

Stable perovskite solar cells with 22 % efficiency enabled by inhibiting migration/loss of iodide ions

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Experimental section

Materials

Titanium tetrachloride (TiCl₄), N,N-Dimethylform amide (DMF), dimethyl sulfoxide (DMSO), isopropanol (IPA) and chlorobenzene (CB) were purchased from Innochem. Polyetheramine (PEA) was obtained from Sigma-Aldrich. Formamide hydroiodate (FAI), methyl ammonium iodide (MAI) and lead iodide (PbI₂) were obtained from Liaoning You Xuan Technology Co. Ltd. 2,2',7,7'-tetrakis(*N,N*-dip-methoxyphenylamine)9,9'-spirobifluorene (Spiro-OMeTAD) and methyl ammonium bromide (MABr) were purchased from Xi'an Polymer Light Technology Corp. Methylammonium chloride (MACl) was purchased from Alfa Aesar. Bis(trifluoromethane) sulfonimide lithium salt (Li-TFSI), 4-*tert*-butylpyridine (TBP) and tris[2-((1 *H*-pyrazol-1-yl)-4-*tert*-butylpyridine)cobalt(III)tris(bis(trifluoromethylsulfonyl) imide)] (FK209) were purchased from Sigma-Aldrich. All the chemicals are used directly without further purification.

Device Fabrication

FTO glasses (15Ω sq⁻¹) were sequentially cleaned with DI-water, acetone, and ethanol in an ultrasonic bath for 20 min, respectively. After dried by a high-purity nitrogen, The FTO substrates were treated UV-ozone for 15min prior to use. For the ETL, the TiO₂ layers was deposited on FTO substrates by chemical bath deposition method. The FTO substrates were then immersed into TiCl₄/DI-water solution (*v:v* = 1: 8) at 70 °C for 30 min. Afterwards the FTO substrates were washed with water and ethanol, then dried in air, finally treated with UV ozone for 20 min. The perovskite films were fabricated by one-step anti-solvent method. The perovskite precursor solution was intended by dissolving 2.1 M PbI₂, 1.16 M FAI, 0.63 M MAI, 0.14 M MABr and 0.07 M MACl in DMF/DMSO mixed solvent (*v: v* = 9: 1). Then, add PEA solution into perovskite precursor solution to obtain perovskite precursor solution containing PEA molecules. The

precursor solution was stirred for 4 h at room temperature in a glove box and was filtered before use. In details, the perovskite precursor solution was spin-coated at 5,000 rpm for 30 s, diethyl ether (1 mL) was poured onto the substrate at start of spin coating 10 s. The yellow transparent films were then transferred to a hot plate and annealed at 150 °C for 16 min to obtain the black perovskite films. For the HTL, The Spiro-OMeTAD solution was prepared by dissolving 76 mg of Spiro-OMeTAD, 30 ul of TBP, 23 ul of FK209 (300 mg mL⁻¹ acetonitrile) and 20 ul of LiTFSI (520 mg·mL⁻¹ acetonitrile) in 1 ml of chlorobenzene, and then was stirred for 12 h at room temperature. Then, the Spiro-OMeTAD solution was spin-coated on the annealed black perovskite film at 4,500 rpm for 20 s to obtain a hole transport layer. Finally, 100 nm thick Au electrodes were deposited via the vacuum evaporation equipment at an atmospheric pressure of 10⁻⁴ Torr (Kurt J. Lesker).

Characterization

The photocurrent density-voltage (*J-V*) curves were measured under AM 1.5 simulated sunlight (100 mW·cm⁻²) from solar simulator (Enlitech Technology Co., Ltd) after spectral correction, which was recorded by IVS-KA5000 measurement software and a digital source meter (Keithley 2400). 25 cells of PSCs with and without PEA were measured the photocurrent density-voltage (*J-V*) curves. The morphology of the perovskite films was measured using a scanning electron microscope (HITACHI Regulus , SU8100). Steady-state photoluminescence (PL) spectra was measured using a fluorescence spectrometer (Edinburgh FLS1000). XPS testing performed on ESCALAB Xi+ (Thermo Fisher) instrument. The trap density of the perovskite films was measured by a Keithley 2400 by space charge limited current (SCLC) test. The absorption spectrum of IPA solution was obtained by UV spectrophotometer (UV-1900). The static contact angle of the perovskite film was obtained by a contact angle meter (OCA15EC). For MPP tests, obtained in the same solar simulator with the sunlight intensity controlled by the filter.

