

## Supporting information

### Highly Reproducible Self-Assembled Monolayer Based Perovskite Solar Cells via Amphiphilic Polyelectrolyte

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**Keywords:** Perovskite, Amphiphilic Conjugated Polyelectrolyte, Self-Assembled Monolayer, Buried Interface, Band bending

## Experimental section

### Material preparation:

Lead iodide ( $\text{PbI}_2$ , 99.99%), lead bromide ( $\text{PbBr}_2$ , 98%), [2-(3,6-Dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic acid (Meo-2PACz, 98%), methylamine hydrochloride (MAHCl, 98%) and SAMs were from TCI. Methylamine bromide (MABr) and formamidinium iodide (FAI) were from Greatcell Solar. Poly(9,9-bis(3'-(N,N-dimethyl)-N-ethylammonium-propyl-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene))dibromide (PFN-Br) was from 1-Material. 1-Methyl-2-pyrrolidinone (NMP, anhydrous, 99.5%), N, N-dimethyl formamide (DMF, anhydrous, 99.8%), 2-propanol (IPA, anhydrous, 99.5%), methanol (MeOH, anhydrous, 99.8%), and ethanol (EtOH, 99.8%) were from Sigma-Aldrich. Diethyl ether (anhydrous, 99.0%) was from JT Baker. All chemicals were used as received without any further purification.

### Precursor solution preparation:

The perovskite precursors solutions,  $\text{FA}_{0.97}\text{MA}_{0.03}\text{Pb}(\text{I}_{0.97}\text{Br}_{0.03})_3$  and  $\text{FA}_{0.6}\text{MA}_{0.4}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ , were prepared by mixing 1.3 M  $\text{FAPbI}_3$  (dissolved in mixed solvents, DMF:NMP=8:2 vol.) and 1.3 M  $\text{MAPbBr}_3$  (dissolved in mixed solvents, DMF:DMSO=8:2 vol.).

### Device fabrication:

The glass-ITO substrates were ultrasonically washed with deionized water, acetone, and isopropanol for 10 minutes in sequence. After drying by  $\text{N}_2$ , the cleaned substrates were treated with ultraviolet ozone for 1 hour. A SAM layer was deposited by spin-coating 1 mM SAMs solution at 3000 rpm for 20 seconds with 10 seconds dwell time before the spin-coating process. Then the ITO/SAMs was placed on a  $100^\circ\text{C}$  hot plate for 10 minutes. For the device with a PFN-Br layer, the PFN-Br solution (0.05 wt% PFN-Br in methanol) was spin-coated onto the ITO/SAMs at 4000 rpm for 220 seconds. Then, 1.3M perovskite precursor solution was spin-coated onto the substrates at 4000 rpm for 20 seconds. At 10 second of the spin-coating process, 0.4 ml diethyl ether was dripped onto the substrate. After spinning, MAHCl (solution in IPA) was coated at 4000 rpm for 20s. Both as-deposited perovskite thin films were heated at  $60^\circ\text{C}$  for 5 min and then placed on  $100^\circ\text{C}$  hot plate for 1 hour. The device was then completed with C60 (40nm, as ETL), BCP (5nm), and Cu (100nm) through thermal evaporation.

### Preparation process to expose the buried interface

The epoxy was sandwiched by the top glass and bottom substrate, followed by UV-light illumination to cure the epoxy. After the epoxy is fully cured, we then removed the perovskite layer from the bottom substrate for further SEM examination. Because of the stronger adhesion between perovskite and cured epoxy, the perovskite thin film remained adhered on the glass/epoxy substrate and become the upside-down perovskite film after the two substrates were separated.

