

RESEARCH ARTICLE

Enhancing performance of two-step fabricated perovskite solar cells with sulfonium triflate-based additive

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Abstract

We incorporated triphenylsulfonium triflate (TPST), a sulfonium-based additive consisting of polar triflate and bulky hydrophobic phenyl rings, to the PbI₂ precursor solution for preparation of less-defect perovskite film via two-step fabrication. TPST induced localized alterations in the array of the PbI₂ structure due to its large size, thereby forming a more discontinuous and coarser surface with a greater number of pinholes and subsequently facilitating more efficient organic–inorganic reactions. As a result, we achieved the production of thick perovskite films with enlarged granules and decreased PbI₂ residuals in the two-step fabrication process. Furthermore, TPST facilitated the passivation of bulk film defects by increasing the binding energy with the defects. Consequently, the ITO/SnO₂ np-based device and the FTO/CBD SnO₂-based device obtained the best PCEs of 23.88% and 24.30%, respectively. Furthermore, the moisture stability of the perovskite was improved by the hydrophobic character of the TPST additive.

KEYWORDS

2 step deposition, additive, perovskite solar cell, sulfonium triflate

1 | INTRODUCTION

Perovskite solar cells have attracted considerable interest due to their remarkable optoelectronic properties, including photo-absorption, with a high absorption coefficient,¹ high carrier mobility,² and long diffusion length for

electrons and holes.^{3,4} They have recently achieved a power conversion efficiency (PCE) of 26.1%,⁵ establishing themselves as the next generation of solar cells for the production of sustainable energy.

To develop efficient and stable perovskite solar cells, it is crucial to fabricate a high quality perovskite film with large grains and few defects. To accomplish this, film deposition methods based on one-step and two-step

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sequential techniques have been widely explored. Most of the related works have employed a one-step method as a simple way to obtain a dense and uniform film morphology.^{6,7} However, for good film reproducibility such methods require the finely controlled crystallization of two precursors within a limited processing window.⁸ With two-step sequential deposition, the film fabrication is less sensitive to the processing time. This can be favorable for mass production, high reproducibility and eventual commercialization.^{9,10}

Two-step deposition involves the deposition of inorganic materials, such as PbI_2 , followed by the diffusion of organic ammonium salts, such as FAI and MABr, for the reaction to occur. To obtain a high-quality film, a perfect and complete reaction during the second deposition is crucial. The growth and crystalline structure of the PbI_2 films is essential for the subsequent intercalation of organic ammonium compounds and, consequently, the transformation into perovskite phases. Well-ordered and densely packed layers of PbI_2 film can hinder the effective diffusion of the organic ammonium salts into the bulk film, making it difficult to accomplish a perfect reaction using the two-step method.¹¹ When exposed to light, any remaining unreacted PbI_2 can decompose into defect sites, resulting in poor performance and severe degradation.^{12,13}

To address the issue of incomplete reaction in the two-step method, a great deal of research and study has been conducted. Initial research has focused on the use of Lewis bases such as DMSO and NMP to generate stable intermediate phases or adduct complexes upon binding with PbI_2 .^{14,15} This can provide adequate time for the reaction to occur. In addition, researchers have sought to construct environments that organic molecules can access freely, thereby facilitating more efficient organic-inorganic reactions, to completely convert the perovskite crystals.

Similarly, research has been performed to alter the crystalline structure of PbI_2 in order to improve its reactivity with organic molecules. Notably, researchers have examined effectiveness of additive assisted two step method, such as CsI, HCl or even organic salts, to the PbI_2 precursor solution in order to disrupt the original PbI_2 structure and generate a less-ordered (or amorphous) state.^{16–19} In addition, some researchers have investigated the use of polymers to generate an uneven surface on PbI_2 that results in a porous structure.²⁰ This creation of a less-ordered or porous structure within the PbI_2 layer can facilitate the penetration of organic materials into the layers. Many attempts have explored that objective, with small-size succinimide additives using nanoimprint techniques,²¹ the selective formation of porous PbI_2 crystals with large clusters^{22–24} and the removal of DMSO from the formed PbI_2 layer.²⁵ Overall, these efforts aim to

enhance the performance and efficiency of the perovskite solar cells by altering the structure of PbI_2 to increase its reactivity with organic salts.

To passivate the bulk defects of the perovskite film, various ammonium-based additives are currently being applied in the perovskite precursor. In a similar manner, trimethylsulfonium (TMS) is employed as sulfonium-based additives.²⁶ TMS was used to accelerate the crystallization of the quasi-2D Ruddlesden-Popper (RP) perovskite structure by controlling intermediate phases. 1D sulfonium-based lead triiodides were formed by replacing all organic cations within the perovskite structure with trimethyl- or butyldimethyl-sulfonium salt, resulting in enhanced moisture stability in the 1D/3D mixed perovskites.^{27–29}

In this work, we incorporated triphenylsulfonium triflate (TPST), a sulfonium-based additive with bulky and hydrophobic phenyl rings and polar triflate moiety, into the PbI_2 precursor solution to induce structural alternation in PbI_2 layered structure, enhance reactivity with the organic amine salt, and prepare a less-defective perovskite layer for two-step fabrication. TPST molecules were embedded in the PbI_2 layered structure, thereby generating less-ordered, discontinuous and rough PbI_2 films with nano-scale pinholes. Locally reducing the crystallinity of the PbI_2 film in this way is beneficial because it allows the organic amine salt to penetrate the bulk film underneath, and helps control the growth of the perovskite crystals.

By adding the TPST, we successfully prepared thick perovskite films with enlarged grains and reduced PbI_2 residuals in the two-step fabrication. In addition, TPST helped passivate the defects in the bulk film by enhancing the binding energy with the defects (like iodine vacancies and undercoordinated Pb^{2+}) and effectively eliminating Pb-I anti-site defects, thus inhibiting non-radiative recombination in the perovskite film. As a consequence, the photovoltaic devices with TPST exhibited a PCE of 23.88%, with a forward bias V_{oc} of 1.19 V, a J_{sc} (short-circuit current density) of 24.44 mA/cm^2 , and FF (fill factor) of 81.91%. The device also showed enhanced stability in humid conditions (maintaining $\sim 90\%$ of its initial performance after 1500 h under 20% $\sim 30\%$ humidity). Our findings provide simple and practical methods for preparing high-quality perovskite film via two-step method. Adding a bulky sulfonium triflate can further enhance the performance and stability of perovskite solar cells.

