

Supporting Information

Dual Function-Enabled Novel zwitterion to Stabilize Pb-I Framework and Passivate Defects for Highly Efficient Inverted Planar Perovskite Solar Cells

Deng Wang,^{‡ac} Lei Huang,^{‡ac} Qiyin Chen,^{‡b} Luyao Hu,^{ac} Feng Zeng,^{ac} Xianyong Zhou,^{ac} Luo Zheng Zhang,^{ac} Chang Liu,^{ac} Xingzhu Wang,^{*abc} Lei Yan^{*b} and Baomin Xu^{*ac}

^a Department of Materials Science & Engineering and SUSTech Academy for Advanced Interdisciplinary Studies, Southern University of Science and Technology, Shenzhen, Guangdong Province 518055, China

^b Xiangtan University, College of Chemistry, Xiangtan, Hunan Province 411105, China

^c Shenzhen Engineering Research and Development Center for Flexible Solar Cells, Southern University of Science and Technology, Shenzhen, Guangdong Province 518055, China

Experimental details

Materials

ITO coated glass with sheet resistance of $15 \Omega/\text{sq.}$ was purchased from Ying Kou You Xuan Trade Co. Ltd. PTAA (MW=5000~15000), $\text{CH}_3\text{NH}_3\text{Cl}$ (MACl), $\text{CH}(\text{NH}_2)_2\text{I}$ (FAI), $\text{CH}_3\text{NH}_3\text{Br}$ (MABr), C_{60} and BCP were purchased from Xi'an Polymer Light Technology Corp. PbI_2 (99.9985%) was obtained from Alfa Aesar. Bethanechol chloride (BTCC) was purchased from Tokyo Chemical Industry Co. Ltd. (TCI, Japan). All solvents including isopropanol (IPA, 99.5%), Dimethyl sulfoxide (DMSO, 99.5%), N, N-dimethylformamide (DMF, 99.5%) and chlorobenzene (CB, 99.5%) were purchased from Sigma-Aldrich. These materials were used as received without further purification.

Device fabrication

ITO glass substrates were cleaned with detergent, deionized water, acetone and isopropanol ultrasonically for 15 min each. After UV-ozone treatment for 20 min, ITO glasses were subsequently moved into N_2 -filled glovebox. PTAA solution (2 mg/mL in CB) was spin-coated onto ITO glass at 4000 rpm for 25 s, and then the substrates were baked at 100°C for 10 min.

The preparation of the perovskite precursor solutions for two-step deposition is shown as follows: Firstly, 553.2 mg PbI_2 was dissolved in 1 mL mix solvent of DMF and DMSO (V:V= 95:5) and stirred at 65°C for 1 h. Then, 60 mg FAI, 6 mg MACl, 6 mg MABr and BTCC with different doping concentrations (wt% = 0.5, 1, 2, 4) were

dissolved in 1 mL IPA and stirred at 40°C for 1 h. Before used, all the precursor solutions were filtered by 0.22 μm PTFE filter. 50 μL PbI_2 solution was spun onto PTAA substrates at 2000 rpm for 30s, and then let it on stand for 2 min. 100 μL salt-mixed solution was spun onto PbI_2 at 2000 rpm for 30s. After that, the prepared films were thermal annealed at 150°C for 15 min in ambient air (RH: 30~40 %). C_{60} (40 nm), BCP (8 nm), and Ag (100 nm) were deposited in sequence onto perovskite films by thermal evaporation through a shadow mask with an active area of 0.1 cm^2 .

Characterization

Characterization of PSCs: Photocurrent density-voltage (J - V) curves were measured under AM 1.5 G one sun illumination (100 mW/cm^2) with a solar simulator (Enlitech SS-F7-3A) equipped with a 300 W xenon lamp and a Keithley 2400 source meter. The external quantum efficiency (EQE) was measured using a DSR100UV-B spectrometer with an SR830 lock-in amplifier. The steady-state PCE was measured by monitoring current with the largest power output bias voltage and recording the value of the photocurrent. The morphologies of perovskite films were characterized by scanning electron microscopy (SEM, TESCAN MIRA3) at 10 kV accelerating voltage. Atomic force microscope (AFM) images of HTMs were obtained on a multimode SPM (Bruker) with tapping mode. The XRD spectra of the prepared films were measured using a Bruker eco D8 with 40 kV and 25 mA. Ultraviolet-visible (UV-vis) spectra was carried out using an UV-vis spectrophotometer (Cary 6000, Agilent). X-ray photoelectron spectroscopic (XPS) was measured by Escalab 250Xi (Thermo Fisher, USA). Fourier transform infrared spectra (FTIR) were measured

