Tremendously Enhanced Photocurrent Enabled by Triplet-Triplet Annihilation Up-conversion for High-Performance Perovskite Solar Cells

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Materials: All chemicals were used directly without any treatment after purchase. Chlorobenzene (CB, anhydrous, 99.8%), dimethyl sulfoxide (DMSO, anhydrous, ≥99.9%), N, N-dimethylformamide (DMF, anhydrous, 99.8%), 4-tert-butylpyridine (tBP), bis(trifluoromethylsulfonyl) amine lithium salt (Li-TFSI), rubrene (Rub, 99.99%) and dibenzotetraphenylperiflanthene (DBP, 98% HPLC) were obtained from Sigma-Aldrich. Lead iodide (PbI_2, 99.999%) and stannic oxide (SnO_2) colloid precursor were obtained from Alfa Aesar. Methylamine iodide (CH_3NH_3I, 99.0%) was purchased from TCI. 2,2′,7,7′-tetrakis(N, N-di-p-methoxyphenylamine)-9,9′-spirobifluorene (Spiro-OMeTAD) was purchased from Xi'an Polymer Light Technology Crop. Acetonitrile (99.9%) was purchased from J&K Scientific Ltd.

PVSCs Fabrication and Characterization: Perovskite precursor solution was prepared by dissolving PbI_2 and CH_3NH_3I in DMF/DMSO (9:1, v/v) with a molar ratio of 1:1. Indium tin oxide (ITO) glass substrates were cleaned by sequential ultrasonic treatment with detergent solution, acetone, deionized water, and isopropyl alcohol for 20 min, respectively. After drying with a stream of nitrogen, then the substrates were treated with UV-ozone for 20 min in plasma cleaner. The SnO_2 solution (1 mL SnO_2 colloid precursor was diluted by 3 mL of deionized water) was spin-coated on ITO at 3000 rpm for 30 s, followed by annealing at 150 °C for 30 min in air. For one-step anti- solvent method to fabricate the perovskite film, the perovskite precursor was directly spin-coated onto the SnO_2 substrate at 4000 rpm for 30 s followed with a dripping of CB (0.15 mL, with and w/o Rub:DBP) after spin coating step for 9 s. The various concentrations Rub:DBP solution were prepared by dissolving different weights of Rub and DBP (mass ratio 10:1) in 1 mL CB. Then the substrate annealed on a hot plate at 100 °C for 10 min. For bilayer structure device preparation, the Rub:DBP solution was spin-coated onto the perovskite layer at 4000 rpm for 30 s. After the substrate cooled to room temperature, then Spiro-OMeTAD solution [72.3 mg Spiro-OMeTAD with 17.5 μL LiTFSI solution (520 $mg \cdot mL^{-1}$ in acetonitrile) and 28.8 μL tBP in 1 mL CB] was spin-coated at 4000 rpm for 30 s on

the perovskite films. Finally, 90 nm Ag electrode was evaporated on the films to complete the preparation of PVSCs with an effective area of 0.04 cm^2.

Device Characterization: Current density-voltage (*J-V*) characteristics were measured using a source meter (Keithley 2400), equipped with a light source (100 $mW \cdot cm^{-2}$) under AM 1.5 G filter. The reverse scan range is from 1.2 V to 0 V, with 20 mV for each step. The ultraviolet-visible (UV-Vis) spectra was conducted using a SHIMADZU, UV-2600 spectrophotometer. The steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra were recorded by an Edinburgh instruments FLS920 spectrometer (Edinburgh Instruments Ltd.). Atomic force microscopy (AFM) images were measured by MultiMode 8-HR (Bruker) atomic force microscope. A Rigaku D/Max-B X-ray diffractometer with Bragg-Brentano parafocusing geometry was employed to test X-ray diffraction (XRD) patterns. The Two-dimensional grazing incidence X-ray diffraction (2D-GIXRD) measurement was performed at the BL14B1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF). External quantum efficiency (EQE) values were measured under monochromatic illumination (Oriel Cornerstone 260 1/4 m monochromator equipped with an Oriel 70613NS QTH lamp), and the calibration of the incident light was performed using a monocrystalline silicon diode. Electrical impedance spectroscopy (EIS) of the PVSCs was performed in a frequency range from 1 MHz to 10 mHz using Zahner electrochemical workstation at an applied bias equivalent to the open-circuit voltage of the cell under 1 sun illumination.