2 | RESULTS AND DISCUSSION

In Figure 1A, we depict the molecular structure of triphenylsulfonium triflate (TPST), which was used as the sulfonium-based additive in this work. To explore

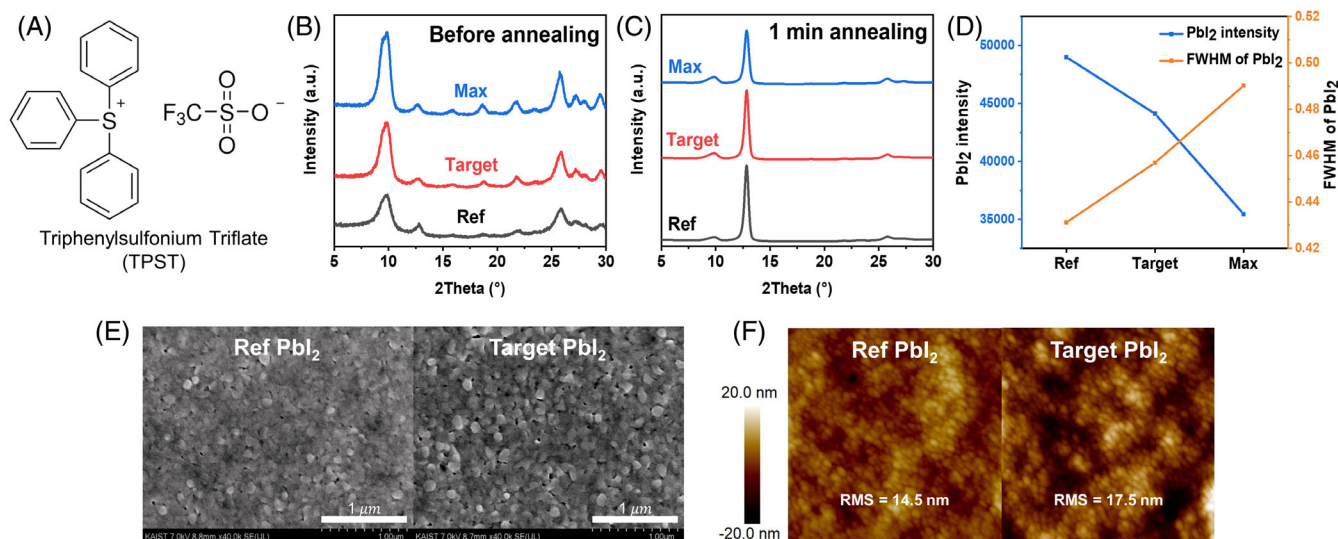


FIGURE 1 (A) The structure of triphenylsulfonium triflate (TPST). XRD spectra of PbI₂ (B) before annealing and (C) after 1 min-annealing. (D) Intensity and FWHM of PbI₂ of Ref, Target and Max. (E) SEM surface images of Ref and Target PbI₂. The scale bar is 1 μ m. (F) Top-view AFM images of Ref and Target PbI₂. The scale bar is 1 μ m.

the effect of TPST as an additive on the PbI₂ film and the perovskite film, we prepared three samples with varying quantities of the additive. The film without any additive was designated “Ref,” the film with the optimal amount of TPST (0.7 mg) was designated “Target,” and the film that was dissolved with the maximal amount of TPST (1.8 mg) was labeled “Max.”

Figure 1B,C shows the XRD spectrum of the as-prepared PbI₂ film prior to thermal annealing. The peak at 9.9° is well-known to correspond to the PbI₂(DMSO) complex. The Target film showed a higher peak intensity than the Ref film. This peak became strongest in the Max film, which indicated that more DMSO molecules were inserted into the PbI₂ layers.^{30,31} After annealing for 1 min (Figure 1C), the intensities of the PbI₂(DMSO) complex peak at 9.9° became weaker while the intensities of the PbI₂ peak at 12.8° became stronger.

In Figure 1D, the intensity of the PbI₂ peak at 12.8° ranged from 49 000 for the Ref film to 35 000 for the Max film, and the full width at half maximum (FWHM) of the PbI₂ peak was 0.4312 for the Ref film and 0.4902 for the Max film. Despite this large variation in the intensity of the peak, we observed no change in their positions and no emergence of additional peaks.³² Consequently, we hypothesize that the TPST additives embedded between the PbI₂ layers may locally reduce the order of the PbI₂ layered structure, which is expected to provide a more favorable environment for the penetration of FAI molecules.^{23,24}

This is indirectly supported by the morphological changes observed in the scanning electron microscopy (SEM) images of the Ref and Target PbI₂ films, as

presented in Figure 1E. Compared to the Ref film, the surface of the Target film is more discontinuous, coarser, and contains a greater number of pinholes. A similar phenomenon was also observed by atomic force microscopy (AFM), as shown in the images in Figure 1F, which clearly shows that the Target film became more uneven and rough as compared to the Ref film. In fact, the roughness of the PbI₂ increased from 14.5 nm for the Ref film to 17.5 nm for the Target films. This difference in the morphology of the PbI₂ film may be attributed to the local disruption of the ordered arrays of PbI₂ by the insertion of the bulky TPST additive. This can be expected to help facilitate the diffusion of organic amine salt into the PbI₂ film, and induce a more efficient conversion to the perovskite.^{20–22,32}

Considering the effect of TPST on the PbI₂ structure, we anticipated that the crystal growth process of the perovskite structure would also undergo modifications. Figure 2A displays the XRD spectrum of the perovskite films. Notably, the characteristic peak of δ -FAPbI₃ at 11.8° was not observed in all perovskite films. However, the addition of TPST led to a reduction in the intensity of the peak of α -FAPbI₃ at 12.8°. This may be associated with the crystal orientation, which will be discussed later.

In contrast, the (111) peak of α -FAPbI₃ at 24.5° exhibited a significant increase in intensity, from 11 000 for the Ref film to 13 000 for the Target film. Additionally, the introduction of TPST contributed to a decrease in the PbI₂ peak at 12.8°, due to the more effective conversion into perovskite. In Figure 2B, the ratio of the PbI₂/FAPbI₃ peak intensity of the films is plotted, and it shows

