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60 cm² perovskite-silicon tandem solar cells with an efficiency of 28.9% by homogenous passivation

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Abstract

Inverted perovskite solar cells face performance limitations due to non-radiative recombination at the perovskite surfaces in devices, including functional layers. Advanced characterization and density functional theory reveal that phosphonic acids passivate perovskite surface defects, while piperazinium chloride mitigates interface recombination by improving energy level alignment, introducing a field effect, and homogenizing the surface. Together, the quasi-Fermi level splitting of the perovskite is homogeneously increased by ca. 100mV. This enables two-terminal perovskite-on-silicon tandems to achieve a certified open-circuit voltage of 2V for a 1 cm² device and high performance in excess of 31%. The scalability of the passivation is furthermore demonstrated with homogeneously passivated devices reaching certified efficiencies of 28.9% for an active area of 60 cm².

Introduction

In inverted (p-i-n) perovskite solar cells (PSCs), the electron transport layer (ETLs) is typically composed of fullerene (C_{60}) or its derivatives^{1,2}. These layers effectively extract electrons, and C_{60} has proper band alignment with medium bandgap (~ 1.52 eV) Pb-based perovskite absorbers, enabling p-i-n devices to achieve certified power conversion efficiency (PCE) beyond 26%³. However, a significant drawback arises from the defective interface between the wide bandgap (>1.63 eV) perovskite absorbers and fullerenes, leading to increased non-radiative recombination⁴. Additionally, the wide bandgap perovskite absorber itself poses challenges due to bulk and surface defects⁵. Furthermore, wide bandgap absorbers suffer from a higher conduction band minima (E_{CBM}) offset to the lowest-unoccupied-molecular-orbital (LUMO) of C_{60} ⁶, enhancing Shockley-Read-Hall (SRH)-like interface recombination at this critical interface, leading to high surface recombination velocities (SRVs), reducing the quasi-Fermi level splitting and consequently device- V_{OC} ^{7,8}.

Passivation of surface defects (e.g., vacancies, interstitials, substitutional defects, or metallic Pb^0)^{9,10} of Pb-based perovskite absorbers (surface passivation) has been demonstrated using various compounds, including organohalides (oleylammonium iodide¹¹, butylammonium iodide, 3-methylthiopropylammonium iodide (3-MTPAI), ...) ¹², organometals ($FcTc_2$)^{13,14}, zwitterions (phenformin hydrochloride)¹⁵, and inorganic halides (LiF)¹⁶. To suppress recombination between perovskite and C_{60} (interface passivation), thin evaporated dielectric interlayers (LiF, MgF_x)^{17,18}, ALD-deposited AlO_x ¹⁹, and solution-processed organohalides (diammonium salts like propane-diammonium iodide ($PDAI_2$)²⁰, ethylenediammonium iodide and piperazinium salts like $PI^{21,22}$) and phosphonic acids (pentafluorobenzyl phosphonic acid (pFBPA) have been utilized effectively^{23,24}. To fully exploit the potential of inverted perovskite solar cells, simultaneously suppressing interface and surface recombination holds significant promise. A bimolecular approach can be employed where two molecules with complementary passivation abilities are combined at the surface/interface. This approach has been recently demonstrated by Liu *et al.*¹² in medium bandgap perovskite absorbers, where surface passivation with 3-MTPAI increased the photoluminescence quantum yield (PLQY) beyond 10% while interface recombination was suppressed by a diammonium halide ($PDAI_2$), resulting in a certified single-junction efficiency of 25.1%. In their later work, combining a bimolecular approach at the interface with additive engineering to minimize bulk defects, Hao *et al.*²⁵ achieved a certified efficiency of 26.1%, one of the highest efficiencies for single-junction perovskite solar cells²⁵. Likewise, Ugur *et al.* combined additive engineering using a diammonium chloride with the shortest alkyl chain (methylenediammonium chloride) to minimize bulk defects and LiF/ $PDAI_2$ bilayer at the perovskite/ C_{60} interface. A certified perovskite-silicon tandem efficiency of 33.7% could be demonstrated with this approach²⁶. Such a dielectric/diammonium halide bilayer (LiF/ $EDAI_2$) was also shown by Liu *et al.*, who recently achieved a certified tandem performance of 33.89% with an open-circuit voltage of 1.97V²⁷. An effective combination of two thin films at an absorber/contact interface has also been used in the crystalline (c-)Si industry. In passivated emitter and rear contact (PERC) and tunnel oxide passivating contact (TOPCon) solar cells, the AlO_x/SiN_x stack provides a high-quality interface (low SRV) with the combination of field effect (via fixed negative charges in AlO_x) and chemical passivation (via dangling bond passivation and hydrogenation by the AlO_x/SiN_x stack)^{28,29}.

Mitigating voltage losses at the perovskite/ C_{60} interface is imperative to exploit the full potential of wide bandgap perovskite absorbers. These strategies are crucial not only for enhancing the performance of individual inverted PSCs but also for tandem/multi-junction devices incorporating inverted perovskite sub-cells. In this work, we combine two molecules (a phosphonic acid, PA, and a piperazinium halide) with complementary passivation abilities. The former passivates perovskite top surface defects, and the latter improves band alignment, introduces a field effect, homogenizes the surface potential overall enables reduced losses when in contact with the electron transport layer.

Experimental results and discussions

Surface passivation – molecule family phosphonic acids (PAs)

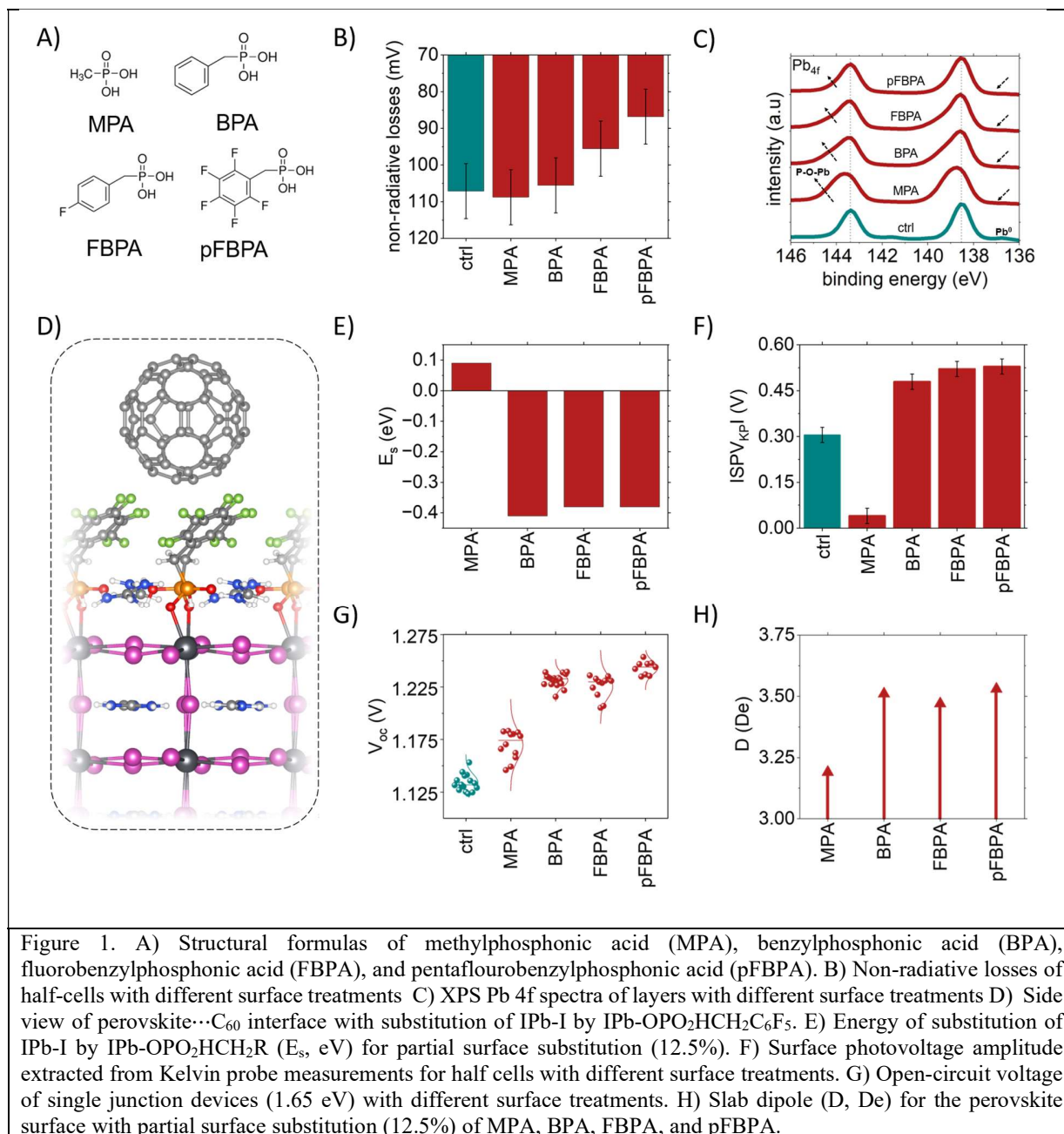


Figure 1. A) Structural formulas of methylphosphonic acid (MPA), benzylphosphonic acid (BPA), fluorobenzylphosphonic acid (FBPA), and pentafluorobenzylphosphonic acid (pFBPA). B) Non-radiative losses of half-cells with different surface treatments C) XPS Pb 4f spectra of layers with different surface treatments D) Side view of perovskite...C₆₀ interface with substitution of IPb-I by IPb-OPO₂HCH₂C₆F₅. E) Energy of substitution of IPb-I by IPb-OPO₂HCH₂R (E_s, eV) for partial surface substitution (12.5%). F) Surface photovoltage amplitude extracted from Kelvin probe measurements for half cells with different surface treatments. G) Open-circuit voltage of single junction devices (1.65 eV) with different surface treatments. H) Slab dipole (D, De) for the perovskite surface with partial surface substitution (12.5%) of MPA, BPA, FBPA, and pFBPA.

We begin by attempting to passivate top surface defects with PAs (**Fig.1(a)**) via a post-deposition treatment of the herein used triple halide triple cation³⁰ perovskite absorbers. For that purpose, we fabricate half-cell test structures (ITO/(4-(3,6-Dimethyl-9H-carbazol-9-yl)butyl)phosphonic acid(Me-4PACz)/SiO_x-np/perovskite) to track the changes in PLQY upon deposition of PAs (**Fig.1(a)**) atop the perovskite. Then, we extract the non-radiative (NR) losses from PLQY measurements (measured from absolute steady-state PL) following: $\Delta V_{OC,non-r} = \frac{kT}{q} * \ln(PLQY)$. The average NR loss of the bare absorber is 107 mV (on the hole transport layer stack) at carrier densities of ca. 1 sun (**Fig.1(b)**). Upon deposition of methyl phosphonic acid (MPA), the non-radiative loss increases slightly to an average of 109 mV, decreases slightly to 105 mV with benzyl PA (BPA), with fluorobenzyl PA (FBPA), it decreases to 93 mV and with pentafluorobenzyl PA (pFBPA) it decreases to 85 mV. The decrease in the non-radiative loss with pFBPA

deposition shows that either the surface defect density is reduced (e.g., chemical passivation), or the minority/majority carrier concentrations are altered so that the effect of surface recombination is minimized, e.g., via field-effect passivation. To understand the cause of this surface passivation, X-ray photoelectron spectroscopy (XPS) measurements were conducted. Samples treated with the phosphonic acids show suppression of Pb^0 . Furthermore, we identify the formation of P-O-Pb bonds³¹ through the emergence of a shoulder in the Pb 4f signal at ~145 eV signal (**Fig.1(c)**)^{23,24}. All the PAs show a similar degree of Pb^0 suppression, albeit it is unclear whether the phosphonic acids protected the perovskite absorber from X-ray or vacuum-induced degradation during the measurements, which prevents the formation of Pb^0 , or non-saturated Pb^{2+} is chemically passivated with phosphonic acids which, in turn, reduces the amount of Pb^0 . This raises two questions 1) Why did MPA not show any surface passivation effect, whereas BPA-derivatives, especially fluorinated ones, did? 2) Since Pb^0 suppression is common to all the tested PAs – **Fig.1(c)** is Pb^0 , in fact, an active defect center without the presence of C_{60} ? The strength of the P-O-Pb signature is anti-correlated with the size of the molecule, where smaller molecules being likely more mobile and causing less steric hindrance, appear to be creating denser layers. The highest P-O-Pb signal is observed for MPA, followed by BPA, FPBA, and pFBPA in decreasing order. At the same time, the size of the molecule is correlated with its effectiveness in passivating, as observed above, where smaller molecules passivate worse. To understand these phenomena we turn to density function theory (DFT) calculations focusing on the surface of a halide perovskite in the presence of the PAs.

All reasonable phosphite orientations, including rotamers created by CH_2R -rotation, were considered to choose the lowest energy orientations. Stabilization of the perovskite surface is achieved due to the formation of the P-O-Pb covalent bond, as well as stronger hydrogen bonding of the phosphite with the formamidinium cations ($\text{P}=\text{O}\cdots\text{HN}$) and weaker hydrogen bonding with iodine ($\text{P}-\text{OH}\cdots\text{I}$). For $\text{R} = \text{C}_6\text{H}_5$ (BPA), $\text{C}_6\text{H}_4\text{F}$ (FBPA), and C_6F_5 (pFBPA), the phenyl ring adopts a horizontal position due to the weak halogen ($\text{C}-\text{F}\cdots\text{I}$ and intermolecular $\text{P}=\text{O}\cdots\text{F}-\text{C}$), hydrogen ($\text{C}-\text{H}\cdots\text{I}$ and intermolecular $\text{P}=\text{O}\cdots\text{H}-\text{C}$), and $\pi\cdots\pi$ bonding of phenyl with the formamidinium – **Fig.1(d)**. The energy of substitution of IPb-I by $\text{IPb-OPO}_2\text{HCH}_2\text{R}$ (E_s , eV) for each PA (12.5% of the surface iodide is substituted by the phosphite) can be seen in **Fig.1(e)**, showing that surface substitution with phenyl-modified phosphites is energetically favorable, achieving $E_s = -0.41$, -0.38 , and -0.38 eV for $\text{R} = \text{C}_6\text{H}_5$, $\text{C}_6\text{H}_4\text{F}$, and C_6F_5 , respectively, as compared to energetically unfavorable 0.09 eV for $\text{R} = \text{CH}_3$ in the case of 12.5% substitution. Surprisingly, despite the large size of the phenyl group, complete surface substitution is more energetically favorable, achieving $E_s = -0.41$, -0.42 , and -0.55 eV for $\text{R} = \text{C}_6\text{H}_5$, $\text{C}_6\text{H}_4\text{F}$, and C_6F_5 in the case of 100% substitution due to $\pi\cdots\pi$ bonding and the softness of the perovskite lattice allowing alternation of the I_5PbO octahedra tiltings, see **Fig.S1**. Such differences in energy of substitution indicate superior surface passivation, thereby decreasing non-radiative losses for BPA-derivatives in contrast to MPA, **Fig1(e)**.

To further understand the interface passivation mechanism in the presence of the top-electrode stack ($\text{C}_{60}/\text{SnO}_x/\text{Ag}$) by the BPA molecules, we conducted Kelvin probe measurements to track changes in work function (WF). By measuring the WF under dark and light conditions, we extracted the surface photovoltage (SPV) in the presence and absence of C_{60} . With C_{60} , the SPV ($\text{WF}_{\text{dark}} - \text{WF}_{\text{light}}$) follows the trend of the V_{oc} for all BPA derivatives and control devices – **Fig1(f-g)**. HTL/perovskite/ C_{60} stacks were used in these experiments, and SPV values were measured at the electron selective interface (C_{60}). The SPV amplitude increases by 155 mV with BPA, 215 mV with FBPA, and 225 mV with pFBPA. MPA leads to a decrease of 265 mV compared to the control device (**Fig.1(f)**), suggesting that the electron selectivity at this interface is hampered, delivering the smallest surface polarization in DFT calculations, **Fig. 1(h)**. Increasing SPV amplitude in the presence of the full device stack (HTL and ETL) measured from the ETL suggests that the electron concentration in the C_{60} layer is increased due to suppressed non-radiative losses at the perovskite/ C_{60} interface. The highest SPV amplitude (original signal is negative since p-i-n devices are measured from the n-side) is achieved with pFBPA, which benefits from simultaneous interface and surface passivation effects.

We then conducted UPS and KP measurements to compare control and pFBPA passivated devices. Extracting band energetics from UPS, the E_{VBM} barely changed with pFBPA (from -5.7 eV to -5.65 , within the margin of error) – **Fig.S4**. The E_{VBM} offset increases slightly from 0.4 eV to 0.6 eV, and the WF stays constant around -4.9 eV. Since the difference between the E_{VBM} and EF decreases with pFBPA, it signifies

reduced n-type surface characteristics, which is not beneficial at the electron selective interface. Despite an increasing E_{VBM} offset, which should minimize the minority carrier concentration, decreasing recombination and reduced n-doping can also introduce a surface field increasing minority carrier concentration. Hence, at this interface, due to these two compensating effects, we deem improved energetics causing the reduced recombination unlikely and used DFT to understand the interactions between perovskite, PAs, and C_{60} .

The densities of states of the interfaces of the phosphite-modified perovskite surfaces with C_{60} do not show the emergence of recombination-dominating in-gap states originating from the phosphite (**Fig.S2**). This includes states stemming from the perovskite being in contact with C_{60} or any remote coupling, irrespective of the distance between the two. This is in contrast to previous results, irrespective of full or partial substitution at the perovskite; see **Fig.S1**. In the case of a partial pFBPA substitution at the surface, the charge transfer to C_{60} appears to be still efficient, indicated by the mild negative Bader charge accumulation of -0.03 electrons (see **Table.S1**) via the surface-aligned conductive π -system, preserving high FFs, **Fig.S3**. This indicates that a priori, the electrostatics at this interface align more favorably. Fortunately, the favorable alignment does not result in any additional resistive losses, unlike it is the case with dielectric layers¹⁹. In addition, the interface passivation also results in a higher slab dipole moment with the systems with different PAs, **Fig.1(h)**. The system with MPA exhibits the smallest slab dipole moment, 3.2 De. For the BPA derivatives, surface polarization increases, indicated by the slab dipole moment of approximately 3.5 De. Among them, the pFBPA system shows the highest slab dipole moment, albeit only marginally higher than the other BPAs. This enhanced surface polarization suggests the introduction of a more favorable dipole for electron extraction, which is also reflected as a change in the E_{VBM} by 0.15 eV (**Fig.S4**).

After revealing the beneficial effect of the BPA-modified surfaces on the charge-accumulation efficiency, we aimed to understand if the effect can be translated into higher voltages in devices. To do so, we fabricated single-junction perovskite solar cells (ITO/Me-4PACz/SiO_x-np/perovskite/passivation/ C_{60} /SnO_x/Ag) and measured the photovoltaic device performance and PLQY to quantify the non-radiative recombination losses in full devices. On the one hand, all BPA derivatives (BPA, FBPA, pFBPA) achieve high V_{oc} values above 1.225 V by passivating the C_{60} interface and without compromising carrier transport, resulting in PCEs close to 22% in single junction devices (**Fig.1(g)** and **Fig.S3**). The pFBPA devices also benefited from the initial increase in PL due to the surface passivation, achieving a V_{oc} up to ~1.25V and slightly outperforming other BPA derivatives (efficiency of 22%). On the other hand, MPA shows minor interface passivation, delivering a V_{oc} up to 1.19V, whereas the reference devices are limited to <1.14V. The improvement (<40 mV) with MPA is attributed to the suppression of Pb^0 defects (**Fig.1(c)**), which act as deep trap centers in the presence of C_{60} ³². Despite pFBPA providing surface passivation and decreasing non-radiative losses at the C_{60} interface, upon deposition of the negative electrode contacts (C_{60} /SnO_x), the non-radiative recombination loss increases by 35 mV to ~120 mV (**Fig.2(a)**), showing that pFPBA (defined as surface passivation (SP) in the next section) does not entirely suppress interface recombination presumably because of the imperfect band energetics – **Fig.S4**. Even though promising performances (PCE~22%, $V_{\text{OC}} > 1.24\text{V}$) were demonstrated with pFBPA, these results suggests that there is still room for improvement by addressing the perovskite/ C_{60} interface. For that purpose, we aim to combine the surface passivation with a second interfacial modifier that allows for better interface passivation (e.g., enhancing n-type behavior at the interface, introducing a favorable field effect, maximizing the E_{VBM} offset, and minimizing the E_{CBM} offset to improve the charge selectivity).

