Supporting Information

Synergistic Cooperation between Photovoltaic and Thermoelectric

Effects in Solar Cells

Ping Fu^a, Dong Yang^a, Yihua Chen^b, Ruixue Lu^a, Md Azimul Haque^c, Yucheng Liu^d, Yaoyao Han^e, Hui Li^a, Ruotian Chen^a, Jieqiong Liu^a, Wei Qin^a, Luis Huerta Hernandez^c, Fengtao Fan^a, Kaifeng Wu^e, Derya Baran^c, Huanping Zhou^f, Can Li^{*a}

^aState Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, 457 Zhongshan Road, Dalian 116023, China ^bExperimental Centre for Advanced Materials, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China.

^cPhysical Science and Engineering Division, KAUST Solar Center (KSC), King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Kingdom of Saudi Arabia

^dKey Laboratory of Applied Surface and Colloid Chemistry; School of Materials Science and Engineering, Shaanxi Normal University, Xi'an 710119, China.

^eState Key Laboratory of Molecular Reaction Dynamics and Dynamics Research Center for Energy and Environmental Materials, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

^fSchool of Materials Science and Engineering, Peking University, Beijing 100871, China.

Correspondence to: *Prof. Can Li: <u>canli@dicp.ac.cn</u> Phone: (86)-411-84379070*

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Experimental

Materials

Tin Oxide (SnO₂) nanoparticle (15 wt % in water, Alfa-Aesar Inc.), Titanium Tetrachloride (TiCl_{4.} Alfa-Aesar Inc.) methylammonium chloride (MACl, > 99%, Luminescence Technology Corp), methylammonium iodine (MAI, > 99%, Luminescence Technology Corp), formamidine iodide (FAI, 99.9 %, Advanced Election Technology CO.Ltd), 2,2',7,7'-Tetrakis(N,N-di-p-methoxyphenylamino)-9,9'spirobifluorene (spiro-OMeTAD) and bathocuproine (BCP) were used as received from Xi'an Polymer Light Technology Corp., China. Lead iodide (PbI₂, 99.9985%) was purchased from Tokyo Chemical Industry (TCI). Nickel (II) nitrate hexahydrate (≥98%) was purchased from Tianjin Damao Chemical Reagent Factory. N, N-Dimethylformamide (DMF, anhydrous, 99.8%), dimethyl sulfoxide (DMSO, anhydrous, 99.8%), gamma-Butyrolactone (GBL, 98%), isopropyl alcohol (IPA, anhydrous, 99.8%), chlorobenzene (CB, anhydrous, 99.8%), toluene (anhydrous, 99.8%), 2% (in volume) formic acid (CH_2O_2) , lithium bis (trifluoromethyl sulphonyl) imide (Li-TFSI, 99.8%) and tert-butyl pyridine (TBP, 96%) were used as received from Sigma-Aldrich.

NiO_x ink solution

NiO_x nanoparticles were produced using a chemical precipitation method. First, 0.5 mol Ni $(NO_3)_2 \cdot 6H_2O$ was dissolved in 100 mL deionized water with stirring at roomtemperature. And then, 10 mol/L NaOH was added into the solution to adjust the pH at 10. The colloidal precipitate was obtained after stirring for 5 min, and thoroughly washed for three times using deionized water by centrifugation. The products were dried at 80 °C for 6 h to obtain green powder. Finally, the green powder was calcined at 270 °C for 2 h to obtain dark-black NiO_x nanoparticles. The NiO_x ink was prepared by 20 mg NiO_x nanoparticles dispersed in 1 mL deionized water. NiO_x films were fabricated using NiO_x ink by spin-coating at 2000 rpm for 60 s at room-temperature.

