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# A Multifunctional Molecular Bridging Layer for High Efficiency, Hysteresis-Free, and Stable Perovskite Solar Cells

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At present, the dominating electron transport material (ETL) and hole transport material (HTL) used in the state-of-the-art perovskite solar cells (PSCs) are tin oxide and 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine)-9,9'-spirobifluorene (Spiro-OMeTAD). However, the surface hydroxyl groups of the SnO<sub>2</sub> layer and the Li<sup>+</sup> ions within the Spiro-OMeTAD HTL layer generally cause surface charge recombination and Li<sup>+</sup> migration, significantly reducing the devices' performance and stability. Here, a molecule bridging layer of 3,5-bis(fluorosulfonyl)benzoic acid (FBA) is introduced onto the SnO<sub>2</sub> surface, which provides appropriate surface energy, reduces interfacial traps, forms a better energy level alignment, and, most importantly, anchors (immobilizes) Li<sup>+</sup> ions in the ETL, and consequently improves the device power conversion efficiency (PCE) up to 24.26% without hysteresis. Moreover, the device with the FBA passivation layer shows excellent moisture and operational stability, maintaining over 80% of the initial PCE after 1000 h under both aging conditions. The current work provides a comprehensive understanding of the influence of the extrinsic Li<sup>+</sup> ion migration within the cell on the device's performance and stability, which helps design and fabricate high-performance and hysteresis-free PSCs.

## 1. Introduction

Organic-inorganic halide perovskite solar cells (PSCs) have great potential for next-generation solar cells due to their long charge-carrier diffusion length, wide absorption range, tunable energy bandgap, and low-cost and low-energy solution processing.<sup>[1–5]</sup> So far, the power conversion efficiency (PCE) of single-junction perovskite solar cells has reached 25.7%,<sup>[6]</sup> which is close to the silicon heterojunction solar cell record.<sup>[7]</sup> The most used electron-transport material (ETL) and hole-transport material (HTL) in the state-of-the-art PSCs are tin oxide (SnO<sub>2</sub>) and lithium bis-(trifluoromethanesulfonyl) imide salt (LiTFSI) doped 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine)-9,9'-spirobifluorene (Spiro-OMeTAD), respectively. However, there are still some issues with these materials for commercialization.

For the SnO<sub>2</sub> ETL, some unavoidable charge-trap states, including hydroxy, oxygen, tin vacancies, interstitials, surface hydroxyl groups, and anti-site defects,<sup>[8]</sup> exist in bulk and at the interface between the ETL and the perovskite layer. These charge-trap states act as

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recombination centers, leading to increased non-radiative recombination, reducing the PCE and stability of the devices. Hence, some passivation methods have been extensively investigated for bulk SnO<sub>2</sub> and the interface between the SnO<sub>2</sub> and active layer. The passivation methods include doping using ionic compounds,<sup>[9]</sup> acid treatments,<sup>[10]</sup> bilayer ETL formation,<sup>[11]</sup> and the use of polymer as additive<sup>[12]</sup> and buffer layers.<sup>[13]</sup> The molecular bridging layer can be very promising considering a method of simultaneously controlling the surface roughness, work function alignment, trap passivation, and the mechanical reliability interface modification leading to non-radiative recombination and instability. Yang and coworkers indicated that a 3-aminopropyltriethoxysilane (APTES) self-assembled molecules (SAM) as an interfacial layer could modify the interface, enhancing the interfacial contact and improving the morphology and crystallinity of perovskite films.<sup>[14]</sup> Wang et al. reported that C<sub>60</sub>-SAM facilitates electron transfer from the perovskite layer to the SnO<sub>2</sub> ETL due to its high electron affinity.<sup>[15]</sup> Dong et al. found that the novel 2,4,5-trichlorobenzenesulfonic acid potassium salt (3Cl-BSAK) could eliminate the device hysteresis and the V<sub>OC</sub> loss due to the efficient interaction between carbon-chlorine bonds with uncoordinated Sn, effectively filling oxygen vacancies in the SnO<sub>2</sub> surface.<sup>[16]</sup> Dai et al. demonstrated an iodine-terminated self-assembled monolayer (I-SAM) used in perovskite solar cells (PSCs) to achieve a 50% increase in adhesion toughness at the interface between the ETL and the halide perovskite thin film to enhance mechanical reliability. These successful examples suggest that interfacial engineering with multifunctional molecules is a great option to enhance the PCE and stability of the n-i-p PSCs with SnO<sub>2</sub> ETL.

On the other hand, for spiro-OMeTAD HTL, some chemical dopants such as 4-tertbutylpyridine (tBP) and lithium bis-(trifluoromethanesulfonyl) imide salt (LiTFSI) are indispensable to achieving efficient hole extraction and sufficient conductivity.<sup>[17]</sup> These deliquescent dopants have a profound negative influence on the stability of the PSCs, due to the hygroscopicity of lithium salt and the migratory nature of Li<sup>+</sup> ions.<sup>[18,19]</sup> So far, various dopants have been studied to replace LiTFSI, such as AgTFSI,<sup>[20]</sup> Cu(TFSI)<sub>2</sub>,<sup>[21]</sup> and Zn(TFSI)<sub>2</sub>.<sup>[22]</sup> However, considering the active spiro-OMeTAD radical cation species generation<sup>[21]</sup> and Li<sup>+</sup> ions serving as the supporting ion to complete the electrochemical cycle,<sup>[23]</sup> Li-TFSI is still the most common p-dopant for spiro-OMeTAD. However, Li<sup>+</sup> ions could migrate from spiro-OMeTAD to the surface leading to more pinholes on the surface of spiro-OMeTAD<sup>[24]</sup> and changing the perovskite film toward more n-doping and raising the surface potential.<sup>[25]</sup> Moreover, it could even pass through the perovskite layer and accumulate at the surface of the ETL, and higher Li-TFSI doping concentration could aggravate the hysteresis issue<sup>[26]</sup> and the “burn-in” effect.<sup>[27]</sup> recently, some researchers indicated that Li<sup>+</sup> ions migration is also an essential factor affecting the stability of PSCs at high temperatures.<sup>[28,29]</sup> At present, the methods to eliminate the migration of Li<sup>+</sup> ions include adding MoS<sub>2</sub> with flower-like microstructures into spiro-OMeTAD acting as a powerful sorbent for Li<sup>+</sup> ions;<sup>[30]</sup> doping reduced graphene oxide (rGO) to spiro-OMeTAD to provide adsorption sites for Li<sup>+</sup> ions<sup>[31]</sup> and using a “cross-linkable” PCBM derivative to blocks this migration of Li<sup>+</sup> ions.<sup>[27]</sup> However, there have been no reports of inhibition of ion mobility while passivating ETL.

