< Electronic Supplementary Information>

Self-Assembled Hierarchical Structure to keep the

3D Crystal Dimensionality in *n*-butylammonium

Cation-capped Pb-Sn Perovskites

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EXPERIMENTAL SECTION

Materials

Formamidinium iodide (FAI, Greatcell Solar), Cesium iodide (CsI, 99.999 %, Alfa Aesar), *n*butylammonium iodide (*n*-BAI, Greatcell Solar), lead(II) iodide (PbI₂, 99.99 %, Tokyo Chemical Industry Co., Ltd.), tin(II) iodide (SnI₂, 99.999 %, Alfa Aesar), and tin(II) fluoride (SnF₂, 99 %, Sigma-Aldrich) were purchased and used without purification as precursors for Pb-Sn binary perovskites. Dimethylformamide (DMF, 99.5 %, Samchun Chemical) and dimethyl sulfoxide (DMSO, 99.8 %, Samchun Chemical), toluene (99.8 %, Samchun Chemical), and chlorobenzene (CBZ, 99 % - GR grade, Wako) were used as solvents. Acetone (\geq 99 %, Samchun Chemical), Isopropanol (IPA, \geq 99.5 %, Samchun Chemical) and methanol (\geq 99.5 %, Samchun Chemical) were used as cleaning solvents for Indium tin oxide (ITO)coated glasses. Poly(3,4-ethylenedioxythiophene) polystyrenesulfonate (PEDOT:PSS, PVP AI 4083) was sourced from CleviosTM (Germany). Phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM, 99.5 %) was sourced from Organic Semiconductor Materials (OSM, Republic of Korea) and Bathocuproin (BCP, 98 %) was purchased from Alfa Aesar. Poly(3-hexylthiophene-2,5-diyl) (P3HT, 4002-EE, *Mw* = ca. 60 K, *RR* = ~90 %) was purchased from Rieke Metals.

Preparation of perovskite precursor solution

A FA_{0.83}Cs_{0.17}Sn_{0.5}Pb_{0.5}I₃ precursor was prepared from FAI, CsI, PbI₂, and SnI₂, with 1.2 M concentration (the stoichiometric ratio of FAI:CsI:PbI₂:SnI₂: is 0.83:0.17:0.5:0.5). An *n*-BAI precursor was prepared by replacing the amount of FAI:CsI in the perovskite components with 2 mol%, 5 mol%, or 10 mol%. Two perovskite precursors were dissolved in a mixed solvent of DMF:DMSO with 4:1 volume ratio, which has an excess SnF₂ of 0.06 M (it is the amount for the 10 mol% of SnI₂). The perovskite solution was stirred at room temperature (RT) for 2 hours in the nitrogen (N₂)-filled glove box.

Fabrication of Perovskite Solar Cells (PSCs) and hole-only devices

ITO-coated glasses were sequentially cleaned with acetone, methanol, and IPA in the ultrasonic bath for 15 min, respectively. After cleaning, the glass substrates were dried in the dry oven at 95 °C to evaporate residual solvents. The cleaned substrates were then subjected to a UV-ozone treatment for 20 min. PEDOT:PSS was spin-coated onto the substrates at 4000 rpm for 50 s in ambient condition, and annealed at 150 °C for 20 min on a hotplate as a hole transport layer (thickness is ca. 30 nm). The surface treatment was performed by spin-coating of DMSO with 200 µL onto the PEDOT:PSS films. The surface-treated PEDOT:PSS/ITO substrates were dried at 150 °C for 20 min. The perovskite precursor solutions with/without n-BA were spincoated at 5000 rpm for 30 s in the N₂-filled glove box. A 300 µL of PC₆₁BM solution dissolved in toluene (1 mg mL⁻¹) was applied dropwise in the center of the substrate during the spincoating. The perovskite-coated substrate was annealed at 65 °C for 1 min, sequentially annealed at 100 °C for 30 min (thickness is ca. 400 nm). For an electron transport layer, a PC₆₁BM solution with 20 mg mL⁻¹ dissolved in CBZ was spin-coated onto the perovskite film at 1500 rpm for 35 s and annealed at 80 °C for 10 min (ca. 30 nm). A BCP solution (0.5 mg mL⁻¹ dissolved in IPA) was spin-coated at 4000 rpm for 20 s without any post-annealing treatment. The silver (Ag) top electrodes (ca. 100 nm) were thermally evaporated under a high vacuum condition (< 1×10^{-6} Torr) with a shadow mask (the size of each solar cell device is 4 mm²). The hole-only devices for space-charge limited current (SCLC) were fabricated with a structure of ITO/PEDOT:PSS/perovskite/P3HT/Ag. All fabrication processes were followed in the same manner with the PSCs except for a P3HT layer. A P3HT solution dissolved in CBZ (10 mg mL⁻¹) was spin-coated onto the perovskite film at 1500 rpm for 35s and annealed at 85 °C for 5 min.

