

Supplementary materials for

**Improved efficiency and stability of flexible perovskite solar cells by
a new spacer cation additive**

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1. Experiment

1.1 Materials

The tin oxide (SnO₂, 15% in H₂O) colloid precursor was purchased from Alfa Aesar. The PET/ITO substrate was purchased from dAdvanced Election Technology CO.Ltd. Related solution such as dimethyl sulfoxide (DMSO), N, N-dimethylformamide (DMF), isopropanol (IPA), acetonitrile, 4-tertbutylpyridine (4-TBP), and chlorobenzene (CB) were obtained from Sigma-Aldrich. The involved

organic salts include methylammonium iodide (MAI, >99.5%), formamidinium iodide (FAI, >99.5%), formamidinium bromide (FABr, >99.5%), and, methylammonium chloride (MACl, >99.5%), aladdin phenylethylammonium iodide (PEAI, >99.5%), together with the spiro-OMeTAD (>99.5%) and lead iodine (PbI₂, >99.99%), which were also purchased from Xi'an Polymer Light Technology Corp. 2-(chloromethyl)pyridine hydrochloride (CPHC) and CoCl₃.6H₂O was ordered from Aladdin. All reagents and solvents were used as received.

1.2 Device fabrication

PET/ITO substrates were cleaned by a sequential sonication treatment in the deionized water, acetone and isopropanol for 15 min, followed by ultraviolet-ozone treatment for 15 min. After that, SnO₂ (Volume ratio, Water:NH₄.H₂O:SnO₂=2:1:1 and 3 mg/mL CoCl₃.6H₂O) solution was coated on the cleaned substrate at 4,000 rpm for 30 s, followed by annealing under 120 °C for 30 min in the air. 691.5 mg of PbI₂ was dissolved in 950 μL DMF and 50 μL DMSO. Organic salts (FAI:MAI:MACl(CPHC) = 73.5 mg:16.5 mg :18 mg (0.5 mg)) were dissolved in 1 mL IPA. The perovskite layers were then fabricated by using a two-step spin-coating process reported previously (first step 1800 r.p.m. for 30 s; second step 2400 r.p.m for 40 s). Then the substrates were annealed at 70 °C for 1 min in the glove box (first step) and under 150 °C for 15 min in the air environment (humidity = 30~40%). After that PEAi (5 mg/L) IPA solution were spin coated on the perovskite layers (5000 r.p.m for 30 s). The hole transport layers (HTL) were deposited by spin coating the spiro-OMeTAD solution (72.3 mg spiro-OMeTAD in 1 mL CB and mixing 30 μL 4-TBP and 40 μL LiTFSI (260 mg/mL in acetonitrile)). The above solutions were spin coated on the perovskite layers (5,000 r.p.m for 30 s). Finally, 80 nm Au electrode was evaporated under a high vacuum of 8*10⁻⁴ Pa. Our PSCs of area is 0.1 cm² and aperture area of 0.04 cm².

1.3 Characterization of Device and Materials

The current density–voltage (J - V) measurement was performed via a Keithley 2400 Source Meter under a solar simulator (AM1.5G). The external quantum efficiency curves were obtained with a Zolix SCS10-X150-DSSC system. Capacitance–voltage relationships were measured under 10 mV AC voltage at 1 kHz. The surface morphology was obtained using a field-emission scanning electron microscopy (SEM, Hitachi, SU9000), using an electron beam accelerated at 5 kV. The X-ray diffraction (XRD) patterns were recorded using Cu- K_{α} conventional pattern (XRD, Bruker D8 Advance, $\lambda=1.5406$ Å). The absorption spectra were recorded with Jasco V-670. FTIR spectroscopy was conducted in the IR spectrometer instrument (Bruker IFS66V/S). The high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was carried out using a F200X-G2 microscope equipped by an aberration corrector for probe forming lens, operated at 300 kV. The steady-state PL spectrum was obtained by using a laser scanning confocal microscope (Witec, alpha 300). The transient photocurrent (TPV) spectra were recorded by a high resolution oscilloscope (Tektronix DPO2022B) using 550 nm excitation derived from a pulsed laser. (Opolette HE 355 LD) The trap density measurements were performed by using an Agilent B1500A precision meter in the drive-level capacitance profiling (DLCP) module. The DLCP measurement were conducted in the same DC bias range with that for the standard C-V measurement from 0 to 1.5 V. While the amplitude of the ac biases was ranging from 20 to 200 mV.

