

Electronic Supplementary Information

Effective surface passivation with 4-bromo-benzonitrile to enhance the performance of perovskite solar cells

Jiahui Li,^a Fei Gao,^{a} Jialun Wen,^a Zhuo Xu,^a Chaoqun Zhang,^a Xiaodong Hua,^a Xuediao Cai,^{a*} Yuanrui Li,^a Bonan Shi,^a Yu Han,^a Xiaodong Ren,^a and Shengzhong (Frank) Liu^{a,b*}*

^a Key Laboratory of Applied Surface and Colloid Chemistry, National Ministry of Education; Shaanxi Key Laboratory for Advanced Energy Devices; Shaanxi Engineering Lab for Advanced Energy Technology, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an 710119, China.

^b Dalian National Laboratory for Clean Energy; iChEM, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

*Corresponding author.

E-mail address: feigao@snnu.edu.cn, xdcai@snnu.edu.cn, liusz@snnu.edu.cn ;

Fax: +86 29 81530702

Films Preparation and Solar Cell Fabrication

FTO glass was cleaned ultrasonically using 2% Hellmanex aqueous solution, ethanol and ultra-pure water sequentially for 25 min each, and processed in an O₂ plasma for 10 min. A TiO₂ film of ~ 30 nm thickness was prepared on the FTO glass by chemical-bath deposition using 0.2 M TiCl₄ aqueous solution at 70°C for 1 h. The TiO₂/FTO sample was annealed at 200°C for 30 min. The perovskite precursor solution was prepared by adding FAI (245.1 mg), PbI₂ (656.9 mg), PbBr₂ (27.5 mg), MACl (33 mg), and MABr (8.4 mg) into 1 mL DMF/DMSO (8 : 1, v/v), which was then vibrated for 4 h. Then, the PBBN was dissolved in chlorobenzene (CB) with various concentrations for the surface passivation of perovskite films.

The prepared perovskite precursor solution was spin-coated onto TiO₂/FTO at 4000 rpm for 30 s. 0.15 mL chlorobenzene was dripped on the spinning sample 25 s prior to the end of the process, and then the film was annealed at 150°C for 20 min. To passivate the perovskite film, 50 µl of PBBN/CB solution was spin-coated onto the perovskite film at 5000 rpm for 30 s. The film was then heated at 100°C for 10 min. A spiro-OMeTAD solution, consisting of 90 mg spiro-OMeTAD, 36 µL t-BP, and 22 µL of LiTFSI solution (520 mg LiTFSI in 1 mL acetonitrile) in 1 mL of chlorobenzene, was spin-coated onto the perovskite films at 5000 rpm for 30 s. All processes were performed in a nitrogen-filled glovebox. Finally, a 60 nm gold electrode with area of 3 mm × 3 mm was deposited onto the spiro-OMeTAD film by vacuum evaporation.

Characterization and Measurement

X-ray diffraction (XRD) spectra were recorded by an x-ray diffractometer (XRD, DX-2700) using Cu K α radiation ($\lambda=0.154$ nm). Top-view and cross-sectional