DFT calculation

The structural optimization and electronic structure calculations were carried out by Cambridge Serial Total Energy Package (CASTEP) in Materials studio. The generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) functional was employed. Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm was used for the structural optimization of the model with the following optimization parameters: the calculation was expanded by using the ultrasoft pseudopotential with a cutoff energy of 490 eV, and the total energy was converged to 2×10⁻⁵ eV. The structural optimization was optimized until the force tolerance on each atom was smaller than 0.05eVÅ⁻¹, the stress tolerance was smaller than 0.1 GPa, and the displacement tolerance was smaller than 0.002 Å. The Monkhorst-Pack grids with the actual spacing of 0.052 Å⁻¹ and SCF tolerance of 2×e⁻⁶ eV/atom were used in all DFT simulations.

FAPbI₃ possesses cubic structure with space group Pm-3m at room temperature with a 3×3×1 super cell and a 20 Å vacuum slab to investigate the adsorption of I⁻, I₂ and PEA. All the adsorption molecules were placed on the super cell surface to optimize to convergence.

Table S1. Performance parameters of PSCs with different concentrations of 0, 2, 5, 8 and 11 $\mu\text{l}\cdot\text{mL}^{-1}$.

sample	Jsc	Voc	FF	PCE
Control	24.09	1.06	73.02	18.79
2 μl	24.41	1.09	75.77	20.18
5 μl	24.55	1.12	80.11	22.02
8 μl	24.47	1.12	77.63	21.45
11 μl	24.35	1.08	74.55	19.77

Table S2. Statistical distribution of device parameters of PSCs with different concentrations of 0, 2, 5, 8 and 11 $\mu\text{l}\cdot\text{mL}^{-1}$.

sample	Number of cells	Highest PCE	Lowest PCE	Average of PCE
Control	25	19.71	16.59	18.50 \pm 0.81
2 μl	25	20.18	18.87	19.23 \pm 0.58
5 μl	25	22.02	21.15	21.53 \pm 0.28
8 μl	25	21.45	20.01	20.76 \pm 0.41
11 μl	25	19.77	17.79	18.61 \pm 0.71

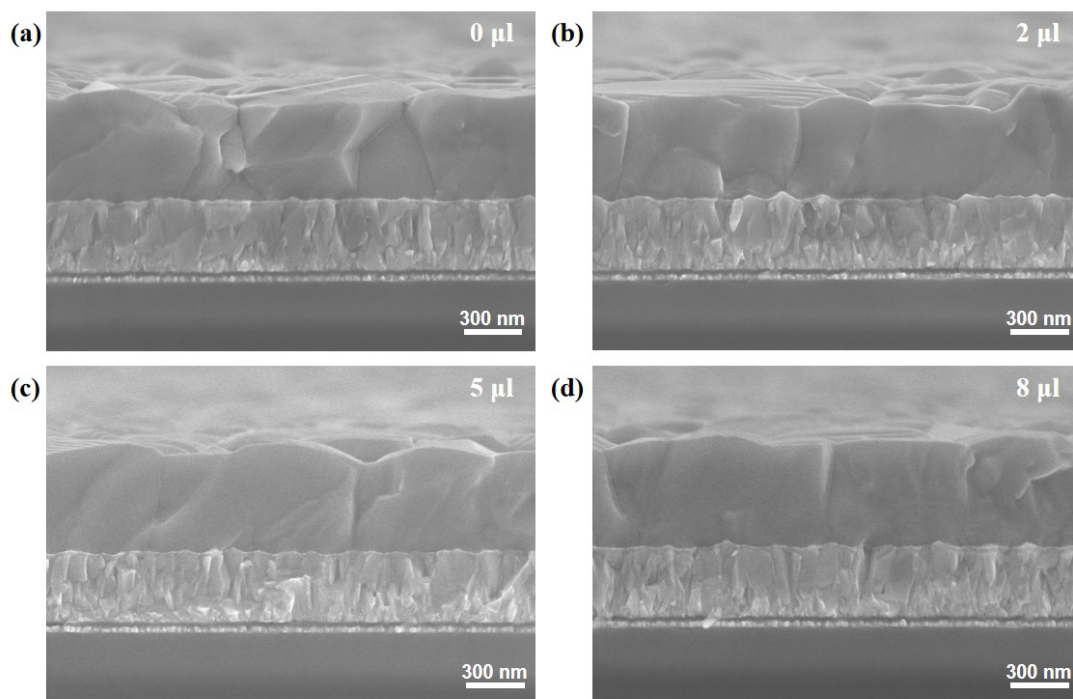


Fig. S1 The cross-section SEM images of perovskite films (a) without PEA; with PEA (b) 2 μl ; (c) 5 μl ; (d) 8 μl .