### Characterizations:

The current density-voltage (J-V) characteristics were measured by AM 1.5G solar simulator purchased from Enlitech. The light intensity was calibrated by a certified silicon reference cell. The reverse scan started from  $V_{oc}$  to  $J_{sc}$  ( $1.2\text{ V} \rightarrow -0.2\text{ V}$ ) and the forward scan started from  $J_{sc}$  to  $V_{oc}$  ( $-0.2\text{ V} \rightarrow 1.2\text{ V}$ ), with a scan speed of  $20\text{ mV s}^{-1}$ . Scanning electron microscope (SEM) images were obtained using the German brand Zeiss ULTRA PLUS. X-ray diffraction patterns were acquired by Bruker D8 Discover. Contact angle measurements were acquired by *Kriiss* G10. The steady-state photoluminescence (PL) measurement of the thin film and the PL quenching efficiency of the device measured under open circuit and short circuit conditions

(PLQEoc-sc) were measured by the FS5 spectrofluorometer of Edinburgh Instruments Ltd. The excitation wavelength was set at 600 nm, and the signal was collected at 1 nm s<sup>-1</sup> and scanned twice. Time-corrected single photon counting system (TCSPC) measurements (OC conditions and SC conditions) were also conducted on an Edinburgh Instruments Ltd. FS5 spectrofluorometer. AFM, C-AFM, and KPFM measurements were performed by the Bruker Dimension ICON with Scan Asyst. C-AFM measurements were used to scan the electrical anomaly of the film surface at 200 mV condition. Then, the KPFM measurement of perovskite film was scanned with a small bias voltage applied for the actual measurement. XPS was measured using PHI 5000 VersaProbe III of ULVAC-PHI Ltd. We conducted ambient photoemission spectroscopy (APS) measurements using an SKP5050 instrument (KP Technology). The samples were prepared and kept in the dark before the measurements were taken. The valence band edge (or HOMO) of the samples was determined by measuring the photoemission in the 4-7 eV energy range under UV-light illumination. A ToF-SIMS depth profile analysis was carried out using the ION-TOF TOF-SIMS V instrument on thin films of ITO/MeO-2PACz/Perovskite and ITO/MeO-2PACz/PFN-Br/Perovskite, which were prepared with a surface area of 1x1 cm<sup>2</sup>. During the analysis, Cs<sup>+</sup> primary ions were used to sputter the surfaces, while a pulsed Bi<sup>+</sup> primary ion beam was used for analysis. The analysis area was positioned within the Cs<sup>+</sup> raster scanning area to ensure that the analysis was performed on the same region of the sample.

