ADVANCED ENERGY MATERIALS

Supporting Information

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Indigo: A Natural Molecular Passivator for Efficient Perovskite Solar Cells

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Materials

All the materials were mentioned is purchased from Greater solar, Alfa Aesar, or Xi'an Polymer Light Technology Corp. In detail, lead iodide (PbI2, 99.999%) from Advanced Election Technology Co., Ltd, lead bromide ($PbBr_2$, 99.99%) and cesium iodide (CsI, 99.99%) from Alfa Aesar and FAI and methylammonium bromide (MABr, 99.99%) from Great solar, Spiro-OMeTAD [2,2',7,7'-tetrakis-(N,N-dipmethoxyphenylamine)-9,9'-spiro-bifluorene] from Xi'an Polymer Light Technology Corp. Solvents used for perovskite solar cell include anhydrous N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) from Alfa Aesar, the chlorobenzene used for antisolvent process were purchase from Sigma-Aldrich. ITO and FTO substrate were obtained from Advanced Election Technology Co., Ltd. All other chemicals were used as received without any further purification. More specifically, the 1 mL precursor (DMF:DMSO=4:1) contains 1.2 M perovskite and the perovskite thin film were made by the composition of mixed halides $Cs_{0.05}FA_{0.85}MA_{0.10}Pb(I_{0.90}Br_{0.10})_3$.

Characterization

Top-view and cross-section SEM images were obtained by a Zeiss Supra 55 field in high vacuum mode at 15 kV accelerating voltage. AFM images (tapping mode) were captured through an Asylum Research Cypher S AFM microscope. UV-Vis spectra were recorded on a PerkinElmer model Lambda 750. The steady-state and time-resolved PL spectra were recorded with a FluoroMax-4

spectrofluorometer excited at 460nm(HORIBA Scientific). GIWAXS measurements were performed at the Shanghai Synchrotron Radiation Facility Laboratory on Beamline BL14B1 using X-rays with a wavelength of λ= ~1.24 Å. The XPS spectra were obtained using a Kratos AXIS Ultra DLD ultrahigh vacuum photoemission spectroscopy system, with an Al Ka radiation source. And the FTO/c-TiO_2/ $Cs_{0.05}FA_{0.85}MA_{0.10}Pb(I_{0.90}Br_{0.10})_3$ perovskite/ Spiro-OMeTAD/MoO_3/Ag structure was adopted to fulfill this measurement EIS measurements carried out through Zahner IM6 electrochemical workstation while applying a bias of under open-circuit with a frequency between 1 MHz and 100 Hz under a monochromatic LED (500 nm, 100 mW/cm^2) light irradiation.

The computational method of first-principles calculations based on density functional theory (DFT)

The projector-augmented wave method (PAW) was employed to represent the ionic cores and the following electronic states were considered as valence: Pb 6p and 5d; I 4d 5s and 5p; C 2s and 2P; O 2s and 2p; H 1s; N 2s and 2p. A 1×1×1 Gamma k-point grid was employed for the slab calculations due to the large computational cost involved. The geometry optimizations were halted when the forces in the atoms were all below 0.05 eV/Å. The binding energy associated with Indigo docking on $FAPbI_3$ ($E_{binding}$) was calculated with the formula:

$$E_{binding} = E_{indigo@FAPb_{1-x}I_3} - E_{indigo} - E_{FAPb_{1-x}I_3slab}$$

where $E_{indigo@FAPb_{1-x}I_3}$, E_{indigo} and $E_{FAPb_{1-x}I_3slab}$ stand for the ground-state energy of the defective/non-defective indigo@$FAPbI_3$ system, Indigo molecular and defective/non-defective $FAPbI_3$ slab.