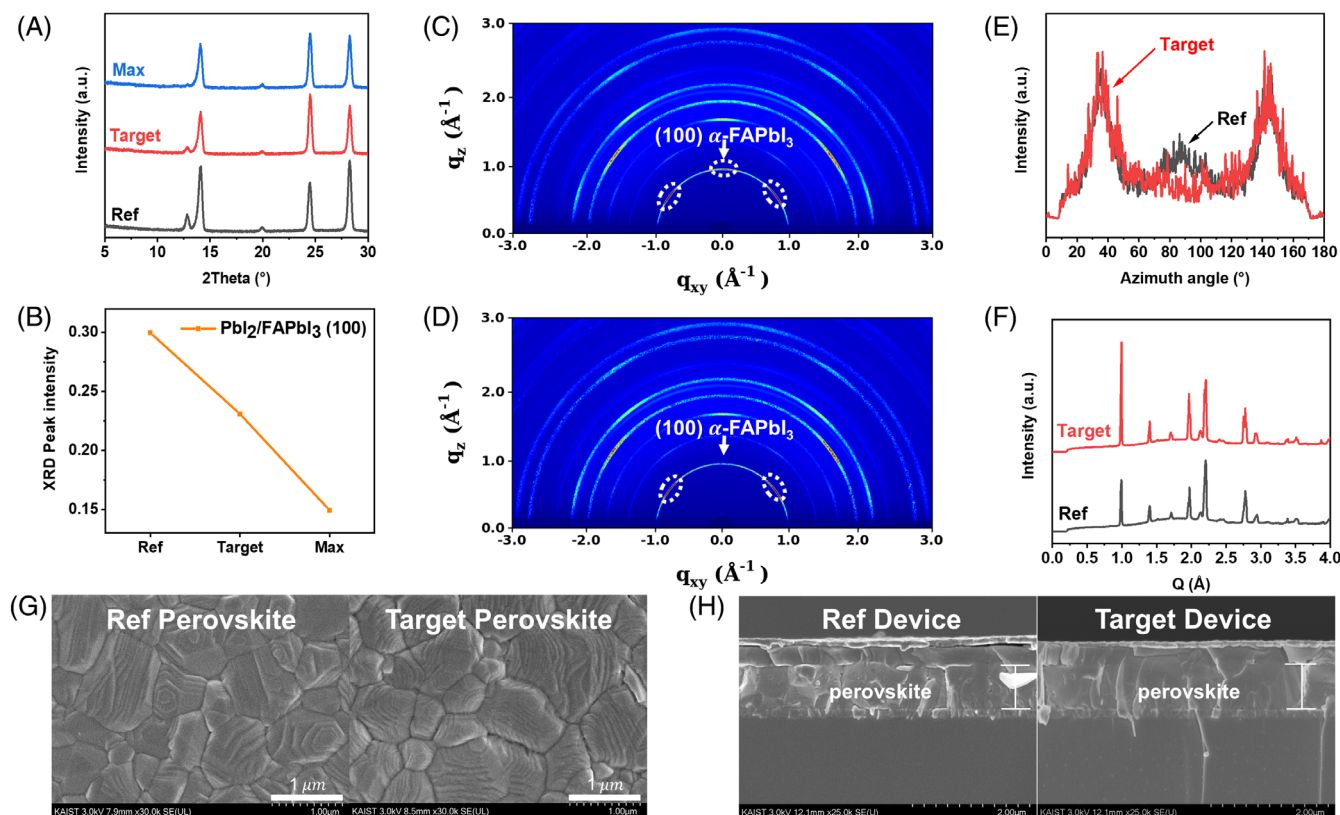


FIGURE 2 (A) XRD spectra of perovskite films. (B) XRD Peak intensity of $\text{PbI}_2/\text{FAPbI}_3$ (100) in Ref, Target and Max perovskite films. GIWAXS images of (C) Ref and (D) Target perovskite films. (E) The azimuth angle and intensity plot cut along the ring at $q = 1 \text{ \AA}^{-1}$ based on GIWAXS data. (F) GIWAXS data cut along the 40° . (G) SEM surface images of perovskite films of Ref and Target. (H) SEM cross-section images of the devices of Ref and Target.

a decreasing trend with increasing amounts of TPST additive. Its lower value implies a decrease in unreacted PbI_2 following conversion to perovskites. Thus, we concluded that the introduction of TPST promotes a chemical reaction between FAI and PbI_2 effectively converting the perovskite, thereby resulting in a reduction in residual PbI_2 .^{15,33,34}

Grazing incidence wide-angle x-ray scattering (GIWAXS) images were obtained and are shown in Figure 2C,D. The GIWAXS images of the Ref and the Target perovskite films appeared to be nearly identical, except for the peaks at $q = 1.0$ and $2.0 \text{ \AA}^{-1}$, corresponding to the (100) and (200) plane of $\alpha\text{-FAPbI}_3$. In Figure 2C, the two films clearly exhibited a different crystal orientation of the (100) plane $\alpha\text{-FAPbI}_3$. The Ref perovskite film displayed three distinct regions with relative higher intensity along the circle line. Among them, the intensity of the central region became weaker and similar to that of the circle line for the Target perovskite film in Figure 2D.

For further detail about the crystal orientation, we plotted the azimuthally circular-cut at the $q = 1.0 \text{ \AA}^{-1}$ in Figure 2E. The Ref perovskite film exhibited three main

peaks at the azimuthal angles of $\sim 40^\circ$ ($180-140$), 90° , and 140° ($180-40$). On the other hand, for the Target perovskite film, only two main peaks at $\sim 40^\circ$ ($180-140$) and 140° ($180-40$) were enhanced while, the peak at 90° was significantly attenuated. This observation implies that the addition of TPST could affect the preferential crystal orientation of the perovskite during the growth of the crystal.

Next, we plotted the radial line profiles at different angles of ~ 40 , 90 , and 140° . In Figure 2F (from data at the $\sim 40^\circ$), the $\alpha\text{-FAPbI}_3$ peak at $q = 1.0 \text{ \AA}^{-1}$ was considerably enhanced for the Target perovskite film, as compared to that for the Ref film. This behavior was consistent with the observations of the line cut data at the azimuthal angle of 140° (Figure S1a). However, the radial line data at 90° (in Figure S1b) clearly showed that the intensity of the $\alpha\text{-FAPbI}_3$ peak for the Target film was much lower than that of the Ref film, which is the same result as the XRD data shown in Figure 2A. On the basis of the GIWAXS data, it can be considered that TPST induces a change in the crystal orientation of the perovskite, suppressing the vertical orientation in the perovskite film along the q_z axis. This is mainly attributed

