Electronic Supporting Information

Cation and anion optimization of ammonium halide for interfacial passivation of inverted perovskite solar cells

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Contents

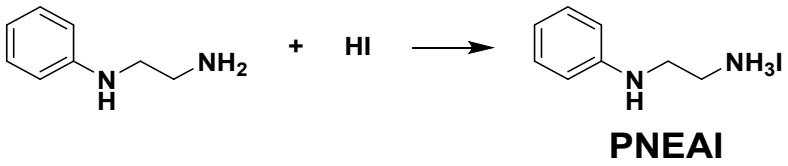
1. Experimental section

The ^{1}H NMR spectra were collected on a Bruker AVANCE III HD 400 MHz spectrometer in d6-DMSO solution with TMS as a reference. The morphology of the samples was recorded by scanning electron microscopy (SEM, Germany ZEISS Sigma 300). Steady-state photoluminescence (PL) and time-resolved photoluminescence spectrum (TRPL) spectrum were conducted with FLS1000 spectrofluorometer (Edinburgh) with a pulsed excitation laser of 375 nm. UV-Vis absorption spectra were collected on a UV-Vis spectrometer (PerkinElmer model Lambda 365). X-ray photoelectron spectrometer (ThermoFischer, ESCALAB Xi+, USA) was used for testing. Among them, the analysis room is 8×10^{-10}Pa, the excitation source is, Al ka ray (emission hv = 1486.6 eV), the working voltage is 12.5 kV, the filament current is 16 mA, and the signal is accumulated according to the condition of the sample. The full spectrum of the Passing-Energy test is 100eV, the narrow spectrum is 20eV, the step size is 0.05eV, the dwell time is 40-50 ms, and the charging is performed with the binding energy of C1s = 284.80 eV as the energy standard. Correction. X-ray diffraction (XRD) characterization was Equipment Model (Nippon Rigaku Ultima IV). The samples were deposited on ITO glass with the same solution compositions as those for the solar cells. *J-V* characteristics were measured in N_2-filled glove box by Vigor source meter under simulated sunlight from a solar simulator (Enlitech, SS-F5, Taiwan). EQEs were collected by an EnLiTechnology (Taiwan) EQE measurement system. A National Renewable Energy Laboratory calibrated silicon solar cell was used to obtain the AM 1.5G solar simulator's light intensity. The devices were shielded with a shading mask with an aperture area of 0.043 cm^2.

2. Synthesis

Commercially available reagents and solvents were purchased from Energy or Admas and used without further purification.

Synthesis of PNEAI

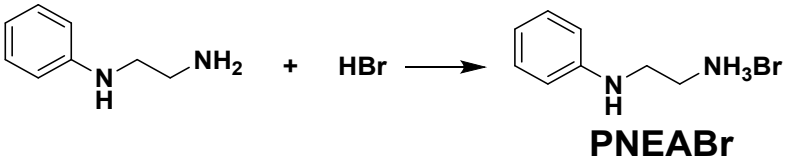


Scheme S1. Synthetic route of PNEAI

PNEAI

HI (2.56 g, 55%, 11.01 mmol) was added dropwise to a solution of *N*[1]-phenylethane-1,2-diamine (1.5 g, 11.01 mmol) in ethanol at 0 □°C under a nitrogen atmosphere. After being stirred at room temperature for 2 h, the mixture was concentrated in vacuo. The precipitate was washed with petroleum ether and recrystallized in diethyl ether three times. The product was collected and dried under a high vacuum overnight, providing the pure **PNEAI** (2.45 g, 84%) as a white solid powder. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.72 (s, 3H), 7.12 (t, *J* = 7.8 Hz, 2H), 6.60 (dd, *J* = 12.1, 7.5 Hz, 3H), 5.68 (t, *J* = 6.1 Hz, 1H), 3.26 (d, *J* = 7.1 Hz, 2H), 2.97 (t, *J* = 6.4 Hz, 2H).

