

Supporting Information

Enhanced Stability and Photovoltage for Inverted Perovskite Solar Cells via Precursor Engineering

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Experimental Section

Patterned ITO glass with a sheet resistance of $15 \Omega \text{ sq}^{-1}$ was purchased from Ying Kou You Xuan Trade Co. Ltd. PbI_2 (99.9985%) was obtained from Alfa Aesar. TAPC (97%), CsI, PTAA (Mn=3200, Mw=4900), MAI, MABr, FAI, PbBr_2 (99%), PbCl_2 (99%), C_{60} (99%), and BCP (>99%) were purchased from Xi'an Polymer Light Technology Corp. DMF (99.8%), DMSO ($\geq 99.9\%$), and chlorobenzene (99.8%) were purchased from Sigma Aldrich.

Perovskite precursor preparation: FAPbI_3 (A) precursor was prepared by mixing 1M FAI and 1.05M PbI_2 in 1 mL DMF/DMSO (v/v, 4:1). MAPbBr_3 (B) precursor was prepared by mixing 1M MABr and 1M PbBr_2 in 1 mL DMF/DMSO (v/v, 4:1). $\text{MAPbI}_{3-x}\text{Cl}_x$ (C) precursor was prepared by mixing 1.2M MAI, 1.1M PbI_2 , and 0.12M PbCl_2 in 1 mL DMF/DMSO (v/v, 4:1). Then 0.83 mL A and 0.17 mL B was mixed to form the control precursor $\text{A}_{0.83}\text{B}_{0.17}$. For the alloyed perovskite precursors, certain amount of C (0 μL , 93 μL , 147 μL , or 208 μL) was added to the control precursor to form the alloyed precursor $(\text{A}_{0.83}\text{B}_{0.17})_{1-y}\text{C}_y$ with $y = 0, 0.1, 0.15, \text{ or } 0.2$, respectively. For the $\text{Cs}_{0.05}(\text{A}_{0.83}\text{B}_{0.17})_{0.95}$ precursor, 1M FAI, 1.05M PbI_2 , 0.2M MABr, and 0.2M PbBr_2 were dissolved in 1 mL DMF/DMSO (v/v, 4:1), then 5% vol CsI (1.5M stock solution in DMSO) was added to the mixed precursor as described elsewhere.¹

Device fabrication: Patterned ITO-coated glass substrates were cleaned ultrasonically with detergent, deionized water, acetone, and isopropanol in sequence for 20min each. After UV-ozone cleaning for 30min, ITO glass was moved into N_2 -purged glovebox. TAPC+PTAA HTL were deposited on the ITO substrate, as reported previously.² The alloyed precursor $(\text{A}_{0.83}\text{B}_{0.17})_{1-y}\text{C}_y$ was spin coated onto the TAPC-coated ITO substrates at 1000 rpm for 10s and 5000 rpm for 30s, and

100 μL of chlorobenzene were rapidly dropped on the substrates after 15 s of the spin coating. Then the samples were annealed at 100 $^{\circ}\text{C}$ for 1h. Finally, C_{60} (30 nm), BCP (8 nm), and Ag (100 nm) were sequentially deposited onto the perovskite layer by thermal evaporation through a shadow mask with an active area of 0.10 cm^2 .

Characterization: The morphologies of perovskite and HTLs films were characterized by scanning electron microscopy (SEM, TESCAN MIRA3) at a 5kV accelerating voltage. Atomic force microscope (AFM) images of HTLs films were collected on a multimode SPM (Bruker) with tapping mode. UPS analysis was conducted to measure the energy level of HTLs with an unfiltered He I (21.22 eV) gas discharge lamp and a hemispherical analyzer. Steady-state and time-resolved PL spectra were measured using an Edinburgh FLS920 spectroscopy system, using pulsed laser excitation at 405 nm. The time-resolved PL measurements were carried out by a Deltaflex TCSPC system (Horiba) at 950 nm with a 479 nm laser. Electrochemical impedance spectroscopy (EIS) measurements were performed on an electrochemical workstation (Zahner). Photocurrent density-voltage (J - V) curves were measured under AM 1.5 G one sun illumination (100 mW/cm^2) with a solar simulator (Enlitech SS-F7-3A) equipped with a 300 W Xenon lamp and a Keithley 2400 source meter. The light intensity was adjusted by an NREL-calibrated Si solar cell. During measurement, the cell was covered by a mask with an aperture of 0.1 cm^2 .