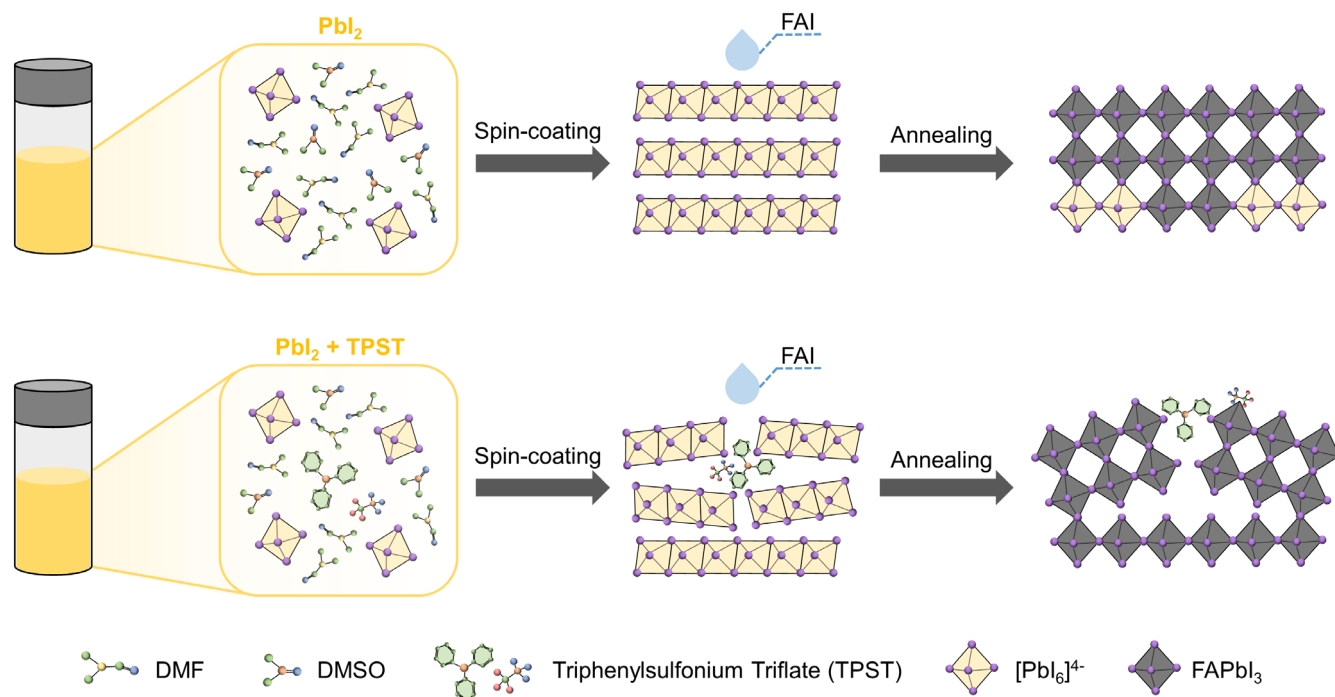


FIGURE 3 Schematic illustration in fabricating PbI_2 and FAPbI_3 assisted by TPST.

to the local disruption of the ordered arrays of PbI_2 by inserting a bulky TPST additive before reacting with the organic amine salt.

SEM images of the Ref and Target perovskite films are shown in Figure 2G. It can be clearly observed that the grain in the Target film is slightly larger than that of the Ref film. More interestingly, the crystal facet orientation of the two films show different behaviors. The facet orientation of granules in the Ref film is vertical (90°) and diagonal (40° , 140°) along the normal axis of the film. In contrast, the Target film displays fewer grains oriented vertically and a greater proportion of diagonally oriented grains (40° , 140°). This observation is consistent with the GIWAXS data, as the intensity of the $\alpha\text{-FAPbI}_3$ peak in the diagonal direction is greater in the target film. The cross-sectional SEM images of the devices in Figure 2H indicate that both the Ref and Target perovskite films have the similar thickness.

In Figure 3, we suggested a schematic illustration of the PbI_2 layer with the controlled ordering induced by the TPST additive, sequentially forming perovskite crystal via two-step fabrication. Upon PbI_2 deposition, TPST induces localized alterations in the array of the PbI_2 structure due to its large size, thereby forming a more discontinuous and coarser surface with a greater number of pinholes. In such a morphology, FAI molecules such as organic amine salts can readily diffuse into the bottom layer of the PbI_2 , allowing for more complete reactions, resulting in less unreacted PbI_2 . This alteration in the

array of the PbI_2 structure can also influence the crystal facet orientation of the perovskite film during the conversion of the PbI_2 into perovskite. As a result, (100) facet grains with diagonal orientation are strongly promoted in the generated perovskite film, while grains with a vertical orientation have been suppressed.

To study the chemical interaction of the TPST additive in the perovskite film, X-ray photoelectron spectroscopy (XPS) was conducted. Figure 4A shows the XPS spectrum of the Pb 4f, in which the Pb $4f_{7/2}$ and $4f_{5/2}$ peaks for the Ref film are located at 138.28 and 143.13 eV, respectively. The corresponding peaks are shifted to a higher binding energy by 0.1 eV (for the Target film) and 0.2 eV (for the Max film), respectively. This is due to the coordination of Pb with a sulfur atom of higher electron affinity.³⁵ This may be due to the chemical interaction between sulfur (S) in the TPS cation of the TPST and the undercoordinated Pb^{2+} ion on the film surface^{36,37} thus contributing to defect passivation of the perovskite film. This Pb-S interaction is strong enough to help retard the fast growth of the perovskite film and result in a higher quality perovskite film.²⁷

Figure 4B displays the carbon 1s XPS spectrum, with the magnified spectrum of the Max film (sky blue line), to clarify its peak. At 292.0 eV, the broad peak corresponds to the $\pi-\pi$ stacking interaction between the phenyl groups of the TPST molecules. Accordingly, it is expected that the rigidity and hydrophobic nature of the three benzene rings of TPST would prevent the ingress of

