

Multifunctional Dual-interface Layer Enables Efficient and Stable Inverted Perovskite Solar Cells

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1. Experimental Section

1.1 Materials

Laser etched ITO ($1.5 \times 1.5 \text{ cm}^2$, 7-9 Ω , 0.7 mm) glass substrates Lead iodide (PbI_2 , 99.9%), Formamidinium hydroiodide (FAI, >98%) were purchased from Advanced Election Technology Co. Ltd., China. Poly [bis (4-phenyl) (2, 4, 6-trimethylphenyl) amine] (PTAA, $M_w \approx 33500$), Poly[9,9-bis(3'-(N,N-dimethyl)-Nethylammonium-propyl-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] dibromide (PFN-Br), Lead bromide (PbBr_2 , 99%), bathocuproine (BCP), Cesium chloride (CsI, 99%), (pyridin-3-yl)methanaminium iodide (3-PyAI), Spiro-MeOTAD (99.5%), Bis(tri-fluoromethane) sulfonimide lithium salt (Li-TFSI, 95%), FK209 ($\geq 99\%$) and 4-tert-butylpyridine (4-tBP, 96%) were purchased from Xi'an Polymer Light Technology Corp, China. Anhydrous DMF (99.8%) and DMSO (99.8%), Chlorobenzene (CB, 95%), Acetonitrile (ACN, 99.8%), Isopropyl alcohol (IPA, 99.8%) were acquired from Aladdin.

1.2 Device Fabrication

Glass/ITO substrates ($1.5 \text{ cm} \times 1.5 \text{ cm}$) were cleaned by sonication in deionized water, ethanol and isopropanol (IPA) and then dried in an oven. Next, the dry substrates were treated with UV-ozone for 15 min before used. 5 mg/mL PTAA solution (dissolve in chlorobenzene) was spin-coated (5000 rpm for 30 s, ramp rate: 4000 rpm/s) on the ITO glass substrate, and immediately transferred to a 100 °C heating stage for annealing for 10 minutes. Then the PFN-Br solution was covered on the upper layer of PTAA at 6000 rpm for 30 s to increase the hydrophilicity. 1.4 M $\text{FA}_{0.9}\text{Cs}_{0.1}\text{PbI}_{2.8}\text{Br}_{0.2}$ precursor

solution was prepared by dissolving all of the powders in DMF and DMSO mixed solvents with a volume ratio of 4:1. The perovskite film was deposited using the one-step antisolvent assisted deposition method, 50 μL precursor solution was spin coated onto the ITO/PTAA substrate in two steps at 1000 rpm for 10 s (ramp rate: 1000 rpm/s) and 6000 rpm for 30 s (ramp rate: 3000 rpm/s), respectively. During spin-coating, about 195 μL of chlorobenzene (CB) was added dropwise on the film, 10 s before the end of the spinning. 50 μL of 3-PyAI solution (1 mg/mL) is spin coated onto the surface of perovskite. After deposition, the substrates were immediately transferred to a hot plate and annealed at 100 $^{\circ}\text{C}$ for 30 min. The PCBM solution (20 mg/mL dissolve in chlorobenzene) was coated at 3000 rpm for 30 s (ramp rate: 2500 rpm/s). Finally, isopropanol saturated solution of BCP was applied at a rate of 5500 rpm with a time of 30 s and the Ag with a thickness of 80 nm to form an electrode through evaporation.

1.3 Characterizations

The current-voltage (J - V) curves, maximum power output (MPP) tracking test and the space-charge-limited current (SCLC) were measured by a Keithley 4200 source meter unit under an AM 1.5G solar (100 mW cm^{-2}), the active area is 0.04 cm^2 (Newport, 91192A). ESP is calculated by Gaussian 5.09 software. The surface morphology and energy dispersive spectrum mapping of the perovskite film was obtained by scanning electron microscope (Hitachi, SU-70, Japan). X-ray diffraction patterns (XRD) were collected using a Bruker instrument using Cu $K\alpha$ radiation at scan rate of $4^{\circ}\text{ min}^{-1}$ (D8 advance, Germany). The surface roughness was studied by atomic force microscopy of

