Supporting Information

Suppressing Surface and Interface Recombination to Afford Efficient and Stable Inverted Perovskite Solar Cells

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Materials and Methods

Materials

Dimethyl sulfoxide (DMSO, 99.9%), N, N-dimethyl formamide (DMF, 99.8%), isopropanol (IPA, 99.5%), ethanol (EtOH, 99.5%), chlorobenzene (CB, 99.8%), toluene (Tl, 99.8%), and anisole (AS, 99.7%) were supplied by Millipore Sigma. Methylammonium iodide (MAI) and Formamidinium iodide (FAI) were supplied from Great cell Solar Materials. [2-(9H-Carbazol-9-yl)ethyl]phosphonic acid (2PACz), lead iodide (PbI$_2$, 99.99%), lead bromide (PbBr$_2$, 99.99%), and lead chloride (PbCl$_2$, 99.99%) were supplied by TCI America™. Methylammonium chloride (MACl), CsI (99.99%), C$_{60}$ fullerene, bathocuproine (BCP), PMAI, and PDMAI$_2$ were supplied by Xi'an Polymer Light Technology. All the used precursors and solvents were used as received without any further purification.

Device Fabrication

Fluorine-doped tin oxide (FTO) glass substrates were sequentially cleaned using detergent, deionized water (DIW), acetone (ACE), and isopropanol each for 15 min in an ultrasonic bath, followed by ozone treatment for 30 min. A 0.5 mg/mL 2PACz in EtOH solution was spin-coated on FTO at 4,000 r.p.m. for 30s, followed by 10 min of thermal annealing at 100℃. The perovskite layer with around 600nm of thickness was deposited in the N$_2$ inert environment with H$_2$O and O$_2$ concentrations less than 1 ppm.

A 5 mol% MAPbCl$_3$ with a concentration of 1.6 M MAPbCl$_3$ was introduced to Cs$_{0.05}$MA$_{0.05}$FA$_{0.90}$PbI$_3$ perovskite precursors in a mixed DMF and DMSO solvent system (4:1 v/v). The colloidal solution was filtered using a 0.22 μm polytetrafluoroethylene (PTFE) filter and spin-coated at 1000 r.p.m for 10 s (acceleration 200 r.p.m./s) and 5000 r.p.m. for 30 s (acceleration 2000 r.p.m./s), respectively. At the 20th s of the second step, 300 μL antisolvent (anisole) was dropped. The films were then annealed for 15 min at 100°C. For the surface treatment, 100 μL 3 mM PMAI or PDMAI$_2$ in IPA/CB (1:1 v/v) solution was coated on the perovskite films by dynamic spinning at 4500 r.p.m for 25 s, followed by further annealing at 100°C for 5 min. For the electron transport layer (ETL), 30 nm C$_{60}$ was evaporated on the perovskite films under a vacuum of ~10^{-6} Torr, followed by 7 nm BCP thermal evaporation as an HTL. In the last, 200 nm silver (Ag) electrode was evaporated under a vacuum of ~10^{-6} Torr.

Characterizations

SEM images were taken with a JEOL JSM-7900FLV microscope to analyse the film morphology and device structure. XRD spectra of the surface-treated perovskite films were measured with a Rigaku Smart Lab SE X-ray diffractometer. The *J-V* curves of the prepared devices were measured with a Keithley 2420

source meter under a simulated AM 1.5G spectrum and a solar simulator (XES-300T1, SAN-EI Electric), which was calibrated using a standard silicon reference cell. The J-V curves of all PSCs were measured by covering the active area with a metal mask of 0.09 cm^2 with a voltage step of 20 mV and a scanning rate of 70 mV/s. EQE was recorded by an Enli Technology IPCE measurement system with a dual xenon/quartz halogen light source. Time-resolved photoluminescence (TRPL) and confocal PL mapping were recorded with a laser confocal Raman spectrometer (Princeton Instruments, Acton Standard Series SP-2558) and a 405 nm laser (OBIS LX-405) using a home-built confocal microscope. X-ray photoelectron spectroscopy (XPS) was recorded on Thermo Scientific ESCALAB 250Xi with an X-ray spot size of 500 μm. The luminescence quantum yield was measured by a LuQY Pro System (Quantum Yield Berlin) with an excitation wavelength of 532 nm (100 mW). The operational stability test was conducted by putting the encapsulated devices in the air with a relative humidity of ~50% under 1-sun illumination at 65˚C which was continuously monitored by an IR thermometer. The device performance was evaluated periodically.