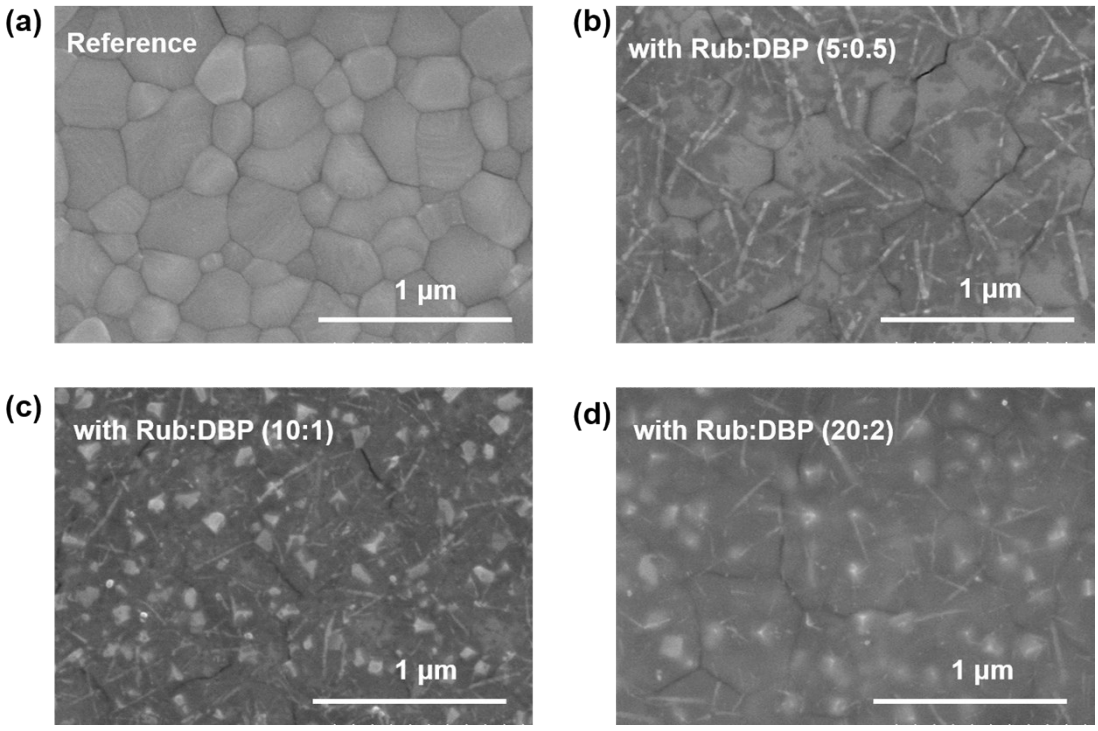


Fig. S1. SEM images of (a) the reference and (b-d) Rub:DBP incorporated perovskite films with different mass ratio concentration.

