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## **Optimized Carrier Extraction at Interfaces for 23.6% Efficient Tin–Lead Perovskite Solar Cells**

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**Abstract**

Carrier extraction in mixed tin–lead perovskite solar cells is improved by modifying the top and bottom perovskite surfaces with ethylenediammonium diiodide and glycine hydrochloride, respectively. Trap densities in the perovskite layers are reduced as a result of surface passivation effects and an increase in film crystallinity. In addition, the orientated aggregation of the ethylenediammonium and glycinium cations at the charge collection interfaces result in the formation of surface dipoles, which facilitate charge extraction. As a result, the treated mixed tin–lead perovskite solar cells showed improved performance, with a fill factor of 0.82 and a power conversion efficiency up to 23.6%. The unencapsulated device also shows improved stability under AM1.5G, retaining over 80% of the initial efficiency after 200 h continuous operation in inert atmosphere. Our strategy is also successfully applied to centimeter-scale devices, with efficiencies up to 21.0%.

## Introduction

Due to their strong optical absorption, tunable bandgap, and efficient charge generation<sup>1,2</sup>, metal halide perovskites are promising materials for printable, cost effective next-generation photovoltaics. The power conversion efficiency (PCE) of perovskite solar cells (PSCs) can be optimized for solar radiation by bringing the perovskite bandgap closer to the ideal range of 1.1–1.4 eV<sup>3,4</sup>. Although most lead perovskite materials have bandgaps larger than 1.45 eV<sup>5,6</sup>, smaller bandgaps can be obtained with tin–lead (Sn–Pb) compositions<sup>7-9</sup>, where about half of the lead ions are substituted with tin<sup>10</sup>. Introducing tin into the perovskite lattice, however, can adversely affect the device performance<sup>11-13</sup> – primarily by self-doping due to the oxidation of Sn(II) to Sn(IV)<sup>14</sup>. This process readily occurs through reactions with the solvent<sup>15,16</sup> or trace oxygen<sup>17,18</sup>. Suppressing these oxidation processes is therefore the key to realizing high device performance. Several means have been reported to reduce the Sn(IV) content in tin-containing perovskite films, including reducing agents<sup>19-23</sup>, as well as antioxidants<sup>24-26</sup>.

Currently, the highest PCE of mixed Sn–Pb perovskite devices reaches over 22%<sup>27-31</sup>. Tan et al. achieved this by using a zwitterionic antioxidant, formamidinium sulfinic acid, as a bifunctional additive, which both suppressed Sn(II) oxidation and passivated defects at the perovskite grain surfaces<sup>27</sup>. Yan et al. used a reducing agent, 4-hydrazinobenzoic acid, and vertical Pb/Sn compositional gradients to enhance photocarrier separation and suppress carrier recombination<sup>29</sup>. Zhu et al. were able to passivate structural defects in Sn–Pb perovskite by adding guanidinium thiocyanate, which increased the charge carrier lifetimes ( $>1 \mu\text{s}$ ) and diffusion lengths ( $>2.5 \mu\text{m}$ )<sup>32</sup>. Meanwhile, very recently, we achieved ultra-long carrier lifetimes ( $>7 \mu\text{s}$ ) by applying a Sn(IV) scavenging method<sup>22</sup> and treating the purified Sn–Pb films with maltol<sup>33</sup>. Even with these long lifetimes, however, the efficiencies of mixed Sn–Pb devices<sup>10,27,28,32,34-41</sup> still remain below those of their pure lead counterparts<sup>42-47</sup>. As the quality of the material already appears to be sufficiently high, we believe that the efficiency of Sn–Pb PSCs is now primarily limited by poor carrier

dynamics at the interfaces with the charge collection layers<sup>48</sup>. We therefore aim to improve the structural and electronic properties at the top and bottom regions of the perovskite films by modifying them with surfactants containing methylammonium terminal group. Methylammonium surfactants with different functional groups, such as  $\text{NH}_3^+\text{-CH}_2\text{-R}$  ( $\text{R} = \text{-CH}_2\text{-NH}_3^+$ , (Ethylenediammonium,  $\text{EDA}^{2+}$ )<sup>49,50</sup> or  $\text{-COOH}$ , (Glycinium,  $\text{GlyH}^+$ )<sup>51</sup>), offer the means to systematically tailor the electrostatics at perovskite interfaces (Fig. 1a). Moreover, the challenge for improving the property of the perovskite films is to selectively and reliably apply these simple surfactant molecules to specific charge extraction surfaces with favorable orientation in an easy and efficient way.

### Design strategy

We propose the use of  $\text{EDAI}_2$  for the post-treatment of the perovskite top surface. The  $\text{EDA}^{2+}$  is sufficiently small to allow for electronic contact between the perovskite and the top charge transport layer (Fig. 1a). In addition, since  $\text{EDA}^{2+}$  is too short to occupy two A-sites of the perovskite lattice simultaneously<sup>52,53</sup>, 2D phases should not be formed. Unlike the EDA (ethane-1,2-diamine), a bidentate neutral base with lone pairs<sup>54</sup>, for  $\text{EDA}^{2+}$ , we speculate that one methylammonium group of it binds to the surface of the perovskite films, reducing the density of structural defects, especially the acceptor-like defects, and unsatisfied dangling bonds. The other methylammonium group would then point away from the perovskite surface, inducing a surface dipole<sup>55</sup>, which may facilitate electron extraction from the top surface into the electron collecting layer of positive-intrinsic-negative (p-i-n) structured (inverted) PSCs.

When glycine hydrochloride ( $\text{GlyHCl}$ ) is added into the perovskite precursor solution, the methylammonium head of  $\text{GlyH}^+$  is expected to bind to the surface of the perovskite crystallites, stabilizing the formation of larger particles<sup>56</sup>. These particles, which sediment at the bottom interface, serve as nucleation centers in the film growth process<sup>51</sup>. Therefore, the electronegative

carboxyl groups at the bottom surface face outwards from the perovskite, towards the hole collection layer. The orientation of the resulting dipole creates an electric field<sup>57</sup> which assists in driving the holes to the hole collection layer.