Synthesis of PNEABr

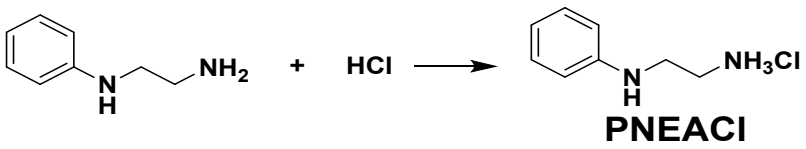


Scheme S2. Synthetic route of PNEABr

PNEABr

HBr (1.86 g, 48%, 11.01 mmol) was added dropwise to a solution of *N*[1]-phenylethane-1,2-diamine (1.5 g, 11.01 mmol) in ethanol at 0 □°C under a nitrogen atmosphere. After being stirred at room temperature for 2 h, the mixture was concentrated in vacuo. The precipitate was washed with petroleum ether and recrystallized in diethyl ether three times. The product was collected and dried under a high vacuum overnight, providing the pure **PNEABr** (1.80g, 75%) as a white solid powder. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.91 (d, *J* = 18.2 Hz, 3H), 7.11 (t, *J* = 7.6 Hz, 2H), 6.61 (dd, *J* = 16.1, 6.9 Hz, 3H), 5.78 (d, *J* = 8.1 Hz, 1H), 3.29 (q, *J* = 6.1 Hz, 2H), 2.97 (t, *J* = 6.4 Hz, 2H).

Synthesis of PNEACl



Scheme S3. Synthetic route of PNEACl

PNEACl

HCl (1.49 g, 36%, 14.68 mmol) was added dropwise to a solution of *N*[1]-phenylethane-1,2-diamine (2 g, 14.68 mmol) in ethanol at 0 □°C under a nitrogen atmosphere. After being stirred at room temperature for 2 h, the mixture was concentrated in vacuo. The precipitate was washed with petroleum ether and recrystallized in diethyl ether three times. The product was collected and dried under a high vacuum overnight, providing the pure **PNEACl** (2.10 g, 83%) as a white solid powder. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.15 (m, 3H), 7.11 (t, *J* = 7.6 Hz, 2H), 6.60 (dd, *J* = 22.2, 7.6 Hz, 3H), 6.02 – 5.78 (m, 1H), 3.29 (dt, *J* = 7.7, 3.8 Hz, 2H), 2.95 (t, *J* = 6.4 Hz, 2H).

3. Device fabrication:

ITO glass (15 Ω sq-1) was ultrasonically cleaned with deionized water, acetone, and isopropanol for 15 minutes, respectively. Then, the cleaned ITO substrate was treated with ultraviolet ozone for 6 minutes. PTAA (2 mg/mL solution in toluene) was spin-coated on clean ITO at 6000 rpm for 30 s and then annealed at 100°C for 10 min. The ITO substrates were cooled to room temperature before use. 1M perovskite precursor solutions were constructed by mixing FAI, PbI2, CsI, and PbBr2 in DMF:DMSO mixed solvent (4:1; v/v) with a chemical formula of FA0.83Cs0.17Pb(I0.86Br0.14)3. 45 μL of the prepared precursor solution was spin-coated at 1000 rpm for 10 s and 5000 rpm for 30 s onto the PTAA-coated ITO substrate, 150 μL CB as anti-solvent was dripped on the film at 15 s before the end of the last procedure, and then annealed at 100 ℃ for 10 min. After deposition of the perovskite active layer, 35 μ L of PNEACl (1mg/mL, IPA), PNEABr (0.5mg/mL, IPA), or PNEAI (0.5mg/mL, IPA) solution was spin-coated on to the film at 4000 rpm for 30 s. Finally, 15 nm C60, 5 nm BCP and 80 nm silver electrode was evaporated under a high vacuum (< 6×10-4 Torr) sequentially. The active area for all solar cells was 0.04 cm2, defined by the shadow mask.