Surface and interface passivation

To address across-interface recombination between the perovskite and C_{60} by introducing a favorable dipole and n-type enhanced surface doping, we use a piperazinium halide molecule, similar to Li *et al.*, Mariotti *et al.* and Scheler *et al.*^{33,34,40}, but with the counter ion, Cl^- , which we have simulated to exhibit stronger binding to C_{60} than the iodine salt (**Fig. S1, Table S1**). Interestingly, piperazinium chloride (PCl), when utilized by itself, does not provide any surface passivation but rather results in a >10 mV increase in non-radiative losses without C_{60} in place (**Fig. 2B**, right panel). When completing the stack, PCl strongly suppresses the interface

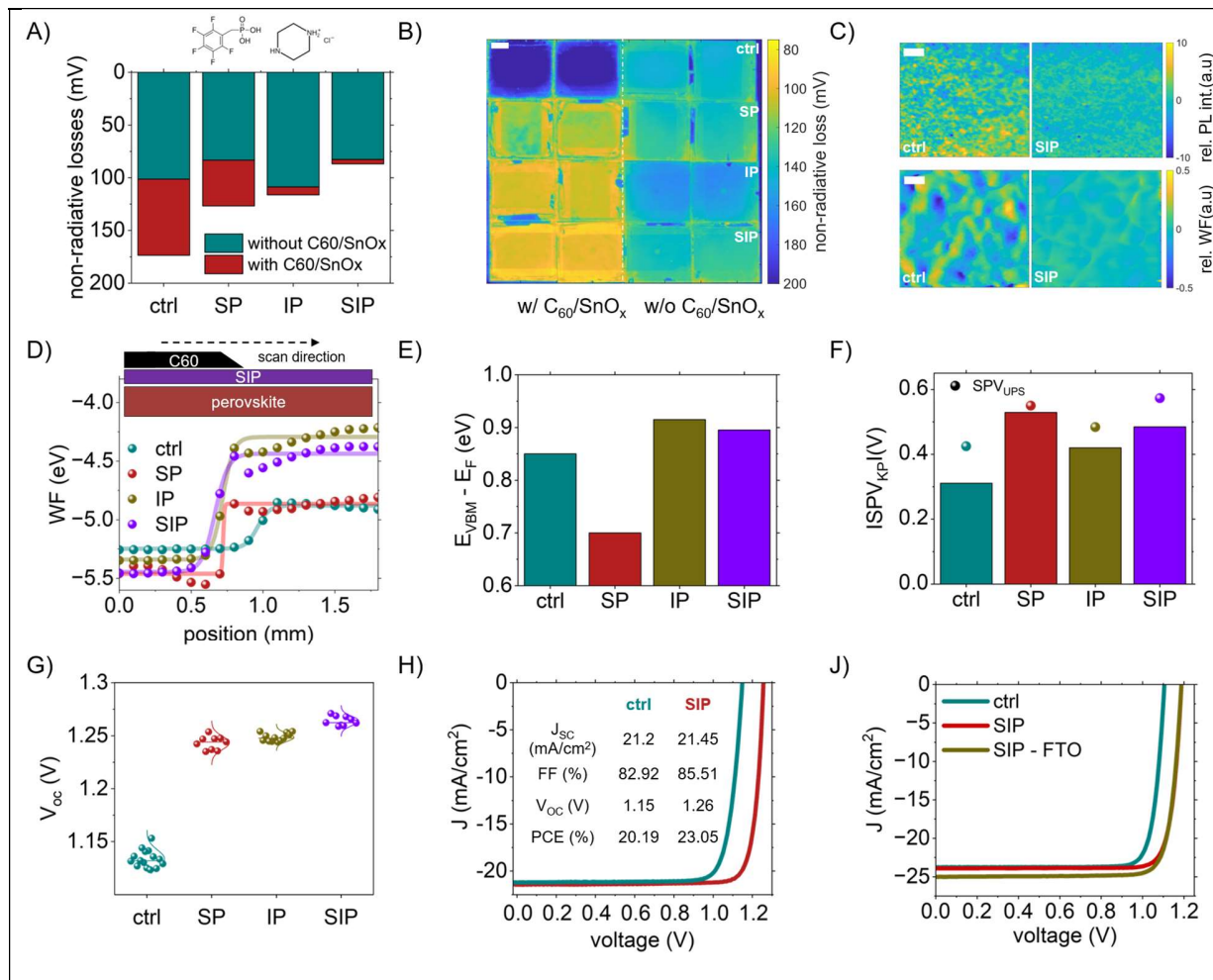


Figure 2. A) Non-radiative loss analysis with and without C₆₀/SnO_x for different conditions, SP (pFBPA), IP (PCI), and SIP (PCI/pFBPA). B) Non-radiative loss mapping measured using wide-field absolute PL (1 cm scale bar) with and without C₆₀/SnO_x for different conditions on 2.5 x 2.5 cm² substrates. C) Hyperspectral imaging (25 μm scale bar) and Kelvin probe force microscopy (250 nm scale bar) maps for control and SIP samples, where the z-axis represents the relative non-radiative loss and relative WF within the sample, respectively. D) Work function results from scanning UPS measurements under light along graded perovskite/C₆₀ (control, SP, IP, SIP). E) The distance between E_{vbm} and E_f for samples with control, SP, IP, and SIP. F) SPV amplitude extracted from KP and UPS measurements for control, SP, IP and SIP samples. G) Open-circuit voltage of single junction devices (with 1.65 eV absorber) with different passivation, surface passivation (SP), interface passivation (IP), and surface and interface passivation (SIP). H) Champion reverse scan JV curves of wide bandgap (1.65 eV) devices with control and SIP. J) Champion reverse JV curves of medium bandgap (1.55 eV) devices with control and SIP on ITO and SIP on FTO substrates.

recombination (**Fig. 2B**, left panel) when depositing C₆₀ and performs better than the best BPA derivative by itself (pFBPA); **Fig.S5-S6**. Hence, we propose to combine an interface passivation agent (IP) (e.g., PCI) and a surface passivation agent (SP), (e.g., pFBPA) with complementary passivation functionalities. When SP and IP are combined (defined as SIP), non-radiative recombination losses due to surface defects and interfacial recombination - even after C₆₀/SnO_x deposition - are strongly suppressed. In contrast to the control devices with a PLQY of ca 0.1%, corresponding to a non-radiative loss of 170 mV, the combined SIP passivation allows ~3% PLQY and thereby a low loss of ~90 mV in complete devices, **Fig.2(a)**. Likewise, the SPV amplitude increases by 65 mV with SIP compared to IP, owing to the increasing carrier concentration - (**Fig.2(f)**). Using absolute wide-field PL mapping, the QFLS of half- and full-cells is mapped across 2.5x2.5 cm² samples. SIP samples exhibit homogeneous passivation, comparable to the former results looking at a smaller area (~0.5 cm²). The homogeneous passivation across the whole surface is highly encouraging for a scale-up of devices as it shows that the method appears to self-assemble into effective

passivation layers, even for manufacturing-relevant dimensions of several cm^2 (**Fig.2(b)** and **Fig.S7-9**). The decrease in the non-radiative loss upon deposition of the negative electrode stack shows the robustness of the bulk and interfaces under ALD deposition conditions. Moreover, PL mapping revealed macro-scale homogeneity of the surface treatments across the samples. SP itself introduces inhomogeneity (standard deviation of NR-loss = 42 mV), especially in the presence of a top-electrode stack (**Fig.2(b)**). However, when SP is combined with IP, i.e., SIP samples show a more uniform distribution (standard deviation of non-radiative loss = 23 mV) and around an overall high QFLS (~ 1.29 eV), **Fig.2(b)-S7,9** across the whole sample. We hypothesize that the excess PA that remains on the surface as an overlayer is washed away with the sequential application of IP.

After investigating the homogeneity on the cm scale, we aimed to understand whether the homogeneity is maintained at the micro-nano scale. When the WF distribution across the surface is investigated via Kelvin probe force microscopy (map size of $2 \times 2 \mu\text{m}$) and absolute PL spectra using hyperspectral imaging (map size of $100 \times 100 \mu\text{m}$), a decrease in the standard deviation of the WF (from 150 meV to 42 meV) and improved homogeneity in PL is observed (**Fig.2(c)**). Improved homogeneity in the WF and PL distribution can contribute to minimizing scaling-up losses and achieving higher fill factors with minor optoelectronic fluctuations^{20,35}. Furthermore, the changes in the surface microstructure are investigated with top-view scanning electron microscopy (SEM) and grazing-incident wide-angle x-ray scattering (GIWAXS), where it can be seen that with SP, and SIP the average domain size shows a slight increase (**Fig.S10**). We likewise observe a slightly improved crystallinity derived from the stronger signal of the “main” perovskite GIWAXS peak (as probed under every angle) in the case of SIP compared to the control films, suggesting a slight improvement in the film’s top morphology²⁰. In contrast to many alternative surface modifications, we did not observe the formation of a low dimensional (e.g., 2D) perovskite, or any other diffracting feature, suggesting the formation of a thin amorphous layer, **Fig. S10**.

Surface energetics

To understand the influence of the surface treatments on the surface work function (under light and dark conditions deducing surface photovoltage), we have conducted KP and UPS measurements for different layer stacks. We fabricated test samples ITO/HTL/perovskite/ C_{60} (graded) with specific geometry (**Fig.2(d)**) and constructed an array (20 points) of measurements for UPS separated by $100 \mu\text{m}$ starting in the C_{60} coated area and then ending in the perovskite zone while passing over the graded region (more details in the UPS mapping section in Methods) to capture the band energetics starting from C_{60} and down to the perovskite surface within a single sample. A similar sample geometry is utilized for KP measurements, but only 2 points on the C_{60} coated area and non- C_{60} coated are measured instead – **Fig.S11**. Exemplary output for the UPS spectra (secondary electron cut-off and E_{VBM} and fits) and KP measurements can be seen in **Fig.S12-S13**, respectively. For all of the samples (control, SP, IP, SIP) in UPS measurements, the WF converges to similar values ~ -4.9 eV in the dark and -5.4 ± 0.1 eV under light conditions – **Fig.2(d)** on C_{60} which shows similar electronic characteristics of C_{60} layers despite being deposited on different surfaces. When illuminated, the WF decreases with IP and SIP from -4.6 eV to -4.2 eV – **Fig.2(d)** and **Fig.S14**. - This does not necessarily signify a modulation towards more n-type without knowing how the band-edges shift relative to E_{f} . Since the valance band maxima (E_{VBM}) also changes upon different passivation schemes – **Fig.S14** - we plot the distance between E_{f} and the E_{VBM} – **Fig.2(e)** - which shows increasing distance with the IP and SIP showing enhanced n-type behavior bringing the Fermi level closer to the conduction band. We observed similar direction and magnitude of shifts in KP results showing enhanced n-type behavior, which aligns with the literature³⁶. At the electron extraction interface (perovskite/ C_{60}), modulating the WF towards more n-type potentially decreases the minority carrier concentration (holes, p_{n}), resulting in lower non-radiative recombination. Hence, we conclude that the IP treatment does not alter the interface defect density but introduces a field effect that decreases p_{n} , which reduces recombination. For the SIP-treated samples, we observe the highest SPV amplitude (~ 0.57 eV for SIP and 0.41 eV for control), which is in line with the KP results, **Fig.2(f)**. Also, the increase in the SPV_{UPS} amplitude is similar to SPV_{KP} (~ 0.16 eV), confirming higher carrier concentrations due to enhanced surface and interface passivation. Moreover, from DFT calculations (see **Table.S1**), the Bader charge accumulation on C_{60} increases further to -0.04 electrons with the partial (12.5%) PCl and pFBPA substitution, confirming the improved electron extraction efficiency.

The combination of pFBPA and PCl introduces a WF n-type shift, creating a favorable field effect at the electron extraction interface. This is complemented by the increased valance band maxima offset minimizing the minority carrier concentration, **Fig.S14**. In addition to the changes in the surface work function, the valance band minima (E_{VBM}) is also measured across the perovskite/ C_{60} interface, as seen in **Fig. S14**. The E_{VBM} offset increases significantly from (0.4 eV) with IP (1.05 eV) and SIP (0.95 eV) compared to the control devices, resulting in a higher offset for holes. A higher offset for minority carriers at the electron charge extraction interface is beneficial to minimize their concentration, decreasing non-radiative recombination. As a result, owing to the enhanced n-type surface characteristics and higher minority carrier offset of the IP, despite the SP treatment introducing a WF shift towards more p-type itself, the combination of SP & IP (SIP) preserves n-type modulation – **Fig.S14**.

Single junction device performance

In single junction wide bandgap devices, the increase in open-circuit voltage with the utilization of SIP compared to SP or IP is ~ 25 and ~ 20 mV, respectively, **Fig.2(g)** with a champion PCE (SIP treatment) reaching 23%. In contrast, the control devices without any passivation yield ca. 20% - **Fig.2(g) and Fig.2(h)**. The significant improvement in FF originates (**Fig.2(h)**) from the decreased non-radiative losses, increasing the pFF (**Fig.S15**) up to $\sim 88\%$ and FFs up to 85.5%. We did not observe statistically relevant differences in the short circuit current density (**Fig. S16**). To compare different combinations of PAs with PCl we fabricated devices with BPA/PCl, which showed similar device performance to PCl alone. We explain this by noting that BPA shows no notable surface passivation compared to the other PAs (**Fig.1(b)**), which does not enable improvements compared to PCl alone – **Fig.S17**. We further showcase the SIP strategy being applicable to other absorbers as well, by using a medium-bandgap absorber (1.55 eV) $\text{Cs}_{0.05}\text{FA}_{0.90}\text{MA}_{0.05}\text{PbI}_3$ (with an additional 3% MAPbCl_3)¹² and demonstrate $>24\%$ PCE on ITO-substrates and $>24.75\%$ (**Fig.2(j)**) PCE on FTO-substrates (with only 0.22 mA/cm^2 discrepancy in J_{sc} measured from EQE (24.79 mA/cm^2) and JV (25.01 mA/cm^2) – **Fig.S18**).

Perovskite-silicon tandem device performance

We successfully integrated the newly developed SIP into the top cell of front-side polished perovskite-silicon heterojunction tandem solar cells, **Fig.S19**. First of all, on 1 cm^2 , we fine-tuned the bandgap ($\sim 1.65 \text{ eV}$, with the final composition $\text{Cs}_{0.05}(\text{FA}_{0.9}\text{MA}_{0.1})_{0.95}\text{Pb}(\text{I}_{0.8}\text{Br}_{0.2})_3 + 3\%\text{MAPbCl}_3$), and by increased the absorber thickness to 600 nm – **Fig.S19** - for optimal performance in monolithic tandems. The improvement from the control devices to SIP was primarily driven by increased FF and V_{oc} . Our top-performing device reached a PCE of 32.9% (JV scan; with a V_{oc} of 1.983 V, J_{sc} of 20.24 mA/cm^2 , and FF of 81.96% - **Fig.3(a)**) and $\sim 32.45\%$ when tracking the MPP, **Fig.S20**. The certified steady-state efficiency of two similar device is measured at 31.6% and 31.14% by JRC-ESTI, **Fig.S21-22**. The open-circuit voltage achieved in the latter certification is 2.0006V. The passivation strategy is seamlessly transferred to the tandem devices, which results in a substantial increase in average PCE with SIP compared to SP and IP, respectively **Fig.3(b-c)**. The EQE of one of the champion devices is depicted in **Fig.3(d)**. The photogenerated currents for the perovskite top cell and the silicon-heterojunction bottom cell are 20.90 and 20.33 mA/cm^2 , respectively, resulting in a cumulative photogenerated current of 41.23 mA/cm^2 , excluding shadowing losses from the metal fingers (estimated as $\sim 1.5\%$). Moreover, V_{oc} and PCE distribution of the devices among six batches (including shunted devices) utilizing SIP can be seen in **Fig.S23** and the best three batches (excluding shunted devices) in **Fig.S24**, which shows repeatable performance over hundreds of devices in different batches.

Furthermore, upon the successful integration of SIP into our 1 cm^2 tandem baseline and with the knowledge of homogenous passivation we then fabricated larger devices with 4 cm^2 and 60 cm^2 active areas. Screen-printed metallization is utilized in devices with an area bigger than 1 cm^2 instead of evaporated Ag contacts which requires curing the paste at 130°C for 10 min in ambient conditions³⁷. The bottom cell processing was simplified compared to the 1 cm^2 bottom cells (no nc-SiOx(n) index matching layer and no SiOx-np

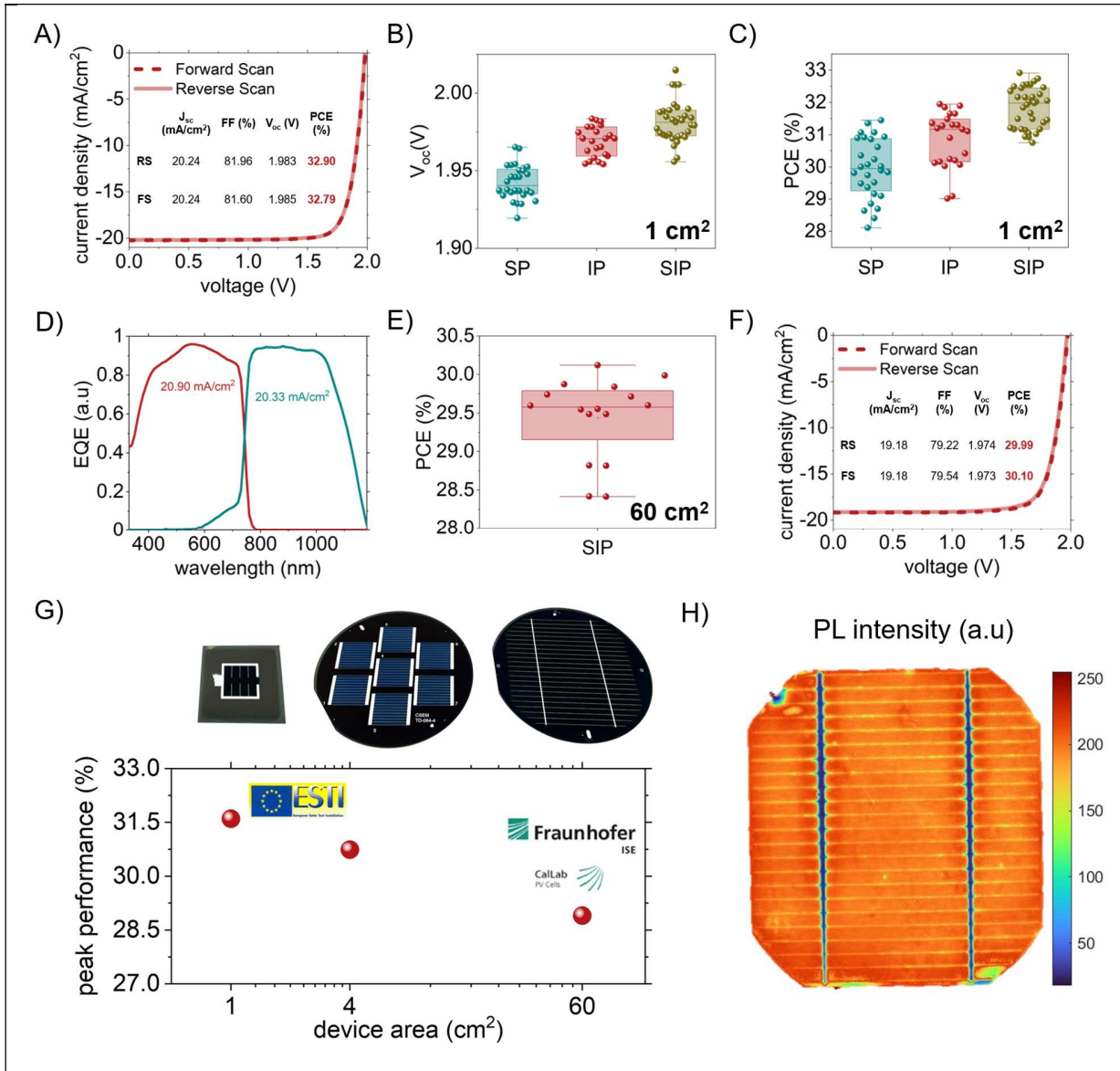


Figure 3. A) Champion reverse and forward scan JV curve of SIP device and PV performance parameters. B-C) Open-circuit voltage and PCE (both reverse and forward scan) statistics of tandem devices fabricated with SP, IP and SIP over multiple batches. D) EQE spectrum of a SIP device. E) PCE statistics of large area (60 cm²) devices with SIP. F) Champion reverse and forward JV curves of 60 cm² device and PV performance parameters. G) Peak efficiency versus device active area graph and image of corresponding devices. 1 cm² device is certified by JRC-ESTI and 60 cm² device by Fraunhofer ISE CalLab. H) PL imaging (top-cell) of the 60 cm² tandem device showing the high level of top cell homogeneity, including the passivation.

back reflector). It is also worth mentioning that the certified 60 cm² champion device features a double-side sub-micron textures. The bandgap of the absorber was also reduced from 1.65 to 1.63 eV to benefit from higher current mismatch due to the higher pFF of the bottom cell (towards the bottom cell, reducing the impact of possible shunts in the large area top cell)²⁴. The decreasing V_{oc} due to the decreasing bandgap in the top cell is compensated by the suppressed perimeter recombination (since cell size becomes much larger than the diffusion length) in the bottom cell as the area increases from 1 cm² to 60 cm² preserving V_{oc} 's ~1.97V. The peak device performances achieved are 31.6% (certified by JRC-ESTI), 30.74% (in-house), and 28.90% (certified by Fraunhofer ISE CalLab) on 1, 4 and 60 cm², respectively **Fig.3(g)**. The in-house reverse and forward JV curves of the champion 60 cm² and 4 cm² devices can be seen in **Fig.3(f)** and **Fig.S25**, respectively, the maximum power point tracking of 60 cm² device (**Fig.S26**) and the certified results (1.965V, 18.87 mA/cm², 28.9% steady state efficiency, 77.94% FF, 29.0% reverse scan efficiency and EQE)

from Fraunhofer ISE CalLab can be seen in **Fig.S27**. Open-circuit voltages of ~ 1.96 V were achieved across these different length scales, showing that the surface & interface passivation is robust and homogenous (from nanometer to cm scale) and transferable to larger areas as confirmed by PL images of a large area device (**Fig.3(h)**) with a tight intensity distribution (**Fig.S28**). Moreover, the average PCE from two batches composed of eight large-area devices is 29.5% (both reverse and forward scan data points are included since the hysteresis is not significant) (**Fig.3(e)**), a testimony to the high repeatability of the SIP treatment.

Stability - stabilization of perovskite surface but weak interface and enhanced ionic loss

Upon dark N_2 storage, a SIP device with an initial efficiency of 31.88% showed no sign of degradation (**Fig.S29**) after > 1400 h, which aligns with our previous reports where similar hydrophobic fluorinated phosphonic acid were utilized²³. While shelf stability is essential, solar cells must also withstand external stresses, particularly heat and light, to perform reliably under real-world operating conditions. Therefore, we focused next on testing the device under these operational conditions. To check the influence of the SIP (control vs SIP) on the stability of the single junction devices, we tracked the maximum power point of devices in N_2 , without encapsulation, at $\sim 35^\circ\text{C}$. After 115 hours, the performance of the SIP devices decreased from 21% to 16%, whereas the performance of control devices increased from 17.5% to 20%, **Fig.S30**. We hypothesize that the performance loss of the SIP devices can be attributed to the ionic losses through the additional mobile ions at the interface (e.g., piperazinium⁺, Cl⁻, pFBPA⁻)^{38,39}, and a weakened perovskite/ C_{60} interface.

First, we conducted fast hysteresis (FH) JV and bias-assisted charge extraction (BACE) measurements to test the former hypothesis (see **Fig.S31-S32**)³⁸⁻³⁹. In the FH measurements, the significant losses in J_{SC} , FF, and consequently PCE observed in the SIP device between fast (ion-freeze) and slow (steady-state) measurements are attributed to enhanced ionic loss. In contrast, the control sample exhibited only minor performance losses between ion-freeze and steady-state conditions. The BACE measurements further confirmed the increased ionic losses in the SIP device, which shows an order of magnitude higher density of ions (**Fig.S32**). These results demonstrate that faster degradation of SIP devices is related to enhanced ionic losses, which are exacerbated under illumination in line with the observations from Scheler *et al.*⁴⁰.