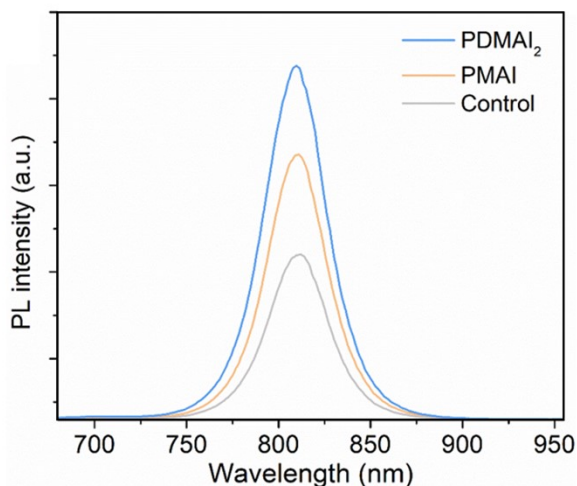**Fig. S1.** Steady-state photoluminescence of the perovskite films with different surface passivation.
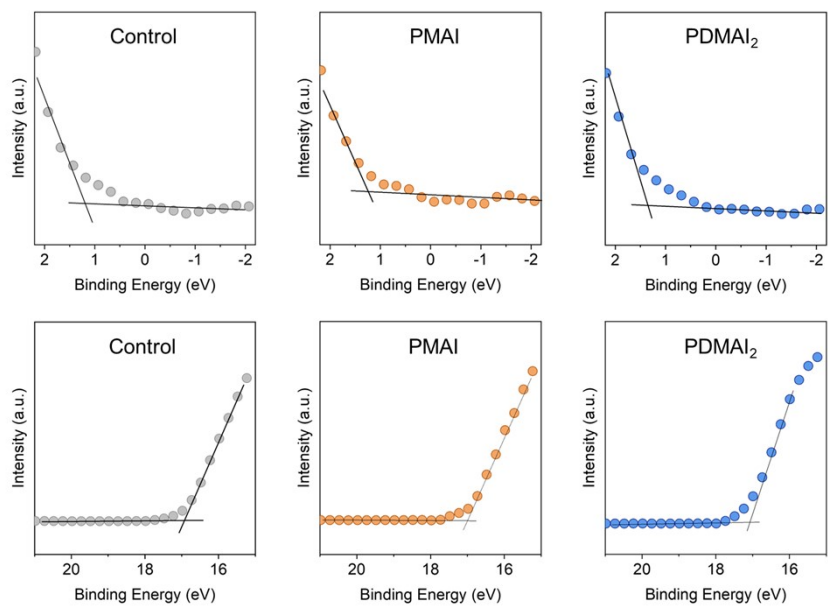
Fig. S2. UPS spectra the control, PMAI-treated, and PDMAI2-treated perovskite films.
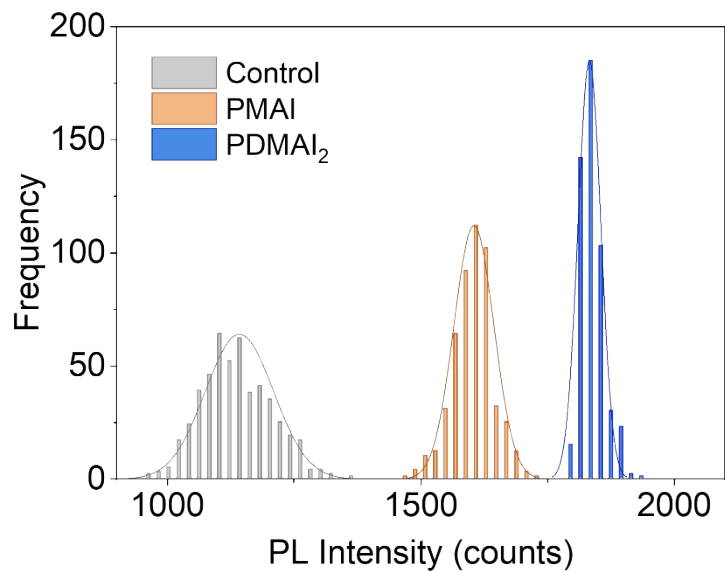