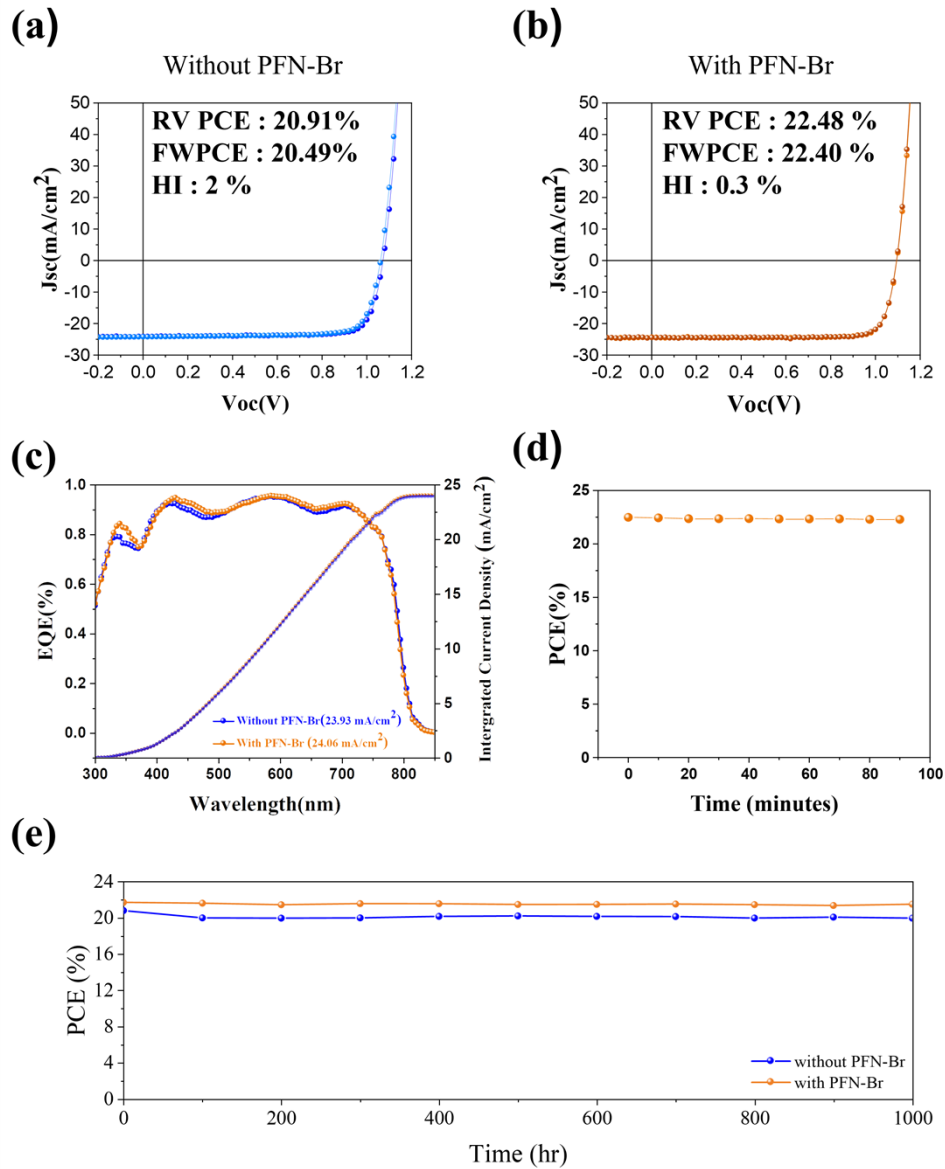


Figure S1. Representative JV curves of the champion perovskite solar cells (a) without PFN-Br (b) with PFN-Br under the illumination of 1 sun intensity and (c) the corresponding device's EQE. (d) Stabilized PCE of champion perovskite device with PFN-Br under solar simulator (AM 1.5G). The JV characteristics were performed every 10 minutes, and the device held at maximum power point between the intervals of the measurements. (e) The long-term stability of the devices stored in N<sub>2</sub> filled glove box.