The charge density difference distribution is defined as:

$$\Delta\rho = \rho_{indigo@FAPb_{1-x}I_3} - \rho_{indigo} - \rho_{FAPb_{1-x}I_3slab}$$

where $\rho_{indigo@FAPb_{1-x}I_3}$ is the total charge density of the defective/non-defective indigo@FAPbI3 slab system, and $\rho_{FAPb_{1-x}I_3}$ and ρ_{indigo} are the charge densities of the defective/non-defective $FAPbI_3$ slab and Indigo molecule by separate.

The calculation of TRPL fitting:

The test results of TRPL were fitted by a biexponential function as follows:

$$f(t) = A_1 e^{(-\frac{t}{\tau_1})} + A_2 e^{(-\frac{t}{\tau_2})} + A_0$$

where A_0 is a constant, t is the time, A_1 and A_2 are the decay amplitudes, τ_1 and τ_2 is the decay times, and the average PL lifetime (τ_{ave}) can be obtained by the equation as follows:

$$\tau_{ave} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}$$

The hysteresis index calculation

The hysteresis index of target and control device were calculated by a function as follows:

$$H = \frac{PCE_{reverse} - PCE_{forward}}{PCE_{reverse}}$$

SCLC measurements

A structure of Glass/FTO/PEDOT:PSS (ca. 30 nm)/perovskite (ca. 400 nm)/Spiro-OMeTAD (ca. 80 nm)/Ag (ca. 80 nm) was applied. The trap-state density (N_{trap}) of the QD film can be calculated by the equation:

$$N_{trap} = \frac{2\varepsilon_0\varepsilon_r V_{TFL}}{qL^2}$$

where ε_0 is the vacuum dielectric constant, ε_r is the relative dielectric constant of perovskite about 25, V_{TFL} represents the trap-filled limit voltage, q is the elemental charge and L is the distance between the electrodes.

tDOS measurements

The energetic profile of trap density of states (tDOS) can be derived from the angular frequency dependent capacitance using the equation:

$$N_T(E_\omega) = -\frac{V_{bi}}{qW}\frac{dC}{d\omega}\frac{\omega}{k_B T}$$

where C is the capacitance, ω is the angular frequency, q is the elementary charge, k_B is the Boltzmann's constant and T is the temperature. V_{bi} and W are the built-in potential and depletion width, respectively, which were extracted from the Mott–Schottky analysis. The applied angular frequency ω defines anenergetic demarcation, where ω_0 is the attempt-to-escape frequency.

