

1. Experimental part

1.1 Material Preparation

In this experiment, Methylammonium iodide (MAI, 99.5%), lead iodide (PbI_2 , 99.99%), 4(5)-Iodoimidazole(4II), 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spiro-bifluorene(Spiro-OMeTAD, $\geq 99.5\%$) were purchased from Xi'an Polymer Light Technology Corp. Titanium diisopropoxide bis(acetylaceto-nate), 4-tert-butylpyridine (tBP, 96%), dimethyl sulfoxide(DMSO, $\geq 99.9\%$) anhydrous, N,N-dimethylformamide(DMF, 99.8%), ethyl acetate (99.8% anhydrous) and chlorobenzene (CB, 99.5%) anhydrous were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. Acetone (AR) was ordered from Sinopharm Chemical Reagent. Acetonitrile (ACN, 99.9% anhydrous) and 2-Propanol (IPA, $\geq 99.5\%$) were purchased from Shanghai Macklin Biochemical Technology Corp. Bis(trifluoromethane)sulfonamide lithium salt (Li-TFSI, 99.95%) was purchased from Sigma-Aldrich.

1.2 Preparation process of the PSCs

ETL: The etched fluorine-doped tin oxide (FTO) glass substrates were ultrasonically cleaned with detergent, deionized water, acetone, and anhydrous ethanol for ten minutes in turn, and then it was dried in a drying cabinet for a few hours, and then it was taken out and further treated with an oxygen plasma cleaning machine for fifteen minutes. The TiO_2 precursor solution was obtained by mixing 1.589 mL of n-butanol with 125 μL bis(acetylacetonate) diisopropyl titanate and stirred for 2.5-3h. Then, the precursor solution was spin-coated onto the treated FTO glass at 500 rpm 3 s and 2000 rpm 30 s, and then annealed at 135 $^\circ\text{C}$ for 10 minutes, and finally sintered at 500 $^\circ\text{C}$ for 30 min in ambient air.

MAPbI₃: The perovskite precursor solution was obtained by dissolving MAI and PbI_2 (1.4M) in a mixture of DMSO and DMF (V:V=1:9). Appropriate amount of 4II was completely dissolved in DMSO, and then 72 μL was extracted from the solution and added into the pure phase perovskite precursor solution without DMSO to obtain perovskite precursor solutions with different concentrations of 4II (12.5mg mL^{-1} , 15mg mL^{-1} , 17.5mg mL^{-1} , 20mg mL^{-1}). The glass containing c- TiO_2 was treated by

plasma cleaning machine for 10 minutes, and then the precursor solution was subsequently spin-coated on the TiO₂/FTO substrates at 4000 rpm for 25 s. 135 μ L ethyl acetate was quickly added as the antisolvent 8 s before the spin coating was finished. Finally, the sample was annealed at 105 °C for 10 minutes.

HTL: Firstly, 108.5 mg of Spiro-OMeTAD was dissolved in 1.5 mL of chlorobenzene, then 43.2 μ L of 4-tert-butylpyridine (tBP) and 26.3 μ L of Li-TFSI solution (520 mg of Li-TFSI dissolved in 1mL of anhydrous acetonitrile) were added to obtain the precursor solution of the hole transport layer. The precursor solution was spin-coated onto the perovskite layer at 3000 rpm 30 s. The sample is then oxidized in a drying oven for 12 hours. Finally, 0.12 cm² silver electrode is evaporated by thermal evaporation.

1.3 Characterization and Measurement

Scanning electron microscopy (SEM) (Regulus 8230, Hitachi, JPN) was used to observe the surface morphology and cross section morphology of perovskite films. The crystal structure of the prepared perovskite films was analyzed by X-ray diffraction (XRD) (D/MAX2500V). Ultraviolet-visible (UV-vis) absorption spectra of perovskite films in the range of 400 ~ 900 nm were obtained using the CARY 5000 (Agilent, Australia) UV-VIS spectrophotometer. The steady-state photoluminescence (PL) spectra of 532 nm excited laser were obtained using LabRAM HR Evolution (HORIBA JOBIN YVON, FR) to analyze the charge transport characteristics of perovskites. The molecular structure and valence states of perovskite films were studied using monochromatic Al K α (photon energy: 1486.6 eV) X-ray photoemission spectroscopy (XPS)(ESCALAB250Xi, Thermo, USA). Surface current and voltage were measured using Dimension Icon (BRUKER, Germany) in light and dark states using conductive Atomic Force microscopy (C-AFM) and Kelvin Probe Force microscopy (KPFM), respectively. To record the current signal between the specimen and the tip, C-AFM operates in contact mode. In this process, a constant voltage of 1 V is applied to the sample. Current-voltage (J-V) and space-charge-limited current (SCLC) curves were obtained by Keithley 4200 SMU instrument under AM1.5 irradiation (100 mW cm⁻², XES-301S solar simulator) under dark state conditions and