4. ^{1}H NMR spectra

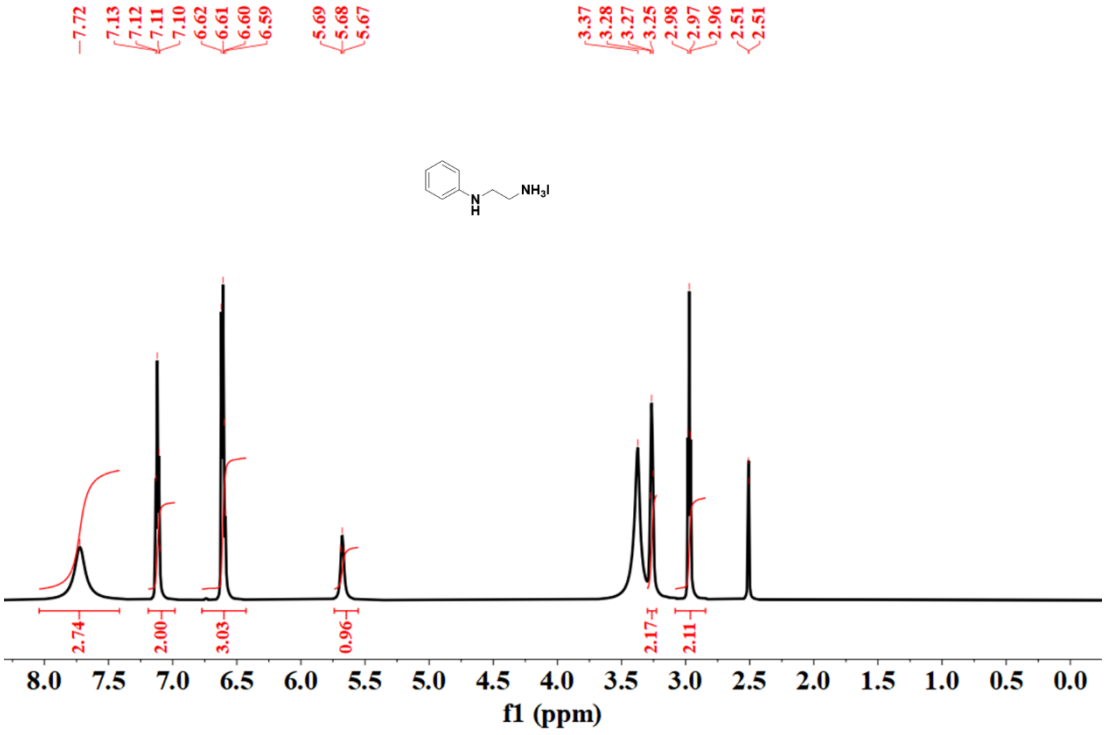


Figure S1. ^{1}H NMR spectrum of compound **PNEAI**.

