Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

1. Figures

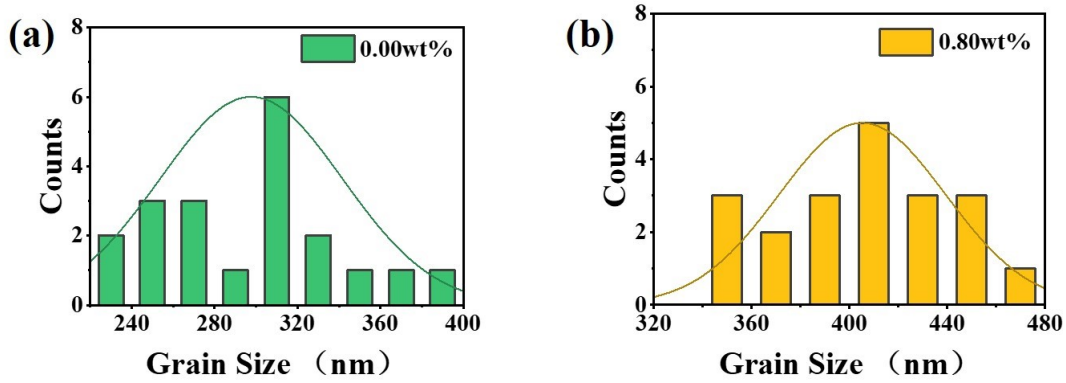

Fig. S1 Grain size distribution calculated from SEM images for (a) control and (b) 0.80 wt% EU-modified perovskite film. The corresponding values of STD are 44.01 and 34.07, respectively.

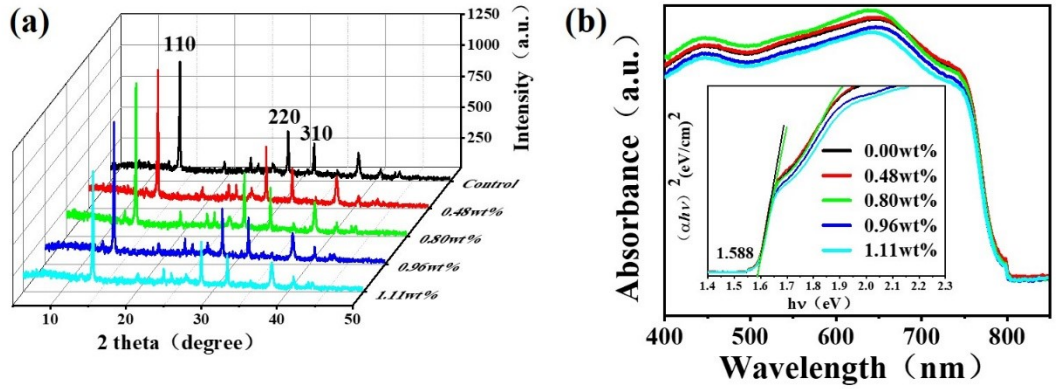

Fig. S2 Perovskite films with and without EU additive: (a) X-ray diffraction spectra; (b) UV-vis absorption plot with the inset of Tauc plot.

