Supporting Information

Post-Treatment Additives Enable Synergistic Surface Passivation and Secondary Grain Growth Regulation toward High-Performance Air-Processed Perovskite Solar Cells

Kelan Wang[a,1]; Shuai Xu[a,1]; Rong Cao[b], Xinyi Zhang[a]; Haocong Wang[a]; Chongzhen Tang[a]; Ran Fansheng[b,*]; Yipu Wang[a,*]; Minmin Wang[a,*]; Yanqiang Hu[a,*]

[a] School of Chemistry and Chemical Engineering, Nantong University, Nantong 226001, Jiangsu, China.

[b] School of Pharmacy and Jiangsu Province Key Laboratory for Inflammation and Molecular Drug Target, Nantong University, Nantong 226001, China.

Corresponding Author

*E-mail: ranfansheng1992@163.com; wangyipu@ntu.edu.cn; mmwang0528@ntu.edu.cn; HUYQNTU@ntu.edu.cn

Experimental Section:

Chemicals and reagents: Methylammonium bromide (MABr, 99.5%), formamidinium iodide (FAI, 99.99%), cesium iodide (CsI, 99.999%), lead bromide ($PbBr_2$, 99.99%), lead iodide (PbI_2, 99.99%) were purchased from Advanced Election Technology Co., Dimethyl sulfoxide (DMSO), N, N-dimethylformamide (DMF) and isopropanol (IPA), N-(2-fluoropyridin-6-yl)-2-(4-amino-4-formamido-1H-pyrazol-2-yl)acetamide (FPA) were purchased from Sigma-Aldrich. Commercial tin (IV) oxide solution (SnO_2, 15% in H_2O colloidal dispersion) was purchased from Alfa Aesar. All salts and solvents were used as received without any further purification.

Perovskite solar cell fabrication: FTO substrate was sequentially ultrasonically cleaned by deionized water, acetone, ethanol, and isopropanol for 30 min, and then treated with UV/O_3 light for 60 min. The SnO_2 film was fabricated on the FTO substrate from a SnO_2 nanocrystal solution (diluted with H_2O to 2.5%) at 3,000 rpm for 30 s and subsequently thermal annealing at 150 °C for 30 min in an ambient environment. KCl solution with a concentration of 5 mg/ml was spin-coated on the substrates for 20 s at 4000 rpm. The substrates were annealed at 100 °C for 10 min. The substrate was treated with UV-ozone for 30 min before spin-coating of the perovskite solution. Then, a 0.221 g FAI, 0.648 g PbI_2, and 0.03 g MACl were dissolved in DMF/DMSO (8:1, v/v) and stirred at 70 °C for 2 h, and then spin-coated on the substrate at 3000 rpm for 30 s. During the spin-coating, 200 μL of ethyl acetate was dripped after spinning for 10 s. Subsequently, the perovskite film was annealed at 150 °C for 15 min in an ambient environment. Afterward, 40 μL of isopropanol solution with different FPA concentrations was deposited on the perovskite film by spin-coating at 4,000 rpm for 30 s, and then at 150 °C for 5 min. Finally, a 100 nm thick Au electrode was deposited on top of the device by thermal evaporation under vacuum conditions. The active area is 0.09 cm^2, as defined by the mask.

Measurement and Characterization: Powder X-ray diffraction (XRD) patterns of the perovskite films were recorded by a Bruker D8 diffractometer with Cu Kα radiation (λ=1.5406 Å). FTIR spectra were measured using a Bruker Vertex 80v Fourier transform infrared spectrometer. The surface morphology of the perovskite films was observed by field-emission scanning electron microscopy (FE-SEM; Quanta 250FEG) and atomic force microscope (AFM; Brook Multimode 8). Absorption spectra of the prepared films were measured with a UV-vis-NIR spectrophotometer (UV-3600, Shimadzu). Ultraviolet photoelectron spectroscopy (UPS) was performed using a PHI5000VERSA PROBE II instrument. The PL spectra of the films were obtained at room temperature by using a steady-state lifetime spectrofluorometer (Varian Cary Eclipse). The time-resolved photoluminescence decay of the perovskite film was measured using a Horiba Fluorolog-3 Time Correlated Single Photon Counting (TCSPC) system. The current-voltage characteristic curves of the fabricated PSCs were measured under standard AM 1.5 sunlight (100 mW cm^{-2}, WXS-90L2, Wacom).