Then, using DFT, we compared the binding energy (E_b , eV) of C_{60} for different systems to understand further the accelerated degradation of devices with SIP, see **Table S1**. All reasonable binding sites were considered to choose the lowest energy site. We obtained (E_b) of -0.86 and -0.96 eV for partial (12.5%) and full (100%) surface substitution of IPb-I by IPb-OPO₂HCH₂C₆F₅ (pFBPA), respectively, indicating stabilization of the interface with denser surface coverage with the phosphites. The energetically favorable site for partial substitution is not above the phenyl rings but closer to the phosphite group, creating O $\cdots$ C_{60} and F $\cdots$ C_{60} contacts (in addition to the strong I $\cdots$ C_{60} contact with the perovskite surface), see **Fig. S1 and Table S1**. This increase in negative E_b amplitude signifies a stabilization of the surface and interface with pFBPA. Experimental results show that the interface stability changes significantly when piperazinium chloride is added onto the pristine perovskite surface. To understand this effect, we modeled the interface of a piperazinium-chloride-modified perovskite surface with C_{60} . Substitution of FAI by HNC₄H₈NH₂·Cl (PCL) achieves E_s of -0.07 eV, indicating stabilization of the piperazinium-chloride-modified surface due to Pb-Cl bonds, stronger NH $\cdots$ Cl contacts created by HNC₄H₈NH₂ (as compared to NH $\cdots$ I contacts created by FA) and additional sp³ CH $\cdots$ Cl and CH $\cdots$ I contacts created by HNC₄H₈NH₂. However, the binding of C_{60} to the perovskite surface is reduced ($E_b = -0.38$ eV) indicating a destabilization of the piperazinium-chloride-modified interface due to weaker N $\cdots$ C_{60} contacts created by HNC₄H₈NH₂ (as compared to the O $\cdots$ C_{60} , F $\cdots$ C_{60} , and I $\cdots$ C_{60} contacts created by the phosphite-modified surfaces) and inaccessibility of the Cl atoms of the perovskite because of capping by the piperazinium, see **Fig.S1**.

The presented DFT results imply that strong binding is created at halogen $\cdots$ C_{60} contacts that could be realized either on top of a dense layer of halogenophenyl-functionalized phosphites (without piperazinium halide) on the fully substituted surface or near halogenophenyl-functionalized phosphites (with piperazinium halide) on the partially substituted surface where they do not block halogen $\cdots$ C_{60} contacts. The second case was modeled for a surface with partial substitution of Pb-I by IPb-OPO₂HCH₂C₆F₅ and one HNC₄H₈NH₂·Cl

ion pair in the vicinity of a I···C₆₀ contact. Indeed, E_b of C₆₀ reaches -0.99 eV, indicating a synergetic effect of the halogenophenyl-functionalized phosphite and piperazinium chloride as long as partial substitution is preserved, **Fig.S1** and **Table S1**. Even though experimentally determining the surface substitution fractions with utilized concentrations (1mM) is challenging, the significantly accelerated degradation of the devices might points towards high PCl fractions lowering binding energies and causing a weak interface.

To experimentally evaluate whether the destabilization at the interface due to the high fraction of PCl substitution is the main driver of accelerated degradation, we conducted a comparison of device stability by forming a SIP layer on top and below the perovskite layer (SIP-top and SIP-bottom configurations), as shown in **Fig. S33(a)**. Given that the SAM/perovskite interface is already of high quality (with a voltage loss of less than 15 mV), the SIP-bottom devices did not exhibit an enhanced open-circuit voltage. The accelerated degradation observed in SIP-top devices, where the perovskite/SIP/C₆₀ interface is present, was not seen in SIP-bottom devices, even though in this configuration high energy photons are absorbed closer to the SAM/SIP/perovskite interface, potentially providing more energy to drive chemical interactions. This difference in stability suggests that rather than the chemical reactions between the perovskite and SIP, the weakened perovskite/C₆₀ interface and enhanced ionic losses (also points out towards the importance of C₆₀ in ionic loss mechanism) are the primary cause of the accelerated degradation^{40,41}, making the devices more vulnerable to external stress factors such as light, humidity, and heat. We confirm this by peeling off, cleaning the top surface, and replacing the top-electrode stack (SIP/C₆₀/SnO_x/Ag), in an attempt to repair degraded SIP devices. Indeed, this approach partially restored performance, as shown in **Fig. S33(b)**. The PCE could be restored to > 80% of its initial value, indicating that full recovery is not possible, even when SIP and C₆₀ were redeposited, likely due to bulk degradation of the absorber potentially made more vulnerable due to the weakened perovskite/C₆₀ interface and enhanced ionic losses. Reducing the concentration, and thus the surface fraction, of piperazinium chloride to preserve the halogen···C₆₀ contact that promotes high binding energy could be a potential strategy to achieve a better balance between efficiency and stability.

Discussion

We believe that many passivation agents are, in fact, destabilizing the interface and, despite short-term improvements, are finally detrimental. It is noteworthy that recently Chen *et al.*²⁵ in a similar device architecture, adding a chlorinated functional group to the benzyl ring of a passivating agent increased the binding energy at the interface with C₆₀. Moreover, Yang *et al.*⁴³ further enhanced the stability of the interface by utilizing a chemically resilient head group (amidinium) instead of the commonly used ammonium, which retarded deprotonation reactions. Scheler *et al.*⁴⁰ modified the counter-ion of the piperazinium halides to tosylate and the piperazinium tosylate-modified devices suffered less from ion-induced losses. These points towards potential solutions to engineer the surface and interface passivating molecules towards stable and efficient perovskite photovoltaics where the strong halide-C₆₀ interaction could be attached to a chemically passivating moiety, chemically resilient head groups can be utilized instead of ammonium groups and ionic losses can be minimized with counter ion engineering.

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Author contributions: Conceptualization of the idea by KA and FS. Experimental design by KA and CMW. Single junction and tandem top cell fabrications (1 and 60 cm²) by KA. DFT calculations and analysis by AO and US. PLQY measurements and analysis by KA. 1 cm² bottom cell development and fabrication by DT and JH, and 60 cm² bottom cell development and fabrication by CA. XPS/UPS measurements and analysis MM and KA. Large area tandem developments (>1 cm²) by KA, MDB, and LC. KPFM and SEM measurements MO, GIWAXS analysis by AK. KP measurements by AM, FL. Wide-field PL, and HI measurements by AL, JBP, and DO. Writing-review & editing KA and CMW. Supervision and funding acquisition by AWH, QJ, CB, and CMW. Manuscript revision, all authors.

Competing interests:

The authors declare no conflict of interest.

References

- Chiang, C. H. & Wu, C. G. Bulk heterojunction perovskite-PCBM solar cells with high fill factor. *Nat Photonics* **10**, 196–200 (2016).
- Liu, X. *et al.* Novel efficient C60-based inverted perovskite solar cells with negligible hysteresis. *Electrochim Acta* **288**, 115–125 (2018).
- Yoo, J. J. *et al.* Efficient perovskite solar cells via improved carrier management. *Nature* **590**, 587–593 (2021).
- Warby, J. *et al.* Understanding Performance Limiting Interfacial Recombination in pin Perovskite Solar Cells. *Adv Energy Mater* **2103567**, 1–10 (2022).
- Tong, J. *et al.* Wide-Bandgap Metal Halide Perovskites for Tandem Solar Cells. *ACS Energy Lett.* **6**, 1, 232–248 (2021).
- Lin, Y. *et al.* Matching Charge Extraction Contact for Wide-Bandgap Perovskite Solar Cells. *Advanced Materials* **29**, 1–8 (2017).
- C. M. Wolff, P. Caprioglio, M. Stolterfoht, D. Neher, Nonradiative Recombination in Perovskite Solar Cells: The Role of Interfaces. *Adv. Mater.* **31**, 1902762, (2019).
- Caprioglio, P. *et al.* On the Relation between the Open-Circuit Voltage and Quasi-Fermi Level Splitting in Efficient Perovskite Solar Cells. *Adv Energy Mater* **9**, (2019).
- Jiang, Q. *et al.* Surface passivation of perovskite film for efficient solar cells. *Nat Photonics* **13**, 460–466 (2019).
- Aydin, E., De Bastiani, M. & De Wolf, S. Defect and Contact Passivation for Perovskite Solar Cells. *Advanced Materials* **31**, 1–20 (2019).
- Azmi, R. *et al.* Damp Heat-Stable Perovskite Solar Cells with Tailored-Dimensionality 2D/3D Heterojunctions. *Science* **376**, 73–77 (2022).
- Liu, C. *et al.* Bimolecularly Passivated Interface Enables Efficient and Stable Inverted Perovskite Solar Cells. *Science* **382**, 810–815 (2023).
- Li, Z. *et al.* Organometallic-Functionalized Interfaces for Highly Efficient Inverted Perovskite Solar Cells. *Science* **376**, 416–420 (2022).
- Li, B. *et al.* Highly Efficient and Scalable p-i-n Perovskite Solar Cells Enabled by Poly-metallocene Interfaces. *J Am Chem Soc.* **146** (19), 13391–13398 (2024).
- Isikgor, F. H. *et al.* Concurrent cationic and anionic perovskite defect passivation enables 27.4% perovskite/silicon tandems with suppression of halide segregation. *Joule* **5**, 1566–1586 (2021).
- Mao, K. *et al.* Unveiling and Balancing the Passivation-Transport Trade-Off in Perovskite Solar Cells with Double-Side Patterned Insulator Contacts. *Adv Energy Mater* **13**, 2302132 (2023).
- Liu, J. *et al.* Efficient and stable perovskite-silicon tandem solar cells through contact displacement by MgF_x. *Science (1979)* **377**, 302–306 (2022).

18. Menzel, D. *et al.* Field Effect Passivation in Perovskite Solar Cells by a LiF Interlayer. *Adv Energy Mater* **12**, 2201109 (2022).
19. Artuk, K. *et al.* A Universal Perovskite/C60 Interface Modification via Atomic Layer Deposited Aluminum Oxide for Perovskite Solar Cells and Perovskite–Silicon Tandems. *Advanced Materials* **2024**, *36*, 2311745 (2024)
20. Chen, H. *et al.* Regulating surface potential maximizes voltage in all-perovskite tandems. *Nature* **613**, 676–681 (2023).
21. Mariotti, S. *et al.* Interface engineering for high-performance, triple-halide perovskite-silicon tandem solar cells. *Science* **381**, 63–69 (2023).
22. Li, F. *et al.* Regulating Surface Termination for Efficient Inverted Perovskite Solar Cells with Greater Than 23% Efficiency. *J Am Chem Soc* **142**, 20134–20142 (2020).
23. Chin, X. Y. *et al.* Interface passivation for 31.25%-efficient perovskite/silicon tandem solar cells. **63**, 59–63 (2023).
24. Turkay, D. & Artuk, K. *et al.* Synergetic substrate and additive engineering for over 30%-efficient perovskite-Si tandem solar cells. *Joule* **8**, 1735–1753 (2024).
25. Chen, H. *et al.* Improved Charge Extraction in Inverted Perovskite Solar Cells with Dual-Site-Binding Ligands. *Science* **384**, 189–193 (2024).
26. Ugur, E. *et al.* Enhanced Cation Interaction in Perovskites for Efficient Tandem Solar Cells with Silicon. *Science* **385**, 533–538 (2024).
27. Liu, J. *et al.* Perovskite-silicon tandem solar cells with bilayer interface passivation. *Nature* (2024) doi:10.1038/s41586-024.
28. Feldmann, F. *et al.* Tunnel oxide passivated contacts as an alternative to partial rear contacts. *Solar Energy Materials and Solar Cells* **131**, 46–50 (2014).
29. Green, M. A. The Passivated Emitter and Rear Cell (PERC): From conception to mass production. *Solar Energy Materials and Solar Cells* **143**, 190–197 (2015).
30. Xu, J. *et al.* Triple-halide wide-band gap perovskites with suppressed phase segregation for efficient tandems. *Science (1979)* **367**, 1097–1104 (2020).
31. Xiong, S. *et al.* Reducing nonradiative recombination for highly efficient inverted perovskite solar cells via a synergistic bimolecular interface. *Nat Commun* **15**, 5607 (2024).
32. Liang, J. *et al.* Origins and influences of metallic lead in perovskite solar cells. *Joule* **6**, 816–833 (2022).
33. Li, F. *et al.* Regulating Surface Termination for Efficient Inverted Perovskite Solar Cells with Greater Than 23% Efficiency. *J Am Chem Soc* **142**, 20134–20142 (2020).
34. Mariotti, S. *et al.* Interface engineering for high-performance, triple-halide perovskite-silicon tandem solar cells. *Science* **381**, 63–69 (2023).
35. Kerner, R. A., Xu, Z., Larson, B. W. & Rand, B. P. The role of halide oxidation in perovskite halide phase separation. *Joule* vol. 5 2273–2295 (2021).
36. Chen, H. *et al.* Regulating surface potential maximizes voltage in all-perovskite tandems. *Nature* **613**, 676–681 (2023).
37. Kamino, B. A. *et al.* Low-Temperature Screen-Printed Metallization for the Scale-Up of Two-Terminal Perovskite-Silicon Tandems. *ACS Appl Energy Mater* **2**, 3815–3821 (2019).
38. Thiesbrummel, J. *et al.* Universal Current Losses in Perovskite Solar Cells Due to Mobile Ions. *Adv Energy Mater* **11**, (2021).
39. Thiesbrummel, J. *et al.* Ion-induced field screening as a dominant factor in perovskite solar cell operational stability. *Nat Energy* **9**, 664–676 (2024)
40. F. Scheler, *et al.*, Correlation of Band Bending and Ionic Losses in 1.68 eV Wide Band Gap Perovskite Solar Cells. *Adv. Energy Mater.* **2024**, 2404726.
41. De Bastiani, M. *et al.* Mechanical Reliability of Fullerene/Tin Oxide Interfaces in Monolithic Perovskite/Silicon Tandem Cells. *ACS Energy Lett* **7**, 827–833 (2022).
42. Ren, X. *et al.* Mobile iodides capture for highly photolysis- and reverse-bias-stable perovskite solar cells. *Nat Mater* **23**, 810–817 (2024).
43. Yi Yang *et al.* Amidination of ligands for chemical and field-effect passivation stabilizes perovskite solar cells. *Science* **386**, 898–902 (2024).
44. Antognini, L. *et al.* Influence of the Dopant Gas Precursor in P-Type Nanocrystalline Silicon Layers on the Performance of Front Junction Heterojunction Solar Cells. *IEEE J Photovolt* **11**, 944–956 (2021).
45. Turkay, D. *et al.* Self-aligned silica nanoparticle rear reflectors for single-junction Si and perovskite-Si tandem solar cells. Submitted (2024)
46. P. Giannozzi *et al.*, Advanced capabilities for materials modelling with Quantum ESPRESSO, *J. Phys.: Condens. Matter* **29**, 465901 (2017).
47. P. Giannozzi *et al.*, QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials, *J. Phys. Condens. Matter* **21**, 395502 (2009).

48. M. J. van Setten et al., The PseudoDojo: Training and grading a 85 element optimized norm-conserving pseudopotential table, *Comput. Phys. Commun.* 39, 226 (2018).
49. O. A. Vydrov and T. V. Voorhis, Nonlocal van der Waals functional made simple, *Phys. Rev. Lett.* 103, 063004 (2009).
50. O. A. Vydrov and T. V. Voorhis, Nonlocal van der Waals density functional: The simpler the better, *J. Chem. Phys.* 133, 244102 (2010).
51. J. Calbo et al., The nonlocal correlation density functional VV10: A successful attempt to accurately capture noncovalent interactions, *Annu. Rep. Comput. Chem.* 11, 37 (2015).
52. P. Würfel, The chemical potential of radiation, *J. Phys. C: Solid State Phys.*, vol. 15, no 18, p. 3967-3985, (1982)
53. Jiang, Z. (2015). GIXSGUI: a MATLAB toolbox for grazing-incidence X-ray scattering data visualization and reduction, and indexing of buried three-dimensional periodic nanostructured films. *J. Appl. Cryst.* 48, 917-926 (2015).

Supplementary Materials for

60 cm² perovskite-silicon tandem solar cells with an efficiency of 28.9% by homogenous passivation

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The PDF file includes:

Materials and Methods
Figs. S1 to S34

Materials and Methods

Perovskite fabrication & deposition

1. Triple cation triple halide absorber (TC-TH) - wide (1.65 eV) bandgap perovskite absorber

Triple cation perovskite (TC-TH) absorber utilized in this work is $\text{Cs}_{0.05}(\text{FA}_{0.90}\text{MA}_{0.10})_{0.95}\text{Pb}(\text{I}_{0.80}\text{Br}_{0.20})_3 + \sim 3\% \text{MAPbCl}_3$. The absorber is fabricated with one-step anti-solvent method. Three separate stock solutions are prepared which are composed of 1.36M FAl. (Dyename, >99.99%), 1.5M PbI_2 (TCI, >99.99%) in 4:1 (volume ratio) DMF:DMSO and 0.78M MABr (Dyename, >99.99%), 0.78M FABr (Dyename, >99.99%), 1.5M PbBr_2 (TCI, >99.99%) in 4:1 (volume ratio) DMF:DMSO and 1.5M CsI (Alfa Aesar, >99.9%) in DMSO. Then these solutions are mixed in a vial containing 15 mg/mL PbCl_2 (TCI, >99.99%) and 5 mg/mL

MACl (Dyename, >99.99%) with 800:200:40 volume ratio respectively. The precursor solution (100 μ L) is spread onto the substrate (2.5x2.5 cm²), then spun at 3500 rpm with 2000 rpm/s for 35 s. When 10 s left during the spin-program, 250 μ L of Anisole (Sigma Aldrich, Anhydrous >99.8%) is dropped onto the substrate. Then the samples are annealed at 100°C for 15-20 min inside the glovebox.

2. Triple cation medium (1.55 eV) bandgap perovskite absorber

The medium bandgap (MBG) absorber utilized in this work is Cs_{0.05}FA_{0.9}MA_{0.05}PbI₃ with 5% excess PbI₂ and 5% excess MAPbCl₃. The solution is prepared by mixing, 1.68M PbI₂, 0.048M PbCl₂, 0.08M MAI, 0.2M MACl, 1.43M FAI, 0.08M CsI in DMF:DMSO 4:1 (volume ratio). The absorber is fabricated with the one-step antisolvent method. The precursor solution (100 μ L) is spread onto the substrate (2.5x2.5cm²), then spun at 3500 rpm with 1000 rpm/s for 35 s. When 10 s are left during the spin-program, 250 μ L of Anisole is dropped onto the substrate. Then the samples are annealed at 100°C for 15-20 min inside the glovebox.

Surface and interface passivation

For the PA molecule family study, 1 mM MPA (Sigma Aldrich, >98%) or BPA (Sigma Aldrich, >97%) or FBPA (Sigma Aldrich, >97%) or pFBPA (Sigma Aldrich, >97%) is dissolved in IPA and spin-coated at 6000 rpm dynamically and spun for 30 s followed by an annealing for 5 min at 100 °C.

For interface passivation, 1 mM PCl (Dyename,>98%) in IPA, for surface passivation 1 mM pFBPA (Sigma, >97%) in IPA and for the surface and interface passivation 1 mM PCl and 1 mM pFBPA in IPA utilized. Upon deposition of the perovskite absorber, the SP, IP, or SIP is spin-coated at 6000 rpm dynamically and spun for 30 s followed by an annealing of 100 °C for 5 min.

For the passivation of medium bandgap perovskite, piperazinium iodide (Dyename, 1 mM in IPA) or propane-diammonium iodide (TCI, 2 mM in IPA) is utilized instead of piperazinium chloride.

There are two other methods to apply SIP and reach similar performance;

- 1) To use 1 mM pFBPA as an additive into the perovskite ink that accumulates on interfaces²⁴ (demonstrated in our previous work) providing surface passivation and then 1 mM PCl is spin-coated on top of the absorber with pFBPA additive.
- 2) To use sequential application of 1 mM pFBPA followed by 1 mM of PCl on the top surface. Samples are annealed in between PCl and pFBPA at 100 °C for 5 min. Likewise, a 6000 rpm spin recipe is utilized.

Solar cell fabrication

Fabrication of single-junction perovskite solar cells

0.7 mm ITO (15 ohm/square - TKing) coated glass substrates are cleaned with Helmanexx and DI respectively using ultrasonic baths for 15 min. Samples are exposed to UV-ozone for 30 min right before the SAM deposition. SAM (e.g., Me-4PACz) solution (1 mg/mL) is spin-coated onto substrates for 100 μ L with a program of 10 s resting time, 3000 rpm, 300 rpm/s. Then the substrates are annealed for 10 min at 115°C. To improve the wetting, 0.1% SiO_x-np in EtOH (20 nm diameter) spin-coated for 100 μ L with a program of 2000 rpm with 500 rpm/s for 30 s and annealed for 115 °C for 10 min²⁴. For the deposition of the perovskite absorber, the one-step absorber (TC-TH) that is mentioned in the above sections is utilized. Details of the passivation solutions (IP, SP or SIP) have been given in the section above. 20-25 nm of C₆₀ (Creaphys, >99.9% - resublimed) is deposited via thermal evaporation with a rate of 0.2 Å/s in the Angstrom thermal evaporator. Then ALD-SnO_x is deposited at 95-100°C with pulse purge times of 0.3s / 6s / 0.1s / 6s for 150-175 cycles with TDMASn and H₂O sources. The utilized thicknesses for baseline devices are 20-22.5 nm measured with an ellipsometer on c-Si. For the metal contact, 150 nm of Ag is deposited via thermal

evaporation with a rate of 1.5-2 A/s. 110 nm of MgF_x evaporated on the glass side for anti-reflective coating. The device active area is 0.2 cm^2 .

