

# Multifunctional Ion-Lock Interface Layer Achieved by Solid–Solid Contact Approach for Stabilizing Perovskite Solar Cells

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It has been a hindering issue in perovskite solar cells that the interfaces between the perovskite and charge transport layers show significantly high concentrations of defects with an amount about 100 times more than inside the bulk perovskite layer. The issue causes substantial reduction in both the efficiency and stability of the devices. Herein, a solid–solid contact approach is demonstrated to realize a multifunctional ion-lock layer with strong chemical interaction to the perovskite layer. The multifunctional ion-lock layer remarkably suppresses the interface defects and tunes the work function, contributing to promoting the carrier extraction, increasing the open-circuit voltage, and enlarging the photocurrent. In addition, the multifunctional ion-lock layer successfully locks ions from movement and thus improves the stability of the devices. Finally, with a multifunctional ion-lock layer, the perovskite solar cells deliver an efficiency of up to 23.13% along with desirable long-term operational, storage, and humidity stability. Consequently, the work offers guidelines for establishing defect-suppressed interfaces between perovskites and hole transport layers.

## 1. Introduction

Metal halide perovskites (MHPs) have emerged as revolutionary semiconductors because of their excellent photophysical properties including high absorption coefficients, long carrier

diffusion lengths, high defect tolerance, and low-cost solution processing.<sup>[1–3]</sup> Particularly, perovskite solar cells (PSCs) have delivered a record certified power conversion efficiency (PCE) up to 25.5%, rivaling polycrystalline silicon solar cells.<sup>[4–7]</sup> Despite these notable results, the operational stability of PSCs is still a grand challenge to hinder their commercial applications. More efforts are needed to make devices more stable while not compromising the performance of PSCs.

The interfaces between perovskite and carrier transport layers (CTLs) play a vital role in the performance and stability of PSCs. Because of the soft crystal lattice properties of perovskites and high concentrations of interface defects (about 100 times that within the perovskite layer), the damage of perovskite normally initializes at the surface under external stimuli con-

ditions including electric fields, moisture, oxygen, heat, and illumination.<sup>[8–13]</sup> For example, the high deliquescent lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) in the hole transport layer based on 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene can easily absorb water to accelerate the hydrolysis of the underneath perovskite layer.<sup>[14–21]</sup> Moreover, abundant defects at interfaces will inherently favor ion migration arising from trap-induced fields, resulting in the deterioration of both organic CTLs and perovskite layers.<sup>[22,23]</sup> Hence, it is necessary to tailor a special interface layout to make outstanding improvements in defects passivation and ions permeation, unlocking the full potential of PSCs.<sup>[24]</sup> The majority of currently reported works focus on the surface traps passivation by organic-based solution post-treatment method. These works typically pay more attention to the chemical passivation of surface defects/traps but are rarely involved in the suppression of ion migration between different layers.<sup>[14,15,25–28]</sup> Moreover, the solution post-treatment method strongly relies on the solvent (usually chlorobenzene or isopropanol) that will dissolve and destroy the perovskite and cause an insurmountable constraint to the development of more efficient interface layers.

In this study, we propose a solid–solid contact (SSC) strategy to form a thin sulfonated tetrafluoroethylene-based fluoropolymer-copolymer (Nafion) multifunctional ion-lock layer, which not only reduces the surface defects of perovskite but also suppresses serious ion migration at interfaces. The

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Nafion film firstly forms on the Si/SiO<sub>2</sub> substrate and then laminates on the top of perovskite film with annealing at 100 °C for 2 min, which avoids solvent damage to the perovskite films. Through solid-state contact transfer, an ultra-thin Nafion multifunctional ion-lock interfacial layer is formed on the surface of perovskite. The strong chemical interaction between metal cations and Nafion can eliminate the surface defects/traps of perovskite to improve carrier dynamics. Moreover, the dense Nafion acts as an ion-lock layer to lock the movement of ions between perovskite and CTLs. Finally, the PSCs with Nafion multifunctional ion-lock interface layer show a high power conversion efficiency of 23.13% with excellent humidity and operational stability.

## 2. Results and Discussion

Figure 1a shows the chemical structure of Nafion composed of perfluorovinyl ether groups terminated with sulfonate groups onto a tetrafluoroethylene backbone, which features with abundant fluorine (-F) atoms. Considering the solvent-induced degradation concerns of forming Nafion film from its water-based solution on perovskite active layer of PSCs, an SSC strategy is successfully developed to achieve an ultra-thin Nafion layer on the surface of FA<sub>0.92</sub>Cs<sub>0.08</sub>PbI<sub>3</sub> perovskite (denoted as FA<sub>0.92</sub>Cs<sub>0.08</sub>PbI<sub>3</sub>/Nafion) (Figure 1b). The Nafion film is firstly formed on the Si/SiO<sub>2</sub> substrate and then stacked on the surface of FA<sub>0.92</sub>Cs<sub>0.08</sub>PbI<sub>3</sub> film with heating at 100 °C for 2 min.

