

Supporting Information for

Effect of Functional Groups in Passivating Materials on Stability and Performance of Perovskite Solar Cells

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Experimental section

Materials Synthesis

Formamidinium iodide (FAI) was synthesized by reacting 20 mL hydroiodic acid (55-58%, Junsei) with 10 g of formamidine acetate (99%, Alfa Aesar) at 2 °C with stirring for 2 h. Brownish salt was collected by evaporating the solvent at 60 °C using a rotary evaporator, which was followed by washing with diethyl ether (99.0%, Samchun) several times until the color was bleached. The product was recrystallized in anhydrous ethanol, filtered and dried under vacuum for 24 h, which was stored in a glove box filled with Ar. Benzylammonium iodide (BnAMI) and phenylamidinium (benzamidinium) iodide (PhADI) were synthesized in a similar manner. In this case benzylamine (99%, Sigma Aldrich), benzamidine (99%, Sigma Aldrich) was used as precursor.

Formamidinium lead triiodide (FAPbI₃) black powder was synthesized by mixing 1.2 M FAI and PbI₂ (99%, Acros) in γ -butyrolactone (GBL, 99.5%, SAMCHUN) and heating at 130 °C for 2 h under vigorous stirring. The black powder was washed with acetonitrile (ACN, 99.9%, DAEJUNG) and diethyl ether for several times, which was followed by drying at 150 °C for 30 min.

Methylammonium lead triiodide (MAPbBr₃) single crystals were synthesized by mixing 1.0 M methylammonium bromide (MABr, 99.99%, Greatcellsolar) and PbBr₂ (98%, TCI) in dimethylformamide (DMF, 99.8%, Sigma-Aldrich), where the solution was heated at 110 °C

for 2 h. To remove unreacted chemicals, the single crystals were washed with ACN and diethyl ether for several times, which was dried at 100 °C for 30 min.

Device Fabrication

Fluorine-doped tin oxide (FTO) glass substrates (Pilkington, TEC-8, 8 Ω /sq) were patterned by laser etching machine and ultrasonically cleaned with detergent and ethanol. Ultraviolet ozone (UVO) was treated for 60 min to remove residual organic contaminants. For chemical bath deposition (CBD) to prepare SnO₂ film, the coating solution was prepared by mixing 137.5 mg of SnCl₂·2H₂O (99.99%, Sigma-Aldrich), 625 mg of urea (99%, Sigma-Aldrich), 625 μ L of HCl (37wt%, Sigma-Aldrich), 12.5 μ L of thioglycolic acid (99%, Sigma-Aldrich) and 50 mL of deionized water, in which the cleaned FTO was dipped at 85 °C for 5 h. After CBD, the SnO₂-coated FTO substrate was washed with deionized water and isopropanol for 10 min using sonication bath, which was followed by heating at 170 °C for 60 min. Perovskite precursor solution was prepared by mixing 433 mg of the home-made FAPbI₃ powder, 2.9 mg of MAPbBr₃ single crystal, 16.9 mg of MAcl (99.99%, synthesized), 444 μ L of dimethyl formamide (DMF), 56 μ L of dimethyl sulfoxide (DMSO, 99.9%, Sigma-Aldrich). The solution was filtered with 0.20 μ m pore-sized PTFE-H filter (Hyundai MICRO). The perovskite precursor solution was spin-coated on the SnO₂-coated FTO substrate at 1000 rpm for 5 s and then 5000 rpm for 20 s, in a dry room with relative humidity less than 2%, where 1000 μ L of diethyl ether (99.9%, Sigma-Aldrich) was poured drastically on the rotating substrate at 10 s before end of coating process. The as-deposited perovskite film was annealed at 100 °C for 5 min and at 150 °C for 10 min using hot plate. For post-treatment, 50 μ L of the BnAMI, PhADI or tBADI solution with 10 mM concentration (concentration was also varied to find optimal performance) dissolved in isopropyl alcohol (IPA) was dynamically spin-coated on the annealed perovskite film at 3000 rpm for 20 s, followed by annealing at 100 °C on a hot plate for 5 min. Hole transporting layer (HTL) was overcoated on the post-treated perovskite film by spin-coating 20 μ L of the spiro-MeOTAD solution at 3000 rpm for 20 s, where the spiro-MeOTAD solution was prepared by dissolving 72.3 mg of spiro-MeOTAD (2,2',7,7'-tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene) (99%, Sigma Aldrich), 28.8 μ L of 4-*tert*-butyl pyridine (98%, Sigma Aldrich) and 17.5 μ L of lithium bis(trifluoromethanesulfonyl)-imide (LiTFSI, Sigma Aldrich) solution (520 mg LiTFSI in 1 mL ACN (99.8%, Sigma Aldrich)) in 1 mL of chlorobenzene (99.8%, Sigma Aldrich). Finally,

Au electrode was deposited by using thermal evaporator at evaporation rate of 0.5 Å/s to form about 70 nm thick Au electrode.

