Supporting Information

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Experimental Section

Materials and solution preparation: Unless stated otherwise, all the materials were purchased from commercial sources and used without purification. For the hole transport layer (HTL), PEDOT:PSS aqueous dispersion (PVP Al 4083) was purchased from Heraeus Clevios and filtered by a PVDF syringe filter (0.45 µm) before use. Poly(triaryl amine) (PTAA) was dissolved in toluene at a concentration of 3 mg mL$^{-1}$ and stirred overnight at 60 °C. For the sequential solution-processed Pb-Sn hybrid perovskite precursor solutions, a 1.2 mmol PbI$_2$ (Sigma-Aldrich, beads, 99.999% trace metal basis) and SnI$_2$ (Sigma-Aldrich, beads, 99.99% trace metals basis) mixture was dissolved in N,N-dimethylformamide (DMF, 0.876 mL) (Sigma-Aldrich, anhydrous 99.8%) and dimethyl sulfoxide (DMSO, 0.0864 mL) (Sigma-Aldrich, anhydrous 99.9%). In the solution mixture, the molar fraction of SnI$_2$ ($\chi$) was varied between 0, 0.25, 0.4, 0.5, 0.6, 0.75, and 1, and 10 mol% SnF$_2$ (Sigma-Aldrich, 99%) with respect to SnI$_2$ was added. The precursor solutions were stirred at 60 °C for 1 hour and filtered by a PTFE syringe filter (0.22 µm) before use. Formamidinium iodide (53.48 mg) (FAI, Greatcell Solar) and methylammonium iodide (25.6 mg) (MAI, Greatcell Solar) mixture was dissolved in 1 mL of 2-propanol (Sigma-Aldrich,
anhydrous 99.5%) at 60 °C. For the perovskite surface passivation, ammonium thiocyanate (NH₄SCN) (Sigma-Aldrich, ACS reagent, ≥ 97.5%) was dissolved in 2-propanol at a concentration of 1 mg mL⁻¹ at room temperature. For the electron transport layers (ETLs), both C₆₀ (SES Research, 99.95%) and bathocuproine (BCP) (Lumtec, 99%) were used as received.

Solar cell fabrication: Patterned glass/ITO (Naranjo Substrates) were cleaned by sonication in acetone, sodium dodecyl sulfate (Acros, 99%) soapy water, deionized water, and 2-propanol, each step for 15 min. The ITO substrate was then treated under UV-ozone for 30 min before use. For the Sn-containing solar cells ($x \geq 0.25$), PEDOT:PSS solution was spin coated on the ITO substrate at 3000 rpm for 60 s and dried at 140 °C for 15 min in the ambient atmosphere. For the Pb-only ($x = 0$) device, PTAA was spin coated at 5700 rpm for 30 s and annealed at 100 °C for 10 min in the N₂ glovebox. In the same glovebox, the perovskite film was deposited on the HTL using a sequential solution process, first the (1−$x$)PbI₂: $x$SnI₂ mixture was spin coated at 3000 rpm (with a 2000 rpm/s acceleration) for 30 s, and dried at room temperature for 30 min. Afterward, the FAI/MAI solution was dynamically spin coated on the (1−$x$)PbI₂: $x$SnI₂ film at 3000 rpm for 60 s. The substrate was then annealed at 100 °C for 30 min before cooling down. For the FA₀.₆₆MA₀.₃₄Pb₀.₅Sn₀.₅I₃ perovskite film with additional surface treatment, the NH₄SCN solution was dynamically spin coated on top at 5000 rpm for 30 s. Finally, the device was completed by evaporating C₆₀ (20 nm), BCP (8 nm), and Ag (100 nm) layers under a high vacuum (~$3 \times 10^{-7}$ mbar). For the ambient stability test a Cu (100 nm) electrode was used instead of Ag. The active area of the solar cell was determined by the overlap of the Ag and ITO contacts (0.09 or 0.16 cm²).