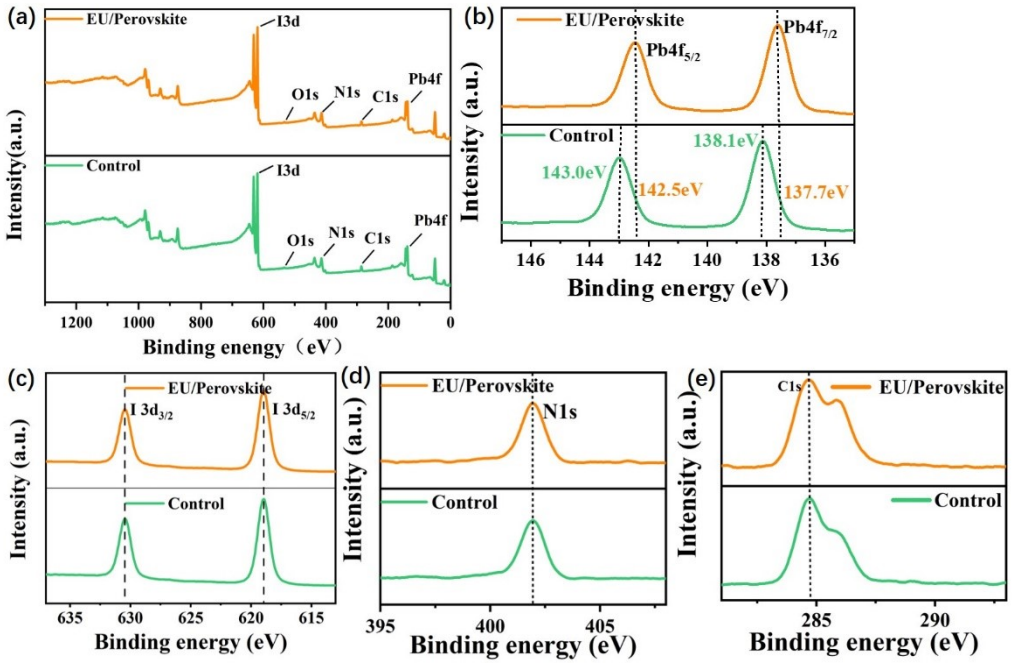

Fig. S3 XPS spectra for the perovskite films with and without EU addition: (a) full range; (b) Pb 4f; (c) I 3d; (d) N 1s; (e) C 1s.

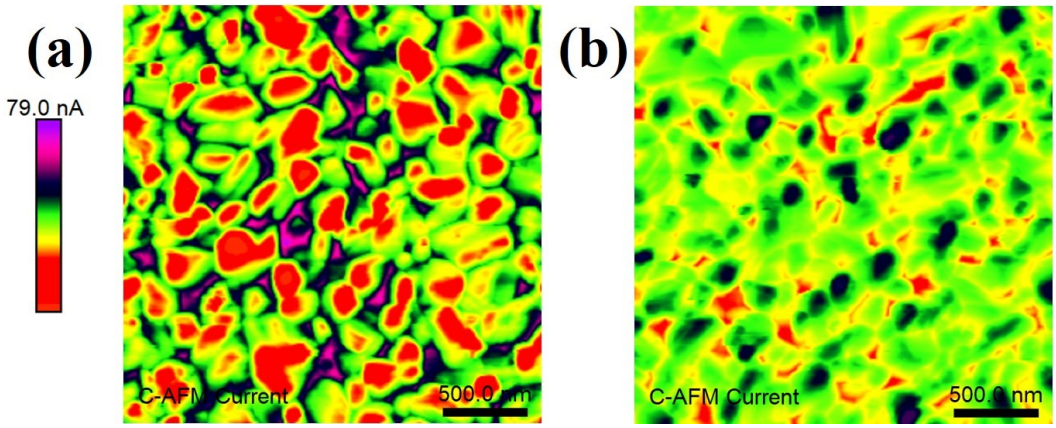

Fig. S4 C-AFM current mappings overlay on the corresponding topological images for perovskite films: (a) without and (b) with EU agent.

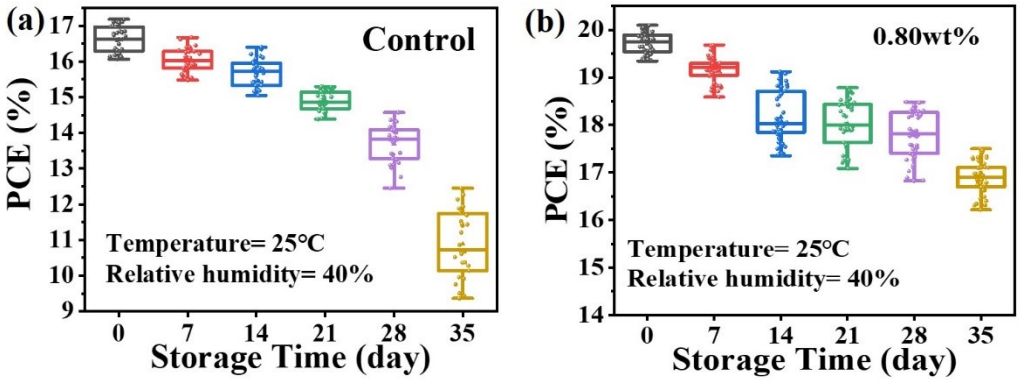

Fig. S5 Statistical stability test based on 32 cells for 35 days in ambient with a relative humidity ~40%: (a) control and (b) 0.80 wt% EU-modified devices.