### Realizing the modifications to the top and bottom regions

We started with a three A-site cations mixed Sn–Pb perovskite,  $\text{Cs}_{0.1}\text{FA}_{0.6}\text{MA}_{0.3}\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ , (MA = methylammonium, FA = formamidinium), fabricated, as reported in our previous work<sup>33</sup>, from a 1.8 M precursor solution prepared in *N,N*-dimethylformamide and dimethyl sulfoxide with a volume ratio of 3:1. 10 mol% tin fluoride ( $\text{SnF}_2$ ), with respect to  $\text{SnI}_2$ , and 2 mol% ammonium thiocyanate ( $\text{NH}_4\text{SCN}$ ), with respect to the total amount of B-site precursor ( $\text{SnI}_2 + \text{PbI}_2$ ), were added to the perovskite precursor solution.  $\text{SnF}_2$  suppresses Sn(II) oxidation<sup>22,58,59</sup>, while thiocyanate salts mediate the perovskite crystal growth<sup>10,60,61</sup>. This perovskite is the control to which the treated perovskite layers are compared. For top interface modification, a solution of  $\text{EDAI}_2$  in isopropanol/toluene (volume ratio of 1:1) is spin-coated on the top of perovskite films. This perovskite will be referred to as “ $\text{EDAI}_2$ -treated”. To modify the bottom interface, GlyHCl (2 mol% with respect to the total amount of B-site precursor) is added into the precursor solution. The perovskite layer to which both  $\text{EDAI}_2$  and GlyHCl treatments have been applied will be referred to as “ $\text{EDAI}_2/\text{GlyHCl}$ -treated”.

To pinpoint the regions affected by each treatment, time-of-flight secondary-ion mass spectrometry (ToF-SIMS) was used to track the distributions of the  $\text{EDA}^{2+}$  and  $\text{GlyH}^+$  ions throughout the perovskite film (Fig. S1–5). The ToF-SIMS results show that the  $\text{EDA}^{2+}$  cations introduced by the post-treatment are mainly distributed on the perovskite top surface (Fig. 1b, c, S6–8). In contrast,  $\text{GlyH}^+$  cations are found to be mainly located at the bottom region of the perovskite films (Fig. 1b, c, S9–18).

Further experiments were performed to better understand why GlyH<sup>+</sup> cations preferentially aggregate towards the bottom region of the perovskite films. Although it has been reported for additives that the concentration gradients in perovskite layers can depend on the substrates, such as NiO<sub>x</sub>/ITO<sup>62</sup> and NiO<sub>x</sub>/FTO<sup>63</sup> (ITO and FTO is indium tin oxide and fluorine-doped tin oxide, respectively.). The distribution of GlyH<sup>+</sup> in the perovskite layers was concentrated near the substrate, regardless of the substrate examined (Fig. S9 and S10). Similar ion distributions were observed within the perovskite films fabricated on poly-(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS)-coated, PTAA/PFN-coated, and bare FTO (PFN and PTAA is poly[9,9-bis(3'-(*N,N*-dimethylamino)-propyl-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)] and poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine], respectively.) The distribution of GlyH<sup>+</sup> is therefore more likely governed by interactions with the perovskite surfaces, as indicated by the nuclear magnetic resonance (NMR) results (Fig. S19). Furthermore, dynamic light scattering (DLS) measurements were conducted to study the formation of particles in the perovskite precursor solutions with and without the addition of GlyH<sup>+</sup> (Fig. S20). The results show that the size distribution of the perovskite colloidal particles formed in the solution was significantly altered after introducing GlyH<sup>+</sup>, with the big particles dominate the colloidal system. We therefore propose that the GlyH<sup>+</sup> is initially bound to the colloidal particles in the perovskite precursor solution (Fig. 1a). Large perovskite particles sediment at the substrate surface, where they serve as nucleation sites for the subsequent growth of the perovskite layer after the anti-solvent addition. While GlyH<sup>+</sup> bound to the top surface of the nuclei are most likely replaced by the A-site cations stoichiometrically required for the continuous growth of the 3D perovskite layer, GlyH<sup>+</sup> bound to the bottom surfaces remains, since there are no A-site components in solution nearby. Note that no low dimensional perovskite phases were observed by XRD, even as the amount of GlyH<sup>+</sup> was increased to 8 mol% (Fig. S21). Although extensive study would be necessary to examine the further detail of the underlying mechanism, we assume that the residual GlyH<sup>+</sup> is located as deposits at the bottom surface and grain boundaries as suggested by the ToF-SIMS results.

### Effects of the treatments on film quality

The morphology of the perovskite layers was examined with scanning electron microscopy (SEM) and atomic force microscopy (AFM). All samples show good coverage with large grains. Post-treatment with the EDAl<sub>2</sub> solution appears to have a polishing effect<sup>64</sup>, washing away the surface layer of the perovskite film. In the control sample, some deposits, probably from SnF<sub>2</sub><sup>65-67</sup>, are visible between the grain boundaries (Fig. 1d). These deposits are less prominent after the perovskite films are post-treated with EDAl<sub>2</sub> solution, and the surface roughness is reduced from 42 nm for control to 37 nm for the films treated with EDAl<sub>2</sub> solution (Fig. S22).

Viewed in cross section, all the perovskite films show evenly-sized, monolithic grain structure. The average thickness is 870, 830, and 860 nm for the control, EDAl<sub>2</sub>-treated, and the EDAl<sub>2</sub>/GlyHCl-treated perovskite films, respectively (Fig. 1e, S23). The EDAl<sub>2</sub>-treated film is notably thinner than the control, confirming the polishing effect of the post-treatment with EDAl<sub>2</sub> solution. The isopropanol/toluene co-solvent system was found to be critical for this top surface modification. The details are given in the supplementary information (Fig. S23 and S24). The polarity of the isopropanol helps the organic ammonium salts to anchor to the film surface, enhancing defect passivation<sup>68</sup>. Sn-containing perovskites are soluble in isopropanol<sup>69</sup>, however, so toluene was added to reduce the overall viscosity of the solution and accelerate the dispersion of the EDAl<sub>2</sub> solution on the films before spinning.