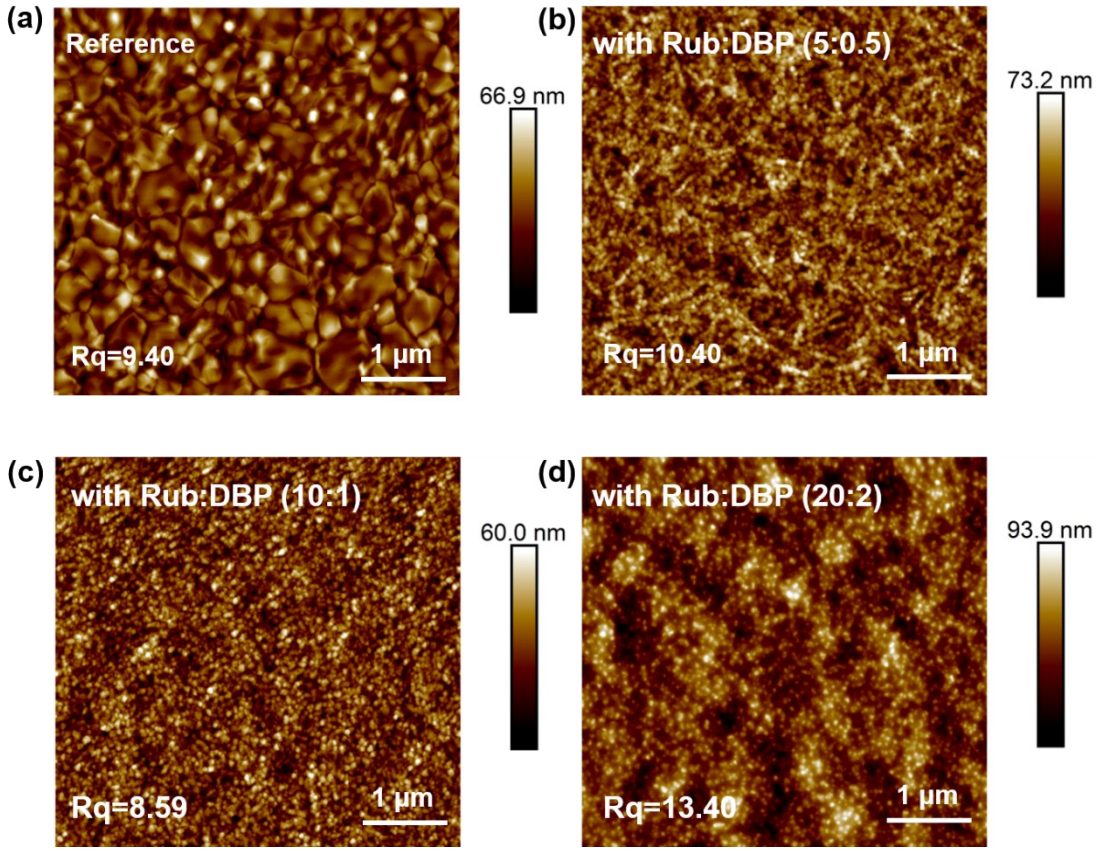
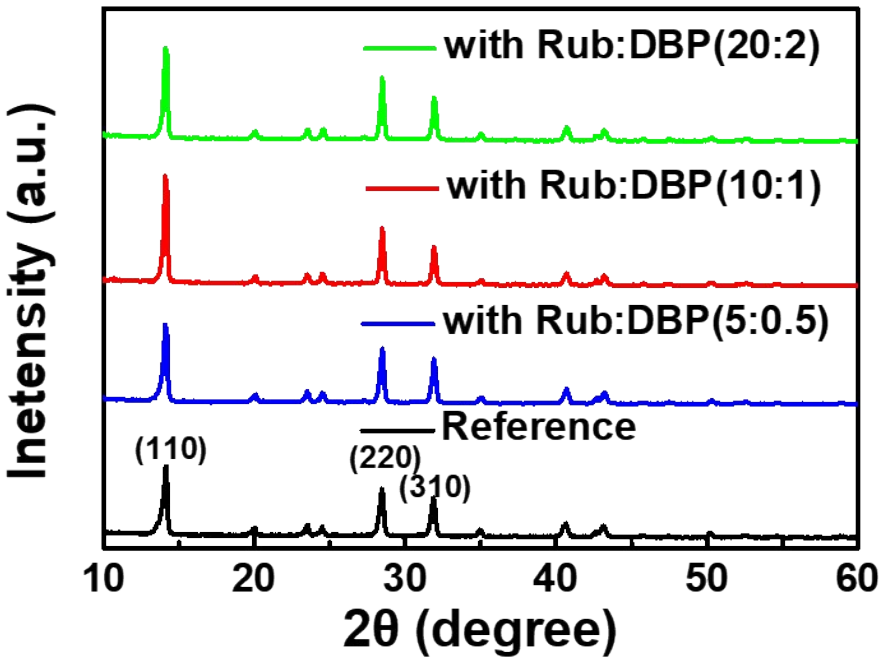


Fig. S2. AFM images of (a) the reference and (b-d) Rub:DBP incorporated perovskite films with different mass ratio concentration.



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76 **Fig. S3.** XRD patterns of the reference and Rub:DBP incorporated perovskite films.