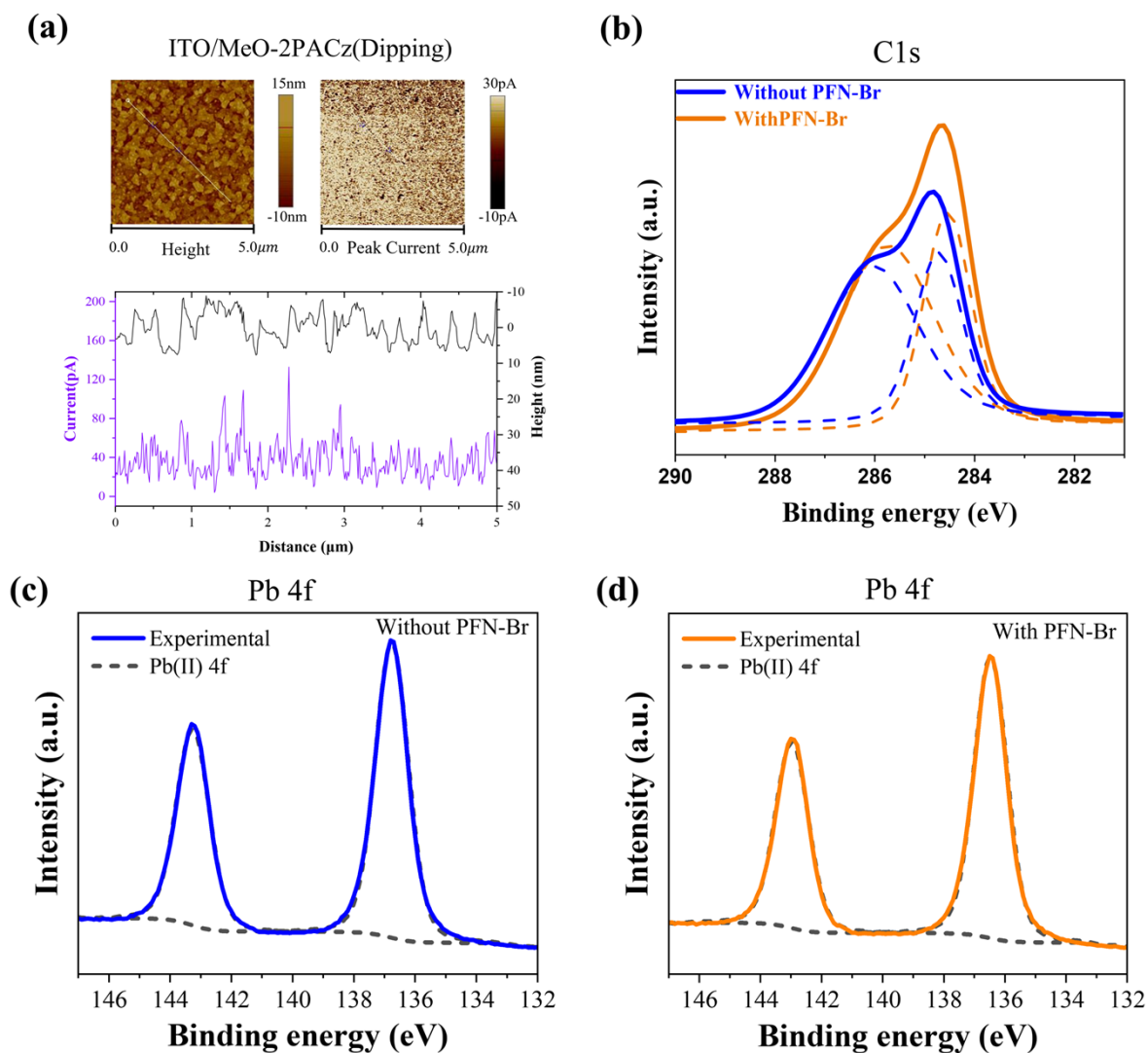


Figure S2. (a) Conductive atomic force microscopy (c-AFM) of the height and current map of ITO/MeO-2PACz substrate, in which the MeO-2PACz is deposited by the dipping method. (b) Fitting of the C1s peak in XPS spectra of the perovskite with and without the presence of the PFN-Br layer. Fitting of the Pb 4f peak in XPS spectra of the perovskite: (c) without the PFN-Br layer, and (d) with the PFN-Br layer

Table S1. Characteristics of the C1s and Pb 4f Peaks from XPS Analysis of Perovskite Films, detailing Peak Center, Full Width at Half Maximum (FWHM), Height, and Integrated Peak Area, corrected area using an RSF of 1 (C 1s) and 8.329 (Pb 4f) for both films without (W/O) and with PFN-Br.

W/O PFN-Br	Center (eV)	FWHM	Area	Corrected Area	C:Pb
C-N	285.9	2.35	14584	12467	0.2:1
C-C	284.8	1.22	11028		
Pb 4f7/2	136.8	1.28	272707	54217	
Pb 4f5/2	143.3	1.28	178868		
With PFN-Br	Center (eV)	FWHM	Area		
C-N	285.7	2.37	15487	15412	0.3:1
C-C	284.6	1.18	11484		
Pb 4f7/2	136.5	1.28	260390	51592	
Pb 4f5/2	143.0	1.28	169320		