using a Spectrum Two FTIR within 800 to 4000 cm^{-1} . Contact angles (CAs) were measured by AST VCAoptima. Electrochemical impedance spectra (EIS) were performed on an IM6 electrochemical workstation (Zahner Ennium, China) in the dark condition with a bias near the corresponding V_{OC} of individual cells. The time-resolved PL (TRPL) spectra were measured by the fluorescence spectrophotometer (Horiba-FM-2015, France).

Computed electrostatic potential (ESP) of Bethanechol chloride (BTCC): Density functional theory (DFT) calculations were performed by using the B3LYP functional and the all-electron double- ξ valence basis sets with polarization functions 6-31G*, implemented in the Gaussian 03 program. Geometry optimizations of BTCC were performed with full relaxation of all atoms without solvent effects. Vibrational frequency calculations were performed to assure that the optimized structure of BTCC has no imaginary frequency.

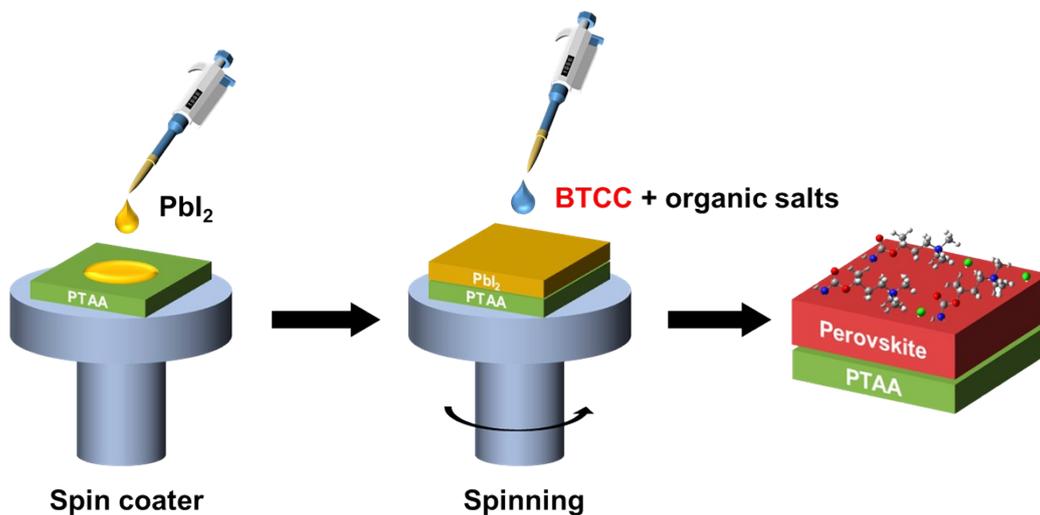


Fig. S1 The schematic fabrication procedure of perovskite film treated with BTCC via a two-step method.