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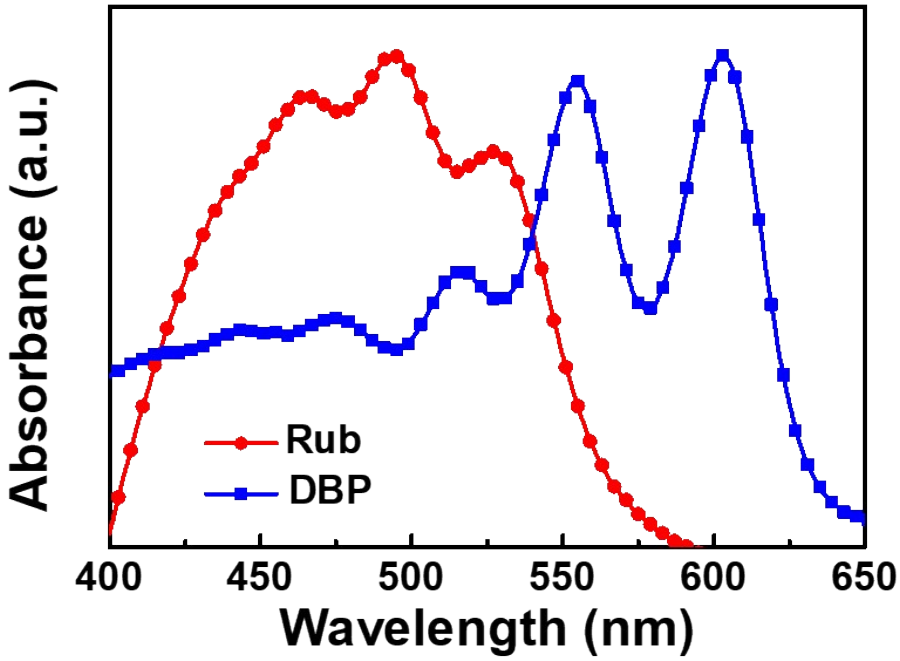


Fig. S4. UV-Vis absorption spectra of Rub and DBP films.

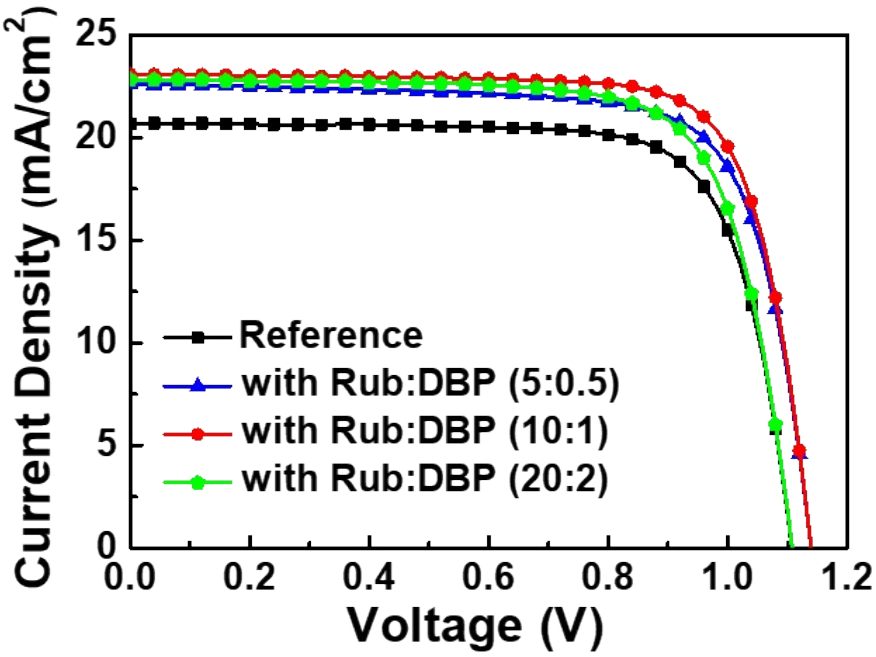


Fig. S5. *J-V* curves of the reference and Rub:DBP incorporated PVSCs under standard AM 1.5 G illumination (100 mW·cm^{-2}).