$$E_\omega = k_B T ln\frac{\omega_0}{\omega}$$

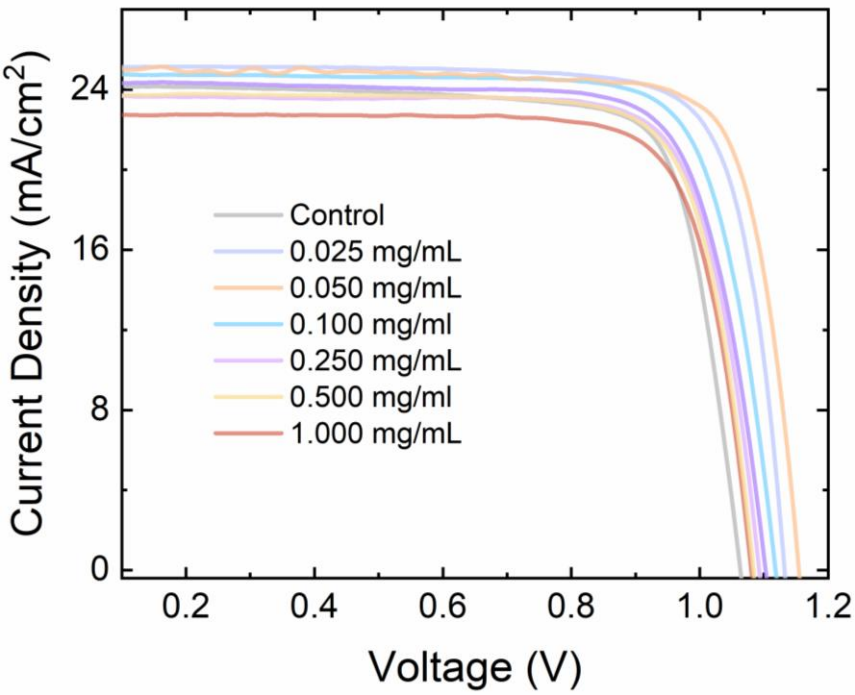

Figure S1. The *J-V* curves of devices at different indigo concentrations

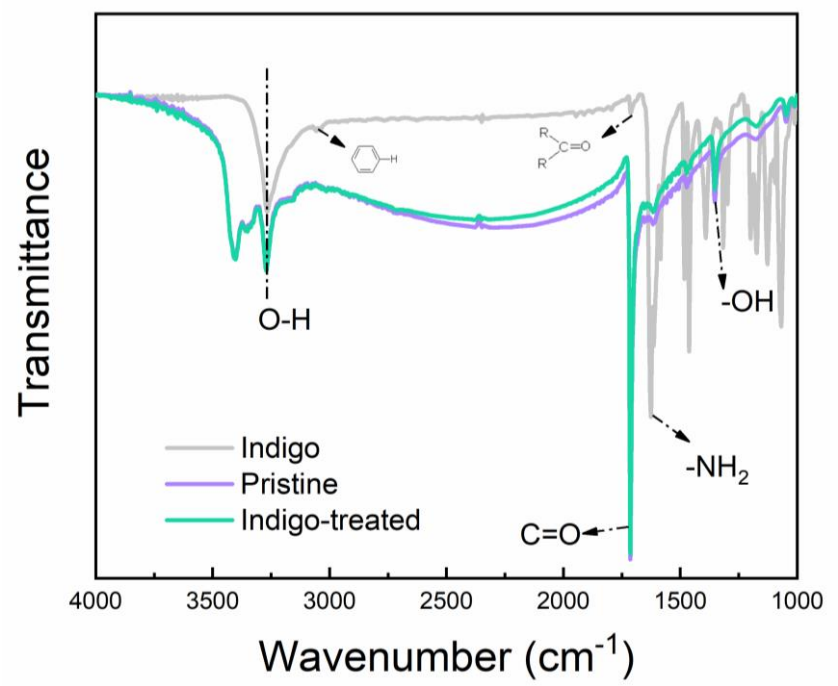

Figure S2. The FTIR spectra of Indigo, pristine, and Indigo-treated perovskites.