Characterizations

Current density-voltage (J - V) curves were measured under AM 1.5G one sun (100 mW/cm²) intensity using a solar simulator (Oriel Sol 3A, class AAA) equipped with 450 W Xenon lamp (Newport 6280NS) and a Kiethley 2400 source meter. The light intensity was adjusted by NREL-calibrated Si solar cell having KG-2 filter. The device was covered with a metal mask with aperture area of 0.1 cm². Optical absorption was measured using a UV-visible spectrometer (Lambda 45, PerkinElmer). External quantum efficiency (EQE) spectra were collected by using an QEX-7 series system (PV measurements Inc.) in which a monochromatic beam was generated from a 75 W Xenon source lamp (USHIO, Japan) under DC mode. Steady-state PL and TRPL were measured by a FLS1000 photoluminescence spectrometer (Edinburgh Instruments). The samples were excited with a 450 W ozone free Xenon arc lamp for steady-state PL. For TRPL, 405 nm diode lasers (EPL, Edinburgh Instruments) pulsed at repetition frequency 5 MHz was used for excitation. Surface morphology was investigated using atomic force microscope (AFM, NX10, Park Systems) with FTO/SnO₂/perovskite by non-contact mode in the N₂ glove box. X-ray diffraction (XRD) data were collected from a Rigaku SmartLab diffractometer, where Cu K α radiation was used ($\lambda = 1.5406$ Å) and a scan rate was 4°/min with 0.02°/step. X-ray photoelectron spectroscopy (XPS) was carried out with an ESCALAB250 instrument (Thermo Fisher Scientific) by using a monochromatized Al source ($h\nu = 1486.6$ eV). Binding energy was calibrated with respect to C 1s peak of 284.6 eV. Ultraviolet photoelectron spectroscopy (UPS) measurements were carried out with ESCALAB 250 XPS system (Thermo Fisher Scientific) using He I (21.22 eV). Electrochemical impedance spectroscopy (EIS) measurement data were obtained from the Autolab electrochemical working station with an amplitude of 20 mV at voltage ranging from -0.1 V to 0.1 V by 0.1 V step voltage in the dark with frequency range from 1 MHz to 0.1 Hz. The measured data were fitted using Z-view software.