scanning electron microscopy (SEM) images were gotten on a field emission SEM (FESEM, SU-8020, Hitachi). Atomic force microscopy (AFM) images were recorded by a Bruker Dimension FastScan Scanning Probe Microscope (SPM) in the tapping mode. Ultraviolet-visible spectra were obtained using a spectrophotometer (Lambda 950, Perkin-Elmer). Photoluminescence (PL) spectra and time-resolved PL (TRPL) spectra were collected by exciting the $(\text{FAPbI}_3)_{0.95}(\text{MAPbBr}_3)_{0.05}$ films deposited on compact TiO_2/FTO substrate using a PicoQuant Fluo Time 300 with 510 nm laser excitation pulsed at a frequency of 40 MHz for PL or 1 MHz for TRPL. Fourier transform infrared (FTIR) spectra were acquired with a Bruker VERTEX 70 in the range of $4000\text{--}400\text{ cm}^{-1}$. The elemental chemical states of the perovskite films were measured by X-ray photoelectron spectroscopy (XPS, Thermo K-Alpha VGS) using the Fermi edge as the energy reference. The $J\text{--}V$ curves of the PSCs were measured on a Keithley 2400 SourceMeter in ambient conditions at room temperature. The simulated sunlight source was a 450-W xenon lamp and the illumination intensity was calibrated to 100mWcm^{-2} . The power output of the AM 1.5G Oriel solar simulator was calibrated with an NREL-traceable KG5-filtered silicon reference cell. The fabricated PSCs were tested from 2 to -0.1 V at a scan rate of 0.1 Vs^{-1} , scan of 0.02 V , and scan delay time of 10 ms. External quantum efficiency (EQE) measurement was performed using a QTest Station 2000ADI system (Crowntech Inc.), including a tungsten-halogen lamp, a Si detector and a monochromator. Electrochemical Impedance spectroscopy (IS) was measured by an electrochemical workstation (IM6ex, Zahner, Germany) in the frequency range from 1MHz to 1Hz under 0.9 V under dark. The water contact angles of perovskite films were measured by a DataPhysics OCA 20.

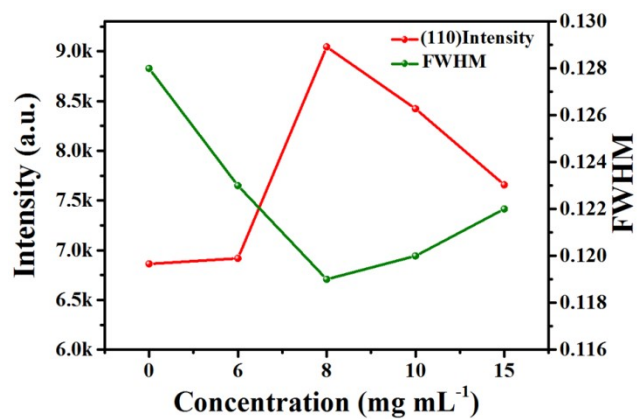
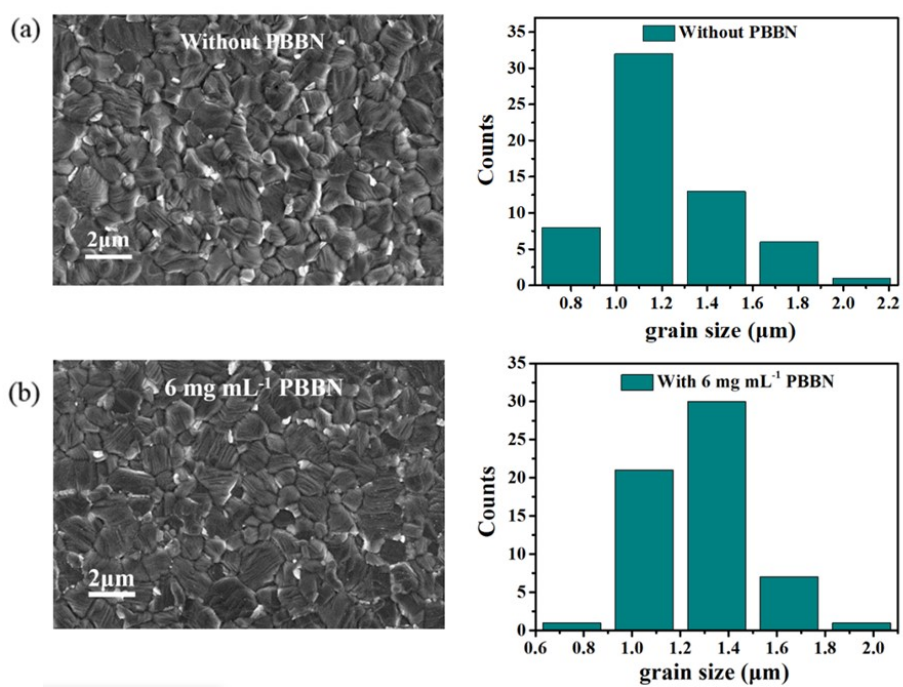


Figure S1 Intensity and full width at half maximum (FWHM) of the main (110) XRD peak of the perovskite films treated with different concentration PBBN.