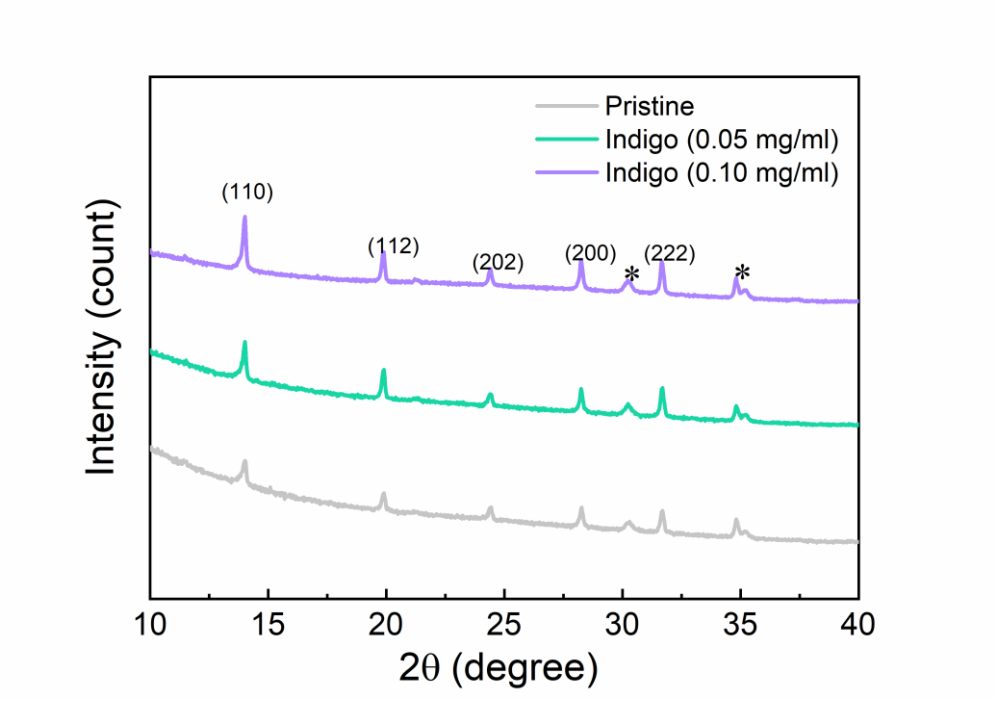

Figure S3. The XRD patterns and of the pristine and different concentration Indigo-treated perovskite thin films.

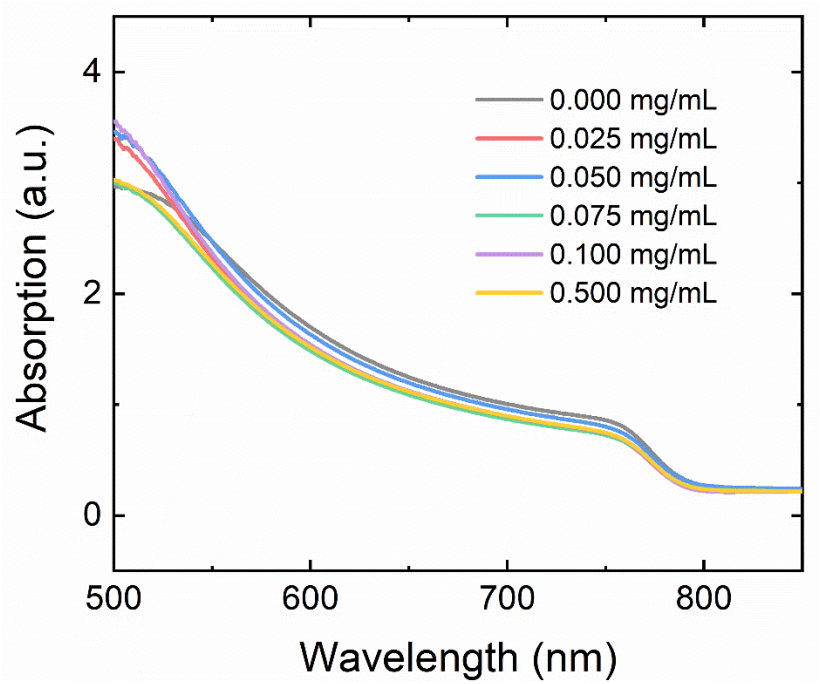

Figure S4. The Absorption of difference concentration Indigo-treated perovskite thin film.