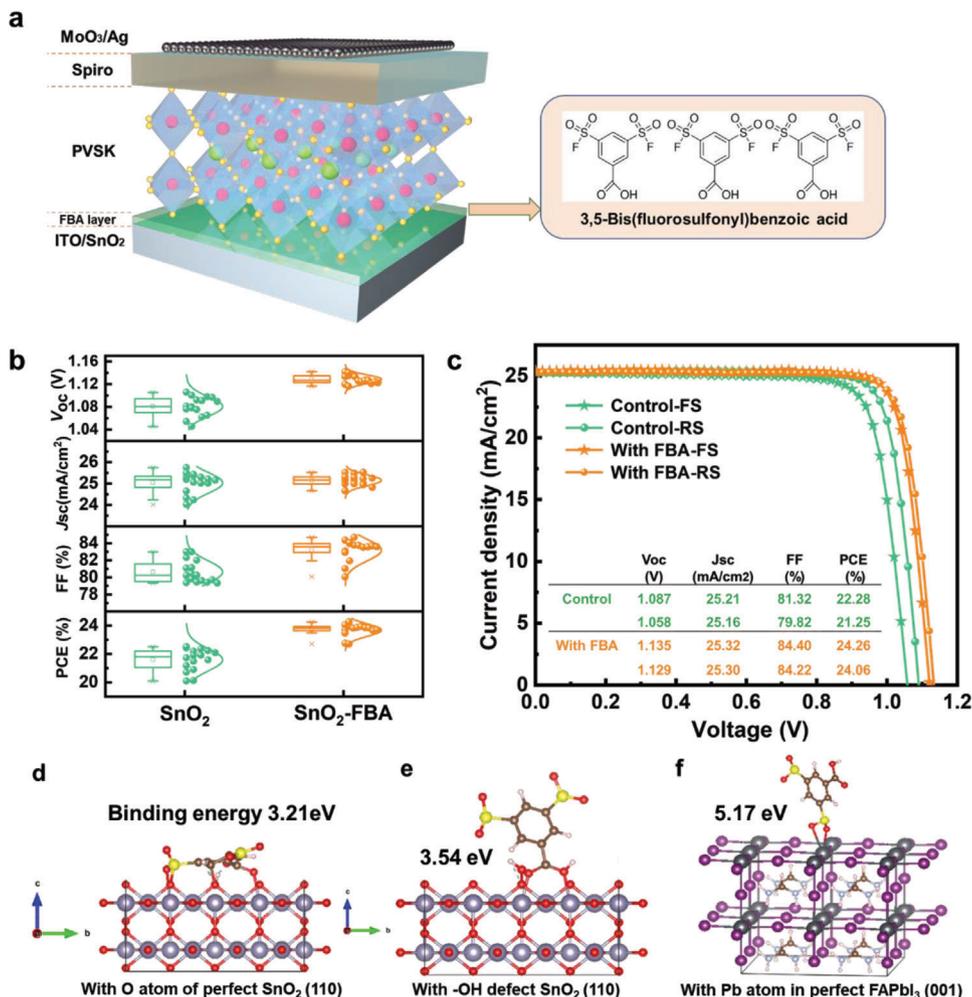
Here we devise a strategy to passivate the defects at the interface between SnO<sub>2</sub> and perovskite while inhibiting Li<sup>+</sup> ions migration using the molecule 3,5-bis(fluorosulfonyl)benzoic acid (FBA). The carboxyl group in FBA acts as an effective multifunctional passivating agent at the interface between SnO<sub>2</sub> and perovskite due to filling oxygen vacancies and reducing the -OH group. Moreover, FBA optimizes the ETL's surface energy and flatness, leading to a larger perovskite grain size. Additionally, the FBA passivation layer modifies the work function of the SnO<sub>2</sub> with a favorable energy level difference between the perovskite and ETL, significantly improving the charge collection and transport properties in the device, resulting in a higher open circuit voltage (Voc) and fill factor (FF). Finally, the fluorosulfonyl group can anchor Li<sup>+</sup> ions, thereby minimizing hysteresis and enhancing the device's stability.<sup>[32]</sup> Thanks to these favorable synergistic effects, the device based on FBA passivation achieved a high PCE of 24.26%. Moreover, the unencapsulated devices show better moisture-resistance stability and operation stability performance.

## 2. Result and Discussion

### 2.1. FBA as SnO<sub>2</sub> Passivation Layer

The device with an ITO/SnO<sub>2</sub>/FAPbI<sub>3</sub>/Spiro-OMeTAD/MoO<sub>x</sub>/Ag planar structure and the structure of 3,5-bis(fluorosulfonyl)benzoic acid is shown in Figure 1a. The detailed device performance is summarized in Figure 1b and Table S1, Supporting Information. EQE spectra (Figure S1, Supporting Information) show slight improvement, as seen in the short-circuit current density (J<sub>SC</sub>). However, the V<sub>OC</sub> is significantly increased from 1.08 to 1.13 V. As shown in the J–V curves (Figure 1c), the FBA passivation layer delivers higher performance, increasing the PCE from 22.28% to 24.26%. Additionally, the hysteresis issue is also inhibited but not eliminated. Moreover, the higher FF indicates better charge transport (higher shunt resistance) and efficient charge extraction through the contacts (lower series resistance).<sup>[33]</sup>

The first critical issue for the FBA to have these properties is to ensure the FBA molecule's orientation. Through first-principles density functional theory (DFT) calculations, the binding energy of perfect SnO<sub>2</sub> and FBA molecules in three different adsorption conditions, including an Sn-atom, hollow, or O-atom site (Figure 1d and Figure S2a,b, Supporting Information), can be calculated as −0.39, −1.27, and −3.21 eV, respectively. However, in the actual situation, some traps mentioned above inevitably exist in the SnO<sub>2</sub> ETL layer. The binding energies of the FBA molecule and SnO<sub>2</sub> with -OH groups and O vacancy were calculated as −3.54 and −0.43 eV, shown in Figure 1e and Figure S2c, Supporting Information. On the other hand, the binding energy of the FBA molecule and FAPbI<sub>3</sub> in different adsorption methods also can be achieved. (Figure 1f and Figure S3a–c, Supporting Information). The maximum binding energy condition is FBA molecules with Pb atom, reaching −5.17 eV, as shown previously,<sup>[34]</sup> indicating that the fluorosulfonyl group could coordinate with lead atoms to improve the stability of the devices. All the DFT results are shown in Table S2, Supporting Information. On the other hand, through the sum-frequency generation spectroscopy (SFG) result in Figure S4, Supporting Information, we observe that the peak of -OH groups found at



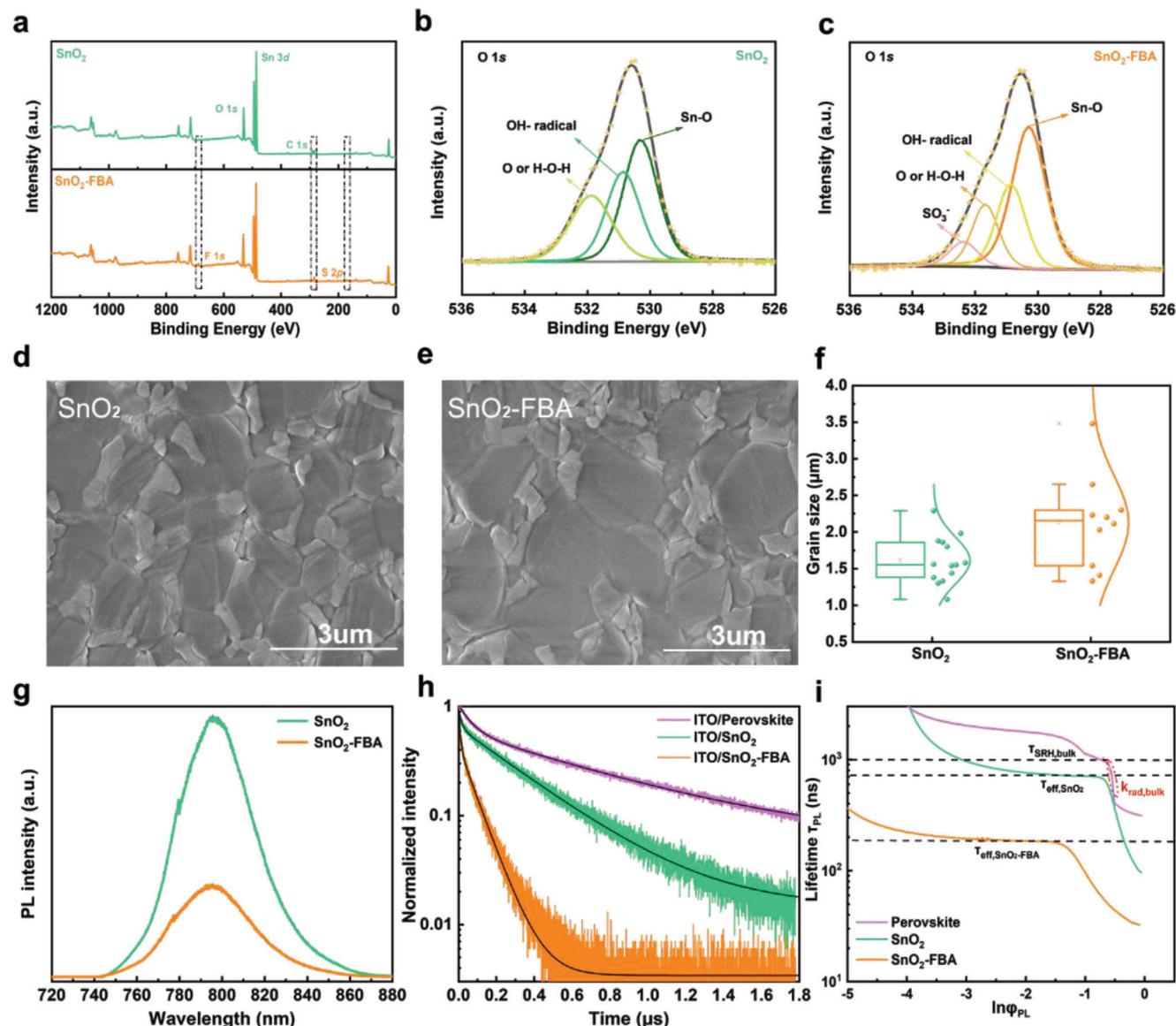
**Figure 1.** a) Schematic diagram of the passivation layer formed between the SnO<sub>2</sub> ETL and perovskite layer. b) Statistical distribution diagram of the performance of the control group and devices with the FBA passivation layer. c) *J*–*V* curves of devices based on SnO<sub>2</sub> and SnO<sub>2</sub>-FBA ETL. Theoretical models of FBA molecular with different SnO<sub>2</sub> structures: d) with perfect structure e) with OH group traps. f) Theoretical models of FBA molecular with FAPbI<sub>3</sub> perovskite.