2. Supplementary experimental results

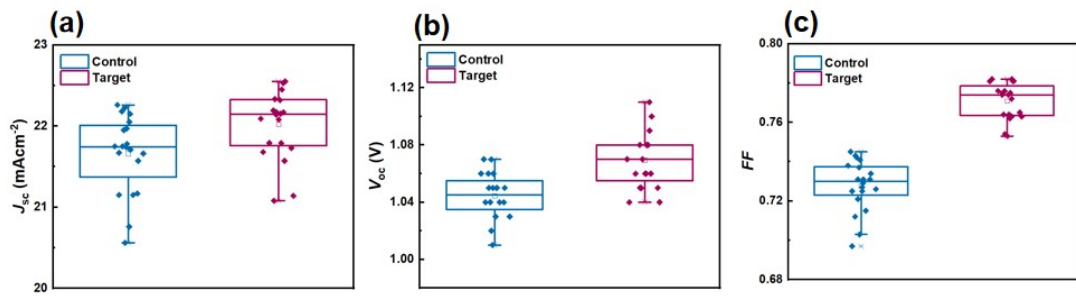


Figure S1. The statistically evaluated J_{sc} (a), V_{oc} (b) and FF (c) of 20 different devices.

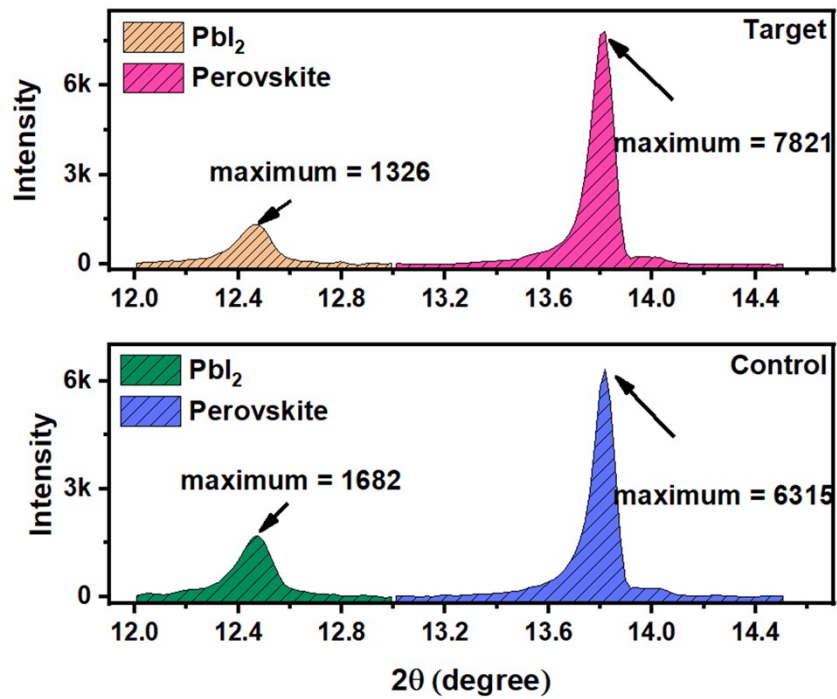


Figure S2. Magnified XRD pattern of perovskite and PbI_2 peaks.