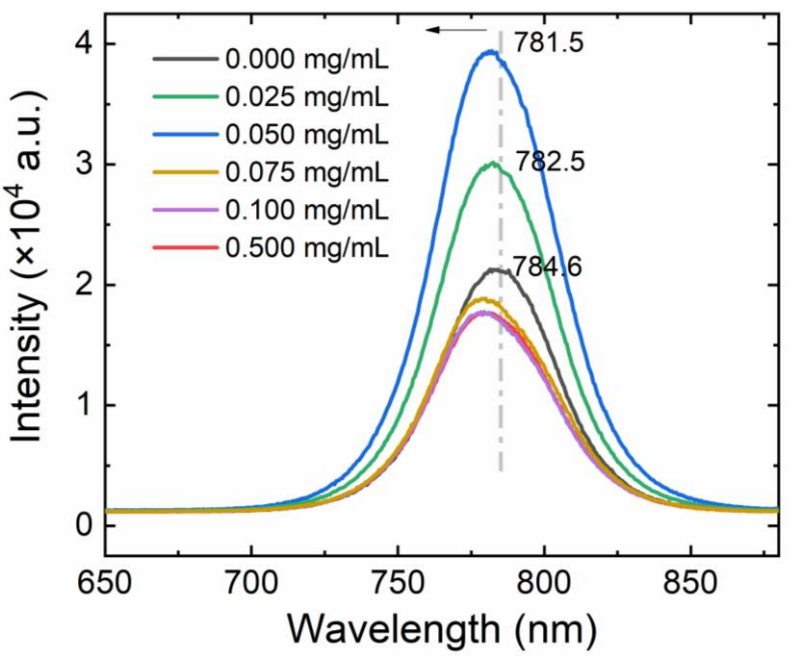

Figure S5. The Intensity of difference concentration Indigo-treated perovskite thin film.

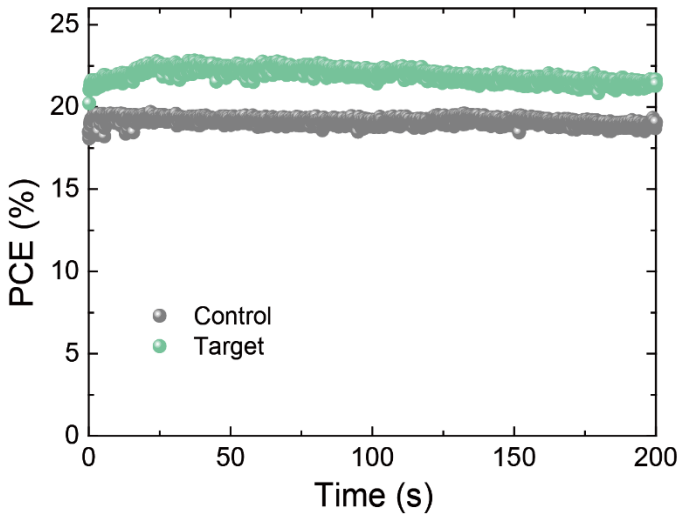

Figure S6. stabilized power output of the champion Indigo-treated PSCs under maximum power point (MPP) tracking for 200 s.

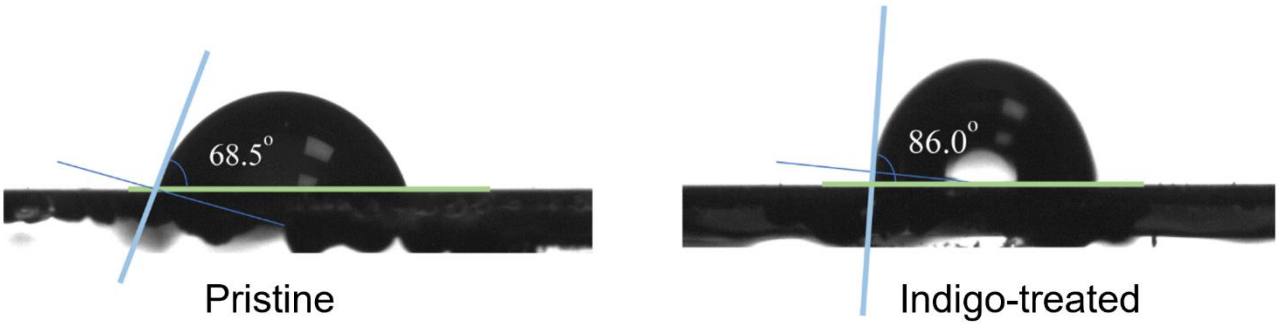

Figure S7. The contact angle of water drop on control and the Indigo-treated film.

