Electronic Supplementary Information (ESI)

Surface Ligand Manipulation enables ~15% Efficient MAPbI$_3$ Perovskite Quantum Dot Solar Cell

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Materials

Methylamine acetate (MAAc, 99.99%, Greatcell solar), lead iodide (PbI$_2$, 99.9%, Adamas), oleic acid (OA, 90%, Aldrich), oleylamine (OAm, 90%, Aladdin), 1-octandecene (ODE, 90%, J&k), Acetic acid (99.5%, TCI), methyl acetate (MeOAc, anhydrous 99%, J&k), n-hexane (anhydrous 97.5%, J&K), n-octane (>98%, Alfa Aesar), toluene (98%, Chinasun Specialty Products Co.,Ltd.), isopropyl alcohol (IPA, >99.9%, J&K), methylamine thiocyanate (MASCN, 97.0%, TCI), methylamine iodide (MAI, Greatcell, 99%), titanium tetrachloride (TiCl4, ≥ 98% purity, Sinopharm Chemical Reagent Co.,Ltd.), tris(pentafluorophenyl)borane (95%, Acros Organics), poly(bis(4-phenyl)(2,4,6 trimethylphenyl) amine) (PTAA, Xi'an Polymer Light Technology Crop.). All these materials were used without further purification. Fluorine-doped tin oxide (FTO) covered glass substrates were purchased from Advanced Election Technology Co., Ltd.

Experimental Section

Synthesis of MA-OA precursor

0.455 g of MAAc and 10 mL of OA were loaded into a 50 mL three-neck flask and degassed under vacuum for 2 hours at 70 °C with continuously stirred. The flask was then filled with N$_2$ and kept at 70 °C for injection.

Synthesis of MAPbI$_3$ PeQDs

1 g PbI$_2$ was added into a 250 mL three-neck flask along with 50 mL ODE and dried under vacuum for 1 hour at 90 °C with continuously stirred. Then, 4 mL OAm and 8 mL OA were injected under N$_2$ and degassed for about 1 hour. Then, 0.5 mL acetic acid was injected under N$_2$ atmosphere and kept for 5 min. After that, this solution was cooled to 70 °C and swiftly injected with 10 mL MA-OA solution, 5s later, the reaction was quenched quickly by the ice-water bath. The crude solution was then added with 4 mL toluene and 20 mL MeOAc and centrifuged at 8000 rpm for 10 min to remove the excess precursors and unreacted ligands. The precipitation was collected and re-dispersed into 30 mL Toluene and then added with 10 mL MeOAc and centrifuged at 8000 rpm for 10 min. The precipitants were then collected and re-dispersed in 10 mL n-hexane. Before use, this solution needed to be concentrated to 100 mg mL^{-1} MAPbI$_3$ PeQD n-octane solution.

PeQD solar cell device fabrication

The glass/FTO substrate was ultrasonic cleaned with deionized water, acetone isopropyl

alcohol and acetone for 15 minutes each, respectively. After that, the substrate was dried with N_2 stream and treated with ultraviolet ozone for 30 min before use. Then, the TiO_2 electron transport layer was deposited on the FTO substrate by chemical bath deposition. Before depositing the active layer, the substrate was annealed on a hot plate at 200 ℃ for 30 minutes and treated with ultraviolet ozone for 15 minutes. Then, for preparing active layer, 15 μL of PeQD solution was dropped on the substrate and coated at 1000 rpm 15 s and 2000 rpm 20 s to prepare the $MAPbI_3$ PeQD film. Subsequently, 150 μL IPA solution was dropped onto the as-cast $MAPbI_3$ PeQD film for 5 s and spin-coated at 2000 rpm for 20 s to remove the excess long chain insulted ligands. For MA-salts treated sample, desired MA-salts are dissolved in IPA as ligands. This process was repeated 2 times to obtain a 200-300 nm thickness $MAPbI_3$ PeQD film. After that, for preparing hole transport layer, 30 μL solution of PTAA in Tol (15 mg mL^{-1}) doped with 4 tris(pentafluorophenyl)borane was spin-coated on the active layer at 3000 rpm for 30 s. Finally, 100 nm of Au electrode were thermally evaporated through a shadow mask with an active area of 0.075 cm^2.