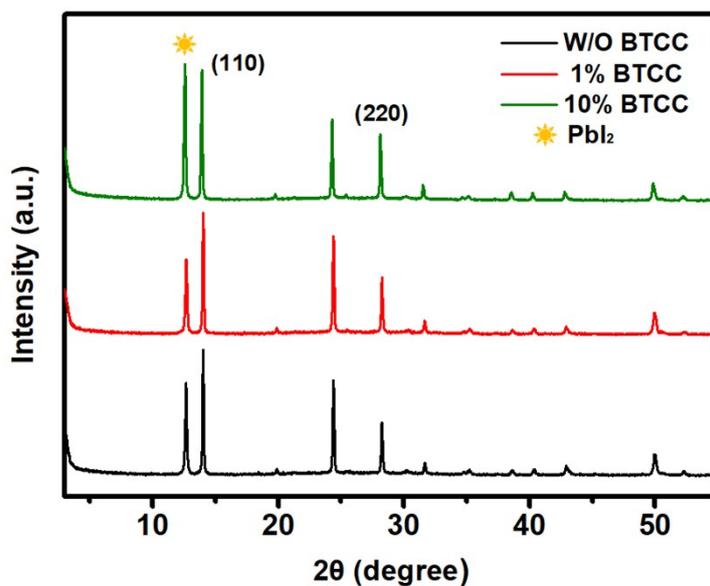


Fig. S2 XRD spectra of perovskite films with and without BTCC treatment.

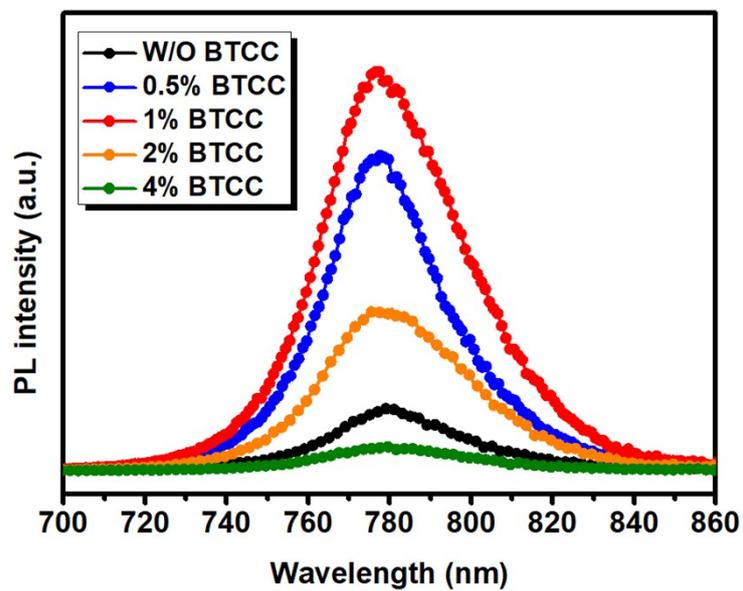


Fig. S3. Steady-state PL spectra of perovskite films with 1% and without BTCC treatment.

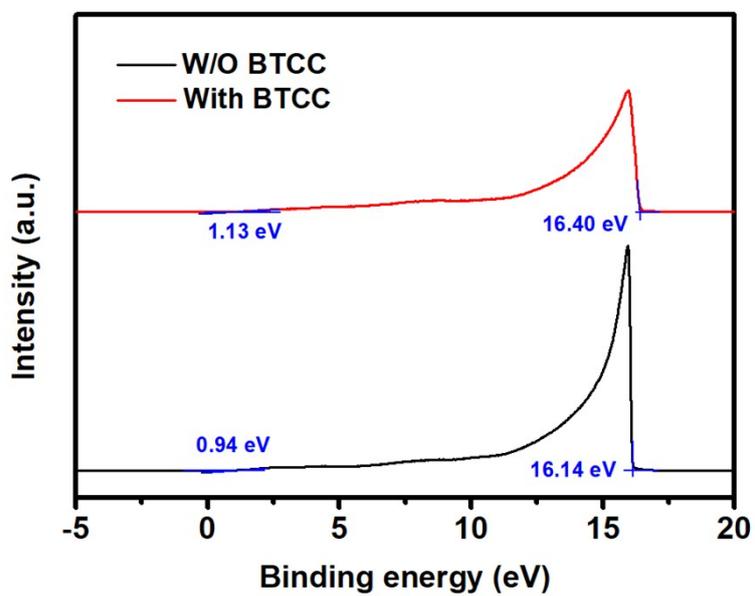


Fig. S4. UPS spectra of perovskite films with and without BTCC treatment.