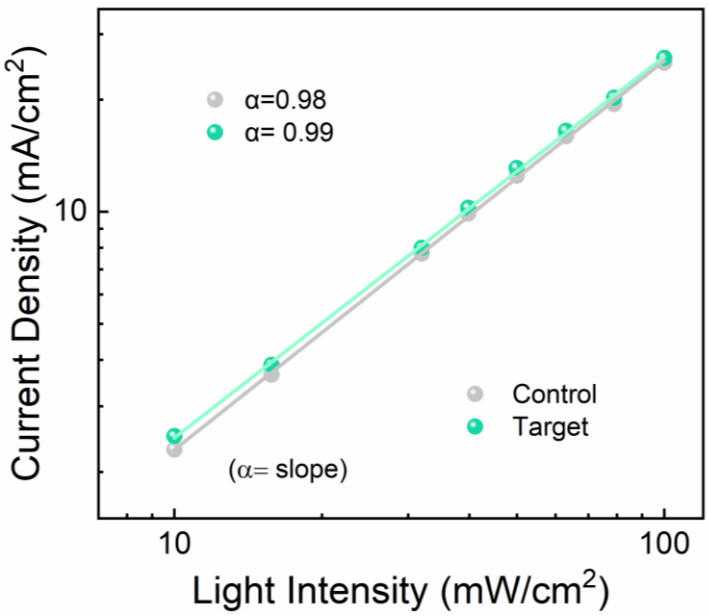

Figure S8. The relationship of J_{sc} with respect to light intensity for the control and target perovskite device.

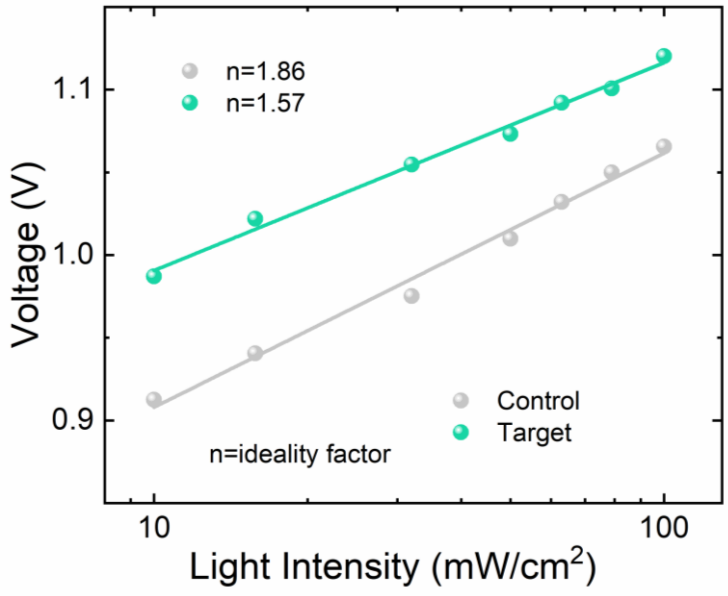

Figure S9. The light intensity dependence of V_{oc} of the mixed perovskite devices.

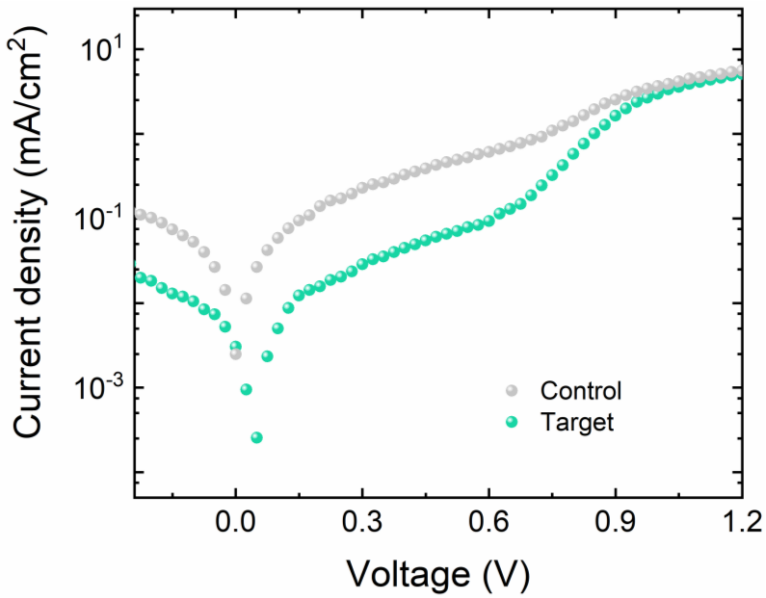

Figure S10. The dark-current pattern of the pristine and Indigo-treated perovskite thin films.