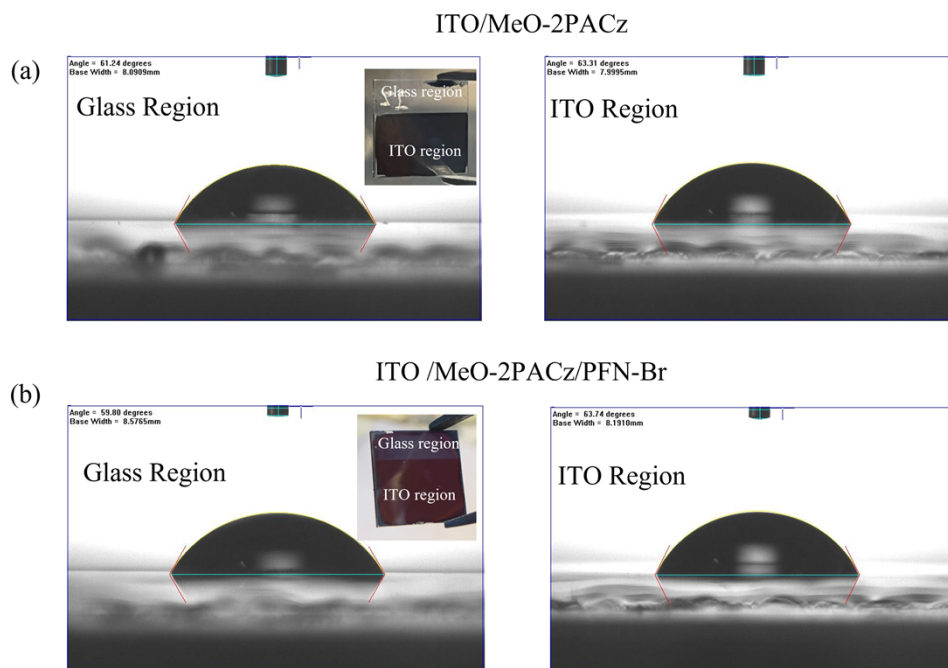


Figure S3. Contact angle test of different layers (a) ITO/Meo-2PACz (b) ITO/Meo-2PACz/PFN-Br. The inserted picture is the corresponding substrate deposited with a perovskite layer.

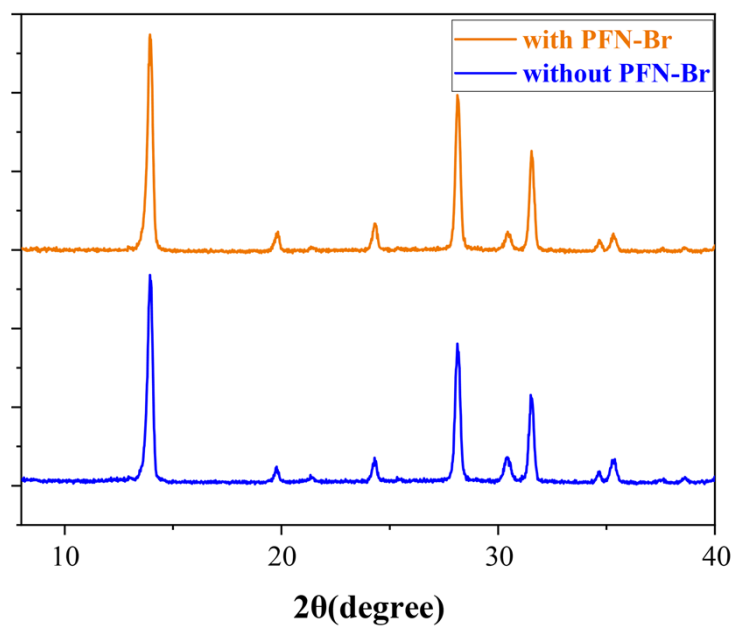


Figure S4. The XRD pattern of perovskite thin films with PFN-Br and without PFN-Br.