3200–3500 wavenumbers<sup>[35]</sup> decreases with the increasing immersion time of SnO<sub>2</sub> in FBA, proving that the carboxyl group binds to SnO<sub>2</sub>. Therefore, these results demonstrate that the fundamental molecular orientation of FBA is that -OH is found to bind to tin oxide, while the sulfonic fluoride group is bound to the perovskite layer.

Secondly, X-ray photoelectron spectroscopy (XPS) is conducted to investigate how the electronic structure of SnO<sub>2</sub> changes with the addition of FBA. **Figure 2a** shows the whole spectra of SnO<sub>2</sub> and SnO<sub>2</sub>-FBA. For the SnO<sub>2</sub>-FBA spectra, some new peaks, including F 1s and S 2p, are detected. Moreover, in Sn 3d orbital (Figure S5, Supporting Information), the peaks of FBA shift to the direction of higher binding energy with 0.2 eV (exceeds the instrument uncertainty), illustrating the presence of extra electrons around an Sn atom.<sup>[36]</sup> This evidence supports that the FBA molecules bind to the SnO<sub>2</sub> film surface. For the O 1s orbital, the binding energies at 530.2, 530.8, and 531.8 eV are attributed to Sn-O, surface-absorbed hydroxyl groups, and an O vacancy. O vacancy is the most typical charge state in SnO<sub>2</sub>,<sup>[37]</sup>

and -OH groups could result in traps during the SnO<sub>2</sub> film-fabrication process, leading to lower device performance.<sup>[4]</sup> The defect percentage (calculated as  $\frac{O_v + O_{-OH}}{O_{all}}$ ) shows a noticeable decrease from 58.4% to 41.4%, as measured in (Figure 2b,c), and shown in Table S3, Supporting Information. The excellent passivation performance of FBA is due to carboxylic acid forming an ester bond with SnO<sub>2</sub> via the esterification reaction<sup>[38]</sup> and reacting with both tin and oxygen dangling bonds on the SnO<sub>2</sub> surface, thereby passivating the surface with high coverage and reducing surface recombination.<sup>[8]</sup> Moreover, from the absorption spectra and transmission spectra data of each ETL, the effect of the FBA passivation layer on optical properties could be ignored (Figure S6, Supporting Information).

Lastly, inserting the FBA interfacial layer between ETL and the perovskite layer can improve the crystal quality and film coverage of perovskite film. The ETL must balance hydrophilicity and hydrophobicity to form a uniform film with a large grain size because the substrate is over-hydrophilic; although the film uniformity increases, the grain size tends to be smaller due to the



**Figure 2.** a) XPS full spectra of SnO<sub>2</sub> and SnO<sub>2</sub>-FBA. b-c) XPS high-resolution spectra of SnO<sub>2</sub> and SnO<sub>2</sub>-FBA in O 1s orbit. SEM images and box chart of grain size of perovskite films deposited on SnO<sub>2</sub> and SnO<sub>2</sub>-FBA ETLs. d) SnO<sub>2</sub>; e) SnO<sub>2</sub>-FBA; f) box chart. g) PL and h) TRPL spectra of perovskite films deposited on SnO<sub>2</sub> and SnO<sub>2</sub>-FBA ETLs. i) Differential lifetime as a function of the logarithm of the TRPL intensity

high density of nuclei. On the other hand, the perovskite film could not completely cover the hydrophobic substrate, resulting in pinholes in the film.<sup>[39]</sup> As seen from the water contact angle in Figure S7, Supporting Information, the water contact angle of SnO<sub>2</sub> is 5.4°. The water contact angle is also increased with the ascension of FBA precursor concentration. When the concentration of FBA precursor reaches 0.1 mg ml<sup>-1</sup>, the water contact angle is 16.4°. Moreover, from top-view scanning electron microscope (SEM) images in Figure 2d,e, the average grain size of the perovskite film based on SnO<sub>2</sub>-FBA (2.13 μm) is much larger than that of the film on pristine SnO<sub>2</sub> (1.61 μm). Figure 2f demonstrates the statistical distribution of grain sizes of the perovskite film deposited on different ETL. These results confirm that suitable surface energy is achieved by introducing the FBA passivation layer. However, a higher concentration of FBA pre-

cursor (0.5 mg ml<sup>-1</sup>) could cause grain boundary defects and pinholes in the perovskite film, as shown in Figure S8, Supporting Information. Through the atomic force microscopy (AFM) images of the FBA layer with different concentrations (Figure S9, Supporting Information), the agglomeration phenomenon can be observed when the FBA concentration is over 0.3 mg ml<sup>-1</sup>. It could be the reason for grain boundary defects and pinholes in the perovskite film. Moreover, the performance demonstrated in Figure S10 and Table S4, Supporting Information also proves that the moderate concentration of FBA (0.1 mg ml<sup>-1</sup>) is beneficial for crystallization. Hence, from the SEM images, AFM results, and performance of the device, 0.1 mg ml<sup>-1</sup> FBA concentration should be more appropriate. The cross-section SEM image (Figure S11, Supporting Information) illustrates that the interface between SnO<sub>2</sub>-FBA ETL and the perovskite layer is

uniform and pinhole free. Additionally, from the atomic force microscopy (AFM) images (Figure S12, Supporting Information), the surface roughness with the FBA passivation layer is significantly reduced, indicating the FBA could fill the nanopores on the surface of SnO<sub>2</sub>, thus enhancing the flatness and mobility of SnO<sub>2</sub> ETL. Moreover, from the root means square (RMS) roughness of each perovskite film (Figure S13, Supporting Information), the parameter barely changed, indicating that the morphology of perovskite film has not changed basically. The modified ETL's extraction properties are also improved as measured using photoluminescence (PL). From the PL curves shown in Figure 2g, the perovskite film on SnO<sub>2</sub>-FBA shows the best PL quenching phenomenon thanks to better carrier extraction capacity. For the time-resolved photoluminescence (TRPL) of pure perovskite film (Figure 2h), two regimes can be distinguished: a carrier density-dependent lifetime at high TRPL signals (short delay times) and a constant lifetime at low TRPL signals (long delay times). However, it has been clearly shown by Kirchartz that we cannot use simple exponential lifetimes to decouple the effects in the bulk and at the interface.<sup>[40]</sup> Instead, we employ the differential lifetime to distinguish these effects. The differential lifetime is defined as.