General Characterization

The optical absorption spectra were characterized using ultraviolet-visible (UV-Vis) spectroscopy (UV-2700, Shimadzu). Before scanning the perovskite samples, a baseline correction was conducted with a scan range of 300 nm - 1100 nm. The measurement conditions are 100 nm/min for the scan speed and 1 nm for the interval step size. The steady-state photoluminescence (PL) spectra were measured using a spectrofluorometer (Fluorolog3 with TCSPC, HORIBA SCIENTIFIC) with a laser excitation wavelength at 374 nm. A crystal structure of the perovskite films was evaluated by X-ray diffraction (XRD, D8-Advance, Bruker-AXS). A diffracted beam monochromator was equipped in the X-ray diffractometer (Cu K α radiation, $\lambda = 1.541$ Å). All the XRD data were recorded in the two-theta range from 10° to 40° with a 1° min⁻¹ scanning rate at RT. Grazing incidence wide-angle X-ray scattering (GIWAXS) experiments were performed at the SAXS-3C beamline (X-ray wavelength = 0.1213 nm) at the Pohang Accelerator Laboratory (PAL) in Korea. The scattering signal was recorded on an EIGER detector (pixel size of 75 µm) and the sample to detector distance (SDD) was 220.3 mm. Each scattering pattern was obtained with an X-ray beam exposure time of 150 s. The incident angles were positioned to three different points, 0.08°, 0.12°, or 0.26°. Grazing incidence small-angle X-ray scattering (GISAXS) measurement was performed in a vacuum chamber with an X-ray wavelength of 1.542 Å on a Xenocs XEUSS 2.0 system. The incident angle was aligned to 0.2°. The sample-to-detector distances (SDDs) was 2500 mm. X-ray beam exposure time was 600 s. The surface morphologies and cross-sectional images were investigated by field emission scanning electron microscopy (FE-SEM; AURIGA, Carl Zeiss). The roughness of the perovskite films was observed by atomic force microscopy (AFM, NX-10 Complete AFM, Park Systems). Time of Flight Secondary Ion Mass Spectrometer (ToF-SIMS, TOF.SIMS-5) was used to obtain depth profiles of ions involved in the perovskite films. Analysis was performed using a 30 keV Bi primary ion gun. The depth profiling was

accomplished with a 5 keV argon cluster source with a $300 \times 300 \,\mu\text{m}$ area. From the profiles, three-dimensional (3D) rendering images were obtained. Water contact angles to investigate hydrophobicity or hydrophilicity for the perovskite films were measured using a contact angle instrument (Surface Electro-Optics, Phoenix 300). X-ray photoelectron spectroscopy (XPS) measurement was performed with a K-alpha system (Thermo Fisher Scientific) using a monochromatic Al Ka irradiation (1486.6 eV). Ultraviolet photoelectron spectroscopy (UPS) measurement was performed using an XPS-Theta Probe (Thermo Fisher Scientific) with Al Ka radiation (1486.6 eV).