This file includes **Figure S1-S13**:

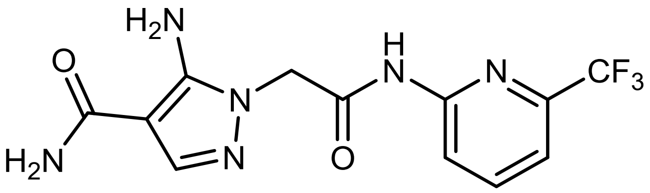

Figure S1. The molecular structure of FPA.

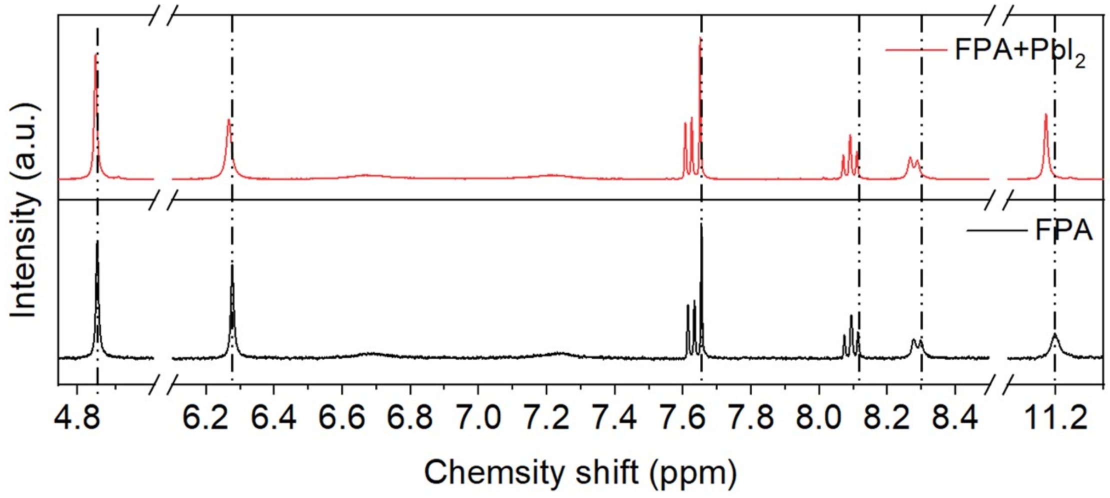

Figure S2. ^{1}H NMR spectra of FPA and FPA+PbI_2 mixture.

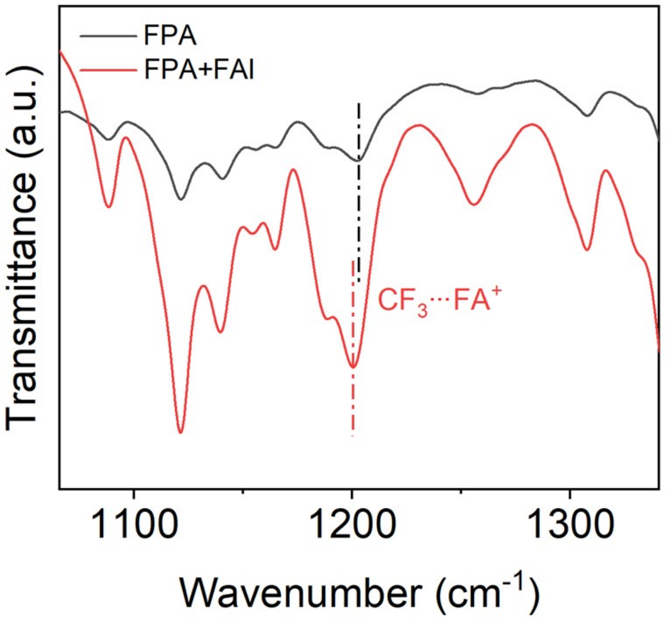

Figure S3. FTIR spectra of FPA and FPA+FAI mixture.