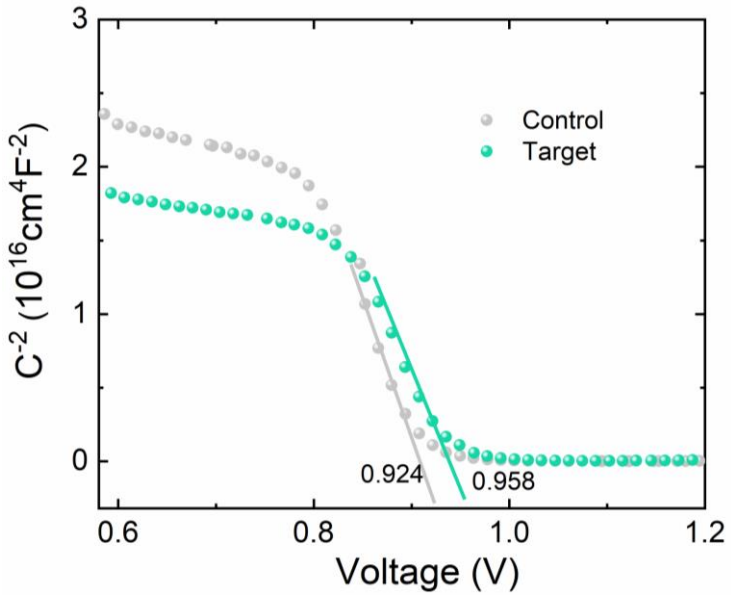

Figure S11. The Voltage dependence of capacitance of the mixed perovskite devices.