Characterization

The UV-vis absorption spectroscopy was performed on a Perkin Elmer model Lambda 750 spectrophotometer. The PL spectra were recorded by a FluoroMax-4 spectrofluorometer (HORIBA Scientific) with excitation wavelength at 410 nm. The TRPL spectra were obtained using a Hamamatsu streak camera. The PL data were analyzed on a Nikon 50x objective (N.A. 0.55) in a Nikon ME600 optical microscope. The FTIR spectra were collected using a Bruker HYPERION FTIR spectrometer and cumulated 32 scans at a resolution of 4 cm^{-1}. The TEM images were recorded by a Tecnai G2 F20 S-Twin system operated at 200 kV. The XRD patterns were performed on a desktop diffractometer (D2 PHASER, Bruker) with a Cu Kα source (λ = 1.54056 Å). The XPS measurements were carried out at a Kratos AXIS Ultra DLD ultrahigh vacuum photoemission spectroscopy system equipped with an Al-Kα (1486.6 eV) radiation source and a hemispherical electron energy analyzer (Scienta R3000). The top view and cross-section SEM images were obtained from SEM (a Zeiss G500 with the extra high tension of 10 kV). The AFM images were obtained by a Veeco AFM. *J-V* curves of the devices carried out at a Keithley 2400 Digital Source Meter under N_2 glovebox and simulated AM 1.5G spectrum at 100 mW cm^{-2} with a solar simulator (Class AAA, 94023A-U, Newport). The external quantum efficiency (EQE) measurement of the solar cells was measured by a Solar Cell Scan 100 system (Zolix Instruments Co. Ltd.).
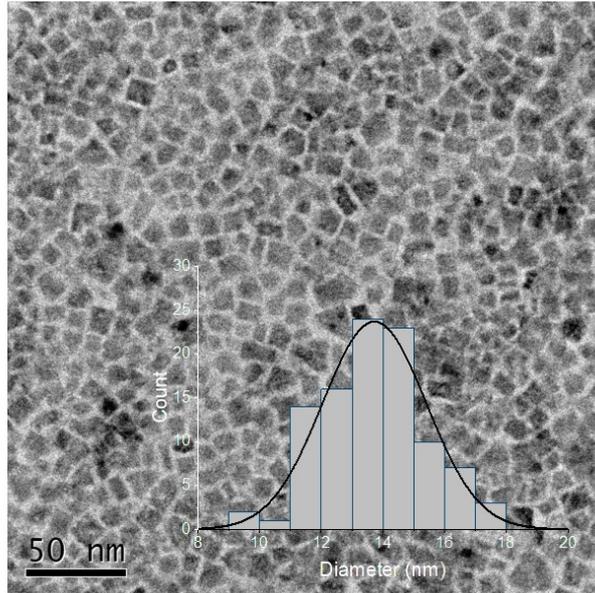
Fig. S1 TEM image and the corresponding size distribution of MAPbI$_3$ PeQD.
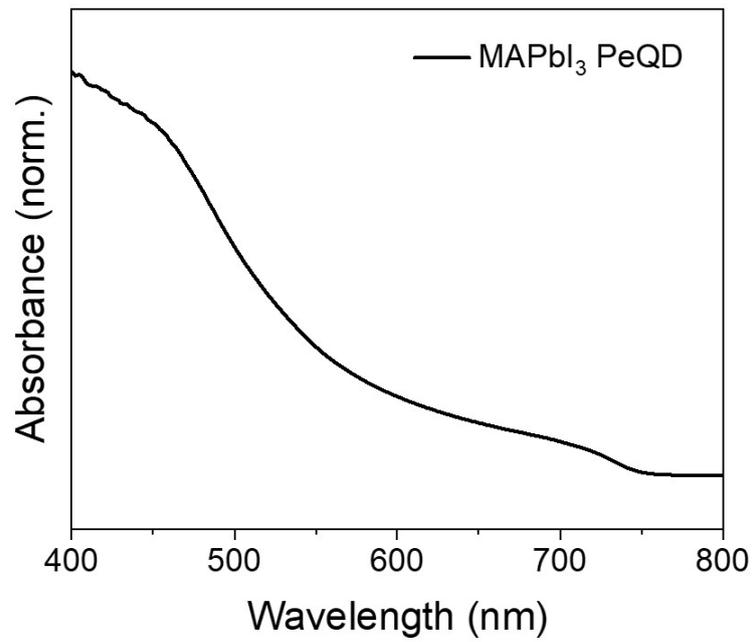