Fabrication of monolithic perovskite-silicon heterojunction tandem solar cells – 1 cm^2

The bottom cell fabrication process is performed on 200 or 280 μm -thick n-type, 2 $\text{ohm}\cdot\text{cm}$, FZ Si wafers. A layer of SiN_x is applied to the front side using PECVD, and the rear side is textured using a KOH solution to create a random pyramid pattern. The SiN_x masking layer is then removed and samples undergo a cleaning sequence prior PECVD process. Through PECVD, hydrogenated amorphous and nanocrystalline Si layers are deposited on both sides. On the front side, a-Si:H(i), a-Si:H(n), nc-Si:H(n), and nc-SiOx:H(n) are deposited at 200°C . On the rear side, a-Si:H(i) is deposited at 200°C , followed by ultra-thin SiOx and nc-Si:H(p) layers at 175°C^{45} . On the rear side, a 40 nm-thick ITO is deposited by sputtering through a shadow mask. The samples then receive a SiO_2 -np coating on the pyramid textures acting as an infrared rear reflector, which is then capped with an Ag layer through the same shadow mask used for the ITO deposition⁴⁵. A 500 nm-thick SiOx layer covers the rear side, including both metalized and non-metalized regions. Additional Ag is sputtered onto the active area to finalize the rear contact. The front side is completed by sputtering a 20 nm-thick ITO layer for interconnection. As the final step before top cell processing, 4" wafers are then laser-cut into $2.5 \times 2.5 \text{ cm}^2$ substrates, which are annealed at 210°C for 30 min in ambient to optimize the properties of the solar cells.

Me-4PACz (TCI or Dyenamo) is spin-coated with the same spin recipe utilized in single-junction devices. In tandems (for 1, 4, 60 cm^2), 30 $\mu\text{L}/\text{mL}$ DMF is added into the SAM solution to improve solubility to avoid micelles formation. After SAM deposition, the surface is washed by spinning 150 μL ethanol at 3000 rpm to clean residual SAM and DMF followed by annealing at 115 degrees. To improve the wetting of the perovskite precursor on Me-4PACz, 0.1% wt SiOx-np ($\sim 20 \text{ nm}$ diameter) in ethanol or 0.1% wt AlOx-np (Sigma Aldrich, $<50 \text{ nm}$, 20 wt.% in isopropanol) diluted (1:200) solution in isopropanol is spin-coated statically at 2000 rpm with 500 rpm/s acceleration followed by an annealing step of 10 min at 115°C . The absorber utilized in tandems is $\text{Cs}_{0.05}(\text{FA}_{0.9}\text{MA}_{0.1})_{0.95}\text{Pb}(\text{I}_{0.80}\text{Br}_{0.20})_3 + 3\%$ (MAPbCl₃). The absorber is fabricated with the one-step anti-solvent method. The molarity of the solution is increased to 1.7M from 1.5M to adjust the thickness of the absorber. When 10 s are left during the spin program, 250 μL of Anisole (Sigma Aldrich, $>99\%$) is dropped onto the substrate. Then the samples are annealed at 100°C for 15-20 min inside the glovebox. The thickness of C_{60} is reduced down to 15-20 nm for the tandem devices and 150-175 cycles of ALD-SnO_x is used in tandems. After the ALD-SnO_x, 35 nm of IZrO with sheet resistance around 225 ohm/square is deposited from 4-inch 98% $\text{I}_2\text{O}_3 + 2\%$ ZrO target with deposition power of 70W and working pressure 2.7 μbar with $\sim 0.14\%$ of O_2 to Ar ratio. After the TCO, $\sim 500 \text{ nm}$ of Ag grid is evaporated with a rate of 2 A/s which is followed by 100 nm evaporation of LiF or MgF_x with 1 A/s rate in Angstrom thermal evaporator.

Fabrication of monolithic perovskite-silicon heterojunction tandem solar cells larger than 1 cm^2

The certified 60 cm^2 device employed double-side sub-micron textured bottom cells. In the large area bottom cells, on the front side, a-Si:H(i), a-Si:H(n) were deposited, and on the rear side a-Si:H(i) and a-Si:H(p) layers. For the processing of the top cell, all the solutions used for the small area were scaled by $\times 10$. 25 nm C_{60} was evaporated, and 125 cycles of ALD-SnO_x was deposited using an Oxford Instruments ALD tool. 40 nm ITO with R_{sh} 130 ohm/sqr was sputtered on top of SnOx. Instead of the evaporated metal contacts, screen-printed Ag ($\sim 20 \mu\text{m}$) with low-temperature curing was used³⁷. To withstand curing (130°C , 10 min, in ambient), the PbI_2 -excess amount in the absorber is decreased from 6% to 3%. Triple-cation triple halide (CsFAMA) absorbers showed enhanced resilience to such stress compared to CsFA-triple halide absorbers (MACl addition is not considered as MA-inclusion in this work) **Fig.S34**. The shadowing losses from the metal contacts for the 60 cm^2 metallization design are estimated at $\sim 2.85\%$ which is higher than the 1 cm^2 design ($\sim 1.5\%$).

Characterization

Density Functional Theory

Quantum Espresso was used for modeling by plane wave density functional theory^{46,47}. The wavefunctions were constructed using norm-conserving scalar-relativistic pseudopotentials with Pb $5d^{10}6s^26p^2$ and I $5s^25p^5$ valence electrons⁴⁸. The kinetic energy cutoff was set to 80 Ry and the charge density cutoff to 320 Ry. The Brillouin zone was integrated on a Monkhorst-Pack k-grid with 50 k-points per $\text{\AA}^{-1}$ and the revised Vydrov-Voorhis (rVV10) electron density functional was adopted to properly account for the non-covalent bonding^{49,50,51}. In the structure relaxations, the atomic positions were updated using the Broyden-Fletcher-Goldfarb-Shanno algorithm until the residual forces were reduced to $\leq 10^{-4}$ Ry Bohr⁻¹.

(0 0 1)-oriented FAPbI₃ slabs with FAI-termination and eight surface formula units were modeled, see Fig. S2. A vacuum layer of 25 $\text{\AA}$ thickness was employed with saw-tooth electrostatic potential centered in the middle of the vacuum layer for dipole correction.

The energy of substitution of IPb-I by IPb-OPO₂HCH₂R was calculated as $E_s = (E_{\text{perovskite-OPO}_2\text{HCH}_2\text{R}} + xE_{\text{PbI}_2} - E_{\text{perovskite-I}} - xE_{\text{IPbOPO}_2\text{HCH}_2\text{R}})/x$, where $x = 1$ and 8 for 12.5% and 100% substitution, respectively, and IPb-I and IPb-OPO₂HCH₂R are molecules, according to the reaction scheme $\text{perovskite-I} + \text{IPb-OPO}_2\text{HCH}_2\text{R} \rightarrow \text{perovskite-OPO}_2\text{HCH}_2\text{R} + \text{PbI}_2$. This descriptor was chosen due to the fact that phosphonic acids are strong enough to dissociate in the polar solvent providing phosphite-anions to create Pb(II) phosphites that modify the perovskite surface. The energy of substitution of FAI by HNC₄H₈NH₂·Cl was calculated as $E_s = (E_{\text{perovskite-Cl}\cdot\text{H}_2\text{NC}_4\text{H}_8\text{NH}_2} + 8E_{\text{FAI}} - E_{\text{perovskite-I}\cdot\text{FA}} - 8E_{\text{HNC}_4\text{H}_8\text{NH}_2\cdot\text{Cl}})/8$, where FAI and HNC₄H₈NH₂·Cl are tight ion pairs, according to the reaction scheme $\text{perovskite-I}\cdot\text{FA} + \text{HNC}_4\text{H}_8\text{NH}_2\cdot\text{Cl} \rightarrow \text{perovskite-Cl}\cdot\text{H}_2\text{NC}_4\text{H}_8\text{NH}_2 + \text{FAI}$. The binding energy of C₆₀ with the perovskite surface was calculated as $E_b = E_{\text{perovskite}\cdots\text{C}_{60}} \rightarrow E_{\text{perovskite}} - E_{\text{C}_{60}}$, where C₆₀ is a molecule, according to the reaction scheme $\text{perovskite} + \text{C}_{60} \rightarrow \text{perovskite}\cdots\text{C}_{60}$.

JV

The 4PP measurement method is used. JV measurements were obtained using a two-lamp (Halogen and Xenon) class AAA WACOM sun simulator with an AM1.5G irradiance spectrum at 1.000 W/m². 0.1 cm² shadow masks are used to measure cells with an area of 0.2 cm² unless otherwise stated. Opaque devices are illuminated from the glass side. The single junction cells are measured with a scan rate of ~ 0.50 V/s, first, reverse scan and then forward scan. Both reverse and forward scan are included in the JV statistic plots. Three-point weight MPP measurements are performed using an in-house written LabVIEW code. For the measurement of tandem devices, before each measurement, the calibration of the AAA WACOM system is checked with three different certified cells with different spectral responses to minimize the spectral mismatch of the sources. Then the cells with ~ 1 cm² are measured with a scan rate of ~ 0.1 V/s and a similar MPP tracking algorithm is utilized as the single junction perovskite solar cells. A temperature-controlled (25 °C) brass chuck was used.

All IV measurements for devices bigger than 1 cm² were made on a large area class A+A+A+ solar simulator from WACOM using two light sources (xenon and halogen). The spectral response and overall light intensity of the simulator were verified with externally calibrated reference cells to approximate 1-sun AM1.5G equivalent intensity. All measurements were done using a four-point method. All cells were measured on a metallic vacuum chuck with an active temperature-controlled set to 25 °C. Cell areas were masked with laser-cut aperture masks whose physical areas were optically measured. All IV curves were scanned between 2 V -0.1 V. At a scan rate of approximately 80 mV/s. Maximum power-point tracking was achieved using a 3-point algorithm which actively modified the voltage throughout the measurement. Small areas (4 cm²) were contacted using two-Kelvin probes on either side of the metal grid. Large area cells (60 cm²) were contacted using 4-Kelvin probes with one contacting each end of each bus bar. The contact point was approximately

2 cm from the end of the bus bar. Shading due to probe bars is corrected after the measurements by application of the correction factor ($\times 1.016$) to J_{sc} .

Long-term stability

Cicci Research stability measurement setup is utilized where the samples are kept in N_2 atmosphere, under 1-sun illumination by tracking the MPP with perturb & observe algorithm. The N_2 chambers are temperature controlled and cells saturate ~ 10 - 15°C higher than the chamber temperature.

For stability testing, the PbX_2 excess amount is reduced to 3% from 6% and 2PACz HTL is utilized for simplicity.

EQE

EQE spectra were measured with a custom-made spectral response set-up where the samples were irradiated with chopped light at a frequency of ~ 200 Hz and the response was measured with a lock-in amplifier. For tandem cells visible and IR light biases are used to saturate complementary sub-cells and to measure each sub-cell near short-circuit conditions 0.7V and 1.2V bias voltages are applied to the cell when measuring top and bottom cells respectively.

FH Measurements

JV curves were obtained by applying a triangular voltage pulse to the cells, starting approximately at the V_{oc} . This was followed by a reverse sweep from open-circuit to -0.1 V and a forward sweep from -0.1 V back to V_{oc} at variable frequencies or scan speeds (V/s) using a system developed by FastChar UG^{38, 39}.

BACE

The device was initially biased at a voltage equivalent to the open-circuit voltage. After a delay time of 30 seconds, a bias of 0 V was applied to extract the injected and capacitive charge within the device. The transient current was recorded using a Keithley 2400 instrument controlled by a custom LabView program. The extracted charge was calculated by integrating the transient current, while the charge carrier density was determined by dividing the total charge by the elementary charge and the cell volume^{38, 39}.

SEM

SEM images were acquired with acceleration voltages ranging from 1 to 5 kV using either an Everhart-Thornley or an in-lens detector (JEOL JSM-7500TFE or Zeiss NVision 40 microscopes).

Steady-state PL

Custom built steady state PL setup is utilized to measure in-situ PL and PLQY. The light from the laser diode is coupled into a fiber directed into the integrating sphere and sample is illuminated. Then the emission from the sample is homogenized by multiple reflections within the integrating sphere and coupled out into another fiber that is connected to a spectrometer. As long as the emission and the excitation which in our case the values are (750 to 800 nm) and (532 nm), careful comparison of the peaks enables to measure PLQY (down to 10^{-6}). OD filter wheel helps to change the light intensity in between 0.01 sun to 3 sun. As a calibration check, three fluorescent test samples with high specified PLQY ($\sim 70\%$) supplied from Hamamatsu Photonics where measured where the specified value could be accurately reproduced within a

small relative error of less than 5%. For QFLS measurements the light intensity is tuned to 1-sun depending on the bandgap of the absorber using an external c-Si photodetector.

Intensity-dependent steady-state PL

The samples were illuminated in the steady-state PL setup as described above. A neutral density filter wheel was used to attenuate the laser power to measure at different intensities which was compared to the initial measured. The samples were illuminated at a given intensity for 3 s illumination time using an electrical shutter.

The pseudo-J-Vs were deduced from the intensity-dependent QFLS measurements. This was done by calculating the dark-current density from the generated current density at a given light intensity in equivalent suns. For example, 1 sun corresponds to 21.0 mA/cm², and 1% of one sun to 0.210 mA/cm². The obtained dark current was then plotted against the measured QFLS at the given light intensity to create a transport-free dark J-V-curve which was then shifted to the J_{sc} in the JV-measurement to create the pseudo-JV curve allowing to read of the pseudo-FF and V_{oc} of the measured partial cell stack (e.g., glass/absorber, or half-cell, or the complete cell).

Hyperspectral imaging (HI)

Two hyperspectral imaging (HI) systems with different fields of view were used. Both record luminescence intensity signal along three dimensions $\{x,y,\lambda\}$.

The wide-field (~10 cm scale, 130 μ m spatial resolution) hyperspectral photoluminescence images were acquired with Grand-EOS equipment from PhotonEtc (2 nm spectral resolution). A wide-field illuminating LED system at 525 nm homogeneously brightens the samples at a power of 42 mW/cm² (~0.6 Sun for 1.65 eV bandgap).

Micro-scale (~1 μ m spatial resolution) hyperspectral photoluminescence images were acquired with a home-built microscope with Thorlabs optomechanical elements, a 2D bandpass filtering system from company PhotonEtc with 2 nm resolution, and a 4Mpix silicon-based sCMOS camera Hamamatsu ORCA Flash v4. The sample is illuminated with a 405 nm LED at varying powers from 75-750 mW/cm² (~1-10 Sun for 1.65 eV bandgap) through an infinity-corrected $\times 50$ Nikon objective with numerical aperture of 0.6. The luminescence is collected through the same objective. The excitation beam and luminescence signals are separated with appropriate dichroic beam splitter and filters.

Both imaging systems are absolutely calibrated, and the obtained absolute PL spectra are fitted according to Generalized Planck's law⁵² to obtain the quasi-fermi level splitting (QFLS) and bandgap maps. The QFLS are corrected to match 1 sun fluence condition, based on illumination intensity, bandgap of the samples and optical ideality factor extracted from illumination power dependent broadband PL images.

Measurements were performed under nitrogen atmosphere at room temperature.

Bichromatic PL mapping

Photoluminescence imaging was performed using a custom setup. Excitation of the perovskite layer is done using an array of blue light emitting diodes (450 nm central wavelength), effective generation is roughly equivalent to 1sun. The sample emission is filtered using long pass filters and imaged using a Thorlabs Kiralux CCD camera mounted with a 6mm focal length objective. Reference of the filters in case: Thin film filter for PK PL: ThorLabs FELH-0650 and Absorbing filter for PK PL: SCHOTT RG-695 and SCHOTT RG-715.

Kelvin probe (KP)

KP measurements were performed using a KP Technology Ltd. SKP5050 probe using a 2 mm gold tip. The work function of the samples was measured during 3 cycles of dark and illumination (10 min each) on at least 2 different points. The illumination was performed with a white LED previously calibrated with a silicon diode to obtain 1 sun of intensity. The SPV of the samples was calculated by the difference of the average work function under dark and illumination.

Kelvin probe force microscopy (KPFM)

KPFM maps were generated using an AFM Dimension Edge Bruker microscope with a Pt-coated Si tip (Model SCM-PIT-V2), having a spring constant (k) = 3 N m⁻¹. Scans were performed over 2 μm at 512 pixels and 1 Hz frequency in a dual-pass setup, the first pass to record topography and the second to measure the contact-potential difference (CPD) with a tip potential of 5 V (both passes are in tapping mode). The WF of the Pt tip was precisely calibrated by measuring the CPD relative to a freshly cleaved highly oriented pyrolytic graphite (HOPG); a material with a standard work function of about 4.6 eV. This allowed us to estimate locally the surface potential values of the different perovskite films with high spatial resolution.

XPS/UPS and UPS mapping

XPS measurements were performed using an Axis Supra (Kratos Analytical) with a monochromatic Al Kα X-ray line. The pass energy was set to 20 eV with a step size of 0.1 eV for XPS, and to 40 eV with a step size of 0.15 eV for AR-XPS. The emission current was set to 15 mA. The samples were electrically grounded to limit charging effects. UPS was measured using a He I UV source, with the pass energy set at 10 eV and a step size of 0.025 eV. The intensity of the UV source together with the measurement area was selected in order to prevent the energy analyzer from saturating. Secondary electron cutoff (SECO) was used to assign the work function of the material, while the valence band onset, was used to estimate the valence band maximum with respect to the Fermi level.

For the UPS-mapping experiment (Fig.2(d)), to extend the evaporation edge formed while evaporating C₆₀, the evaporating mask is placed 5 mm away from the substrate instead of 1 mm (noted as graded C₆₀ in the main text)

Grazing Incidence Wide Angle X-ray Scattering (GIWAXS)

Data were acquired at a 2° incidence angle using a point-collimated beam on a Bruker D8 Discover Plus diffractometer equipped with a Copper rotating anode and an Eiger2 500K detector. The beam was shaped by a focussing Göbel mirror, followed by a 0.3 mm pinhole, and then collimated by a 0.2 double-pinhole collimator. The detector was mounted at 117 mm sample-detector distance in gamma-optimized orientation, to collect one quadrant by taking three separate images, which were then merged into the shown images using DiffraC.EVA. Raw data images were converted to Q using GIXSGUI⁵³.

A number of repeating rectangular shapes are visible on the GIWAXS images, these shapes stem from Kapton tape used to cover minor damage on the detector, and they have no impact on data interpretation.

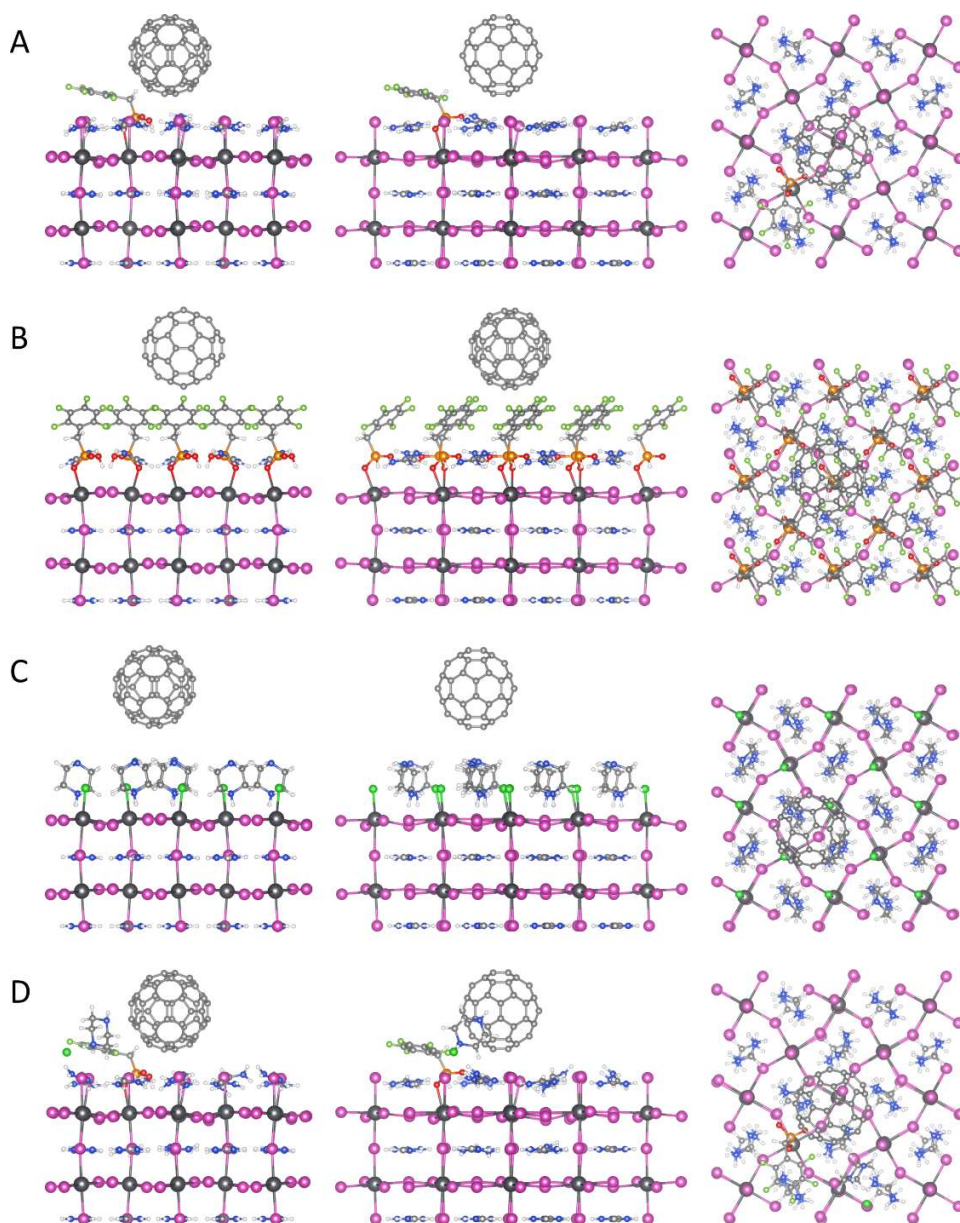


Figure S1. Side and top views of perovskite...C₆₀ interfaces with (A) 12.5% and (B) 100% surface substitution of IPb-I by IPb-OPO₂HCH₂C₆F₅, (C) 100% surface substitution of FAI by HNC₄H₈NH₂·Cl, (D) 12.5% surface substitution of IPb-I by IPb-OPO₂HCH₂C₆F₅ with one HNC₄H₈NH₂·Cl ion pair in the vicinity of a I...C₆₀ contact.