illumination conditions. The electrochemical impedance spectroscopy (EIS) was measured at 0.7 V bias in the dark with the frequency ranging from 500 mHz to 1 MHz. EIS and incident photon current conversion efficiency (IPCE) spectra were both tested by the Zahner electrochemical station (Zahner, Germany). Mass spectroscopy was performed using Agilent Technologies VNMRS600. For liquid-state ^1H NMR, samples were prepared by dissolving in 0.5 mL DMSO. The samples were vigorously stirred until the single crystals were completely dissolved. Afterward, it was transferred to a 5 mm NMR tube.

2. Table

Table S1 corresponding photovoltaic parameters of the best performance cells measured at reverse and forward scans of the control and 15 4II devices

		V_{oc} (V)	J_{sc} (mA/cm ²)	FF(%)	PCE(%)	HI
control	forward	1.042	22.35	48.86	11.38	0.34
	reverse	1.052	22.77	71.87	17.22	
4II	forward	1.081	23.90	63.08	17.52	0.16
	reverse	1.091	23.88	80.40	20.95	

3. Figure

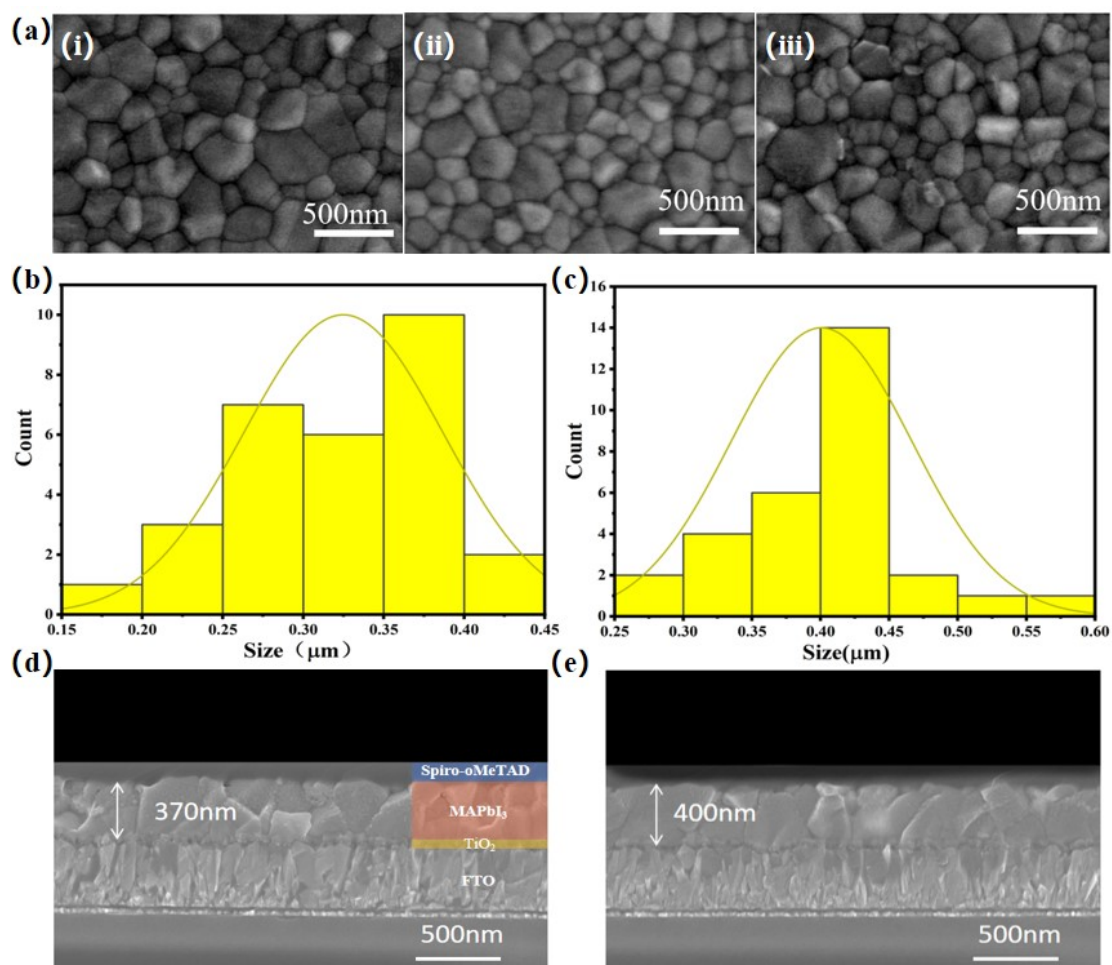


Fig.S1 (a) Top-view SEM image of perovskite film with varied amounts of 4II agents: (i) 12.5 mg mL⁻¹; (ii) 17.5 mg mL⁻¹; (iii) 20 mg mL⁻¹; Grain size distribution calculated from SEM images for (c) control and (b) 15 4II perovskite film. Cross-sectional SEM images of PSCs: (d) pristine; (e) 15 4II.