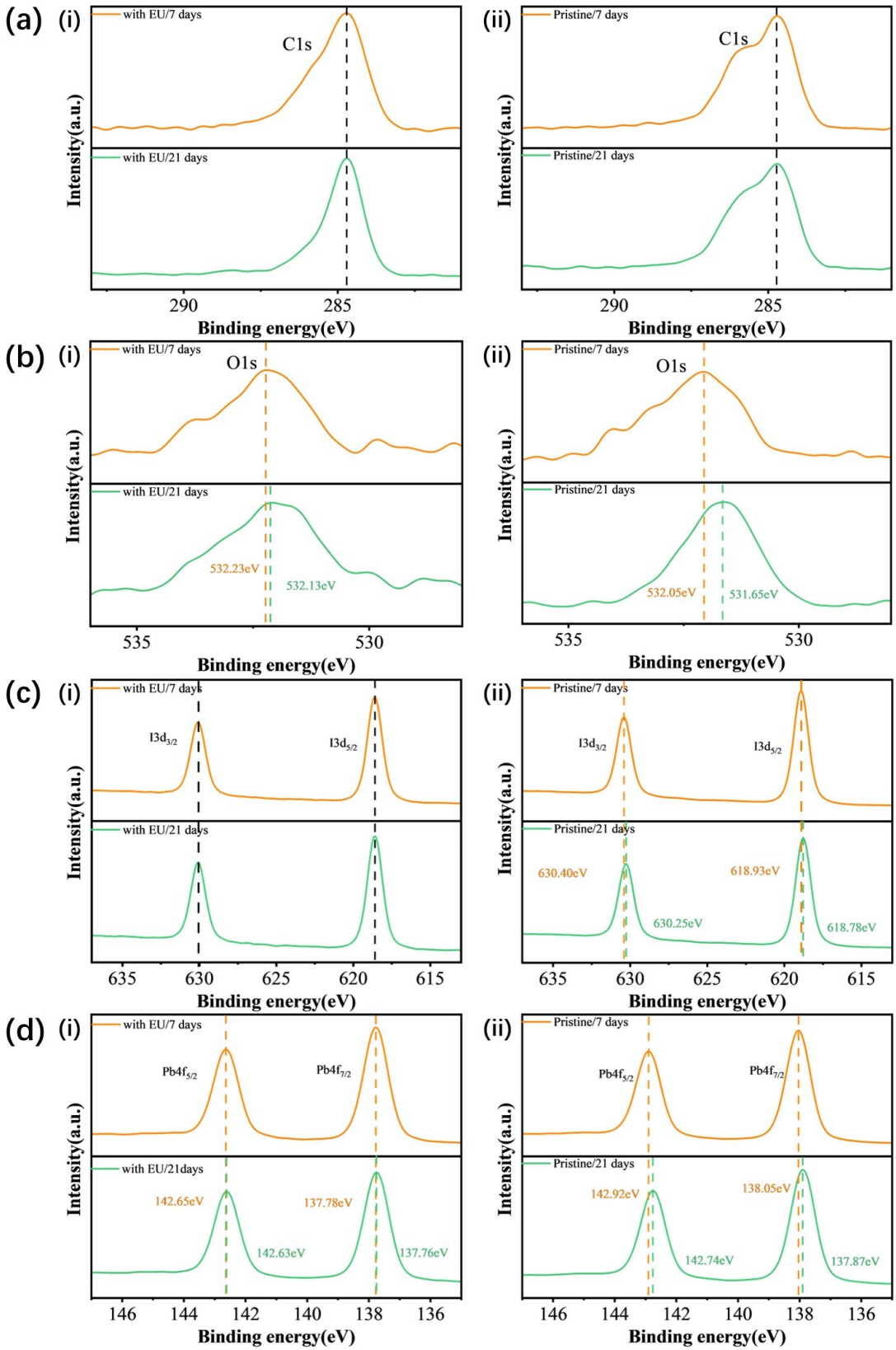

Fig. S6. XPS spectra of (a) C 1s; (b) O 1s; (c) I 3d and (d) Pb 4f of the EU-added and control perovskite films stored for a period of time: (i) 7 days; (ii) 21 days.

2. Tables

Table S1 The photovoltaic parameters of PSCs without and with EU additive under different scan directions

EU additive concentration (wt%)		V_{oc}(V)	J_{sc}(mA cm^{-2})	FF(%)	PCE(%)	HI
Control	forward	1.065	22.57	47.88	11.52	0.26
	reverse	1.061	22.40	72.63	17.27	
0.80	forward	1.073	23.98	64.33	16.56	0.14
	reverse	1.092	24.04	76.61	20.10	

Table S2 EIS fitting parameters for the control and EU-modified PSCs

EU additive concentration (wt%)	R_s(Ω）	R_{ct}(Ω）	CPE-P	CPE-T	τ_n(ms)
Control	25.13	41421	0.999	1.77E-08	0.727
0.48	22.69	77514	0.997	2.58E-08	1.964
0.8	27.95	117530	0.996	2.10E-08	2.405
0.96	23.63	64474	0.992	2.09E-08	1.275
1.11	28.36	52981	0.997	2.08E-08	1.082

3. Experimental section

Reagents and materials: Titanium diisopropoxide bis (acetylacetonate), 4-*tert*-butylpyridine (tBP), N, N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), ethyl acetate (EA), chlorobenzene (CB) and carbamic acid ethyl ester (EU) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. MAI, PbI_2 and Spiro-OMeTAD were supplied by Xi'an Polymer Light Technology Corp. Bis (trifluoromethane) sulfonamide lithium salt (Li-TFSI) was ordered from Sigma-Aldrich. Acetonitrile (ACN) was purchased from Shanghai Macklin Biochemical Technology Corp. Acetone and isopropanol were supplied by Sinopharm Chemical Reagent.