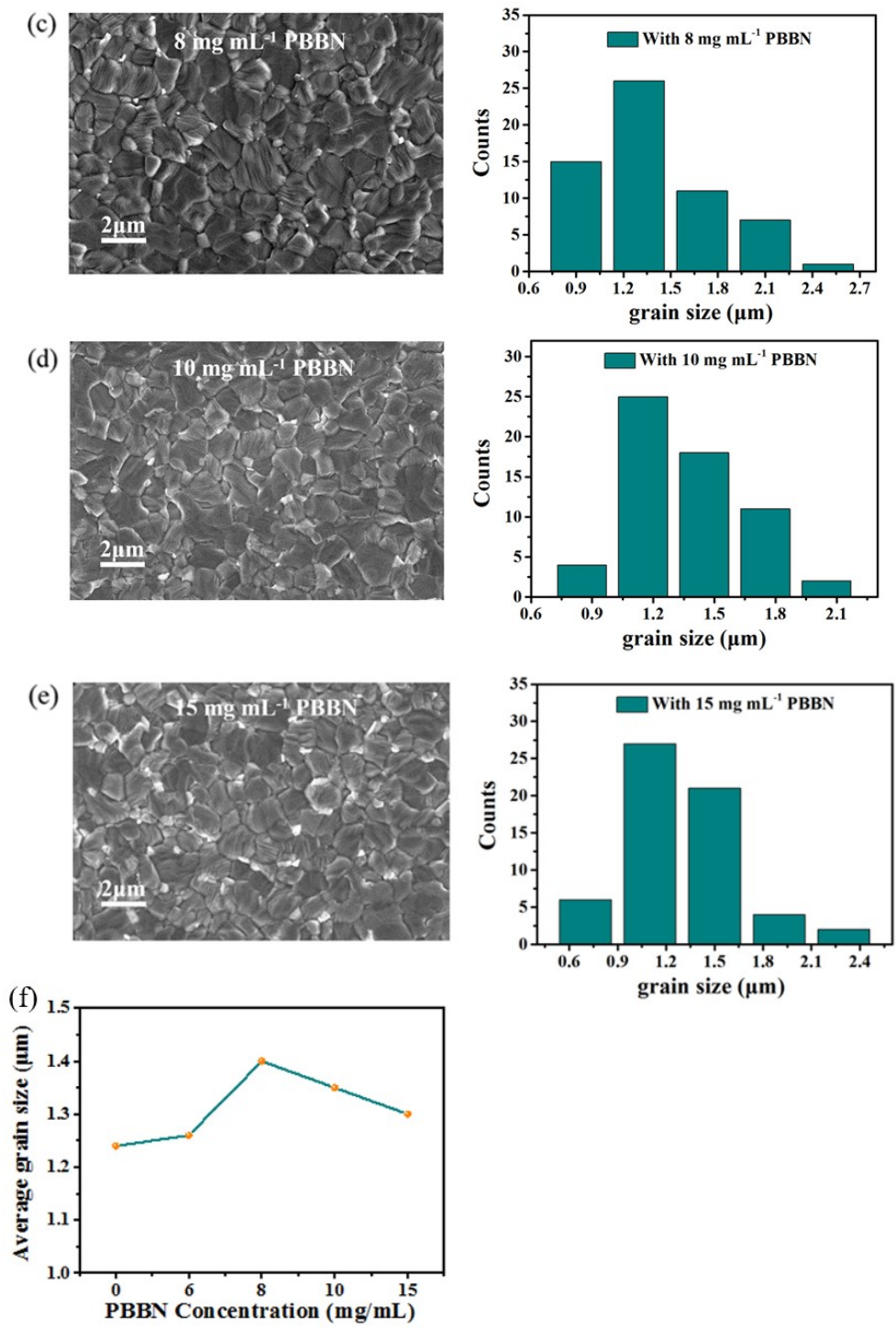


Figure S2 Surface SEM images and Grain-size distributions of the perovskite films treated without and with different concentration PBBN (a~e); Average grain size of the perovskite films as a function of PBBN concentration (f).