Device testing

All device characterizations were carried out in ambient conditions (RT and relative humidity (RH) of 25 - 30 %). Current-voltage (J-V) curves of the perovskite solar cells were measured using a solar simulator (PEC-L01, Peccell Technologies) under standard AM1.5 illumination (power, 100 mW cm⁻²). The light intensity was calibrated with a silicon photodiode detector (BS-500BK, BUNKOUKEIKI CO., LTD.). Each device was measured with a scan rate of 100 mV s⁻¹ using a Keithley 2400 source meter. The external quantum efficiency (EQE) spectra were characterized using a CompactStat instrument (Ivium Technologies; Eindhoven, Netherlands) comprised of a power source (Abet Technologies 150 W xenon lamp, 13014) and a monochromator (DongWoo Opteron, MonoRa500i). The system was calibrated with the same photodiode detector for the solar simulator.

Space-charge limited current (SCLC) measurement was performed using a Keithley 2400 source meter. The scan range of the voltage was 0 V - 7 V and the measurement was conducted in a dark condition. Transient photovoltage (TPV) was measured with a nanosecond-pulsed Nd:YAG laser source (OPOTEK, Vibrant 355 LD, repetition rate of 10 Hz, and pulse width of 5 ns). A continuous light illumination from a xenon lamp was simultaneously monitored by a

Keithley 2400 source meter for V_{oc} generation. A small perturbation of a laser pulse (532 nm) modulated with neutral density filters (purchased from Newport) was applied to the devices. A digital oscilloscope (Agilent DSO3202A) with an input terminal of 1 M Ω was used to record the TPV signals.

DFT calculation

All calculations used a density functional theory (DFT) code implemented in the Vienna Abinitio Simulation Package (VASP), using the projector augmented wave (PAW) method.^{1,2} The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was used for the exchangecorrelation functional parameterization. Projector operators were evaluated in real space. All crystal structures were fully relaxed until the force acting on each atom was less than 0.01 eV Å⁻¹. Electron convergence criteria were set to 10⁻⁴ eV when the energy cut-off set 520 eV for the plane-wave basis points.^{3,4} All calculation results were spin-polarized calculations to describe the molecular oxygen (O₂).⁵ The Brillouin zone integration was performed with Gamm point sampling for surface and Monkhorst-Pack k-point grid of $3 \times 3 \times 1$ for bulk. The thermodynamic formation energy (ΔE_f) of iodine defect in the FA_{0.83}Cs_{0.17}Pb_{0.5}Sn_{0.5}I₃ perovskite was described as Equation S1;

$$\Delta E_f = (E(I) + E(FA_{0.83}Cs_{0.17}Pb_{0.5}Sn_{0.5}I_{3-\delta}) - E(FA_{0.83}Cs_{0.17}Pb_{0.5}Sn_{0.5}I_3)$$
(1)

where $E(FA_{0.83}Cs_{0.17}Pb_{0.5}Sn_{0.5}I_3)$ and $E(FA_{0.83}Cs_{0.17}Pb_{0.5}Sn_{0.5}I_2)$ are the DFTcomputed energy of the perfect cubic perovskite and defected cubic perovskite, respectively. E(I) is the single-atom energy in a super large cell. In this stage, we investigated O_2 adsorption energy to check the oxidation effect on the perovskite based on the DFT modeling (we make an iodine defect and attach oxygen molecule). The O_2 adsorption energies on the FA_{0.83}Cs_{0.17}Sn_{0.5}Pb_{0.5}I₃ and BA_{0.02}(FA_{0.83}Cs_{0.17})_{0.98}Sn_{0.5}Pb_{0.5}I₃ were calculated by following equation:

$$E_{oxi} = E(FACsPbSnI_{3-\delta}O_2) - E(FACsPbSnI_{3-\delta}) - E(O_2)$$
⁽²⁾

where $E(FACsPbSnI_{3-\delta}O_2)$ is the total free energy of O₂ adsorbed on the FA_{0.83}Cs_{0.17}Sn_{0.5}Pb_{0.5}I_{3-\delta} or BA_{0.02}(FA_{0.83}Cs_{0.17})_{0.98}Sn_{0.5}Pb_{0.5}I_{3-\delta}. $E(FACsPbSnI_{3-\delta})$ is the total free energy of an iodine defected FA_{0.83}Cs_{0.17}Sn_{0.5}Pb_{0.5}I₃ or BA_{0.02}(FA_{0.83}Cs_{0.17})_{0.98}Sn_{0.5}Pb_{0.5}I₃, where iodine defect (I) was generated on the top surface.