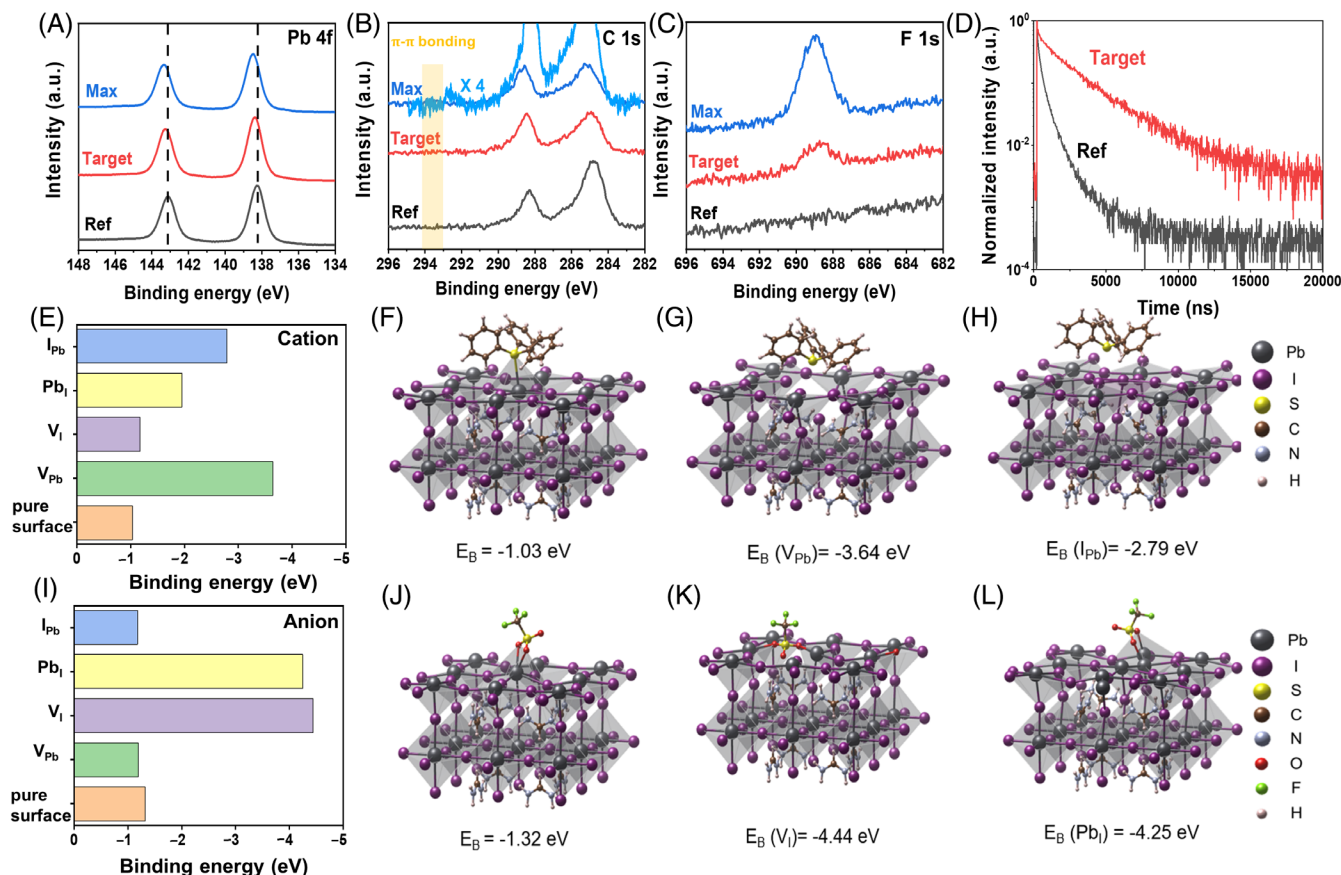


FIGURE 4 XPS spectrum of (A) Pb 4f, (B) C 1s and (C) F 1s. (D) TCSPC spectrum of Ref and Target perovskite films. (E) DFT calculation of binding energy of triphenylsulfonium cation. Optimized structure and binding energy of triphenylsulfonium cation at (F) pure surface, (G) Pb vacancy (V_{Pb}), (H) I_{Pb} antisite on FAPbI_3 surface. (I) DFT calculation of binding energy of triflate anion. Optimized structure and binding energy of triflate anion at (J) pure surface, (K) I vacancy (V_{I}), (L) Pb_{I} antisite on FAPbI_3 surface.

humid air into the film and enhance its moisture stability.^{38,39}

In Figure 4C, we found the F 1s peak at 689.03 eV in both the Target and Max films. The intensity of the F 1s peak was enhanced as the amount of TPST increased, indicative of its presence on the surface.

To gain better insight into the effect of the TPST additive on the bulk film, we employed time-of-flight secondary ion mass spectrometry (ToF-SIMS), as depicted in Figure S2. Notably, for the Target film in Figure S2b, the F and S atoms of the TPST showed significantly higher intensities throughout the perovskite layer compared to the Ref film in Figure S2a. Intriguingly, the majority of the TPST resides on the perovskite surface and at the interface between the perovskite and SnO_2 (ETL).

To analyze the optical properties of the perovskite film containing TPST, we conducted ultraviolet–visible (UV–Vis) absorption spectrum measurements. As shown in Figure S3a, the absorption spectrum of the film was almost the same as that of the Ref perovskite film. Based on the absorption spectrum, we obtained the Tauc plot,

as presented in Figure S3b. It confirmed that both the Ref and Target perovskite film had the same bandgap value of 1.54 eV.⁴⁰

Subsequently, we performed steady-state photoluminescence measurements, depicted in Figure S4. Notably, the peak intensity increased in the Target film, while the peak position remained unaltered. Also, the time-correlated single photon counting (TCSPC) data in Figure 4D indicates a prolonged PL lifetime ($\tau_2 = 807\text{ ns}$) in the Target perovskite film as compared to that ($\tau_2 = 186\text{ ns}$) of the Ref perovskite film, due to fewer defects.⁴¹ As a result, the carrier lifetime in the perovskite film with TPST was longer than that without it, which is a consequence of reduced defects, by suppressing non-radiative recombination.⁴²

We carried out DFT calculations to investigate the passivation effect of TPST on the FAPbI_3 surface, as demonstrated in Figure 4E,I. The formation energy of possible defects was examined to determine the dominant defect on the FAPbI_3 surface in Figure S5. The formation energy of I_{Pb} antisite was the lowest (Figure S5d,