Fig. S3. Statistical distribution of PL intensity counts against the number of tested control, PMAI, and PDMAI$_2$-treated perovskite.
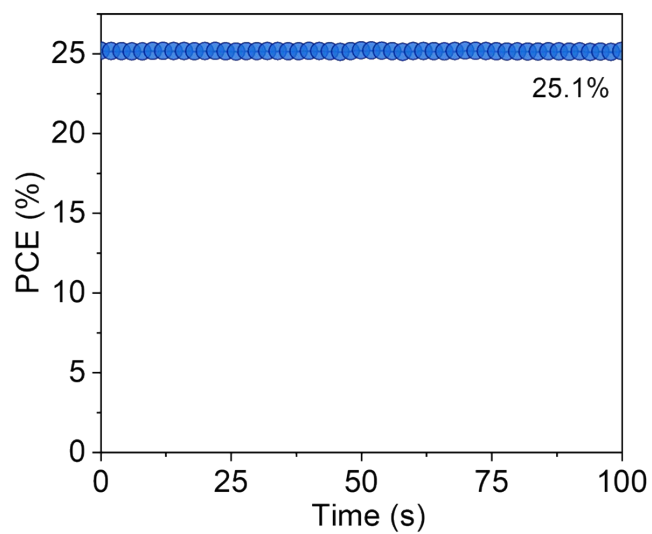
Fig. S4. Stabilized PCE curve of the best-performing device based on PDMAI$_2$ surface treatment.
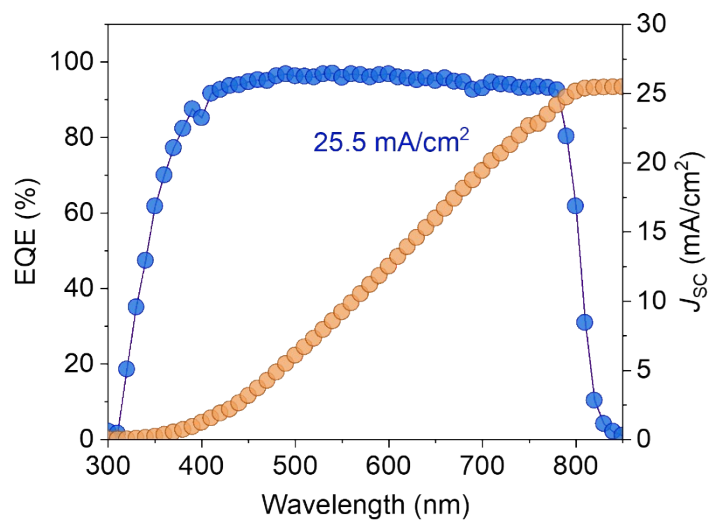