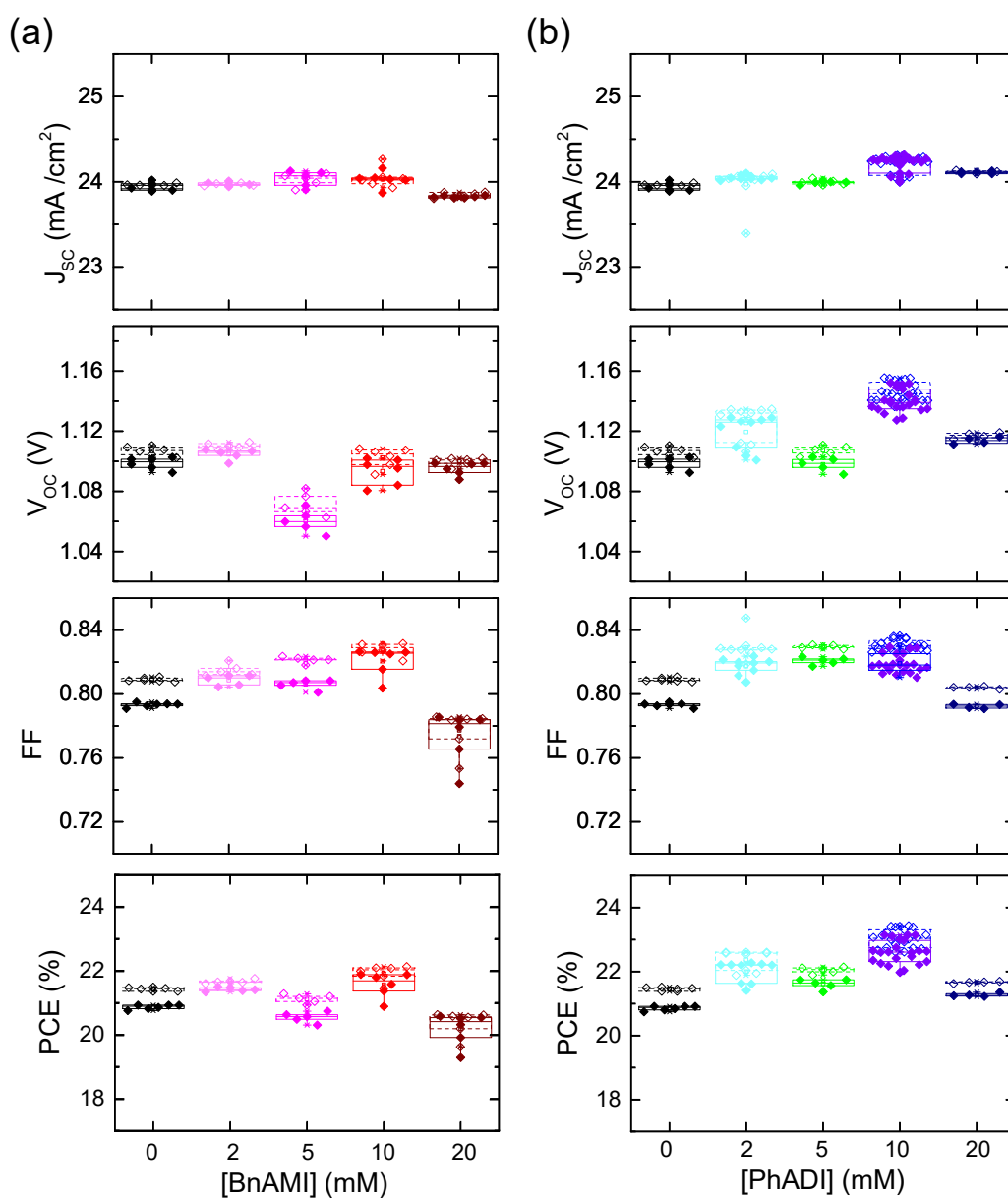


Figure S1. statistical photovoltaic parameters for PSCs employing perovskite films before (w/o) and after post-treatment with different concentration of (a) BnAMI and (b) PhADI. Dashed and solid lines represent forward scan and reverse scan, respectively.

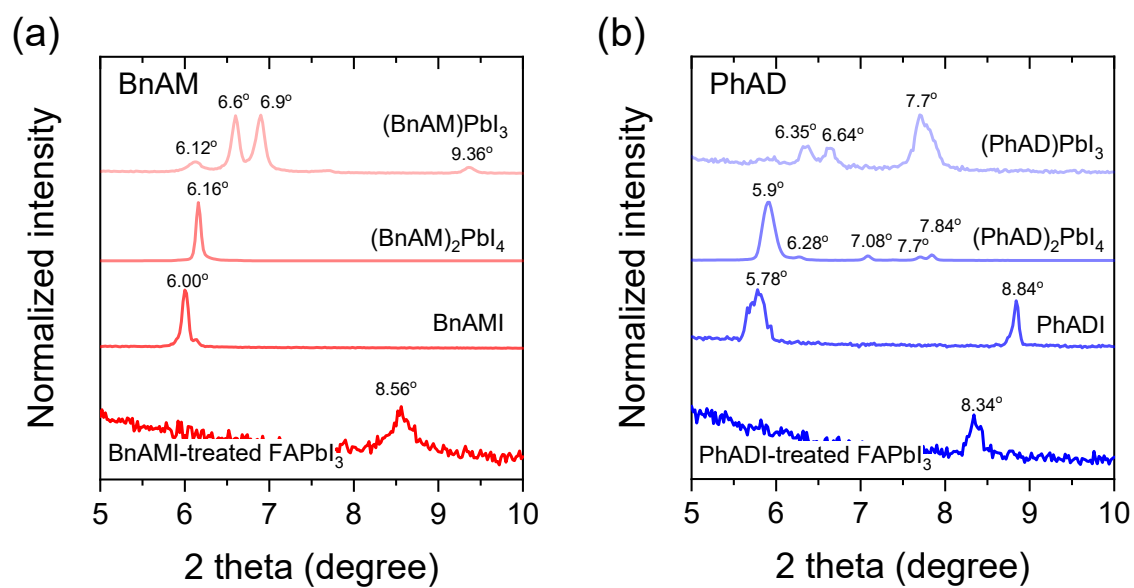


Figure S2. Film XRD patterns of (a) BnAMI-treated FAPbI₃, BnAMI, (BnAM)₂PbI₄ and (BnAM)PbI₃ and (b) PhADI-treated FAPbI₃, PhADI, (PhAD)₂PbI₄ and (PhAD)PbI₃. All films were prepared on a bare FTO.