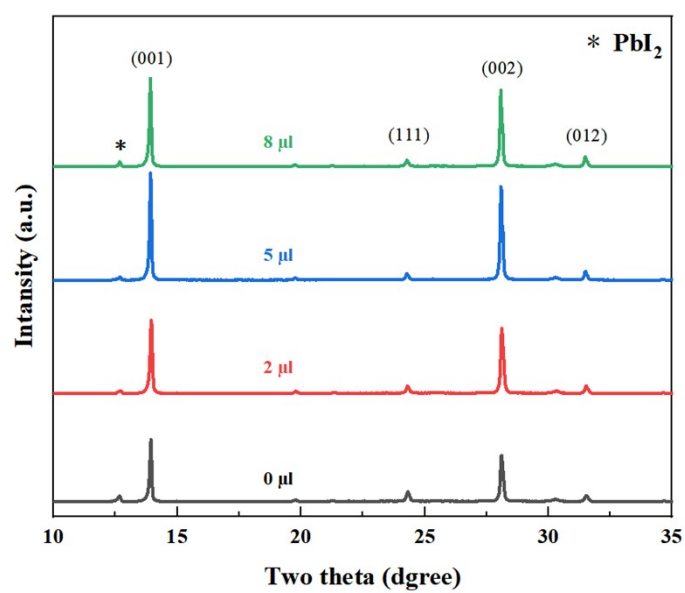


Fig. S2 XRD spectra for the perovskite with various PEA concentration

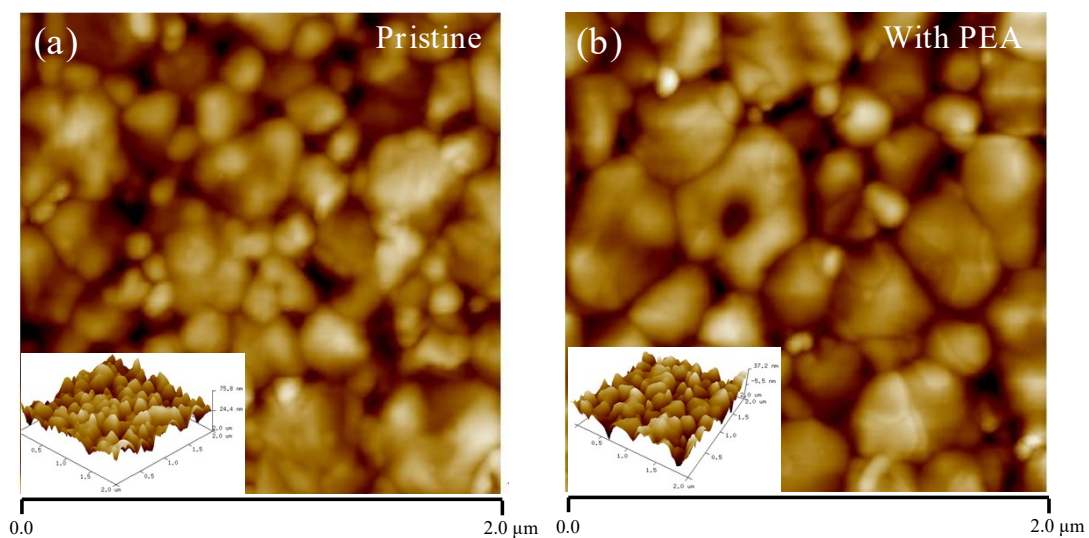


Fig. S3 AFM images for the topography and roughness of (a) pristine perovskite and (b) perovskite with PEA.