Perovskite precursor solution

The FAPbI₃ perovskite solution, FAI: MAI: MACI (70 mg: 4 mg: 10 mg) were dissolved in 1 ml IPA and 1.4 M PbI₂ was dissolved in a mixture solution of DMF and DMSO (94:6 v/v). These solutions were filtered through 0.4- μ m-pore PTFE filter after stirring one night and stored under a dry nitrogen atmosphere. The MAPbI₃ solution with initial mole ratio of 1 MAI : 1 PbI₂ were dissolved in a mixture solution of DMF and DMSO (4:1 v/v). The MAPbI₃ precursor solution was spin-coated at 4000 rpm for 30 s by onestep method and chlorobenzene (CB) as antisolvent was dropped after the first 10 s, then annealed at 130 °C for 10 min. Spiro-OMeTAD solution was prepared by dissolving spiro-OMeTAD (90 mg), tert-butyl pyridine (TBP, 36 μ L) and lithium bis (trifluoromethyl sulphonyl) imide (Li-TFSI, 22 μ L) solution (520 mg Li-TFSI in 1 mL acetonitrile) in 1 mL of chlorobenzene. About 50 nm thick TiO₂ layer was deposited on FTO substrates by the chemical bath deposition method .The substrates were immersed in the 0.2 M TiCl₄ aqueous solution and placed in an oven at 70 °C for 1h.

FAPbl₃ Single-crystal (SC)

To grow FAPbI₃ SC, FAI and PbI₂ were dissolved in gamma-Butyrolactone (GBL) with a molar ratio of 1:1 at 20 °C, and the concentration of the solution was controlled at 0.8 M. After vigorous stirring for 24 hours, clear FAPbI₃ precursor solution was obtained. Before using the solution, 2% (in volume) formic acid (CH₂O₂) was added into the precursor solution with stirring for 5 minutes to disperse it completely. Then, the solution was filtered through 0.8 μ m pore size PTFE filters into a clear crystallizing dish. To grow large FAPbI₃ SC, two steps were needed. First, small (1-2 mm) crystals were grown by heating the solution at 105 °C for 8 h, and the small crystals were selected as seeds. Second, to obtain large crystals, three to five seeds were transferred

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to another clear crystallizing dish with fresh solution. Then the new crystallizing dish was placed in a quiet air heating oven, and the oven was heated to 105 °C and maintained for five days. To further grow larger size crystals, the temperature was gradually increased to 120 °C. For the SC tests, a 150 nm thick interdigital electrode of Au (with an interelectrode distance of 50 μ m) was thermally evaporated as a counter electrode under a pressure of 4 × 10⁻⁴ Pa.

Other Characterizations

UV-visible absorption spectra were conducted on a Cary 60 (Agilent Technologies) with a LH101C temperature control device (Hailankeyi Company, Beijing). X-ray Diffraction (XRD) patterns were characterized by X-ray powder diffraction system (Bruker D8 discover, Cu K α : λ = 1.54 Å) at different temperature at a voltage of 40 kV and 200 mA currents with a liquid nitrogen cryostat (Oxford Instruments, OptistatDN-V). The diffraction data were collected with angular range $10 \approx 60$ degrees. Rietveld refinements were performed with GSAS-II². Rietveld refinement of the perovskite film on ITO glass indicates a preferred orientation of the crystallites in the film. To account for the experimental condition, the preferred orientation was modeled using 20 spherical harmonic functions³. Diffraction peaks were fitted with a Pseudo-Voigt peak profile. Steady-state Photoluminescence (PL) spectra were obtained by FLS980 (Edinburgh Instruments Ltd) equipped with a 450W Xe lamp, a photomultiplier tube (PMT) detector and a liquid nitrogen cryostat (Oxford Instruments, OptistatDN-V). Femtosecond pump-probe transient absorption (TA) spectra were performed at different temperature. The femtosecond laser pulse was generated by a Ti: sapphire femtosecond regenerative amplifier with 800 nm wavelength and 1 kHz repetition