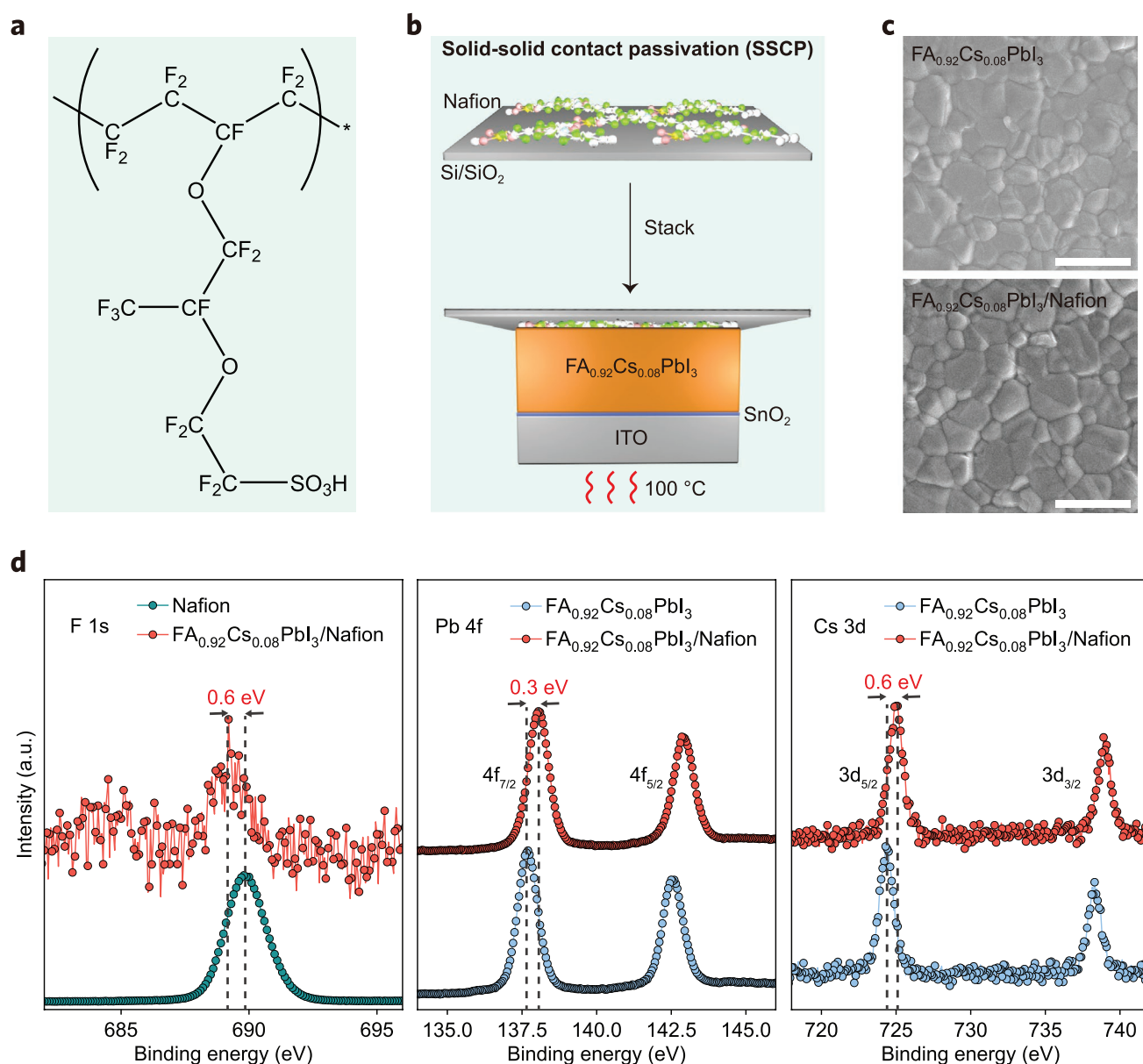


**Figure 1.** a) Molecular structure of Nafion. b) Schematic of solid–solid contact passivation strategy. c) Top-view SEM images of pristine perovskite and with Nafion surface modification. The scale bar is 200 nm. d) High-resolution XPS spectra of F 1s, Pb 4f, and Cs 3d of pristine perovskite and perovskite with Nafion modification films.

Through the solid-state contact transfer, an ultra-thin Nafion film forms on the surface of perovskite, confirmed by F 1s X-ray photoelectron spectroscopy (XPS) signal on the surface of  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$  (Figure 1d). Based on these Nafion-modified perovskites as light absorber layers, we fabricate PSCs with a configuration of glass/ITO/electron-transport layer/perovskite/hole-transport layer/Au. All  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ /Nafion-based PSCs except for excessive Nafion modification exhibit improved device efficiency compared with the  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$  ones (Figure S1 and Table S1, Supporting Information). Notably, the device based on perovskite film covered with blank Si/SiO<sub>2</sub> with the same heating condition has also been fabricated and studied to exclude the effect from the Si/SiO<sub>2</sub> substrate. Our results show that the process with blank Si/SiO<sub>2</sub> makes no difference to the device performance of the control PSCs without any Nafion. Considering that the Nafion at 0.5 wt.% concentration provides the optimal photovoltaic (PV) performance, we then choose the case of  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$  modified by 0.5 wt.% Nafion for detailed investigations on the effect of Nafion on the perovskite film and device performance.

