Supporting information

Experimental Section

Materials:

The reagents used in the work were purchased from the following companies without further purification.

ITO (Advanced Election Technology Co., Ltd), SnO_2 (Tin(IV) oxide, 15% in H_2O colloidal dispersion, Alfa Aesar), BiI_3 (Bismuth (III) iodide, 98%, Macklin), CsI (Cesium iodide, 99.9%, Advanced Election Technology Co., Ltd), MoO_3 (Molybdenum (VI) oxide, 99.9%, 3A Chemicals), Spiro-OMeTAD (2, 2', 7, 7'-tetrakis (N, N-di-p-methoxy-phenylamine)-9, 9'-spirobifuorene, Advanced Election Technology Co., Ltd), Li-TFSI (Lithium bis (triuoromethanesulfonyl) imide, Xi 'an p-OLED Corp), tBP (4-tert-butyl pyridine, Xi 'an p-OLED Corp), DMSO (Dimethylsulfoxide, 99.9%, Sigma-Aldrich), DMF (N, N-Dimethylformamide, 99.8%, Sigma-Aldrich), CB (Chlorobenzene, 99.8%, Sigma-Aldrich).

Preparation of perovskite solutions:

1 mmol BiI_3 and 0.333 mmol CsI were added into the mixture of 900 uL DMF and 100 uL DMSO solution and stirred for 8 h to prepare $CsBi_3I_{10}$ precursor solution in the glove box.

Device fabrication:

ITO glass was cleaned in detergent, deionized water, acetone and isopropanol sequentially by ultrasonication for 15 min and then treated with UV-ozone for 20 min. The SnO_2 solution (3.75% in H_2O) was coated onto ITO at 3000 rpm for 30s and annealed at 200 °C for 40 min in air. The CBI precursor solution was spin coated on top of SnO_2 layers at 3000 rpm for 30s and then annealed at 160 °C for 5min in air environment (RH=30%). For the perovskite prepared by hot-casting method, the substrates were preheated at 85 ℃ for 5 minutes before coated with CBI precursor. Similarly, the SnO_2 substrate should be placed on a cold table (-5℃) for 5 minutes

before spinning the precursor solution for the cold-casting method. The Spiro-OMeTAD solution, which was prepared by mixing 72.3 mg Spiro-OMeTAD in 1 mL chlorobenzene with 28.8 µL tBP and 17.5µL Li-TFSI salt (520 mg/mL in acetonitrile) was spin-coated at 3000 rpm for 30 s. Finally, 5 nm MoO_3 and 80 nm silver counter electrode were deposited by vacuum evaporation method.

Characterization:

Top-view and cross-section SEM photograph of CBI films and device were taken by field-emission scanning electron microscopy (JSM-7800F, Japan). Atomic force microscopy (AFM) measurements were carried out on Asylum Research MFP-3D-BIO (US) in Kelvin Probe Force Microscope mode. X-ray diffraction (XRD) spectra were recorded by X-ray diffraction (XRD, Bruker D8 Advance) and used with Cu Kαradiation irradiation at 40 mA and 40 kV. All samples were scanned from 5° to 55° (2 detector). The absorption spectra measured on UV-Vis spectrometer (Shimadzu UV-2550) was to evaluate the light absorption ability of perovskite. The I-V curves was obtained from the Probe station for semiconductor measurement (Lake Shore CRX-6.5K). The photoluminescence (PL) spectra of the films were obtained from Fluorescence spectrophotometer (FLS920) using 395 nm incident light to excite. The Current–voltage (J–V) curves of devices were measured under AM 1.5 G sunlight (100 mW cm^{-2}) from a solar simulator (Keithley 2400 source meter) with a 0.09 cm^2 aperture mask. The Electrochemical impedance spectroscopy (EIS) curves were performed on the Electrochemical Workstation (CHI600E, China). The water contact angle of CBI films were obtained from the contact angle goniometer (Kruss SA20, Germany).