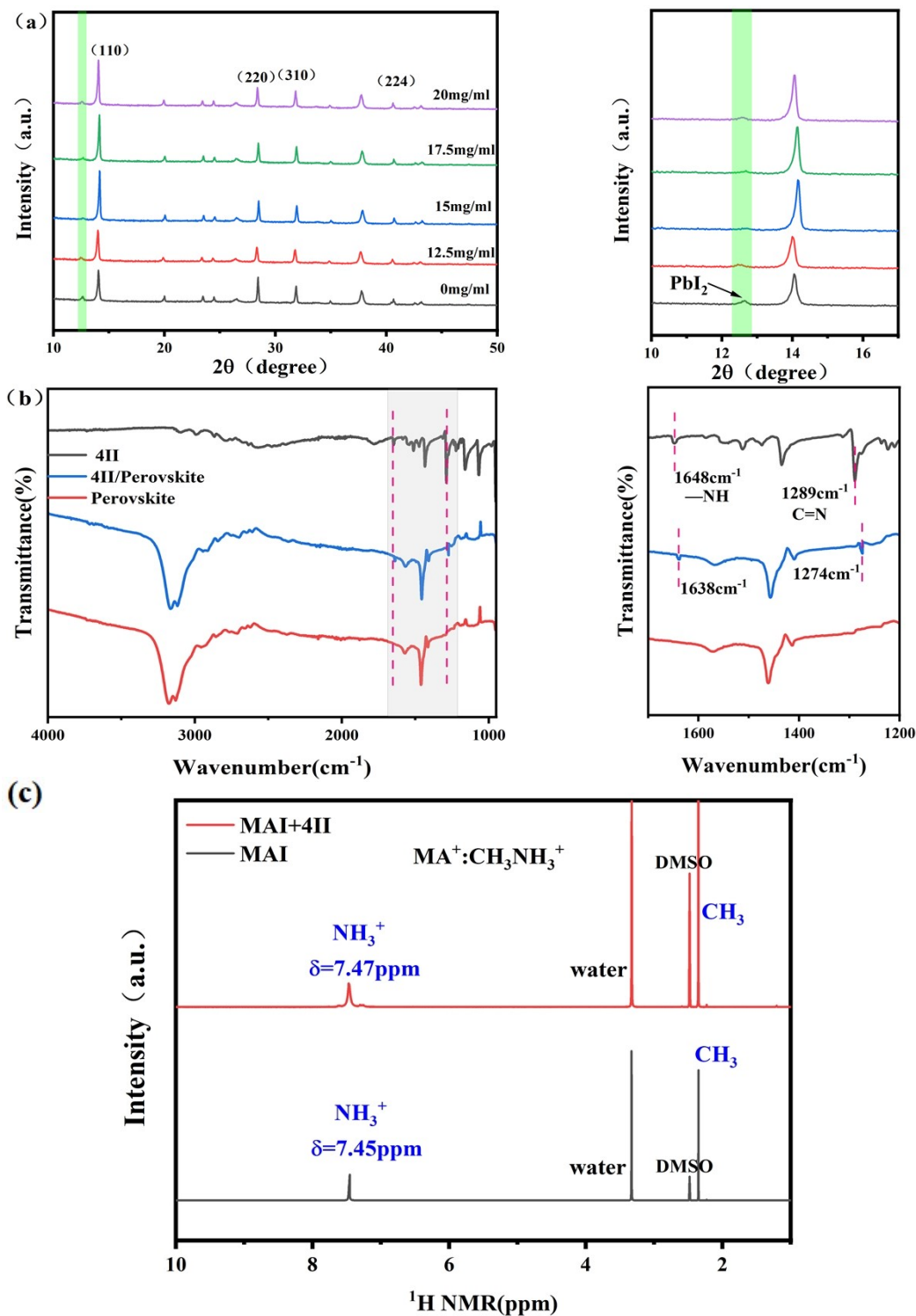


Fig.S2 (a) XRD patterns of perovskite film with diverse amounts of 4II agents and the enlarged XRD pattern; (b) FTIR spectra of pure 4II molecule, the pristine and 4II-modified perovskite films and the enlarged view of the area of the underlined area; (c) ^1H NMR spectra of perovskite powders with and without 4II agents