

## Supporting Information

### **Additive Engineering with 2, 8-dibromo-dibenzothiophene-S, S-dioxide Enabled Tin-Based Perovskite Solar Cells with 14.98% Power Conversion Efficiency**

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## **Materials and Methods**

**Materials:** Germanium (II) iodide ( $\text{GeI}_2$ , >99.8%),  $\text{SnI}_2$  (99.99%),  $\text{SnF}_2$  (99%) and ethylenediammonium diiodide ( $\text{EDAI}_2$ , >98.0%) were purchased from Sigma-Aldrich Company. 2,8-dibromo-dibenzothiophene-S,S-dioxide (BrDS) was obtained from Aladdin Company. 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) was obtained from SunaTech Inc. PEDOT:PSS (PVP AI4083) was obtained from Heraeus Precious Metals North America. 1-Ethyl-3-methylimidazolium chloride (EMIC) was acquired from Aladdin Industrial Corporation. Fullerene derivative indene- $\text{C}_{60}$ -bisadduct (ICBA) and formamidine iodide (FAI) were acquired from Xi'an Polymer Light Technology. The metal copper was purchased from ZhongNuo Advanced Material (Beijing) Technology Co., Ltd. Anhydrous N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), as well as anhydrous chlorobenzene (CB, 99.8%) were obtained from Sigma-Aldrich Company.

**EMIC-PEDOT: PSS Thin Films:** 1.5 wt % EMIC was added to the PEDOT:PSS aqueous solution according to the reported literature <sup>[1, 2]</sup>. After that, the resulting solution was magnetically swirled for two hours (room temperature), then filtered by PTFE (polytetrafluoroethylene) filters (0.45 $\mu\text{m}$ ). EMIC-PEDOT:PSS thin films were then made ready via spin-coating the above blended solution. Subsequently, the film was annealed at 130 °C for 20 minutes in the air.

**Fabrication of perovskite precursor solutions:** The control perovskite precursor solutions were prepared by adding  $\text{EDAI}_2$  (2.8 mg),  $\text{SnF}_2$  (14.1 mg),  $\text{GeI}_2$  (14.7 mg), FAI (151.7 mg) and  $\text{SnI}_2$  (335.3 mg) into 1 mL mixed solvent (DMF:DMSO = 4:1). The perovskite was modified by adding different amounts of BrDS (1 mg, 2 mg, 3 mg).

**Fabrication of Perovskite Solar Cells:** Pre-patterned ITO glass substrates were sequentially cleaned using detergent, deionized water, acetone, and isopropanol. Subsequently, the PEDOT:PSS aqueous solution (1.5 wt % EMIC) was spin-coated on ITO glass at about 4000 rpm for 50 seconds and annealed at 130 °C for about 20 minutes in air. Subsequently, ITO/EMIC-PEDOT: PSS substrates were immediately shifted to nitrogen-filled glovebox, where perovskite layers were deposited on the EMIC-PEDOT:PSS substrate via a one-step solution casting step at about 5000 rpm for 50 seconds. During the spin-coating, 500  $\mu\text{L}$  of chlorobenzene was dropped onto the spinning substrate. Subsequently, the perovskite film was baked at 70

°C for about 20 minutes. After that, ICBA (dissolved in chlorobenzene, 15 mg/ml) was deposited on the perovskite at about 1200 rpm for 30 seconds, followed by annealing at 100 °C for 10 min. After cooling, C<sub>60</sub> (30 nm), BCP (8 nm) and the metal copper (100 nm) electrode was thermally evaporated in vacuum chamber at pressure set at  $< 4 \times 10^{-4}$  Pa through a shadow mask, respectively. The active area of each device was 0.0576 cm<sup>2</sup> defined through a shadow mask.