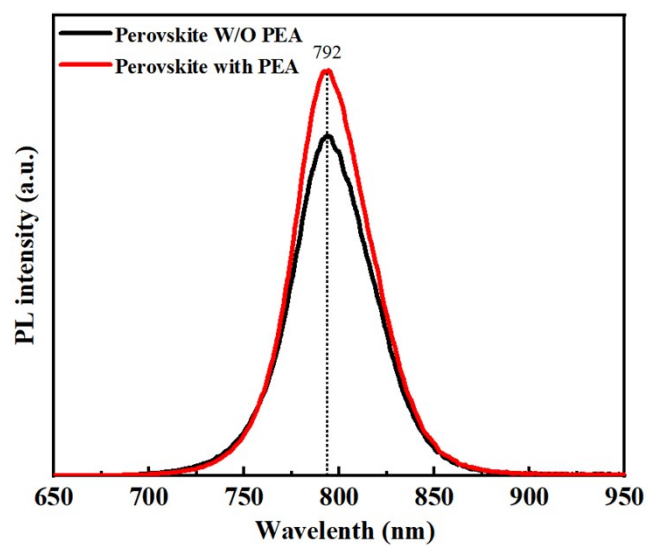


Fig. S4 steady-state PL spectra of perovskite films W/O (control) and with PEA

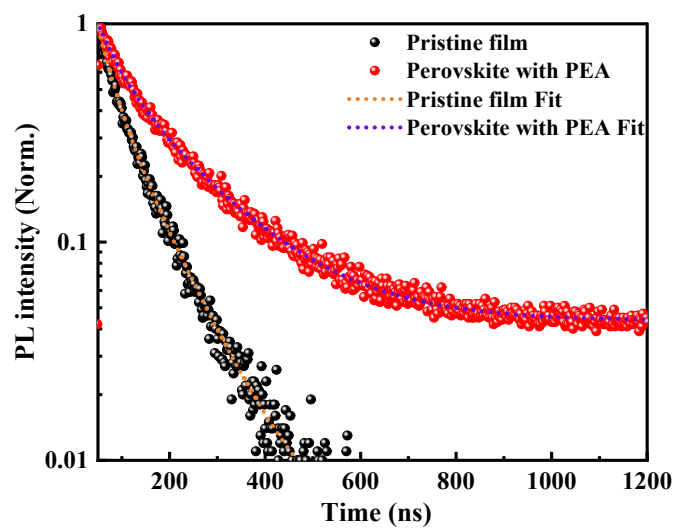


Fig. S5 Time-resolved photoluminescence decay spectrum results of perovskite films W/O (control) and with PEA.

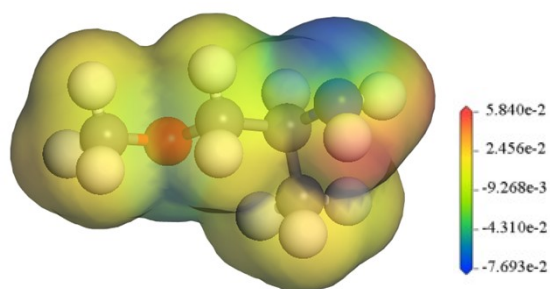


Fig. S6 The electrostatic potential (ESP) of PEA. The illustration on the right shows the scale of ESP equipotential line, blue is negative potential, red is positive potential.

