

Crystallization control and multisite passivation of perovskites with amino acid to boost efficiency and stability of perovskite solar cells

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Experimental section

Materials: Formamidinium iodide (FAI, 99.99%), PbI₂ (99.99%), AHBA (99.9%), lead dibromide (PbBr₂, 99.99%) and poly[bis (4-phenyl)(2,4,6-trimethylphenyl)amine]

(PTAA, $M_n = 6000-15000$) were purchased from Xi'an Polymer Light Technology Corp. Methylamium bromide (MABr, 99.5%) was purchased from Materwin Corp. Chlorobenzene (CB, anhydrous, 99.8%), toluene, ethyl acetate (EA, anhydrous, 99.8%), dimethyl sulfoxide (DMSO, anhydrous, 99.9%), *N,N*-dimethylformamide (DMF, anhydrous, 99.8%), cesium iodide (CsI, 99.5%) and bathocuproine (BCP, 99.9%) were purchased from Sigma-Aldrich. 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4 -TCNQ, 99%) was purchased from Nichem. [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) and buckminsterfullerene (C₆₀, 99%) were purchased from Nano-C Tech. All chemicals were used as received without further purification.

Perovskite precursor solution: The Cs_{0.03}(FA_{0.85}MA_{0.15})_{0.97}Pb(I_{0.85}Br_{0.15})₃ perovskite films were deposited from a precursor solution containing FAI (190.06 mg), PbI₂ (548.06 mg), MABr (21.84 mg), PbBr₂ (77.07 mg) and AHBA (X mg, X=0, 0.25, 0.5, 1) in anhydrous DMF (0.64 mL) and DMSO (0.16 mL). Then, the 35 μ L of CsI, predissolved as a 1.5 M stock solution in DMSO, was added to the mixed perovskite precursor to achieve the desired triple cation composition. Note that a small molar excess of PbI₂ (3.3%) in the precursor solution was used in this study to fabricate the perovskite active layers.

Device Fabrication: The ITO glasses were washed with acetone, ethanol and deionized water in sequence, followed by ultrasonic cleaning with deionized water, acetone and ethanol for 20 min. After drying with high purity N₂ and vacuum drying

in an oven, the ITO substrates were treated with UV-ozone for 30 min. Then the F₄-TCNQ-doped PTAA solution (4 mg/mL in toluene doped with 0.25 wt% F₄-TCNQ) was spin-coated onto the ITO substrates at 6000 rpm for 30 s, and then the samples were heated at 100 °C for 10 min in a N₂-filled glovebox. To improve the wettability of perovskite precursor solution on the PTAA hole-extraction layer, the PTAA-coated ITO substrates were pre-treated by spin-coating 70 μL of DMF. Then perovskite precursor solution was spin-coated on the PTAA-coated ITO substrates at 6000 rpm for 30 s, and 100 μL EA was used as the anti-solvent to treat the perovskite films at the 25th s. Thereafter the samples were immediately annealed on a hotplate at 100 °C for 60 min. The electron transport material, PC₆₁BM solution (10 mg mL⁻¹ in CB) was spin-coated on the top of perovskite layer at the speed of 1000 rpm for 45 s. Finally, C₆₀ (20 nm), BCP (9 nm) and Ag electrode (80 nm) were sequentially deposited by thermal evaporation under a pressure of 1.4×10⁻⁴ Pa. The active area for all devices is 0.1 cm².

Device characterization: The scanning electron microscope (SEM) images were obtained by using a Hitachi S-4800 field emission scanning electron microscopy. The UV-vis absorption spectra were measured with a PerkinElmer Lambda 650S spectrophotometer. The X-ray diffraction (XRD) patterns were carried out using a Bruker D8 ADVANCE XRD equipment. The current density-voltage (*J-V*) characteristics were carried out using Keithley 2400 under AM 1.5 G illumination (100 mW cm⁻²) from a solar simulator (Oriel Sol3A Class Solar Simulator). Steady-state photoluminescence (PL) and time-resolved PL (TRPL) were measured

with a Hamamatsu C12132 fluorescence lifetime spectrometer using a 1.5 ns pulsed laser (frequency 15 kHz) at an excitation wavelength of 479 nm and an excitation power of 1 mW. The incident photon to current efficiency (IPCE) spectra were carried out by QTest Station 500AD Solar Cell Quantum Efficiency System (CROWNTECH, INC). The X-ray photoelectron spectroscopy (XPS) spectra of perovskite films on ITO glass substrates were carried out by using PHI Quantera SXM (ULVAC-PHI). XPS measurements were tested in an ultrahigh-vacuum environment as low as 5×10^{-11} mbar. The ultraviolet photoelectron spectroscopy (UPS) was operated with a He discharged lamp (He I 21.22 eV, Kratos Axis Supra). The electrochemical impedance spectra (EIS) were studied with a CHI660 electrochemical workstation (CH Instrument Inc.), which were measured within a frequency range of 10^5 -1 Hz at 0.4 V under dark condition. The AFM spectra were measured with Dimension icon and the KPFM results were measured with MFP-3D Infinity AFM.