**Characterization of Solar Cells:** The J-V characteristics of the devices were measured by using a computer-controlled Keithley 2400 Source Measure Unit under the illumination of the simulator illumination (Enlitech Solar Simulator SS-F7-3A, Xenon lamp) at AM1.5G solar 100 mW cm<sup>-2</sup> in nitrogen glove box at room temperature without encapsulation using a shadow mask. The devices were measured both in reverse scan (1.0 / -0.2, step 0.01 V) and forward scan (-0.2 / 1.0, step 0.01 V) with 10 ms delay time. A standard silicon solar cell 91150 was used to calibrate the light intensity. The EQE (external quantum efficiency) was measured by using a DSR100UV-B spectrometer (SR830 lock-in amplifier) under ambient air at room temperature. The steady-state efficiency is obtained by the maximum output voltage of the device and the corresponding current value.

**Other Characterizations:** SEM (Scanning electron microscopy) images were acquired by using the field-emission SEM (FEI Nova–Nano SEM 430). The X-ray diffraction pattern results were based on Bruker ECO D8 (Bruker, Germany) system. The UV–vis (ultraviolet–visible) absorption spectra of the films were acquired by using the spectrophotometer (Perkin Elmer Lambda 750). The photoluminescence (PL) and time-resolved photoluminescence (TR-PL) results were obtained with FLS980 (Edinburgh Instruments).

### **Calculation methods**

Our calculation is carried out by the first-principle based on DFT (density functional theory) with the VASP (Vienna ab initio package) and the pseudopotential by the PAW (projector-augmented wave), and the PBE (Perdew-Burke-Ernzerhof) has been used [3-5]. In our work, the cut-off energy has been set to 400 eV and the Brillouin zone has been used with a 2×2×1  $\Gamma$ -centered k-mesh for our structure supercell surface structure with 12 Å Vacuum. All structures have been optimized until the self-consistent force is less than 0.05 eV Å<sup>-1</sup> and the energy between two consecutive steps was less than 10<sup>-6</sup> eV. In our work, the

BrDS has been absorbed on the FASnI<sub>3</sub> surface. To treat the strongly correlated f-electrons we apply a Hubbard correction (+U).

### Thermal admittance spectroscopy (TAS)

TAS was carried out on a CHI660E electrochemical workstation at 0 V bias in dark with a similar procedure to the reported literature,<sup>[9]</sup> and a tuned frequency range from 10 Hz to 1 MHz and an AC amplitude of 10 mV were employed. The static permittivity and the attempt-to-escape frequency were chosen to be 25 and  $5.0 \times 10^{10}$  rad/s respectively. The final DOS value was calculated based on the data extracted from the Mott-Schottky curve and Capacitance-Frequency spectrum with the following equation,

$$DOS(E_\omega) = -\frac{V_{bi} dC \omega}{qWd\omega kT}$$

Where  $V_{bi}$ ,  $W$ ,  $C$ ,  $\omega$ ,  $k$  and  $T$  are built-in potential, depletion width, capacitance, angle frequency, Boltzmann constant, and temperature respectively. The values of  $V_{bi}$  and  $W$  can be obtained from the Capacitance-Frequency spectrum.

$E_\omega$  can be calculated using the following equation,

$$E_\omega = kT \ln \frac{\omega_0}{\omega}$$

where  $\omega_0$  is the attempt-to-escape frequency.