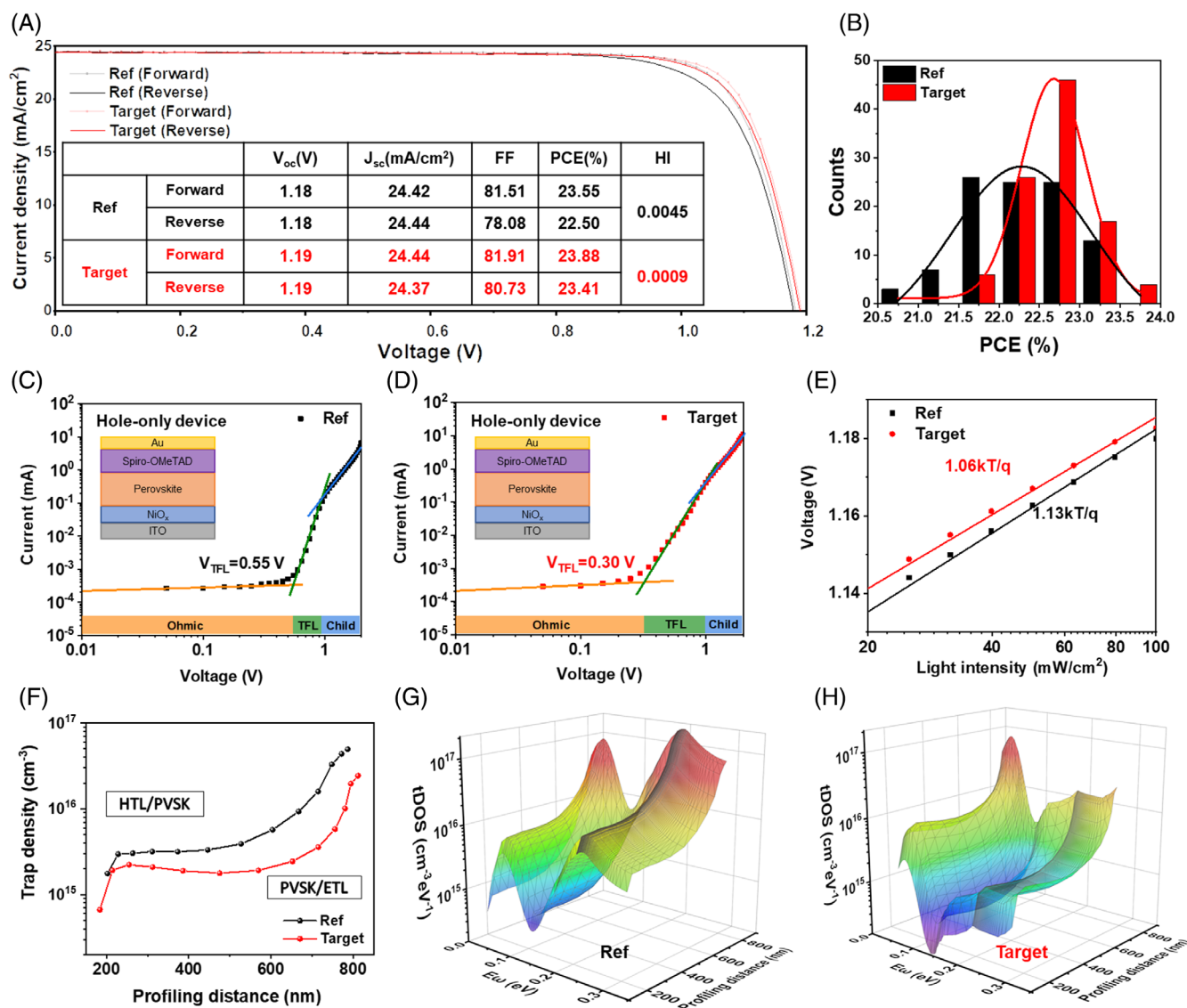


FIGURE 5 (A) J–V curves of Ref and Target devices. The anti-reflective film was used. (B) Statistic distribution charts of PCE for the Ref and Target devices. SCLC measurement of (C) Ref and (D) Target perovskite based on hole-only devices. (E) V_{oc} values with different light intensity. (F) Dependence of the trap density on the profiling distance of a Ref and Target devices measured by DLCP. Energy mapping of the densities of trap states with profiling distance for (G) Ref and (H) Target devices.

$E_{form} = 2.07$ eV) compared to the formation energy of the Pb vacancy (Figure S5a, $E_{form} = 3.08$ eV), I vacancy (Figure S5b, $E_{form} = 2.40$ eV) and Pb_I antisite (Figure S5c, $E_{form} = 3.65$ eV). Thus, the I_{Pb} antisite would be dominant on the $FAPbI_3$ surface.

Then, we investigated the binding of the triphenylsulfonium cation and triflate anion with the $FAPbI_3$ surface to explore their role in defect healing. The triphenylsulfonium cation showed favorable binding with the surface cation defect sites of the Pb vacancy ($E_B = -3.64$ eV) and I_{Pb} antisite ($E_B = -2.79$ eV) as shown in Figure 4G,H. On the other hand, the triflate anion was preferred at the surface anion defect sites of the I vacancy

($E_B = -4.44$ eV) and Pb_I antisite ($E_B = -4.25$ eV) in Figure 4K,L. Therefore, from our DFT calculations, we confirmed that the defect sites of the $FAPbI_3$ surface could be effectively passivated by triphenylsulfonium triflate.

We fabricated a typical n-i-p planar device with ITO/ SnO_2 np/Perovskite/Spiro-OMeTAD/Au to evaluate device performance with and without the TPST additive. As a preliminary step, we optimized the amounts of TPST, as shown in Figure S6. When up to 0.7 mg of TPST was added, the efficiency increased, but then began to decline. At higher amounts, the decreasing trend can be attributed to the accumulation of excess amounts of

TPST, mainly at the interface, thereby impeding charge transfer. Accordingly, we set 0.7 mg of TPST as the optimized amount, designated Target.

Detailed photovoltaic parameter values are outlined in the inset of Figure 5A. The Ref device showed the highest PCE of 23.55% for forward scan with a V_{OC} of 1.18 V, a J_{SC} of 24.42 mA/cm², and a FF of 81.51%. However, for reverse scan the Ref device exhibited a lower PCE of 22.55% due to a lower FF of 78.08%, indicating apparent hysteresis behavior. Meanwhile the Target device showed a champion PCE of 23.88% for the forward scan with a V_{OC} of 1.19 V, a J_{SC} of 24.44 mA/cm², and a FF of 81.91%, exhibiting negligible hysteresis.

External quantum efficiency (EQE) spectra were obtained, as depicted in Figure S8. As shown, the incorporation of TPST resulted in higher efficiency, owing to a substantial increase in V_{oc} and FF. Moreover, as compared to the Ref devices in Figure 5C, the Target devices showed a higher and narrower distribution in PCE. Then, we fabricated TPST-embedded PSCs using an FTO substrate and SnO₂ ETL via chemical bath deposition (CBD), achieving a PCE of 24.30% (as shown in Figure S9). This improvement is attributed to the enhanced J_{SC} as compared with the ITO/SnO₂ np-based PSCs.

We acquired dark I-V curves for space charge limited current (SCLC) measurements, as shown in Figure 5C,D. The inset image illustrates the structure of the hole-only device, configured as ITO/NiOx/Perovskite/Spiro-

OMeTAD/Au. The trap-filled limited voltage (V_{TFL}) for the Ref device was 0.55 V, corresponding to a trap density (N_t) of 3.26×10^{15} cm⁻³.^{43,44} Conversely, the V_{TFL} for the Target device was 0.30 V, corresponding to a N_t of 1.67×10^{15} cm⁻³. Therefore, we can conclude that the TPST effectively reduces trap density.⁴⁵

To deduce the ideal factor (n_{id}), the V_{OC} versus light intensity was plotted in Figure 5E. The Ref device showed a slope (n_{id}) of 1.13, whereas the Target device had a value of 1.06, which is closer to 1. An ideal solar cell has a n_{id} closer to 1, which is indicative of suppressed defect-assisted recombination.^{46,47} The defect passivation effect of TPST is evidenced by the reduction in trap density, leading to diminished defect-assisted recombination.

To gain more insight into the trap passivation of the TPST additive, we employed the drive-level capacitance profiling (DLCP) method, and thermal admittance spectroscopy (TAS) analysis, which is a well-established analysis tool to verify the trap density of perovskite materials. The differences in carrier densities observed at various AC frequencies indicated the existence of trap states within the perovskite thin films. As illustrated in Figure 5F, the trap density of the Target device was entirely diminished across the perovskite film as compared to the Ref device. Specifically, the density of traps decreased considerably in the vicinity of the ETL layer.