The calculated O₂ adsorption energies on the $FA_{0.83}Cs_{0.17}Sn_{0.5}Pb_{0.5}I_{3-\delta}$ and $BA_{0.02}(FA_{0.83}Cs_{0.17})_{0.98}Sn_{0.5}Pb_{0.5}I_{3-\delta}$ show that higher O₂ adsorption energy in the BA(S)Cs(S) (-0.679 eV) provides the oxygen passivation effect compared with I defected $FA_{0.83}Cs_{0.17}Sn_{0.5}Pb_{0.5}I_3$, Cs(S) (-0.949 eV). The higher amount (smaller absolute value) means that the oxidation will hardly occur at the BA(S)Cs(S) structure compared with the Cs(S) system.

To examine the interaction between FA/BA and sulfonates, we calculate interaction energy (E_{int}) between styrene sulfonate (SS) and BA (or FA) using DFT calculation as follows:

$$E_{int} = E(SSFA \text{ or } SSBA) - (E(SS) + E(FA \text{ or } BA))$$
(3)

where E(SS) and E(FA or BA) are the total free energies of SS and FA (or BA), respectively.



Fig. S1. Schematic illustration of the construction of $BA_{0.02}(FA_{0.83}Cs_{0.17})_{0.98}Pb_{0.5}Sn_{0.5}I_3$ (100) slab from the conventional FAPbI₃ unit cell for DFT calculations.



Fig. S2. ToF-SIMS depth profiles and 3D rendering images for all ions involved in the $BA_{0.02}(FA_{0.83}Cs_{0.17})_{0.98}Sn_{0.5}Pb_{0.5}I_3$ perovskite film.



Fig. S3. FE-SEM images (50 K magnification) to evaluate the surface morphology of the Pb-Sn binary perovskite films based on (a) n-BA 0% and (b) n-BA 2%.



Fig. S4. Water contact angle images of (a) *n*-BA 0% and (b) *n*-BA 2% Pb-Sn binary perovskite films after 1 minute of dropping water droplet. The photographs of (a) *n*-BA 0% and (b) *n*-BA 2% Pb-Sn binary perovskite films after 3 minutes of dropping water droplet.



Fig. S5. The calculated interactions of SS-BA and SS-FA and the schematic illustrations of SS-BA and SS-FA molecules, respectively.



Fig. S6. Photographs showing the pristine (first row) and *n*-BA 2% (second row) perovskite solutions of initial (left) and 5 minutes after air exposure (right).



Fig. S7. Molecular oxygen adsorption on the (100) surface of the perovskite crystals: crystal structures of (a) $FA_{0.83}Cs_{0.17}Pb_{0.5}Sn_{0.5}I_3$ with cesium (Cs) positioned on the surface (upper) and (b) $BA_{0.02}(FA_{0.83}Cs_{0.17})_{0.98}Sn_{0.5}Pb_{0.5}I_3$ with both *n*-BA and Cs positioned on the surface (bottom). (c) Calculated adsorption energies of the oxygen molecule on the (100) surface of $FA_{0.83}Cs_{0.17}Pb_{0.5}Sn_{0.5}I_3$ and $BA_{0.02}(FA_{0.83}Cs_{0.17})_{0.98}Sn_{0.5}Pb_{0.5}I_3$.

Δ Aa BCF PCBM ^-BA/FA/Cs Pb-Sn binary perovskite PEDOT:PSS

Fig. S8. Schematic illustration of the Pb-Sn binary PSC structure.