Dimension 3100V (SPM, Veeco, USA). The XPS and UPS measurements were conducted with a Kratos AXIS ULTRA DALD and the UPS measured under the He I (21.22 eV) emission line. The steady-state fluorescence (PL) spectra of the films were measured by fluorescence spectrophotometer (Agilent, USA), with excitation wavelength of 402 nm. The time resolved photoluminescence (TRPL) spectra of the PVK films on glass were tested by PL spectrometer (Horiba, Japan), with 457 nm light to excite. The absorption spectra of films on substrates were determined using a UV-vis spectrophotometer (Agilent Cary 5000, USA). The external quantum efficiency (EQE) of the device was tested using a Newport EQE system in the wavelength range of 300-900 nm. The transient photocurrent (TPC) decay, transient photovoltage (TPV) decay Electrochemical impedance spectroscopy (EIS) was conducted on electrochemical workstation (Zahner, Germany).

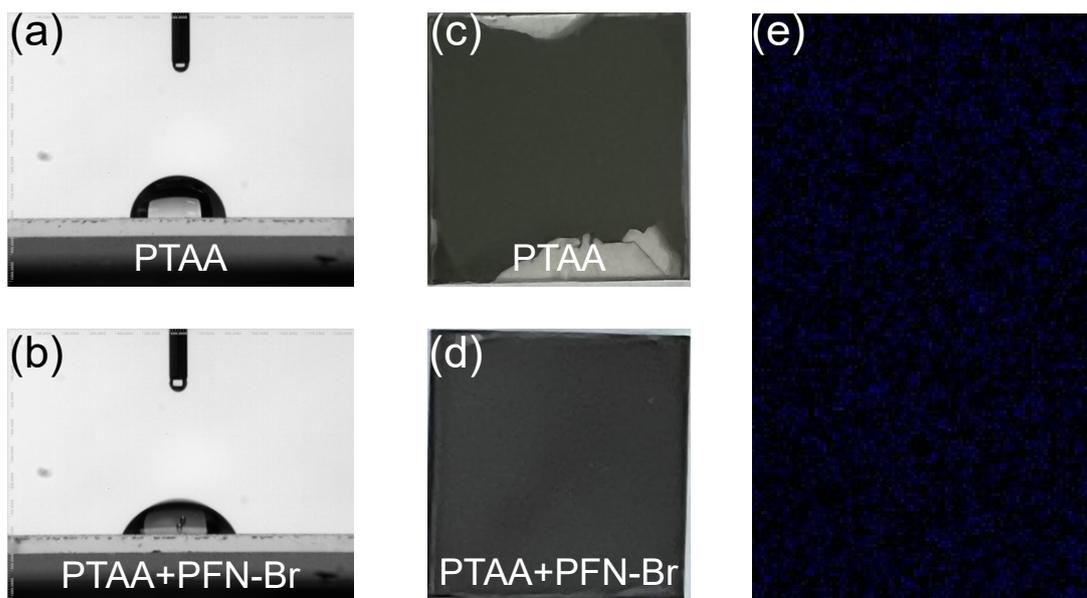


Figure S1. Optical images of (a,b) hydrophilic angle measurement and (c,d) film coverage of PTAA without and with PFN-Br, (e) EDS mapping image of PTAA/PFN-Br layer.

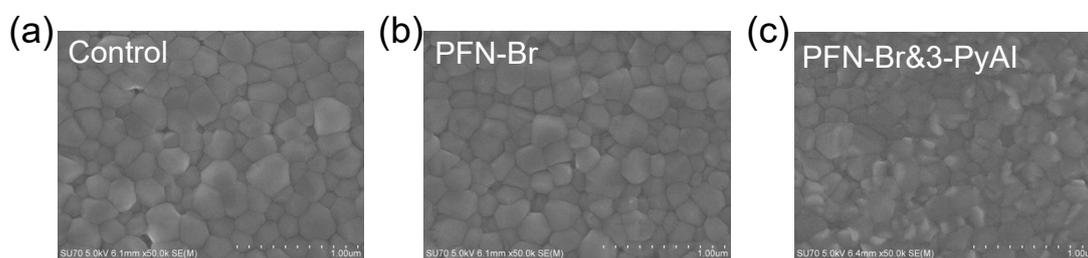


Figure S2. SEM images of three perovskite films at $\times 50K$ resolution.