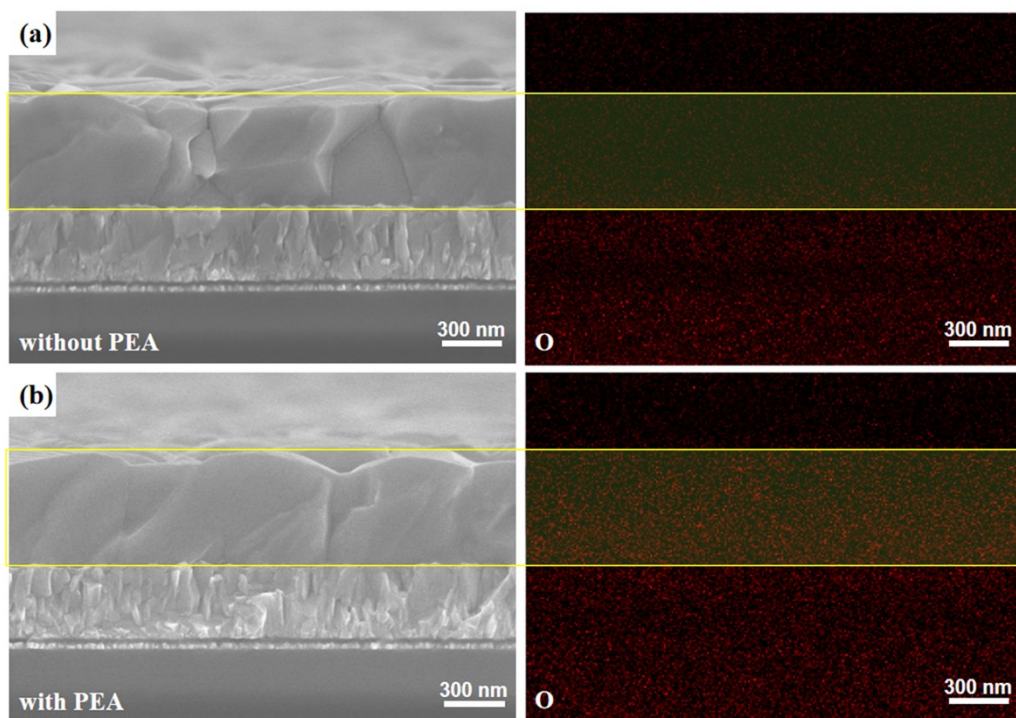


Fig. S7 Cross-sectional SEM-EDS in real PSCs (a) without or (b) with PEA after the annealing. The yellow square marks the O inside the perovskite.

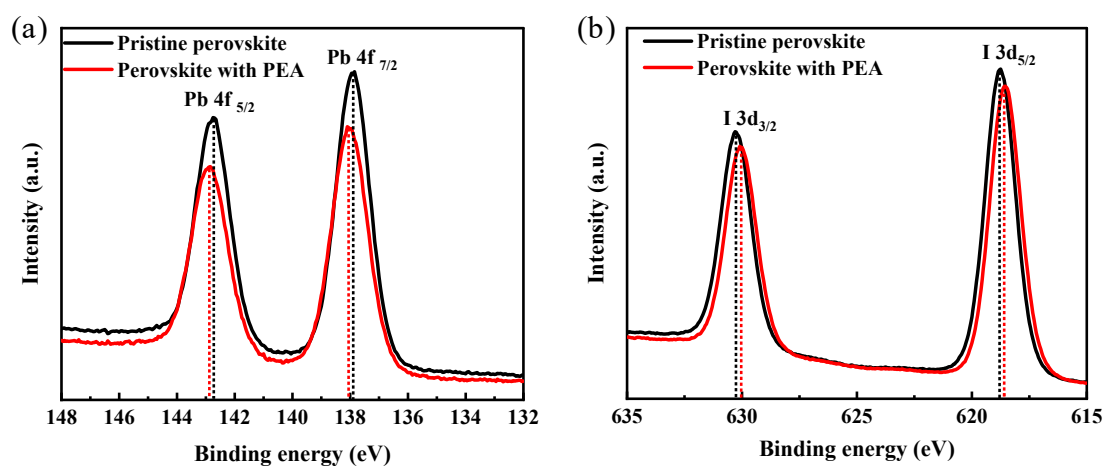


Fig. S8 XPS spectra of perovskite films W/O and with PEA: (a) Pb 4f spectra and (b) I 3d spectra.

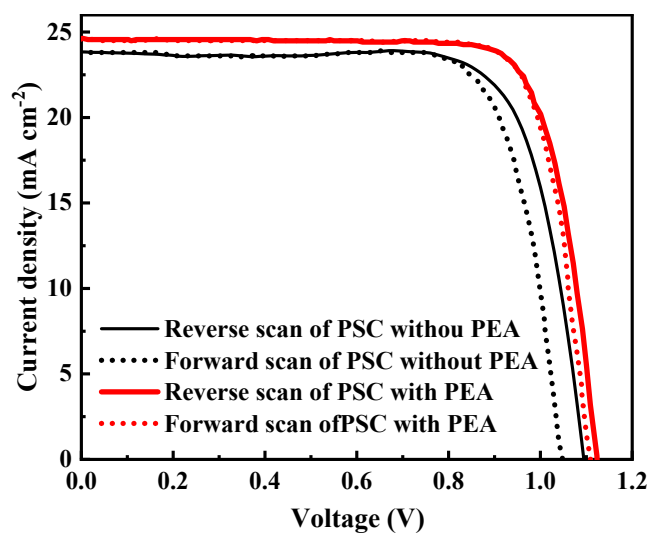


Fig. S9 Forward and reverse scanning J-V curves of the PSCs without and with PEA.