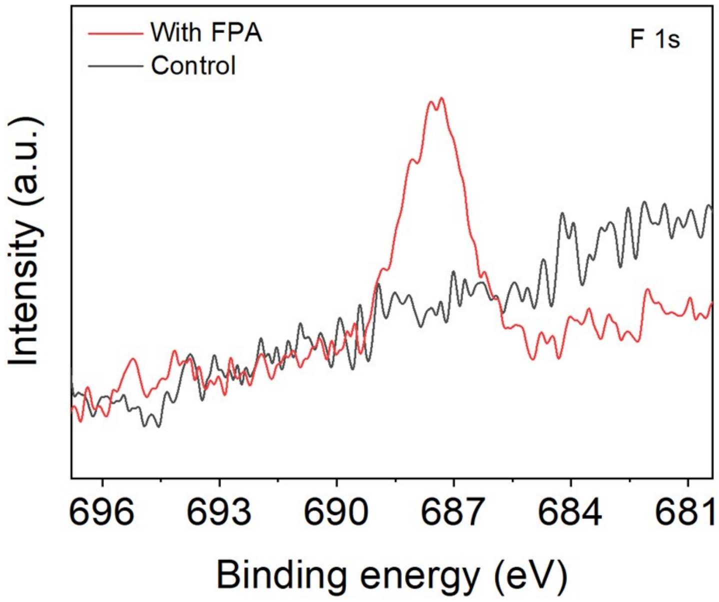

Figure S4. XPS spectra of F 1s with and without FPA.

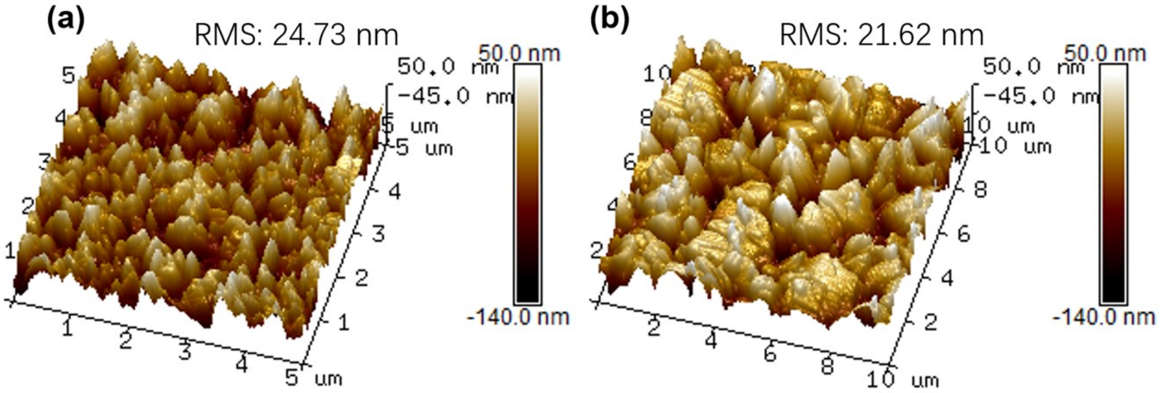

Figure S5. 3D AFM image of the perovskite film without and with FPA.