Fig. S9. Photovoltaic parameter statistic distributions of (a) open-circuit volatge (V_{oc}), (b) short-circuit current (J_{sc}), (c) fill factor (FF), and (d) power converison efficiency (PCE) for the BA_x(FA_{0.83}Cs_{0.17})_{1-x}Pb_{0.5}Sn_{0.5}I₃PSCs as a function of *n*-BA molar ratio (x = 0, 0.02, 0.05, 0.1).



Fig. S10. The representative J-V curves of the $BA_x(FA_{0.83}Cs_{0.17})_{1-x}Pb_{0.5}Sn_{0.5}I_3$ PSCs with various *n*-BA ratio (x=0, 0.02, 0.05, 0.1).



Fig. S11. Steady-state photoluminescence spectra of $FA_{0.83}Cs_{0.17}Pb_{0.5}Sn_{0.5}I_3$ and $BA_{0.02}(FA_{0.83}Cs_{0.17})_{0.98}Pb_{0.5}Sn_{0.5}I_3$ perovskite films.



Fig. S12. Normalized transient photovoltage measurements of the n-BA 0% control device and n-BA 2% perovskite device.



Fig. S13. (a) UV-vis absorption spectra (inset is magnification to determine the band edges) and (b) Plots of $\ln(\alpha)$ versus ho to extract the Urbach energy of the Pb-Sn binary perovskite films without/with *n*-BA 2%.



Fig. S14. UPS spectra of secondary electron cutoff and valence band of perovskite films without (a) and with (b) n-BA 2%. (c) Schematic for the calculated Fermi levels (E_f) and valence band minimum (E_{VBM}). (d) Schematic illustration of energy diagram. The lowest occupied molecular orbital (LUMO) levels of two perovskites were determined from the highest occupied molecular orbital (HOMO) levels and energy bandgaps obtained from tauc plots of Figure S14.



Fig. S15. Tauc plots of Pb-Sn perovskite films with/without *n*-BA 2% cation.



Fig. S16. Steady-state photocurrents for the perovskite solar cells based on *n*-BA 0% (a) and *n*-BA 2% (b) for 1000 s at the maximum power point. The V_m (an applied voltage at the maximum power point) of *n*-BA 0% and *n*-BA 2% devices are 0.640 V and 0.701 V, respectively.



Fig. S17. Photographs with a top-view (top electrode) of the perovskite solar cells without *n*-BA (left) with *n*-BA 2 % (right) after 19 days. Two devices were stored in the N₂-filled glove box. The color of the Ag electrodes was changed to yellow in the *n*-BA 0% device, whereas that of the *n*-BA 2 % device was maintained to silver color. The meaning of the color change is a formation of AgI.



Fig. S18. (a) Energetically favored defect position of iodine and bond distance Sn-I in Sn centered octahedral structure: $FA_{0.83}Cs_{0.17}Pb_{0.5}Sn_{0.5}I_3$ crystal with cesium (Cs) positioned on the surface (upper) and $BA_{0.02}(FA_{0.83}Cs_{0.17})_{0.98}Sn_{0.5}Pb_{0.5}I_3$ crystal with both *n*-BA and (Cs) positioned on the surface (bottom). (b) Calculated I-defect formation energies of Cs(S) and BA(S)-Cs(S) perovskite structures.



Fig. S19. Williamson-Hall plots of the Pb-Sn binary perovskite films without (a) and with n-BA 2% (b).



Fig. S20. Out-of-plane line cuts (q_z direction) from GIWAXS images of Figure 4c-d: (a) surface region, (b) critical angle position, and (c) bulk region.



Fig. S21. The low magnified cross-sectional FE-SEM images of $FA_{0.83}Cs_{0.17}Sn_{0.5}Pb_{0.5}I_3$ perovskite films (a) without and (b) with *n*-BA 2%.



Fig. S22. Out-of-plane profiles from GISAXS patterns of FA_{0.83}Cs_{0.17}Pb_{0.5}Sn_{0.5}I₃ (black line) and BA_{0.02}(FA_{0.83}Cs_{0.17})_{0.98}Pb_{0.5}Sn_{0.5}I₃ (red line) films.