The effect of the treatments on the crystallinity of the perovskite layers was monitored by thin film X-ray diffraction (XRD) measurements (Fig. S21, S25–27). Peaks at 14.2, 20.1, 24.6, 28.4, 31.9, 35.0, 40.7, and 43.2°, were observed for all the films, corresponding to (100), (110), (111), (200), (210), (211), (220), and (300) planes, respectively. The intensity of the (100) peak increases after the EDAl<sub>2</sub> post-treatment, possibly as a result of the surface polishing effect<sup>64</sup> and/or second stage



crystallization<sup>70</sup>. The intensity of the (100) peak was enhanced further in the XRD pattern of the EDAI<sub>2</sub>/GlyHCl-treated film, suggesting that the GlyHCl additive is likely active during the crystal growth phase where it acts to enhance the crystallinity of the film. No low-dimensional phase was detected. The small peak at  $2\theta = 12.7^\circ$  is attributed to PbI<sub>2</sub> from unreacted precursor material or degraded perovskite<sup>71,72</sup>. Although the peak was observed in the patterns of the control and EDAI<sub>2</sub>-treated films, it was absent in that of the EDAI<sub>2</sub>/GlyHCl-treated perovskite film.

For effective charge extraction, high quality perovskite films with long charge carrier lifetimes are necessary. The improvements in the carrier dynamics were evaluated by using steady-state photoluminescence (PL) and time-resolved PL (TRPL). The excitation energy was 1.80 eV, and the excitation photon flux was fixed at  $3.5 \times 10^{11}$  photons cm<sup>-2</sup> (100 nJ cm<sup>-2</sup>), comparable to the incident photon flux under AM1.5G. The perovskite films were excited either from the top surface of the perovskite film (front-side, Fig. S28), or through the quartz substrate (back-side, Fig. 2a, b). Regional sampling specificity is possible, since the thickness of the perovskite films (~850 nm) is considerably greater than the estimated optical penetration depth ( $1/\alpha$ : ~220 nm,  $\alpha$  is absorption coefficient at 688 nm (1.80 eV), Fig. S29). In each condition, a single PL peak around 1.25 eV was observed, with PL lifetimes on the order of microseconds. Note that the PL spectrum is slightly blue-shifted in the control films with the front-side excitation (Fig. S28, Table S1), when compared to the others. One of the possible origins of this blue shift is a Burstein–Moss shift, induced by a significant unintentional hole doping<sup>73</sup>. Another is a bandgap fluctuation due to compositional deviation at the film surface. These assumptions are reasonable considering that the surface quality of the control film is likely somewhat worse than the treated materials. With front-side excitation, the lifetime increased from 2.8  $\mu$ s for the control films, to 4.5  $\mu$ s for the EDAI<sub>2</sub> post-treated films, and 4.9  $\mu$ s for the EDAI<sub>2</sub>/GlyHCl-treated films, indicating that defects are greatly suppressed. At the top surface, most of the improvement originates from the EDAI<sub>2</sub> treatment, as expected. Meanwhile, with back-side excitation, the lifetimes were elongated from 1.5  $\mu$ s for control sample,

to 3.2  $\mu\text{s}$  for EDAI<sub>2</sub>-treated, and finally to 5.5  $\mu\text{s}$  for the EDAI<sub>2</sub>/GlyHCl-treated films. Notably, the influence of the GlyHCl on the lifetimes is more prominent when the bottom region is probed. The steady state PL intensities were also increased (Table S1, Fig. S30). The results clearly show that EDAI<sub>2</sub> post-treatment and GlyHCl additive are able to reduce the density of recombination centers in the EDAI<sub>2</sub>/GlyHCl-treated perovskite films, particularly at the top and bottom regions, respectively<sup>74</sup>.

In order to better characterize the photocarrier recombination dynamics in the EDAI<sub>2</sub>/GlyHCl-treated films, the PL decay was examined under different excitation intensities. The dependencies of PL decay curves, PL lifetimes, and initial PL intensities on photon flux are shown in Fig. 2c, d, S31. The decay curves can be modelled with the rate equations reported in our previous work<sup>75</sup>. The results indicate that bimolecular recombination is dominant under a photon flux equivalent of AM1.5G (initial carrier density  $n_0 = 1.5 \times 10^{16} \text{ cm}^{-3}$ ). The charge carrier trapping rate is  $9.2 \times 10^4 \text{ s}^{-1}$ , three orders of magnitude lower than that of prototypical metal halide perovskite MAPbI<sub>3</sub><sup>75</sup>. The low trap densities for both electrons and holes are confirmed by space-charge-limited current (SCLC) measurements (Fig. S32, Table S2). Most of these traps can be reasonably assumed to be located at the various surfaces of the perovskite layer<sup>76</sup>. From the decay curve fits, the charge carrier density from unintentional doping is estimated to be  $8.2 \times 10^{14} \text{ cm}^{-3}$ , a value similar to the carrier densities reported for the high quality lead perovskite films ( $\sim 10^{15} \text{ cm}^{-3}$ )<sup>75</sup>.

To summarize, the EDAI<sub>2</sub>/GlyHCl-treated perovskite films, modified with both EDAI<sub>2</sub> surface treatment and with the addition of GlyHCl, show improved crystallinity and reduced defect densities, especially at the top and bottom regions. The characteristic p-doping, commonly observed in Sn-containing perovskite materials,<sup>77,78</sup> has been effectively suppressed as suggested with the low unintentional doping induced carrier density.

### Solar cell performance

The cells had the following inverted architecture: FTO/PEDOT:PSS/perovskite/ $C_{60}$ /bathocuproine (BCP)/Ag (Fig. 3a). The active cell area was  $0.0985 \text{ cm}^2$ . Current density–voltage ( $J$ – $V$ ) curves were measured under simulated AM1.5G illumination (Fig. 3b). The best performance of the control cells was 19.6% (Reverse scan,  $V_{OC} = 0.79 \text{ V}$ ,  $J_{SC} = 31.6 \text{ mA cm}^{-2}$ , and  $FF = 0.79$ ). After the  $EDAI_2$  post-treatment, the PCE increased to 21.7% (Reverse scan,  $V_{OC} = 0.85 \text{ V}$ ,  $J_{SC} = 32.3 \text{ mA cm}^{-2}$ , and  $FF = 0.79$ ). The  $FF$  remains the same, but the  $J_{SC}$  and  $V_{OC}$  increased. For the  $EDAI_2$ /GlyHCl-treated device, a maximum PCE of 23.6% was obtained (Reverse scan,  $V_{OC} = 0.89 \text{ V}$ ,  $J_{SC} = 32.5 \text{ mA cm}^{-2}$ , and  $FF = 0.82$ ). The stabilized power output was shown in Fig. S33, which presents the PCE of 22.8% at 300 s. The  $J$ – $V$  curves of the  $EDAI_2$ /GlyHCl-treated devices show small hysteresis (hysteresis index: 0.017), suggesting suppressed ion movements<sup>79</sup>. The suppressed ion movements in the cells fabricated with GlyHCl relates to the enhanced crystallinity. In addition to the increase in  $V_{OC}$ , for these modified cells, the  $FF$  improved as well. This efficiency is the highest reported value for any Sn–Pb perovskite solar cell, as well as being one of the highest reported values for PSC having an inverted structure (Fig. S34)<sup>47,80</sup>. The cell performance measured by the Kanagawa Institute of Industrial Science and Technology (KISTEC) was 23.1% for the reverse scan ( $V_{OC} = 0.88 \text{ V}$ ,  $J_{SC} = 32.5 \text{ mA cm}^{-2}$ , and  $FF = 0.81$ ) and 22.2% for the forward scan ( $V_{OC} = 0.86 \text{ V}$ ,  $J_{SC} = 32.5 \text{ mA cm}^{-2}$ , and  $FF = 0.79$ ) (Fig. S35 and S36). All the related  $J$ – $V$  results are summarized in Fig. S37-39 and Table S3.