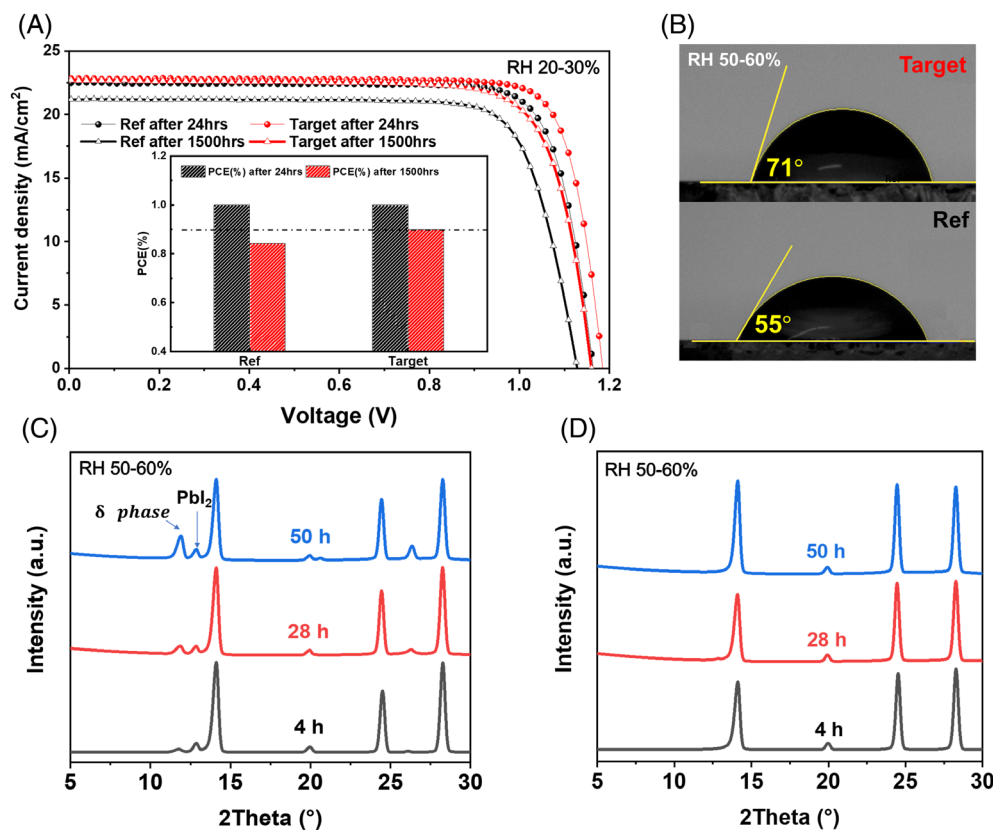


FIGURE 6 (A) J-V curve of Ref and Target devices after 24 and 1500 h under 20%–30% RH. The inset plots are the normalized PCE of Target and Ref. (B) Water contact angle on perovskite film of Target perovskite and Ref perovskite. XRD aging data of (C) Ref perovskite and (D) Target perovskite under 24°C and 50%–60% RH until 2 days.

The tDOS spectra of the Ref and the Target devices, as determined by TAS in Figure S7, revealed a significant decrease in trap density originating from trap band 2 (centered at approximately 0.23 eV), which contains trap states that are comparatively deeper than trap band 1 (centered at approximately 0.05 eV). The presence of Pb-I antisites is likely responsible for the trap's extreme depth, as indicated in Figure 5F. 3D mapping of the spatial and energy trap densities was subsequently performed, as illustrated in Figure 5G,H. Consequently, the passivation of defects in the vicinity of the perovskite/SnO₂ interface is accomplished by the TPST.

We evaluated the moisture stability of the unencapsulated devices in the dark under air conditions (24 °C and 20%–30% RH), as depicted in Figure 6A. After 1500 h of storage, the PCE of the Target device retained ~90% of its initial PCE, while the PCE of the Ref device dropped below ~83% of its initial value within the same time. To support this observation, we carried out water contact angle measurements as shown in Figure 6B. A higher contact angle for the Target perovskite film was found, compared to that of the Ref perovskite film. This higher contact angle is possibly due to the hydrophobic characteristic of TPST, which originates from the three phenyl groups and trifluoromethyl groups.

Further, we performed XRD analysis to observe the degradation of perovskite film under a relatively high humidity condition in Figure 6C,D. Even after exposure for 50 h, the Target film showed only the α -FAPbI₃ peak. In contrast, the Ref film displayed the emergence of both the δ -FAPbI₃ and PbI₂ peaks, except for the original α -FAPbI₃ peak under the same condition, which can be attributed to decomposition of the perovskite upon exposure to humidity. The large size of TPST molecule prevents its incorporation into the lattice of FA-based perovskites. As a result, it is reasonable that the hydrophobic TPST molecules would remain at the grain boundaries. Therefore, the incorporation of TPST into the bulk perovskite film is considered to significantly increase endurance to humidity and mitigate deterioration in air. In addition, we evaluated the operational stability of the devices under maximum power-point (MPP) tracking using white LED. As shown in Figure S10, the Target device maintains the initial efficiency of over 85% after over 140 h, which shows a better stability as compared to the Ref device.

3 | CONCLUSION

In conclusion, we investigated a sulfonium triflate based additive, TPST, to address incomplete reactions when using a two-step method. TPST disrupted the PbI₂ structure, allowing for more PbI₂(DMSO) complexes and

intramolecular exchanges with FAI. It also reduced PbI₂ crystallinity, promoting FAI diffusion to the bottom layer of PbI₂, resulting in complete reactions with less unreacted PbI₂. The TPST's bulkiness caused it to tilt the perovskite structure towards a diagonal orientation, passivating defects like Pb or I vacancies and Pb-I anti-sites. As a result, we achieved the best PCEs of 23.88% and 24.30% for the ITO/SnO₂ np-based device and the FTO/CBD SnO₂-based device, respectively. Furthermore, the hydrophobic nature of the TPST additive enhanced the perovskite's moisture stability, and the TPST-added device retained 90% of its initial PCE for 1500 h under 20% ~ 30% RH air conditions. Our strategy to use a sulfonium triflate additive with bulky phenyl rings for the two-step fabrication of the perovskite film will contribute to ongoing efforts towards the development of efficient and stable perovskite solar cells.

4 | EXPERIMENTAL SECTION

4.1 | Materials

SnO₂ np was purchased from Alfa Aesar. Triphenylsulfonium triflate (TPST), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), methylammonium chloride (MACl), 2-propanol (IPA), chlorobenzene (CB), chloroform (CF), acetonitrile (ACN), tert-Butyl pyridine (tBP) and bis(trifluoromethane) sulfonimide lithium salt (Li-TFSI) were purchased from Sigma Aldrich. Lead iodide (PbI₂) was bought from Tokyo Chemical Industry. 2,2',7,7'-tetrakis(*N,N*-dip-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD) and FK 209 (Co salt) were purchased from Lumtec. Foramidinium iodide (FAI), methylammonium bromide (MABr), and *n*-octylammonium iodide (OAI) were purchased from Greatcell Solar.