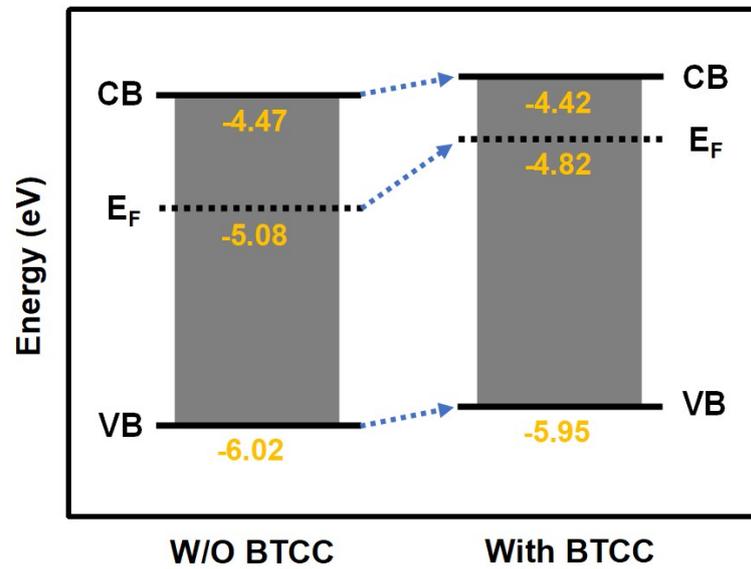


Fig. S5 Energy-level diagrams of perovskite films with and without BTCC treatment.

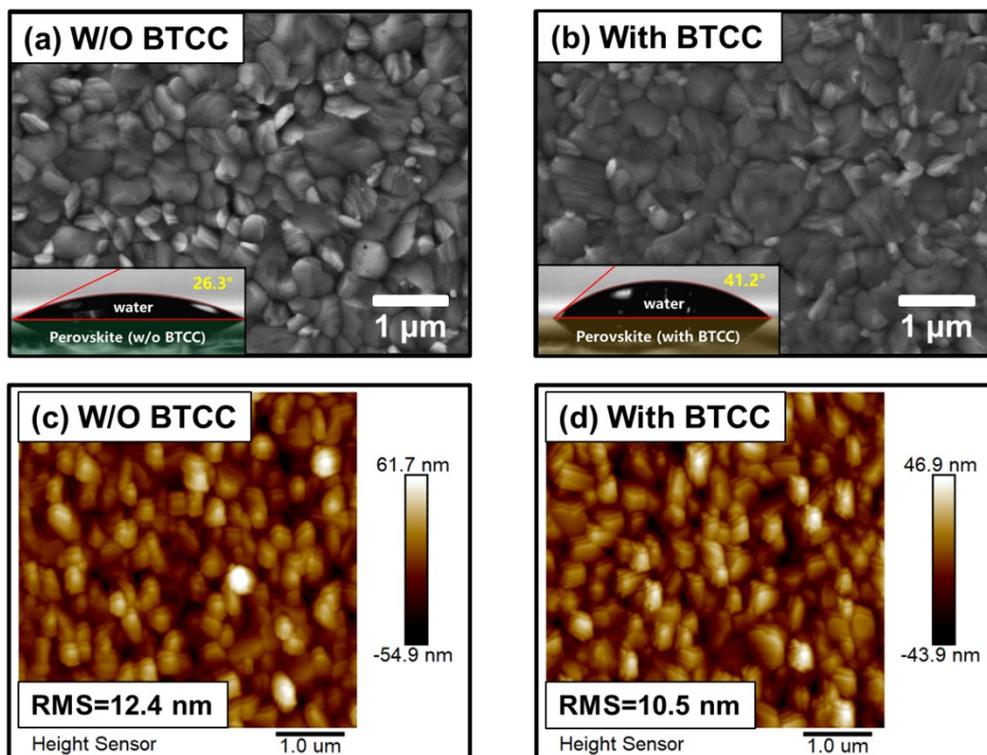


Fig. S6 SEM images of $(\text{FAPbI}_3)_{1-x}(\text{MAPbBr}_3)_x$ films (a) without BTCC and (b) with BTCC treatment. The insets in (a) and (b) are contact angle images of water. AFM images of $(\text{FAPbI}_3)_{1-x}(\text{MAPbBr}_3)_x$ films (c) without BTCC and (d) with BTCC treatment.