	E_b , eV	Distance, Å	Bader charge on C_{60} , electrons
pristine	-0.86	I... C_{60} : 3.7 ($\times 2$)	-0.05
IPb-OPO ₂ HCH ₂ C ₆ F ₅ , 12.5%	-0.86	I... C_{60} : 3.1, F... C_{60} : 3.3, O... C_{60} : 3.6 ($\times 2$)	-0.03
IPb-OPO ₂ HCH ₂ C ₆ F ₅ , 100%	-0.96	F... C_{60} : 3.1 ($\times 3$), 3.3 ($\times 2$)	+0.06
HNC ₄ H ₈ NH ₂ ·Cl, 100%	-0.38	N... C_{60} : 4.1 ($\times 2$), 4.2 ($\times 2$)	0.00
IPb-OPO ₂ HCH ₂ C ₆ F ₅ , 12.5%, HNC ₄ H ₈ NH ₂ ·Cl, 12.5%	-0.99	I... C_{60} : 3.2, F... C_{60} : 3.3, O... C_{60} : 3.5 ($\times 2$), N... C_{60} : 3.3	-0.04

Table S1. Binding energy (E_b , eV), distance of the N/O/F/Cl/I... C_{60} contact (Å), and Bader charge accumulation on C_{60} for the different perovskite surfaces.

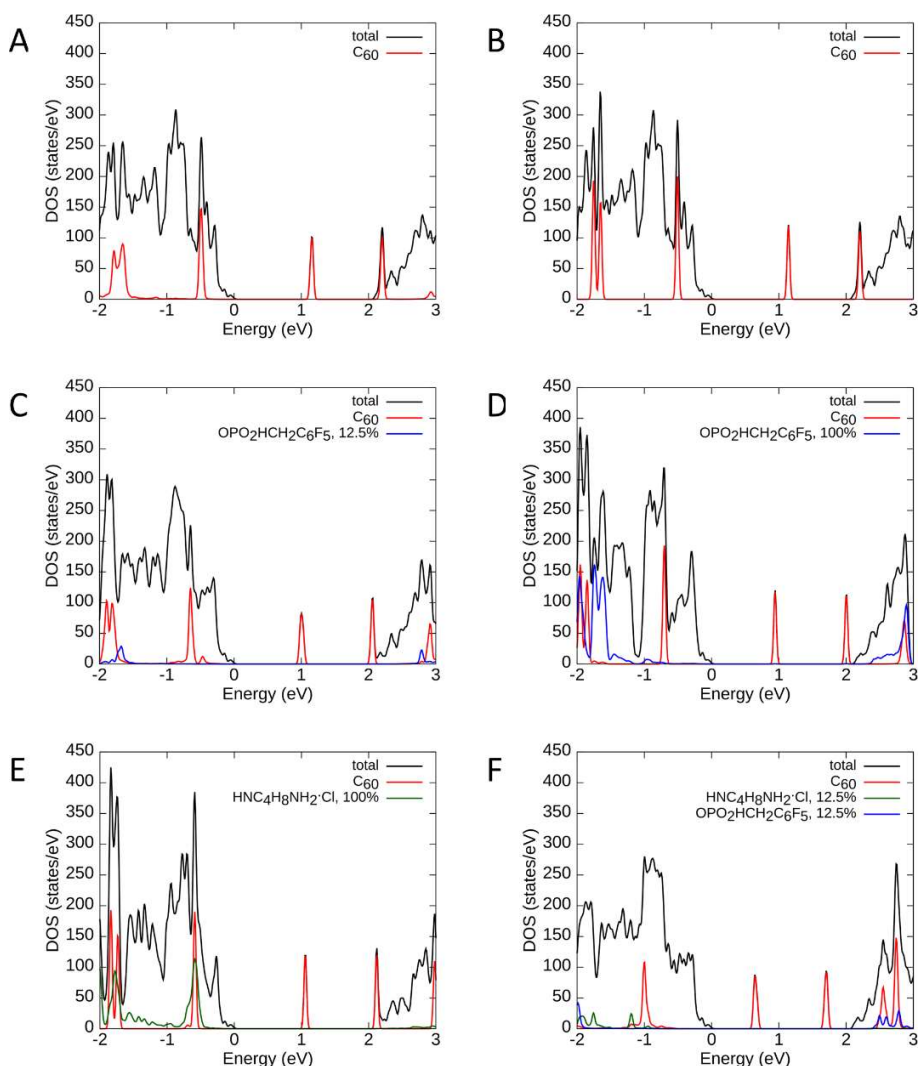
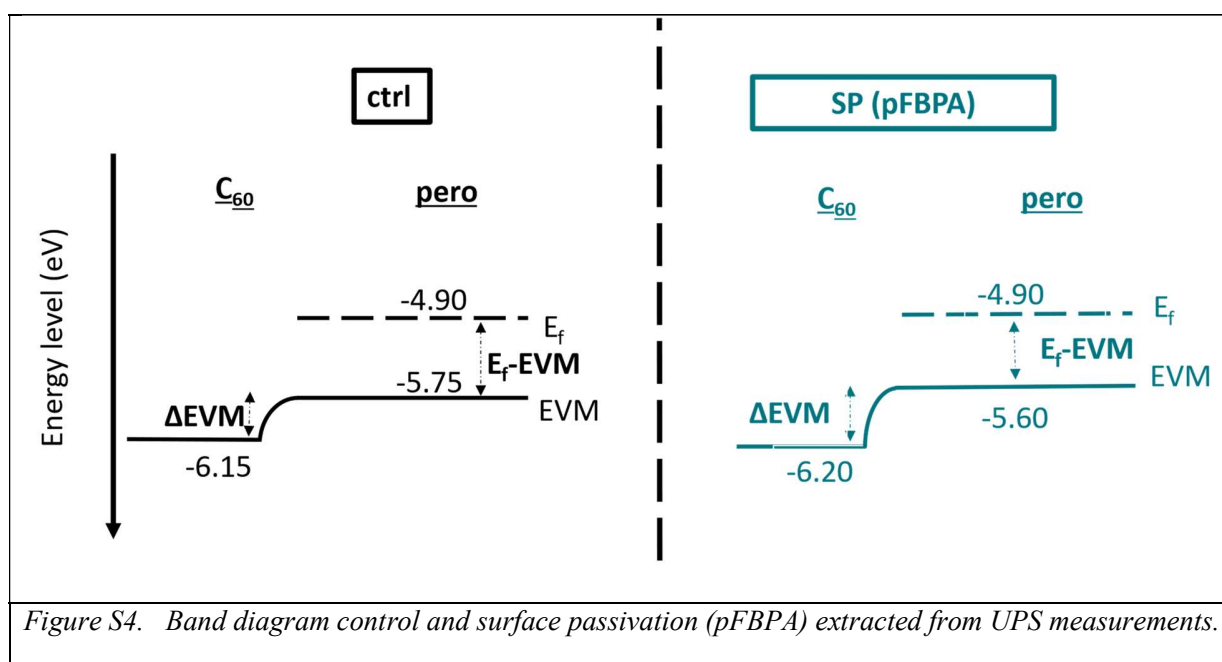
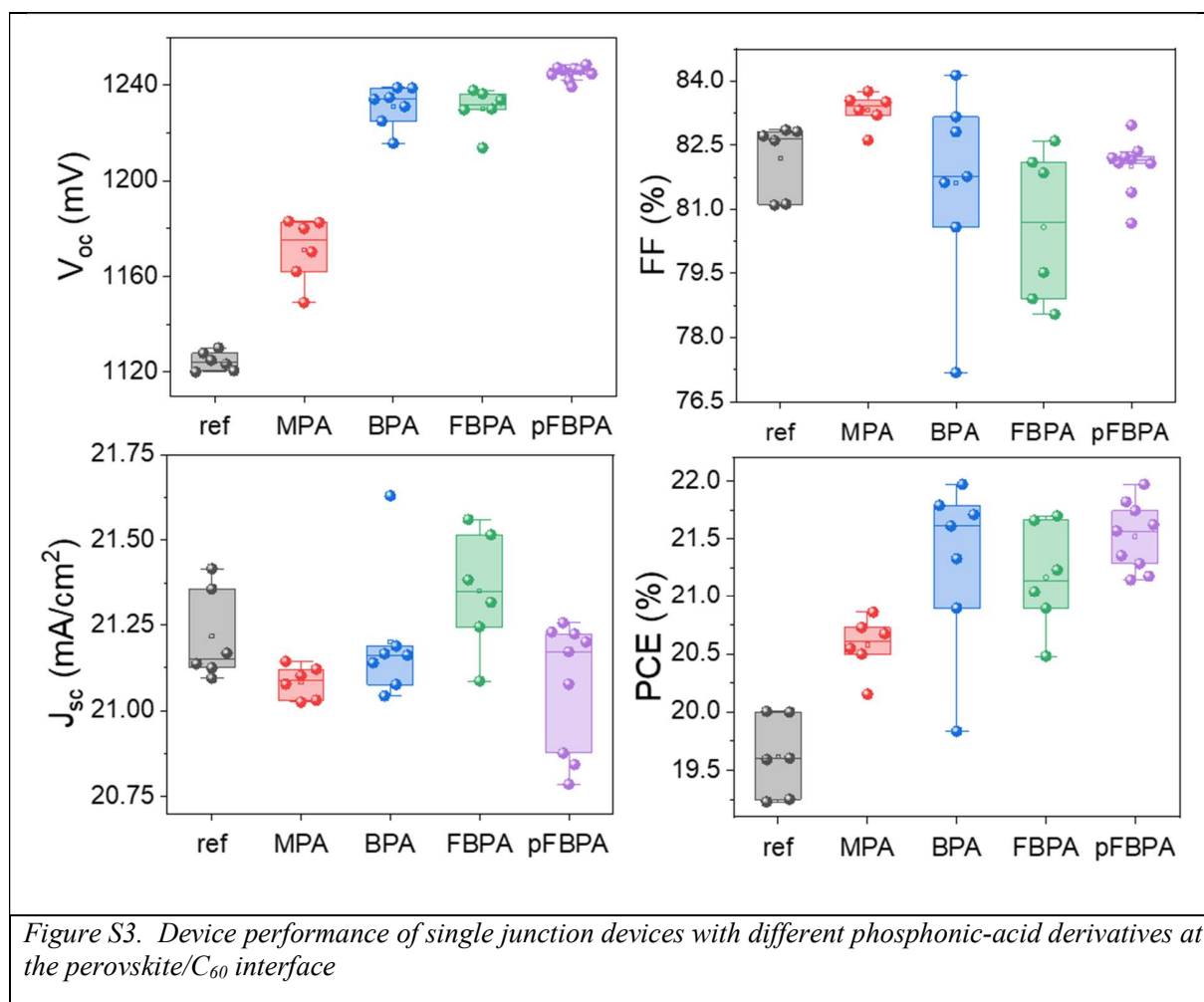
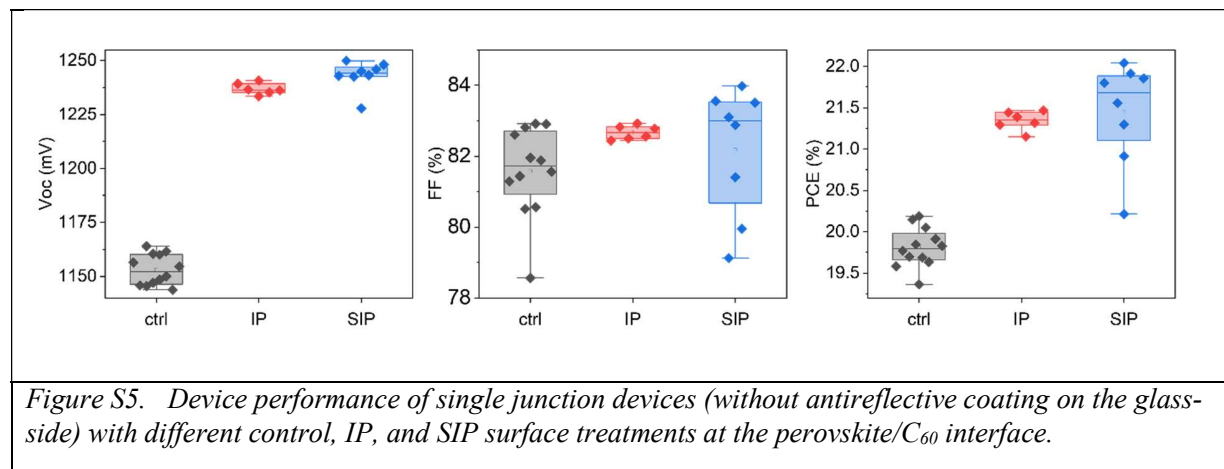


Figure S2. Density of states of perovskite...C₆₀ interfaces: (A) pristine surface with 8.6 Å separation from C₆₀ (negligible interaction), (B) pristine surface with 3.7 Å separation from C₆₀ (maximum interaction), (C) 12.5% and (D) 100% surface substitution of IPb-I by IPb-OPO₂HCH₂C₆F₅, (E) 100% surface substitution of FAI by HNC₄H₈NH₂·Cl, (F) 12.5% surface substitution of IPb-I by IPb-OPO₂HCH₂C₆F₅ with one HNC₄H₈NH₂·Cl ion pair. The resolution of the k-grid was doubled for the density of states calculations and a Gaussian smearing of 0.002 Ry was applied. The overestimation of the band gap is mainly due to negligence of the spin-orbit coupling (computationally too expensive due to the large sizes of the considered systems).





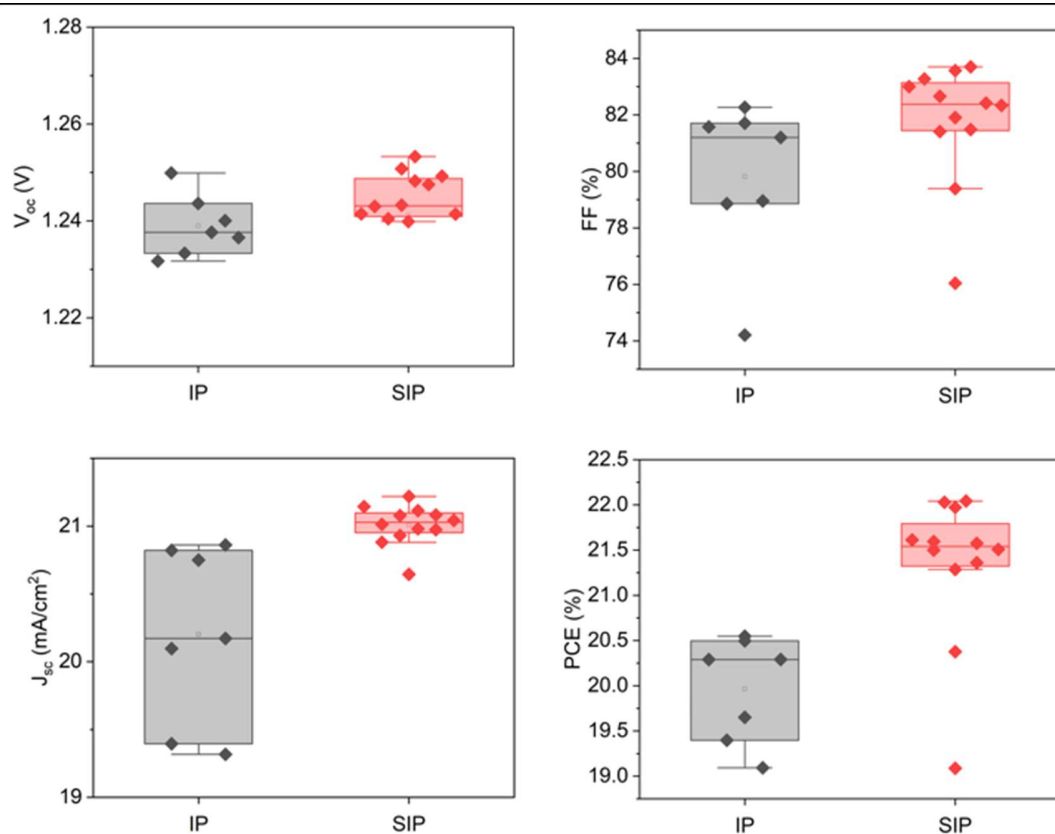


Figure S6. Device performance in another batch of single junction devices with IP and SIP treatments at the perovskite/ C_{60} interface.

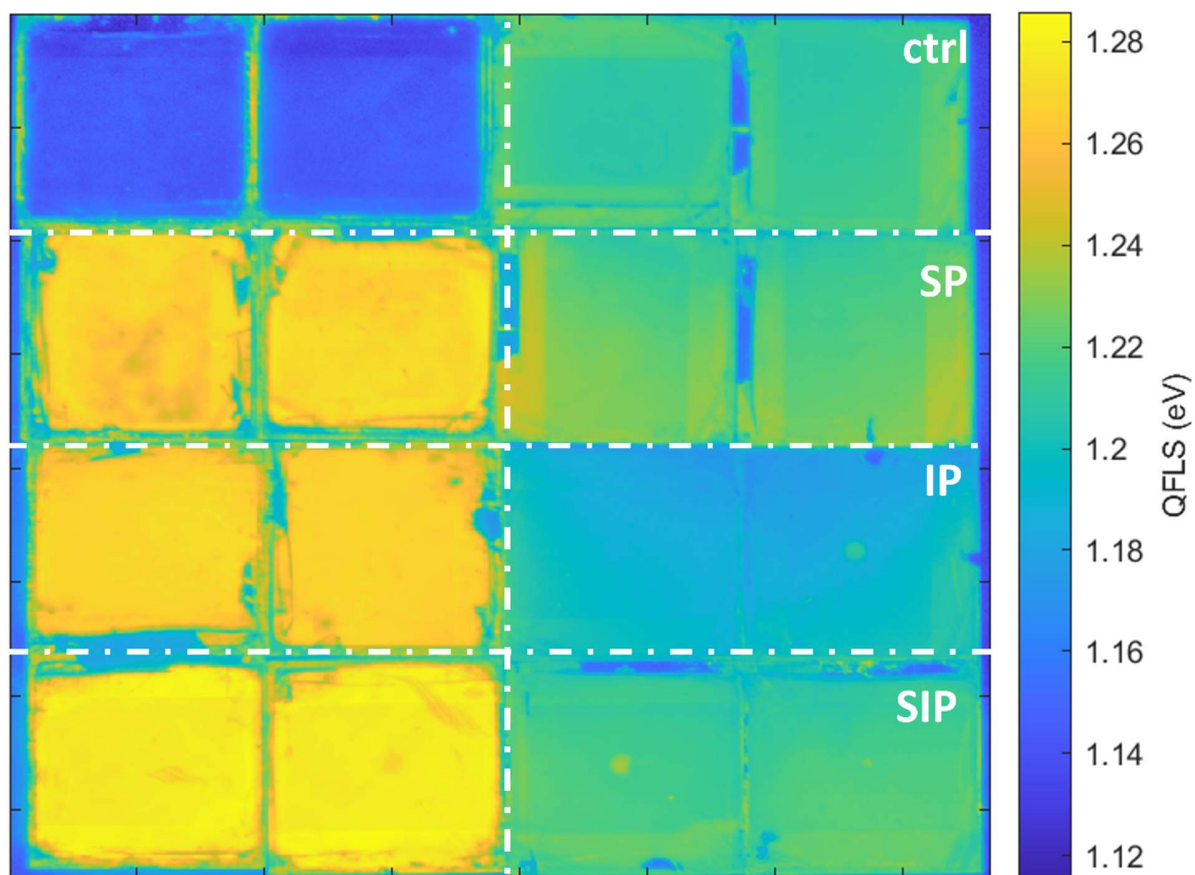


Figure S7. Wide-field PL imaging of QFLS of samples with control, SP, IP and SIP. The left side is with C_{60}/SnO_x stack and the right is without C_{60}/SnO_x . Each sample is $2.5 \times 2.5 \text{ cm}^2$.

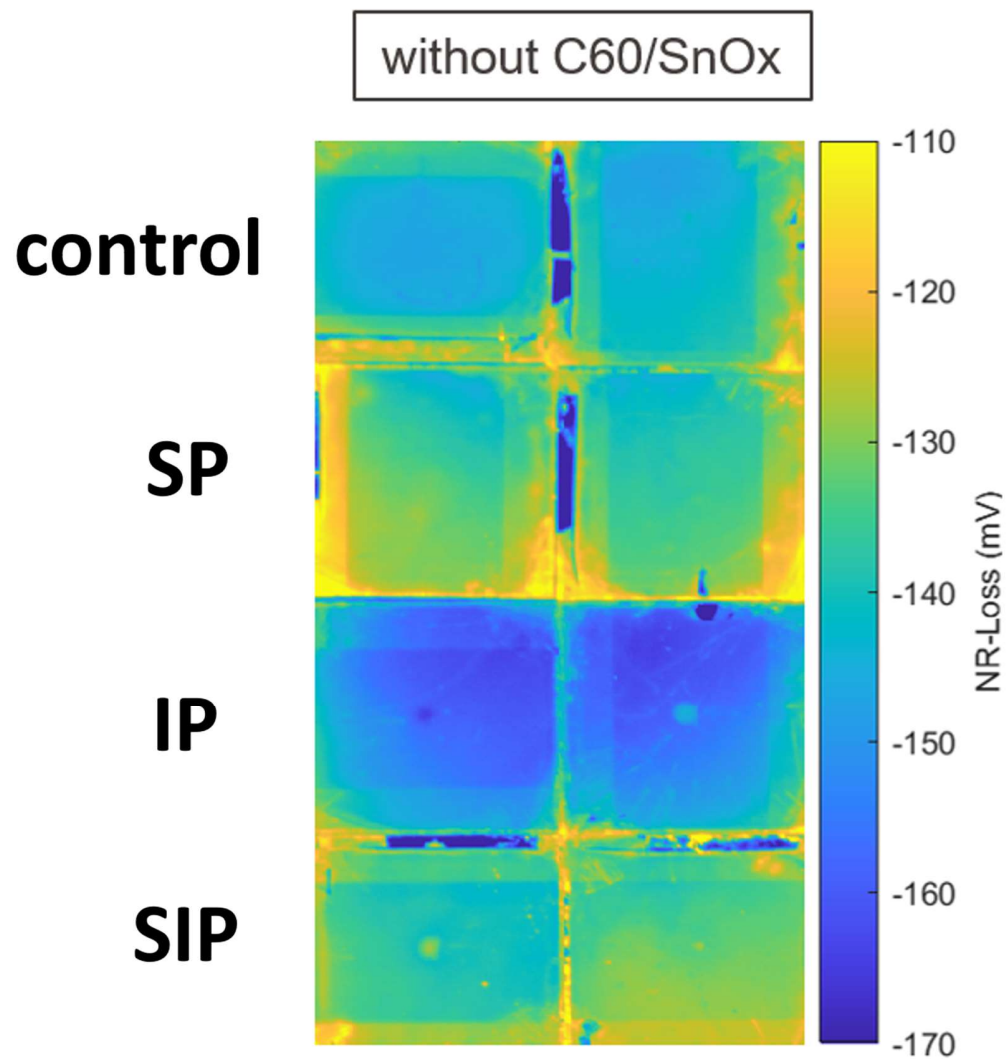


Figure S8. Wide-field PL imaging (non-radiative losses) of samples with control, SP, IP and SIP without C₆₀/SnO_x.