Table S1. The number of atoms of FA, Cs, and BA in the $FA_{0.83}Cs_{0.17}Pb_{0.5}Sn_{0.5}I_3$ and $BA_{0.02}(FA_{0.83}Cs_{0.17})_{0.98}Pb_{0.5}Sn_{0.5}I_3$ perovskite crystals. S and B indicate that elements are positioned on the surface and inside the bulk of the cubic perovskite slab, respectively.

Case	FA	Cs	BA
Cs(S)	7	1	0
Cs(B)	7	1	0
BA(S) Cs(S)	6	1	1
BA(S) Cs(B)	6	1	1
BA(B) Cs(S)	6	1	1
BA(B) Cs(B)	6	1	1

	V _{oc} (V)	$J_{sc}(mA/cm^2)$	FF	PCE (%)
1	0.73	29.75	0.74	16.07
2	0.73	29.52	0.75	16.21
3	0.73	29.32	0.75	16.19
4	0.69	30.30	0.77	16.16
5	0.68	30.35	0.76	15.62
6	0.74	27.97	0.74	15.38
7	0.76	29.93	0.68	15.44
8	0.71	29.56	0.78	15.47
9	0.75	28.45	0.76	16.22
10	0.73	28.70	0.73	15.34
11	0.67	30.08	0.75	15.14
12	0.68	29.96	0.76	15.31
13	0.74	29.75	0.73	16.00
14	0.74	29.46	0.72	15.68
15	0.72	28.61	0.75	15.51
16	0.74	29.15	0.74	16.01
17	0.74	28.83	0.74	15.81
18	0.73	29.31	0.76	16.08
19	0.73	29.05	0.74	15.67
20	0.73	28.86	0.74	15.63
Average	0.72 ± 0.024	29.35 ± 0.64	0.74 ± 0.020	15.75 ± 0.35

Table S2. Photovoltaic performance parameters of *n*-BA 0% $FA_{0.83}Cs_{0.17}Pb_{0.5}Sn_{0.5}I_3$ PSCs under AM 1.5 illustration (power, 100 mW cm⁻²) measured in the air (RT, RH: 25 – 30 %).

No.	V _{oc} (V)	$J_{sc}(mA/cm^2)$	FF	PCE (%)
1	0.78	29.88	0.78	18.18
2	0.78	29.85	0.77	18.02
3	0.77	29.20	0.78	18.10
4	0.77	29.77	0.79	18.29
5	0.76	30.20	0.80	18.39
6	0.76	29.78	0.79	17.88
7	0.78	30.27	0.79	18.23
8	0.80	28.80	0.79	18.20
9	0.77	29.85	0.79	18.26
10	0.76	30.01	0.79	18.07
11	0.78	29.67	0.78	18.03
12	0.79	28.18	0.82	18.25
13	0.79	28.90	0.82	18.26
14	0.79	28.18	0.82	18.33
15	0.79	28.36	0.82	18.49
16	0.79	28.36	0.81	18.35
17	0.80	28.34	0.82	18.59
18	0.80	28.35	0.81	18.42
19	0.81	28.34	0.82	18.66
20	0.80	27.61	0.82	18.28
Average	0.78 ± 0.015	29.10 ± 0.83	0.80 ± 0.018	18.26 ± 0.19

Table S3. Photovoltaic performance parameters of *n*-BA 2% $FA_{0.83}Cs_{0.17}Pb_{0.5}Sn_{0.5}I_3$ PSCs under AM 1.5 illustration (power, 100 mW cm⁻²) measured in the air (RT, RH: 25 – 30 %).