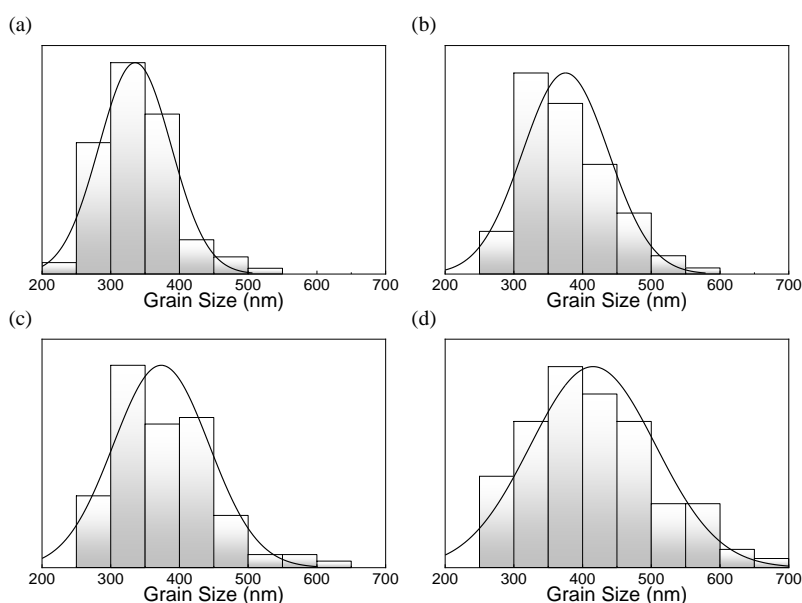


Fig. S1 Grain size statistics of the pristine perovskite and AHBA-incorporated

perovskites with different doping concentration from top-view SEM images: (a) 0 mg/mL, 331.28 ± 3.61 nm, (b) 0.25 mg/mL, 359.22 ± 10.07 nm, (c) 0.5 mg/mL, 364.01 ± 10.50 nm, and (d) 1 mg/mL, 394.35 ± 6.68 nm.

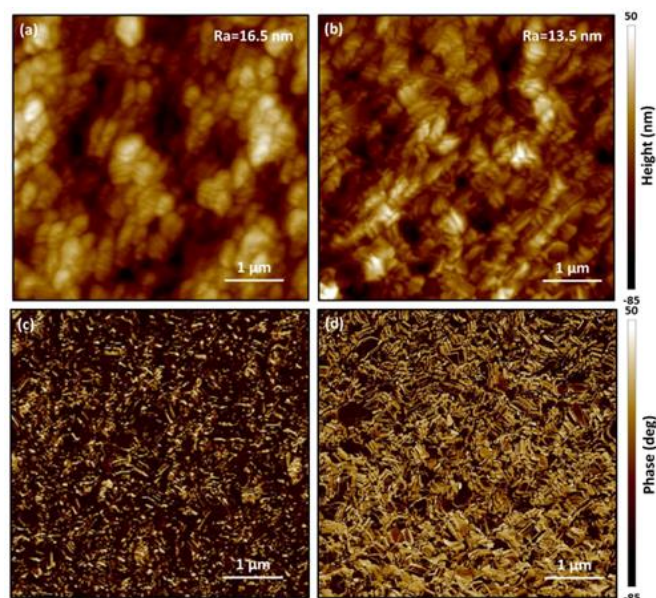


Fig. S2 AFM images of (a, c) the pristine perovskite film and (b, d) the AHBA-doped perovskite film.