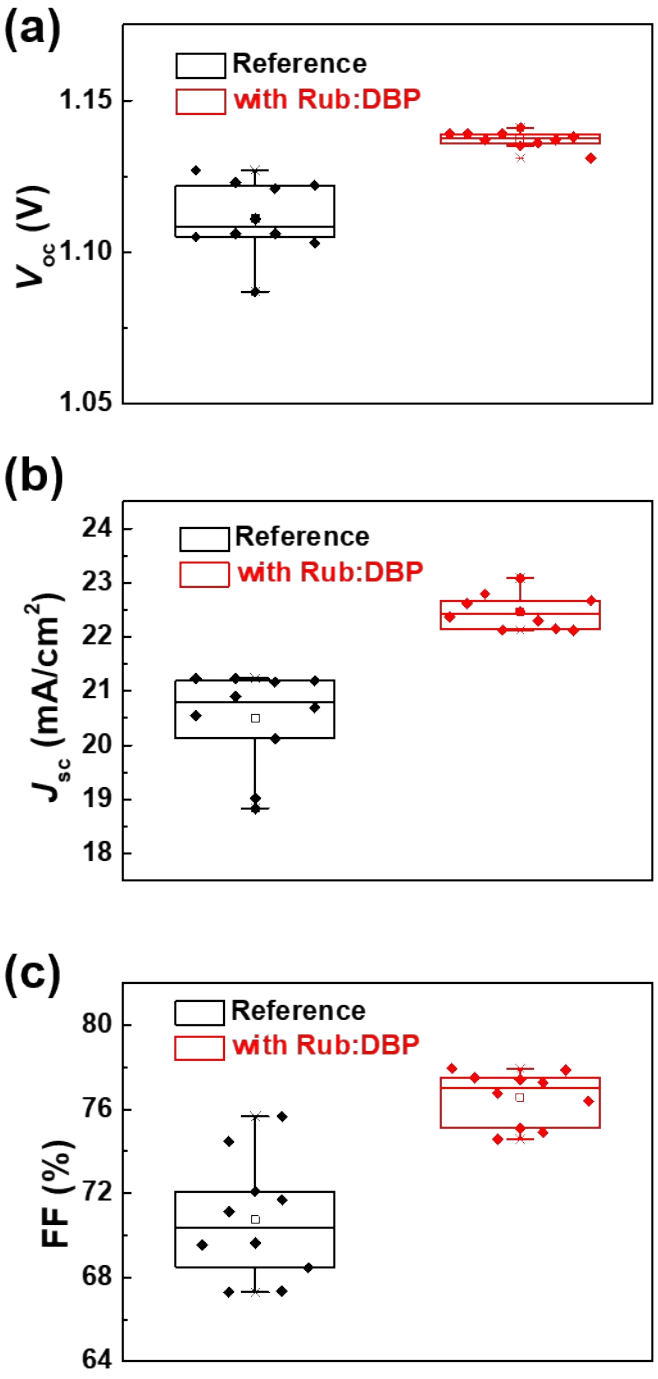
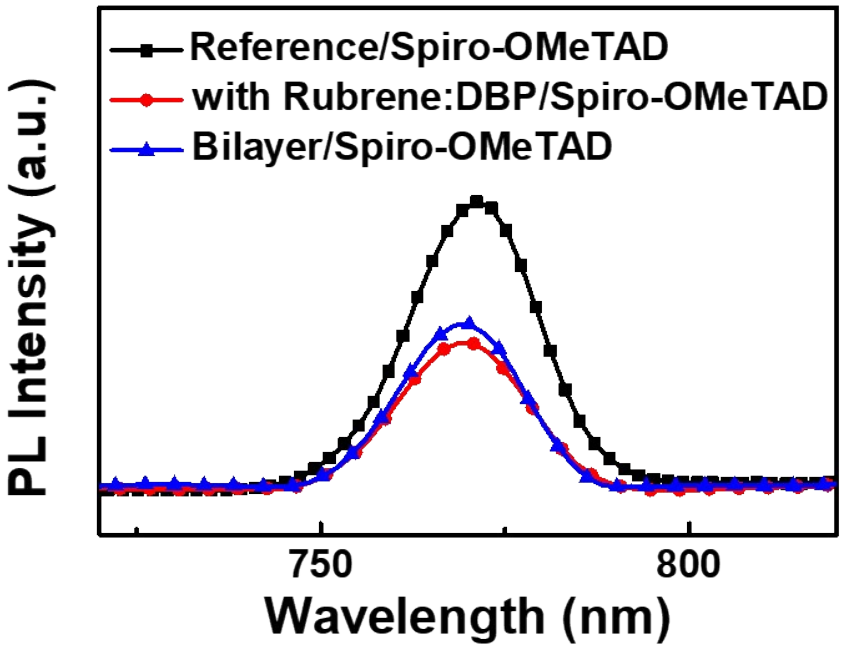


Fig. S6. (a) V_{oc}, (b) J_{sc}, and (c) FF statistical distribution of the reference and Rub:DBP incorporated PVSCs devices.