$$\tau_{PL} = \left( \frac{-1}{m} \frac{d \ln(\varphi_{PL})}{dt} \right)^{-1} \quad (1)$$

where  $\varphi_{PL}(t)$  is the TRPL intensity at a given time after the pulse excitation, and the  $m$  is a factor related to the injection level. For high-level injection,  $m$  can be set to 2, and the perovskite layer can be assumed to be intrinsic or sufficiently low-doped.<sup>[40]</sup> Figure S14, Supporting Information shows the TRPL intensity results, indicating increased interfacial electron transfer due to the presence of the FBA-modified ETL. Moreover, it is advantageous to plot the lifetime as a function of the quasi-Fermi level splitting  $\Delta E_F = k_B T \ln(\Delta n^2/n_i^2)$ , where  $k_B T$  is the thermal energy,  $\Delta n$  the excess carrier density, and  $n_i$  the intrinsic carrier density. Hence, the carrier density is the most significant factor in analyzing recombination and extraction processes. We use the fact that the PL intensity scales with  $\Delta E_F$  according to the following equation.

$$\varphi_{PL} \propto \exp\left(\frac{\Delta E_F}{k_B T}\right) \quad (2)$$

Implying that  $\ln(\varphi_{PL})$  can be used as a relative measure of the quasi-Fermi level splitting shown in Figure 2i. Here, a density-dependent part can be contributed to direct radiative recombination, which could be illustrated as a second-order process that scales with  $k_{rad} \Delta n^2$  ( $k_{rad}$  is the radiative recombination coefficient). The constant part is associated with the slower recombination via traps, which, according to Shockley–Read–Hall (SRH) statistics, resemble a pseudo-first-order process, and the plateau corresponds to an effective SRH lifetime in bulk.<sup>[41]</sup> On the other hand, for the samples with the ETL, the fast decay component represents the extraction of charge carriers at the interface. At longer times, the decay is more rapid than for the perovskite-only film, indicating an additional recombination channel, which can be attributed to interfacial recombination.<sup>[42]</sup> In Figure 2i, The plateau of  $\tau_{PL}$  in this case, the samples with ETL is given by a complex interplay of the bulk SRH lifetime and the surface re-

combination velocity  $S$  of electrons at the ETL. Hence, the surface recombination velocity  $S$  can be calculated using

$$\tau_{SRH,eff} = \left( \frac{1}{\tau_{SRH,bulk}} + \frac{S}{2d} \right)^{-1} \quad (3)$$

where  $d$  is the thickness of the perovskite layer, which can be obtained from Figure S11, Supporting Information, and the related results are shown in Table S5, Supporting Information. Hence, the FBA passivation layer increases the surface recombination velocity, a measure of the electron extraction from the active layer to the electrode, from 35 to 409 cm s<sup>-1</sup>, indicating that most carriers will be more easily extracted through the modified interface.

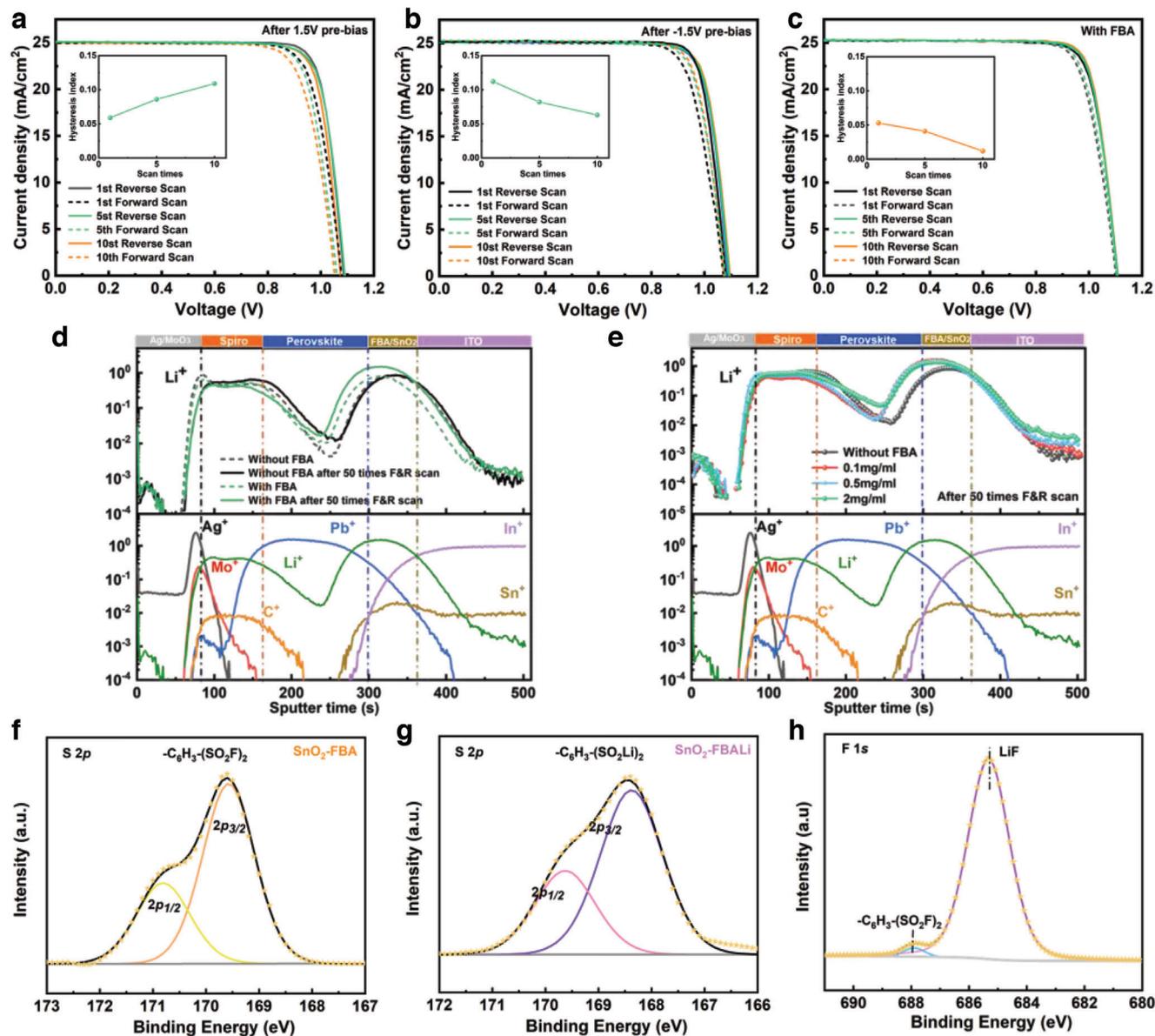
## 2.2. FBA Anchored Li<sup>+</sup> Ions

Another interesting phenomenon is that  $J$ - $V$  hysteresis was modulated by the FBA-modified SnO<sub>2</sub> shown in Figure 1c, and the pre-voltage bias is introduced to investigate this phenomenon. Figure 3a,b delivers the  $J$ - $V$  curve performance under different voltage bias conditions, including 1.5 V forward and 1.5 V reverse bias. Table 1 shows the related parameters, and the hysteresis index (HI) can be calculated as the following equation.<sup>[43]</sup>

$$HI = (PCE_{Reverse} - PCE_{Forward}) / PCE_{Reverse} \quad (4)$$

With a 1.5 V forward pre-bias, the device in the first scan condition shows the best performance after removing the bias. Moreover, with the increased number of scans,  $V_{OC}$  and FF decrease. On the other hand, with a 1.5 V reverse pre-bias, the device performance is improved with the number of scans. Figure 3c demonstrates the device performance with FBA after different scan times. With the increased number of scans, the FF of the forward direction scan shows an upward trend, and the reverse direction scan is stable. However, with the increasing scan times, the device performance with ITO/SnO<sub>2</sub>/PVSK/Spiro/MoO<sub>x</sub>/Ag structure is decreased. In terms of this issue, ion migration is usually considered the main reason for the hysteresis issue. Therefore, time-of-flight secondary ion mass spectrometry (ToF-SIMS) and XPS are used to detect the condition and concentration of each ion in the whole device. The SIMS results are shown in Figure 3d. As mentioned above, the change in Li<sup>+</sup> ion concentration is the most pronounced for the device with/without the FBA layer.