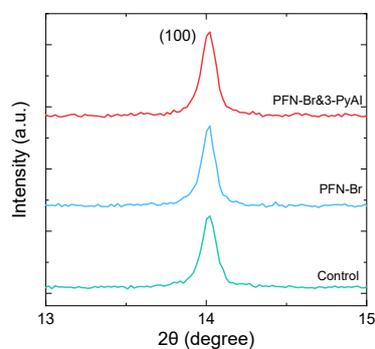


Figure S3. Partial amplification of XRD (100) peak.

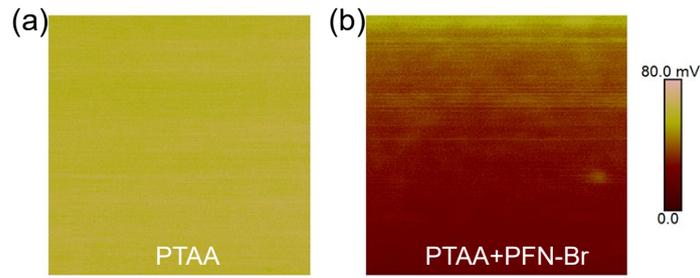


Figure S4. KPFM images of PTAA layer without and with PFN-Br modification, the latter has low CPD and increased work function.

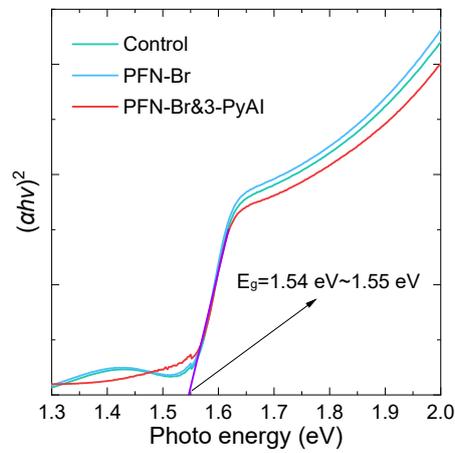


Figure S5. Band gap of different modified perovskite films.

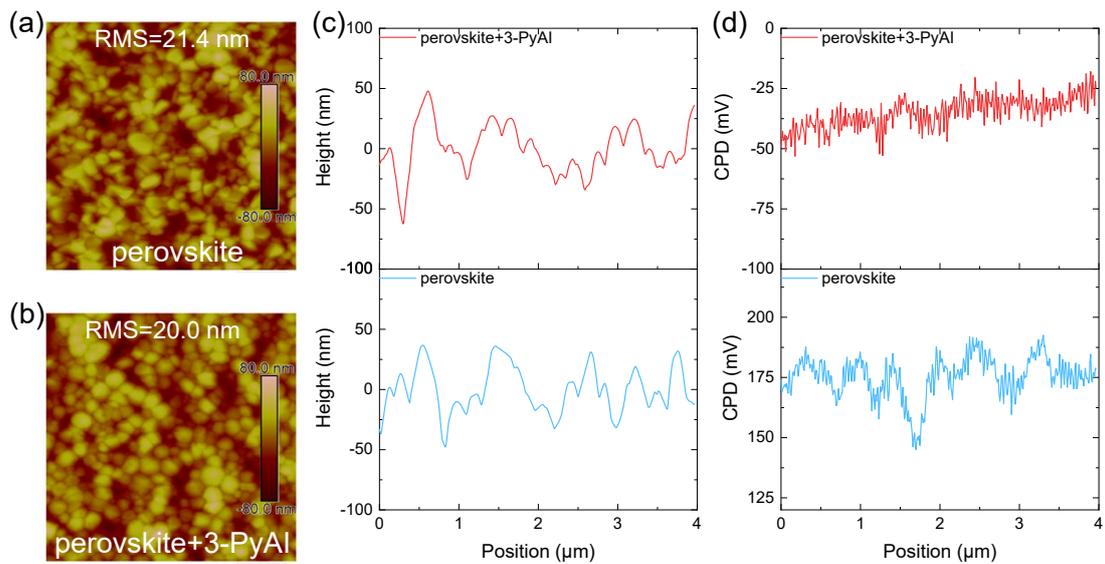


Figure S6. (a,b) AFM images, (c) surface morphology, (d) surface potential of

perovskite films without and with 3-PyAI modification.