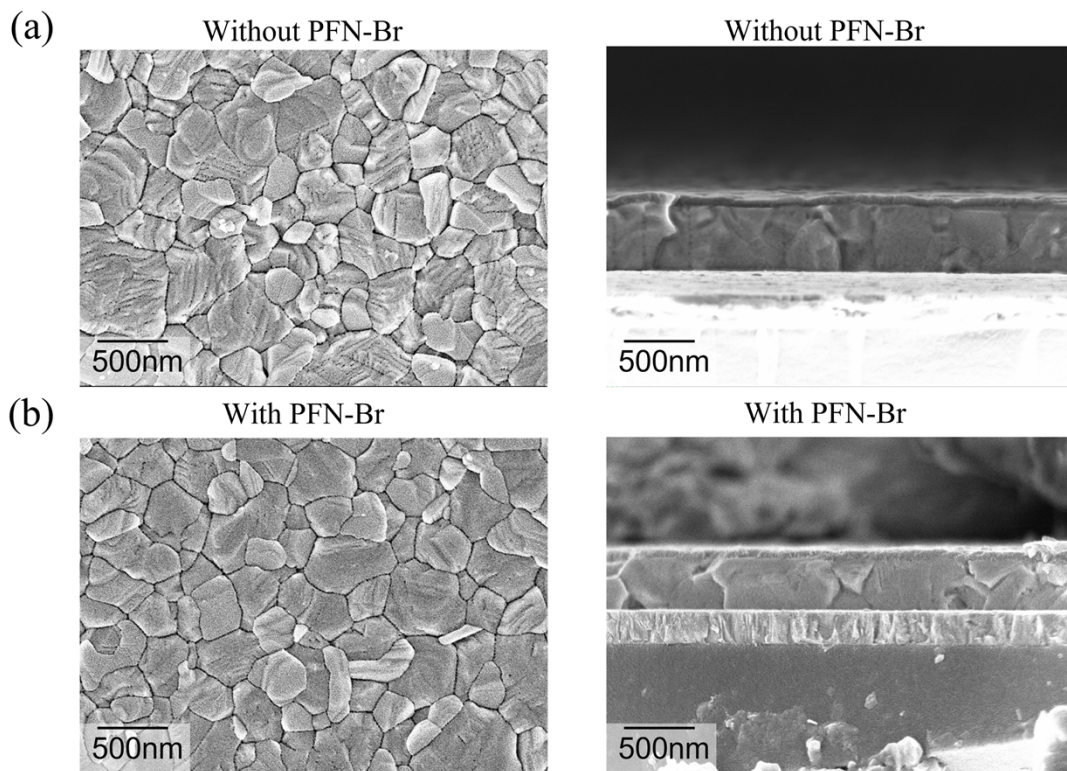


Figure S5. Top view and cross-sectional scanning electron microscopy (SEM) images of (a) ITO/MeO-2PACz/Perovskite (b) ITO/MeO-2PACz/PFN-Br/Perovskite

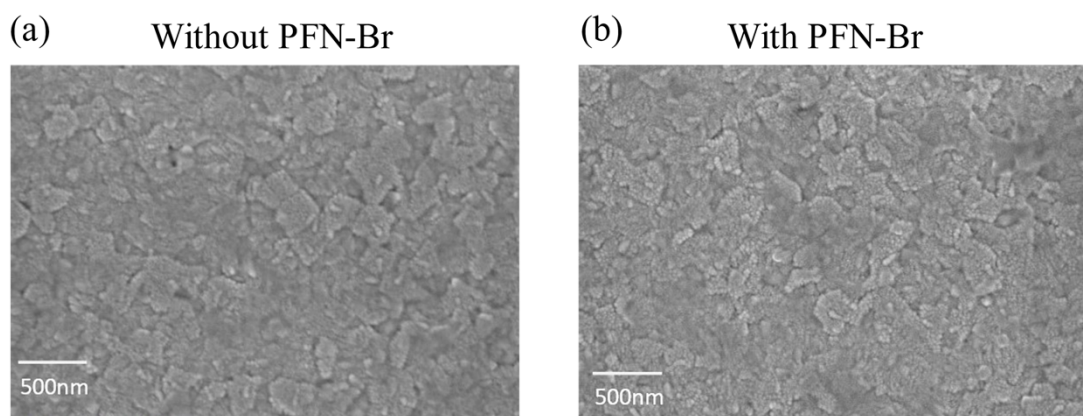


Figure S6. Top view SEM images of ITO detached from the sample consisted of (a) ITO/MeO-2PACz/Perovskite (b) ITO/MeO-2PACz/PFN-Br/Perovskite