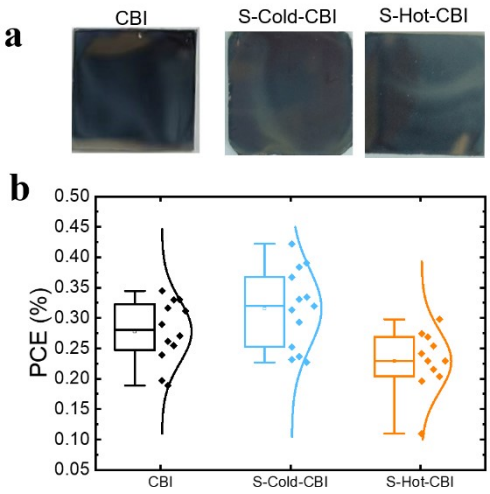


Figure S1. (a) The photographs of CBI film fabricated with preheated, pre-cooled and normal precursor solution. (b) Distribution of PCE of devices fabricated *via* different treatment of precursor solution.

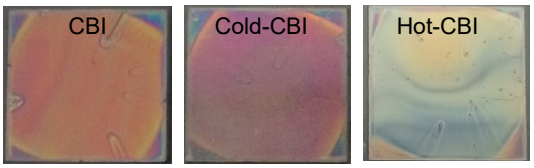


Figure S2. The photographs of films based on CBI, Cold-CBI and Hot-CBI covered by spiro-OMeTAD.

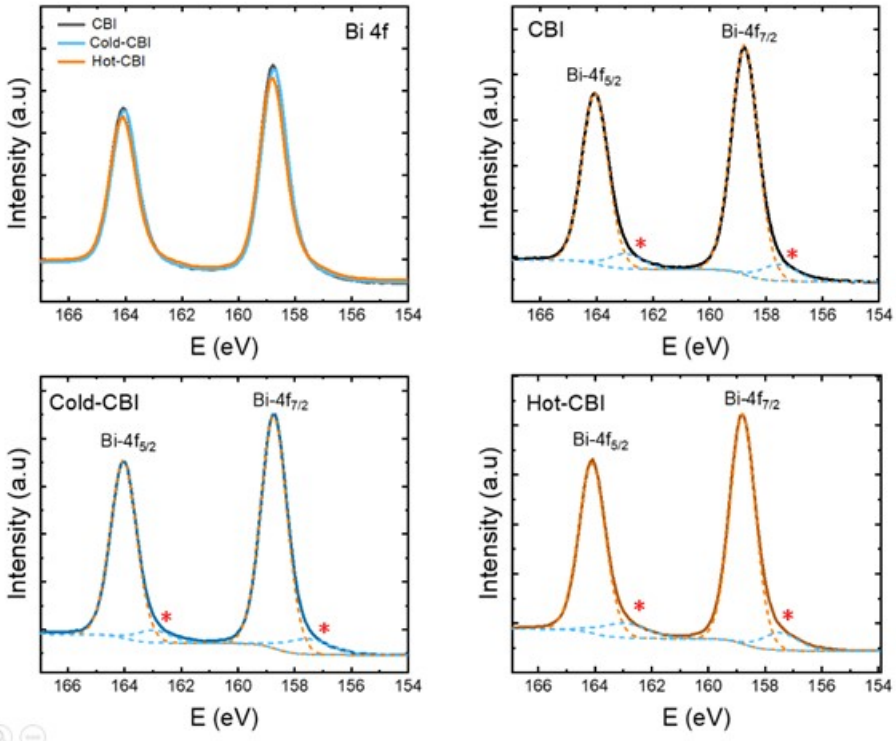


Figure S3. The fine XPS spectra of Bi 4f in CBI, Cold-CBI and Hot-CBI films

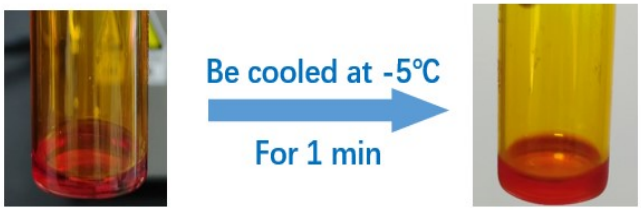


Figure S4. The CBI solution before and after placed on the cold table at -5 ℃ for 1 min, which indicated the solubility of the solution decreases with the declining of temperature.