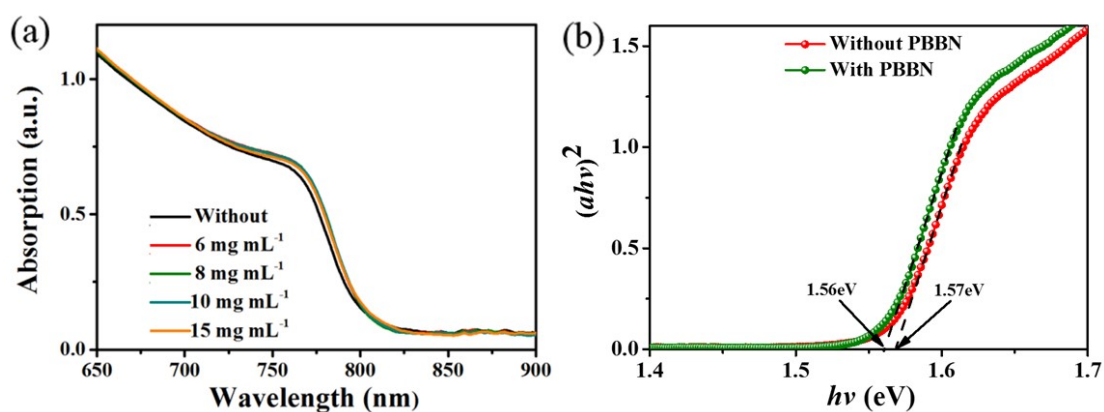


Figure S3 Absorption spectra of perovskite films treated by PBBN with different concentrations (a). Tauc plots: $(\alpha hv)^2$ vs $h\nu$ curves of perovskite films with and without PBBN treatment (b).

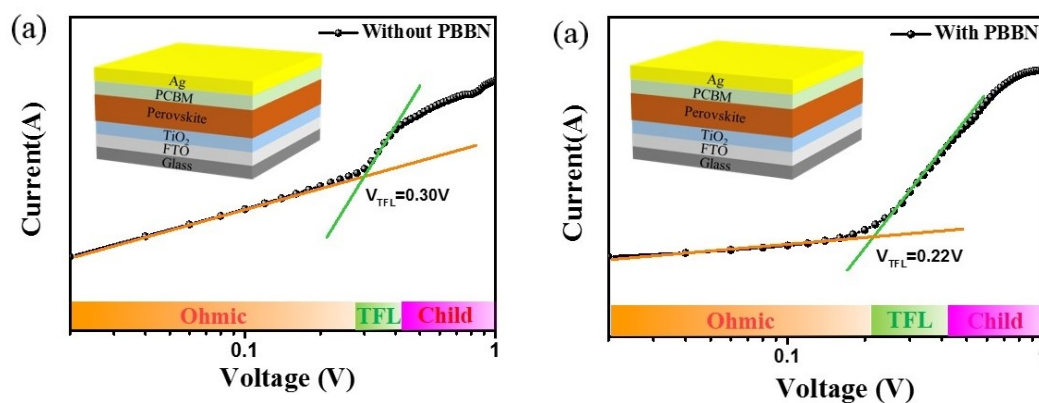


Figure S4 Dark current-voltage properties of the electron-only devices treated without (a) and with PBBN (b).

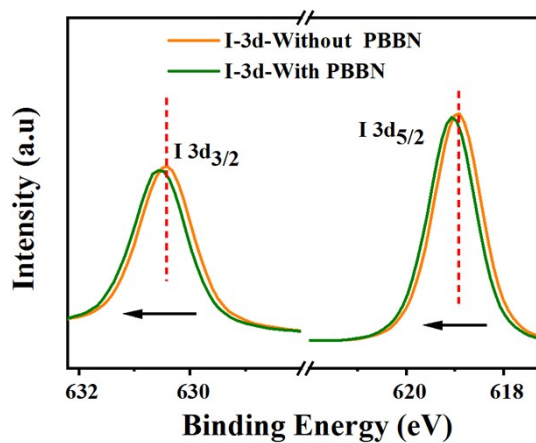


Figure S5 XPS spectra of I 3d of the perovskite films without and with PBBN passivation.