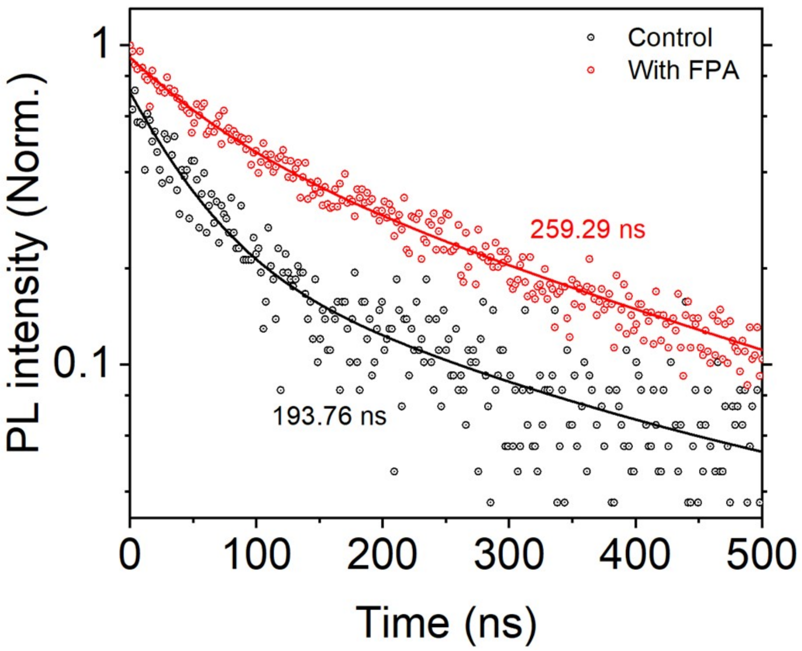

Figure S6. TRPL spectra of the perovskite film without and with FPA.

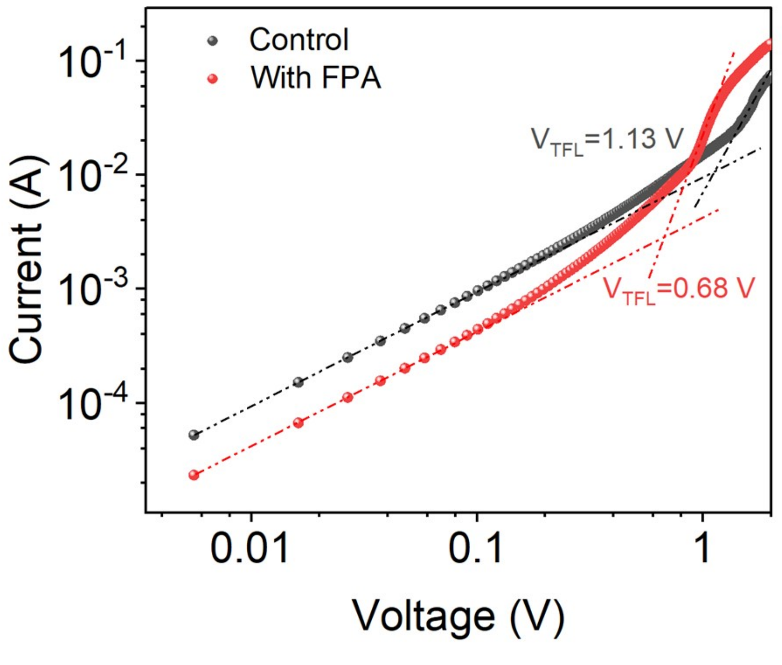

Figure S7. SCLC characterization of electron-only devices based on the perovskite film without and with FPA.

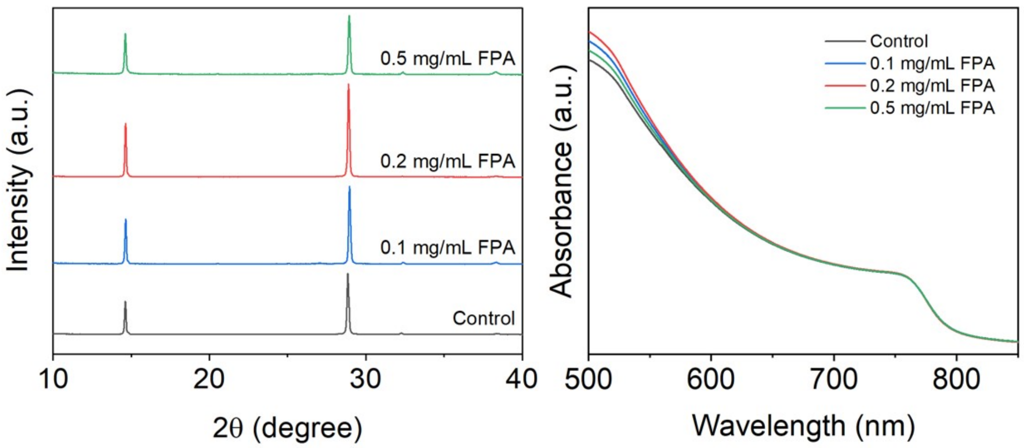

Figure S8. XRD and UV-vis absorption spectra of perovskite films treated with different concentrations of FPA.