Additionally, the Li<sup>+</sup> ions accumulated in the interface and bulk of SnO<sub>2</sub> due to its high Li<sup>+</sup> affinity<sup>[44]</sup> and K<sup>+</sup> in the SnO<sub>2</sub> diffusion into the Spiro-OMeTAD layer provides intracellular ion equilibration.<sup>[23]</sup> For the original device, the concentration of Li<sup>+</sup> ions in the SnO<sub>2</sub> layer is unchanged concerning the device with 50 times forward and reverse scans. It is worth mentioning that a Li<sup>+</sup> ion peak at the interface between MoO<sub>x</sub> and Spiro layer is also observed for the pristine device, which disappeared after 50 forward and reversed scans, indicating Li<sup>+</sup> ion migration under the applied test voltage. However, using SnO<sub>2</sub>-FBA as the ETL, the concentration of Li<sup>+</sup> ions increases by approximately an order of magnitude after 50 times forward and reverse scans. Moreover, more Li<sup>+</sup> ions accumulated in the ETL and perovskite layer interface, indicating that the FBA molecular layer can anchor the Li<sup>+</sup> ions.



**Figure 3.** Reverse (solid) and forward (dash)  $J-V$  curves of the control group device after pre-bias poling, 1st, 5th, and 10th scans. a) 1.5 V pre-bias b) -1.5 V pre-bias. c) Reverse (solid) and forward (dash)  $J-V$  curves for the device with FBA passivation layer with 1st, 5th, and 10th scans. d) ToF-SIMS data of devices deposited on SnO<sub>2</sub> and SnO<sub>2</sub>-FBA ETLs; e) ToF-SIMS data of devices deposited on SnO<sub>2</sub>-FBA ETL with different FBA concentrations. XPS high-resolution spectra of f) SnO<sub>2</sub>-FBA and g) SnO<sub>2</sub>-FBALi. h) High-resolution XPS spectra of F 1s orbit for SnO<sub>2</sub>-FBALi ETL.

Moreover, we also investigated the influence of FBA concentration. As shown in Figure 3e, 0.1 mg ml<sup>-1</sup> is enough to anchor the Li<sup>+</sup> ions. On the other hand, we also used a negative ion gun to investigate the FBA layer (Figure S15, Supporting Information). From the ToF-SIMS results using a negative ion gun, S- and F-ions show a peak in the interface of SnO<sub>2</sub> and the perovskite layer. Moreover, by observing the characteristic elements of FBA, including SO<sup>-</sup>, SO<sub>2</sub><sup>-</sup>, and 34S at the interface between the SnO<sub>2</sub> and the perovskite layer, we show that FBA self-assembles on the SnO<sub>2</sub> surface. From these results, it can be concluded that for the device based on SnO<sub>2</sub> ETL, the Li<sup>+</sup> ions in the device could move back and forth across the whole device under different bias conditions, negatively influencing its performance.

However, for the device with the FBA passivation layer, Li<sup>+</sup> ions are anchored by the SnO<sub>2</sub>-FBA ETL, resulting in negligible hysteresis.

To further explore the FBA layer and its ability to anchor Li<sup>+</sup> ions, we fabricated two devices with Li-free HTL and Li-doped HTL. Then the electrodes, HTL, and perovskite layer are removed after 50 times forward and reverse scans. The XPS spectra of the residual SnO<sub>2</sub> ETL for each device are shown in Figure 3f,g. For the SnO<sub>2</sub>-FBA film, an extra peak could be observed at 169.6 and 170.8 eV in the S 2p orbit, indicating the 2p<sub>3/2</sub> and 2p<sub>1/2</sub> characteristic peak of the -C<sub>6</sub>H<sub>3</sub>-(SO<sub>2</sub>F)<sub>2</sub> group (S-F bonds).<sup>[45]</sup> However, the SnO<sub>2</sub>-FBA layer from LiTFSI doped device (SnO<sub>2</sub>-FBALi) film, due to Li<sup>+</sup> ions in HTL immigration, the S 2p<sub>3/2</sub>

**Table 1.** Photovoltaic parameters of PSCs based on SnO<sub>2</sub> under voltage bias and PSCs based on SnO<sub>2</sub>-FBA measured in both forward and reverse scan directions under AM 1.5 G illumination (100 mW cm<sup>-2</sup>).

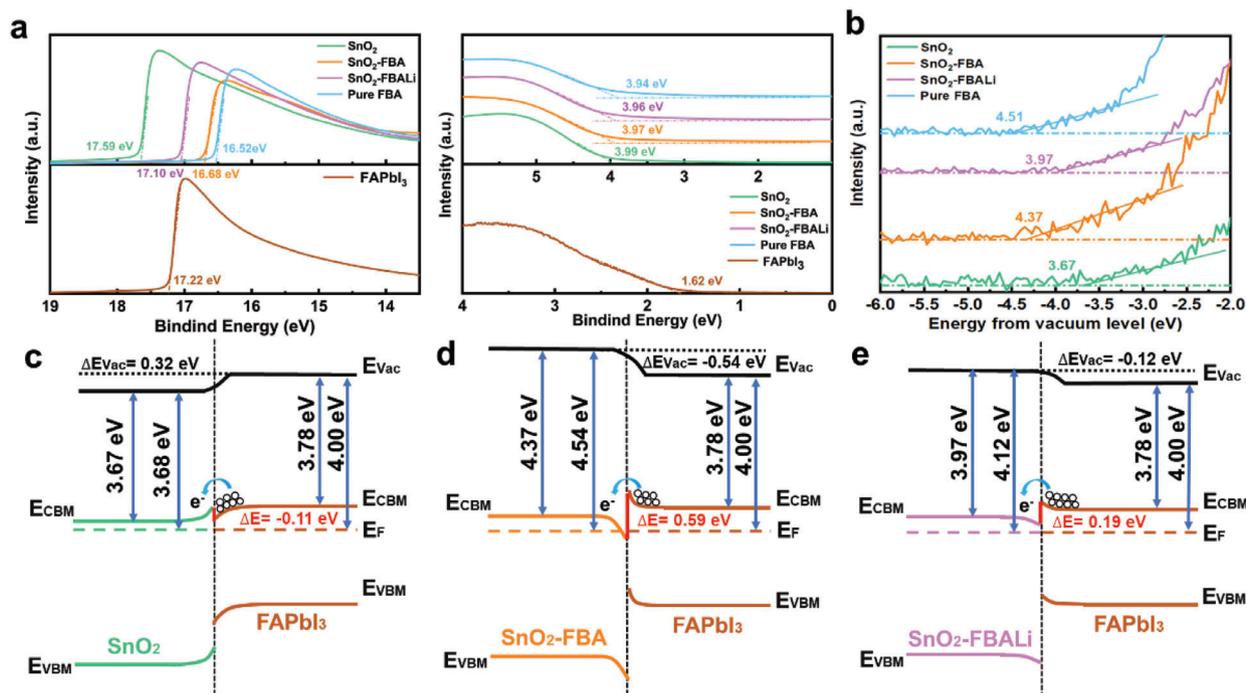
Test condition	Times	Scan direction	V <sub>oc</sub> [V]	J <sub>sc</sub> [mA cm <sup>-2</sup> ]	FF [%]	PCE [%]	HI
1.5 V bias	1 <sup>st</sup>	Forward	1.118	25.04	79.68	22.30	0.059
		Reverse	1.127	25.10	83.85	23.72	
	5 <sup>th</sup>	Forward	1.104	25.06	76.73	21.23	0.086
		Reverse	1.129	25.12	81.94	23.24	
	10 <sup>th</sup>	Forward	1.095	24.96	73.23	20.01	0.109
		Reverse	1.117	25.03	80.32	22.46	
-1.5 V bias	1 <sup>st</sup>	Forward	1.115	25.09	74.78	20.92	0.112
		Reverse	1.122	25.22	83.23	23.55	
	5 <sup>th</sup>	Forward	1.119	25.08	77.48	21.74	0.082
		Reverse	1.135	25.20	82.78	23.67	
	10 <sup>th</sup>	Forward	1.114	25.16	79.22	22.20	0.063
		Reverse	1.137	25.23	82.63	23.70	
With FBA	1 <sup>st</sup>	Forward	1.102	25.20	80.14	22.28	0.053
		Reverse	1.109	25.33	83.76	23.53	
	5 <sup>th</sup>	Forward	1.103	25.21	81.05	22.53	0.041
		Reverse	1.107	25.30	83.92	23.50	
	10 <sup>th</sup>	Forward	1.106	25.20	83.51	23.28	0.012
		Reverse	1.110	25.28	84.03	23.57	