For the 1.57 eV FA₀.₆₆MA₀.₃₄Pb₁.₉₅Br₀.₁₅ semitransparent front cell, both the bottom and the top ITO were deposited at room temperature by RF magnetron sputtering. The deposition was performed under a power of 56 W and a pressure of 2 mTorr (Ar with 0.6 mPa partial pressure of O₂). After UV-ozone cleaning for 30 min., PTAA was spin coated at 5700 rpm for 30 s and
annealed at 100 °C for 10 min. in the N2 glovebox. The FA$_{0.66}$MA$_{0.34}$PbI$_{2.85}$Br$_{0.15}$ was prepared by a sequential deposition protocol, where a PbI$_2$ (1.24 mol L$^{-1}$ in 10.1:1 volume ratio of DMF and DMSO) was spin coated at 3000 rpm (with a 2000 rpm/s acceleration) for 30 s, followed by the spin coating of FAI/MAI/MABr (54.0 mg/14.3 mg/7.6 mg in 1 mL 2-propanol) solution at 3300 rpm for 30 s. The substrate was immediately annealed at 100 °C for 30 min. Afterward, a PCBM (Solenne BV, 99%, 20 mg mL$^{-1}$ in 1:1 volume ratio of CB and CF) solution was spin coated at 1000 rpm (with a 20000 rpm/s acceleration) for 60 s, and annealed at 100 °C for 30 min. Before the top ITO layer deposition, Al:ZnO nanoparticles (Avantama, 2.5 wt% in mixture of alcohols) were spin coated on top twice at 2000 rpm for 60 s, and dried at 75 °C for 5 min. Finally, MgF$_2$ layers were thermally evaporated on the glass and ITO surfaces to enhance the NIR transmission.

**Solar cell characterization:** The current density–voltage ($J$–$V$) characteristics were measured in the N2 glovebox at room temperature. A tungsten-halogen lamp combined with a Schott GG385 UV filter and a Hoya LB120 daylight filter was used to simulate the 100 mW cm$^{-2}$ solar light. To better define the illuminated area, a black shadow mask with an aperture slightly smaller than the cell area (0.0676 or 0.1296 cm$^2$) was used. In the fast and reverse (forward) $J$–$V$ sweep, the Keithley 2400 source meter swept the voltage from +1.5 V (−0.5 V) to −0.5 V (1.5 V) at a scan rate of 0.25 V s$^{-1}$. For the stability test, the laminated narrow bandgap perovskite solar cell was kept in the dark under ambient conditions (25 °C, 20-30 RH%), and fast $J$–$V$ measurements were performed in the N2 glovebox. During the stabilized $J$–$V$ scan, the solar cell was operated at $V_{oc}$ for 5 min under light soaking, followed by a reverse voltage sweep from ($V_{oc}$ + 0.04) V to −0.04 V with a step size of 0.02 V. At each voltage step, the current density was recorded for 5 s. From the stabilized $J$–$V$ curve, the voltage at the maximum power point was extracted, which was then applied to the solar cell during the steady-state power output tracking. For EQE measurement, a modulated monochromatic probe-light (Philips focusline tungsten-halogen lamp, 50 W;
monochromator from Oriel, Cornerstone 130) was used to illuminate the solar cell, which was fixed behind a circular aperture with 1 mm radius and sealed in a nitrogen-filled box with a quartz window. The spectral response was amplified from a pre-amplifier (Stanford Research, SR 570) and measured by a lock-in amplifier (Stanford Research, SR 830). Afterward, the result was converted to the EQE using a reference silicon cell. To mimic the one sun illumination condition used in the $J-V$ measurements, the solar cell was illuminated under a high-power LED (530 nm or 940 nm, Thorlabs, driven by a DC4104 driver) during the EQE measurement.

The light intensity-dependent measurement was performed by using the same EQE setup, where a 730 nm LED was driven between 1-1000 mA, and the $V_{oc}$ at different light intensity was measured with a Keithley 2400 source meter.

The capacitance–voltage ($C-V$) measurements were performed on solar cells using an electrochemical station (Solartron SI1260 impedance/gain-phase analyzer). The measurements were performed in the $N_2$ atmosphere under a dark condition. For the Mott-Schottky analysis, the capacitance was measured by sweeping the (DC) voltage from −0.5 V to 1.2 V with a step of 40 mV. The frequency was kept at 1 kHz with an AC perturbation voltage of 10 mV.