indicating the chemical shift of ^1H . The NMR tubes with perovskite samples in $\text{DMSO-}d_6$ were maintained at 25 $^\circ\text{C}$ during testing.

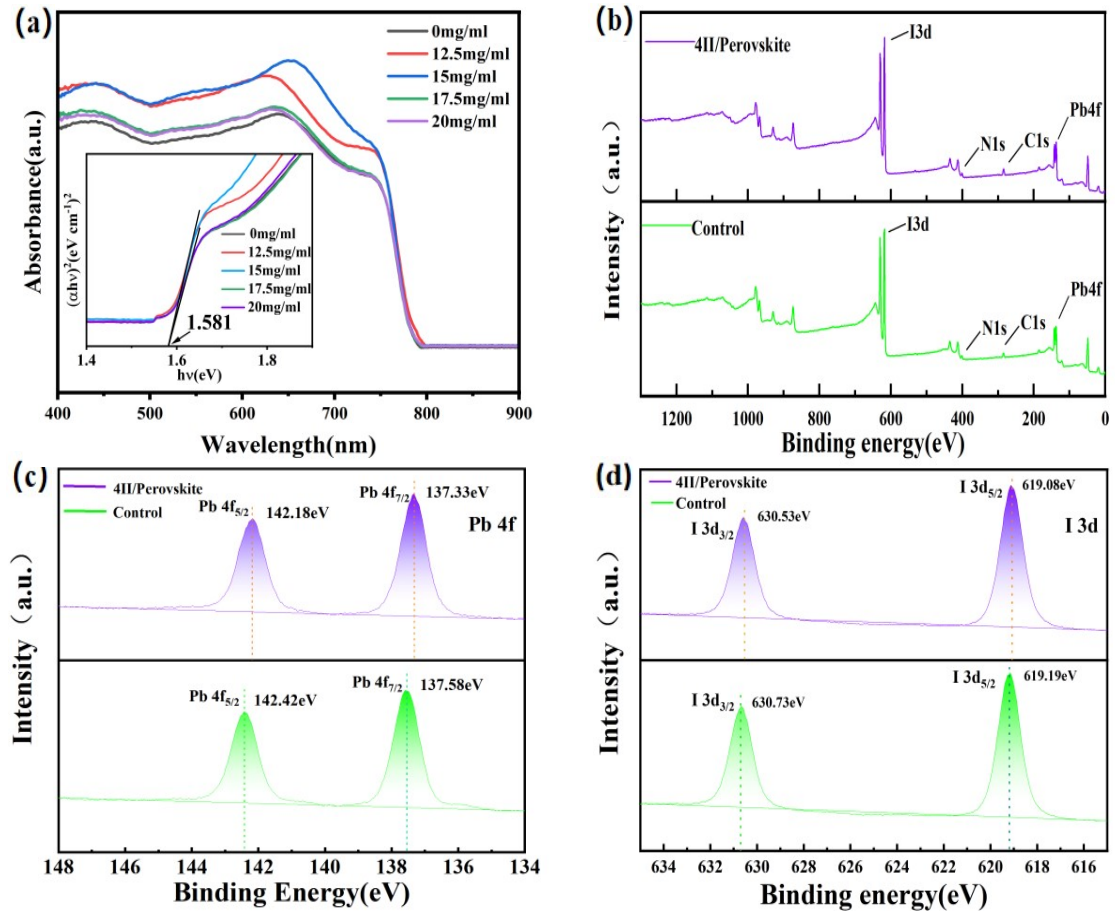


Fig.S3 (a) The UV-vis absorption spectra with the Tauc plots (inset); XPS spectra of the pristine and 15 4II-added perovskite films: (b) survey spectra; (c) Pb 4f and (d) I 3d.