Structural, spectral, and surface chemical state characterizations show that the introduction of the Nafion multifunctional ion-lock layer can strongly interact chemically with  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$  but shows few effects on the morphology and bandgap of  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ . The X-ray diffraction (XRD) results indicate that the introduction of Nafion layer exhibits a neglected effect on the crystalline of  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$  (Figure S2, Supporting Information).<sup>[29]</sup> Both  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$  and  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ /Nafion films show dense morphologies with similar size, as confirmed by scanning electron microscope (SEM) results (Figure 1c). Additionally,  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$  and  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ /Nafion films show similar bandgap ( $\approx 1.53$  eV), as proved by the UV–Vis results (Figure S3, Supporting Information). Then, XPS is conducted to characterize the top surface chemical state to determine the interaction between Nafion and  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ . Compared to  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ , the peaks related to Pb 4f and Cs 3d in the  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ /Nafion show 0.3 eV and 0.6 eV shift to high binding energy, respectively, while the peak assigned to F 1s from Nafion shows 0.6 eV shift to low binding energy (Figure 1d). The binding energy shift of Pb 4f, Cs 3d, and F 1s core levels confirm the strong interaction among the abundant higher electronegativity halogen (F) of Nafion and lower electronegativity Cs and Pb in  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ .<sup>[30]</sup> This strong interaction could passivate uncoordinated  $\text{Pb}^{2+}$ , which induces deep trap states that severely degrade both PCE and long-term stability of PSCs.

We further study the photoluminescence (PL) and transient absorption (TA) of  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$  with Nafion layer on the surface. The PL intensity of  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ /Nafion film is much stronger than that of pure  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$  film (Figure S4a, Supporting Information). In addition, the time-resolved PL (TRPL) spectra in Figure S4b (Supporting Information) show that the PL lifetime ( $\tau$ ) of  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ /Nafion (178.58 ns) is much longer than that of  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$  (112.12 ns) (Table S2, Supporting Information). The enhanced PL intensity and improved PL lifetime indicate that we successfully passivate the surface defects and thus significantly suppress non-radiative recombination in  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ /Nafion arising from the introduction of Nafion, attributing to decreased trap densities.

Transient absorption spectra (TAS) measurement was conducted to explore the ultrafast charge transfer process and recombination mechanism in perovskite films. Figure 2a,b show the contour maps of TAS and femtosecond TA spectroscopy in the range of 2 ps to 800 ps of  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$  and  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ /Nafion films, respectively. Compared to  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ ,  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ /Nafion film shows a much slower decay ratio, in which  $\Delta A$  decreases to 16.7% at 800 ps for pristine  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ , while a higher ratio of 40.4% for  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ /Nafion is achieved during the same time. Figure 2c shows the transition dynamics of decay time. By using the biexponential kinetic model as described in the experimental section to fit the TAS results of pristine  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$  film at 778 nm, we obtain a short time constant of 7.2 ps and a long time constant of 353.2 ps. On the contrary, a much slower decay kinetic process with a short time constant of 14.5 ps and a long time constant of 565.8 ps are fitted for  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ /Nafion film. Figure 2d further simply exhibits the possible ultrafast exciton trapping and recombination process. Upon being excited with a high-energy photon, the generated electron will transit to the conduction band, which rapidly decays to the conduction band edge to form a free carrier. The formed free carrier can recombine directly leading to radiative recombination followed by photon emission or is trapped by trap states from defects into non-radiative recombination without emission. The process of cooling for hot exciton occurs in a very short time. Therefore, the fitted short lifetime belongs to the trapping of excitons and the long lifetime can be assigned to band edge exciton recombination.<sup>[31–33]</sup> The longer lifetime indicates a lower density of surface defect states after being passivated by Nafion, which is direct evidence that the non-radiative recombination is suppressed in  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ /Nafion film compared to pristine  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$  film.

Ultraviolet photoelectron spectroscopy (UPS) results confirm that the introduction of Nafion is beneficial to the extraction of charge carriers. The UPS and valence band spectra results are shown in Figure S5 (Supporting Information) and the energy level alignment at the top interface is shown in Figure S6 (Supporting Information). Compared with  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$  film, the work function of  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ /Nafion film increases from 4.24 to 4.39 eV. The increased work function can enhance the built-in electric field to promote carrier transport and benefit to promote PV high performance.<sup>[34]</sup>

Benefiting from the advantages of the introduced Nafion interface layer,  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ /Nafion-based device with the configuration of glass/ITO/SnO<sub>2</sub>/perovskite/Nafion/Spiro-OMeTAD/Au (Figure S7, Supporting Information) shows much-enhanced PV performance compared with the device without Nafion interface layer. The champion  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ /Nafion based device achieves a PCE of 23.13%, with an open-circuit voltage ( $V_{oc}$ ) value of 1.135 V, a fill factor ( $FF$ ) of 80.9%, and a short-circuit current density ( $J_{sc}$ ) of 25.19 mA cm<sup>−2</sup> (Figure 3a; Table S3, Supporting Information), which is much higher than that of  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$  based device (20.69%) with a  $V_{oc}$  value of 1.052 V, a  $FF$  of 80.1%, and a  $J_{sc}$  of 24.55 mA cm<sup>−2</sup>. Moreover, the  $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ /Nafion-based devices also show lower hysteresis (Figure S8, Supporting Information) and good reproducibility (Figure 3b). By keeping the bias near about the maximum power point (MPP), the stabilized output PCEs are