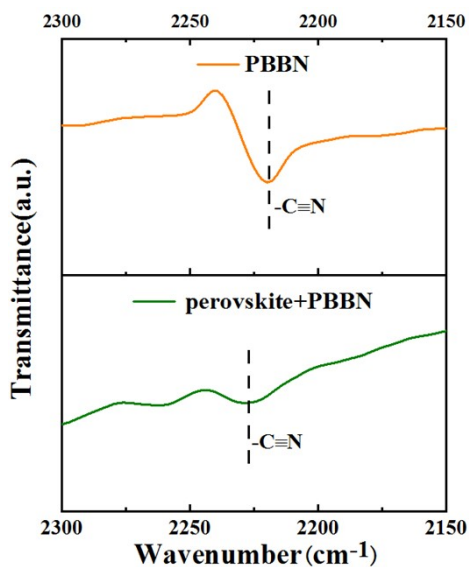


Figure S6 Fourier transform infrared spectra (FTIR) of pure PBBN and perovskite - PBBN mixture.

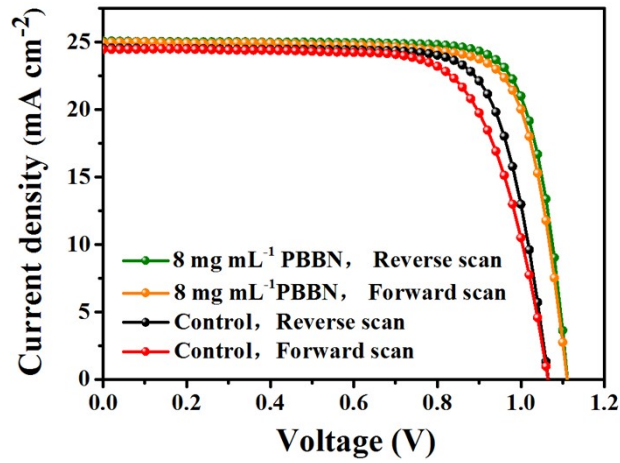


Figure S7 J–V characteristic curves under reverse/forward scanning directions of the PSCs treated without and with PBBN.