*Film characterization:* XRD measurements were performed on a Bruker 2D phaser using Cu Kα ($\lambda = 1.5405$ Å) radiation. The increment step size was 0.05°, and the measurements were performed between 10-40°. Grazing incidence wide angle X-ray scattering (GIWAXS) experiments were carried out on a GANESHA 300 XL+ system from JJ X-ray equipped with a Pilatus 300K detector (pixel size 172 μm × 172 μm). The X-ray source was a Genix 3D Microfocus sealed tube X-ray Cu-source with integrated monochromator and the wavelength used was $\lambda = 1.5408$ Å. SEM images were obtained by a FEI Quanta 3D FEG microscope, using a 5 kV electron beam and a secondary electron detector. To avoid degradation, all the non-annealed perovskite precursor films were stored in the $N_2$-filled tube before quickly transferred to the measuring setup.
AFM measurements were performed using a Veeco MultiMode microscope with Nanosensor PPP-NCHR-50 tips.

A Thermo Scientific K-Alpha was used to measure the surface XPS with a 180° double-focusing hemispherical analyzer and a 128-channel detector. Monochromatic Al Kα (1486.6 eV) radiation was used with a spot size of 400 μm. The measurements were performed under a dark condition, with a base pressure below 8 × 10⁻⁸ mbar. A survey spectrum (15 scans) was first measured with a pass energy of 200 eV, followed by a high-resolution scan (30 scans) of each element with a pass energy of 50 eV. To avoid oxidation, the samples were transferred directly from a N₂ glovebox to the XPS analysis chamber via an air-tight XPS sample holder.

A ~100 nm thick cross-section lamella was prepared by a focused ion beam (FIB) lift-out technique and transferred onto a molybdenum grid. Cross-sectional TEM imaging was performed by a probe-corrected JEOL ARM 200F microscope (200 kV), equipped with a 100 mm² silicon drift detector for EDS elemental mapping. We note that elemental maps based on raw counts (which includes both the peak and background intensity in the energy window) might not represent the real distribution of atoms in the region of interest. Elements with a high atomic number give large background X-ray counts (X-ray continuum), which can contribute to other elemental maps. In order to reduce such background artifacts, we performed quantification of the EDS mappings by binning 5×5 pixels for each pixel to be quantified without reducing spatial resolution.

Ex-situ UV-vis-NIR absorption spectra were measured by PerkinElmer Lambda 900 UV-vis-NIR spectrophotometer between 400 and 1100 nm. To avoid sample degradation, all the samples were stored in an air-tight box, with two glass windows fixed on both sides of the substrate.

In-situ UV-vis-NIR absorption measurements were performed using a previously reported method.\[1\] White paint was applied on the backside of the glass substrate, whereas the (1–x)PbI₂:\nSnI₂ precursor film was deposited on the other side and dried in the N₂ glovebox. The substrate
was then placed on the spin coater, where it was illuminated by a focused light from the halogen lamp. A fiber optical cable was placed at an off-specular angle, which collected the light that was scattered by the white paint and transmitted through the whole layer stack. The optical fiber was connected to a spectrometer, which analyzed the raw photon counts before and after the perovskite layer formation (during the FAI-MAI dripping), and generated an absorption spectrum following the equation

\[
A(\lambda) = -\log_{10}\left(\frac{I_m(\lambda) - I_{m,dark}(\lambda)}{I_{m,blank}(\lambda) - I_{m,dark}(\lambda)}\right)
\]

Here \(I_m\) represents the wavelength-dependent counts; the dark and blank refer to a dark reference and blank reference on the same substrate before the spin coating was started, respectively. By monitoring the absorption spectrum in situ during the spin coating process (\(t = 0\) s when the FAI-MAI was dripped onto the rotating substrate), we obtained the time-evolution of absorbance for the Pb-Sn hybrid perovskites.
Figure S1. XRD pattern of the Pb$_{0.5}$Sn$_{0.5}$I$_2$ precursor film deposited on the ITO substrate, after drying at room temperature for 30 min. ♣: ITO substrate.