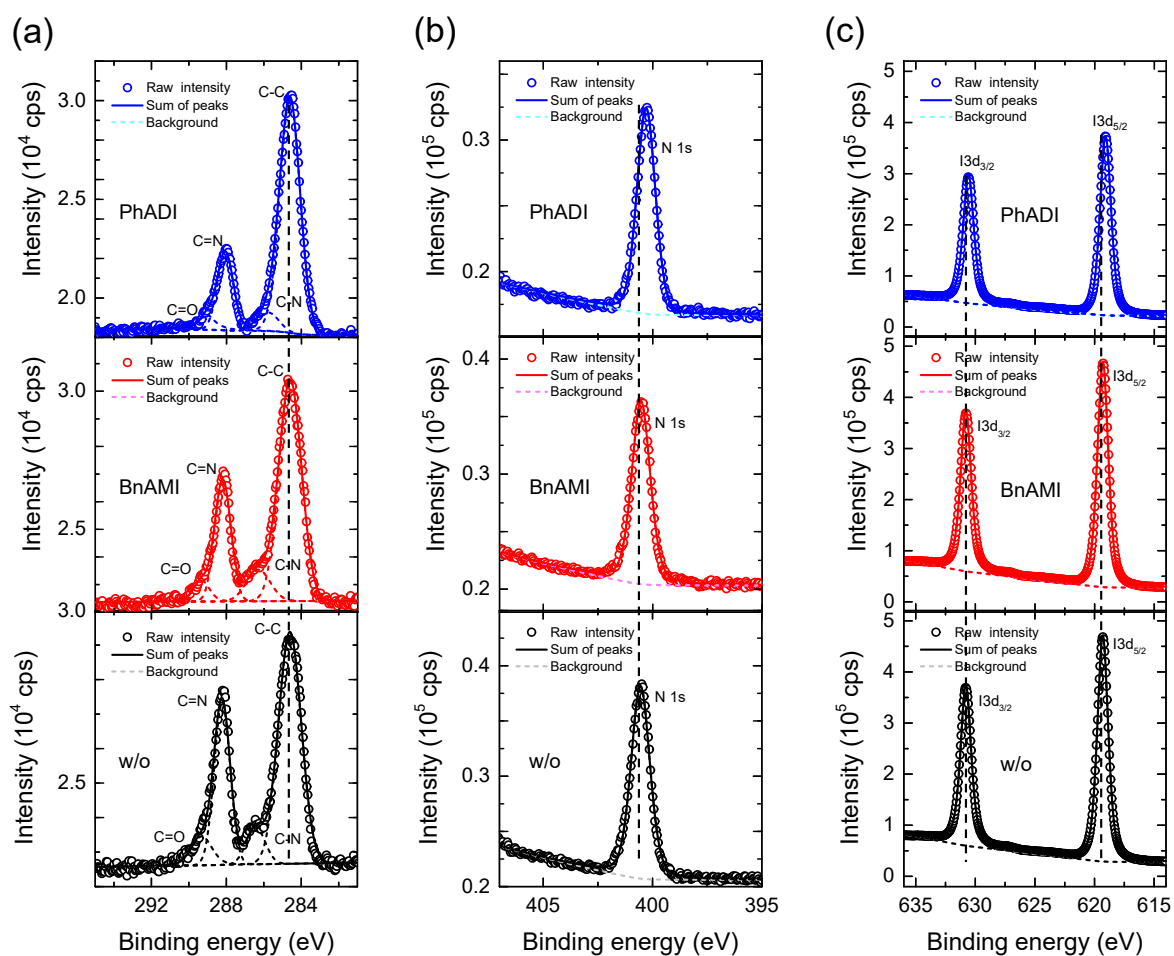


Figure S3. XPS spectra of (a) C 1s, (b) N 1s and (c) I 3d core levels for the perovskite films before (w/o) and after post-treatment with BnAMI and PhADI. Symbols and lines represent measured and fitted data, respectively.

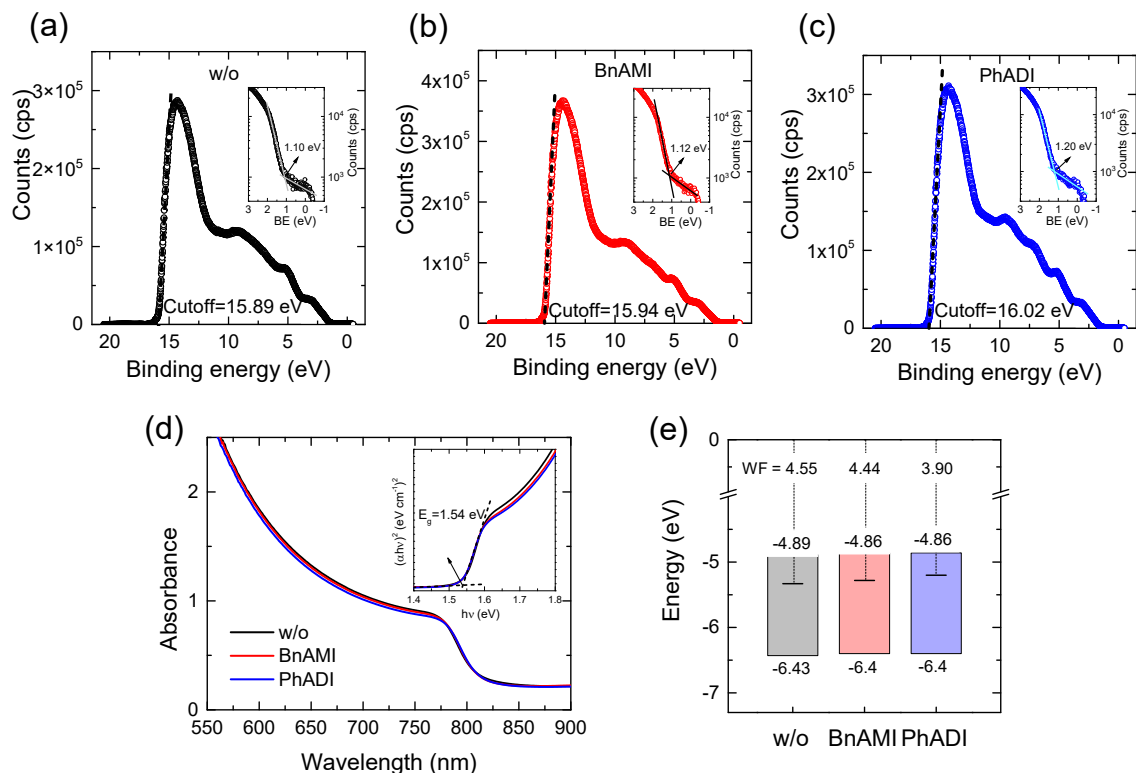


Figure S4. UPS spectra of the perovskite film (a) before (w/o) and after post-treatment with (b) BnAMI and (c) PhADI. Inset shows the log plot at a low binding energy region. (d) Optical absorption spectra of the perovskite film before (w/o) and after post-treatment. Inset shows Tauc's plot. (e) Band diagram (E_{VB} , E_{CB} and WF) of the perovskite surface before and after post-treatment with BnAMI and PhADI.