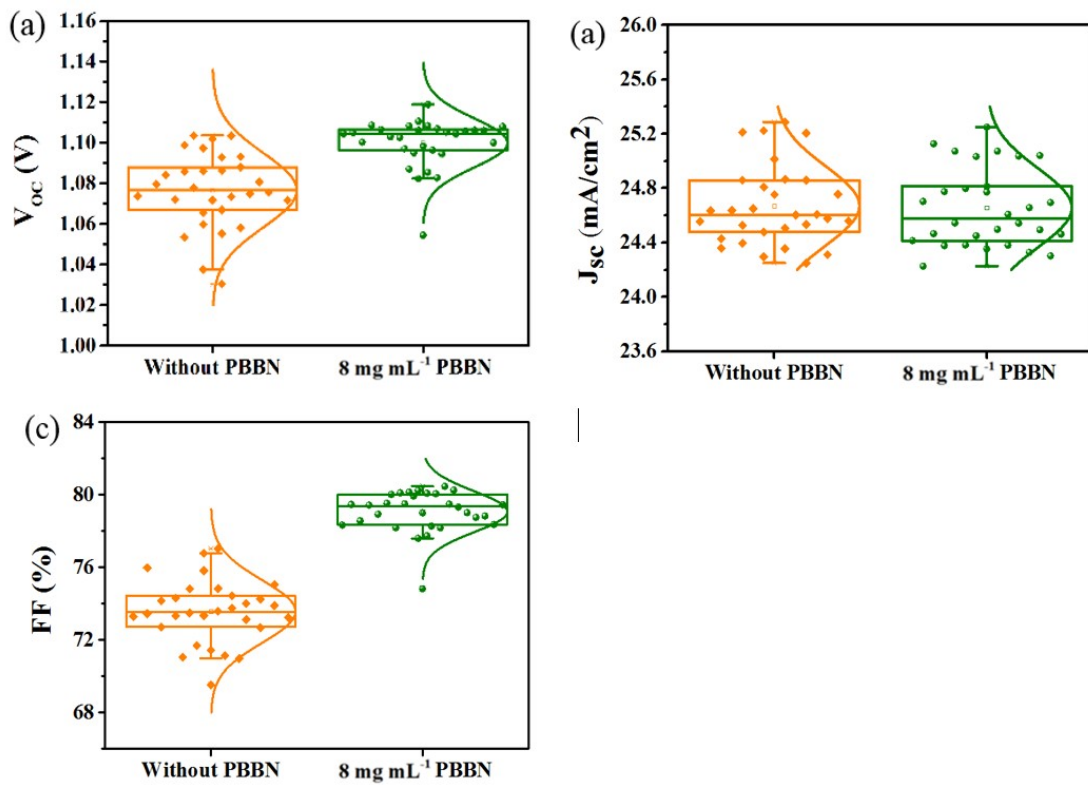


Figure S8 Statistics of V_{OC} , J_{SC} , and FF of the untreated and PBBN treated 30 devices.

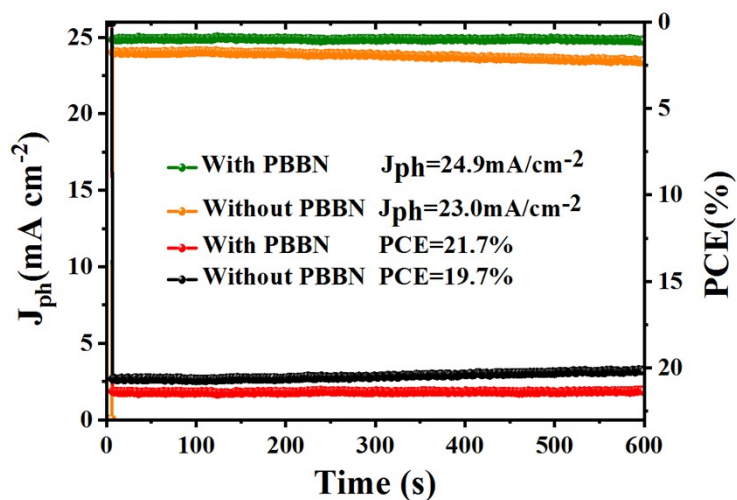


Figure S9 Stable output properties of current density and PCE measured as illumination time of the PSCs without and with PBBN treatment.