Figure S2. Schematic representation of the in-situ absorption measurements during FAI-MAI solution spin coating.[1]
**Figure S3.** In-situ absorption measurements and the time-resolved absorption spectra during spin coating of a FAI/MAI (66:34) solution onto the Pb_{1-x}Sn_{x}I_{2} precursor film (from $t = 0$ s), where $x$ is (a, b) 0, (c, d) 0.25, (e, f) 0.4, (g, h) 0.6, (i, j) 0.75 and (k, l) 1. The apparent absorption between 800 and 1000 nm in panel (b) is due to interference of light reflected from the top of the film and from the glass surface.
Figure S4. Top-view SEM images of non-annealed FA$_{0.66}$MA$_{0.34}$Pb$_{1-x}$Sn$_x$I$_3$ perovskite films (after spin coating), where $x$ is (a) 0, (b) 0.25, (c) 0.4, (d) 0.5, (e) 0.6, (f) 0.75 and (g) 1. Clearly, the grain size of the nonannealed precursor film gradually increases with an increasing Sn content. We note that the voids are formed in some films due to the instant evaporation of residue solvent under the SEM vacuum analysis chamber. Scale bars in SEM images are 500 nm.
Figure S5. XRD patterns of FA$_{0.66}$MA$_{0.34}$Pb$_{1-x}$Sn$_x$I$_3$ ($x$ = 0, 0.25, 0.4, 0.5, 0.6, 0.75, 1) precursor films without thermal annealing. We note that some $\delta$ perovskite phases (marked as *) were formed in the pure-Pb ($x$ = 0) precursor film, which is attributed to the instable $\alpha$ perovskite phase without thermal annealing (nanocrystals). The XRD measurements were performed in the ambient condition.
Figure S6. Top-view SEM images of annealed FA$_{0.66}$MA$_{0.34}$Pb$_{1-x}$Sn$_x$I$_3$ perovskite films, where $x$ is (a) 0.25, (b) 0.4, (c) 0.6 and (d) 0.75. Scale bars are 500 nm. The sheet-like crystals on the perovskite surface visible in panel (a) and (b) are attributed to SnF$_2$.$^{[2-3]}$
**Figure S7.** Grain size distribution of annealed FA$_{0.66}$MA$_{0.34}$Pb$_{1-x}$Sn$_x$I$_3$ ($x = 0, 0.25, 0.4, 0.5, 0.6, 0.75, 1$) perovskite films.
Figure S8. AFM height images of annealed FA$_{0.66}$MA$_{0.34}$Pb$_{1-x}$Sn$_x$I$_3$ perovskite films, where $x$ is (a) 0, (b) 0.25, (c) 0.4, (d) 0.5, (e) 0.6, (f) 0.75 and (g) 1. Scale bars are 800 nm. Similar to the SEM image (Figure 2a-c, S6), AFM images suggest that the grain size increases with Sn contents. Also, the RMS roughness of the films is drastically increased when $x$ is larger than 0.6.
### a)

**FA\textsubscript{0.66}MA\textsubscript{0.34}Pb\textsubscript{0.5}Sn\textsubscript{0.5}I\textsubscript{3}**

| Measure | Fit | Error |
|---------|-----|-------|
| FA\textsubscript{0.5}MA\textsubscript{0.5}Pb\textsubscript{0.5}Sn\textsubscript{0.5}I\textsubscript{3} | PbI\textsubscript{2} R-3m, #73-1754 | Ag-3C, #87-0597 |
| ITO, #39-1058 |  |