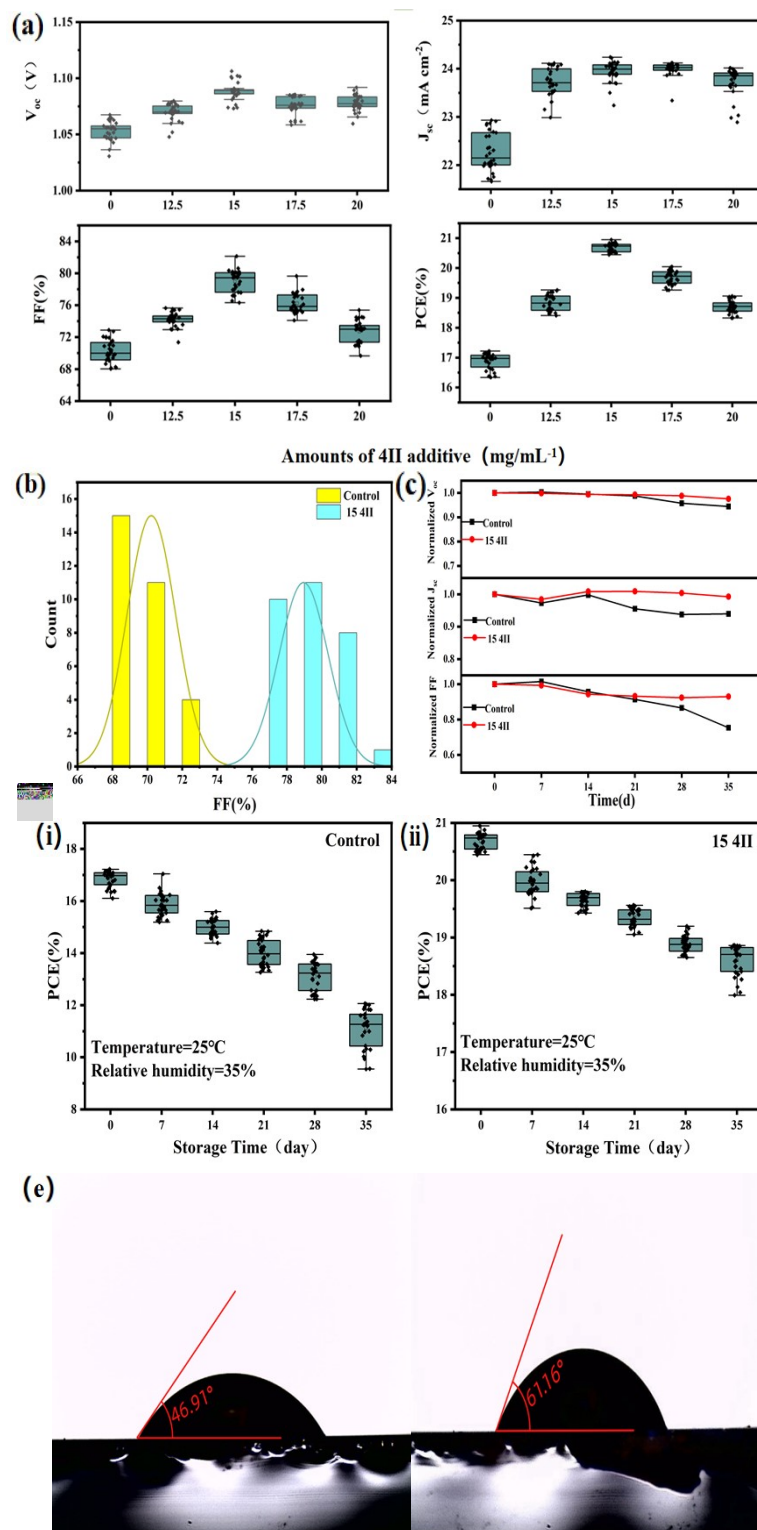


Fig.S4 (a) Statistical of photovoltaic parameters obtained from 30 cells; (b) FF distribution of the control and target group; (c) Evolution of the photovoltaic parameters of the control and 15 4II cells stored in an N₂ glovebox and measured under ambient air condition with 35±5%RH without any encapsulation in 35 days; (d) Statistical stability test based on 32 cells for 35 days; (e) Contact angle of water drop on the surface of pristine and 4II-treated perovskite film.