The external quantum efficiency (EQE) and internal quantum efficiency (IQE) spectra are shown in Fig. 3c. The highest IQE is close to unity, and the EQE reached 90%. The integrated  $J_{SC}$  from the EQE spectrum is  $32.2 \text{ mA cm}^{-2}$ , in close agreement with the values derived from the  $J$ – $V$  scans ( $32.5 \text{ mA cm}^{-2}$ ). The bandgap, estimated from the inflection point of the EQE spectrum<sup>81</sup>, is around 1.25 eV, in line with the PL results.

As mentioned by the previous reports<sup>43</sup>, when the device area is larger than the optical mask used for the  $J$ - $V$  measurements, the recorded  $V_{OC}$  values are slightly below the achievable maximum. With the optical mask removed, the  $V_{OC}$  reached 0.91 V (Fig. 3d), 0.07 V below the thermodynamic limit of 0.98 V<sup>82</sup>. The high  $V_{OC}$  corresponds to a voltage loss of 0.34 V – one of the best results thus far for perovskite solar cell devices<sup>42,83</sup>. The low voltage loss together with the long charge carrier lifetimes observed in the PL experiments confirm the remarkable suppression of non-radiative recombination channels in the EDAl<sub>2</sub>/GlyHCl-treated devices.

The operational stability was evaluated by tracking the maximum power point<sup>84</sup> under AM1.5G. Unencapsulated devices were measured in a N<sub>2</sub>-filled glovebox. The EDAl<sub>2</sub>/GlyHCl-treated cell maintained over 80% of the initial PCE for up to 200 h, and was more stable than either the EDAl<sub>2</sub>-treated (65% in 180 h) or control (60% in 145 h) cells (Fig. 3e, S40). The stability of the PSCs may be limited by the use of PEDOT:PSS as the hole transport layer. This material is known to be hygroscopic, and also its acidity may negatively impact the stability of the perovskite layer<sup>85</sup>. These effects could be mitigated by moving to a different hole selective layer, such as a self-assembled monolayer (SAM)<sup>31</sup> or modifying the acidity of the PEDOT system<sup>86</sup>.

Our top and bottom interface modification strategy was also applied to the fabrication of larger, centimeter-scale PSCs (Table S4, Fig. S41 and 42). For 1 cm<sup>2</sup> active area, a champion PCE of 21.0% (Forward scan,  $V_{OC}$  = 0.88 V,  $J_{SC}$  = 33.1 mA cm<sup>-2</sup>, and FF = 0.72) was achieved. The cells generally showed minimal hysteresis and good reproducibility.

### **Carrier extraction**

For further insights regarding the improved performance, especially the low voltage loss, the effect of the EDAl<sub>2</sub> and GlyHCl treatments on the energy levels of the perovskite films was examined with ultraviolet photoemission spectroscopy (UPS). The UPS experiments probe the vacuum,

Fermi, and valence energy levels near the top surface of the perovskite films, where electrons are extracted in the working solar cells.

Four systems were measured. In addition to the control and EDAI<sub>2</sub> post-treated films with and without GlyHCl additive, a film prepared with GlyHCl additive but without EDAI<sub>2</sub> post-treatment was also examined (Fig. 4a and b). With this sample set, we investigated the influence of the EDAI<sub>2</sub> post-treatment on the perovskite films prepared both without and with, GlyHCl additive. The secondary electron cutoffs, from which the work function of the perovskite surface can be estimated as  $(21.22 \text{ eV} - E_{B,\text{max}})$ , are shown in Fig. 4a. The onset of the valence band relative to the Fermi level is estimated from the spectral data in Fig. 4b. The energy of the Fermi and vacuum levels for each of the four samples relative to the valence band maximum (VBM) and conduction band minimum (CBM) are compiled in Fig. 4c. Comparing the control and EDAI<sub>2</sub>-treated films, we can see that the vacuum level and Fermi levels both shift, by 0.05 eV and 0.11 eV, respectively, to lie closer to the CBM. When the perovskite film contains GlyHCl additive, however, the shift in Fermi level is less pronounced, at only 0.02 eV, while the EDAI<sub>2</sub> post-treatment results in a shift in vacuum energy of 0.04 eV, similar to what was observed for the control films.

In the UPS measurements, a surface dipole is indicated by a change of the vacuum level ( $E_{\text{vac}}$ ) relative to the valence level of the perovskite films (Fig. 4c, S43 and S44)<sup>55,57,87-89</sup>. Post-treatment with EDAI<sub>2</sub> leads to the formation of a surface dipole with a magnitude of about 0.05 eV for the control film, and 0.04 eV for the film fabricated with GlyHCl additive. The positive end of the dipole faces outwards from the perovskite<sup>42,90</sup>. These results support our hypothesis that EDA<sup>2+</sup>, which accumulates at the top surface, is collectively bound to and oriented at the perovskite crystal grains. The potential difference created by the dipole can facilitate electron extraction by helping to sweep electrons away from the perovskite surface and towards the C<sub>60</sub> electron collection layer<sup>90</sup>.