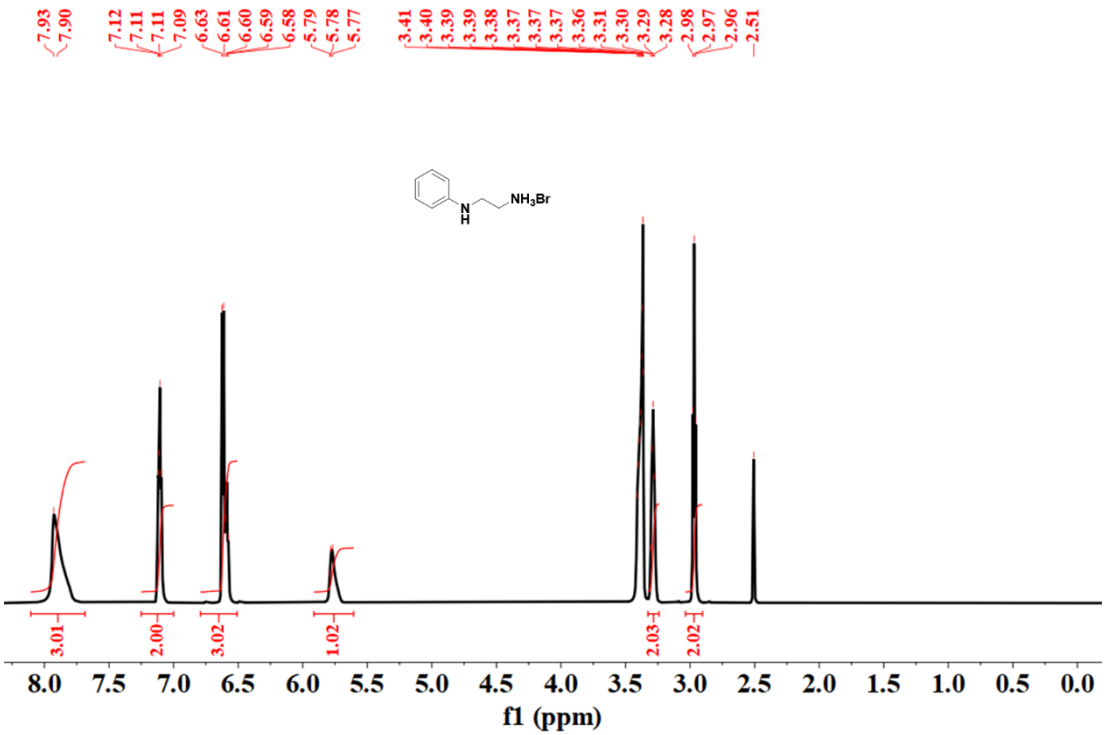


Figure S2. [1]H NMR spectrum of compound **PNEABr**.

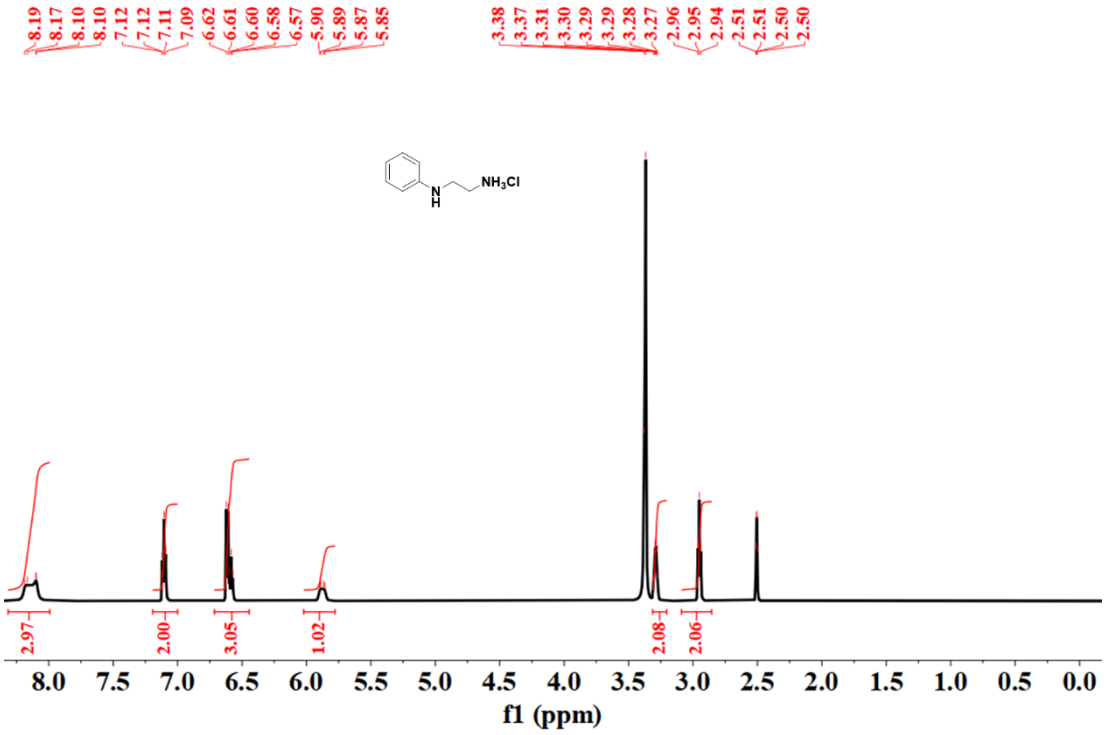


Figure S3. [1]H NMR spectrum of compound **PNEACl**.