No.	V _{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
1	0.73	29.01	0.76	16.09
2	0.72	28.96	0.75	15.64
3	0.72	28.61	0.77	15.80
4	0.71	28.63	0.75	15.24
5	0.71	29.41	0.75	15.66
6	0.71	29.23	0.76	15.73
7	0.71	29.21	0.75	15.55
8	0.68	29.02	0.73	14.43
9	0.71	27.77	0.74	14.70
10	0.70	29.80	0.74	15.40
11	0.71	28.19	0.75	14.99
12	0.69	28.17	0.73	14.24
13	0.71	27.91	0.74	14.74
14	0.71	27.32	0.73	14.05
15	0.70	28.64	0.75	15.09
16	0.70	27.88	0.75	14.73
17	0.70	28.79	0.74	15.02
18	0.71	28.34	0.75	15.11
19	0.70	27.51	0.76	14.63
20	0.70	26.73	0.75	14.00
Average	0.71 ± 0.010	$\textbf{28.46} \pm \textbf{0.77}$	0.75 ± 0.011	15.04 ± 0.60

Table S4. Photovoltaic performance parameters of *n*-BA 5% $FA_{0.83}Cs_{0.17}Pb_{0.5}Sn_{0.5}I_3$ PSCs under AM 1.5 illustration (power, 100 mW cm⁻²) measured in the air (RT, RH: 25 – 30 %).

No.	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	PCE (%)
1	0.69	26.25	0.74	13.40
2	0.68	26.40	0.73	13.07
3	0.69	25.96	0.75	13.30
4	0.68	26.07	0.73	12.94
5	0.68	25.59	0.76	13.20
6	0.68	25.63	0.75	13.00
7	0.68	25.20	0.76	13.06
8	0.68	25.06	0.75	12.78
9	0.66	24.28	0.72	11.54
10	0.67	25.68	0.74	12.65
11	0.65	22.30	0.72	10.38
12	0.65	21.46	0.73	10.24
13	0.64	23.01	0.70	10.34
14	0.66	22.65	0.72	10.64
15	0.65	21.49	0.73	10.13
16	0.66	24.13	0.73	11.48
17	0.66	23.35	0.74	11.24
18	0.66	23.73	0.74	11.55
19	0.65	22.85	0.73	10.83
20	0.65	22.57	0.73	10.64
Average	$\boldsymbol{0.67 \pm 0.015}$	$\textbf{24.18} \pm \textbf{1.64}$	0.73 ± 0.015	11.82 ± 1.21

Table S5. Photovoltaic performance parameters of *n*-BA 10% $FA_{0.83}Cs_{0.17}Pb_{0.5}Sn_{0.5}I_3$ PSCs under AM 1.5 illustration (power, 100 mW cm⁻²) measured in the air (RT, RH: 25 – 30 %).

Perovskite	V _{oc} (V)	$J_{sc}(mA/cm^2)$	FF	PCE (%)
<i>n</i> -BA 0%	0.75	28.45	0.76	16.22
<i>n</i> -BA 2%	0.81	28.10	0.82	18.66
<i>n</i> -BA 5%	0.73	29.01	0.76	16.19
<i>n-</i> BA 10%	0.69	26.27	0.74	13.47

Table S6. Photovoltaic performance parameters of the champion $BA_x(FA_{0.83}Cs_{0.17})_{I-x}Pb_{0.5}Sn_{0.5}I_3PSCs$ with various *n*-BA molar ratios (x = 0, 0.02, 0.05, and 0.1).

Table S7. Summary of TPV decay fitting parameters (bi-exponential equation, $Y = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$)

FA _{0.83} Cs _{0.17} Pb _{0.5} Sn _{0.5} I ₃ perovskite	A_1 (%)	$ au_1(\mu s)$	A_2 (%)	$ au_2$ (µs)	$ au_{average}\left(\mu s ight)$
<i>n-</i> BA 0%	0.25	1.19	0.72	0.19	0.45
<i>n-</i> BA 2%	0.61	4.54	0.21	0.25	3.44

References

- 1 P. Hohenberg, and W. Kohn, *Phys. Rev.*, 1964, **136**, B864.
- 2 G. Kresse, and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758,
- 3 G. Kresse, and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169.
- 4 G. Kresse, and J. Furthmüller, *Comput. Mater. Sci.*, 1996, 6, 15-50.
- 5 Y. Ahn, J. Moon, S. E. Park, J. Shin, J. W. Choi, and K. J. Kim, *Chem. Eng. J.*, 2020, **421**, 127855.