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rate (Coherence) and served as both pump and probe beams. The pump pulse with a wavelength of 400 nm and duration of 50 fs generated via a second harmonic generator (SHG) was used to excite all the samples, and the probe beam was detected by a high-speed spectrometer (HELIOS, Ultrafast Systems). The wavelength range of the detector was set from 400 nm to 850 nm, and the spot size of the TA is approximately 0.5 mm² as evaluated by imaging the laser spot. These films were stable during the transient absorption studies. Seebeck coefficient measurements: For thermal voltage measurement, a homemade setup was used with Peltier devices (Cryo Industries Liquid Nitrogen Dewars equipped with model PSM-LN2 cryogenic temperature controller, Avantgarde Scientific Instruments Co.,) and thermocouples to apply the temperature gradient across the sample, thermal voltage was recorded by a Keithley 4200 electrometer. IR Camera testing: the ground emissivity of the perovskite films was determined according to the calculation formula of emissivity = measured value/standard value, where the measured value is the temperature measured by IR Camera, and the standard value is the temperature measured by the contact thermometer (we use T-type thermocouple for real-time temperature contact detection).

Notes

Note S1 UV-visible absorption spectra analysis

As depicted in Fig.S3, the bandgap peak positions for the films exhibit a band-gap (E_g) shrinkage of merely ~8.0 m eV for the FAPbl₃ films, transitioning from 20 °C (1.533 eV) to -60 °C (1.525 eV). As depicted in Fig.S14, the bandgap peak positions for the films exhibit a band-gap (E_g) shrinkage of merely ~6.0 m eV for the MAPbl₃ films, transitioning from 20 °C (1.575 eV) to -60 °C (1.56 eV). It's evident that such a slight shrinkage of E_g typically leads to a decrease in V_{oc} rather than an increase. Thus, it suggests that there may be other contributing factors to the enhanced V_{oc} for the FAPbl₃ PSCs from 20 °C to -60 °C. FAPbl₃ films exhibits strong absorption in the short-wavelength band and weak absorption in the infrared long-wavelength band (Fig.S5). The absorption below the band gap, namely, in the infrared band, can be directly converted into thermal energy through photo-thermal conversion.

Note S2 XRD data analysis

Based on the Rietveld refinement of XRD for the FAPbl₃ films (Fig.S4), it exhibits a cubic phase (P-43m) for FAPbl₃ films at 20 °C, consistent with the previous reports ⁴, ⁵. The refined lattice parameters for FAPbl₃ films are a = 6.337 Å, and V = 254.472 Å³. The peaks observed at 13.98° and 28.17° for FAPbl₃ films are assigned to the (100) and (200) crystal planes, respectively. Upon lowing the temperature from 20 °C to -50 °C, the refined lattice parameters for the FAPbl₃ films are a = 6.300 and V = 250.465 Å³. Additionally, the peaks associated with the (100) and (200) crystal planes exhibit a slight shift towards high diffraction angle of 14.08 ° and 28.41 °, respectively. These findings collectively suggest that decreasing temperature from 20 °C to -50 °C induce lattice contraction in FAPbI₃ films, without undergoing any phase transition^{6, 7}. Furthermore, the slight lattice contraction of FAPbI₃ films in the detected temperature region could induce self-elimination of intrinsic defects, contributing to the reduced charge carrier recombination discussed above⁵⁻⁷.

Note S3 Heat distribution by COMSOL

In order to study the ΔT across the PSCs, we conducted COMSOL simulations to analyze the heat distribution⁸⁻¹⁰.

The general heat equation (1) is given below:

$$\rho C_{p} \mathbf{u} \cdot \nabla T + \nabla \cdot \mathbf{q} = Q + Q_{\text{ted}}$$
$$\mathbf{q} = -k \nabla T \tag{1}$$

where u, q, k, C_p and ρ are the direction vector, conduction, thermal conductivity of the material as a function of temperature [W/(m.K)], the specific heat [J/(kg.K)], and the density at constant pressure, respectively. Q is a source term that controls the net energy absorbed at the sample surface from both sides.

The materials constituting the PSCs (Glass/ITO¹¹/SnO₂¹²/FAPbI₃¹³/Spiro-OMeTAD¹⁴/Au¹⁵) possess distinct thermal conductivity and Seebeck coefficient¹⁶⁻¹⁸. Under AM 1.5G illumination, the perovskite layer, serving as the primary photoactive material, reaches a temperature of 45°C, as determined by infrared imager (IR) methods (Fig.S6a), consistent with the literature reports¹⁹.