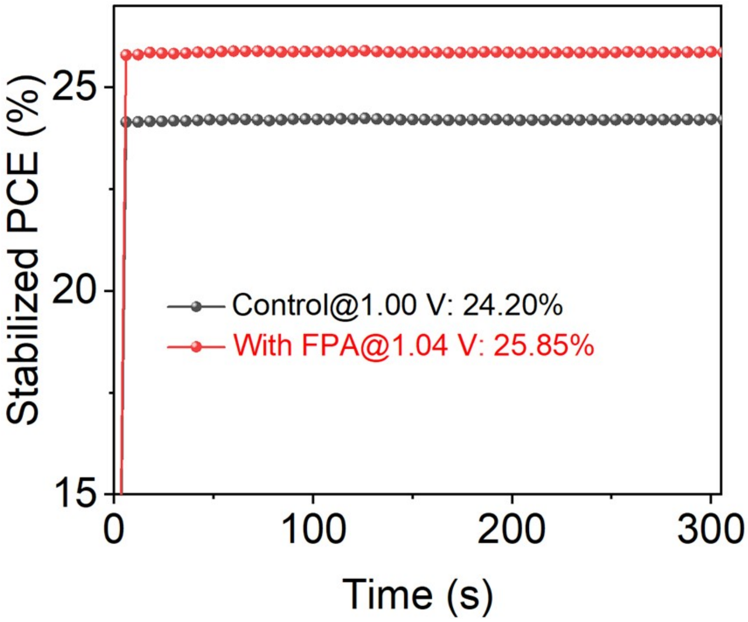

Figure S9. The continuous output for the control and FPA-modified PSCs.

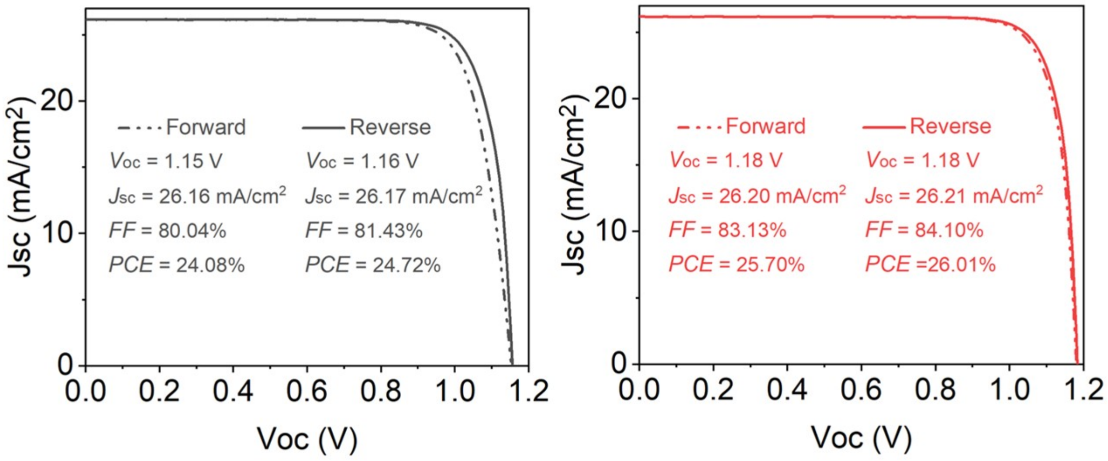

Figure S10. Forward and reverse scan for the control and FPA-modified PSCs. The hysteresis is calculated as follows: HI = ($PCE_{Reverse}$-$PCE_{Forward}$)/$PCE_{Reverse.}$