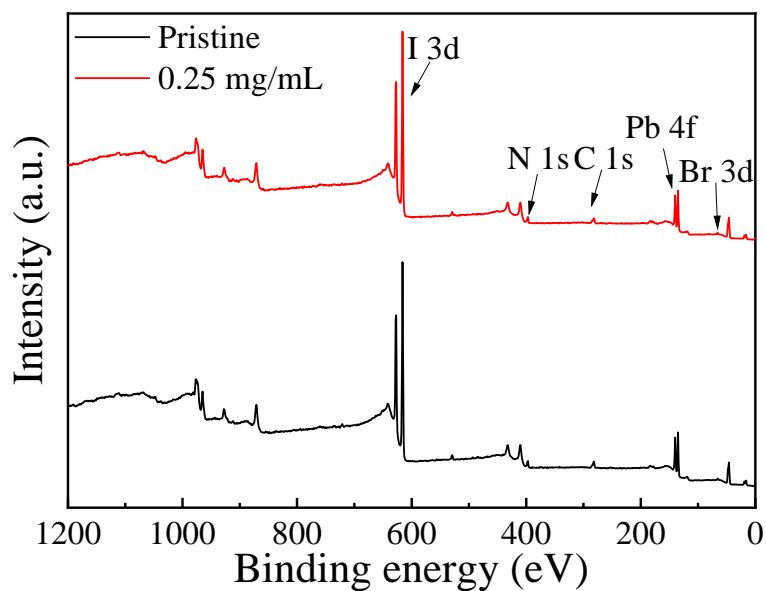


Fig. S3 X-ray photoelectron spectroscopy (XPS). Survey spectra obtained from control perovskite and 0.25-mg/mL AHBA-added perovskite films.

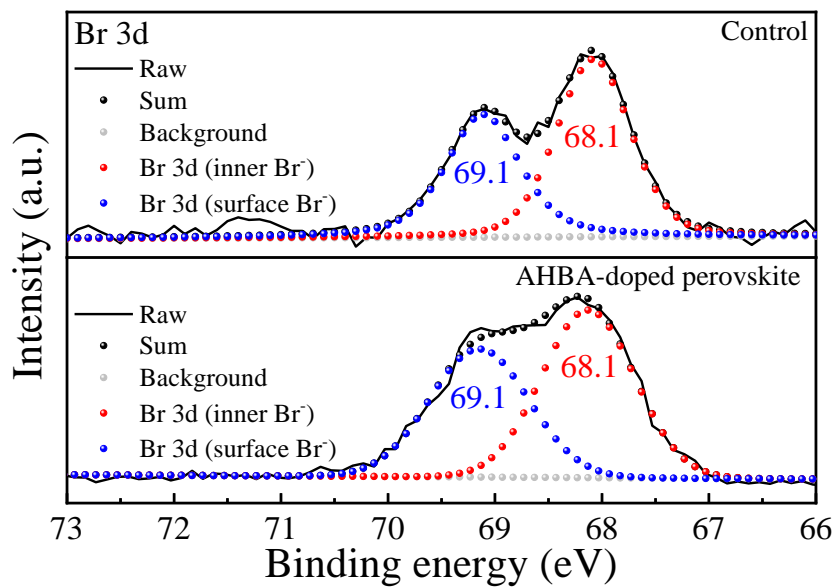


Fig. S4 Br 3d XPS spectra of perovskite films with and without AHBA additive.

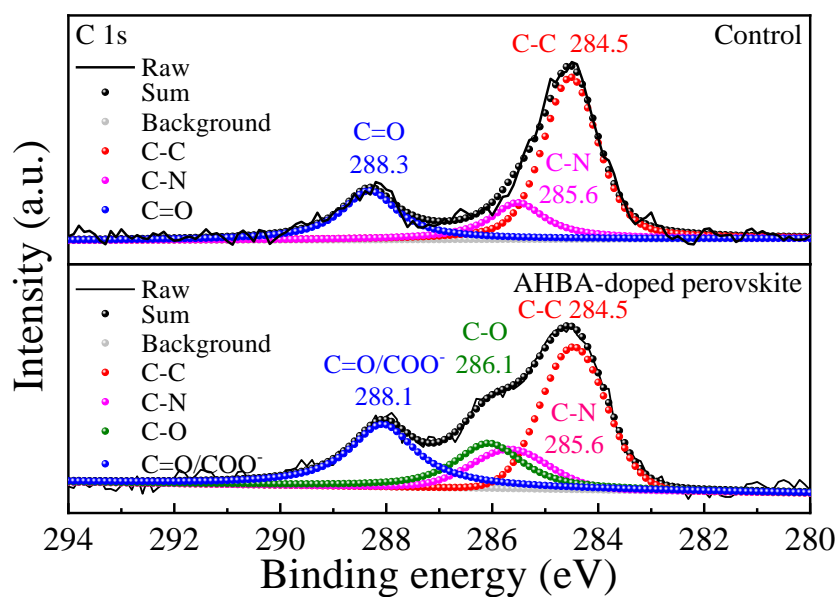


Fig. S5 C 1s XPS spectra of perovskite films with and without AHBA additive.