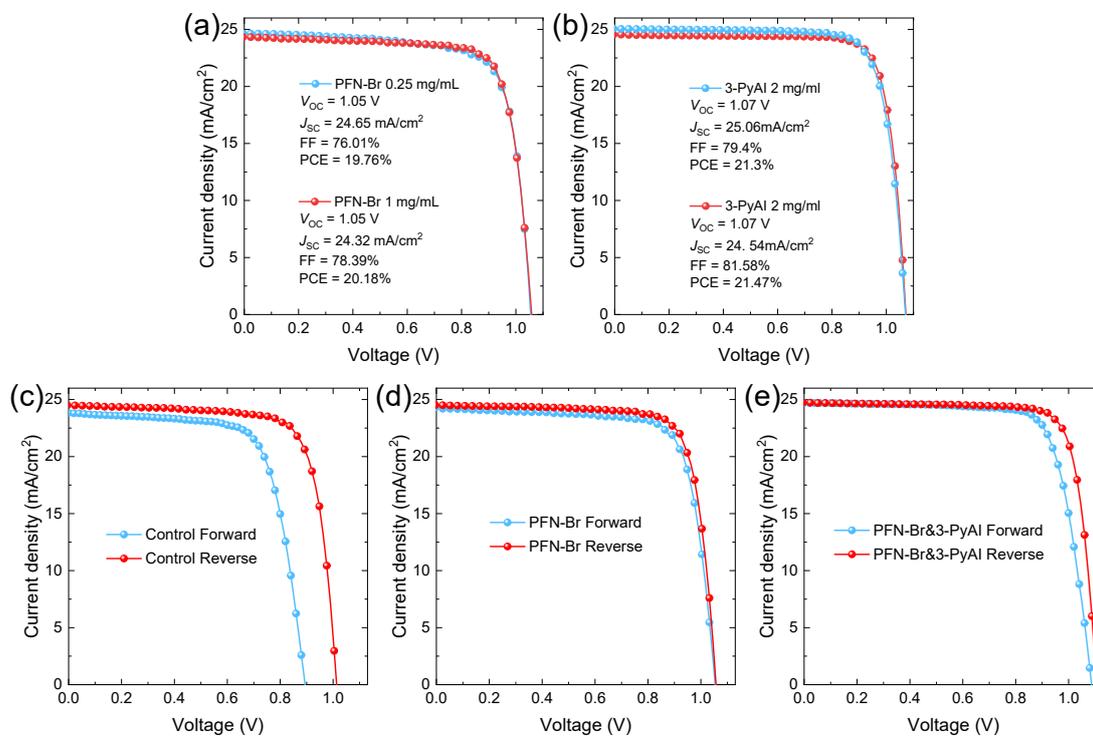


Figure S7. PV performance of devices modified with different concentrations of (a) PFN-Br and (b) 3-PyAI. Forward and reverse J - V curves of (c) control, (d) PFN-Br and (e) PFN-Br&3-PyAI modified devices.