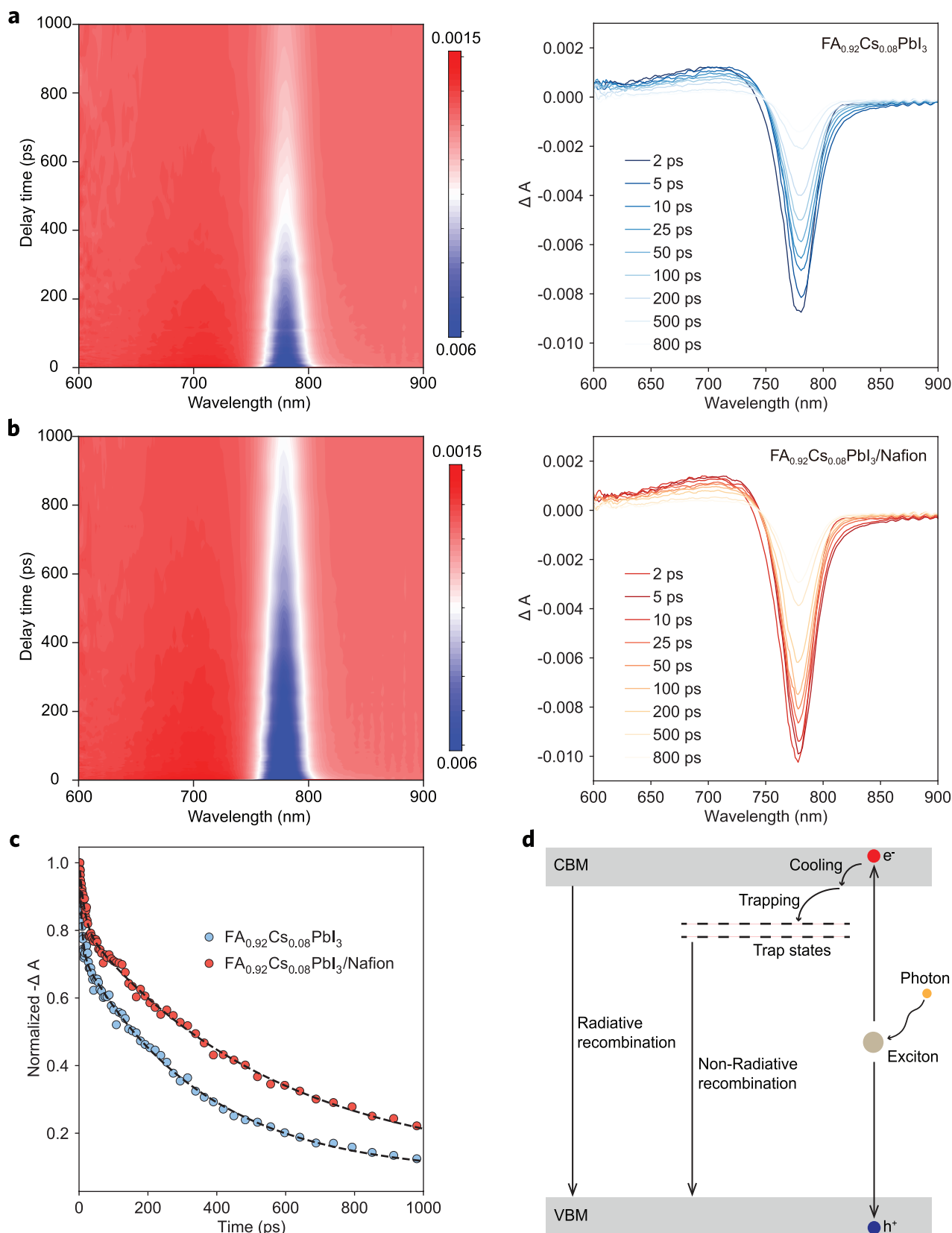


**Figure 2.** a) 2D TA contour map and TA spectra of pristine perovskite film at the denotative delay times. b) 2D TA contour map and TA spectra of perovskite film with Nafion surface passivation at the denotative delay times. c) Decay of the bleaching signal of perovskite film without and with Nafion surface passivation at the wavelength 776 nm. d) Schematic diagram of possible exciton trapping and recombination processes.