characteristic peak moves to 168.5 eV, corresponding to -C<sub>6</sub>H<sub>3</sub>-(SO<sub>2</sub>Li)<sub>2</sub> formation.<sup>[46]</sup> Moreover, in Li 1s orbit and F 1s orbit (Figure S16, Supporting Information and Figure 3h), the peak at 55.7 and 685 eV could prove the formation of LiF<sup>[47]</sup> due to the bond energy of S-F (284 kJ mol<sup>-1</sup>) being far less than C-F (485 kJ mol<sup>-1</sup>).<sup>[48]</sup> Moreover, as shown in Figure 3c, the SnO<sub>2</sub>-FBALi layer is suitable for enhancing performance. The reason that SnO<sub>2</sub>-FBALi ETL becomes better after Li<sup>+</sup> ions are anchored could be analyzed from an energy band perspective. The work function and valence band can be obtained from the UV photoelectron spectroscopy (UPS) of the secondary electron cut-off and Fermi edge (Figure 4a). Generally, the band gap can be calculated from the Tauc-plots of the absorption data. However, due to the exciton binding energy, the optical gap is lower than the electrical bandgap. Hence, inverse photoemission spectroscopy (IPES) is used to accurately estimate the electron affinity (EA) of perovskite and each ETL, shown in Figure S17, Supporting Information and Figure 4b. From the IPES data, the EA of SnO<sub>2</sub>, SnO<sub>2</sub>-FBA, and SnO<sub>2</sub>-FBALi are 3.63, 4.37, and 3.97 eV, respectively. According to these results, the schematic description of the interface band bending of the ETLs and perovskite layer after contact are illustrated in Figure 4c–e. Because the EA of SnO<sub>2</sub> (3.67 eV) is lower than that of the perovskite layer (3.78 eV) before contact (Figure S18, Supporting Information), the CB of SnO<sub>2</sub> bends upwards, and the CB of the perovskite layer bends down when brought into contact. Hence, since the energy level offset  $\Delta E = E_{CB}^{FAPbI_3} - E_{CB}^{SnO_2} = -0.11$  eV, the energy loss will cause lower V<sub>oc</sub>. Furthermore, some electrons will be stuck at the interface leading to the possibility of increased interfacial recombination. However, for the other two ETLs, the situation is the opposite. For the SnO<sub>2</sub>-FBA ETL, the bending orientation is opposite compared to SnO<sub>2</sub> ETL, and  $\Delta E$  increases to +0.59 eV. This means that there will be a diffusion barrier for electrons at this interface. However, one

thing to note is that pure SnO<sub>2</sub>-FBA ETL is nonexistent in a real device since Li<sup>+</sup> ions will always be present due to spiro doping. When the Li<sup>+</sup> ions are anchored to the FBA, the  $\Delta E$  decreases from +0.59 to +0.19 eV, which would lower the energy loss for the electron transfer over this interface, thereby enhancing the V<sub>oc</sub> of the devices.

The calculated electrostatic potential (ESP) profile of FBA is demonstrated in Figure S19, Supporting Information. Due to the solid electron-withdrawing effect of the F atom, the two fluorosulfonyl group shows negative electrostatic potential value. Hence, when the carboxyl group passivated the SnO<sub>2</sub> layer, the FBA layer could act as an electric dipole layer. Thanks to the dipole interlayer, the vacuum level ( $E_{vac}$ ) of the electron energy band at the interface is dramatically shifted upwards illustrated in Figure S20, Supporting Information. Therefore, the work function of SnO<sub>2</sub>-FBA is enlarged. On the other hand, from UPS results, the work function of pure FBA is relatively large. Hence, the larger work function of the SnO<sub>2</sub>-FBA layer could strongly affect the charge carrier transport across the interface. Moreover, with Li<sup>+</sup> ions doped, the electron-withdrawing effect of the F atom is decreased leading to a smaller work function, which reduces the barrier of electron transportation.

Therefore, the appearance shown in Figure 3a,b could also be explained that when the device is on the 1.5 V forward pre-bias, Li<sup>+</sup> ions accumulate at the SnO<sub>2</sub> ETL layer, improving the built-in voltage. A lower built-in voltage means carriers are more difficult to extract since the electric field is lowered and possibly inverted.<sup>[49]</sup> On the other hand, a reverse pre-bias drives Li<sup>+</sup> ions away from the SnO<sub>2</sub> layer, and after removing the reverse pre-bias, the Li<sup>+</sup> ions will accumulate at the SnO<sub>2</sub> layer with more scans. Therefore, the performance of the devices is enhanced, and the hysteresis issues caused by Li<sup>+</sup> ions immigration are eliminated.



**Figure 4.** a) UPS spectra of secondary electron cut-off and valence bands of different ETL and perovskite layers. b) IPES spectra of SnO<sub>2</sub>, SnO<sub>2</sub>-FBA, and SnO<sub>2</sub>-FBALI. The schematic description of the interface band bending of c) SnO<sub>2</sub>/FAPbI<sub>3</sub>; d) SnO<sub>2</sub>-FBA/FAPbI<sub>3</sub>; and e) SnO<sub>2</sub>-FBALI/FAPbI<sub>3</sub> before and after contact. The shift of vacuum energy level ( $\Delta E_{\text{Vac}} = E_{\text{Vac}}^{\text{FAPbI}_3} - E_{\text{Vac}}^{\text{SnO}_2}$ ) and the energy difference between the CB of SnO<sub>2</sub> and FAPbI<sub>3</sub> ( $\Delta E = E_{\text{CB}}^{\text{FAPbI}_3} - E_{\text{CB}}^{\text{SnO}_2}$ ) are shown in these figures directly.

## 2.3. Performance of the PSCs with FBA Passivation Layer

### 2.3.1. Electric Properties of the PSCs with FBA Passivation Layer

A series of electrical characterizations were performed to elucidate further the possible mechanism responsible for the enhancement of  $V_{\text{OC}}$  and FF. The capacitance-voltage (C-V) measurements were also taken to evaluate the built-in potentials ( $V_{\text{bi}}$ ) of each device (Figure 5a). The  $V_{\text{bi}}$  is increased from 1.05 to 1.08 V for the device with FBA passivated layer. A higher  $V_{\text{bi}}$  is favorable for extracting charge carriers from the device.<sup>[50]</sup> Another noticeable feature in the Mott-Schottky (M-S) plots is  $C^{-2}$  of the FBA device is prominently higher than the control device, as would be expected when the FBA has anchored  $\text{Li}^+$  ions (chemical capacitance). Electrical impedance spectroscopy (EIS) also determined the charge transfer dynamics in PSCs (Figure 5b). The fitting results in Table S6, Supporting Information show that the device based on SnO<sub>2</sub>-FBA ETL offers considerably higher charge recombination resistance values ( $R_{\text{rec}}$ ) due to the reduced interfacial defect-assisted traps compared with the optimized device. The diode ideality factor is another good index to check the carrier recombination mechanism in the device. Figure 5c shows the plot of the  $V_{\text{OC}}$  versus the common logarithm of light intensity, and the light ideality factor ( $n$ ) can be calculated as follow.<sup>[51]</sup>