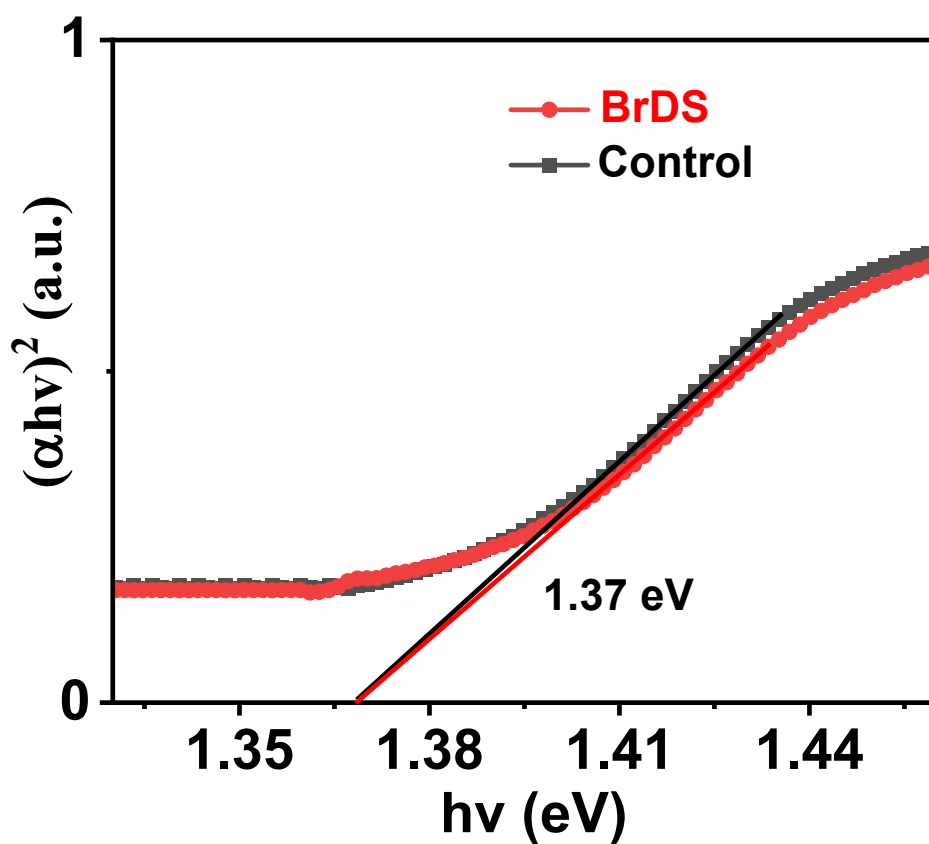


Figure S1. The bandgap of the tin-based perovskite film with and without BrDS. The doping of trace amounts of BrDS does not significantly alter the bandgap of tin-based perovskite films.