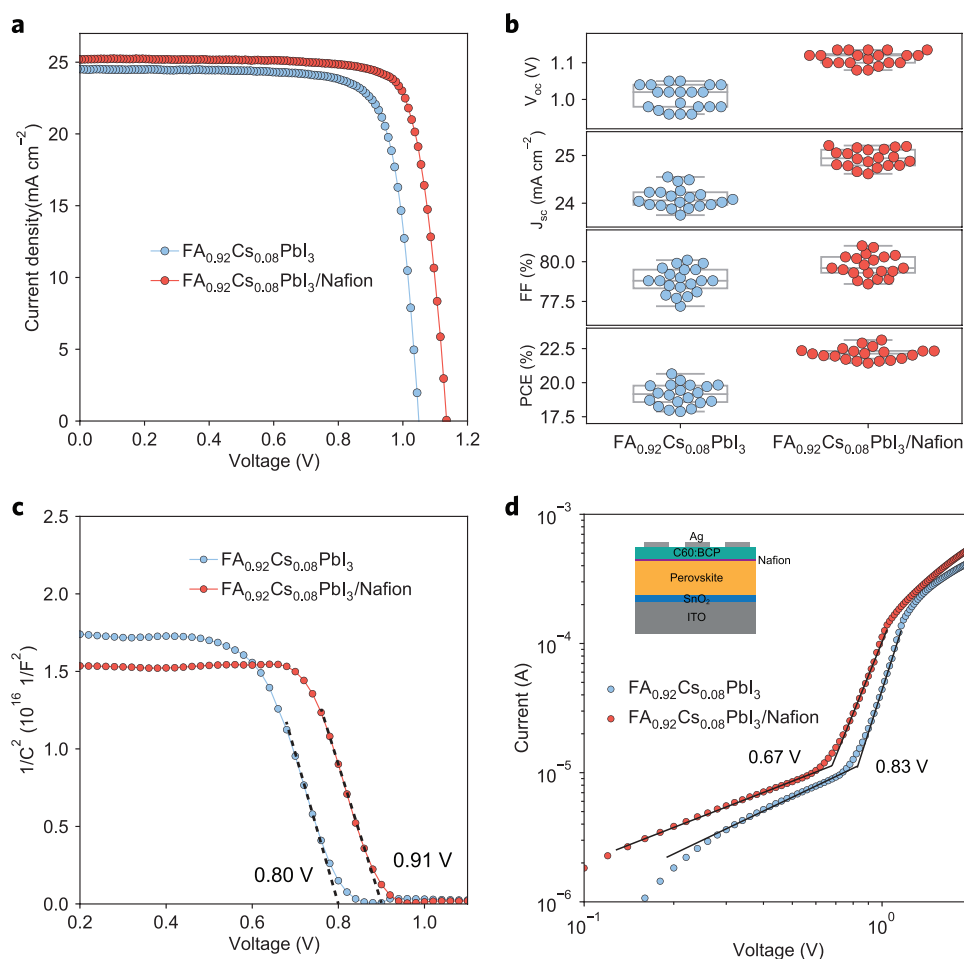


**Figure 3.** a) *J*-*V* curves of PSCs without and with Nafion interface layer with reverse scans. b) Photovoltaic parameter statistics of PSCs without and with Nafion interface layer. c) MS results of the devices without and with Nafion interface layer. d) Space-charge-limited current (SCLC) characteristics of the electron-only devices. The inset showing the structure of devices.

estimated to be 22.97% and 19.77% for FA<sub>0.92</sub>Cs<sub>0.08</sub>PbI<sub>3</sub>/Nafion based device and FA<sub>0.92</sub>Cs<sub>0.08</sub>PbI<sub>3</sub> based device, respectively, which are in good agreement with the PCEs obtained from *J*-*V* measurements (Figure S9, Supporting Information). Furthermore, as shown in Figure S10 (Supporting Information), the integrated photocurrent from external quantum efficiency (EQE) spectra are 24.54 mA·cm<sup>-2</sup> for FA<sub>0.92</sub>Cs<sub>0.08</sub>PbI<sub>3</sub>/Nafion based device and 23.77 mA·cm<sup>-2</sup> for FA<sub>0.92</sub>Cs<sub>0.08</sub>PbI<sub>3</sub> based device, which is consistent with the *J*<sub>sc</sub> derived from the *J*-*V* measurements.

Mott-Schottky (M-S) measurement is performed to identify the increased built-in electric field, contributing to enhancing the carrier extraction to obtain higher *J*<sub>sc</sub> (Figure 3c). The FA<sub>0.92</sub>Cs<sub>0.08</sub>PbI<sub>3</sub>/Nafion based device demonstrates an increased built-in electric field (*V*<sub>bi</sub>) of 0.91 V, compared with 0.80 V of pristine FA<sub>0.92</sub>Cs<sub>0.08</sub>PbI<sub>3</sub> based device. In addition, the electrochemical impedance spectroscopy (EIS) measurement is also adopted to reveal the potential carrier transport behaviors in the PSCs. Figure S11 (Supporting Information) shows the Nyquist plots of the devices without and with Nafion interface layer under dark conditions and the inset represents the equivalent circuit. The lower charge transport resistance (*R*<sub>ct</sub>) and higher

charge recombination resistance (*R*<sub>re</sub>) in devices with Nafion interface layer show the enhanced charge transport, as well as the reduced carrier recombination.

The suppressed non-radiative recombination in the FA<sub>0.92</sub>Cs<sub>0.08</sub>PbI<sub>3</sub> device is consistent with the above photophysical measurements on the films, which indicate that the Nafion introduction can reduce the defects/traps. As shown in Figure 3d, the device with the introduced Nafion layer demonstrates a notable decrease of trap-filled limit voltage (*V*<sub>TFL</sub>) (0.67 V) in space charge limited current (SCLC) measurements, which is linearly proportional to the trap-state density, compared with that of pristine FA<sub>0.92</sub>Cs<sub>0.08</sub>PbI<sub>3</sub> based device (0.83 V).<sup>[35]</sup> Similarly, the linear relationship between *J*<sub>sc</sub> and irradiated light intensity indicates the effective carrier transport and negligible bimolecular recombination in both devices (Figure S12a, Supporting Information). Ideality factor reflects the trap-assisted non-radiative recombination (Figure S12b, Supporting Information). Here, FA<sub>0.92</sub>Cs<sub>0.08</sub>PbI<sub>3</sub>/Nafion device exhibits a slightly less steep slope (1.14 *kT*/*q*) than that of pristine devices (1.43 *kT*/*q*), indicating less trap-assisted recombination.<sup>[36]</sup>

In addition, to improve PV performances, the FA<sub>0.92</sub>Cs<sub>0.08</sub>PbI<sub>3</sub>/Nafion-based devices with the configuration