Fig. S2 Absorption spectra of pristine MAPbI$_3$ PeQD film.
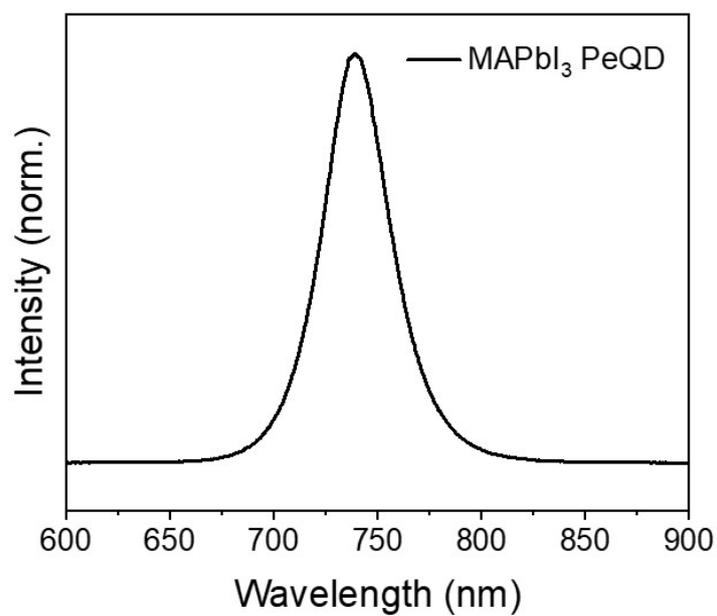
Fig. S3 PL spectra of pristine MAPbI$_3$ PeQD film.
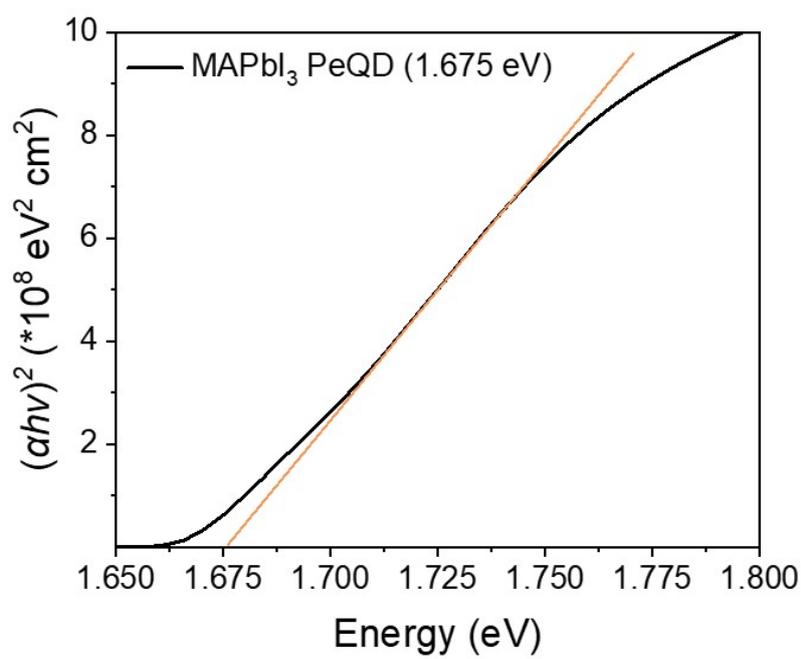
Fig. S4 Tauc plot of pristine MAPbI$_3$ PeQD film.
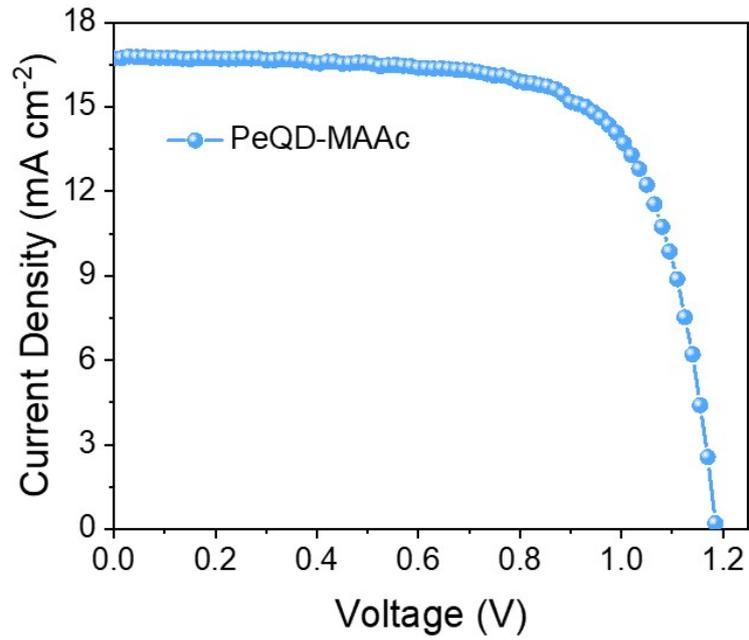
Fig. S5 *J-V* curve of MAAc-treated MAPbI$_3$ PeQD solar cell
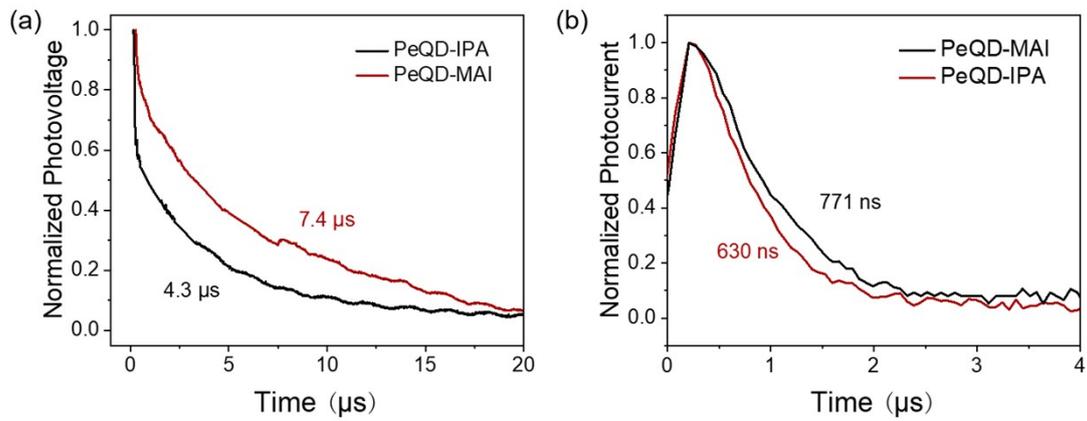
Fig. S6 (a) TPV and (b) TPC spectra of the IPA- and MAI-treated PeQD devices.
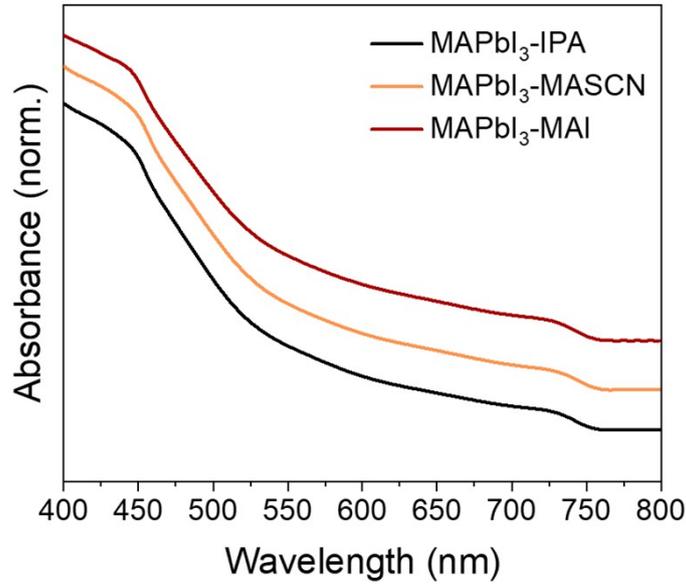
Fig. S7 Absorption spectra of IPA-, MASCN- and MAI-treated MAPbI$_3$ PeQD films.
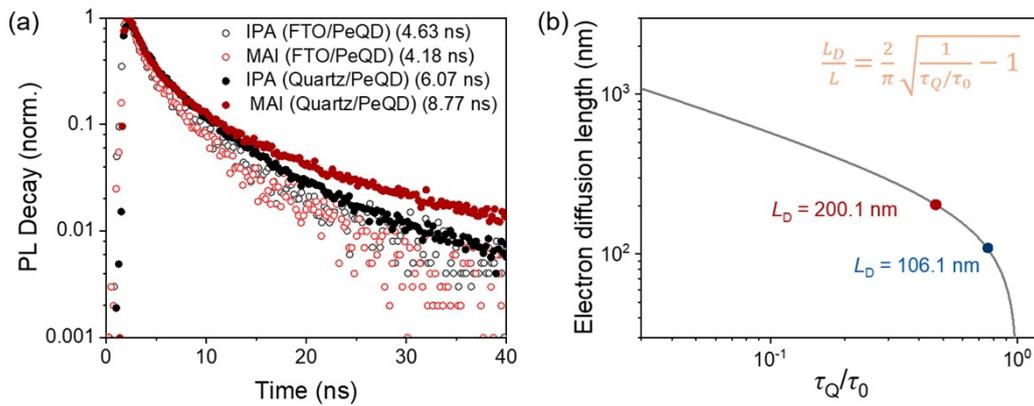
Fig. S8 (a) TRPL of IPA- and MAI-treated PeQD film on FTO and Quartz substrate; (b) Calculated carrier diffusion length of IPA- and MAI-treated PeQD films using the