5. DFT simulation

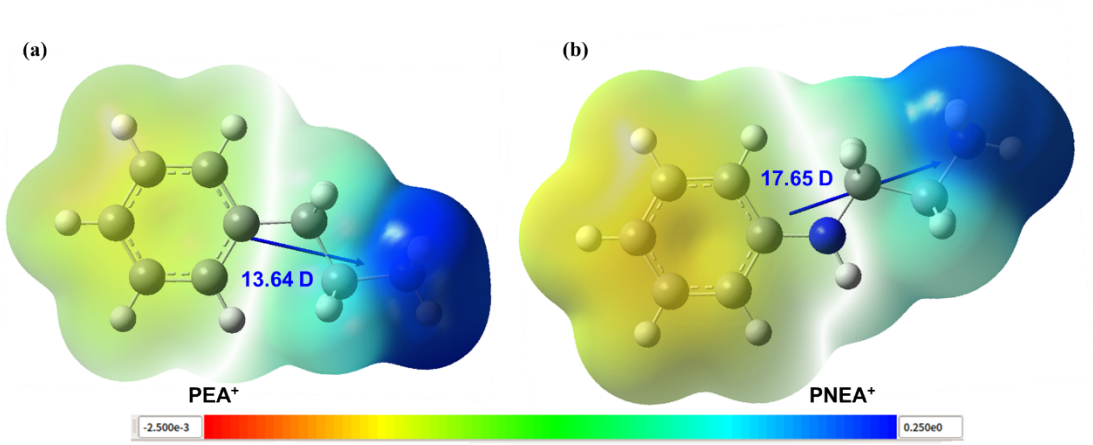


Figure S4. DFT 13.64 of (a) PEA^+ and (b) $PNEA^+$ using Gaussian 16 program.

6. Material Test

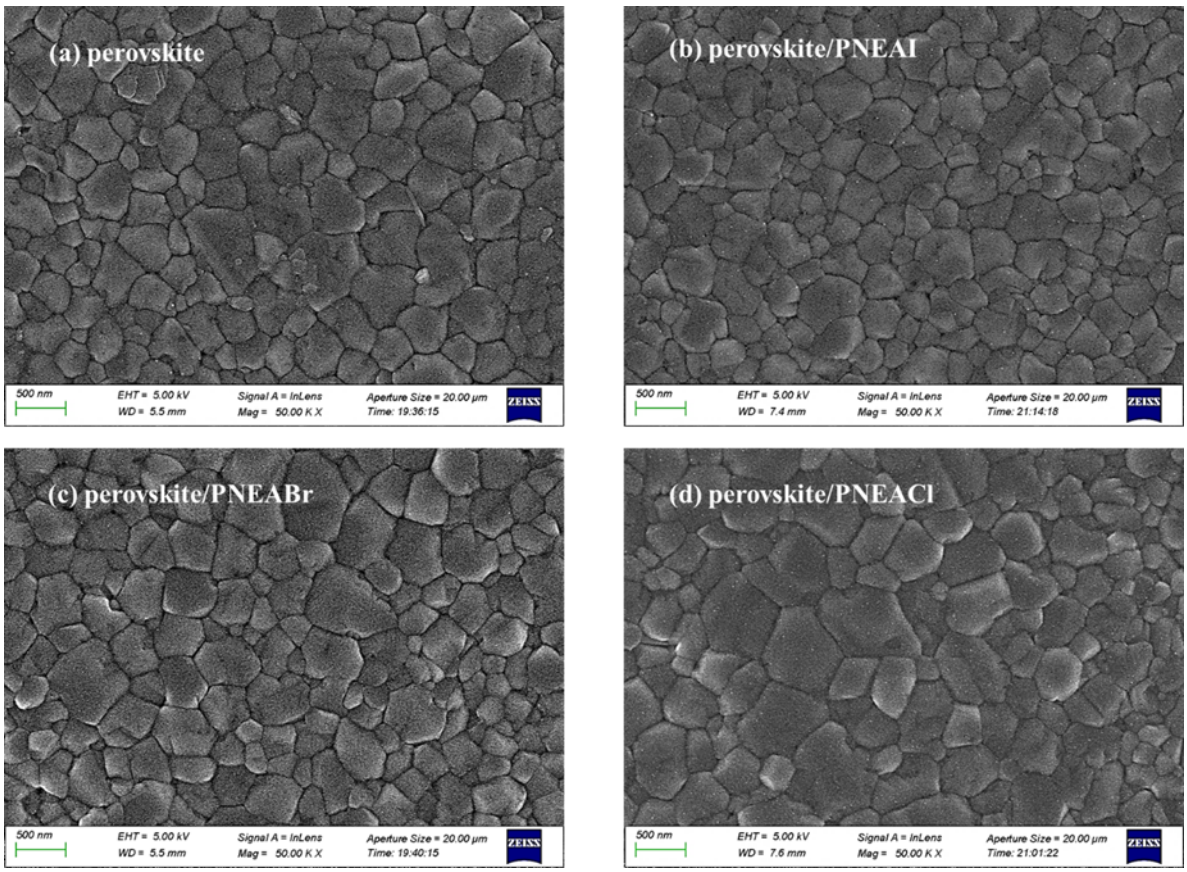


Figure S5. Top-view SEM images of (a) control (b) **PNEAI**-based (c) **PNEABr**-based and (d) **PNEACl**-based perovskite films.