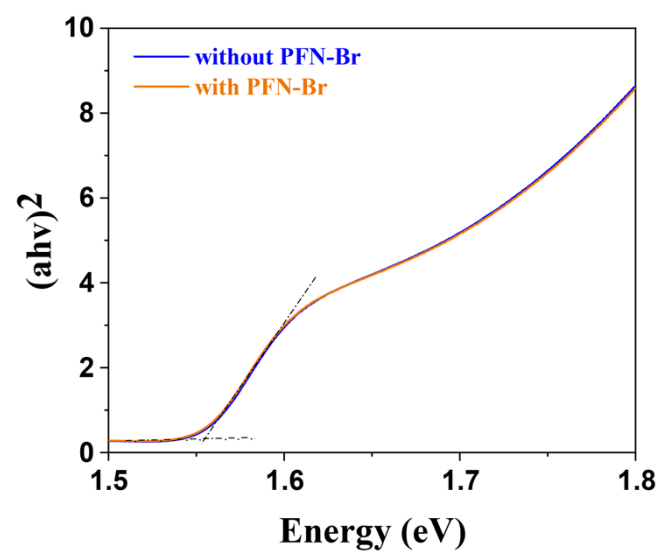


Figure S7. The Tauc plot of perovskite films derived from the UV-absorbance.

Table S2. Double exponential fitting of TCSPC data for perovskite films, illustrating the comparison between samples with and without PFN-Br. The fit is represented by  $y = A_1 \times \exp(-x/\tau_1) + A_2 \times \exp(-x/\tau_2) + y_0$ .

<b>Without PFN-Br</b>	<b>A<sub>1</sub></b>	<b>τ<sub>1</sub> (ns)</b>	<b>A<sub>2</sub></b>	<b>τ<sub>2</sub> (ns)</b>
Open circuit condition	0.68	3.37	0.27	10.38
Short circuit condition	0.58	1.32	0.45	3.74
<b>With PFN-Br</b>	<b>A<sub>1</sub></b>	<b>τ<sub>1</sub> (ns)</b>	<b>A<sub>2</sub></b>	<b>τ<sub>2</sub> (ns)</b>
Open circuit condition	0.69	4.59	0.27	23.40
Short circuit condition	0.57	0.73	0.47	3.46

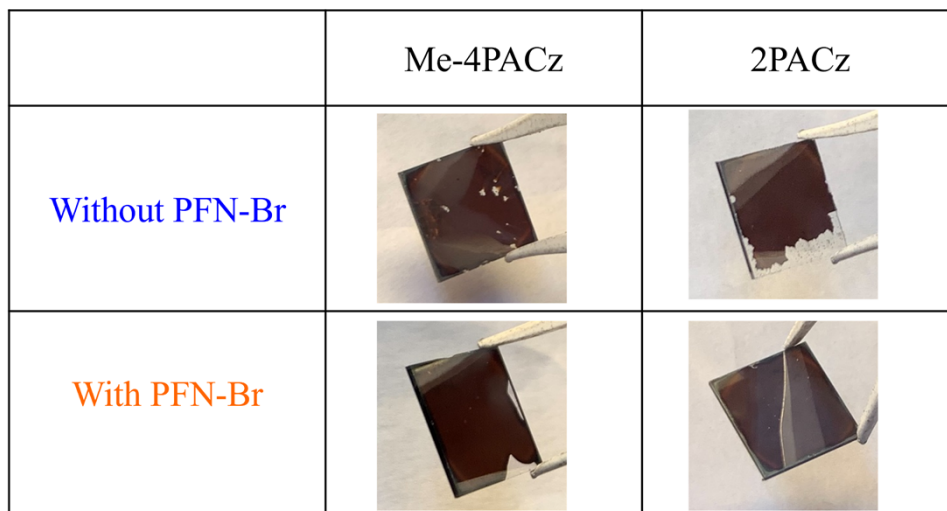


Figure S8. Pictures of the perovskite deposited on (a) MeO-2PACz (b) Me-4PACz (c) 2PACz with/without PFN-Br.