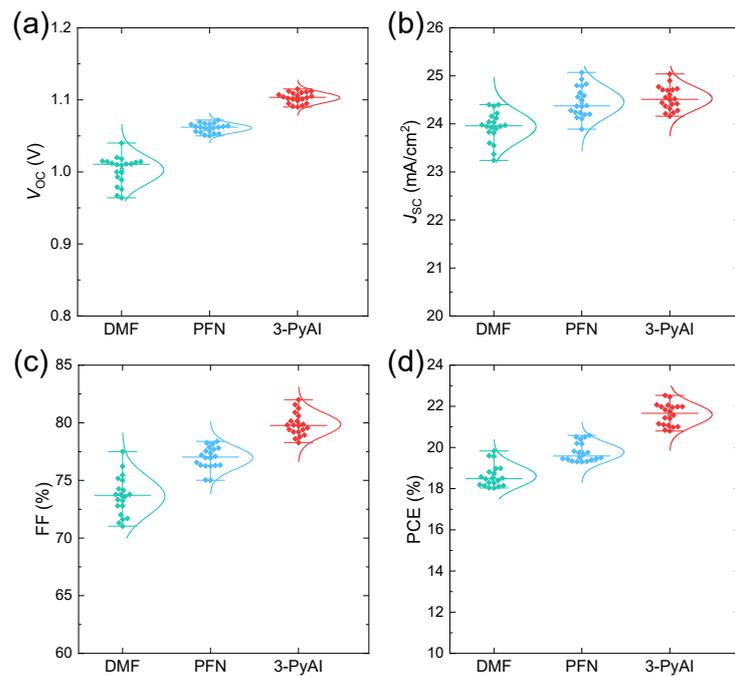


Figure S8. (a) V_{OC} , (b) J_{SC} , (c) FF and (d) PCE parameter statistics of 20 independent photovoltaic devices.

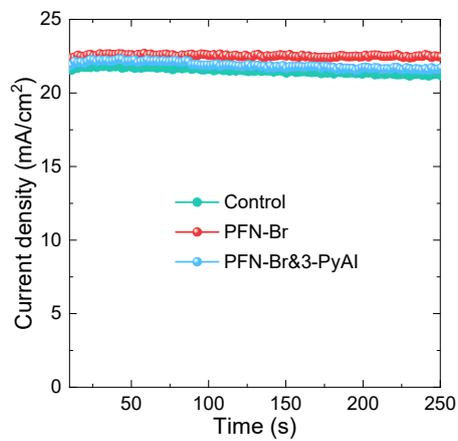


Figure S9. Steady-state output curve of the devices.

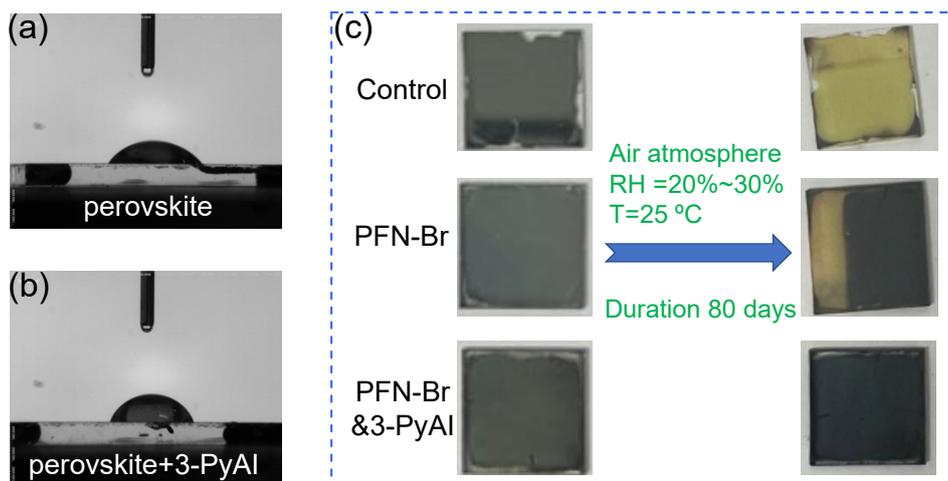


Figure S10. Hydrophobicity measurements on perovskite film surfaces (a) without and (b) with 3-PyAI modification. (c) Optical images of film aged after being left in the air for 80 days.

Table S1. Fitting results of the TRPL spectra of perovskite films deposited on different substrate.

	A_1	τ_1 (ns)	A_2	τ_2 (ns)	τ_{avge} (ns)
PFN-Br	0.42	4.66	0.31	94.44	88.82
PFN-Br&3-PyAI	0.42	8.14	0.28	119.00	108.68