In addition, electron extraction may be enhanced by surface doping effects, indicated by the shifts of the UPS-determined Fermi levels ( $E_F$ ) with respect to the valence and conduction bands. EDAI<sub>2</sub> post-treatment appears to induce the perovskite surface to become more n-type (the  $E_F$  shifts to lie above the center of the band gap, Fig. 4c). The shift is more pronounced for the control film than the film with GlyHCl additive, at  $-0.11$  eV and  $-0.02$  eV, respectively. The result can be understood by noting that while the Fermi level of the control film was nominally at the middle of the bandgap ( $0.60$  eV from the VBM), the Fermi level of the GlyHCl-treated film was already close to the conduction band ( $0.71$  eV from the VBM). Thus, while EDAI<sub>2</sub> post-treatment makes the perovskite surface more n-type, the effect appears to vary depending on how p-type the surface region was initially. The Fermi level shifts correlate well with the difference in Sn(IV) concentrations observed by X-ray photoelectron spectroscopy (XPS, Fig. S45, Table S5). If the top surface is more n-type than the bulk, band bending will be induced in the downwards direction at the perovskite, facilitating electron extraction by drawing electrons to and holes away from the extraction layer.

As GlyH<sup>+</sup> cations mainly accumulate at the bottom region of the perovskite films, electron spin resonance (ESR) spectroscopy was used to examine the charge extraction from the perovskite layers to the PEDOT:PSS substrate. The ESR signal allows us to quantify the charge states in PEDOT:PSS films with and without perovskite capping layers (Fig. 4d, S46, Table S6). The unit intensity is the peak-to-peak ESR intensity of the Mn<sup>2+</sup> standard sample ( $I_{Mn}$ ). The ESR absorption intensity of the PEDOT:PSS film was  $131 I_{Mn}$  units, centered at  $319.2$  mT. When the PEDOT:PSS layer was coated with the control perovskite, the absorption intensity of the PEDOT:PSS ESR signal decreased to  $63.6 I_{Mn}$  units, indicating that, as a result in the difference in Fermi levels between the perovskite layer and the PEDOT:PSS<sup>91</sup>, some electrons from perovskite recombine with holes in the PEDOT:PSS layer at the interface. When the PEDOT:PSS is coated with the perovskite containing GlyHCl additive, however, the absorption intensity is only reduced to  $85.6 I_{Mn}$  units, indicating fewer recombination events.

The change in absorption intensity of the ESR signal correlates with the relative position of the Fermi levels in the PEDOT:PSS and perovskite layers. The results imply that the Fermi level in the PEDOT:PSS and perovskite layers are closer in energy when GlyHCl additive is used. The UPS results, meanwhile, confirm that the work function of the perovskite layer is not evidently altered by the addition of GlyHCl (control: 4.73 eV, GlyHCl: 4.69 eV). The GlyH<sup>+</sup> cation, which accumulates at the bottom interface binds to and aligns with the perovskite crystal face (Fig. 1a, 4e), inducing a surface dipole where the electronegative –COOH group points outwards from the perovskite surface. The resulting dipole, with the negative side facing the PEDOT:PSS layer, creates an electric field which drives the holes to PEDOT:PSS (Fig. 4e)<sup>57</sup>.

## Conclusions

Mixed Sn–Pb solar cells with high open circuit voltages and high fill factors were realized by optimizing charge extraction. Interface modification strategies using surfactants containing methylammonium terminal groups were used to facilitate the extraction of electrons and holes at the top and bottom perovskite surfaces, respectively. Post-treatment with EDAI<sub>2</sub> showed polishing and passivation effects at the top surface, leading to lower carrier trap densities. GlyHCl additive resulted in the accumulation of GlyH<sup>+</sup> cations at the bottom region of the perovskite layer as well as an improvement in film crystallinity. The GlyHCl treatment helped to passivate recombination centers, particularly at the bottom region of the perovskite layer. In addition to improvements to the perovskite layer, EDA<sup>2+</sup> and GlyH<sup>+</sup> cations at the top and bottom regions induced surface dipoles which facilitates electron and hole transfer, respectively, to the charge collection layers.

As a result of the improvements arising from the top and bottom passivation and dipole formation, the PCE of mixed Sn–Pb solar cells with 0.0985 cm<sup>2</sup> aperture area increased to 23.6%, the highest value reported so far for mixed Sn–Pb PSCs, and the one of the highest values reported so far for

PSCs with the inverted structure regardless of perovskite composition. Our top and bottom interface modification strategy was also applied to the fabrication of larger, centimeter-scale PSCs showing high efficiency with small hysteresis and good reproducibility. The easy-to-handle and effective approach should be widely applicable to other perovskite semiconductor devices, such as all-perovskite and perovskite/silicon tandem photovoltaics, perovskite light-emitting diodes, transistors, and X-ray detectors.

#### NOTES AND REFERENCES:

Note: The preliminary manuscript of this work was posted as a preprint by Research Square on July 24<sup>th</sup>, 2021<sup>92</sup>, with the link of <https://www.researchsquare.com/article/rs-727823/v1>.

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**Author contributions:**

S.H. conceived the idea. S.H. measured the SEM. R.M. performed AFM characterization. S.H. conducted the XRD measurement. K.M. conducted the ToF-SIMS measurement. S.H. and K.O. carried out the PL measurements with the help of T.Y., T.H., and Y.K. S.H. fabricated the solar cell devices and did the related characterizations. T.Y., T.H., and Y.K. analyzed the PL dynamics.