### b)

**FA\textsubscript{0.66}MA\textsubscript{0.34}PbI\textsubscript{3}**

### c)

**FA\textsubscript{0.66}MA\textsubscript{0.34}Pb\textsubscript{0.75}Sn\textsubscript{0.25}I\textsubscript{3}**

| Measure | Fit | Error |
|---------|-----|-------|
Figure S9. Experimental XRD patterns and the corresponding fitting profiles for the annealed FA0.66MA0.34Pb1-xSnxI3 perovskites, where x is (a) 0.5, (b) 0, (c) 0.25, (d) 0.4, (e) 0.6, (f) 0.75 and (g) 1. The crystallographic data of a single crystal FA0.5MA0.5Pb0.5Sn0.5I3 were obtained from the report by Kanatzidis and co-workers.[4]
Figure S10. Cubic lattice constant $a$ with different Sn contents ($x$) for the non-annealed (■) and annealed (●) FA$_{0.66}$MA$_{0.34}$Pb$_{1-x}$Sn$_x$I$_3$ ($x = 0$, 0.25, 0.4, 0.5, 0.6, 0.75, 1) perovskite films, respectively, and the integrated peak area (▲) of the (100) peak of the annealed perovskite films. We note that the lattice constant of the pure-Pb ($x = 0$) precursor film does not fit in the monotonic decreasing trend. This can be attributed to the formation of the $\delta$ perovskite phase (Figure S5), which complexes the XRD patterns and hampers the extraction of a reliable lattice parameter.$^{[5]}$
Figure S11. Optical bandgaps of the non-annealed (dash) and annealed (solid) FA$_{0.66}$MA$_{0.34}$Pb$_{1-x}$Sn$_x$I$_3$ ($x = 0, 0.25, 0.4, 0.5, 0.6, 0.75, 1$) perovskite films, respectively. The values were extracted from the UV-vis-NIR absorption spectra.
Figure S12. 2D GIWAX patterns from annealed FA$_{0.66}$MA$_{0.34}$Pb$_{1-x}$Sn$_x$I$_3$ perovskite films, where $x$ is (a) 0.25, (b) 0.4, (c) 0.6 and (d) 0.75.
Figure S13. Azimuthally integrated line profiles along the (100) peak ($q = 1 \text{ Å}^{-1}$) for the annealed FA$_{0.66}$MA$_{0.34}$Pb$_{1-x}$Sn$_x$I$_3$ hybrid perovskite films.
Figure S14. XPS spectra of the (a) Sn 3d and (b) O 1s core-levels of the annealed FA$_{0.66}$MA$_{0.34}$Pb$_{1-x}$Sn$_x$I$_3$ ($x = 0.25, 0.4, 0.5, 0.6, 0.75, 1$) perovskite films. The sample preparation and transfer were done in an inert atmosphere. It is found that the atomic ratio Sn$^{4+}$ remains about 5-10% for all the Pb-Sn hybrid perovskite films, suggesting the uncontrolled oxidation in such films.
Figure S15. (a) Cross-section image of an ITO/PEDOT:PSS/FA$_{0.66}$MA$_{0.34}$Pb$_{0.5}$Sn$_{0.5}$I$_3$/C$_6$0/BCP/Ag perovskite solar cell. (b) EDS line-scan composition profile over the cross section in panel (a).

Figure S16. (a) Mott-Schottky plots ($C^{-2}$–$V$) of the PSCs based on FA$_{0.66}$MA$_{0.34}$Pb$_{1-x}$Sn$_x$I$_3$ perovskite absorber, where $x = 0, 0.25, 0.4, 0.5, 0.6, 0.75$ and 1. The measurements were performed under the dark condition at 1 kHz. (b) The corresponding capacitance–frequency ($C$–$f$) plots of the PSCs, measured at 0 V bias under dark condition.

The background carrier density $N$ is calculated from the equation $C^{-2} = 2 \left( \frac{V_{bi}-V}{q \varepsilon_r \varepsilon_0 N} \right)$; where $C$ is the capacitance, $V_{bi}$ is the built-in potential, $V$ is the applied bias, $\varepsilon_r$ is the relative dielectric constant of the perovskite absorber, $q$ is the elemental charge, and $\varepsilon_0$ is the vacuum permittivity. The $\varepsilon_r$ can be determined from the dark $C$–$f$ measurement at a DC voltage of 0 V and AC perturbation voltage of 10 mV. In the 10 kHz to 100 kHz frequency range, we assume the PSC is a geometric capacitor.
and the geometric capacitance \( C_g = \frac{\varepsilon_r \varepsilon_0 A}{d} \), where \( A \) is the cell area, and \( d \) is the perovskite layer thickness, respectively.

**Figure S17.** Dark \( J–V \) curves of the PSCs based on FA\(_{0.66}\)MA\(_{0.34}\)Pb\(_{1-x}\)Sn\(_x\)I\(_3\) perovskite layers (\( x = 0, 0.25, 0.4, 0.5, 0.6, 0.75 \) and 1).
Figure S18. Stabilized $J-V$ curves of the PSCs based on NH$_4$SCN-treated FA$_{0.66}$MA$_{0.34}$Pb$_{0.5}$Sn$_{0.5}$I$_3$ perovskite films, under different processing conditions: (a) The concentration of NH$_4$SCN solution was varied from 0 to 3 mg mL$^{-1}$ (with no additional thermal annealing). (b) The thermal annealing temperature was varied from room temperature to 120 °C (for 10 min) after the NH$_4$SCN casting. The best performance can be obtained when using 1 mg mL$^{-1}$ of NH$_4$SCN solution (without additional thermal annealing) to passivate the FA$_{0.66}$MA$_{0.34}$Pb$_{0.5}$Sn$_{0.5}$I$_3$ perovskite film.
Figure S19. The statistical distribution of (a) $J_{\text{sc}}$ and (b) FF for the PSCs without (Pristine) and with NH$_4$SCN treatment (1 mg mL$^{-1}$). The $J$--$V$ measurements were done in the fast sweep, both in reverse (left) and forward (right) directions.