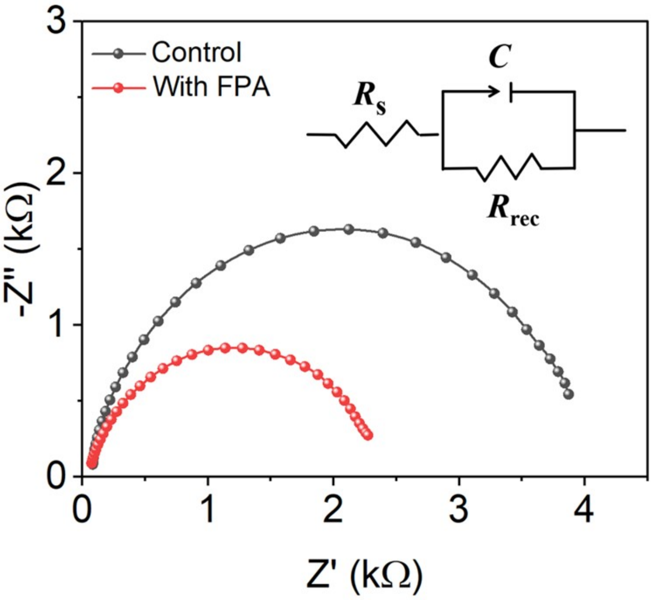

Figure S11. The EIS plot for the control and FPA-modified PSCs.

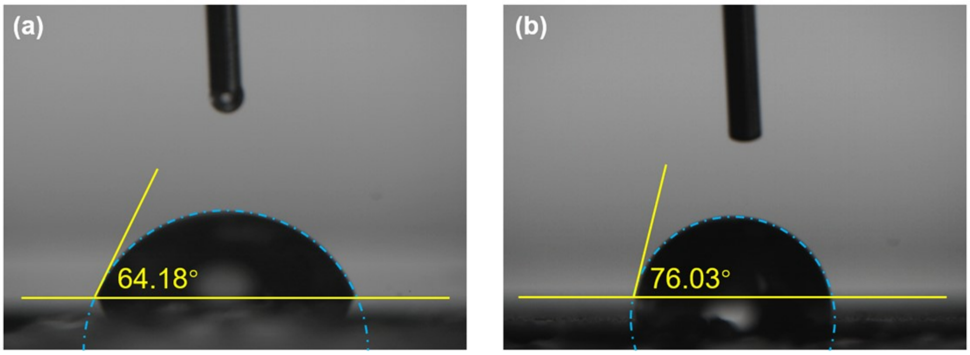

Figure S12. The water contact angle test of the perovskite film without and with FPA.

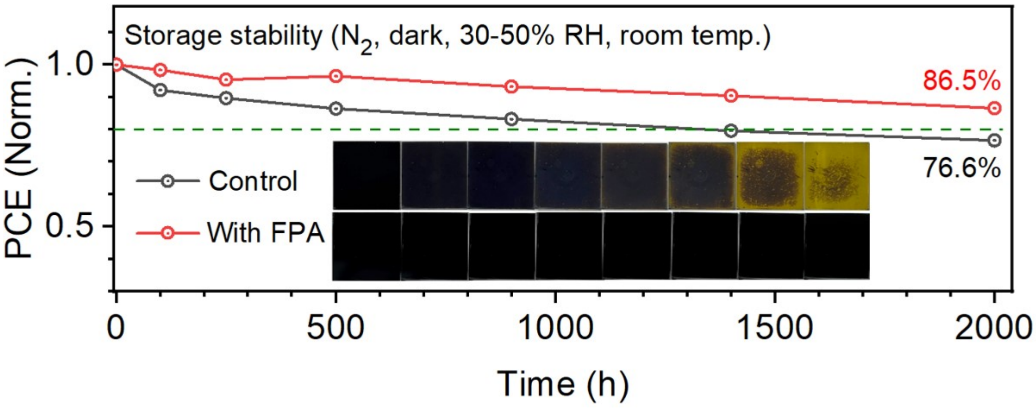

Figure S13. Storage stability for the unencapsulated control and FPA-modified PSCs.