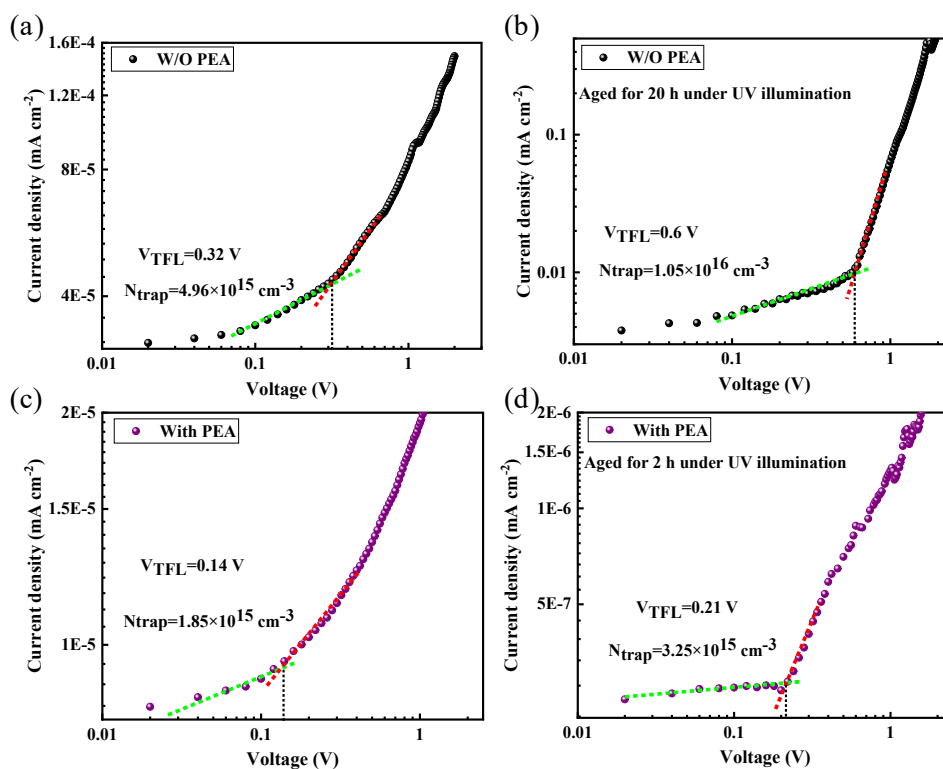


Fig. S10 Dark J - V curves of the devices with the structure of FTO/TiO₂/perovskite/PCBM/Au for (a) perovskite films, and (b) perovskite films after 20 hours of UV illumination; (c) perovskite films with PEA, and (d) perovskite films with PEA after 20 hours of UV illumination.

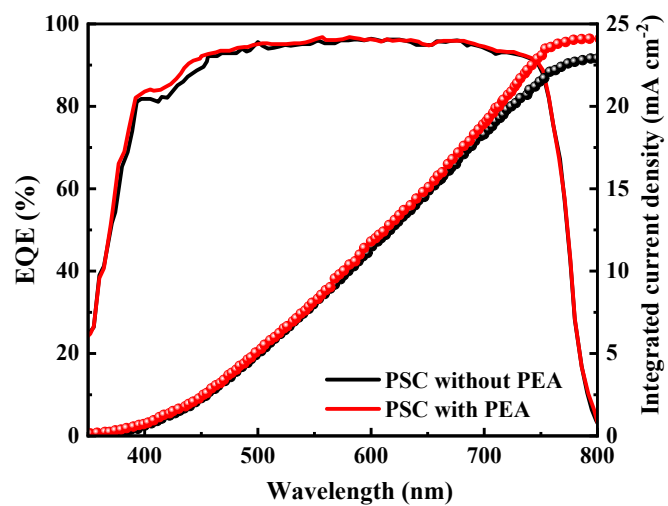


Fig. S11 IPCE spectra obtained for the devices with and without PEA.