Figure S20. Light-intensity dependent $V_{\text{oc}}$ of PSCs based on FA$_{0.66}$MA$_{0.34}$Pb$_{0.5}$Sn$_{0.5}$I$_3$ perovskite film with and without NH$_4$SCN treatment. The device with NH$_4$SCN treatment shows an ideality of 1.7, which is higher than that of the pristine device (1.25). Here, the increased ideality factor can be explained by the reduced surface recombination process in the NH$_4$SCN-treated PSC.$^{[6]}$
**Figure S21.** Mott-Schottky plots ($C^{-2} - V$) of the PSCs based on FA$_{0.66}$MA$_{0.34}$Pb$_{0.5}$Sn$_{0.5}$I$_3$ perovskite absorber with and without NH$_4$SCN post-treatment, respectively. The intercept of the linear regime with the x-axis determines the built-in voltage $V_{bi}$. 
Figure S22. (a) SEM image of the FA$_{0.66}$MA$_{0.34}$Pb$_{0.5}$Sn$_{0.5}$I$_3$ perovskite film after NH$_4$SCN treatment. (b) XRD patterns of the pristine and NH$_4$SCN-treated FA$_{0.66}$MA$_{0.34}$Pb$_{0.5}$Sn$_{0.5}$I$_3$ perovskite film. *: PbI$_2$, ●: Ag electrode. The scale bar is 500 nm.
Figure S23. XPS spectra of the (a) N 1s, (b) I 3d, (c) S 2p, (d) Pb 4f, and (e) Sn 3d core-levels of the pristine and NH₄SCN-treated perovskite films. All the XPS spectra were calibrated using 284.8 eV of C 1s.
Figure S24. Steady-state photoluminescence (PL) spectra of pristine and NH$_4$SCN-treated Pb$_{0.5}$Sn$_{0.5}$ perovskite films deposited on glass substrate.
Figure S25. Photovoltaic parameters (a) $J_{sc}$, (b) $V_{oc}$, (c) FF, and (d) PCE of a laminated narrow bandgap solar cell based with a glass/ITO/PEDOT:PSS/FA$_{0.66}$MA$_{0.34}$Pb$_{0.5}$Sn$_{0.5}$I$_{3}$/C$_{60}$/BCP/Cu device structure. The device was stored under ambient conditions (25 °C, 20-30 RH%) and the $J$–$V$ measurements were performed in the N$_2$ glovebox.
Figure S26. (a) Device structure of a mechanically stacked 4-terminal all perovskite tandem solar cell. (b) $J-V$ curves and (c) the corresponding EQE spectra of a semitransparent front cell with 1.53 eV bandgap perovskite, a 1.23 eV bandgap perovskite stand-alone cell, and a 1.23 eV bandgap perovskite cell measured by using the 1.53 eV cell as an optical filter.
Table S1. Lattice parameter of cubic FA$_{0.66}$MA$_{0.34}$Pb$_{1-x}$Sn$_x$I$_3$ perovskite phase ($x = 0, 0.25, 0.4, 0.5,
0.6, 0.75, 1$).

| Sn content ($x$) | Space group | a (Å) | Integrated peak area at (100) |
|------------------|-------------|-------|-----------------------------|
| 0                | $Pm\bar{3}m$ | 6.3358| 139241                      |
| 0.25             | $Pm\bar{3}m$ | 6.3079| 90444                       |
| 0.4              | $Pm\bar{3}m$ | 3.2987| 52098                       |
| 0.5              | $Pm\bar{3}m$ | 6.2951| 117728                      |
| 0.6              | $Pm\bar{3}m$ | 6.2923| 110793                      |
| 0.75             | $Pm\bar{3}m$ | 6.2824| 149643                      |
| 1                | $Pm\bar{3}m$ | 6.2719| 203951                      |