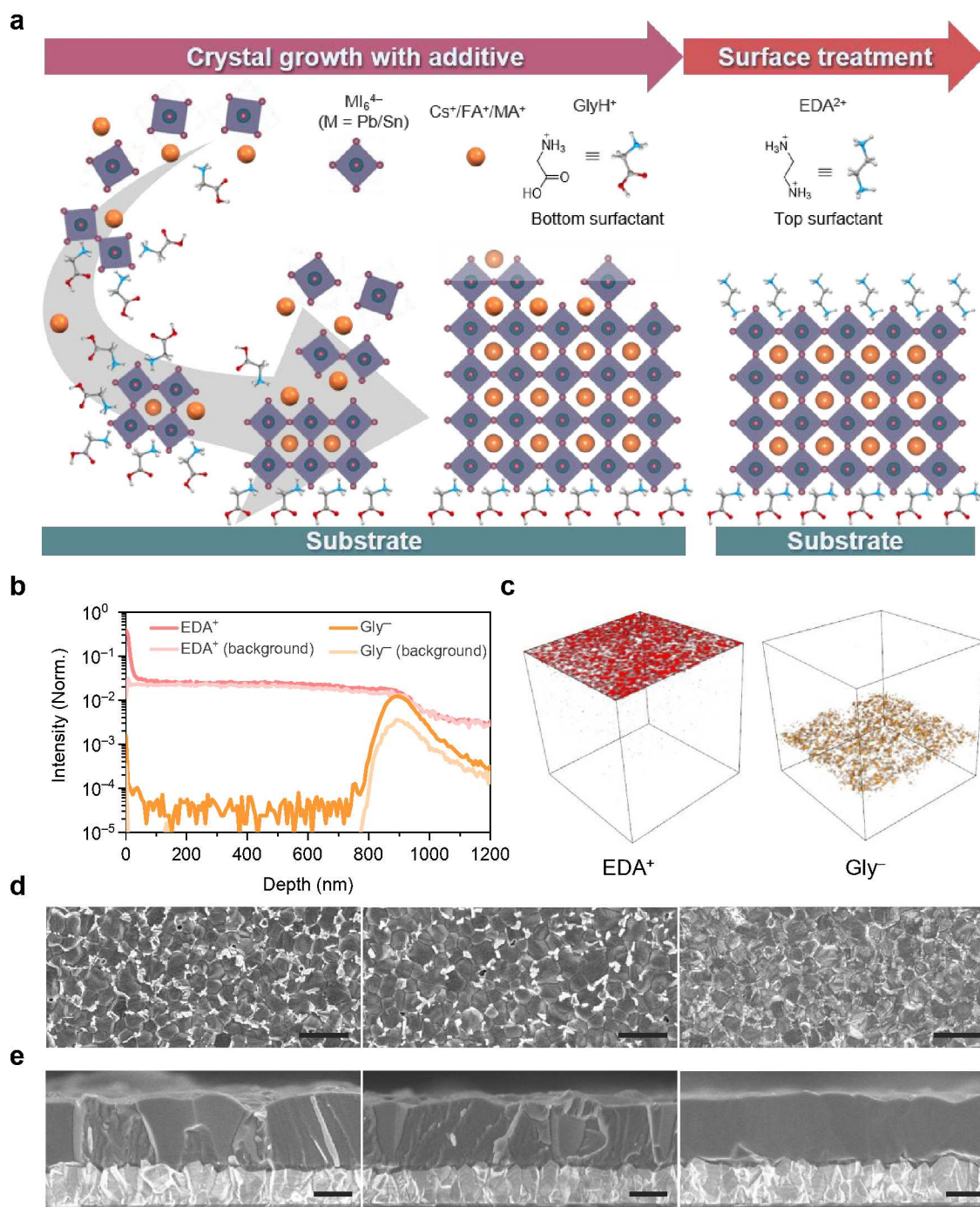
S.H. conducted the XPS measurement with the help of M.A.T. M.A.T., T.Y., and S.H. conducted the optical absorption measurement. K.N. and K.T. conducted the UPS measurement. S.H. conducted the SCLC measurements with the help of R.M. A.S. and K.M. conducted the ESR measurements. R.M. and S.H. performed the impedance measurement. T.N. and S.H. conducted the PLQY and GIXRD measurements. T.N. conducted the NMR characterizations. S.H. prepared the DLS samples. S.H., R.M., and A.W. prepared the manuscript. All authors commented on the manuscript. A.W. supervised the project.

**Competing interests:**

There are no conflicts to declare.