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89 **Fig. S7.** PL spectra of the reference and Rub:DBP incorporated perovskite films on

90 HTL.

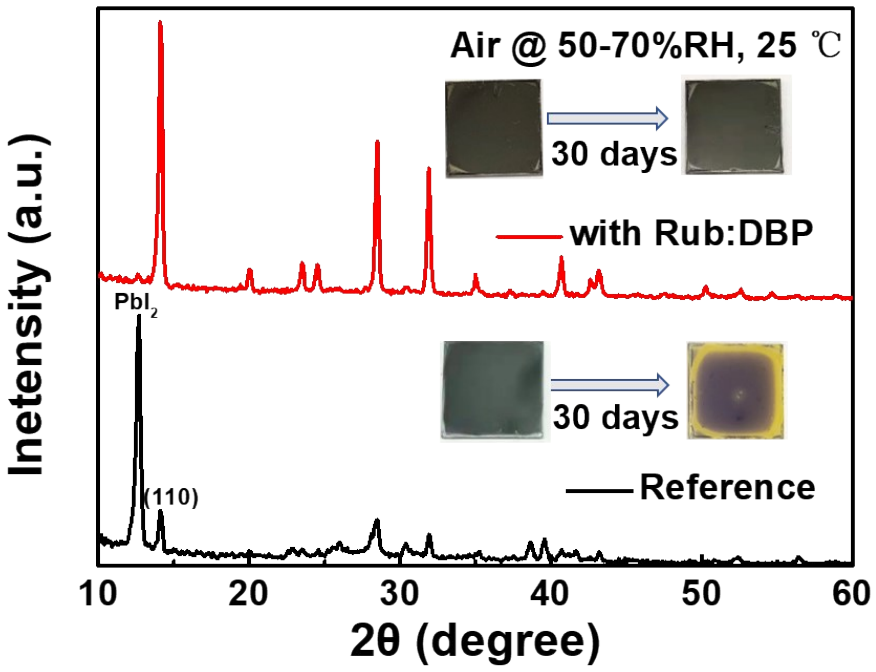

Fig. S8. XRD patterns of the reference and Rub:DBP incorporated perovskite films after aged in air with a RH of 50-70% for 30 days.