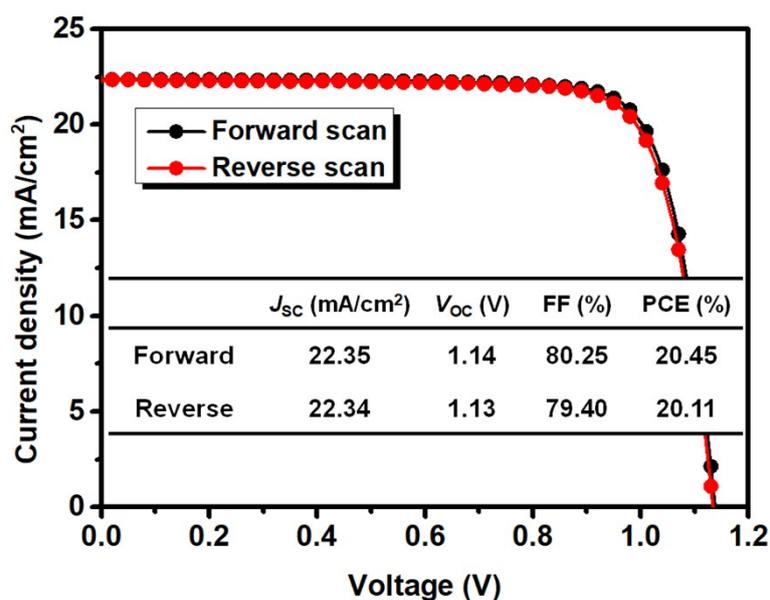


Fig. S7 J - V curves of the champion BTCC-assisted device based on forward and

reverse scans.

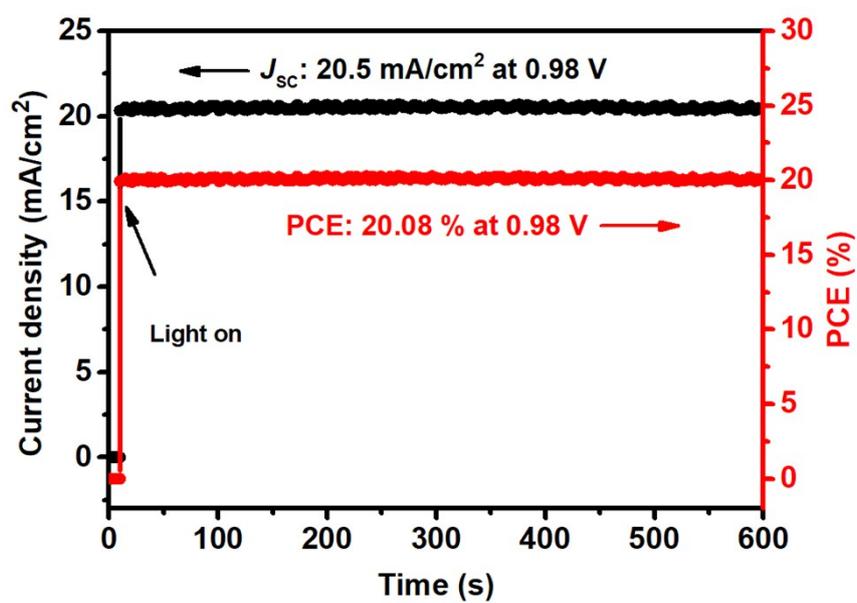


Fig. S8 Steady-state photocurrent and PCE characterization at the maximum power point (MPP) for the champion BTCC-treated device.