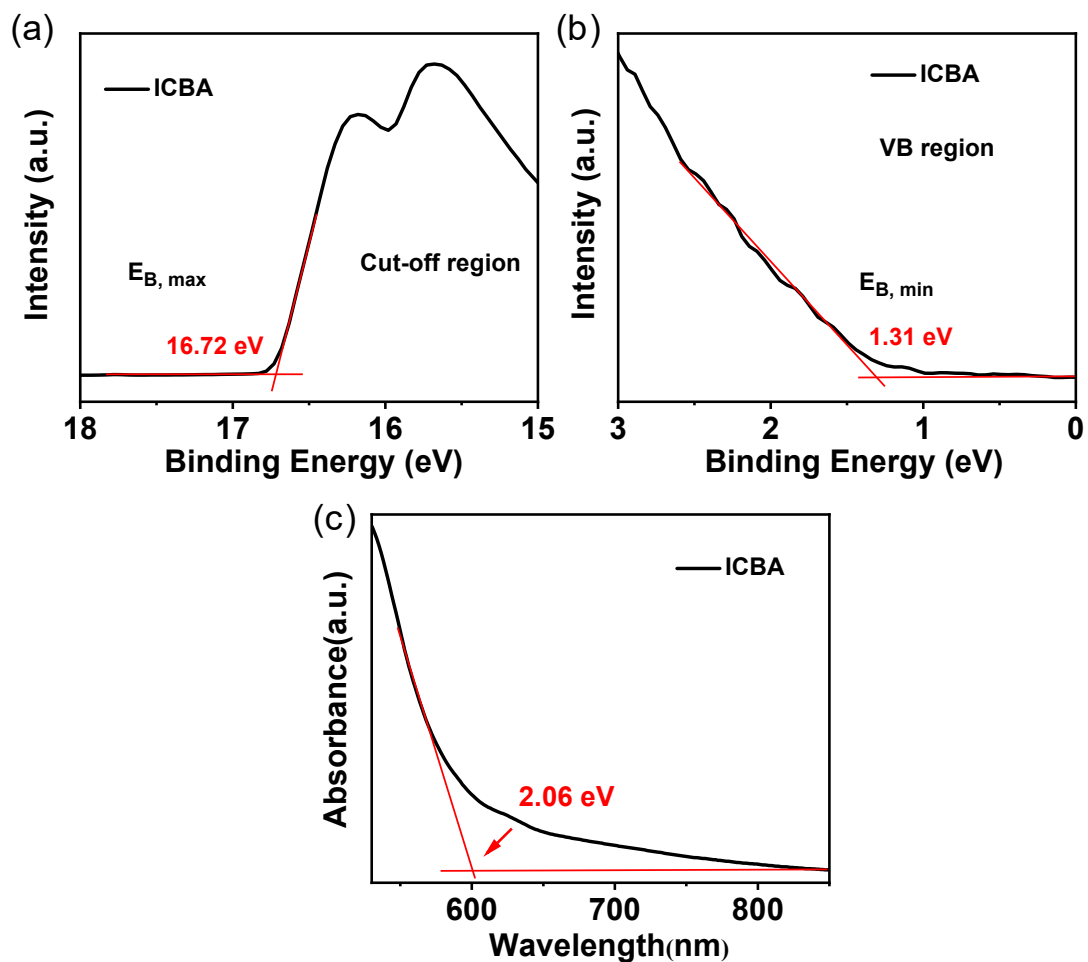


Figure S2. (a-b) The ultraviolet photoelectron spectroscopy (UPS) and the bandgap (c) of the ICBA film. Valence band =  $h\nu$  (21.22 eV) -  $E_{B, \max} + E_{B, \min} = -5.81$  eV; conduction band (LUMO) - valence band (HOMO) = bandgap, conduction band = -3.75 eV.

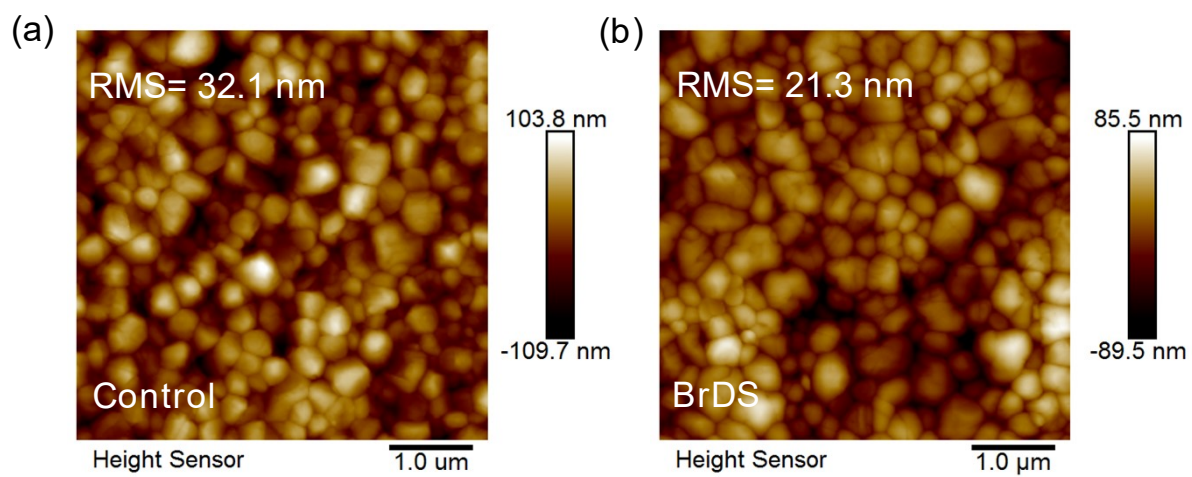


Figure S3. The atomic force microscopy (AFM) images of (a) control tin-based perovskite film and (b) BrDS-doped perovskite film.