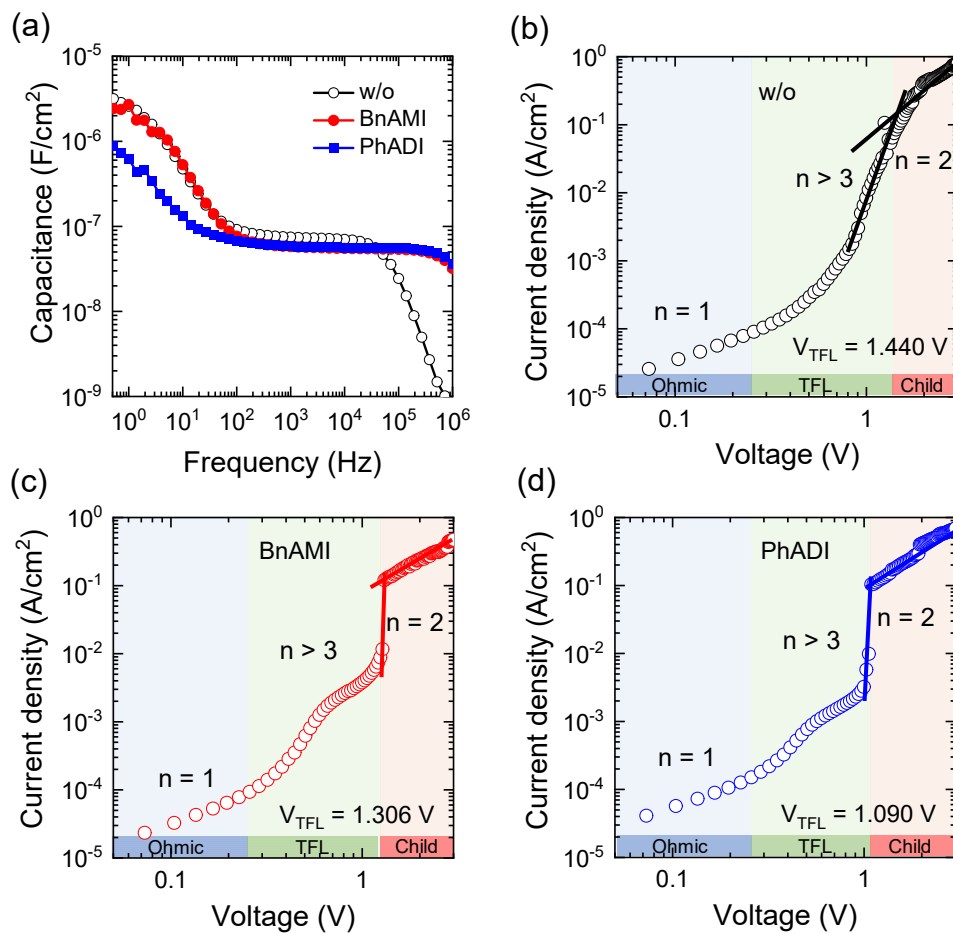


Figure S5. (a) C-f plot before (w/o) and after post-treatment with BnAMI and PhADI. Dark J-V curve (b) before (w/o) and after post-treatment with (c) BnAMI and (d) PhADI. The device structure was FTO/perovskite/Au. V_{TFL} represent trap filled limited voltage.

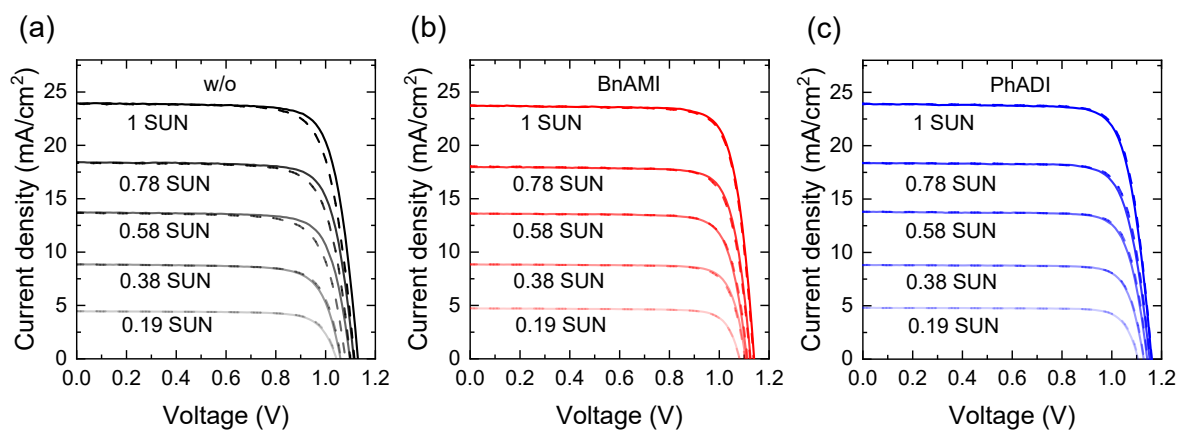


Figure S6. Light intensity-dependent J-V curves of PSCs employing perovskite films (a) before (w/o) and after post-treatment with (b) BnAMI and (c) PhADI. Solid and dashed lines represent reverse-scanned and forward-scanned data, respectively.