In actual test condition, a cooling system is situated near the Au side. The temperatures on glass side and Au side reduce when decreasing the temperature of the cooling system (Fig.S6b). Under the temperature of -50 °C, the temperatures on

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glass side and Au side are almost maintained at 10 °C and 0 °C, respectively (Fig.S6c). Thus, we designed the algorithm by the given temperature of 10 °C and 0 °C for the glass side and Au surfaces, allowing for temperature transitions from FAPbI₃ layer to the other two sides. As depicted in the Fig.S6d, a temperature disparity of approximately 15°C is evident across the FAPbI₃ layer. Thus, significant temperature gradients exist across the perovskite layer and the two sides of PSCs under the cooling system. For simplicity, we adopted the temperature differentials between the two sides of the PSCs as the ΔT throughout the manuscript.

Note S4 Fundmental photovoltaic characterizations for n-i-p planar PSCs

The integrated current obtained from external quantum efficiency (EQE) spectrum for the PSCs at $\Delta T = 1.4$ °C (T = 20 °C) is 24.24 mA cm⁻², thereby corroborating the reliability of the J_{sc} of 25.23 mA cm⁻² from *J*-*V* curve (Fig.S8). The long-term stability analysis was conducted for the n-i-p planar FAPbl₃ PSCs without encapsulation under three distinct conditions 1) relative humidity (RH) < 30% and RT, 2) 65% RH and RT, and 3) 30% RH and 65 °C. As a result, the FAPbl₃ PSCs at $\Delta T = 1.4$ °C maintained their PCE for 6000 h under a relative humidity (RH) of lower than 30% at 20 °C, and retained 65% (80%) cof initial PCE under 65% RH/RT for 1000 h (30% RH/65 °C for 1000 h) as illustrated in Fig.S9.

To assess the reproducibility of FAPbI₃ PSCs, the statistical distribution of the photovoltaic parameters were analysed based on twenty individual PSCs. The statistical findings yielded an average PCE of 22.72% and 25.04% for FAPbI₃ PSCs at ΔT = 1.4 °C or ΔT = 10 °C, respectively (Tables S2,3). For the FAPbI₃ PSCs at ΔT = 10 °C, a

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champion PCE of 25.74% was obtained along with a V_{oc} of 1.23 V, a J_{sc} of 25.79 mA cm⁻², and an FF of 81.08% (Fig.S10a). Moreover, the FAPbI₃ PSCs at $\Delta T = 10$ °C demonstrated a PCE of 25.12% under maximum power point tracking at bias voltage of 1.0 V for 400 secords (Fig.S10b).

Note S5 Surface potential difference measurement

Surface contact potential difference (Δ CPD) and transient Δ CPD signals collected with 5 Hz modulated light were further explored to confirm the p-type and n-type properties for FAPbI₃ films. Δ CPD can be determined by measuring the CPD under illumination and darkness. For a p-type semiconductor with downward surface band bending, due to the separation and transfer of photo-generated electrons towards the surface under illumination, a decreased CPD and a negative Δ CPD are observed. Conversely, for an n-type semiconductor with upward band bending, the CPD increases under illumination, resulting in a positive Δ CPD²⁰. In this manner, the Δ CPDs of the FAPbI₃ films are decreased by 10~20 mV under 680 nm laser illumination. Moreover, the Δ CPD signals for FAPbI₃ exhibited periodic changes of 5 Hz, but with opposite trends when the light is on and off, thus confirming the p-type property of FAPbI₃ films. Additionally, the positive value of the seebeck coefficient also suggests the p-type property of FAPbI₃ films.