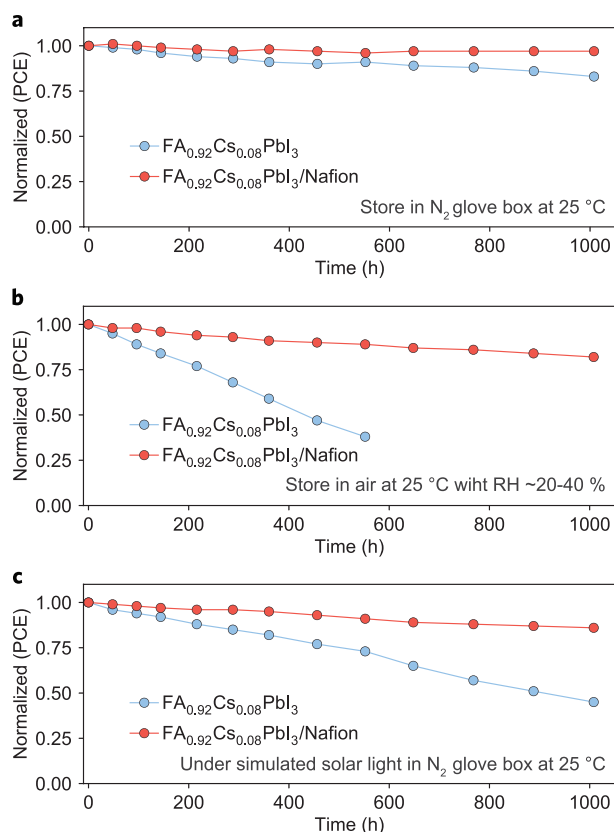


**Figure 4.** a) Stability testing stored in  $N_2$  glove box at ambient temperature. b) Stability testing stored in air at ambient temperature with RH  $\approx 20\text{--}40\%$ . c) Stability testing under simulated solar light in  $N_2$  glove box at ambient temperature.

of glass/ITO/ $SnO_2$ /perovskite/Nafion/Spiro-OMeTAD/Au also exhibit enhanced stability. Compared with the  $FA_{0.92}Cs_{0.08}PbI_3$  based devices, the unencapsulated  $FA_{0.92}Cs_{0.08}PbI_3$ /Nafion based devices show improved stability and retain 97% of their initial efficiency for over 1000 h storage in  $N_2$  glove box and 82% in the air environment, while  $FA_{0.92}Cs_{0.08}PbI_3$  based devices drop to 83% and 38% (Figure 4a,b). We also study the operational stability of the PSCs by exposing unsealed devices to full-sun illumination in  $N_2$  glove box (Figure 4c). After a 1000 h test, the  $FA_{0.92}Cs_{0.08}PbI_3$ /Nafion devices retain over 86% of their initial efficiency, while the control devices only maintain 45% of their initial efficiency.

To probe the effect of the top Nafion interface layer for the stability of devices, we have carried out the time-of-flight secondary-ion mass spectrometry (ToF-SIMS) and obtained the depth profiles of FA, Cs, and Pb ions based on the unencapsulated devices. Figure 5a shows that the  $Pb^{2+}$  and  $Cs^+$  signals shift toward the Au electrode through the HTL for the aged PSCs under the accelerated condition (85 °C) for 24 h in  $N_2$  glove box without top Nafion interface layer, indicating that the perovskite films can easily release the metal and ammonium cations under such an aggressive aging condition, resulting in ions diffusion into other layers.<sup>[15,37]</sup> Encouragingly, the introduction of Nafion ion-lock layer successfully locks  $Cs^+$  or  $Pb^{2+}$  cations escape from the perovskite layer, arising from the strong F-M ( $M = Pb^{2+}$  and  $Cs^+$ ) chemical

interaction and absorption of terminal sulfonate groups of Nafion for metal cations (Figure 5b and c).<sup>[16,17]</sup> Abundant F groups of Nafion will also interact with  $FA^+$  by formation of hydrogen bond (N–H...F). Such interaction and absorption of metal ions is a much more effective and sustainable process for long-term practical applications. Additionally, the  $FA_{0.92}Cs_{0.08}PbI_3$ /Nafion film shows a higher contact angle for a water droplet compared with that of  $FA_{0.92}Cs_{0.08}PbI_3$ , indicating the better water resistance (Figure 5c). This enhanced hydrophobic helps protect perovskite from the attack of moisture, further improving the stability of perovskite, as confirmed by XRD results in Figure S13 (Supporting Information).<sup>[38]</sup>

### 3. Conclusion

We have developed an effective solid–solid contact strategy to construct a multifunctional ion-lock layer on the surface of perovskite. The introduction of Nafion ion-lock layer passivates surface traps of perovskite and increases the built-in electric field at the interface, contributing to an improved  $J_{sc}$  and  $V_{oc}$ . Moreover, the hydrophobic and ion obstruction of Nafion interlayer can lock  $Cs^+$  and  $Pb^+$  from ion migration, resulting in improved stability of PSCs. Finally, the  $FA_{0.92}Cs_{0.08}PbI_3$ /Nafion-based devices achieve a remarkably improved efficiency of 23.13% as well as improved humidity, thermal and operational stability. We anticipate that constructing ion-lock by SSC strategy will not only be a step forwards for developing more efficient perovskite photovoltaics but also enlighten to fabricate perovskite heterojunction devices with other materials in other research areas.