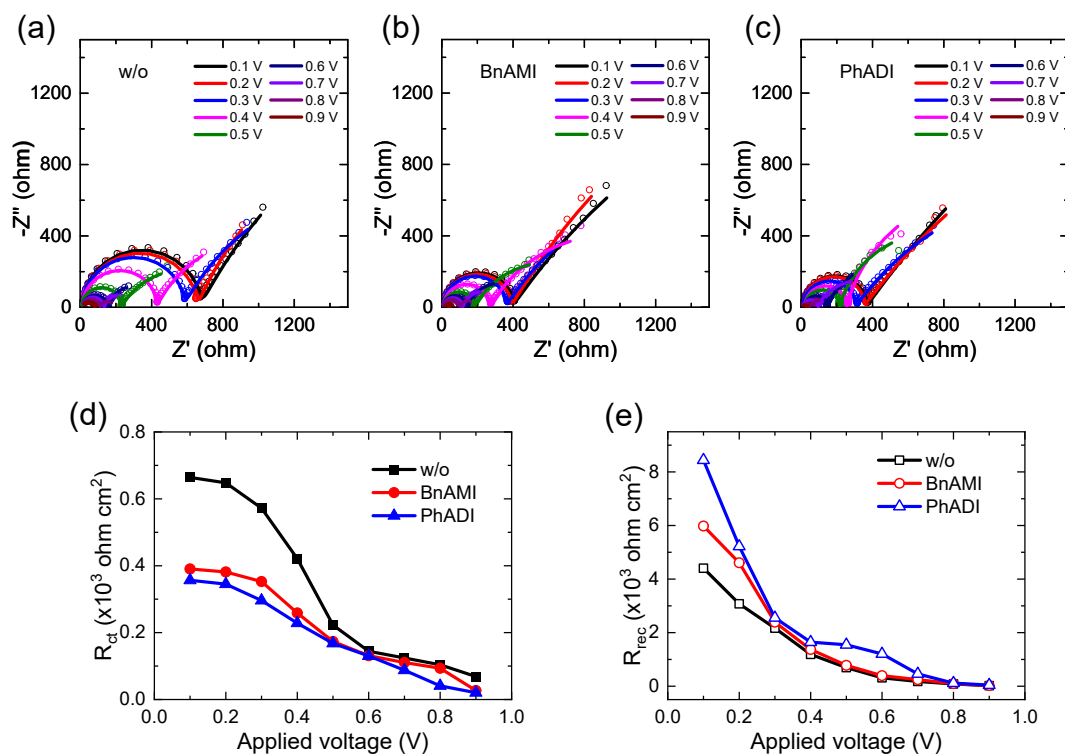


Figure S7. Nyquist plots of PSCs (a) before (w/o) and after post-treatment with (b) BnAMI and (c) PhADI at bias ranging from 0.1 V to 0.9 V under one sun illumination. Symbols and lines are raw data and fitted data, respectively, where the data were fitted with equivalent circuits. (d) Charge transport resistance (R_{ct}) and (e) recombination resistance (R_{rec}).