Preparation of the TiO_2 Solution: Dissolving 125 μL titanium diisopropoxide bis

(acetylacetonate) in 1.589 mL n-butanol.

Preparation of the Perovskite Solution: MAI (0.159 g) and PbI_2 (0.461g) were dissolved in a mixture of DMF (635 μL) and DMSO (72 μL).

Preparation of the EU Perovskite Solution: Dissolving the EU powder in DMSO and adding 72 μL EU solution into the pristine $CH_3NH_3PbI_3$ perovskite precursor solution without DMSO to obtain a series of concentrations (0.48 wt%, 0.80 wt%, 0.96 wt%, 1.11 wt%).

Preparation of the Spiro-OMeTAD Solution: Dissolving 108.5 mg Spiro-OMeTAD, 26.3 μL Li-TFSI solution (520 mg mL^{-1} Li-TFSI in acetonitrile) and 43.2 μL tBP in 1.5 mL CB. All of the solution was stirred at room temperature for 3 h.

Device Fabrication: FTO-coated glass substrates were cleaned sequentially in detergent, deionized water, acetone and ethanol successively for 10 min, and then kept in an oven at 75 ℃ for 3 h [1]. FTO glass substrate should be treated with plasma cleaner for 10 min to enhance the wettability. The electron transport layer (ETL) was obtained by spin-coating TiO_2 solution onto the FTO substrates at 500 rpm for 3 s and 2000 rpm for 30 s and then the substrates were heated at 500 ℃ for 30 min [2]. The precursor solution was spin-coated on the TiO_2-coated FTO in a one-step spin-coating process at 4000 rpm for 25 s. During the step, 135 μL of ethyl acetate was dripped after 17 s as an anti-solvent and after that the substrates were annealed at 105 ℃ for 10 min[2]. Next, the hole transport layer (HTL) was obtained by spin-coating Spiro-OMeTAD solution at 3200 rpm for 30 s. 100 nm of silver electrode was vacuum deposited under 10^{-4} Pa pressure. The device was fabricated with a structure of

FTO/TiO_2/Perovskite/Spiro-OMeTAD/Ag.

Measurements and Characterization: Current density-voltage (J-V) curves were measured using a Keithley 4200 SMU instrument under AM 1.5 irradiation (100 mW cm^{-2}, XES-301S solar simulator). The crystal structures of perovskite were analyzed by X-ray diffraction (D/MAX2500V). The incident-photon-to-current conversion efficiency (IPCE) spectra and the electrochemical impedance (EIS) spectra were measured on an electrochemical workstation (Zahner, Germany) in dark. The frequency ranged from 500mHz to 1MHz with 20 mV perturbation voltage and data was fitted with ZView software. Fourier transform infrared (FTIR) was measured using a Nicolet IS50 iN10 (Thermo Fisher, USA) and UV-visible-near-infrared absorption spectra were measured by CARY 5000 (Agilent, Australia). Steady-state photoluminescence (PL) was carried out by F-4500 Fluorescence Spectrophotometer (Japan). The film morphology was characterized by field emission scanning electron microscope (FE-SEM, SU8020). X-Ray photoemission spectroscopy (XPS) data were obtained by an X-ray source (1486.6 eV) with monochromatic Al Kα (ESCALAB 250Xi, Thermo, USA). The binding energy range was calibrated by setting the C 1s (284.8 eV). Measurement of surface current and potential by conductive atomic force microscopy (C-AFM) and Kelvin Probe Force Microscopy (KPFM) with a tip radius of 25 nm were obtained using Dimension Icon (BRUKER, Germany) under dark. In order to record the current signal between the samples and the tip, C-AFM works in contact mode. In the process, 1 V constant voltage is applied to the as-prepared samples.

References

1. Wang, A.; Cao, Z.; Wang, J.; Wang, S.; Li, C.; Li, N.; Xie, L.; Xiang, Y.; Li, T.; Niu, X.; et al. Vacancy defect modulation in hot-casted NiOx film for efficient inverted planar perovskite solar cells. *Journal of Energy Chemistry* **2020**, *48*, 426-434, doi:https://doi.org/10.1016/j.jechem.2020.02.034.
2. Si, J.; Sha, H.; Qu, B.; Wang, F.; Ma, X.; Jia, C.; Chen, Y. Synergistic effect of surface active agent in defect passivation by for ambient air-synthesized halide perovskite solar cells. *Journal of Power Sources* **2022**, *524*, 231038, doi:https://doi.org/10.1016/j.jpowsour.2022.231038.