Fig. S5. External Quantum Efficiency (EQE) with integrated short-circuit current density (J_{sc}) of the PDMAI-treated perovskite solar cell.
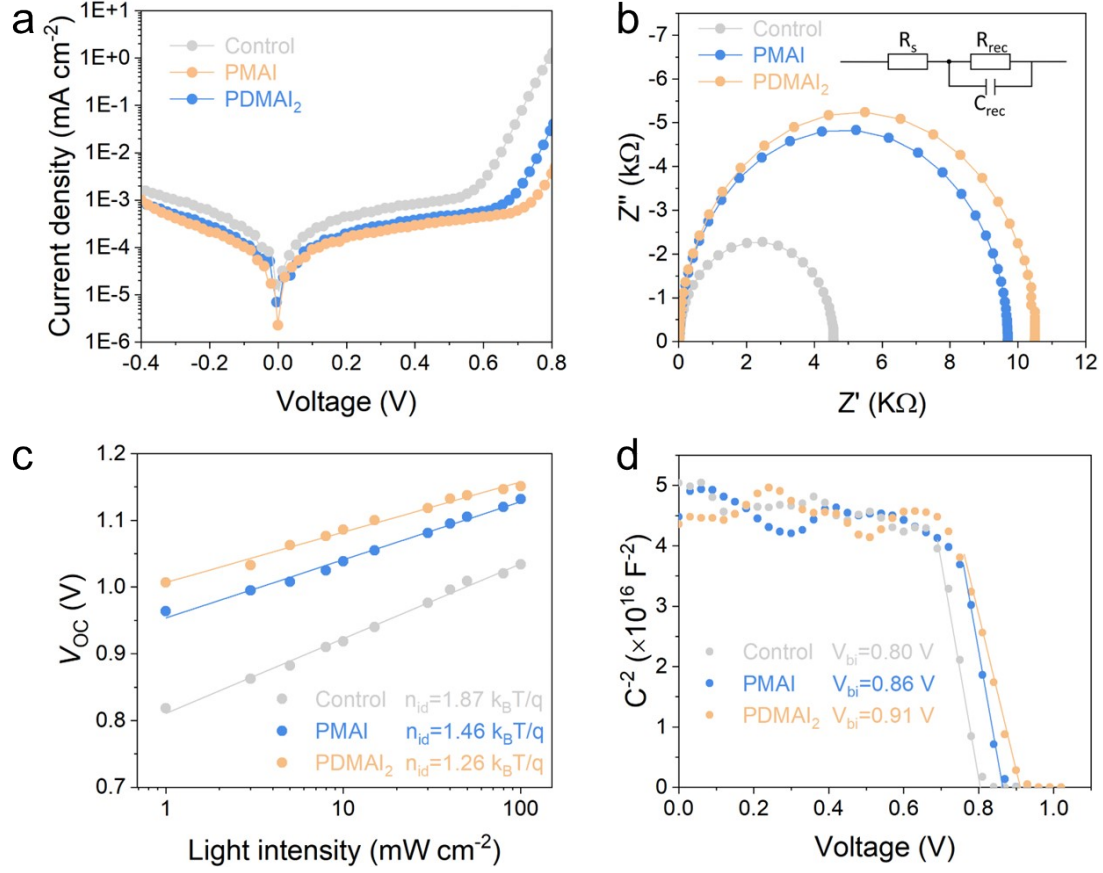
Fig. S6. (a) *J-V* scanning curves of devices under dark conditions. (b) Nyquist plots of the EIS test, (c) V_{oc} dependency on the light intensity, and (d) Mott–Schottky plots of the prepared PSCs.

Table S1. Time-resolved photoluminescence (TRPL) acquired recombination constants and their respective counts of the treated and non-treated samples.

Samples	τ_1 (ns)	A_1 (counts)	τ_2 (ns)	A_2 (counts)	τ_{avg} (ns)
Control	4	2454	1007	215	960
PMAI	4	2802	1452	414	1427
PDMAI$_2$	4	3097	1547	342	1516

Table S2. Space charge-limited measured trap-filled-limited voltage (V_{TFL}) and Equation S1 driven trap-state density (N_t) of the electron-only perovskite device with different surface passivation.

Samples	V_{TFL} (V)	N_t (cm^{-3})

Control	0.79	1.21×10^{15}
PMAI	0.62	0.95×10^{15}
PDMAI$_2$	0.49	0.75×10^{15}

Table S3. Performance parameters with a standard deviation of measured devices based on different surface passivated perovskite.

Samples	V_{oc} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
Control	1.10 ± 0.03	25.8 ± 0.2	79.2 ± 1.4	22.5 ± 1.2
PMAI	1.13 ± 0.03	26.0 ± 0.2	81.6 ± 1.4	24.0 ± 0.9
PDMAI$_2$	1.15 ± 0.03	26.0 ± 0.1	82.3 ± 1.3	24.5 ± 0.8

Trap-State Density (N_t)

$$N_t = 2\varepsilon_0\varepsilon_r V_{TFL}/qL^2 \qquad \textbf{(Equation S1)}$$

Here, ε_0 is the vacuum permittivity, ε_r is the perovskite dielectric constant, V_{TFL} is trap-filled-limited voltage, q is the elementary charge, and L is the active layer thickness.

Ideal Factor (n$_{id}$)

According to the following equation, the V_{OC} ought to possess a linear correlation with the logarithm of light intensity.

$$\frac{dV_{OC}}{d_{\lg I}} = 2.303 \cdot \frac{n_{id}k_B T}{q} \qquad \textbf{(Equation S1)}$$

where k_B is the Boltzmann constant, n_{id} is the ideality factor, T is the thermodynamic temperature, and q is the elementary charge.

Table S4. EIS result of the tested devices after fitting.

	Control	PMAI	PDMAI$_2$
R$_s$ (Ω)	27.11	25.03	22.76
R$_{rec}$ (Ω)	4548	9679	10481