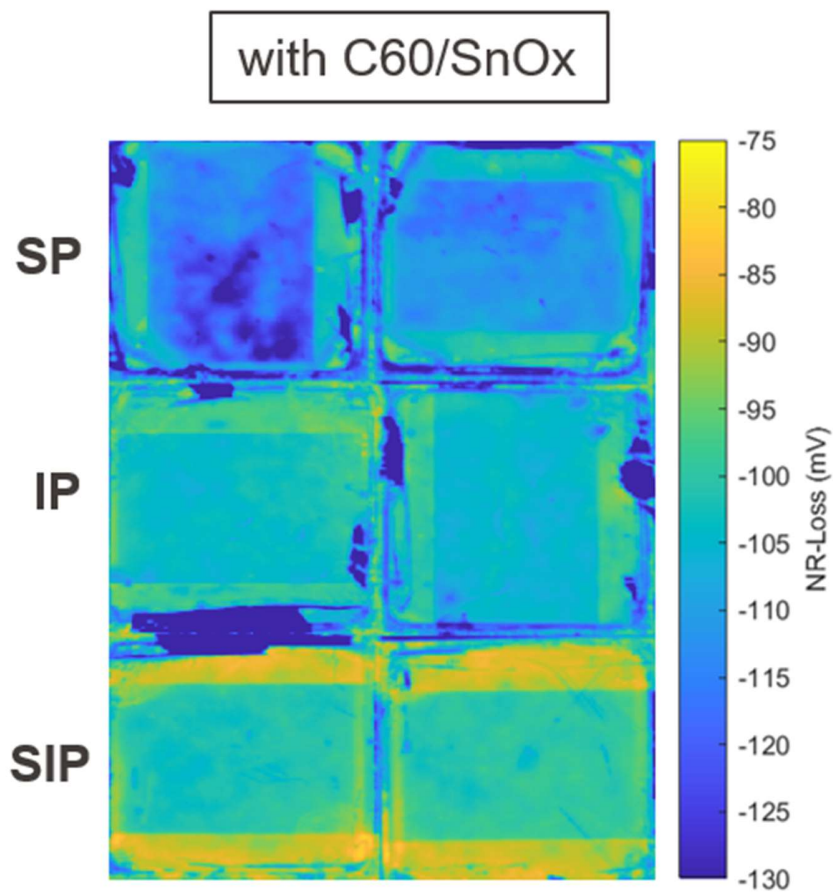
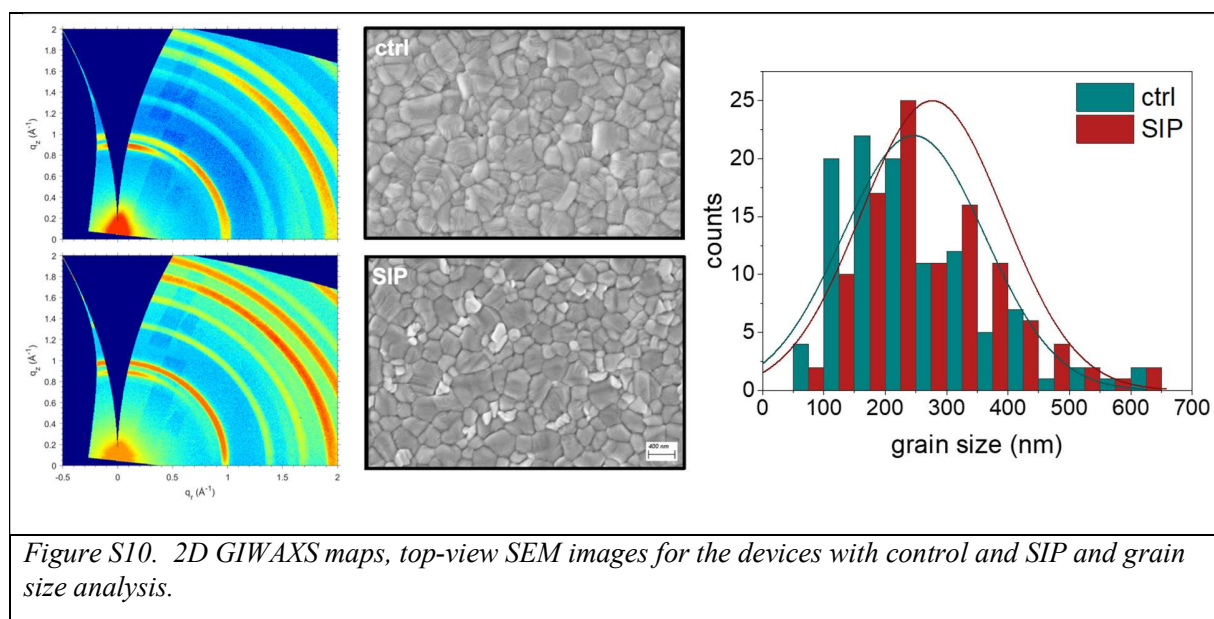


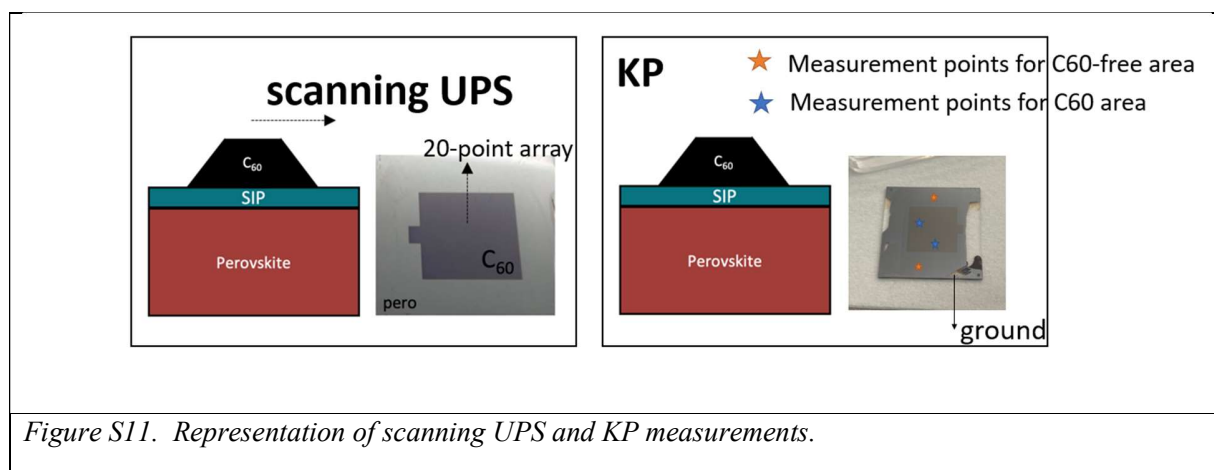
Figure S9. Wide-field PL imaging (non-radiative losses) of samples with control, SP, IP and SIP with C₆₀/SnO_x.

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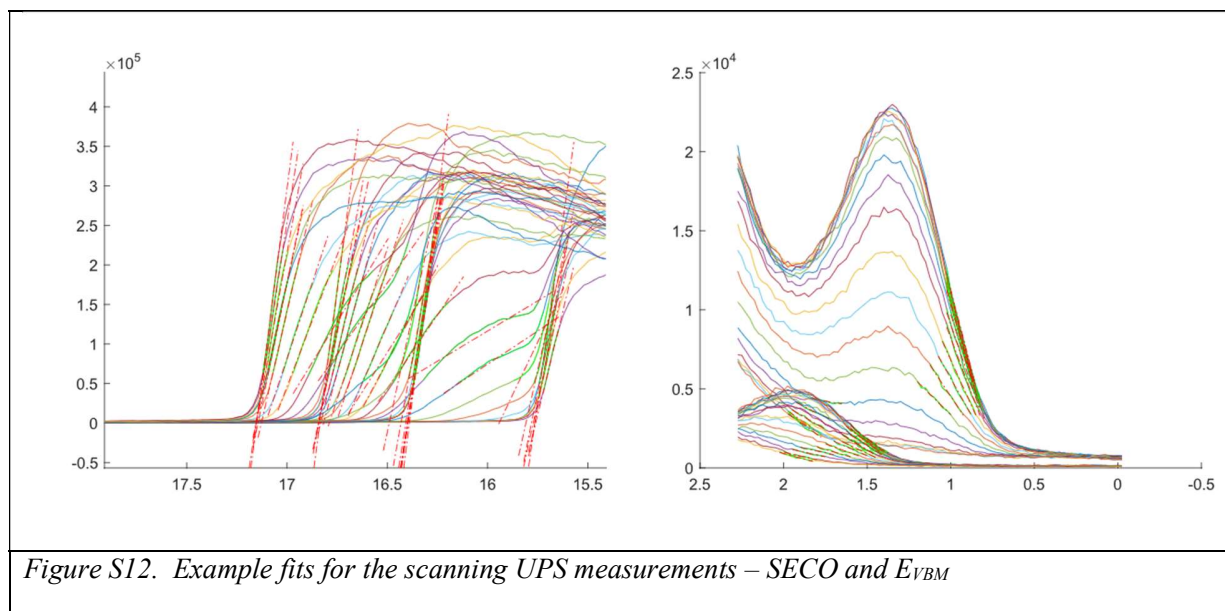


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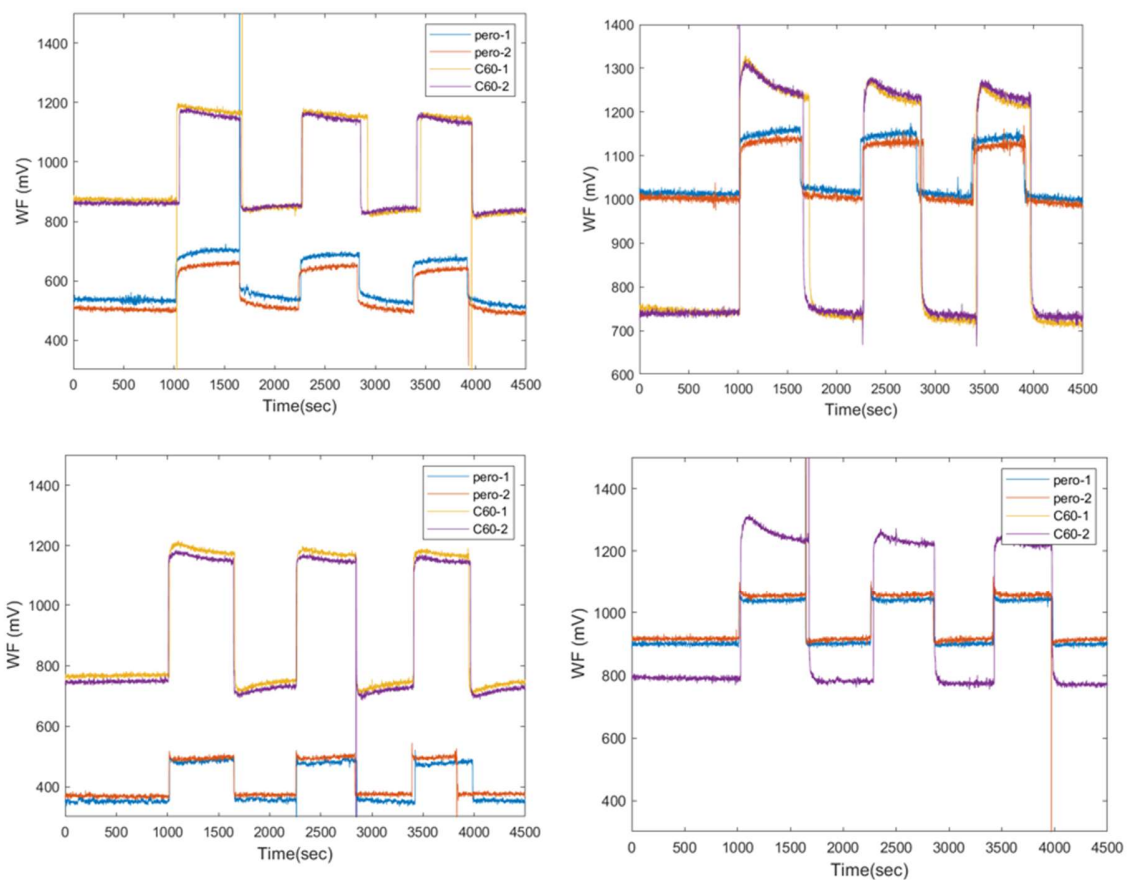
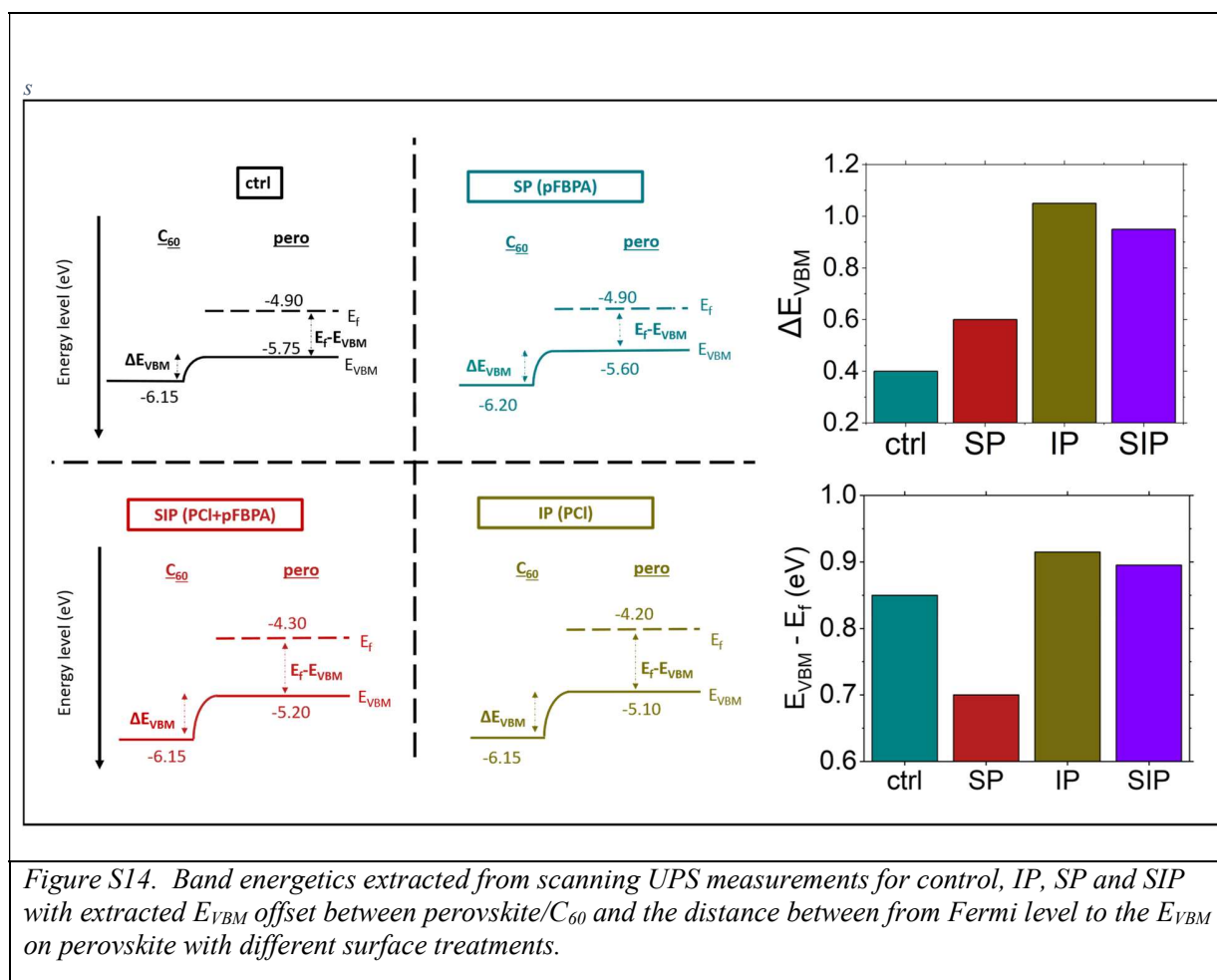


Figure S13. Example dark and light Kelvin probe measurements used for extracting the surface photovoltage.



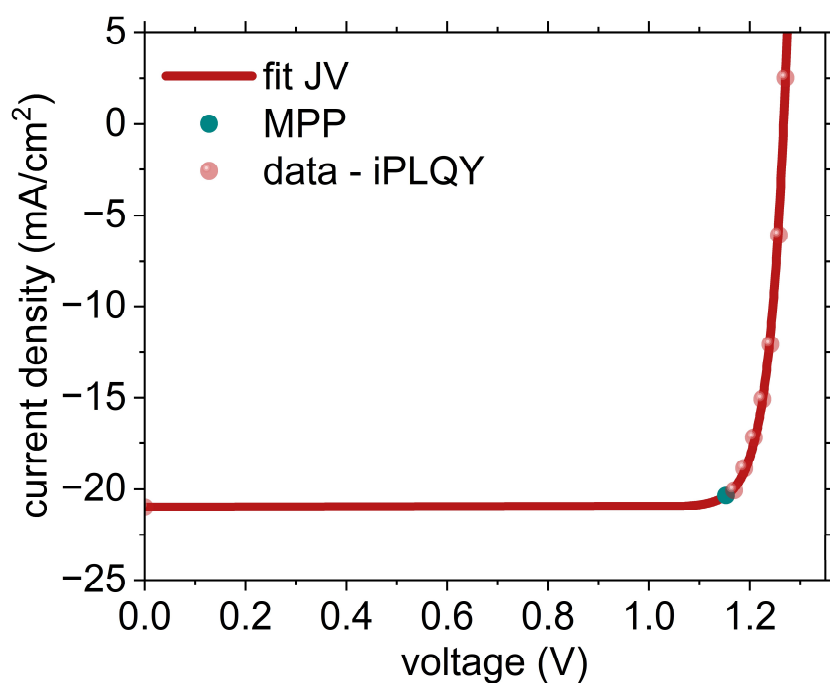


Figure S15. Intensity dependent PLQY measurements for the single junction devices with SIP – pFF of 88.18%

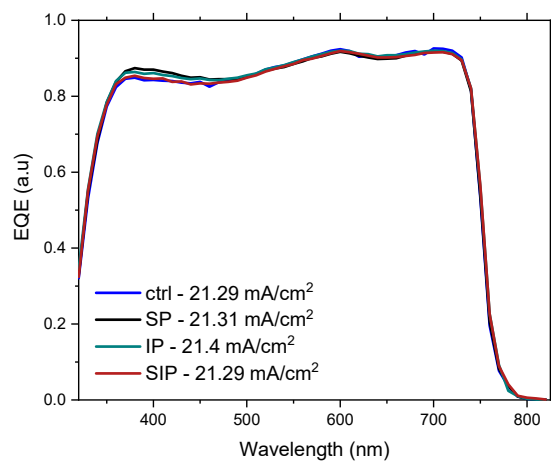


Figure S16. EQE results for control and devices with IP, SP and SIP.

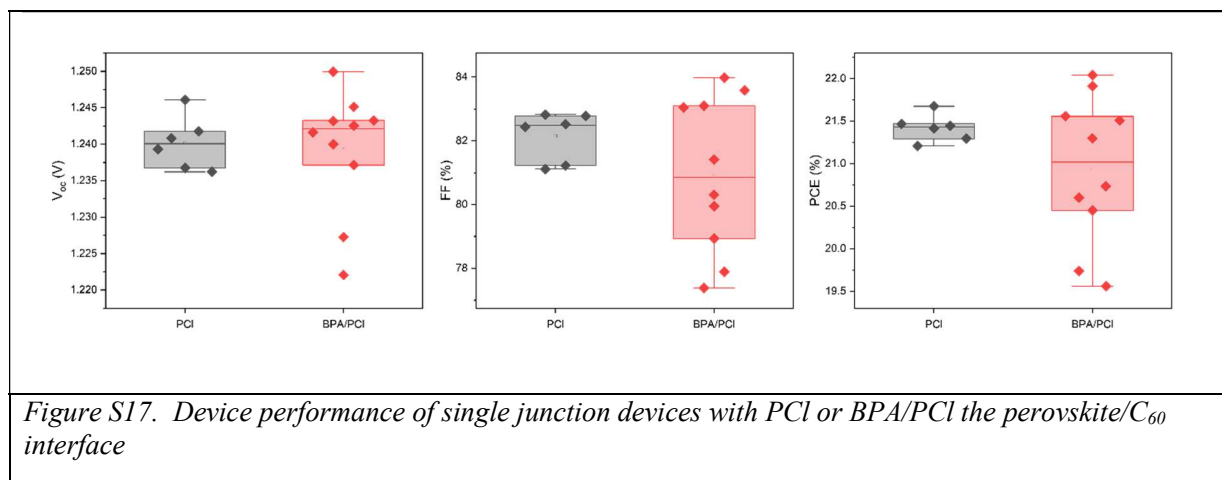


Figure S17. Device performance of single junction devices with PCI or BPA/PCI the perovskite/C₆₀ interface

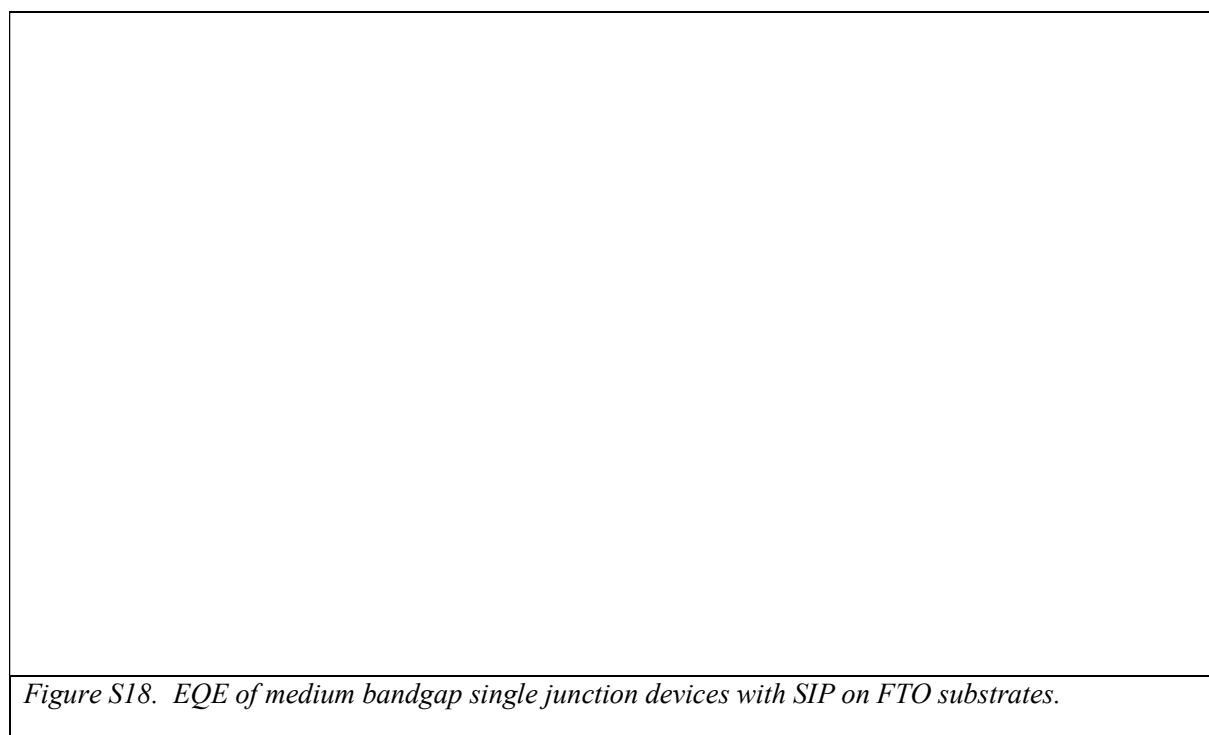


Figure S18. EQE of medium bandgap single junction devices with SIP on FTO substrates.