Note S6 J_{ph} and V_{eff} measurements

To delve deeper into the photoexcitation behaviour of FAPbI₃ PSCs at $\Delta T = 1.4$ °C or 10 °C, an analysis of the charge collection behaviour was conducted by examining the dependence of the photocurrent density (J_{ph}) versus effective voltage (V_{eff})

(Fig.S12). J_{ph} is determined by the equation $J_{ph} = J_L - J_D$, where J_L and J_D are the current densities measured under AM 1.5G illumination and in darkness, respectively. And V_{eff} is defined as $V_{eff} = V_0 - V_{app}$, where V_0 is the voltage when $J_{ph} = 0$ and V_{app} is the applied bias. The ratio of J_{ph}/J_{sat} can be utilized to estimate the charge collection efficiency under operation conditions, where J_{sat} is the saturation photocurrent density. Under short circuit conditions, the J_{ph}/J_{sat} ratios were calculated to be 0.928 and 0.931 for FAPbl₃ PSCs at $\Delta T = 1.4$ °C or 10 °C, respectively. Under the maximal power output conditions, the J_{ph}/J_{sat} ratios were 0.955 for FAPbl₃ PSCs at $\Delta T = 1.4$ °C and 0.977 for the PSCs at $\Delta T = 10$ °C. The larger value of J_{ph}/J_{sat} for FAPbl₃ PSCs at $\Delta T = 10$ °C indicates a superior charge collection efficiency compared to those at $\Delta T = 1.4$ °C, thereby contributing to higher J_{sc} and FF²¹.

Note S7 Origin of the equation of $V_{oc}=kT/q *ln(n/n_0)$

The current density–voltage (*J*–*V*) characteristics of p–n junction solar cells under steady state illumination can be described using single exponential model as, $J = -J_{ph}+J_0(e^{qV/nkT}-1)$, (1) where J_{ph} is the photogenerated current density, J_0 the saturation-current density, q the elementary charge, V the voltage, k the Boltzmann's constant and T the temperature²².

The open-circuit voltage (V_{oc}) is the maximum voltage available from the solar cell. Eq. (1) at J=0: $J_{ph}=J_o(e^{qVoc/kT}-1)$ (2)

Take the ln of each side: $ln (J_{ph}/J_o) = qV_{oc}/kT$ (3)

The expression for V_{oc} : V_{oc} = $kT/q * In(J_{ph}/J_o)$ (4)

In addition, the macroscopic phenomenon of electric current density can be

described by the net motion of microscopic charged carriers.

 $I = \frac{I}{A} = \frac{nqAv}{A} = nqv, (5) \text{ where I} = \text{electric current [A], n=charge carrier density (m}^{3}), q \text{ the elementary charge, v = drift velocity [m/s] and A = area [m^2].}$

Based on the equation (4) and (5), the expression for V_{oc} can be described as:

$$V_{oc} = kT/q * ln(nqv/n_0qv) = kT/q * ln(n/n_0), (7)$$

where k is Boltzmann's constant, T is temperature, q is elementary charge, kT/q is the thermal voltage, n is the carrier concentration and n_0 is the carrier concentration in the initial state.

Figures



Fig.S1 (a) Schematic diagram of the cooling system to control different temperature (Method 1). Photos of the temperature control system in vacuum and the PSCs were operated with temperature-controllable metal directly contacting the illuminated side of the PSCs. (b) Schematic diagram of the cooling system to control the different temperature gradients. Photos of the cooling equipment in an N₂ glove box (Method 2). The cooling system is conducted via the cryogenic reaction bath with circulating ethanol solvent. The temperature of two sides of the PSCs were monitored by T-type thermocouple.



Fig.S2 Photovoltaic parameters distribution of n-i-p planar FAPbI₃ PSCs over a temperature range of -60 °C to 20 °C at $\Delta T = 0$ °C.



Fig.S3 Temperature dependent of (a) UV-visible absorption spectra and (b) corresponding band gap for FAPbI₃ films from 20 °C and -60 °C.



Fig.S4 (a-b) XRD patterns and (c-d) Rietveld refinement for $FAPbI_3$ films at 20 °C and - 50 °C.



Fig.S5 Absorption spectra for FAPbl₃ films/Quartz glass from 300 nm to 2500 nm.