7. Device Test

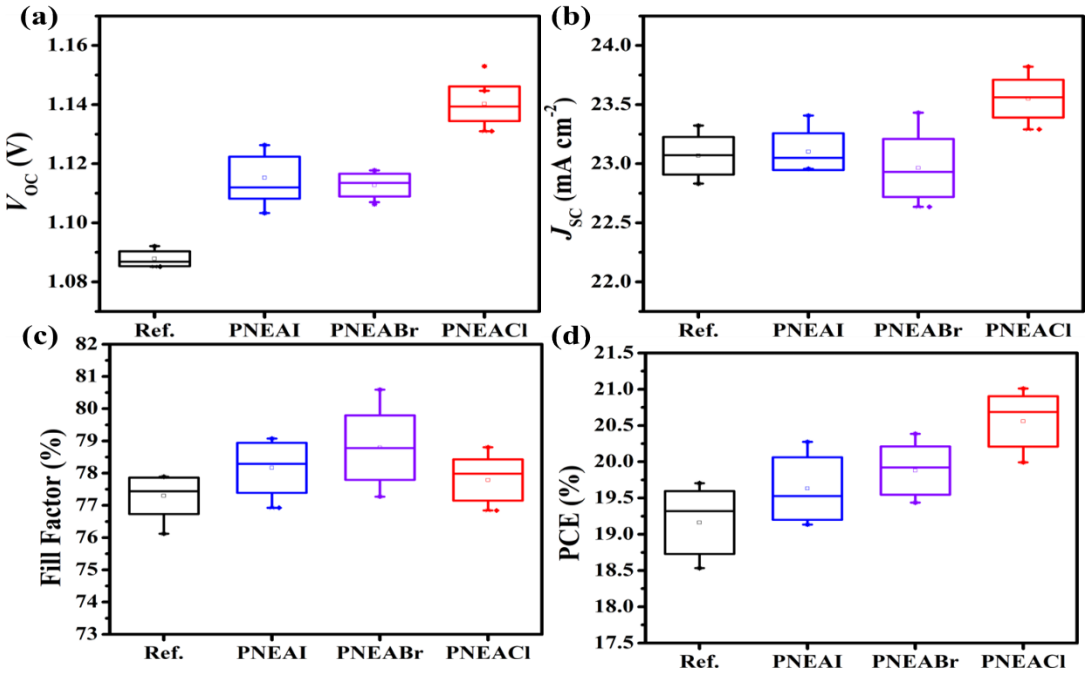


Figure S6. Box plots of (a) PCE, (b) V_{OC}, (c) J_{SC}, and (d) FF of corresponding devices.