Table S1. Typical method of precursor engineering toward increased V_{oc} .

Year	Method	Perovskite	Device type	V_{oc} increment	Ref.
2014	MAI doping	FAPbI_3	Regular	From 0.93V to 1.03V	3
2015	MACl doping	MAPbI_3	Regular	From 0.93V to 1.08V	4
2016	$\text{Pb}(\text{SCN})_2$ doping	MAPbI_3	Regular	From 1.09V to 1.11V	5
2017	$\text{Cu}(\text{Tu})\text{I}$ doping	$\text{MAPbI}_{3-x}\text{Cl}_x$	Inverted	From 1.00V to 1.11V	6
2018	F4TCNQ doping	$\text{MAPbI}_{3-x}\text{Cl}_x$	Inverted	From 1.00V to 1.10V	7
2019	Solvent replacement for DMF	MAPbI_3	Inverted	From 1.00V to 1.06V	8

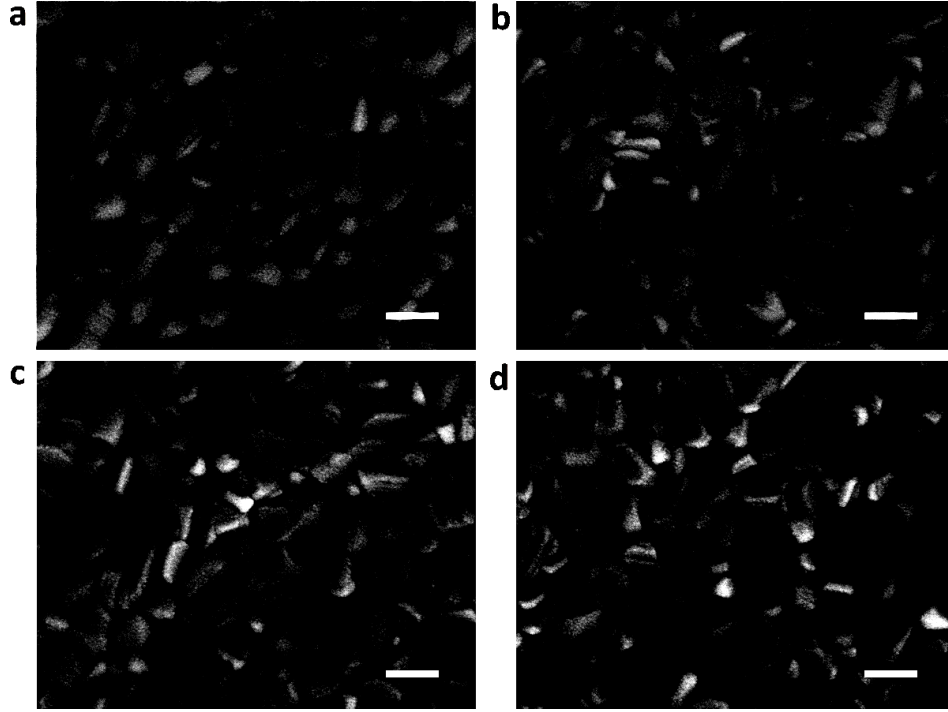


Figure S1. High contrast SEM images of Figure 1. (a) $y = 0$, (b) $y = 0.1$, (c) $y = 0.15$, and (d) $y = 0.2$. Scale bar, 300 nm.