Fig.S6 (a) IR thermal images of FAPbI₃ layer under continuous illumination (AM 1.5G, 100 mW cm⁻²). (b) Temperature of two sides of the PSCs with decreasing the temperature of the cooling system. T₁ and T₂ are the temperatures of illuminated and back side for the PSCs, respectively. (c) T₁ and T₂ vary with time under the cooling temperature of -50 °C. (d) The temperature simulation across n-i-p planar PSCs at $\Delta T = 10$ °C.



Fig.S7 Photovoltaic parameters distribution of n-i-p planar FAPbI₃ PSCs at $\Delta T = 1.4$ °C, 5.8 °C, 7.8 °C and 10.0 °C.



Fig.S8 EQE spectra for n-i-p planar FAPbl₃ PSC at ΔT = 1.4 °C (T = 20 °C).



Fig.S9 Evolution of the normalized PCE of n-i-p planar FAPbI₃ PSCs at ΔT = 1.4 °C (T =

20 °C) aged in (a) RH < 30% at 20 °C; (b) 65% RH at 20 °C and (c) 30% RH at 65 °C.



Fig.S10 (a) *J-V* curves of the champion performance of FAPbI₃ PSCs at $\Delta T = 10$ °C. (b) Stabilized PCE and photocurrent measured at a maximum power point (1 V) for FAPbI₃ PSCs at $\Delta T = 10$ °C.



Fig.S11 Seebeck coefficient for FAPbI₃ film.



Fig.S12 Calculation and statistics of double logarithmic plots of J_{ph} - V_{eff} characteristics of n-i-p planar FAPbI₃ PSCs at $\Delta T = 1.4$ °C and $\Delta T = 10$ °C.



Fig.S13 *J-V* curves of p-i-n planar FAPbI₃ PSCs at $\Delta T > 0$ °C with active area of 0.10 cm².



Fig.S14 Temperature dependent of (a) UV-visible absorption spectra and (b) corresponding band gap for MAPbI₃ films from 20 °C and -60 °C.



Fig.S15 Photo images of instrument for $\mathsf{FAPbI}_3\,\mathsf{SC}$ test.

Supplementary Tables

T (°C)	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF (%)	PCE (%)
-60	1.20	25.13	79.58	23.99±0.32
-50	1.21	25.19	79.98	24.55±0.18
-40	1.20	25.17	79.87	24.21±0.09
-30	1.20	25.18	79.39	23.91±0.50
-20	1.19	25.08	78.96	23.67±0.56
-10	1.19	25.05	79.01	23.58±0.38
0	1.19	25.09	78.84	23.44±0.51
10	1.17	25.06	78.53	23.06±0.47
20	1.16	24.99	77.72	22.60±0.44
30	1.16	24.70	74.02	21.22±0.02

i-p planar FAPbI₃ PSCs at $\Delta T = 0$ °C.

a. The PCE with standard deviations for more than 10 individual PSCs.

Table S2 Summary of the photovoltaic parameter distribution of n-i-p planar FAPbI_3