4.2 | Device fabrication

All devices were fabricated in a dehumidification room controlled under 20 °C, 20% ~ 30% RH. ITO glasses were prepared by sequentially washing with detergent, DI water, and IPA, each for 10 min and moved into the oven. The UVO treatment was performed for 20 min. Then, the ITO glass was spin-coated with SnO₂ np solution diluted by DI (1: 3, v: v) at 4000 rpm for 30 s, and annealed at 150 °C for 30 min. Before deposition of the perovskite layer, the ITO with SnO₂ layer was treated by UVO for 30 min. 1.5 M PbI₂ was dissolved in a solvent mixture of 0.9 mL DMF and 0.1 mL DMSO to prepare the inorganic precursor solution. For the target device, 0.7 mg TPST was added into 1.5 M PbI₂ sol. And 1.8 mg

TPST was added into 1.5 M PbI_2 sol for the max device. The inorganic precursor solution was spin-coated on top of the SnO_2 np layer at 1500 rpm for 30 s. It was annealed at 70°C for 1 min and cooled down to room temperature. For the organic precursor solution, 150 mg FAI, 3 mg MABr, 15 mg MACl were dissolved in 1 mL IPA were sufficiently mixed for 30 min before use. After that, the organic precursor solution was spin-coated on the PbI_2 layer at 3700 rpm for 30 s and annealed at 150°C for 15 min. To deposition of the surface passivation layer, 10 mM of OAI in CB was spin-coated onto the perovskite layer and then annealed at 100°C for 3 min. The hole transporting layer was deposited on top of the surface passivation layer at 3000 rpm for 30 s using Spiro-OMeTAD solution, which consisted of 72.3 mg Spiro-OMeTAD, 35 μL Li-TFSI stock solution (260 mg Li-TFSI in 1 mL ACN), 20 μL Co salt stock solution (100 mg Co salt in 1 mL ACN), 30 μL tBP, and 1 mL CB. Finally, 130 nm of Au film was thermally evaporated onto the hole transportation layer.

4.3 | Characterization

Scanning electron microscopy (SEM) images were taken with a SU8230 (Hitachi) high-resolution microscope. Atomic Force Microscopy (AFM) was conducted by INNOVA-LABRAM HR800. The x-ray diffraction (XRD) data was acquired with a Rigaku Ultima IV x-ray diffractometer by using the $\text{CuK } \alpha$ line ($\lambda = 0.154 \text{ nm}$) at 40 kV and 40 mA source excitation. Absorbance spectra was measured by a UV-Vis spectrophotometer, PerkinElmer (Lambda 1050). Steady-state photoluminescence spectrums were collected by LabRAM HR Evolution Visible_NIR (Horiba) with 635 nm laser. Time-correlated single photon counting (TCSPC) was conducted with TCSPC FluoTime 300 by picoquant (GmbH). Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS) measurements were performed at the PLS-II 6D beamline of the Pohang Accelerator Laboratory (PAL). Moreover, GIWAXS images of the perovskite film were obtained with 18.986 keV x-ray. X-ray photoelectron spectroscopy (XPS) was conducted by a K-alpha (Thermo VG Scientific) and calibrated using C 1s peak at 284.8 eV. Time-of-flight secondary ion mass spectroscopy (ToF-SIMS) was collected by a TOF-SIMS5 (ION-TOF GmbH). J-V curves were measured by using a Keithley 2400 source-meter, under AM1.5G illumination. Before conducting the J-V measurement, we always set the 1 sun using the silicon reference cell. J-V curves were obtained by sweeping between -0.1 V and 1.5 V with an interval of 100 ms. EQE measurements were conducted by Model Quantx-300 (Newport) at room temperature in air. The water

contact angle measurements were performed at 50% RH by using a SEO Phoenix 300.) and analyzed by the Surfaceware software. The operational stability of the device was carried out by MPPT with white LED (Mc science, K3600 solar cell reliability test system and SimuLight SS-LED 150S). For the stability test, poly(triarylamine), PTAA was used as HTL.⁴⁸

The Agilent E4284A Precision LCR Meter and the Keithley 4200A-SCS were utilized for conducting standard C-V (capacitance-voltage), DLCP (Drive-level capacitance profiling), and TAS (Thermal admittance spectroscopy) measurements.^{49,50} In standard C-V measurements for perovskite solar cells, a DC bias was systematically scanned from 0 V to the open-circuit voltage (V_{OC}), typically up to 1.2 V. The AC bias amplitude was set at 14 mV. DLCP measurements covered the same DC bias range as standard C-V measurements, with an AC bias amplitude ranging from 14 to 140 mV. An additional offset DC voltage was applied to maintain a consistent maximum forward bias for each AC bias. The capacitance values obtained at various DC biases were collected using a custom computer program, and C0 and C1 were determined through polynomial fitting. For trap density comparisons, measurements were generally conducted at 10 kHz. This frequency was selected as it does not significantly impact the relative value comparisons, considering that trap densities remain consistent within the range of AC frequencies around 10 kHz. In TAS measurements, the DC bias was fixed at 0 V, and the AC bias had an amplitude of 14 mV. The AC frequency was systematically scanned over a range from 20 Hz to 10 MHz.

4.4 | Calculation

DFT calculations were performed using the Vienna ab initio Simulation Package (VASP).⁵¹ Exchange-correlation energies were treated by Perdew-Burke-Ernzerhof (PBE) functional based on generalized gradient approximation (GGA).⁵² The simulation models were constructed with cell parameters ($a = b = c = 6.366 \text{ \AA}$, $\alpha = \beta = \gamma = 90.00^\circ$) for FAPbI_3 structure. A $3 \times 3 \times 1$ Monkhorst-Pack k-points was used for binding energy calculations.⁵³ A vacuum thickness of 30 $\text{\AA}$ was used to exclude the interaction between periodic images in surface model. A plane wave was expanded with a cutoff of 400 eV and convergence criteria of 10^{-4} eV . Gaussian smearing was used with a width of 0.05 eV to determine partial occupancies. Geometries were relaxed using a conjugate gradient (CG) algorithm until the forces were less than 0.03 eV/ $\text{\AA}$. DFT-D3 was used to correct for van der Waals interactions.^{54,55} The binding energies (E_{B}) of ligands were calculated by $E_{\text{B}} = E_{\text{lig_surf}} - E_{\text{lig}} - E_{\text{surf}}$, where $E_{\text{lig_surf}}$ is the total energy of the system with a ligand

on the FAPbI₃ surface, E_{lig} is the total energy of an isolated gas-phase ligand, and E_{surf} is the total energy of the bare surface, respectively.

AUTHOR CONTRIBUTIONS

Yeeun Kim: Writing- original draft, analysis, experimentation, investigation. **Hyunjun Lee:** Writing- original draft, analysis, experimentation, investigation. **Cheongbeom Lee:** DFT calculation. **Beomjin Kim:** Experimentation. **Nayoon Kwon:** Experimentation. **Taewoong Son:** Experimentation. **Jaehae Lee:** Experimentation, analysis. **Jaegwan Sin:** Analysis of DLCP-TAS. **Taejoo Shin:** Analysis of GIWAXS data, investigation. **Jungyup Yang:** Resources, supervision of DLCP-TAS. **Kyeounghak Kim:** Resources, supervision of DFT calculation. **Jangwon Seo:** Resources, project administration, supervision, writing-review & editing. All authors contributed to the manuscript.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

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SUPPORTING INFORMATION

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