**Corresponding author**

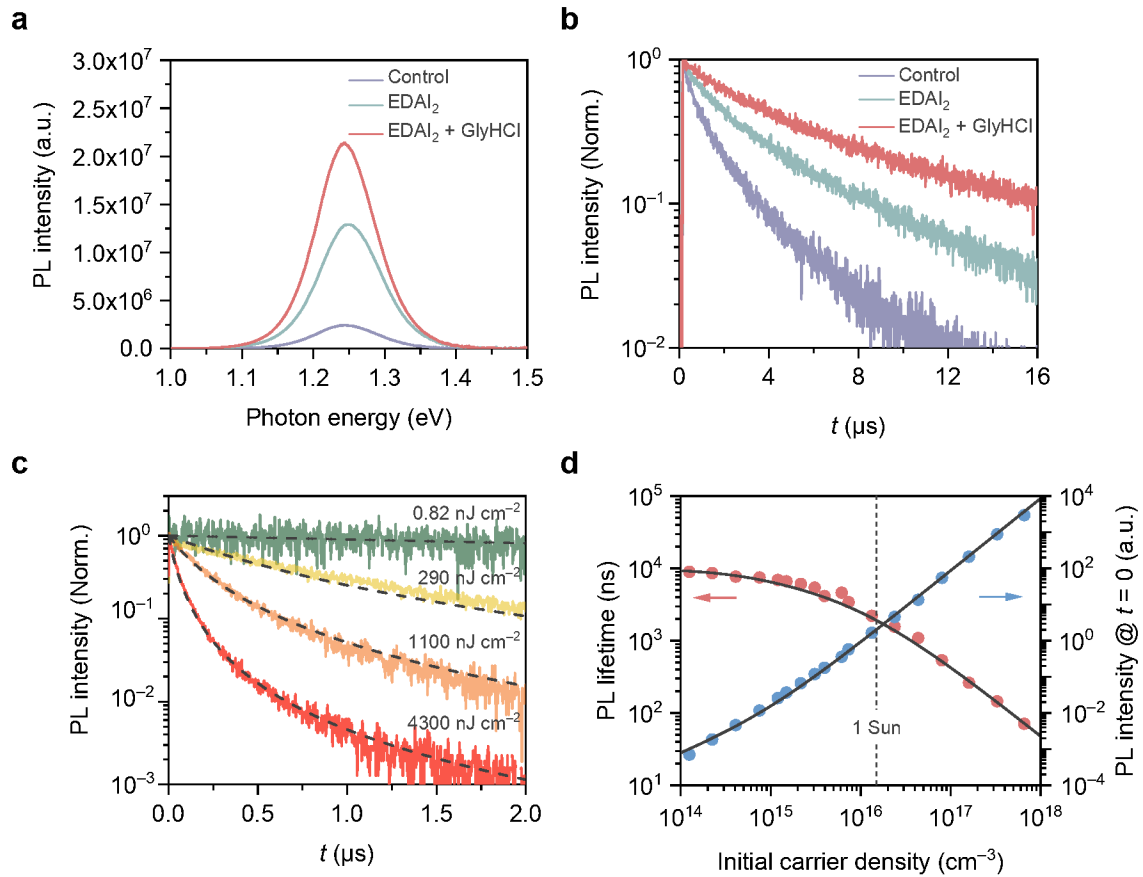
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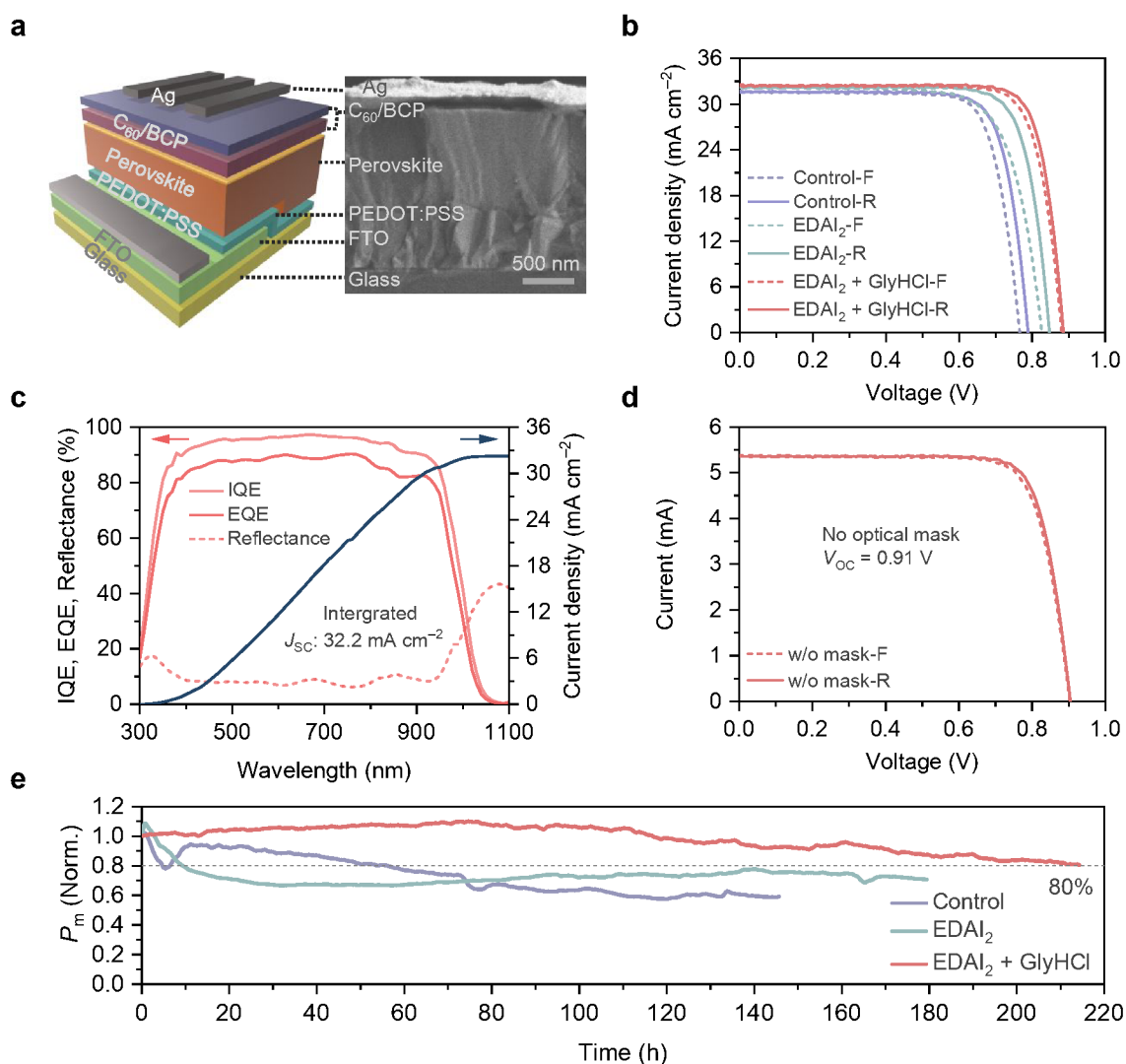
**Fig. 1** | Narrow-bandgap perovskite films with top and bottom interface modification. **a**, Schematic illustration of the interface modifications of mixed Sn–Pb perovskite films by GlyHCl additive and  $\text{EDA}_2$  surface treatment. **b**, ToF-SIMS depth profile of  $\text{EDA}^+$  and  $\text{Gly}^-$  ions for the  $\text{EDA}_2$ /GlyHCl-treated perovskite film on PEDOT:PSS/FTO. Full ion profiles are given in the