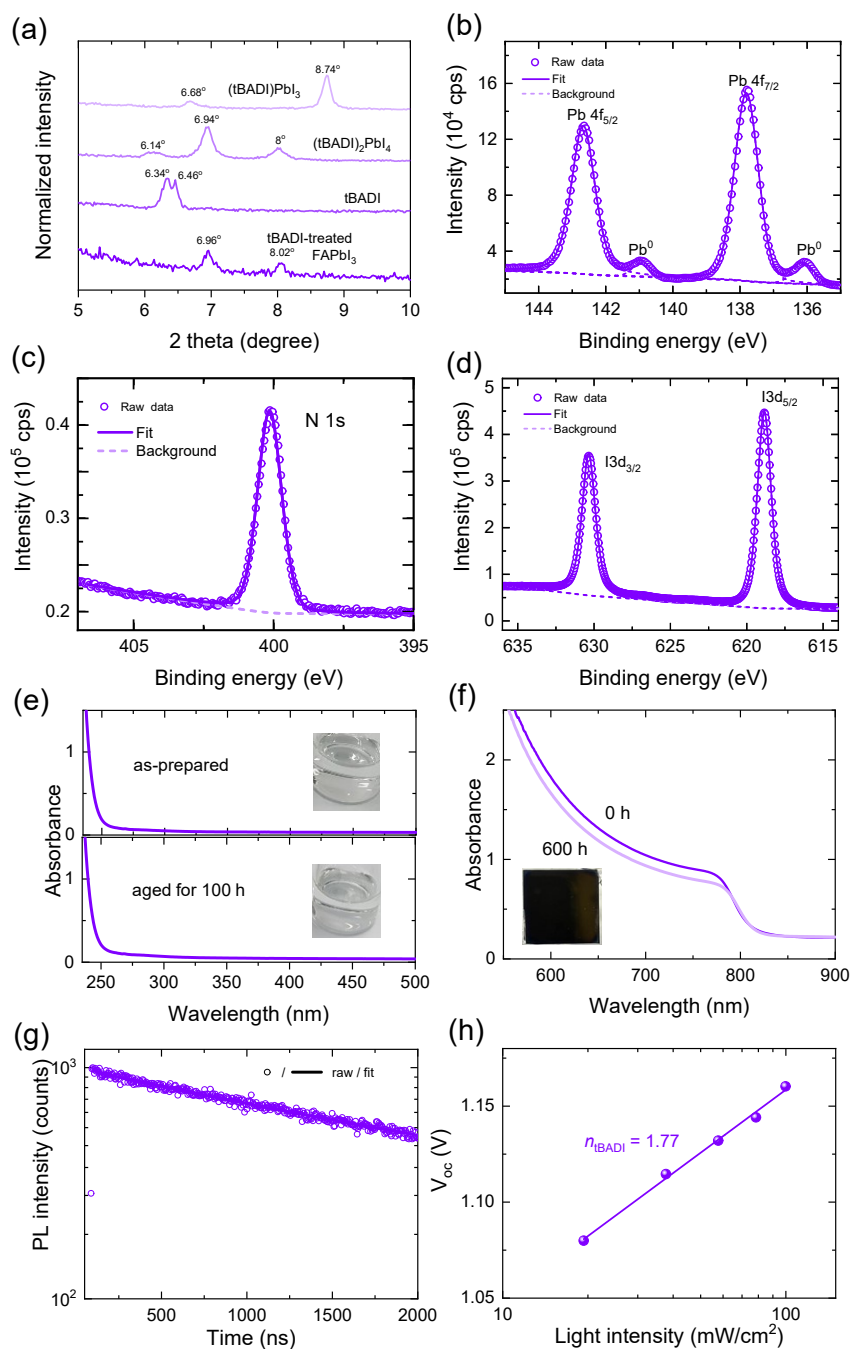


Figure S8. (a) XRD patterns of perovskite treated with tBADI along with tBADI, (tBADI)₂PbI₄ and (tBADI)PbI₃. XPS spectra of (b) Pb 4f, (c) N 1s and (d) I 3d core levels for the perovskite films after post-treatment with tBADI. (e) UV-vis spectra of perovskite precursor solutions with tBADI. Inset pictures represent the real precursor solutions. (f) Absorbance of the fresh and 600 h-aged perovskite films. (g) TRPL of perovskite films treated with tBADI. (h) Light intensity-dependent V_{oc} of PSC employing the tBADI-treated perovskite film.

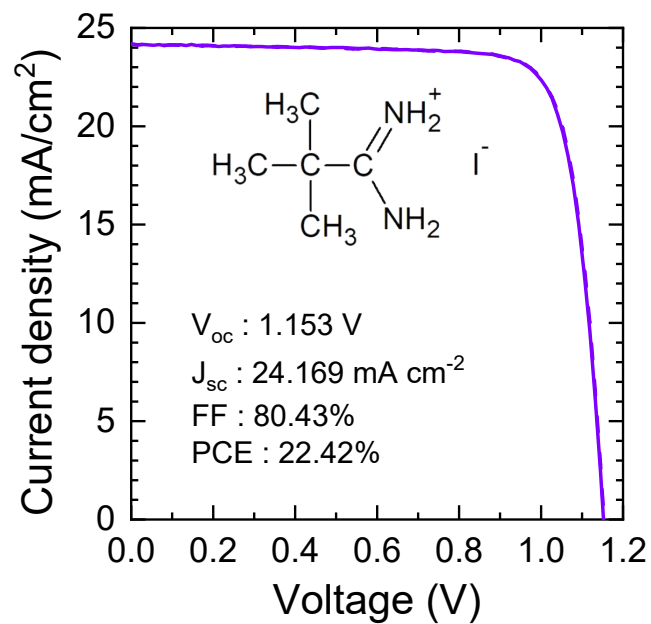


Figure S9. J-V curve of PSC employing perovskite film post-treated with tBADI, measured at 1 sun illumination. Solid and dashed lines represent reverse and forward scanned data. Inset shows a chemical structure of tBADI.