Table S2. Fitting parameters from TRPL spectra.^{a)}

	A_1	τ_1 (ns)	A_2	τ_2 (ns)	$\tau_{average}$ (ns)
$y = 0$	640	4.5	1340	206	203.9
$y = 0.1$	800	7.0	2260	210	207.6
$y = 0.15$	620	7.5	1750	238	235.5
$y = 0.2$	1300	4.3	2630	190	187.9

^{a)}The TRPL spectra were fitted by a bi-exponential decay function,

$$I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$$

and the average PL lifetime is calculated by

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

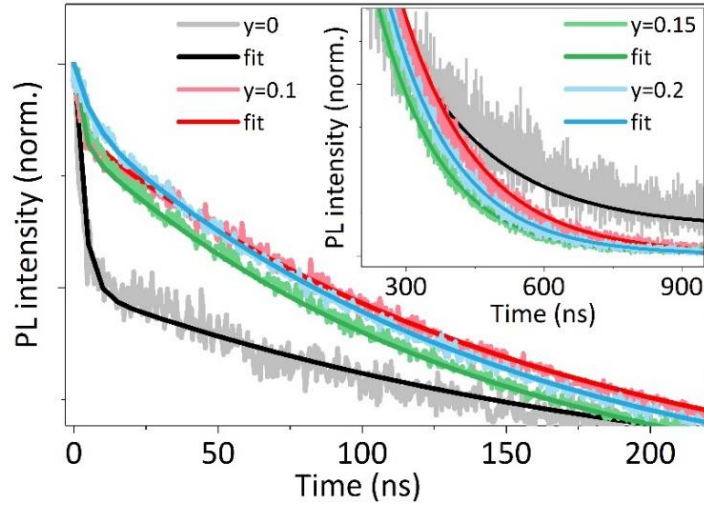


Figure S2. TRPL spectra of perovskite/HTL samples. Inset is the magnification of the region with longer decay time. The decay lifetime is 196.7 ns, 164.5 ns, 137.5 ns, and 146.2 ns for $y = 0, 0.1, 0.15,$ and $0.2,$ respectively.

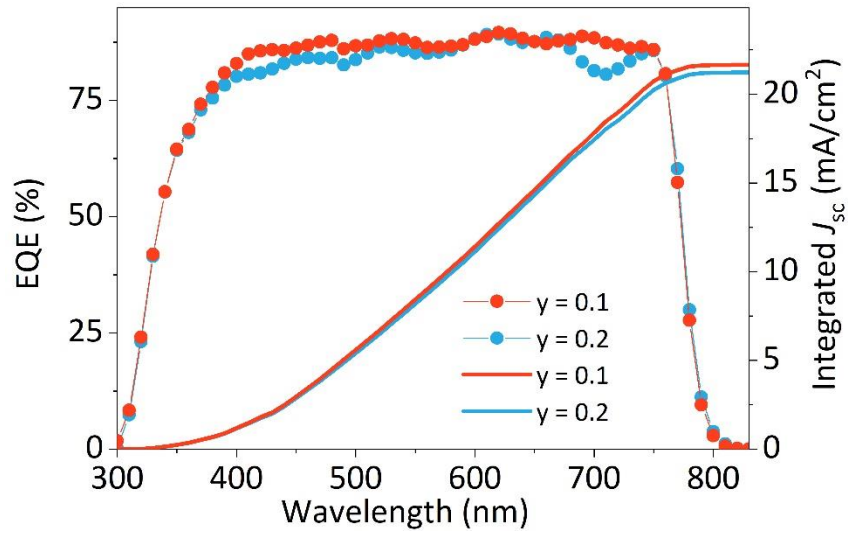


Figure S3. EQE spectra of devices with $y = 0.1$ and $y = 0.2,$ of which the integrated J_{sc} is 21.7 mA/cm^2 and 21.3 $\text{mA}/\text{cm}^2,$ respectively.