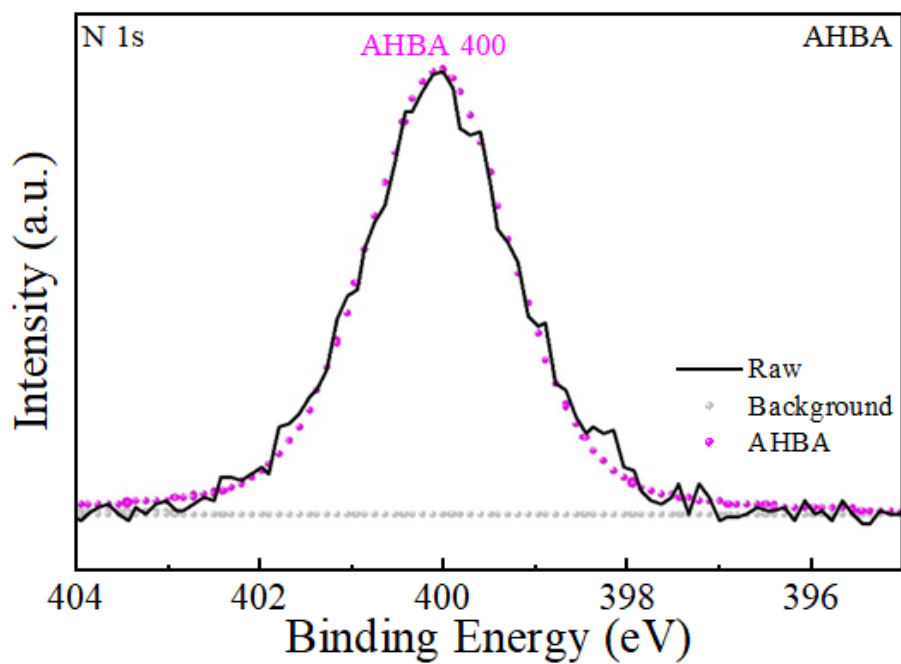


Fig. S6 N 1s XPS spectra of AHBA.

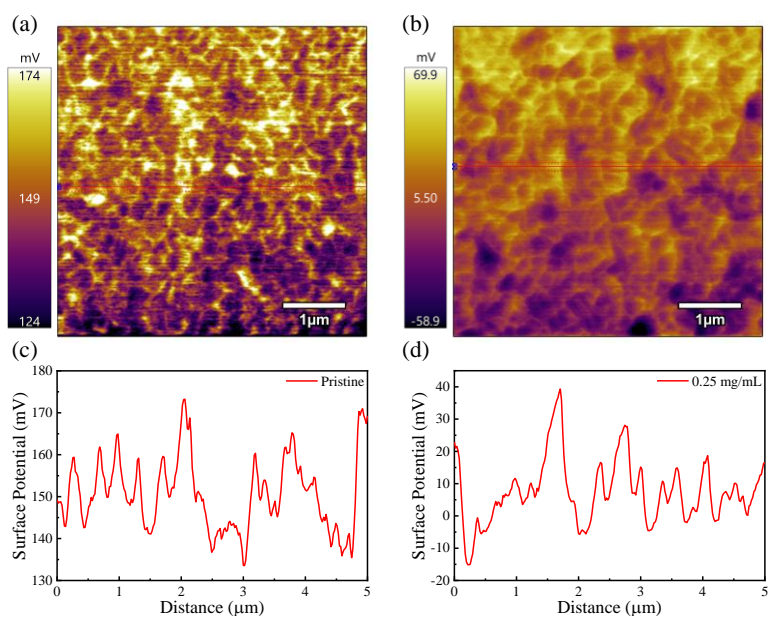


Fig. S7 Kelvin Probe Force Microscopy of pristine perovskite and AHBA-doped perovskite.