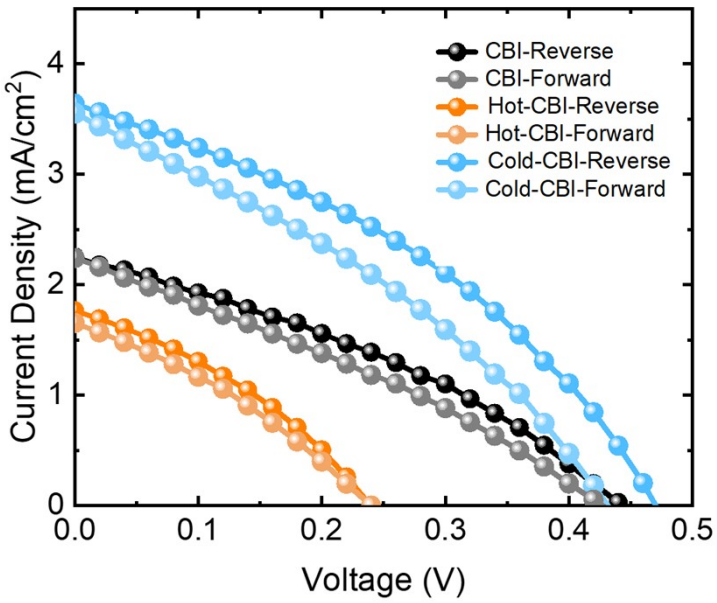
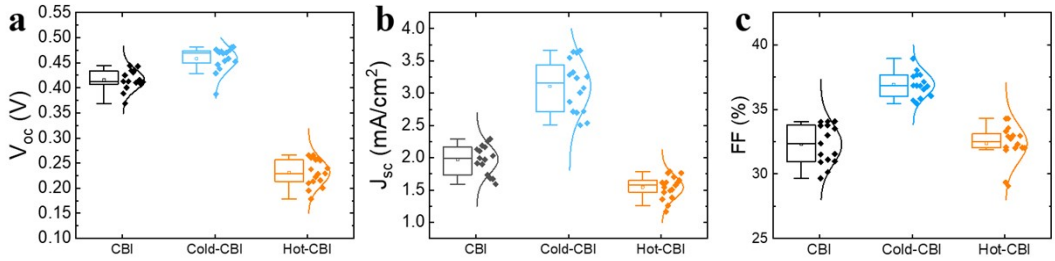


Figure S5. The J−V curves of both forward and reverse scans for different devices

Table S1: The photoelectric characteristic parameters of three kinds of devices.

Samples	V_{oc} (*V*)	J_{sc} (mA/cm^2)	*FF* (%)	*PCE* (%)	*HI*
CBI-Reverse	0.44	2.26	33.50	0.34	0.17
CBI-Forward	0.42	2.24	29.85	0.28	
Cold-CBI-Reverse	0.47	3.64	36.83	0.63	0.21
Cold-CBI-Forward	0.43	3.51	32.81	0.50	
Hot-CBI-Reverse	0.24	1.76	34.28	0.14	0.14

Hot-CBI-Forward	0.24	1.63	32.13	0.12



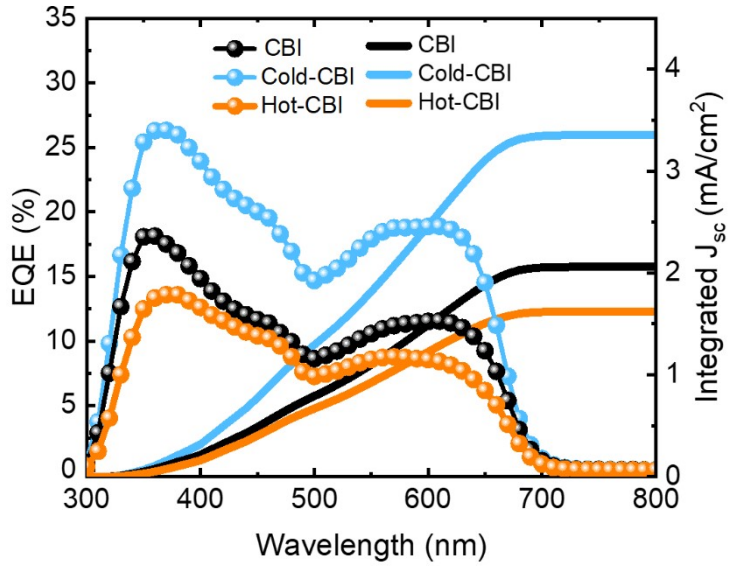


Figure S6. Distribution of (a) V_{oc} (b) J_{sc} and (c) FF of the three types of devices.
Figure S7. The EQE curves of CBI, Cold-CBI and Hot-CBI based devices.