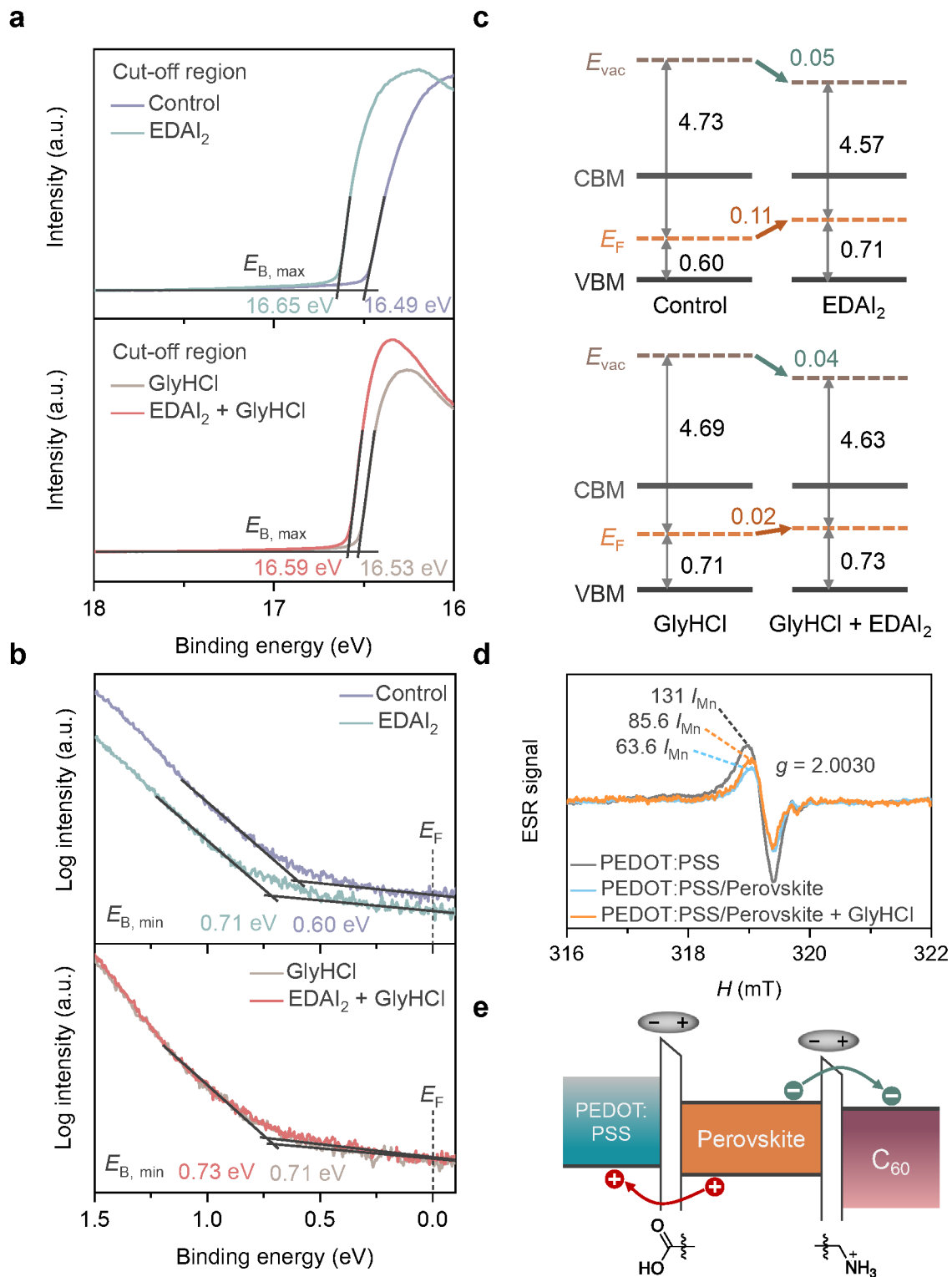
supplementary information (Fig. S1–18). **c**, Reconstructed, background subtracted 3D maps showing the distributions of  $\text{EDA}^+$  and  $\text{Gly}^-$  ions through the modified perovskite films. The raster area of the primary ion beam was  $30\ \mu\text{m} \times 30\ \mu\text{m}$ , and the thickness axis has been expanded for clarity. **d**, Top-view (scale bar:  $2\ \mu\text{m}$ ) and **e**, cross-sectional (scale bar:  $500\ \text{nm}$ ) SEM images of the control,  $\text{EDA}_2$ -treated, and  $\text{EDA}_2/\text{GlyHCl}$ -treated (left to right) perovskite films on PEDOT:PSS-coated FTO/glass substrates.



**Fig. 2 | Carrier dynamics.** **a**, Steady state photoluminescence (PL) spectra and **b**, time-resolved photoluminescence (TRPL) for the perovskite films on quartz substrates with the back-side excitation. **c**, PL decay curves for the EDAI<sub>2</sub>/GlyHCl-treated perovskite film showing the variation in PL lifetimes with excitation intensity. Curve fits used to ascertain the PL lifetimes<sup>75</sup> are shown by the dashed lines, see supplementary information (Fig. S31). **d**, Dependence of the lifetime and initial intensity of the PL signal on the excitation fluence. An initial carrier density of  $1.5 \times 10^{16} \text{ cm}^{-3}$  corresponds to an excitation fluence of  $100 \text{ nJ cm}^{-2}$  (approx. AM1.5G, 1 Sun). Black solid lines are the curve fits obtained using the rate equations reported in our previous work<sup>75</sup>.



**Fig. 3** | Solar cell devices. **a**, Schematic and cross-sectional SEM image. **b**,  $J-V$  curves of the best performing devices. **c**, The EQE, IQE, and reflectance spectra of an EDAl<sub>2</sub>/GlyHCl-treated device. **d**,  $J-V$  curves for the champion device measured with no optical mask and an active area of around 0.16  $\text{cm}^2$ . **e**, Normalized maximum power point tracking (MPPT) curves for the unencapsulated control, EDAl<sub>2</sub>-treated, and EDAl<sub>2</sub>/GlyHCl-treated devices operating under AM1.5G in inert atmosphere. The initial efficiencies were 14.8, 18.2, and 20.1%, respectively.



**Fig. 4 | Band structure and surface dipole formation. a**, Secondary electron cut-off and **b**, valence band regions of the UPS spectra for the perovskite films. **c**, Energy-level scheme based on

the UPS spectra. The full analysis is shown in Fig. S43 and S44. Energy values are given in electron volts relative to the vacuum level,  $E_{\text{vac}}$ , and the conduction band energies are determined from the bandgap of 1.25 eV estimated from the PL measurements. **d**, The ESR spectra for PEDOT:PSS on quartz, with or without a perovskite capping layer. The  $g$ -factor is 2.0030. **e**, Schematic illustrating how electron and hole extraction enhanced by surface dipoles induced by  $\text{EDA}^{2+}$  and  $\text{GlyH}^+$  cations at the top and bottom perovskite interfaces, respectively.

**Broader context**

Monolithic all-perovskite tandem solar cells are a highly promising low cost-per-watt solar technology. Currently, the power conversion efficiency of the narrow gap subcell, which is commonly fabricated from mixed tin–lead perovskite absorber, is relatively poor. High trap densities, particularly at the surface of the tin–lead perovskite film, act as recombination centers. To address this, we applied surfactant molecules to the top and bottom surfaces of the tin–lead perovskite layer. Post-treatment with ethylenediammonium diiodide modified the top surface, resulting in lower carrier trap densities. The bottom surface was passivated using glycine hydrochloride additive, which spontaneously accumulates underneath the perovskite layer during film fabrication. Surface dipoles were formed at both the top and bottom interfaces, promoting charge extraction and leading to a significant improvement to the output voltage and fill factor of the solar cell devices.