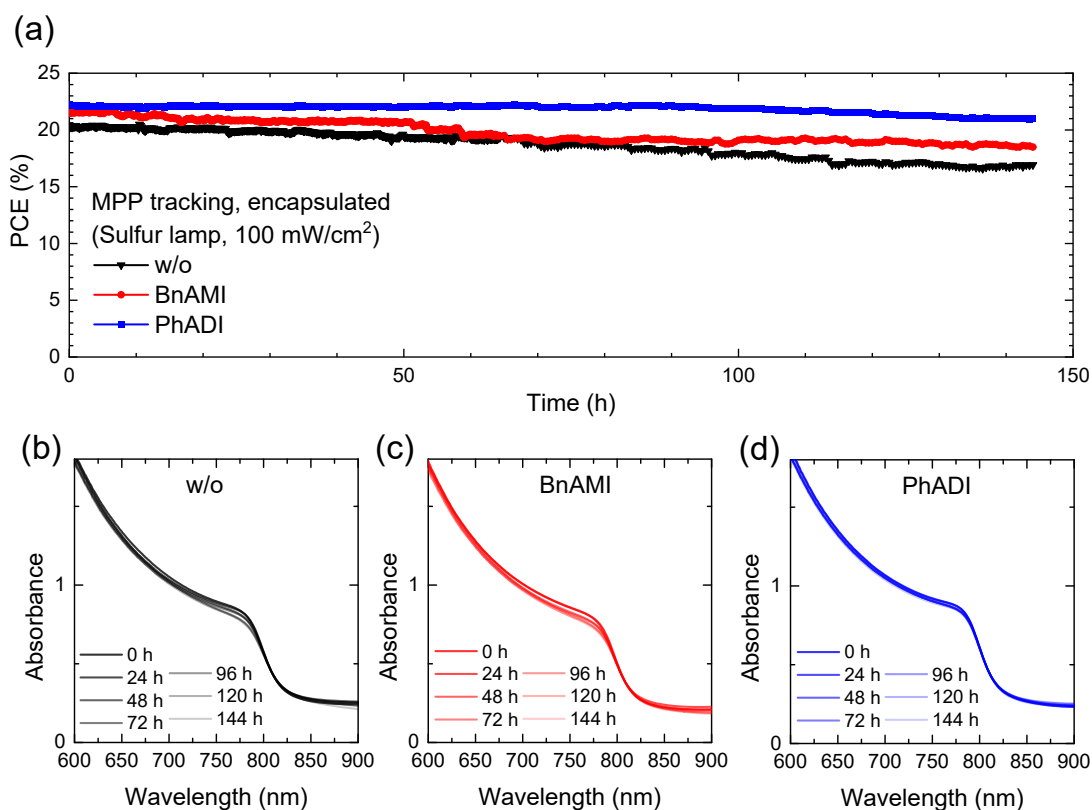


Figure S10. (a) The light soaking stability of the encapsulated PSCs before (w/o) and after post-treatment with BnAMI and PhADI measured at maximum power point (0.963 V for w/o, 0.981 V for BnAMI and 0.995 V for PhADI, respectively.) for 144 h under one sun illumination using the sulfur lamp. The absorbance of perovskite films (b) before and after post-treatment with (c) BnAMI and (d) PhADI under continuous illumination. Perovskite films were unencapsulated.

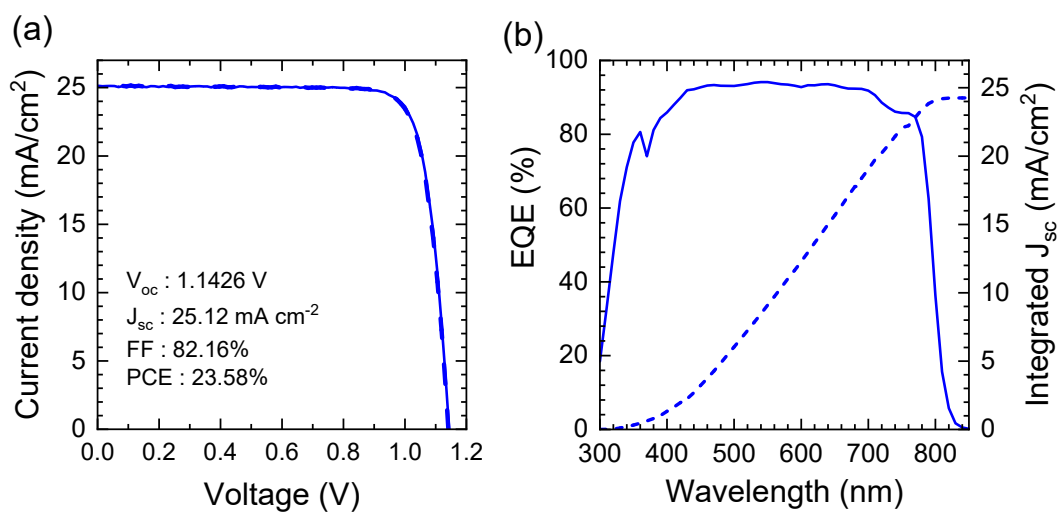


Figure S11. (a) J-V curve (solid: reverse scan; dashed: forward scan) and (b) EQE for the best performing PSC with the PhADI post-treatment fabricated using a highly transparent FTO substrate. Integrated J_{sc} was calculated based on EQE data.

Table S1. Parameters estimated from UPS spectra optical absorption spectra.

Samples	E_g (eV)	$E_{\text{cut-off}}$ (eV)	WF (eV)	VBM (eV)	E_{VB} (eV)	E_{CB} (eV)
w/o	1.54	15.89	5.33	1.10	6.43	4.89
BnAMI	1.54	15.94	5.28	1.12	6.40	4.86
PhADI	1.54	16.02	5.20	1.20	6.40	4.86

Table S2. Parameters estimated from C-f plot and SCLC.

Samples	C_g ($\times 10^{-8}$ F/cm ²)	d ($\times 10^{-5}$ cm)	ϵ_r ($\times 10$)	V_{TFL} (V)	n_t ($\times 10^{16}$ cm ⁻³)
w/o	7.04	470	3.97	1.440	2.53
BnAMI	5.50	470	3.11	1.306	1.79
PhADI	5.65	470	3.19	1.090	1.54