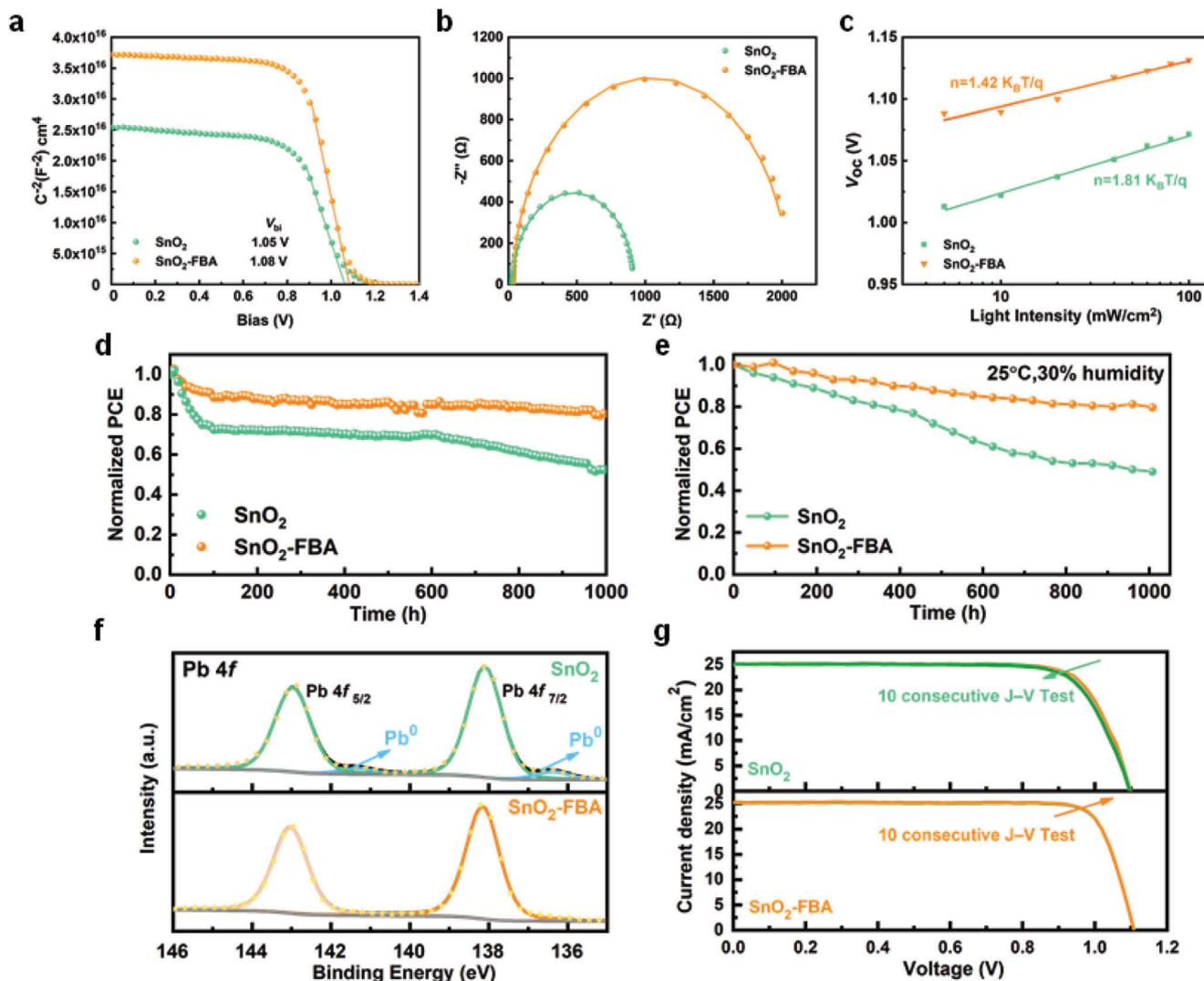
$$V_{\text{oc}} = \frac{nkT}{q} \ln \left( \frac{I_L}{I_0} + 1 \right) \quad (5)$$

Hence, the light ideality factor of the device based on SnO<sub>2</sub> and SnO<sub>2</sub>-FBA is 1.81 and 1.42, respectively, suggesting that

defect-assisted charge recombination is significantly reduced in the FBA-based device.

### 2.3.2. Stability Studies of the PSCs with FBA Passivation Layer

We also detected the stability of the devices based on SnO<sub>2</sub>-FBA. Figure 5d and Figure S21, Supporting Information show the operation stability of each type of device. Compared with the control devices, the devices with the FBA passivation layer offer better stability. After 1000 continuous working hours, the PCE still could maintain over 80% of its initial performance when using FBA as a passivation layer, while the control devices dropped to 60% of their initial PCE. Moreover, we could also observe an apparent burn-in phenomenon for FF and PCE of control group devices. However, this issue is significantly inhibited for the passivated devices due to eliminated  $\text{Li}^+$  ions migration, which is outside the scope of this paper and is discussed elsewhere.<sup>[27]</sup> Moreover, the air stability is also investigated and shown in Figure 5e. The unsealed FBA passivated device showed a noticeable increase in stability and retained more than 80% of the initial PCE after 1000 h, while the control device rapidly dropped to  $\approx 50\%$  of its initial value. To detect the fundamental reason for improving stability, XPS is used to inspect the state of the perovskite crystal. We also move the electrode and HTL of the aged device for each type of device and investigate the state of the perovskite layer. From the XPS spectrum of Pb 4f orbit (Figure 5f), the peak of Pb<sup>0</sup> in Pb 4f5/2 and Pb 4f7/2 orbit at  $\approx 141.5$  and 136.5 eV can be observed clearly for the control group device, illustrating that the chelation of  $-\text{SO}_2\text{F}$  indeed could make perovskite films stable



**Figure 5.** a) Mott–Schottky analysis at 1000 Hz, b) Electrical impedance spectroscopy (EIS) of PSCs, c)  $V_{oc}$  versus light intensity, and normalized averaged PCE of the corresponding devices in d) continuous operation condition; e) 25 °C, 30% humidity. f) XPS high-resolution spectra of perovskite layer after 1000 h operation test for corresponding devices. g) Continuous scanning stability of the device based on  $\text{SnO}_2$  and  $\text{SnO}_2$ -FBA.

and robust against moisture, light, and thermal stresses due to the undercoordinated  $\text{Pb}^{2+}$  or  $\text{Pb}$  clusters readily coordinates with S=O donating a pair of nonbonding electrons,<sup>[16]</sup> which consist with our DFT results. Finally, we also checked the stability of the devices under continuous scanning conditions (Figure 5g); the device with the FBA passivation layer shows excellent constant scanning stability compared with the control group device. Hence, it can be concluded that inhibiting ions migration is the main reason for eliminating hysteresis and improving continuous test stability. However, the decrease of defect density in the bulk and buried interface and the alignment of energy level are factors that cannot be ignored.<sup>[52]</sup>

### 3. Conclusion

In summary, we reported a hysteresis-free perovskite solar cell with a high PCE of 24.26% using a bridged molecule FBA. Firstly,

we find that FBA passivates the trap states on the  $\text{SnO}_2$  film surface and achieves energy level matching, thereby enhancing the electron extraction as seen through an increased surface recombination velocity  $S$ . This leads to better FF and increases  $V_{bi}$ . Secondly, the FBA adjusting the surface energy of the ETL substrates is profitable for forming high-quality perovskite film with enlarged grain size and reducing the defect density of perovskite films. Finally, the sulfonic fluoride groups anchor  $\text{Li}^+$  ions in the ETL, as demonstrated in the TOF-SIMS results and lower hysteresis phenomenon in the  $J$ – $V$  curves. Meanwhile, the devices with FBA interfaces also exhibited improved moisture and operational stability. The PCE of the device remained over 80% of initial values under prolonged operation in humidity, with a minimized burn-in phenomenon. Li-TFSI is commonly used in high-performance n-i-p devices as an additive in the HTL. Hence, understanding the effect of the diffusion of  $\text{Li}^+$  helps design and fabricate high-performance and hysteresis-free PSCs.

## 4. Experimental Section

**Materials:**  $\text{PbI}_2$ , formamidinium iodide (FAI), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), pyridine, 4-(1,1-dimethylethyl)-(t-BP), and Spiro-OMeTAD were purchased from Xi'an Polymer Light Technology Corp. Dimethylformamide (DMF, purity > 99%), dimethyl sulfoxide (DMSO, purity > 99%), isopropanol (IPA, purity > 99%) and chlorobenzene (CB, purity > 99%) were purchased from J&K scientific. The  $\text{SnO}_2$  colloid solution (tin (IV) oxide, 15 wt% in water) was purchased from Alfa Aesar, and the 3,5-bis(fluorosulfonyl)benzoic acid (FBA) was purchased from Aladdin (99.9%).