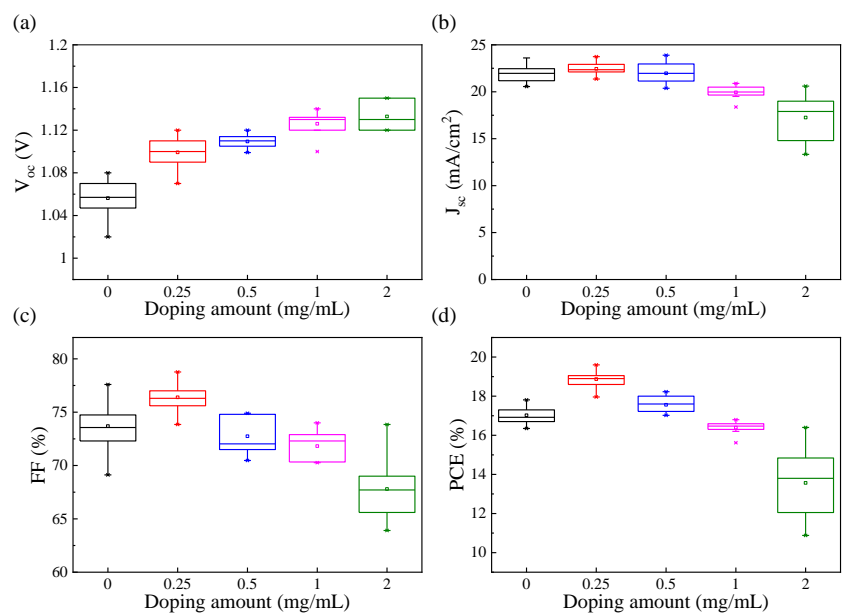


Fig. S8 Statistical data for J_{SC} , V_{OC} , FF and PCE obtained from 20 cells for each doping concentration.

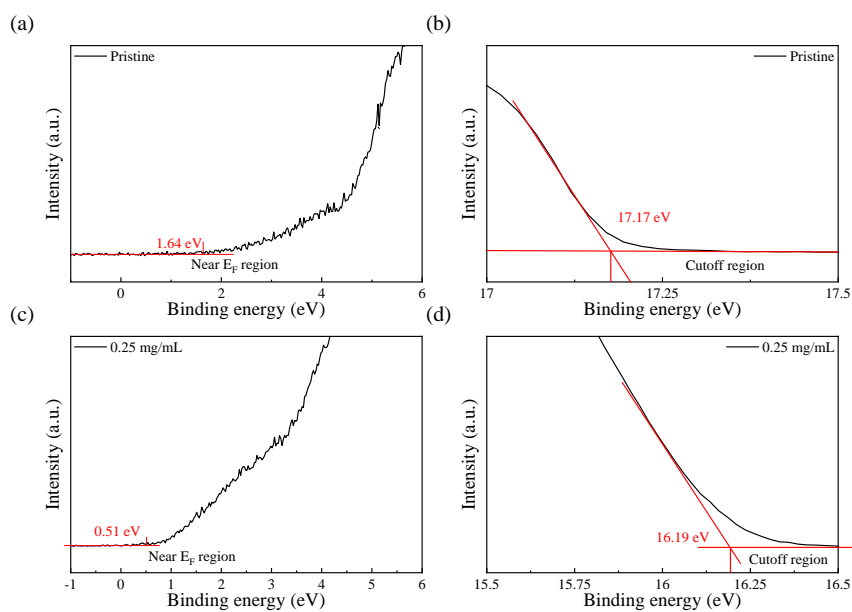


Fig. S9 Helium I α ($h\nu = 21.22$ eV) spectra of secondary electron cutoff and valence band of control and AHBA-incorporated perovskite films.

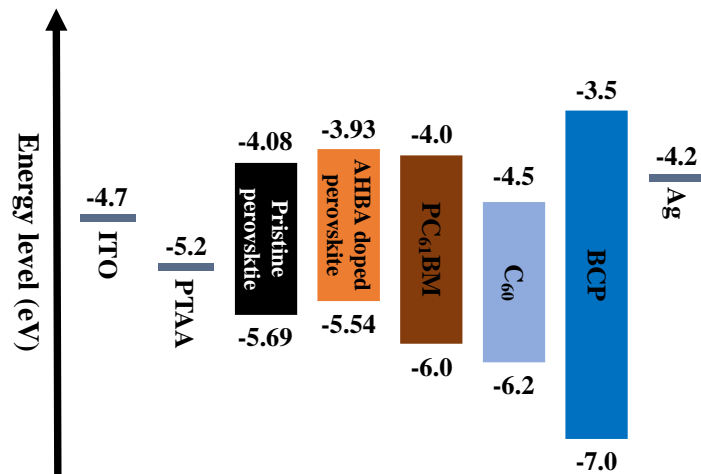


Fig. S10 Schematic illustration of energy levels for the PSCs.