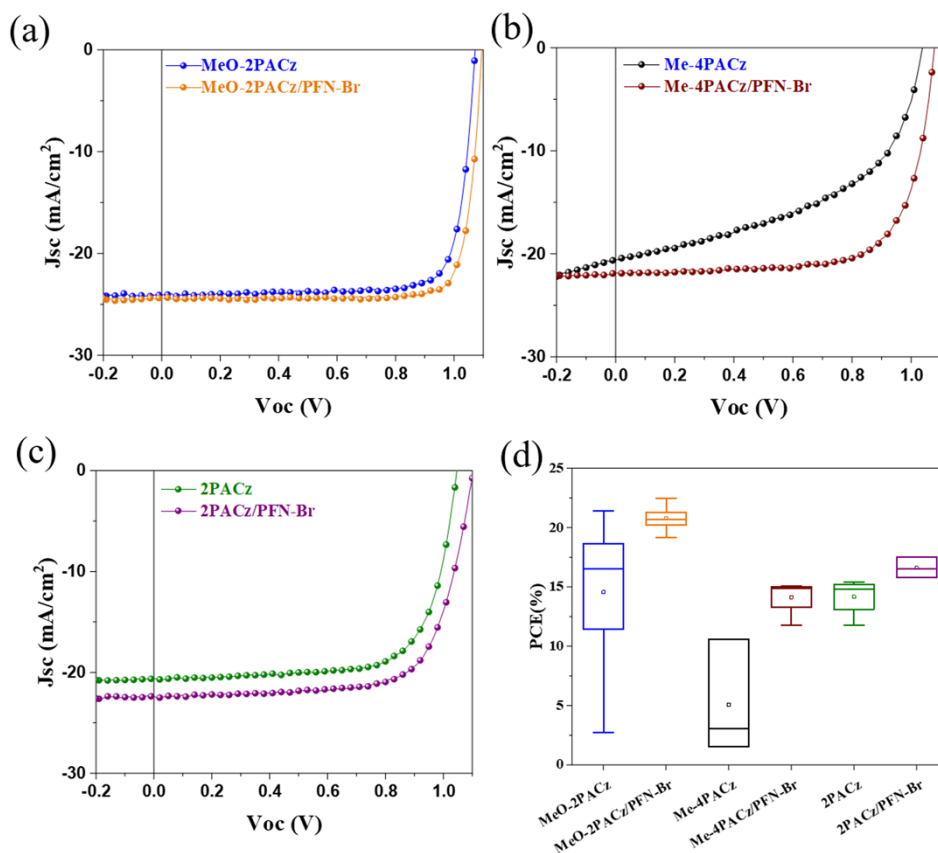


Figure S9. JV curves of devices using different SAMs with/ without PFN-Br (a) MeO-2PACz (b) Me-4PACz (c) 2PACz. The comparison of PCEs of perovskite devices using different SAMs with/without PFN-Br.

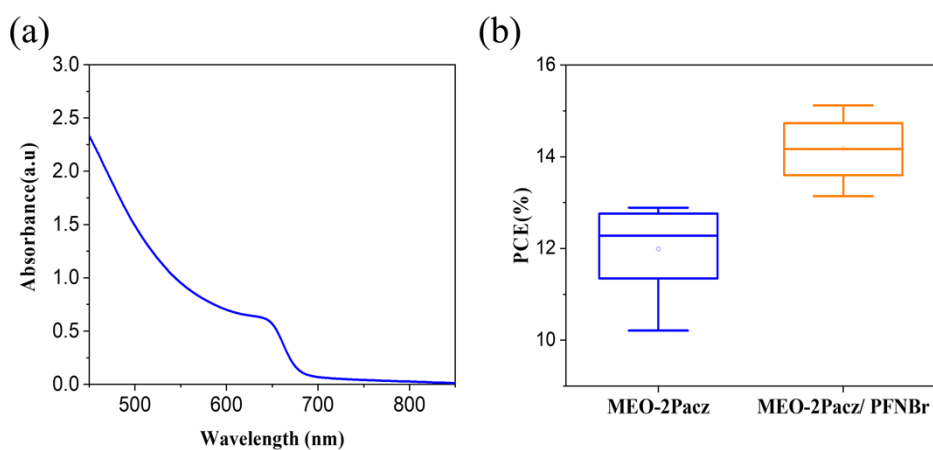


Figure S10. (a) UV-Vis spectrum of  $FA_{0.6}MA_{0.4}Pb(I_{0.6}Br_{0.4})_3$  perovskite film. (b) The PCEs of  $FA_{0.6}MA_{0.4}Pb(I_{0.6}Br_{0.4})_3$  perovskite device with/without PFN-Br.