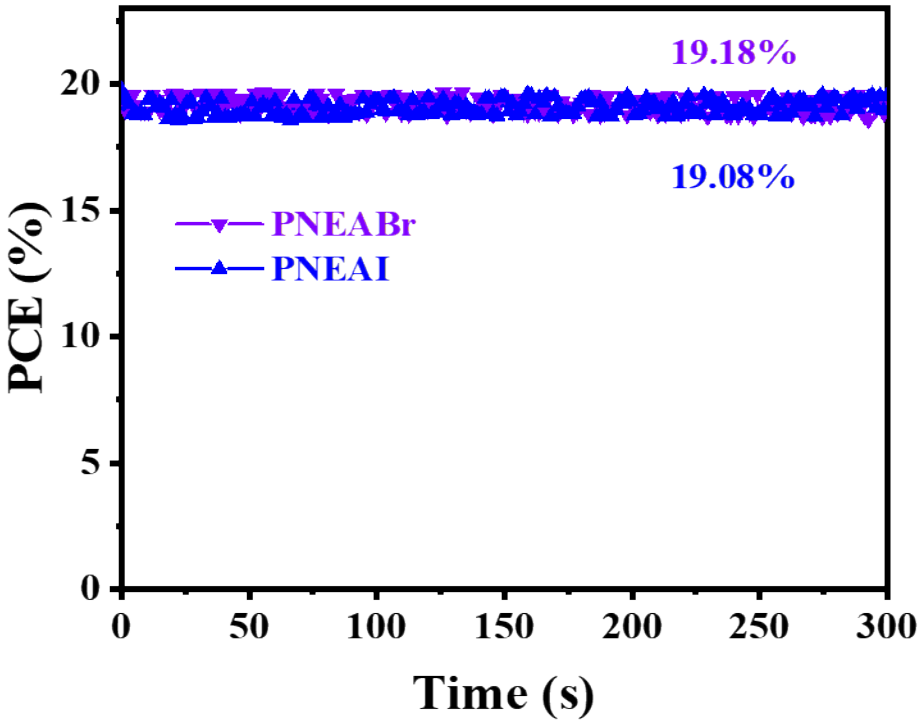


Figure S7. Stabilized power outputs for **PNEABr** and **PNEAI** devices.

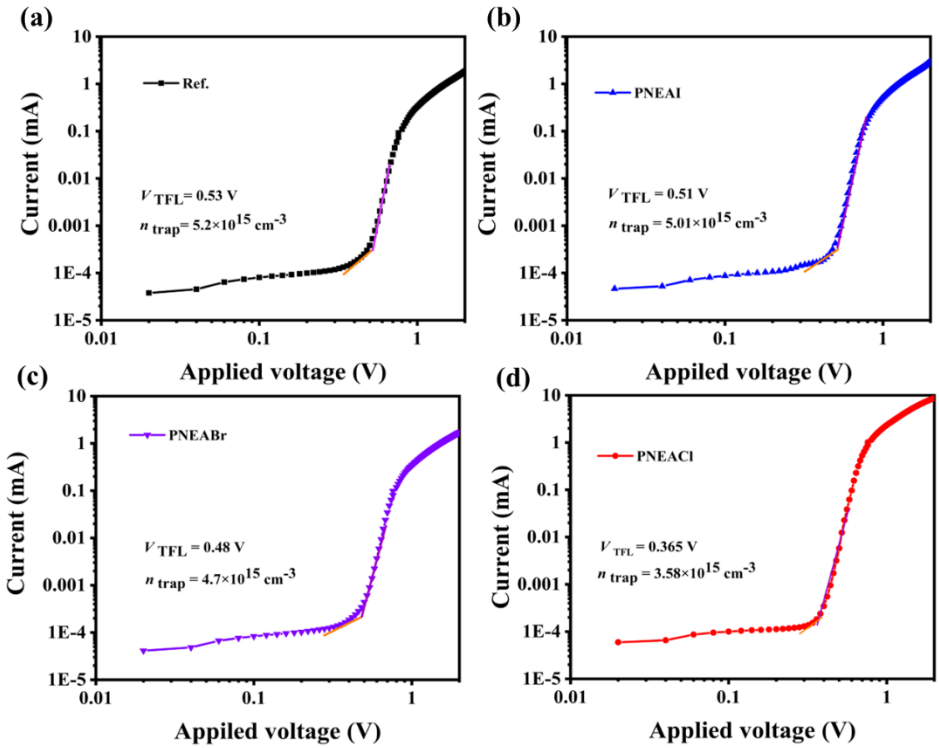


Figure S8. The SCLC curves of hole-only (ITO/PTAA/Perovskites/Au) devices: (a) control, (b) PNEACl-treated (c) PNEABr-treated, and (d) PNEAI-treated devices.