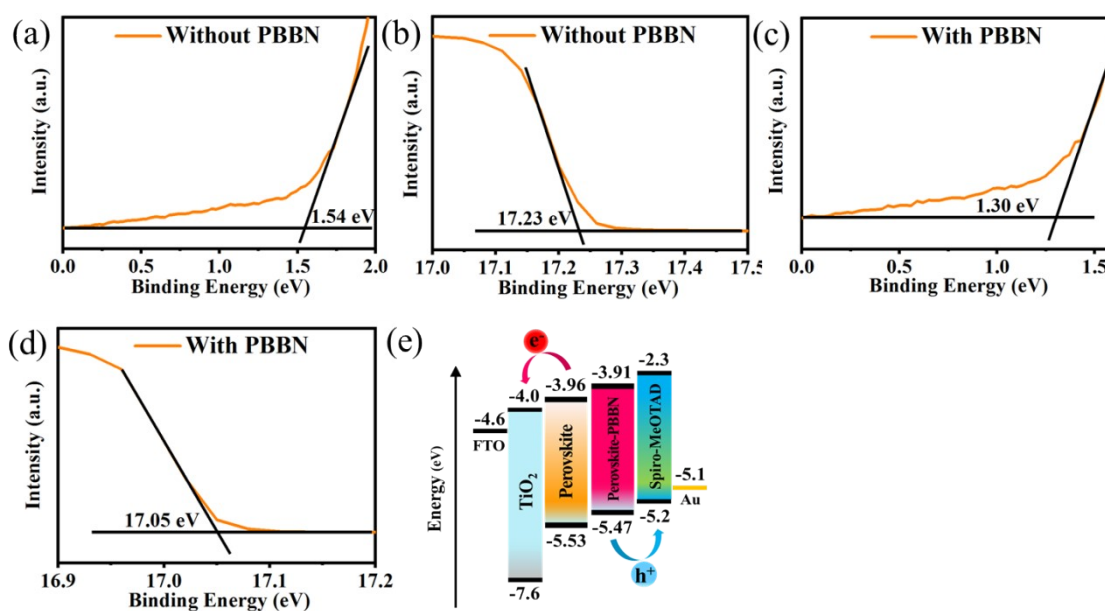


Figure S10 UPS spectra of the perovskite without (a, b) and with (c, d) PBBN treatment for the E_{onset} range (a, c) and E_{cutoff} range (b, d). Energy levels and band structure of PVCs (e).

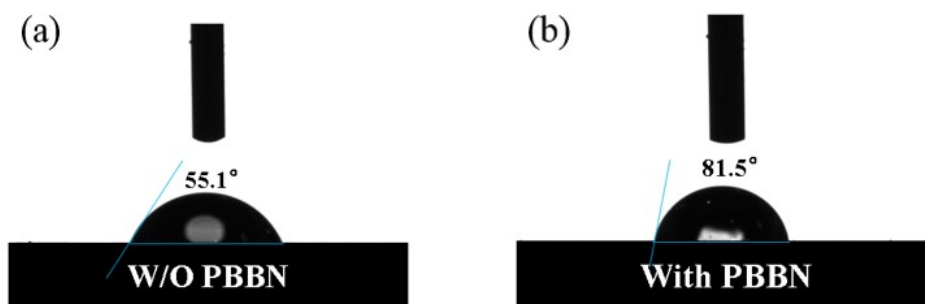


Figure S11 Contact angle of a water droplet on the top of the perovskite films without (a) and with (b) PBBN treatment.

Table S1 The fitted values of τ_1 , τ_2 , A_1 , A_2 and the calculated τ_{ave} of the perovskite films without and with PBBN treatment.

8 mg mL ⁻¹ PBBN	τ_{ave} (ns)	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)
w/o	70	42	642.1	121	3462.4
With	363	136	789.2	542	2474.9

Table S2 Photovoltaic parameters of PSCs treated with different concentrations PBBN.

PBBN	V_{OC} (v)	J_{SC} (mA cm ⁻²)	FF (%)	PCE (%)
Without	1.06	24.56	76.79	20.09
6 mg mL ⁻¹	1.06	24.64	79.00	20.73
8 mg mL ⁻¹	1.11	25.09	79.92	22.28
10 mg mL ⁻¹	1.10	24.91	78.7	21.64
15 mg mL ⁻¹	1.09	24.88	77.88	21.25

Table S3 J–V characteristic curves under reverse/forward scanning directions of the PSC without PBBN treatment.

	V_{oc} (v)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	H-index
Reverse scan	1.065	24.56	76.79	20.09	0.057
Forward scan	1.065	24.49	72.58	18.94	

Table S4 J–V characteristic curves under reverse/forward scanning directions of the PSC with PBBN treatment.

	V_{oc} (v)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	H-index
Reverse scan	1.111	25.09	79.92	22.28	0.029
Forward scan	1.110	24.98	77.96	21.64	

Table S5 Fitted resistances of the perovskite films without and with PBBN treatment.

PBBN	$R_s(\Omega)$	C_{cr} (F)	R_{rec} (Ω)
Without	16.64	3.0×10^{-9}	559.5
With PBBN	16.63	7.2×10^{-9}	2213