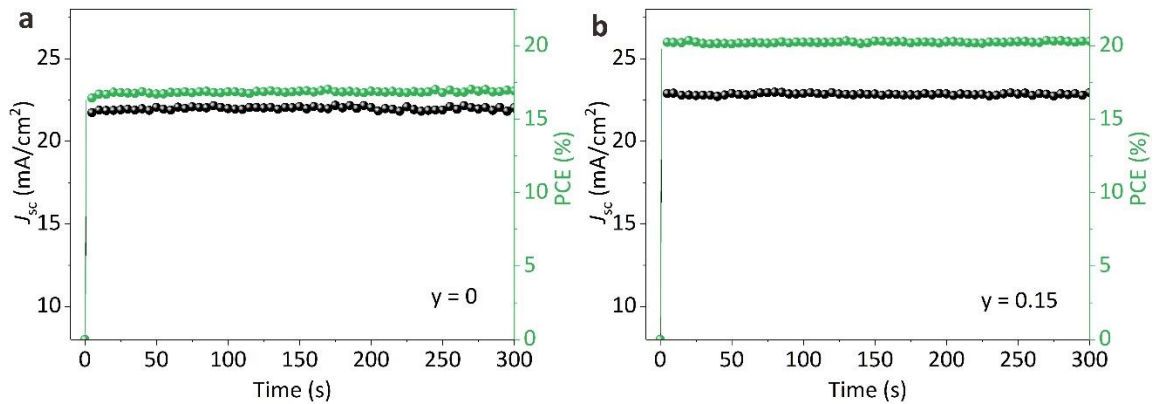


Figure S4. Steady state J_{sc} and PCE up on light exposure for (a) control device, $y = 0$ and (b) optimized device, $y = 0.15$.

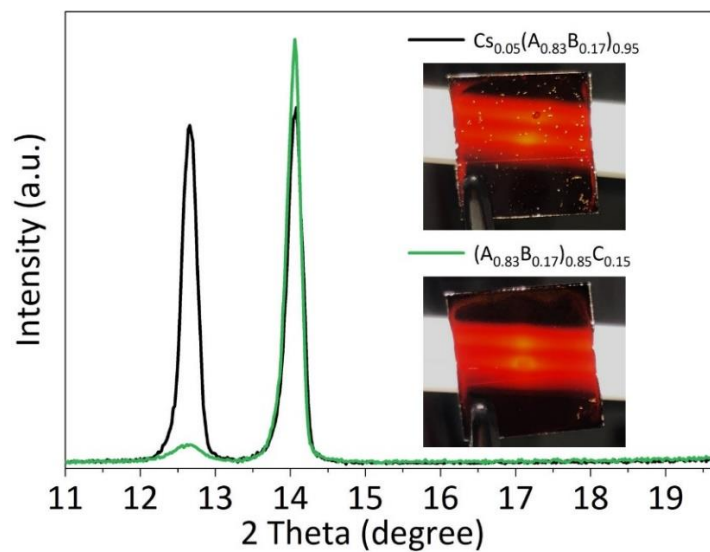


Figure S5. XRD of perovskite films, $\text{Cs}_{0.05}(\text{A}_{0.83}\text{B}_{0.17})_{0.95}$ and $(\text{A}_{0.83}\text{B}_{0.17})_{0.85}\text{C}_{0.15}$, after stored in ambient air under 70% RH for 300h in dark. Insets show the appearance of corresponding films.

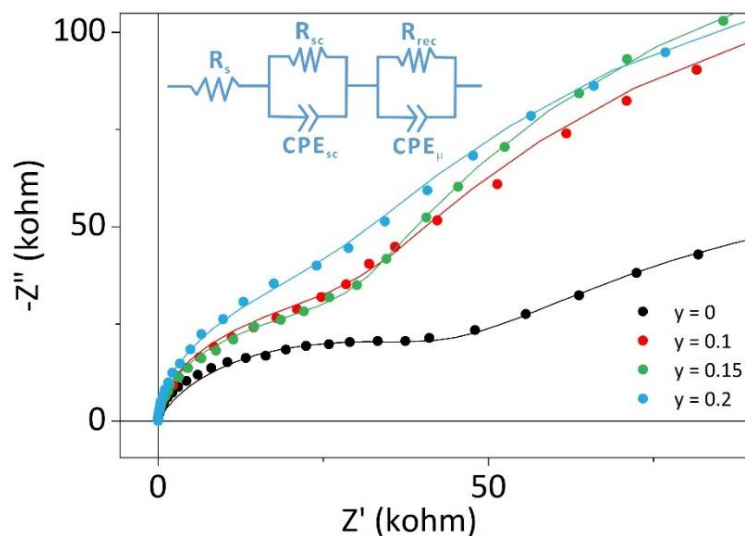


Figure S6. EIS spectra of devices based on control and alloyed perovskites. Inset shows the equivalent circuit.

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