**Instruments and Characterization:** Solar cells' current  $J$ - $V$  characteristics were measured with a Keithley 2400 source meter in an  $\text{N}_2$  glove box under a simulated sun AM 1.5 G (Newport VeraSol- 2 LED Class AAA Solar Simulator) using a mask with  $0.0625 \text{ cm}^2$ . SEM images were gained by a field-emission scanning electron microscope (S-4800) under an accelerating voltage of 10 kV. The atomic force microscopy images of the films of  $\text{SnO}_2$  were studied using a Veeco Dimension 3100 instrument at the ambient temperature in tapping mode. The X-ray and UV photoelectron spectroscopy (XPS and UPS) measurements were conducted at a PHI 5000 Versaprobe system. The electrochemical impedance spectra were measured using an Autolab electrochemical workstation (Autolab PGSTAT 302N, Metrohm Autolab B.V.). The absorption curves of the sample were analyzed by UV-vis spectrometer (Lambda 750, PerkinElmer). PL and time-resolved photoluminescence (TRPL) of solar cells were tested by a home-built defects imaging system (LBIC). The time-of-flight secondary ion mass spectrometry (TOF-SIMS 5-100) was measured with the pulsed primary ions from a Cs+ (2 keV) liquid-metal ion gun for sputtering and a Bi+ pulsed primary ion beam for analysis (30 keV). EIS and M-S measurements were carried out on the electrochemical workstation (PGSTAT302N). The EIS measure conditions were under dark and applied bias at open voltage. The frequency range is 0.1 Hz–10 MHz. The M-S plot measurement conditions were determined to be a 10 kHz frequency. Operational stability of the cells was performed on a multi-channel solar cell performance decay testing system ((PVL-G8001M, Suzhou D&R Instruments Co. Ltd.) inside an  $\text{N}_2$ -filled glove box ( $\text{H}_2\text{O} < 10 \text{ ppm}$ ,  $\text{O}_2 < 10 \text{ ppm}$ ), and the cells were illuminated with a white LED light (D&R Light, L-W5300KA-150, Suzhou D&R Instruments Co. Ltd.) at a simulated one sun intensity (the initial short current equals to the JSC measured under standard condition). The cell's performance was measured by  $I$ - $V$  sweeping from 1.2 to  $-0.2 \text{ V}$ , with a step of  $0.02 \text{ V}$ . The temperature was set at  $25 \text{ }^\circ\text{C}$ . The cells' current  $J$ - $V$  characteristics were measured periodically, and the maximum power output point (MPP) was calculated automatically. An external resistor that matches the MPP point ( $R = I_{\text{max}}/V_{\text{max}}$ ) was then attached to the cells in between  $J$ - $V$  sweepings according to the  $J$ - $V$  sweeping results so that the recorded PCE decay curves directly reflect the performance decay of the cells under the simulated operational situation.

**Preparation of the Solution:** The  $\text{SnO}_2$  colloid solution (15 wt%) was diluted to the concentration of 3 wt% by deionized water. The FBA solution was prepared by dissolving 0.1 mg FBA into 1 ml IPA. The FAPb $_3$  precursor solution was prepared as in the previous work.<sup>[53]</sup> The OAI solution was prepared by dissolving 5 mg OAI into 1 ml IPA. The Spiro-OMeTAD solution was prepared by dissolving 72.3 mg Spiro-OMeTAD into 1 ml CB followed by the addition of 17.5  $\mu\text{L}$  Li-TFSI (520 mg  $\text{mL}^{-1}$  in acetonitrile) and 29  $\mu\text{L}$  t-BP. Both OAI and Spiro-OMeTAD were stirred overnight at room temperature in the glove box.

**Solar Cell Fabrication:** ITO glass was cleaned by ultrasonic cleaning through detergent, DI water, acetone, and isopropanol for 30 min, respectively. Before use, the ITO substrate was cleaned with UV Ozone for 30 min. Then the substrate was spin-coated with a thin layer of  $\text{SnO}_2$  nanoparticles from the  $\text{SnO}_2$  colloid solution at 4000 rpm for 30 s with an accelerated speed of 2000 rpm. Then the substrate was annealed in ambient air at  $150 \text{ }^\circ\text{C}$  for 30 min.

For the FBA passivation layer, the FBA solution was coated on the  $\text{SnO}_2$  layer with 5000 rpm for 30 s. Then the films were annealed at  $90 \text{ }^\circ\text{C}$  for 10 min.

For FAPb $_3$  active layer, the spin rate of this step is 5000 rpm for 30 s with an accelerated speed of 5000 rpm. During the end of 10–12 s, 300  $\mu\text{L}$  of

CB was drop-coated to treat the perovskite films, and then the perovskite films were annealed at  $150 \text{ }^\circ\text{C}$  for 15 min and  $100 \text{ }^\circ\text{C}$  for 15 min. Then the film was washed with IPA by dropping several drops at 3000 rpm and heated at  $100 \text{ }^\circ\text{C}$  for 1 min.

After cooling to room temperature, the OAI solution was coated on perovskite films at 5000 rpm for 30 s with an accelerated speed of 5000 rpm. Then the spiro-OMeTAD solution was coated at 3000 rpm for 30 s with an accelerated rate of 3000 rpm.

Finally, 8 nm thick  $\text{MoO}_x$  and 80 nm thick Ag were deposited on the spiro-OMeTAD film by thermal evaporation with the rate of  $0.3$  and  $2 \text{ } \text{\AA} \text{ s}^{-1}$ .

**DFT Calculations:** All calculations were carried out using the projector augmented wave method in the density functional theory framework (DFT) framework, as implemented in the Vienna ab-initio simulation package (VASP). The generalized gradient approximation (GGA) and Perdew–Burke–Ernzerhof (PBE) exchange functional were used. The plane-wave energy cut-off was set to 500 eV, and the Monkhorst–Pack method was employed for the Brillouin zone sampling. The convergence criteria of energy and force calculations were set to  $10^{-5} \text{ eV per atom}$  and  $0.01 \text{ eV } \text{\AA}^{-1}$ , respectively. To explore the interactions between the organic molecule and  $\text{SnO}_2$  or FAPb $_3$  surfaces, including  $\text{SnO}_2$  (110) or FAPb $_3$  (001), the binding energies of the organic molecule on the  $\text{SnO}_2$  or FAPb $_3$  surfaces were calculated. The  $\text{SnO}_2$  surface model was built by the  $2 \times 2$  supercell of  $\text{SnO}_2$  (110), and the FAPb $_3$  surface model was built by the  $2 \times 2$  supercell of FAPb $_3$  (001). A vacuum region of  $15 \text{ } \text{\AA}$  is applied to avoid interactions between the neighboring configurations. The DFT-D2 method accounted for the vdW interactions between the organic molecule and metal surface.<sup>[54]</sup> Here, the binding energies ( $E_b$ ) were calculated by the energy difference of the system after and before binding:<sup>[55]</sup>  $E_b = E(\text{molecule-slab}) - E(\text{molecule}) - E(\text{slab})$ , where  $E(\text{molecule-slab})$ ,  $E(\text{molecule})$  and  $E(\text{slab})$  represent the DFT energies of the molecule adsorbed surface, the energy of an isolated molecule, and the energy of the clean  $\text{SnO}_2$  or FAPb $_3$  surface, respectively.

## 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.

## Author Contributions

L.Y. designed the experiment, fabricated the perovskite solar cells, analyzed the data, and wrote the original draft. C.D. and H..W. helped to analyze the energy level alignment. C.L. helped to design the experiment. L.Z.

contributed to SEM images. W.Z. and X.G. helped to analyze the DFT and electrostatic potential data. Y.L. contributed to PL data fitting. C.D. and Y.H. contributed to EIS data analysis. H.L. contributes to the SFG analysis. I.Z.M., E.G.L., L.Y., R.Ö., S.W., and C.Z. contribute to the revision of the original manuscript. L.Y., with the help of C.Z., E.G.L., and C.M., designed the experiment and wrote the manuscript. All authors contributed to the interpretation and discussion of the results.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Keywords

high moisture and operation stability, hysteresis-free, Li<sup>+</sup> ion migration, multifunctional molecular bridging layers

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