J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF (%)	PCE (%)
25.79	1.17	77.70	23.52
25.08	1.18	78.56	23.34
24.72	1.18	77.02	22.42
24.73	1.15	78.65	22.46
25.21	1.16	77.60	22.73
25.14	1.16	76.91	22.50
24.92	1.16	78.13	22.57
25.46	1.16	76.87	22.73
25.30	1.16	75.81	22.29
25.80	1.15	78.65	23.34
25.78	1.16	78.40	23.35
25.24	1.17	77.14	22.71
24.94	1.16	77.06	22.30
24.77	1.16	76.52	21.98
25.45	1.18	74.67	22.39
25.19	1.19	74.72	22.36
24.53	1.19	76.79	22.40
24.72	1.19	77.46	22.80
24.87	1.18	76.72	22.60
24.55	1.19	76.65	22.48
24.55	1.19	77.39	22.55
24.74	1.18	77.88	22.65
25.23	1.19	78.23	23.42
25.19	1.19	78.05	23.31
25.08	1.17	77.23	22.72
	J _{sc} (mA cm ⁻²) 25.79 25.08 24.72 24.73 25.21 25.14 25.14 25.30 25.30 25.46 25.78 25.78 25.78 25.24 24.77 25.45 25.19 24.53 24.72 24.87 24.55 24.74 25.23 25.19 24.55 24.74 25.23 25.19	J_{sc} (mA cm ⁻²) V_{oc} (V)25.791.1725.081.1824.721.1824.731.1525.211.1625.141.1624.921.1625.461.1625.301.1625.781.1625.781.1625.781.1625.451.1824.771.1625.451.1825.191.1924.531.1924.551.1924.551.1924.551.1924.741.1825.231.1924.741.1825.191.19	J_{sc} (mA cm ⁻²) V_{oc} (V)FF (%)25.791.1777.7025.081.1878.5624.721.1877.0224.731.1578.6525.211.1677.6025.141.1676.9124.921.1678.1325.461.1676.8725.301.1675.8125.801.1578.6525.781.1678.4025.241.1777.1424.941.1676.5225.451.1874.6725.191.1974.7224.531.1976.7924.721.1977.4624.551.1976.7224.551.1977.3924.741.1877.8825.231.1978.2325.191.1978.2325.081.1777.23

PSCs at $\Delta T = 1.4 \,^{\circ}\text{C}$ ($T = 20 \,^{\circ}\text{C}$).

a. Device #12 is chosen as the representative *J*-*V* curve.

PSCs at ∆7	⁻ = 10 °C (<i>T</i> = - 50 °C).			
Device	J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF (%)	PCE (%)
#1	25.79	1.23	81.08	25.74
#2	26.35	1.22	77.14	24.83
#3	26.19	1.22	78.71	25.20
#4	26.32	1.21	78.91	25.14
#5	26.35	1.21	78.78	25.16
#6	26.28	1.20	79.86	25.22
#7	26.27	1.20	78.55	24.82
#8	25.55	1.21	80.27	24.92
#9	25.56	1.21	80.76	24.97
#10	26.39	1.21	77.92	24.97
#11	26.06	1.22	78.20	24.86
#12	26.40	1.22	77.75	25.08
#13	26.42	1.21	77.89	24.96
#14	26.05	1.22	77.87	24.79
#15	25.97	1.21	79.12	24.91
#16	25.94	1.21	78.78	24.74
#17	26.29	1.22	77.41	24.90
#18	25.70	1.23	80.55	25.47
#19	26.08	1.22	79.18	25.27
#20	26.12	1.22	77.47	24.73
#21	25.70	1.23	80.55	25.47
#22	25.99	1.23	77.25	24.79
#23	26.36	1.22	77.54	24.84
#24	25.48	1.22	80.26	25.02
Averag e	26.07	1.22	78.83	25.04

Table S3 Summary of the photovoltaic parameter distribution of n-i-p planar FAPbI_3

a. Device # 19 is chosen as the representative *J*-*V* curve.

T (°C)	Δ <i>Τ</i> (°C)	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF (%)	PCE ^a (%)
-50	10.0	1.23	25.78	81.08	25.74±0.05
-40	7.8	1.23	25.70	80.55	25.46±0.22
-30	5.8	1.22	25.47	80.26	25.02±0.09
-20	4.8	1.22	25.43	78.75	24.41±0.18
20	1.4	1.17	25.08	77.23	22.72±0.06

Table S4 Summary of the photovoltaic parameters of n-i-p planar FAPbI₃ PSCs at $\Delta T >$

0°C.

a. The PCE with standard deviations for more than 10 individual PSCs.