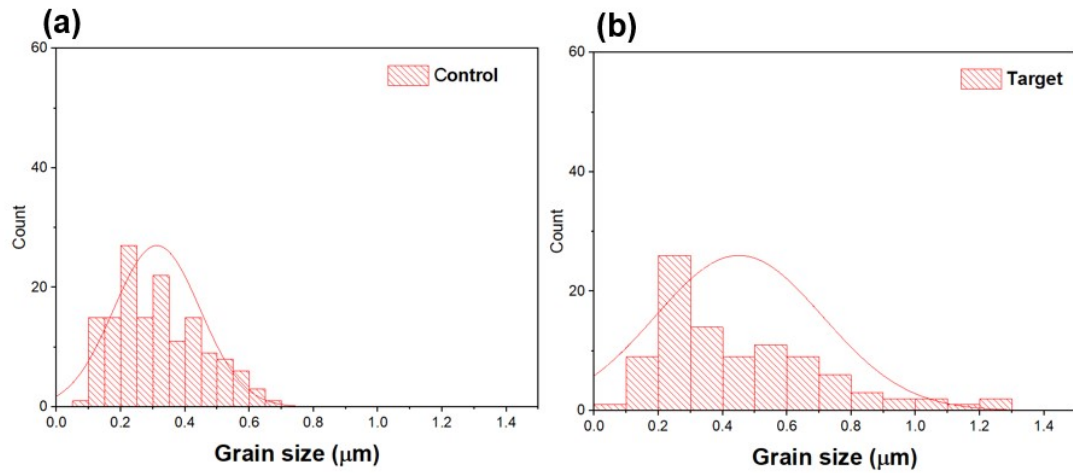


Figure S3. The corresponding particle size statistics of the control (a) and target (b) perovskite film.

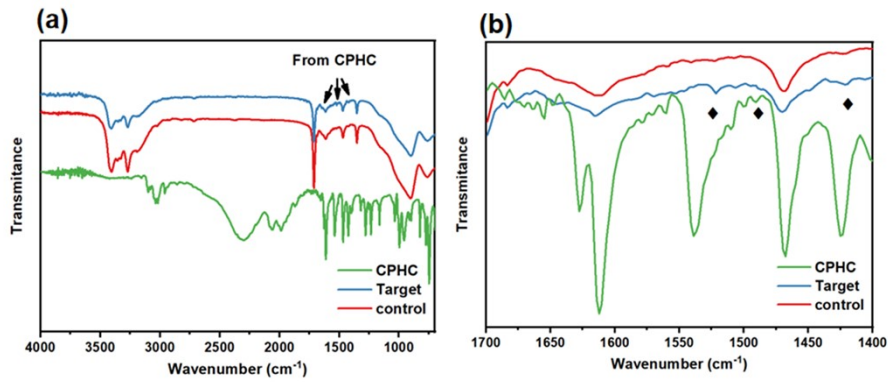


Figure S4. (a) FTIR spectra for the CPHC powder (green), control (red) and the doped film (blue). (b) Magnified FTIR spectra.

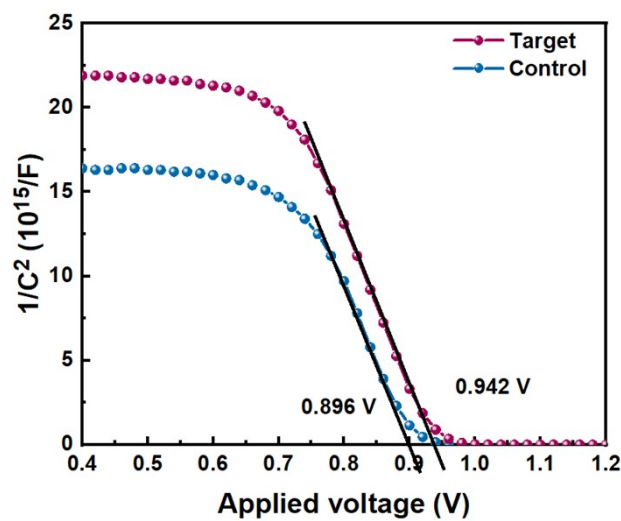


Figure S5. Mott–Schottky plots of the different flexible PSCs. From the M-S plots, we confirm that the target device has a larger V_{bi} (0.942 V), compared to the control device (0.896 V).