Table S1. The photovoltaic performance parameters for devices with different FPA post-treatment concentrations.

Concentration	Voc (V)	Jsc (mA/cm^2)	FF (%)	PCE (%)
0 mg/mL	1.16	26.17	81.43	24.72
0.1 mg/mL	1.17	26.20	83.02	25.45
0.2 mg/mL	1.18	26.21	84.10	26.01
0.5 mg/mL	1.16	26.18	82.64	25.10

Table S2. Summary of recently reported air-prepared efficient PSCs with a formal structure (n-i-p).

Year	**RH (%)**	**Perovskites**	**Methods**	**Types**	**PCE (%)**	**Area (cm^2)**	**Ref.**
2021	50~60	$MAPbI_3$	One-step	n-i-p	20.55	0.09	[1]
2021	~40	$FA_xMA_{1-x}PbI_3$	Two-step	n-i-p	22.09	0.10	[2]
2021	20~90	$FAPbI_3$	Two-step	n-i-p	24.10	0.05	[3]
2022	50~70	$FA_xMA_{1-x}PbI_3$	One-step	n-i-p	23.70	0.0628	[4]
2022	40~55	$FAPbI_3$	Two-step	n-i-p	23.46	/	[5]
2022	20~80	$FAPbI_3$	One-step	n-i-p	23.91	0.05	[6]
2022	~50	$FA_xMA_{1-x}PbI_3$	One-step	n-i-p	24.07	/	[7]
2023	~40	$FA_xMA_{1-x}PbI_3$	Two-step	n-i-p	22.40	0.09	[8]
2023	30±5	$FA_xMA_{1-x}PbI_3$	Two-step	n-i-p	23.30	/	[9]
2023	50~60	$FA_xMA_{1-x}PbI_3$	Two-step	n-i-p	24.42	0.08	[10]
2023	30~40	$FAPbI_3$	One-step	n-i-p	24.00	0.09	[11]
2023	10~50	$FA_xMA_{1-x}PbI_3$	Two-step	n-i-p	24.14	0.09	[12]
2023	30~85	$FA_xMA_{1-x}PbI_3$	Two-step	n-i-p	25.08	0.08	[13]
2024	20~30	$FA_xMA_{1-x}PbI_3$	Two-step	n-i-p	24.16	0.09	[14]
2024	10~15	$FA_xMA_{1-x}PbI_3$	One-step	n-i-p	24.47	0.10	[15]
2024	/	$FA_xMA_{1-x}PbI_3$	One-step	n-i-p	24.63	/	[16]
2024	20~60	$FAPbI_3$	Two-step	n-i-p	24.70	0.09	[17]
2024	20~50	$FAPbI_3$	Two-step	n-i-p	25.08	0.04	[18]
2024	30~60	$FA_xMA_{1-x}PbI_3$	One-step	n-i-p	25.71	0.06	[19]
2025	15~25	$FA_xMA_{1-x}PbI_3$	Two-step	n-i-p	25.18	0.09	[20]
2025	20~40	$FA_xMA_{1-x}PbI_3$	Two-step	n-i-p	25.03	0.10	[21]
2025	10~15	$FA_xMA_{1-x}PbI_3$	One-step	n-i-p	25.30	0.10	[22]
2025	50-60	$FA_xMA_{1-x}PbI_3$	Two-step	n-i-p	26.50	0.08	[23]
2025	~50	$FA_{0.9}Cs_{0.1}PbI_3$	One-step	n-i-p	26.03	0.09	[24]
2025	~50	$FA_{0.9}Cs_{0.1}PbI_3$	One-step	n-i-p	26.18	0.09	[25]
2026	30~40	$FAPbI_3$	Two-step	n-i-p	26.52	0.05	[26]
2026	25~40	$FA_{0.9}MA_{0.1}PbI_3$	One-step	n-i-p	26.01	0.09	**This work**

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