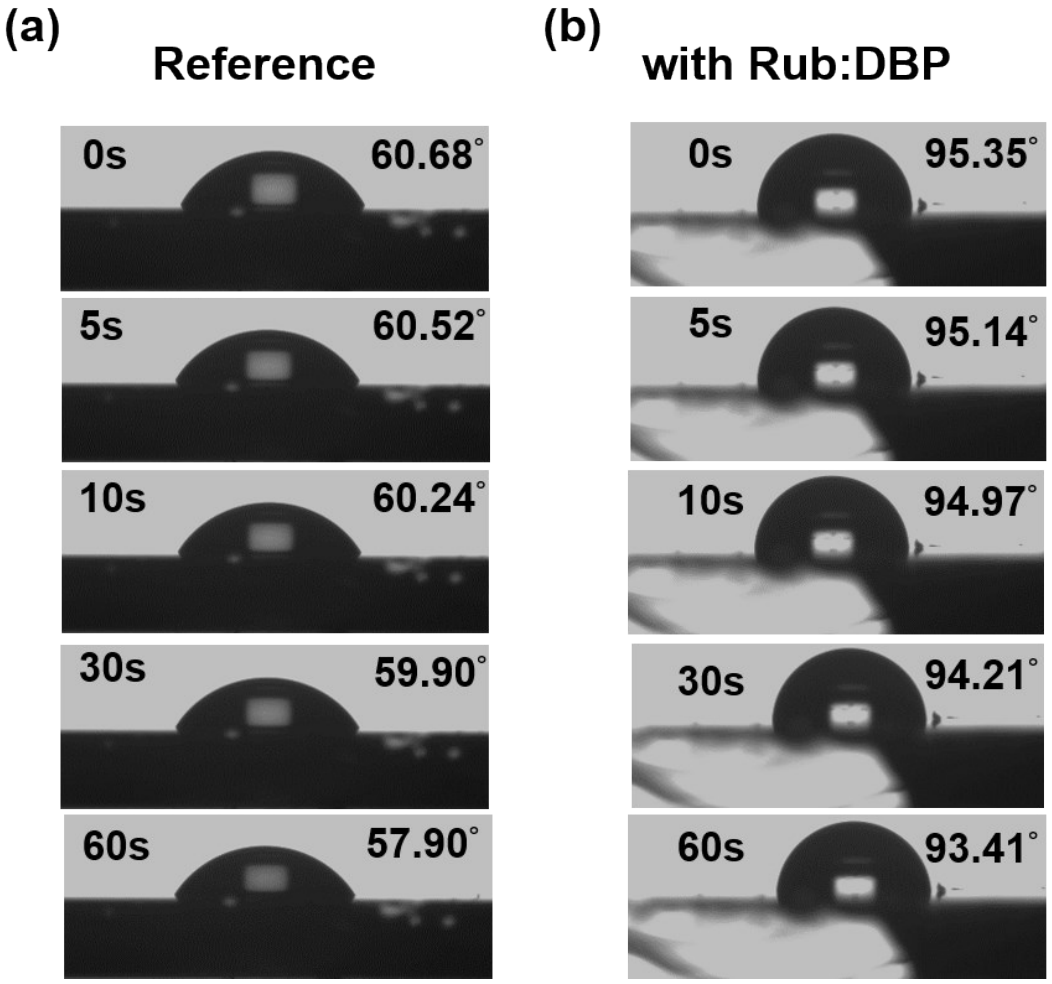

Fig. S9. The contact angle changes of the reference and Rub:DBP incorporated perovskite films.

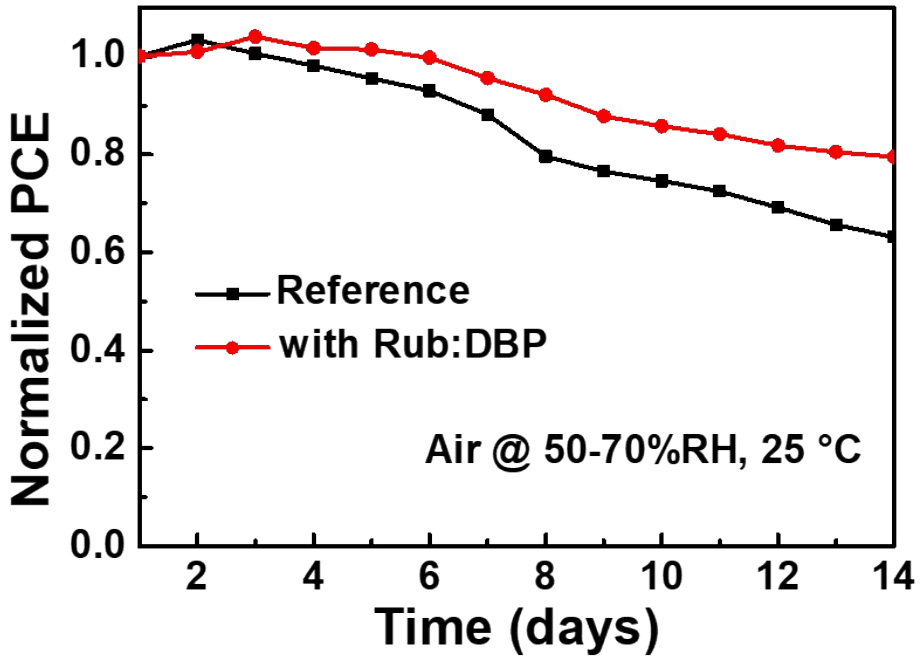

Fig. S10. The long-term moisture stability of the unencapsulated reference and Rub:DBP incorporated PVSCs under air environment with a RH of 50-70%.

Tab. S1. The fitting parameters for time-resolved photoluminescence (TRPL) of the reference and Rub:DBP incorporated perovskite films.

Sample	τ_1 (ns)	τ_2 (ns)	A_1 (%)	A_2 (%)	τ_{ave} (ns)
Reference	45.9	430.0	2.45	97.55	356
with Rub:DBP	2.26	592.1	1.41	98.59	126

Table S2. The charge mobilities of hole-only and electron-only devices based on $MAPbI_3$ (with and w/o Rub:DBP).

Device	Hole mobility ($cm^2 \cdot V^{-1} \cdot S^{-1}$)	Electron mobility ($cm^2 \cdot V^{-1} \cdot S^{-1}$)
Reference	1.69×10^{-2}	6.60×10^{-1}
with Rub:DBP	1.45×10^{-1}	6.94×10^{-1}