equation: $\dfrac{L_D}{L} = \dfrac{2}{\pi}\sqrt{\dfrac{1}{\tau_Q/\tau_0} - 1}$, where L is the thickness of PeQD film, τ_Q is the

quenching lifetime, τ_0 is the intrinsic lifetime.
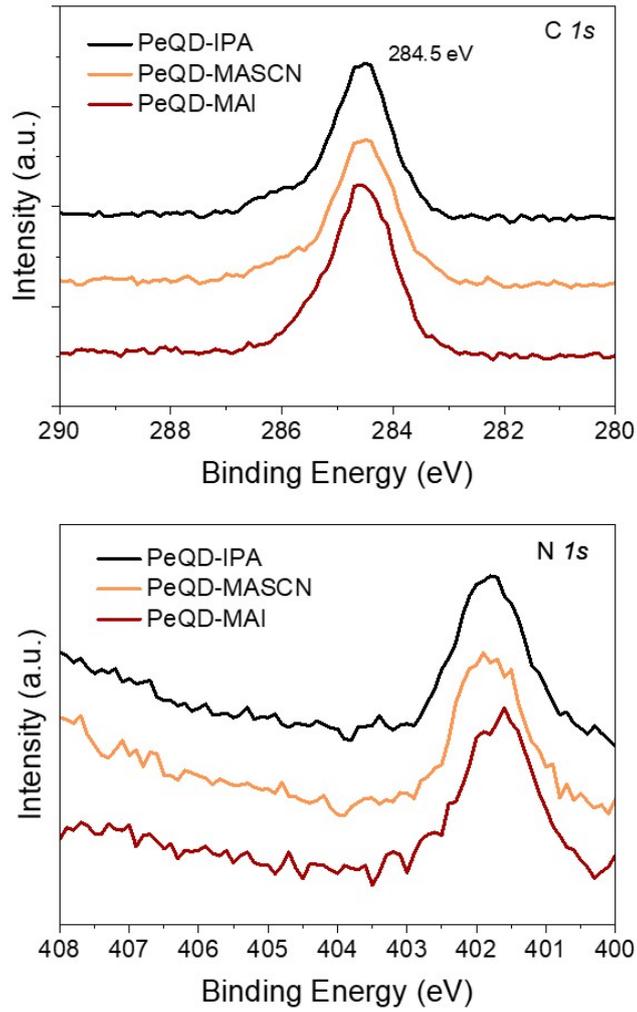
Fig. S9 XPS of C 1*s* and N 1*s* core-level spectra of IPA-, MASCN- and MAI-treated MAPbI$_3$ PeQD films.
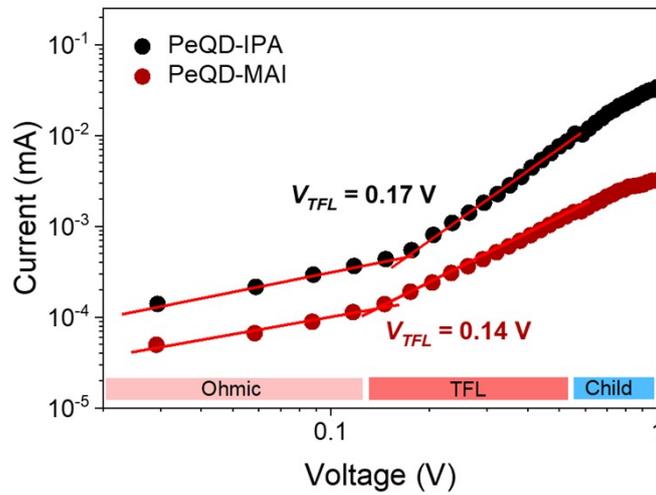
Fig. S10 SCLC curve of the IPA- and MAI-treated devices using the equation:

$$n_e = \frac{2\varepsilon_0 \varepsilon V_{TFL}}{eL^2}$$

, where e is the elementary charge, ε, ε_0 and L are the dielectric constant of bulk film, the vacuum permittivity and the thickness of the $MAPbI_3$ PeQD films, respectively.
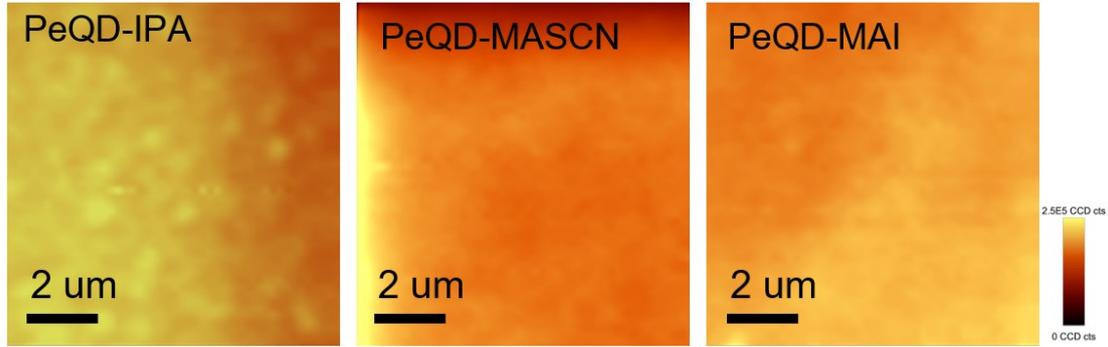
Fig. S11 PL mapping images of IPA-, MASCN- and MAI-treated $MAPbI_3$ PeQD films on quartz substrate

Table S1 The detailed *J-V* parameters of $MAPbI_3$ PeQD solar cells treated by IPA and MA-salts.

Condition	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE (%)
IPA	1.16	16.04	0.70	13.07
MAAc	1.18	16.75	0.70	13.91
MASCN	1.19	16.80	0.72	14.39
MAI	1.20	17.10	0.73	14.98

Table S2 Device efficiency progress of PeQD solar cell.

Composition	Method	V_{OC}	J_{SC}	FF	PCE	*Ref*
$MAPbI_3$	Synthesis engineering	1.02	16.42	0.56	9.30	[1]
$MAPbI_3$	Synthesis engineering	1.20	15.46	0.72	13.34	[2]
$MAPbI_3$	**A-site salts (MAI) post-treatment**	**1.20**	**17.10**	**0.73**	**14.98**	**This work**
$FAPbI_3$	Solvent engineering	1.10	11.83	0.64	8.38	[3]
$FAPbI_3$	A-site salts (FASCN) post-treatment	1.15	18.45	0.68	14.47	[4]
$FAPbI_3$	Solution phase ligand engineering	1.16	20.95	0.67	16.29	[5]
$MA_{1-x}FA_xPbI_3$	A-site salts (MAI) solution phase treatment and	1.14	17.30	0.76	15.10	[6]

	post-treatment					
MA$_{1-x}$FA$_x$PbI$_3$	A-site salts (FAI) post-treatment	1.19	16.42	0.77	15.05	[7]
MA$_{1-x}$FA$_x$PbI$_3$	A-site salts (MASCN) post-treatment	1.17	19.30	0.72	16.23	[8]
MA$_{1-x}$FA$_x$PbI$_3$	A-site salts (MAI) post-treatment	1.16	20.08	0.79	18.94	[9]

Table S3 The detailed fitting parameters of decay lifetime in TRPL measurement.

Condition	A$_1$	τ_1 (ns)	A$_2$	τ_2 (ns)	A$_3$	τ_3 (ns)	τ_{ave} (ns)
IPA	0.49	1.04	0.48	3.64	0.12	11.17	6.07
MASCN	0.65	0.99	0.45	4.17	0.12	14.50	7.91
MAI	0.75	1.01	0.46	4.13	0.11	16.75	8.77

a. The TRPL data was fitted by the equation: $y=A_1e^{-t/\tau_1}+A_2e^{-t/\tau_2}+A_3e^{-t/\tau_3}$.

b. The average lifetime τ_{ave} was calculated by the equation:
$$\tau_{ave} = \frac{A_1\tau_1{}^2 + A_2\tau_2{}^2 + A_3\tau_3{}^2}{A_1\tau_1 + A_2\tau_2 + A_3\tau_3}$$

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