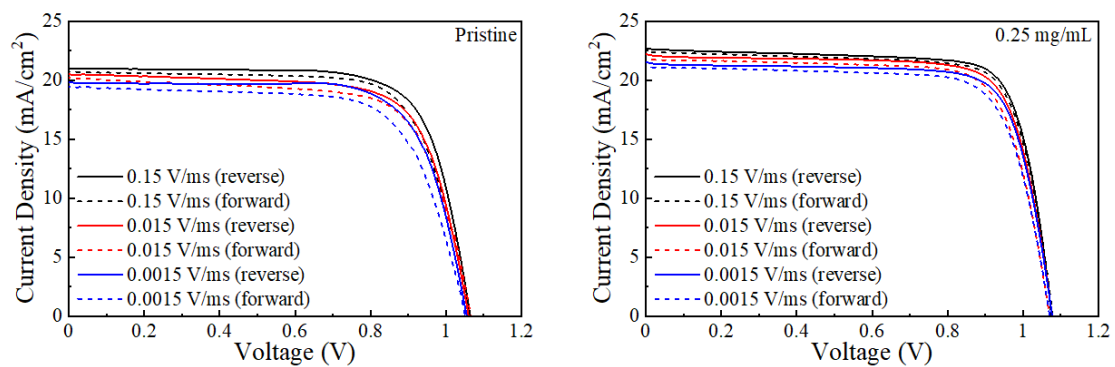


Fig. S11 *J-V* curves of the PSCs under different scan rates.

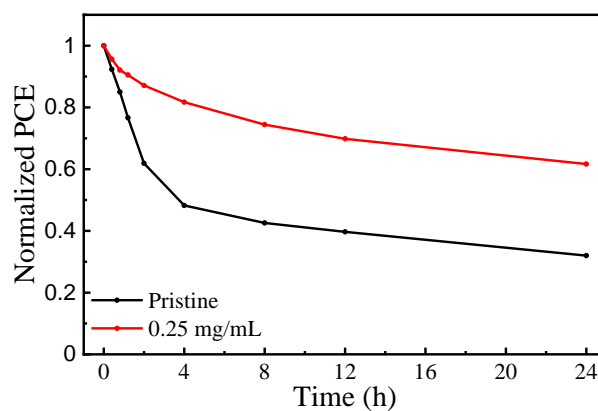


Fig. S12 The stability of PSCs under AM 1.5G one sun constant illumination (unencapsulated, 20-30% RH).

Table S1 Fitted photoluminescence lifetimes for pristine and 0.25 mg/mL AHBA-added perovskite films with a bi-exponential decay model. Here, A_1 and A_2 are fractional intensities, and τ_1 and τ_2 are lifetimes. The average carrier lifetime (τ_{avr}) was calculated with $\tau_{avr} = A_1\tau_1 + A_2\tau_2$.

Sample	τ_1 (ns)/ A_1 (%)	τ_2 (ns)/ A_2 (%)	χ^2	τ_{avr} (ns)
Pristine	13.43/19.28	79.71/80.72	1.106	66.93
AHBA	10.00/1.75	164.13/98.25	1.204	161.43

Table S2 The photovoltaic parameters of PSCs under different J-V scan rates and the calculated hysteresis index (HI) values using the following formula:

$$HI (\%) = \frac{PCE_{reverse} - PCE_{forward}}{PCE_{reverse}} \times 100 \%$$

Sample	Scan Rate (V/ms)	Scan direction	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	HI (%)
Pristine	0.15	forward	1.06	20.71	73.11	16.05	3.25%
		reverse	1.06	20.96	74.67	16.59	
	0.015	forward	1.06	20.22	70.68	15.15	3.50%
		reverse	1.07	20.49	71.61	15.70	
	0.0015	forward	1.05	19.46	69.79	14.26	6.61%
		reverse	1.05	19.81	73.41	15.27	
0.25 mg/mL	0.15	forward	1.08	22.44	76.79	18.61	1.59%
		reverse	1.08	22.68	77.20	18.91	
	0.015	forward	1.08	21.77	75.96	17.86	2.24%
		reverse	1.08	22.19	76.24	18.27	
	0.0015	forward	1.07	21.11	75.31	17.01	4.28%
		reverse	1.08	21.54	76.39	17.77	