Table S2. Photovoltaic parameters of devices based on different FA$_{0.66}$MA$_{0.34}$Pb$_{1-x}$Sn$_x$I$_3$ perovskite 
components, measured under simulated AM 1.5G illumination (100 mW cm$^{-2}$).

| Sn content ($x$) | $J_{sc}^a$ (mA cm$^{-2}$) | $V_{oc}^a$ (V) | FF$^a$ | PCE$^a$ (%) | $J_{sc}^b$ (mA cm$^{-2}$) | PCE$^c$ (%) |
|------------------|---------------------------|----------------|--------|-------------|---------------------------|-------------|
| 0                | 21.7                      | 1.02           | 0.79   | 17.4        | 21.8                      | 17.6        |
| 0.25             | 21.1                      | 0.75           | 0.75   | 12.0        | 21.8                      | 12.2        |
| 0.4              | 24.8                      | 0.75           | 0.72   | 13.3        | 25.7                      | 13.9        |
| 0.5              | 26.3                      | 0.74           | 0.71   | 14.0        | 26.9                      | 14.1        |
| 0.6              | 26.5                      | 0.72           | 0.70   | 13.4        | 27.1                      | 13.7        |
| 0.75             | 22.2                      | 0.5            | 0.63   | 7.1         | 22.3                      | 7.0         |
| 1                | 0.9                       | 0.19           | 0.52   | 0.1         | 1.31                      | 0.1         |

$^a$ The data was extracted from the stabilized $J$–$V$ scans under simulated AM 1.5G illumination (100 mW cm$^{-2}$). $^b$ Calculated by integrating the EQE spectrum with the AM1.5G spectrum. $^c$ Corrected PCE obtained by using the $J_{sc}$ obtained from the EQE spectrum.
Table S3. Photovoltaic parameters of the devices with and without NH₄SCN post-treatment on the FA₀.₆₆MA₀.₃₄Pb₀.₅Sn₀.₅I₃ perovskite film, measured under simulated AM 1.5G illumination (100 mW cm⁻²).

|                | $J_{sc}^a$ (mA cm⁻²) | $V_{oc}^a$ (V) | FF$^a$ | PCE$^a$ (%) | $J_{sc}^b$ (mA cm⁻²) | PCE$^c$ (%) |
|----------------|----------------------|---------------|--------|-------------|----------------------|-------------|
| Without NH₄SCN | 26.3                 | 0.74          | 0.71   | 14.0        | 26.9                 | 14.1        |
| With NH₄SCN    | 27.8                 | 0.78          | 0.73   | 15.8        | 28.0                 | 15.9        |

$^a$ The data was extracted from the stabilized $J–V$ scans under simulated AM 1.5G illumination (100 mW cm⁻²). $^b$ Calculated by integrating the EQE spectrum with the AM1.5G spectrum. $^c$ Corrected PCE obtained by using the $J_{sc}$ obtained from the EQE spectrum.

Table S4. Photovoltaic parameters of a 1.57 eV front cell, a 1.23 eV back cell before and after filtering by the front cell. The $J$-$V$ curves were measured under simulated AM 1.5G illumination (100 mW cm⁻²).

|                | $J_{sc}^a$ (mA cm⁻²) | $V_{oc}^a$ (V) | FF$^a$ | PCE$^a$ (%) | $J_{sc}^b$ (mA cm⁻²) | PCE$^c$ (%) |
|----------------|----------------------|---------------|--------|-------------|----------------------|-------------|
| 1.58 eV        | 19.8                 | 1.02          | 0.79   | 16.0        | 19.8                 | 16.0        |
| 1.23 eV        | 27.2                 | 0.76          | 0.72   | 14.9        | 28.0                 | 15.3        |
| 1.23 eV filtered | 8.3                 | 0.72          | 0.76   | 4.5         | 9.3                  | 5.1         |

$^a$ The data was extracted from the stabilized $J–V$ scans under simulated AM 1.5G illumination (100 mW cm⁻²). $^b$ Calculated by integrating the EQE spectrum with the AM1.5G spectrum. $^c$ Corrected PCE obtained by using the $J_{sc}$ obtained from the EQE spectrum.

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