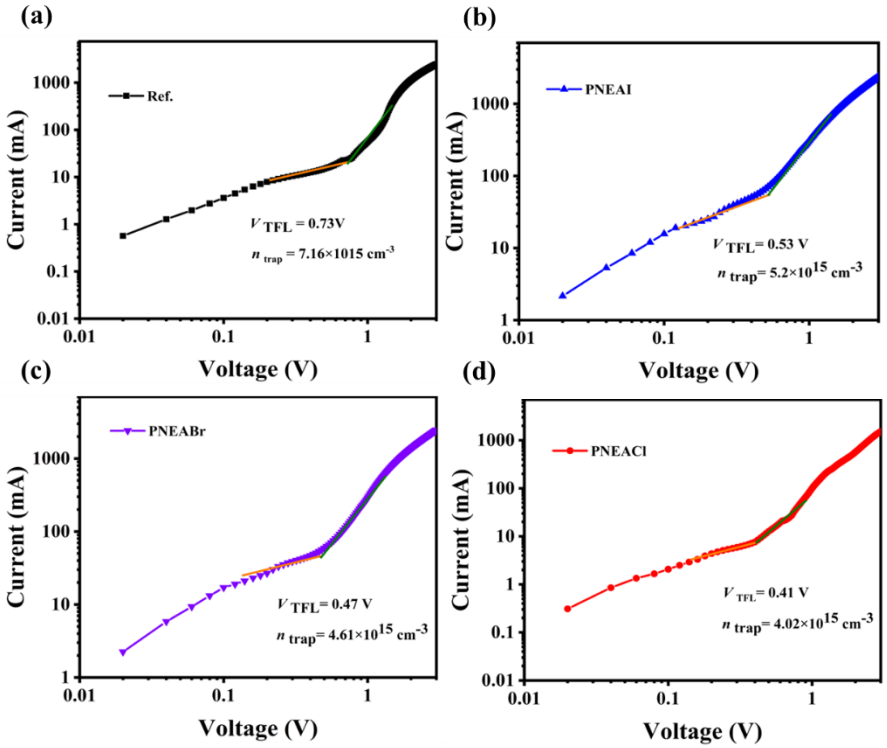


Figure S9. The curves of electron-only (ITO/C_{60}/Perovskites/C_{60}/Cu) devices: (a) control, (b) PNEACl-treated (c) PNEABr-treated, and (d) PNEAI-treated devices.

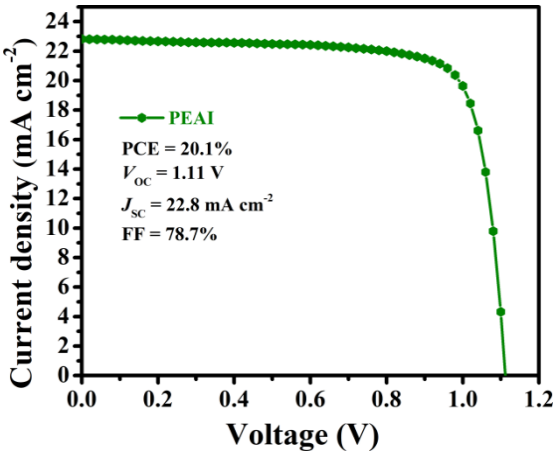


Figure S10. *J-V* curves of PEAI-treated PSCs.

8. Concentration Optimization

Table S1. Devices PCE of perovskite without and with various PNEA halide concentration passivation

Sample		V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
control		1.08 ± 0.00 （1.08）	22.79 ± 0.48 （23.32）	77.30 ± 0.57 （77.70）	19.16 ± 0.43 （19.70）
W/PNEACl	**0.5mg/ml**	1.11 ± 0.01 （1.11）	22.98 ± 0.28 （23.32）	77.52 ± 1.36 （77.38）	19.83 ± 0.28 （20.14）
	1mg/ml	1.13 ± 0.02 （1.15）	23.55 ± 0.16 （23.31）	77.18 ± 1.44 （78.10）	20.55 ± 0.35 （21.01）
	2mg/ml	1.14 ± 0.01 （1.14）	21.93 ± 0.56 （22.94）	74.30 ± 1.79 （75.42）	18.57 ± 0.48 （19.67）
W/PNEABr	**0.1mg/ml**	1.10 ± 0.00 （1.10）	22.27 ± 0.46 （22.77）	78.03 ± 0.68 （78.05）	19.20 ± 0.17 （19.43）
	0.5mg/ml	1.11 ± 0.00 （1.12）	22.82 ± 0.40 （22.64）	78.39 ± 1.39 （80.60）	19.88 ± 0.33 （20.39）
W/PNEAI	**0.1mg/ml**	1.10 ± 0.00 （1.10）	23.40 ± 0.13 （23.57）	78.25 ± 0.21 （78.07）	20.07 ± 0.13 （20.21）
	0.5mg/ml	1.12 ± 0.00 （1.12）	22.60 ± 0.65 （23.07）	77.96 ± 1.25 （78.46）	19.63 ± 0.43 （20.27）