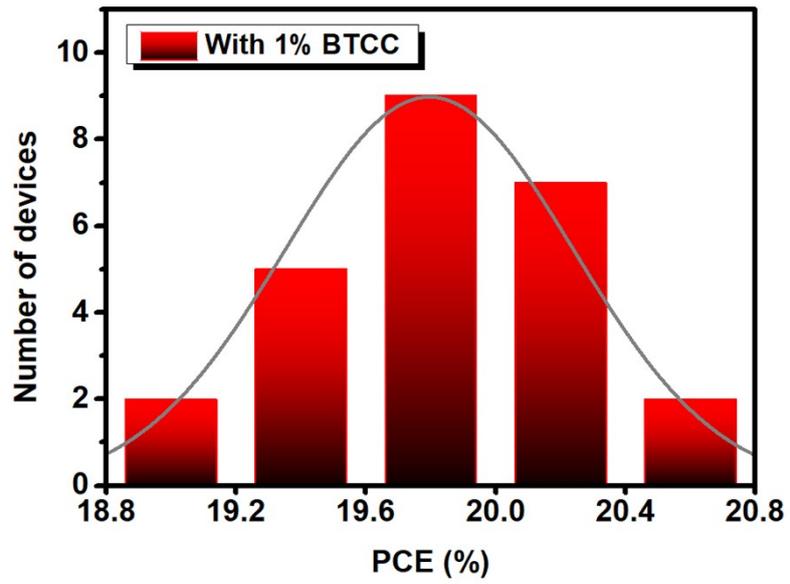


Fig. S9 The PCE distribution histogram of BTCC-treated devices (25 cells).

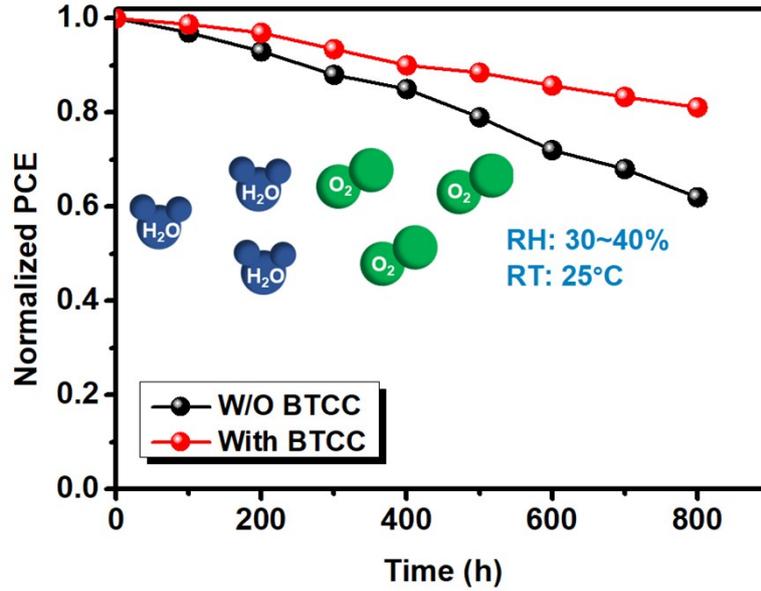


Fig. S10 The variations in PCE of the devices with and without BTCC under ambient condition.

Table S1. Atom ratios (%) of elements from XPS measurements

	Pb (4f)	Cl (2p)	C (1s)	O (1s)	I (3d)
W/O BTCC	15.51	1.99	29.25	5.64	47.60
With BTCC	14.38	2.03	32.48	5.84	45.27

Table S2. Fitting parameters of the TRPL spectroscopy for perovskite films

A_1	$\tau_1(\text{ns})$	A_2	$\tau_2(\text{ns})$	$\tau_{\text{ave}}(\text{ns})^a$

W/O BTCC	0.25	8.07	0.67	35.84	33.69
With BTCC	0.59	10.87	0.38	122.28	108.77

^a Average PL lifetime is calculated according to the equation: $\tau = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$.

Table S3. Photovoltaic parameters of PSCs with different BTCC concentration in organic salt precursor solutions

Concentration (wt%)	J_{SC} (mA/cm ²)	V_{OC} (V)	FF (%)	PCE (%)
0	22.12 ± 0.19	1.04 ± 0.007	77.50 ± 0.70	17.78 ± 0.11
0.5	22.08 ± 0.06	1.08 ± 0.008	78.84 ± 0.45	18.80 ± 0.25
1	22.18 ± 0.15	1.13 ± 0.007	79.62 ± 0.68	19.98 ± 0.37
2	21.80 ± 0.09	1.07 ± 0.011	78.25 ± 0.53	18.24 ± 0.21
4	21.36 ± 0.35	1.03 ± 0.015	77.22 ± 0.54	16.93 ± 0.14