### 4. Experimental Section

**Materials:** All the raw chemicals were used as received from commercial companies, including Formamidinium iodide (FAI) and Methylammonium chloride (MACl) were purchased from GreatCell Solar (Australia). Lead (II) iodide ( $PbI_2$ , 99.999%), Cesium iodide ( $CsI$ , >99%) and 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD, 99.86%) were purchased from Advanced Election Technology Co., Ltd in China. Dimethylformamide (DMF, 99.8%), dimethylsulfoxide (DMSO, 99.9%), chlorobenzene (CB, 99.9%), acetonitrile (ACN, 99.8%), ethanol, acetone, 4-tert-butyl pyridine (tBP, 96%), Tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) tri[bis(trifluoromethane)sulfonimide] (FK 209 Co(III)TFSI, 99.95%) salt, Bis(trifluoromethane)sulfonimide lithium salt (Li-TFSI, 99.95% trace metals basis) and Nafion117 solution (5 wt.% in mixture of lower aliphatic alcohols and water, Du Pont) were purchased from Sigma-Aldrich. Tin Oxide ( $SnO_2$ ) colloidal solution (15 wt.% in  $H_2O$  colloidal dispersion) was purchased from Alfa Aesar.

**Device Fabrication:** Indium tin oxide (ITO) glass substrates were sequentially washed by detergent, deionized water, acetone, and anhydrous ethanol for 20 min, respectively. Then, the ITO glasses were dried by a nitrogen gas gun and treated with Ultraviolet-Ozone (UV-Ozone) for 30 min. The purchased  $SnO_2$  colloidal dispersion (15 wt.%) was first diluted by deionized water (1:6 vol%) and commercial 5 wt.% Nafion117 solutions (DuPont) were diluted to 0.25 wt.%, 0.5 wt.% and 1.0 wt.% using deionized water. After that, diluted  $SnO_2$  colloidal dispersion was spin-coated onto the clean ITO glass substrates at 3000 rpm for 30 s, followed by annealing at 150 °C for 30 min in ambient