Device	J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF (%)	PCE (%)
#1	24.80	1.20	82.52	25.14
#2	24.69	1.20	80.97	25.31
#3	25.00	1.20	82.54	25.22
#4	24.68	1.20	81.39	25.20
#5	25.40	1.19	84.31	25.21
#6	24.86	1.20	82.05	25.18
#7	25.42	1.20	84.02	25.31
#8	25.18	1.20	83.58	25.10
#9	25.19	1.21	81.93	25.39
#10	25.65	1.21	83.11	25.54
#11	25.14	1.21	82.22	25.30
#12	24.66	1.19	82.26	25.24
#13	25.06	1.20	82.60	25.38
#14	25.00	1.19	82.73	25.40
#15	24.99	1.19	83.06	25.34
Average	25.05	1.20	82.62	25.28

Table S5 Summary of the photovoltaic parameters of p-i-n planar FAPbI₃ PSCs at ΔT =1.4 °C (T=20 °C).

Device # 13 is chosen as the representative *J-V* curve.

Table S6 Summary of the photovoltaic parameters of p-i-n planar FAPbI₃ PSCs at ΔT =10.0 °C (T= -50 °C).

Device	Jsc (mA cm-2)	Voc (V)	FF (%)	PCE (%)
#1	25.31	1.22	85.30	26.37
#2	25.90	1.23	84.62	26.97
#3	25.31	1.23	86.30	26.84
#4	25.84	1.23	85.24	27.00
#5	25.94	1.23	84.73	27.02
#6	26.02	1.23	83.59	26.70
#7	25.96	1.23	84.84	27.09
#8	25.94	1.23	85.16	27.17
#9	26.17	1.23	84.39	27.16
#10	25.89	1.23	84.33	26.83
#11	25.84	1.23	84.44	26.82
#12	25.78	1.23	84.44	26.79
#13	25.94	1.23	83.50	26.59
#14	25.79	1.23	83.86	26.57
#15	25.94	1.23	84.33	26.89
Average	25.85	1.23	84.60	26.87

Device # 11 is chosen as the representative *J-V* curve.

Table S7 Photovoltaic parameters of p-i-n planar FAPbI₃ PSCs (0.10 cm²) at $\Delta T > 0$ °C.

FAPbl ₃	Δ <i>Τ</i> (°C)	V _{oc} (V)	FF (%)	J _{sc} (mA cm ⁻²)	PCE ^a (%)
p-i-n	1.4	1.16	81.78	24.20	23.00 ± 0.67
(0.10 cm ²)	10.0	1.19	83.25	25.15	24.93 ± 0.71

a) PCEs with standard deviations for 10 individual PSCs.

Table S8 Summary of the photovoltaic parameters of p-i-n planar FAPbI₃ PSCs (0.10

cm²) at ΔT =1.4 °C (T=20 °C).

Device	J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF (%)	PCE (%)	
#1	24.52	1.18	81.73	23.54	
#2	23.61	1.17	83.44	23.05	
#3	25.27	1.16	80.96	23.81	
#4	23.75	1.16	81.44	22.40	
#5	24.11	1.16	81.44	22.74	
#6	24.34	1.16	81.52	22.97	
#7	23.40	1.16	83.07	22.52	
#8	24.29	1.16	80.44	22.67	
#9	24.29	1.16	80.44	22.67	
#10	24.47	1.16	83.35	23.67	
Average	24.20	1.16	81.78	23.00	

Device # 6 is chosen as the representative *J*-*V* curve.

Table S9 Summary of the photovoltaic parameters of p-i-n planar FAPbl3 PSCs (0.10 cm^2) at $\Delta T = 10.0 \,^{\circ}C$ (T= -50 $^{\circ}C$).

Device	J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF (%)	PCE (%)
#1	25.59	1.19	81.03	24.68
#2	24.65	1.20	84.12	24.80
#3	24.67	1.19	84.40	24.83
#4	25.03	1.19	82.85	24.70
#5	24.73	1.19	83.88	24.69
#6	24.63	1.19	84.34	24.74
#7	25.93	1.19	83.24	25.60
#8	25.51	1.19	81.37	24.76
#9	24.84	1.19	86.00	25.38
#10	25.88	1.20	81.30	25.13
Average	25.15	1.19	83.25	24.93

Device # 4 is chosen as the representative J-V curve.

Supplementary References

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