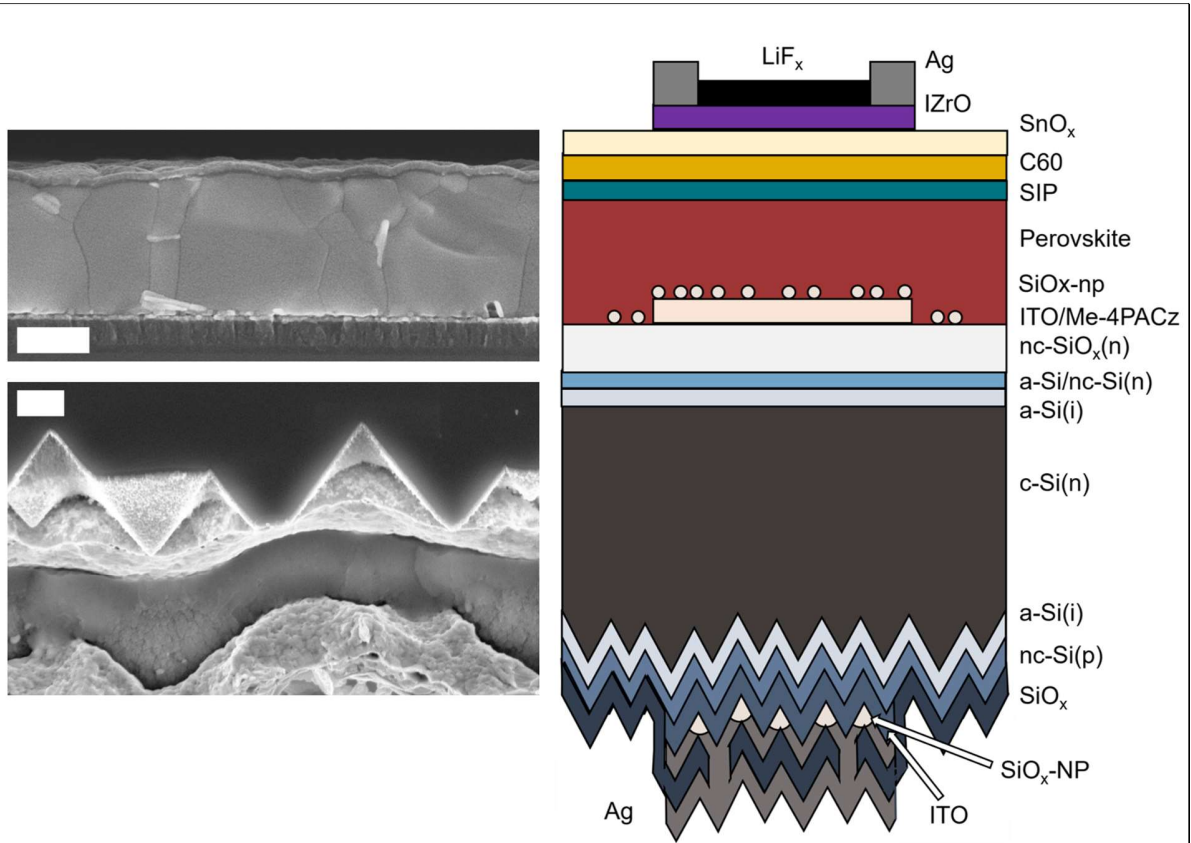


Figure S19. Cross-section SEM images of the top cell and the rear side of the bottom cell of the perovskite-silicon tandem device (scale bar is 300 nm for the top and 400 nm for the bottom image).

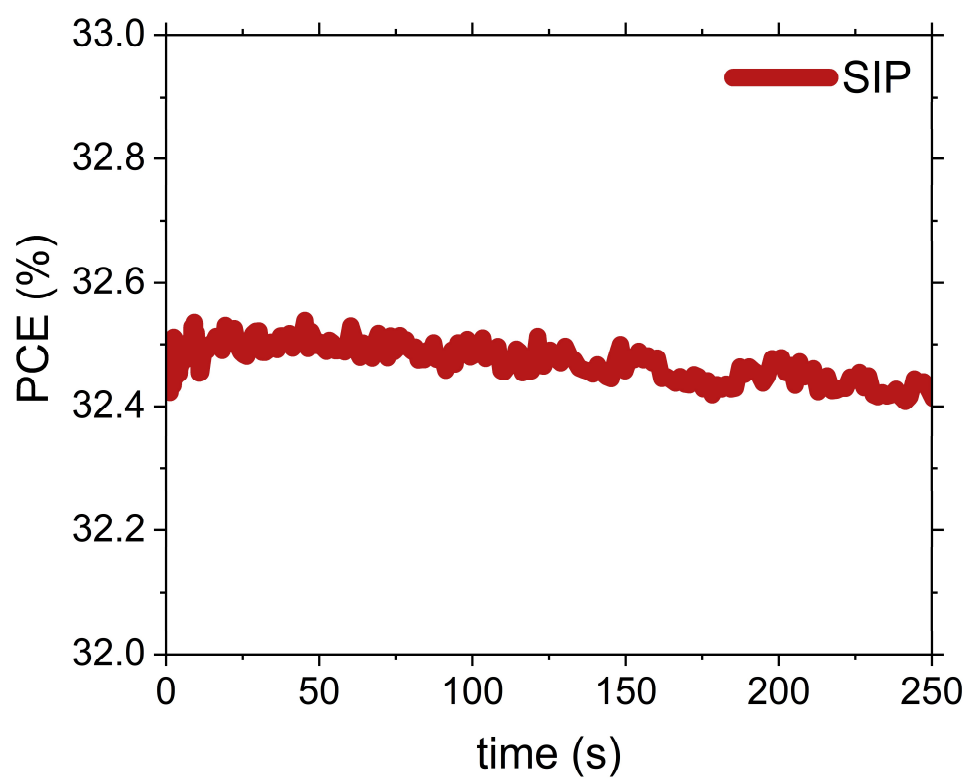


Figure S20. MPP tracking of the champion 1 cm^2 devices.



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CERTIFICATO DI TARATURA LAT 225 DC-23-2246
Certificate of Calibration

Calibration Method: Secondary Calibration with Reference Detector

Procedures for temperature and irradiance corrections to measured I-V characteristics (IEC 60891, ed. 2 2009-12)
Measurement of photovoltaic current-voltage characteristics (IEC 60904-1, ed. 2 2006-09)
Measurement of current-voltage characteristics of multi-junction photovoltaic (PV) devices (IEC 60904-1-1, ed. 1 2017-05)
Requirements for photovoltaic reference devices (IEC 60904-2, ed. 3 2015-01)
Measurement principles for terrestrial photovoltaic (PV) solar devices with reference spectral irradiance data (IEC 60904-3, ed. 4.0 2019-02)
Reference solar devices – Procedures for establishing calibration traceability (IEC 60904-4, ed. 2.0 2019-11)
Computation of the spectral mismatch correction for measurements of photovoltaic devices (IEC 60904-7, ed. 4.0 2019-08)
Measurement of spectral responsivity of a photovoltaic (PV) device (IEC 60904-8, ed. 3 2014-05)
Measurement of spectral responsivity of multi-junction photovoltaic (PV) devices (IEC 60904-8-1, ed. 1 2017-05)

The measurement results reported in this certificate were obtained following procedure No. M41_j, M50_e, M51_d

Instruments or measurement standards which guarantee the traceability chain

Irradiance

Reference detector for

- IV characteristics: ASP009; Calibration laboratory: ESTI; Certificate: n. DC-23-2219
- Spectral Responsivity: ASP010; Calibration laboratory: PTB; Certificate: n. 47050-PTB-20

Temperature

Reference standard type: PRT Isotech 909 sn.1244; Calibration laboratory: UKAS 0175; Certificate n. 22-02-21

Current, Voltage and Resistance

Reference standard type: Fluke 5730/5725 sn.4811502/9085020; Calibration laboratory: DAkkS D-K-15123-01-00 Certificate No sa01075137/sa01077833

Performance Data

Standard Test Conditions

(IEC TS 61836, ed. 3.0 2016-12 par. 3.4.16.5: 1000 Wm⁻², 25°C, AM1.5 Global):

Short Circuit Current (I_{sc}):	<u>23.23 mA ± 0.39 mA</u>
Open Circuit Voltage (V_{oc}):	<u>1.9474 V ± 0.0049 V</u>
Maximum Power (P_{max}):	<u>36.33 mW ± 0.69 mW</u>
Efficiency at STC:	<u>31.6 % ± 1.0 %</u>

Figure S21. Certified PV performance data measured by JRC-ESTI. Measured device area is 1.15 cm².



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Laboratorio Accreditato di Taratura
Accredited Calibration Laboratory



LAT N° 225

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CERTIFICATO DI TARATURA LAT 225 DC-24-2318
Certificate of Calibration

Calibration Method: Secondary Calibration with Reference Detector

Procedures for temperature and irradiance corrections to measured I-V characteristics (IEC 60891, ed. 3 2021-10)
Measurement of photovoltaic current-voltage characteristics (IEC 60904-1, ed. 3 2020-09)
Measurement of current-voltage characteristics of multi-junction photovoltaic (PV) devices (IEC 60904-1-1, ed. 1 2017-05)
Requirements for photovoltaic reference devices (IEC 60904-2, ed. 3 2015-01)
Measurement principles for terrestrial photovoltaic (PV) solar devices with reference spectral irradiance data (IEC 60904-3, ed. 4.0 2019-02)
Reference solar devices – Procedures for establishing calibration traceability (IEC 60904-4, ed. 2.0 2019-11)
Computation of the spectral mismatch correction for measurements of photovoltaic devices (IEC 60904-7, ed. 4.0 2019-08)
Measurement of spectral responsivity of a photovoltaic (PV) device (IEC 60904-8, ed. 3 2014-05)
Measurement of spectral responsivity of multi-junction photovoltaic (PV) devices (IEC 60904-8-1, ed. 1 2017-05)
The measurement results reported in this certificate were obtained following procedure No.: M50_e, M51_f, M66_d

Instruments or measurement standards which guarantee the traceability chain

Irradiance

Reference detector for

- IV characteristics: ASP009; Calibration laboratory: ESTI; Certificate: n. DC-23-2219

- Spectral Responsivity: ASP010; Calibration laboratory: PTB; Certificate: n. 47050-PTB-20

Temperature

Reference standard type: PRT Isotech 909 sn.1244; Calibration laboratory: UKAS 0175; Certificate n. 22-02-21

Current, Voltage and Resistance

Reference standard type: Fluke 5730/5725 sn.4811502/9085020; Calibration laboratory: DAkkS D-K-15123-01-00;
Certificate No sa01230227/sa01230215

Performance Data

Standard Test Conditions

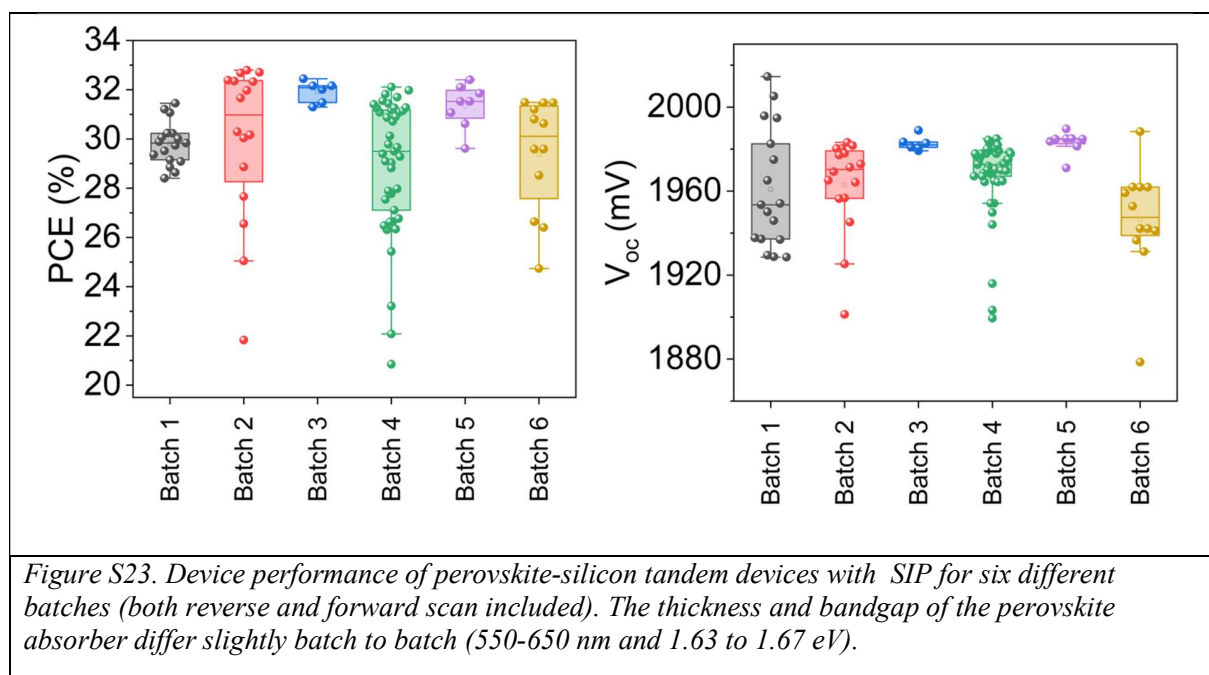
(IEC TS 61836, ed. 3.0 2016-12 par. 3.4.16.5: 1000 Wm^{-2} , 25°C , AM1.5 Global):

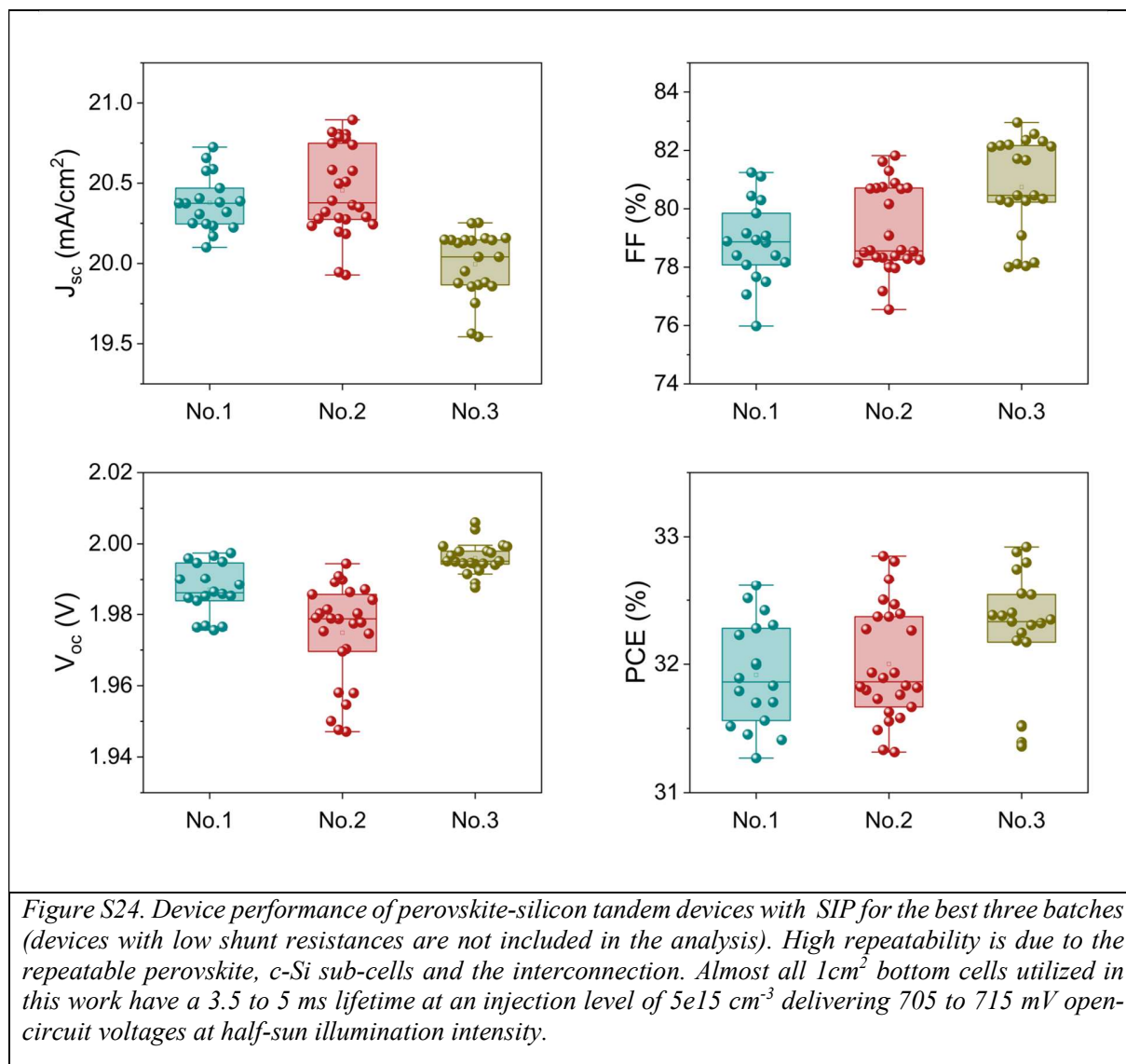
Short Circuit Current (I_{sc}):	<u>$19.96 \text{ mA} \pm 0.24 \text{ mA}$</u>
Open Circuit Voltage (V_{oc}):	<u>$2.0006 \text{ V} \pm 0.0050 \text{ V}$</u>
Maximum Power (P_{max}):	<u>$32.19 \text{ mW} \pm 0.48 \text{ mW}$</u>
Efficiency (η):	<u>$31.11 \% \pm 0.92\%$</u>

JRC.C.2-ESTI E117_v

e-mail: JRC-ESTI-SERVICES@ec.europa.eu

Figure S22. Second round of certification, PV performance data measured by JRC-ESTI. Measured device area is 1.035 cm^2 . Certified open-circuit voltage is 2.0006 V .





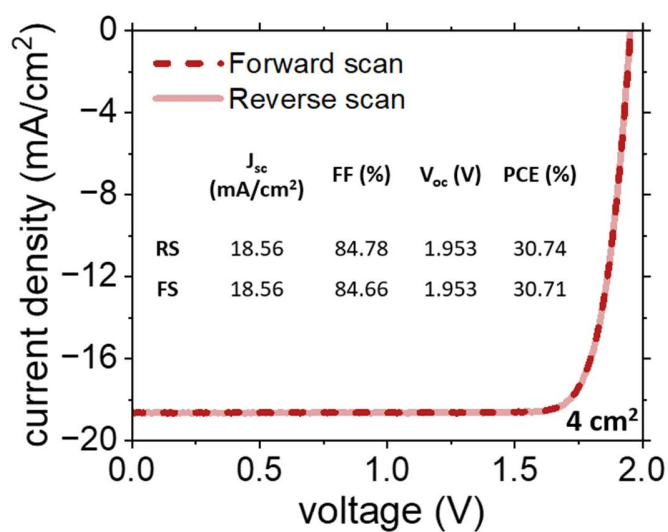


Figure S25. Reverse and forward JV curves of the champion 4 cm² device.