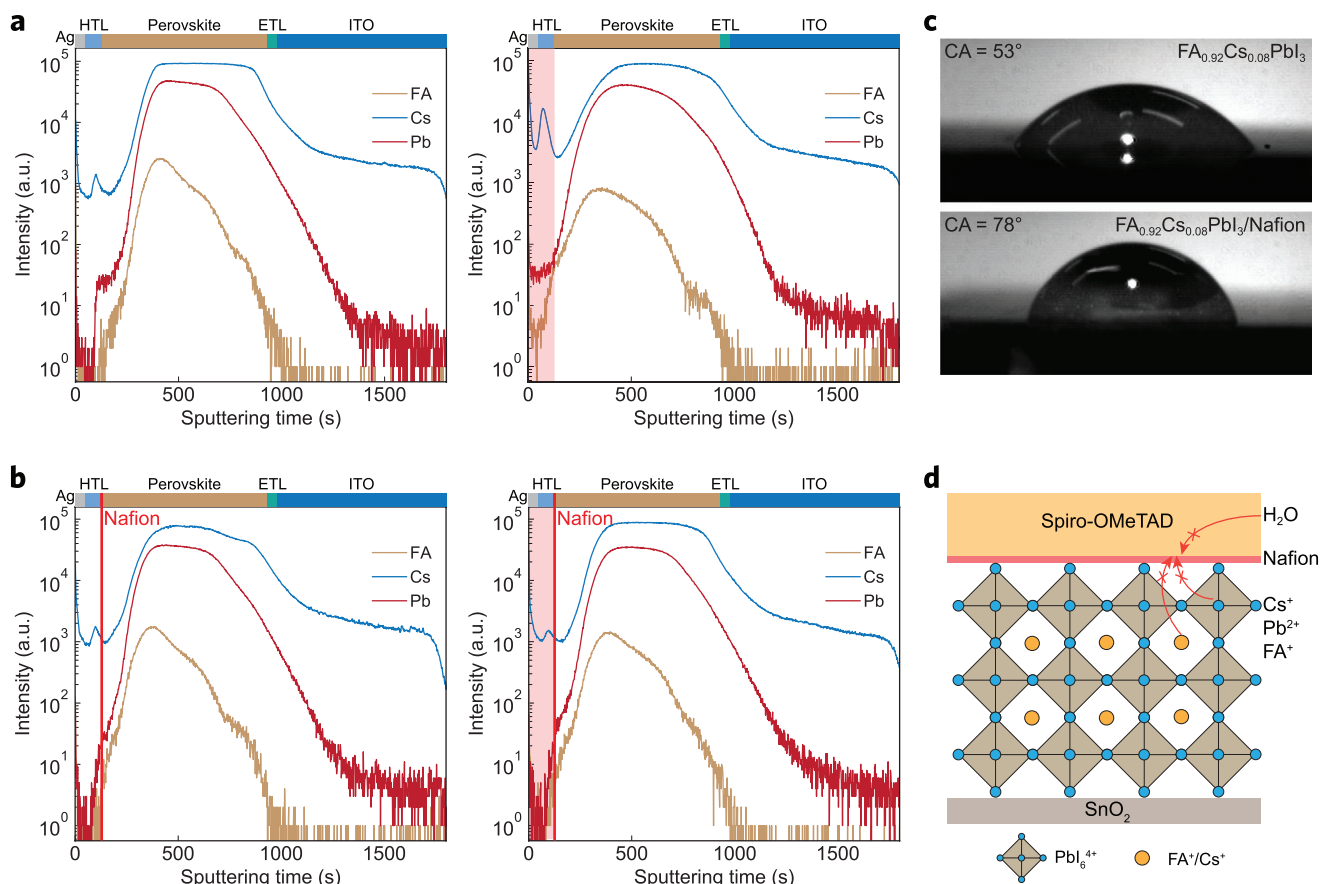


**Figure 5.** a) ToF-SIMS depth profiles of pristine (left) and aged (right) devices without Nafion passivation. b) ToF-SIMS depth profiles of pristine (left) and aged (right) devices with Nafion passivation layer. c) The water contact angles of pristine perovskite and perovskite/Nafion film. d) Schematic of the barrier effect of top Nafion interface layer on ions and water.

air. Here, a typical one-step anti-solvent deposition method was adopted to fabricate pure FA<sub>0.92</sub>Cs<sub>0.08</sub>PbI<sub>3</sub> perovskite films. In detail, 50  $\mu$ L of perovskite precursor solution (29 mg CsI, 221.5 mg FAI, 645.4 mg PbI<sub>2</sub>, and 33 mg MAI were dissolved in 0.9 mL of DMF and 0.1 mL of DMSO mixed solvent) was spin-coated on SnO<sub>2</sub> coated ITO glasses at 4000 rpm for 20 s. Fifteen seconds before the end of the procedure, 150  $\mu$ L chlorobenzene was poured rapidly on the perovskite films. Subsequently, the films were transferred to a hot plate and annealed at 150 °C for 20 min. All these processes were performed in N<sub>2</sub> glove box. After that, the diluted Nafion solutions were firstly spin-coated on the clean Si/SiO<sub>2</sub> substrates at 1000 rpm for 30 s. Then, the Si/SiO<sub>2</sub> substrates were coated with Nafion stacked upside down on the surface of perovskite film with heating at 100 °C for 2 min. After cooling down, a Spiro-OMeTAD solution with consists of 72.3 mg Spiro-OMeTAD, 28.8  $\mu$ L of 4-tert-butyl pyridine, 27.8  $\mu$ L of FK209 Co (III) TFSI solution (300 mg of FK209 in 1 mL of ACN), and 17.5  $\mu$ L of Li-TFSI solution (520 mg of Li-TFSI in 1 mL of ACN) in 1 mL CB was spin-coated on perovskite films at 4000 rpm for 25 s. Finally, 80 nm of Au electrode was thermally evaporated under a high vacuum using an E-beam thermal evaporation system.

**Characterizations:** The SEM images were obtained by Hitachi S-4800 FEG. The XRD was taken using a Bruker D2 Phaser using a Cu K $\alpha$ . The XPS and VBM were tested on Physical Electronics PHI 5802 with a monochromatic Al K $\alpha$  X-ray source. The ToF-SIMS characterization was performed on ION TOF-SIMS 5. The steady-state PL and time-resolved PL spectra were measured on a Pico Quant Fluor Time 300 instrument. A picosecond 375 nm pulse laser (LDH-P-C-75) with a pulse width of <40 ps was used to excite the samples. The current density-voltage (*J*-*V*) curves of PSCs were characterized by using a Keithley 2400 source

meter and a Newport AM 1.5 G solar simulator under a light intensity of 100 mW cm<sup>-2</sup>, calibrated with a standard silicon reference cell. The steady-state PCE was measured at a maximum power point and then tracing the current density. The EQE measurement was performed by a system combining xenon lamp monochromatic chopper, and a lock-in amplifier with a calibrated silicon photodetector (Hamamatsu mono-Si cell). The stability was tested at an N<sub>2</sub> glove box with the illumination of 100 mW cm<sup>-2</sup>. The EIS was measured by an electrochemical workstation (Autolab, PGSTAT 302N) under illumination with an alternative signal amplitude of 5 mV and in the frequency range of 800–0.01 kHz. The transient photovoltage and transient photocurrent decay were recorded on a digital oscilloscope (MDO3102, Tektronix, Inc) with a 532 nm 10 ps pulse width laser (5  $\mu$ J/pulse maximum at 1 MHz) (HE532-5, Fianium).

The space-charge-limited-current (SCLC) method:

$$N_{\text{trap}} = \frac{2\epsilon_0\epsilon V_{\text{TL}}}{eL^2} \quad (1)$$

where  $\epsilon_0$  is the vacuum permittivity,  $\epsilon$  of 46.9 for the perovskite is adopted,  $e$  is the electron charge, and  $L$  is the thickness of the film.

Biexponential kinetic model:

$$I(t) = A_1 \exp\left(-\frac{t-t_0}{\tau_1}\right) + A_2 \exp\left(-\frac{t-t_0}{\tau_2}\right) \quad (2)$$

where  $t_0$  is the start time of the decay process,  $\tau_1$  and  $\tau_2$  represent the first- and second-order decay times,  $A_1$  and  $A_2$  are weighting coefficients of each decay channel.

Carrier lifetime calculation:

$$\tau = \sum A_i \tau_i^2 / \sum A_i \tau_i \quad (3)$$

## Supporting Information

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

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

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

## Keywords

interface, ion lock, Nafion, planar perovskite solar cells, stability

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