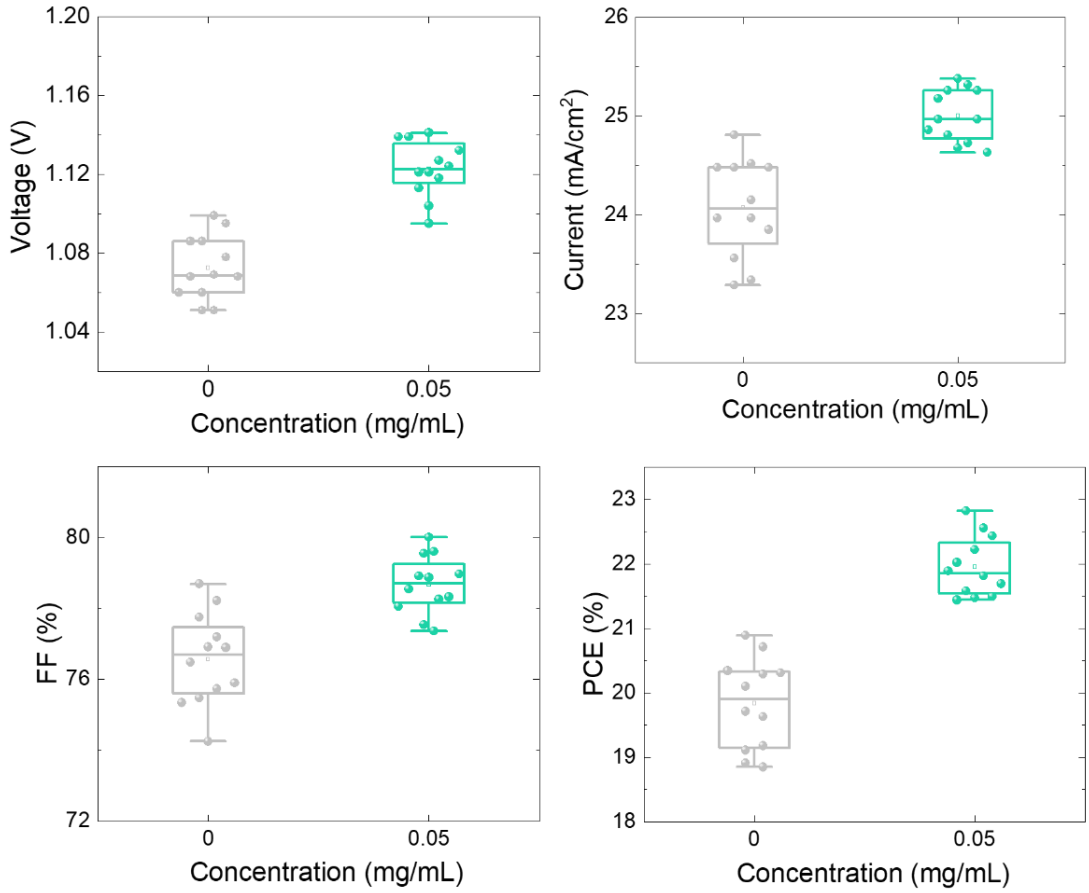

Figure S12. The statistical distribution of J_{sc}, V_{oc}, FF, and PCE for the devices. Statistics from 12 devices for each sample.

Table S1. PV device parameters of the PSCs with different concentrations of Indigo measured under the reverse scan.

Indigo (mg/mL)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)
0.000	1.07	24.15	0.78	20.18
0.025	1.14	24.73	0.79	21.44
0.050	1.16	25.02	0.80	23.22
0.100	1.10	24.30	0.78	20.85
0.250	1.10	23.70	0.79	20.54

0.500	1.09	23.73	0.79	20.43
1.000	1.08	23.34	0.77	19.41

Table S2. Fitting parameters of decay amplitude and decay time obtained from TRPL spectra.

	A_1	τ_1 (ns)	A_2	τ_2 (ns)	τ_{avg} (ns)
Pristine	586.55	2.99	108.94	315.27	300.01
Indigo (0.05 mg/mL)	475.24	4.51	111.59	473.24	454.94

Table S3. The PV device parameters of the PSCs without and with Indigo-treated on the 1×1 cm^2 large-scale area device.

Condition	V_{oc}（V）	J_{sc}（mA/cm^2）	FF	PCE (%)
Control	1.06	23.90	0.72	18.24
Target	1.14	24.50	0.75	20.95

Table S4. EIS parameters of devices based on pristine and Indigo-treated perovskite.

	R_{tr} (Ohm)	R_{rec} (Ohm)	C_{rec} (F)
Control	32.95	116.5	7.41×10^{-9}
Target	30.39	267.2	5.71×10^{-9}

Table S5. The summarized PCE of organic dyes as passivator in perovskite film

Perovskite component	**Organic dye**	**PCE (%)**	**Reference**
$(Cs_{0.15}FA_{0.85})Pb(I_{0.95}Br_{0.05})_3$	Coumarin 343	20.9%	Nano Energy, 2022, 94,106935
$(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$	AQ310 (-COOH)	19.43%	Adv. Energy Mater, 2018, 8,1800715
$MAPbI_3$	Cyanine dye	19.14%	J. Am. Chem. Soc, 2021, 4, 9525
$MAPbI_3$	Quinacridone (QA).	21.06%	Angew. Chem. Int. Ed, 2021, 60, 2485
CsFAMAPbIBr	Merocyanine	22.04%	ACS Energy Lett. 2021, 6, 869
$MAPbI_3$&silicon	N719	26.20%	Adv. Energy Mater, 2021,11,2101662
$CsPbI_{1.5}Br_{1.5}$	FITC	14.05%	Adv. Energy Mater, 2021,11,2003585
$(Cs_{0.05}FA_{0.90}MA_{0.05})Pb(I_{0.90}Br_{0.1})_3$	Indigo	23.2%	This work