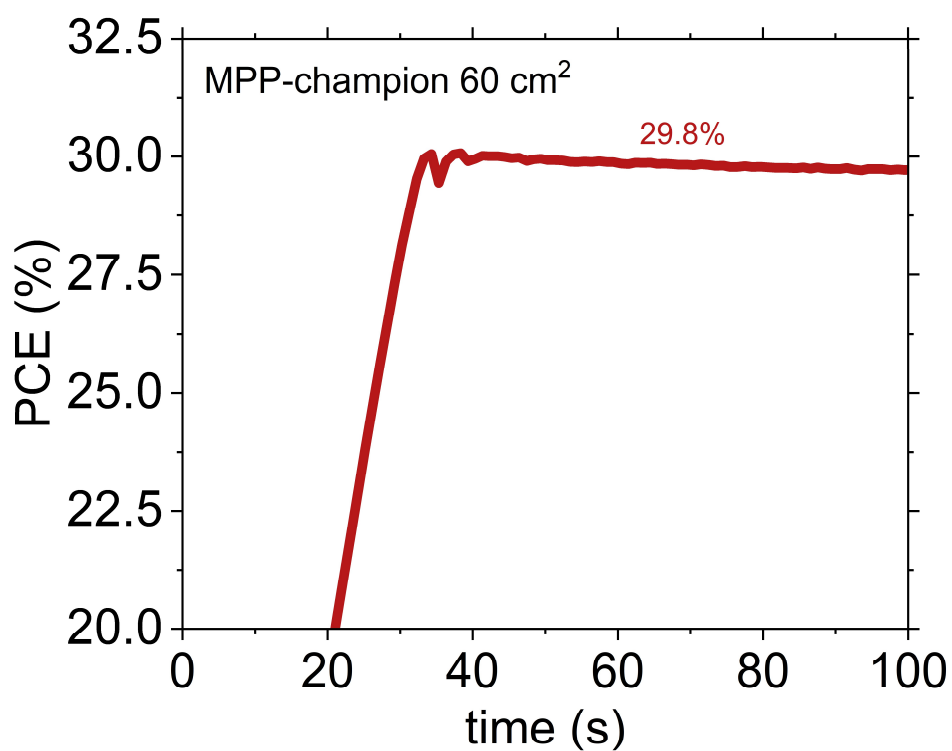
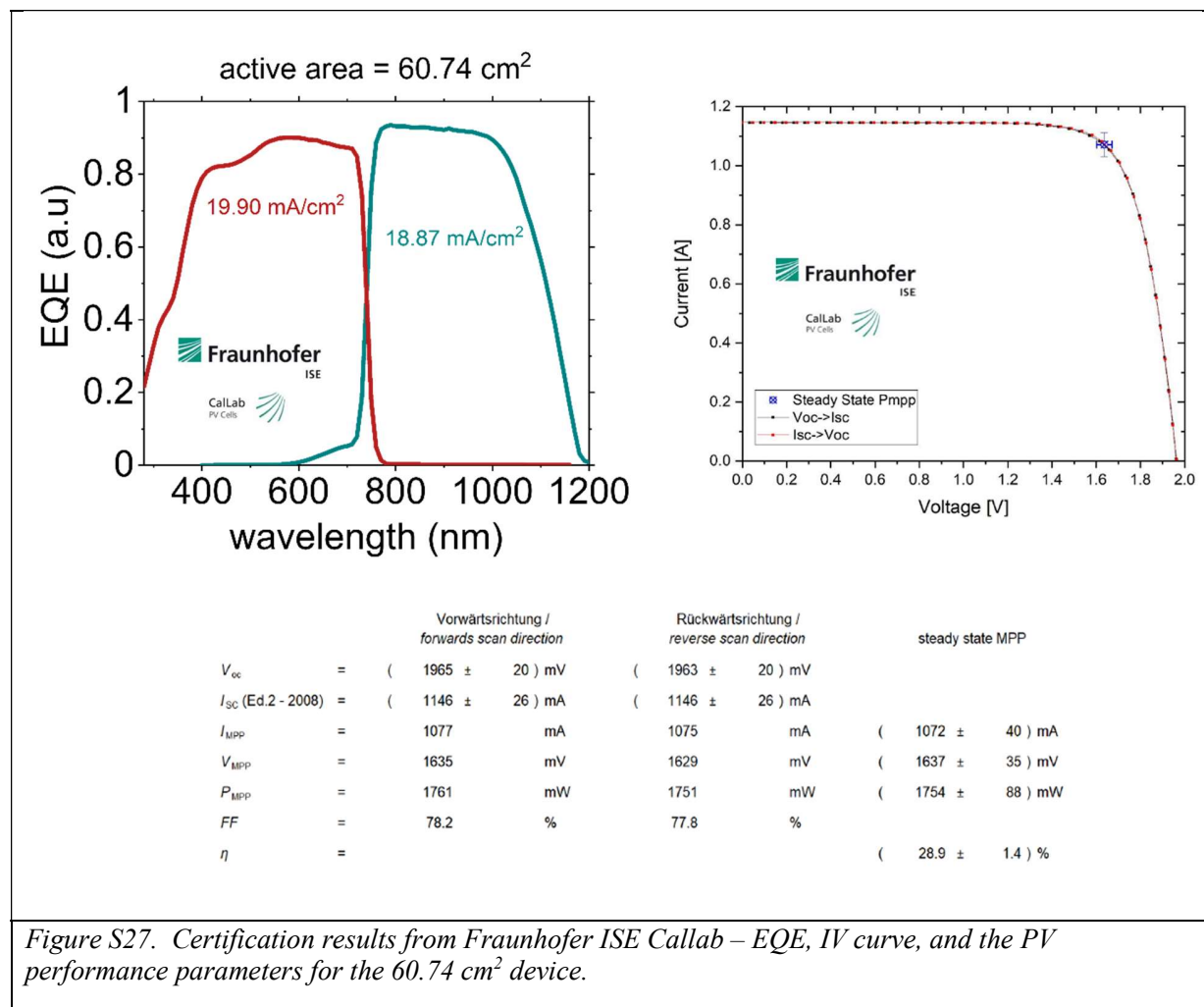


Figure S26. MPP tracking of champion 60 cm² device.



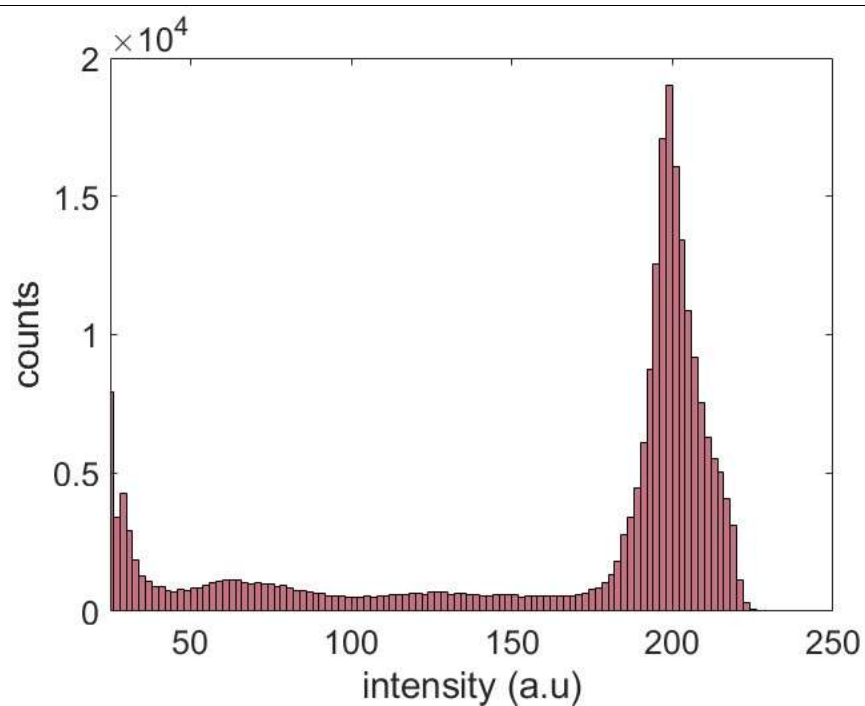


Figure S28. Histogram of the PL intensity (from the top-cell) of the PL mapping of a 60 cm² tandem device.

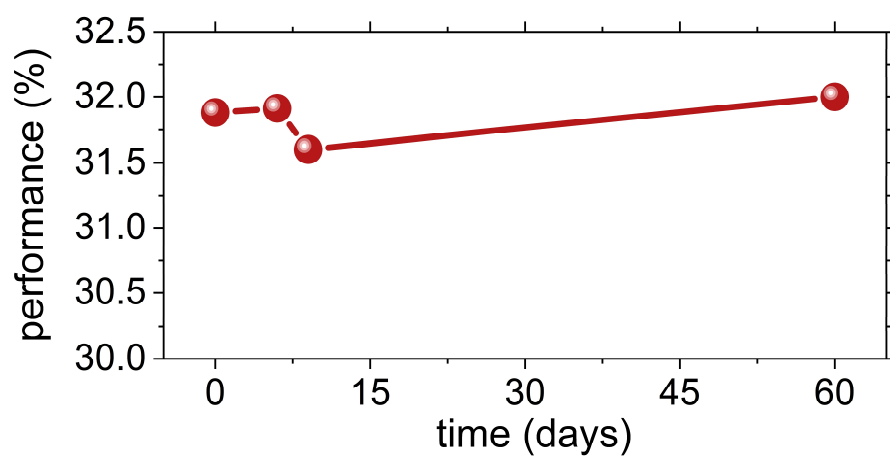
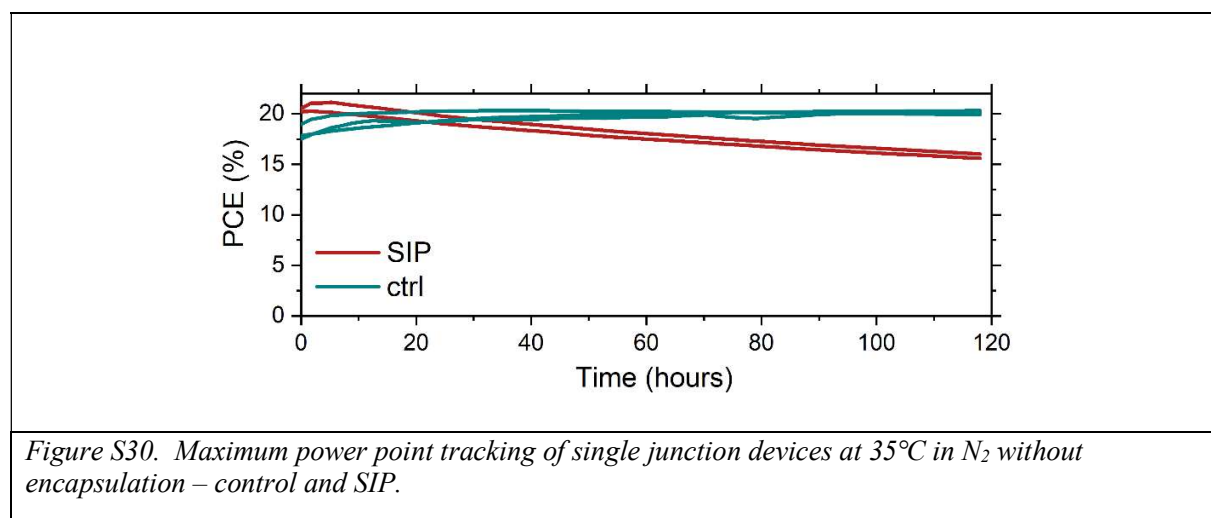


Figure S29. Shelf (dark and N₂) storage stability of SIP tandem devices with initial efficiency 31.88% for 60 days.

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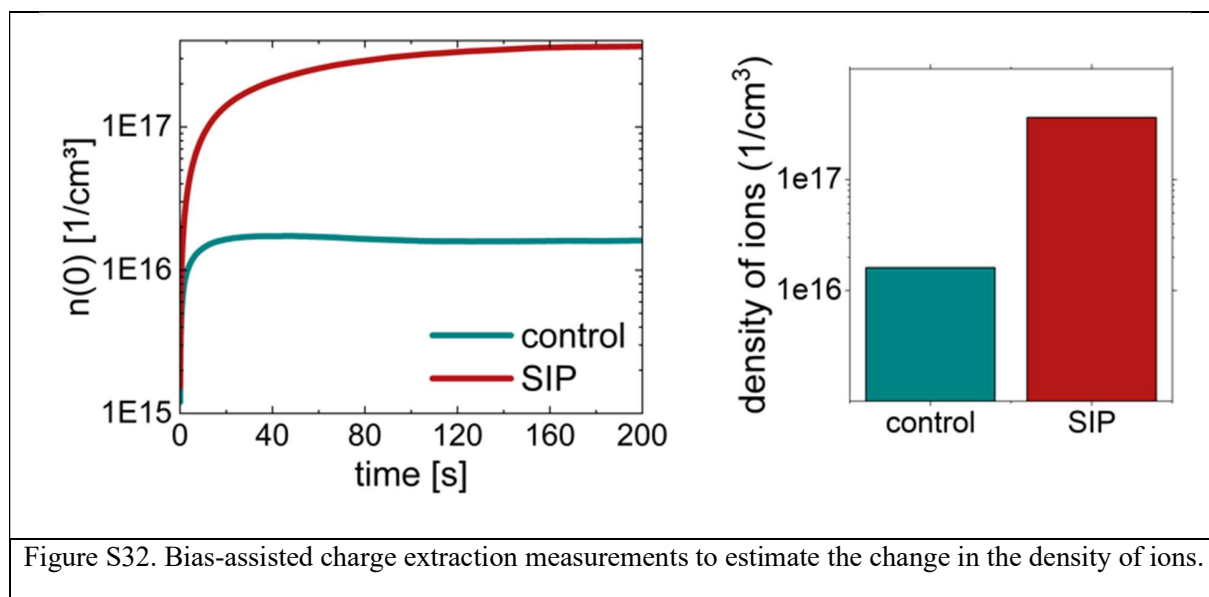
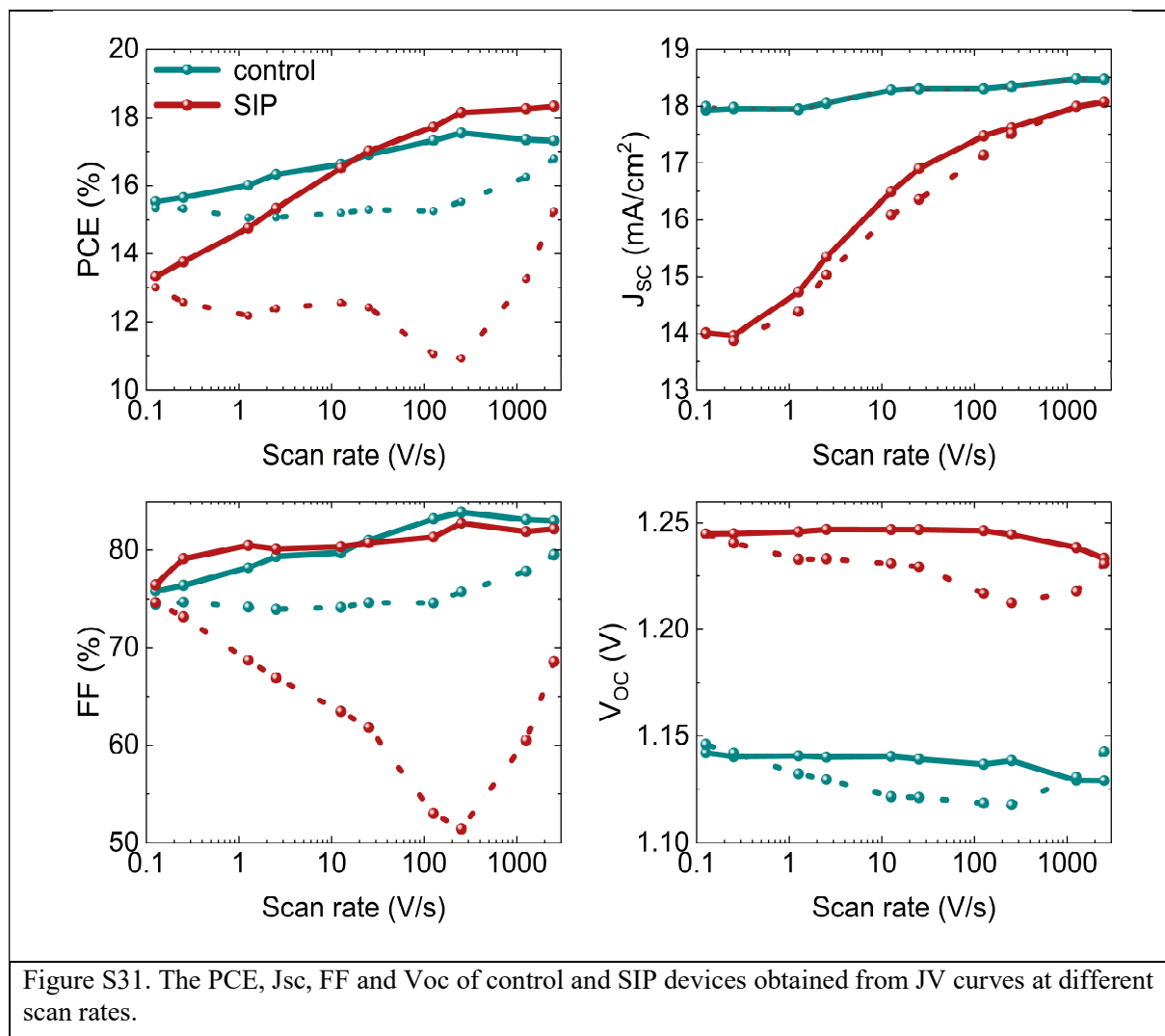
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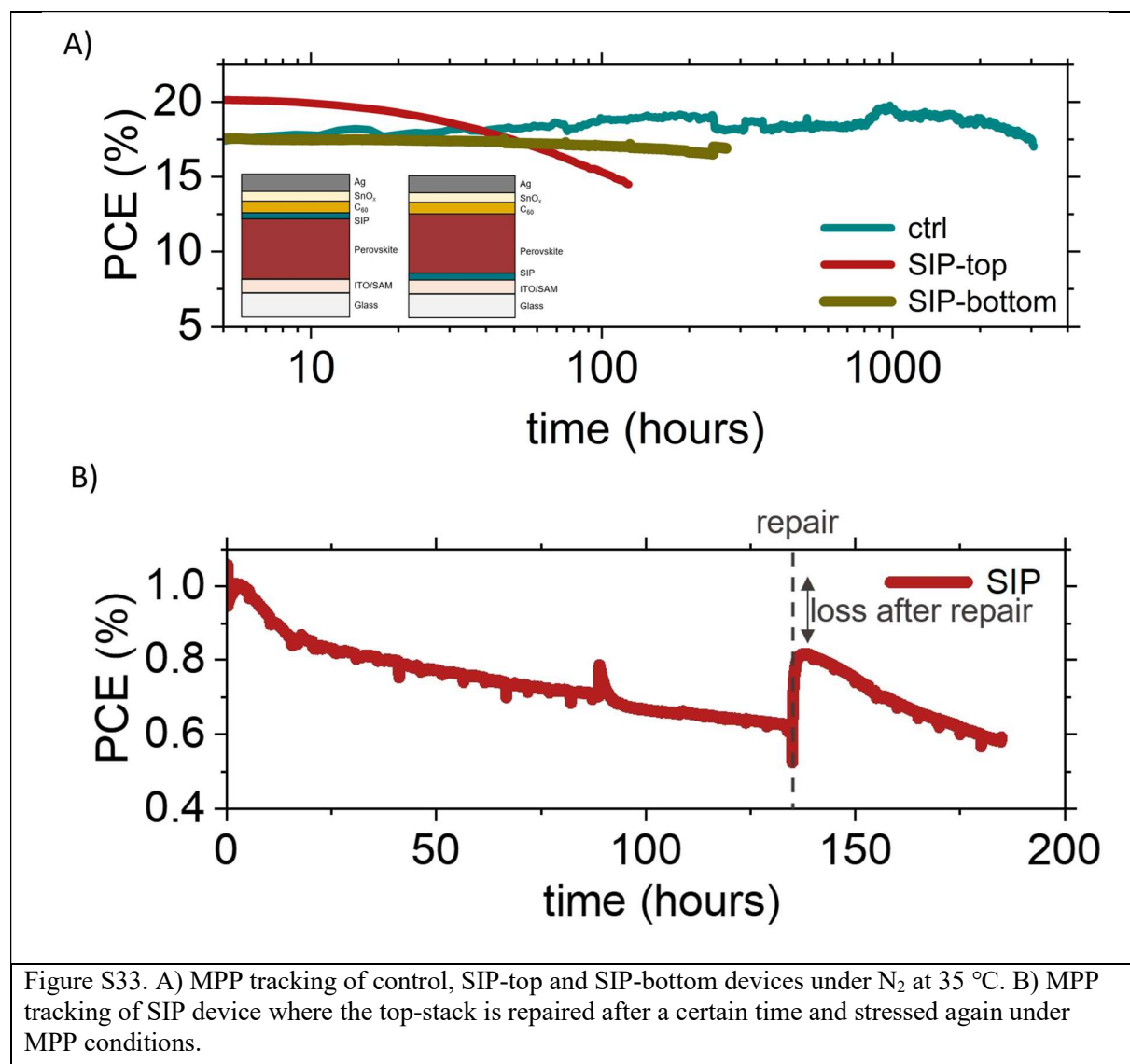
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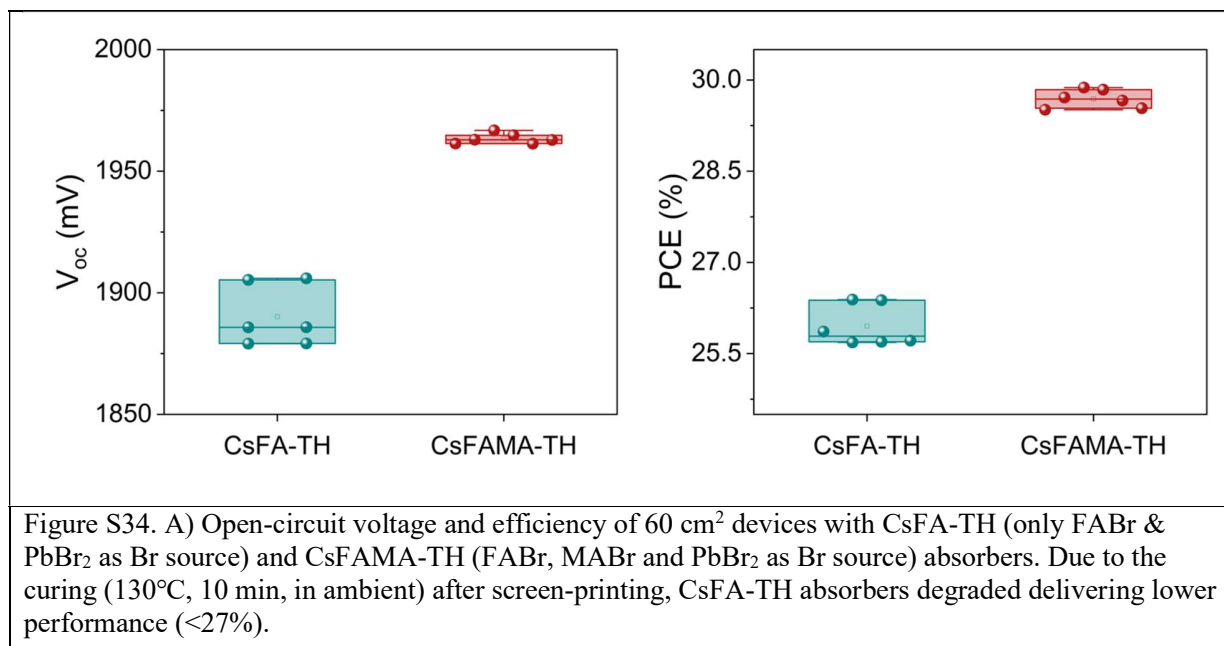
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