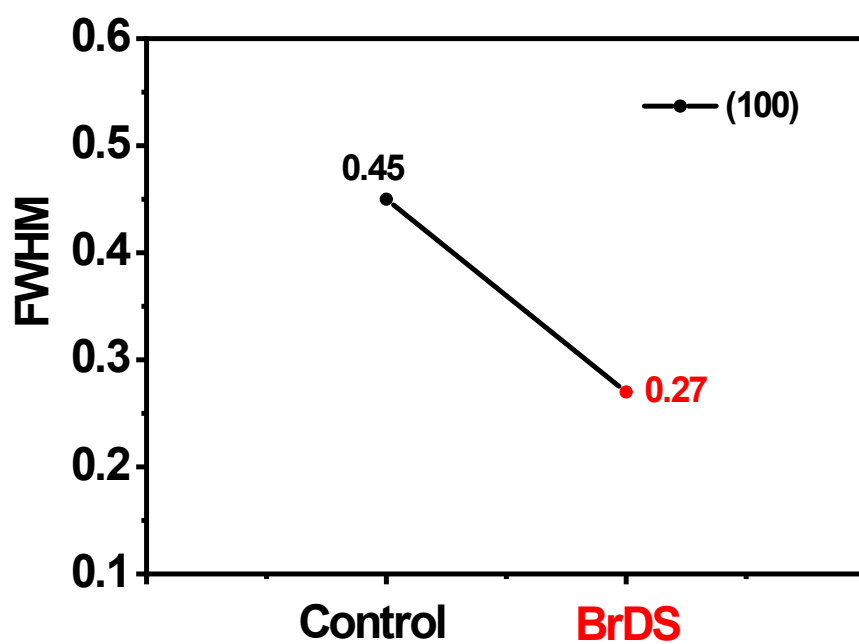


Figure S4. The full width half maximum (FWHM) data of control and BrDS-doped perovskite (100) peaks.



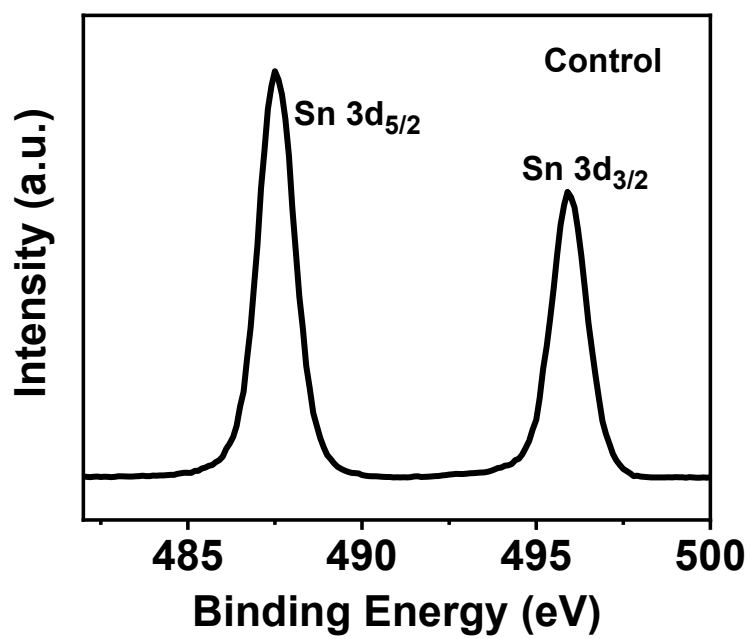


Figure S5. The X-ray photoelectron spectroscopy (XPS) of control tin-based perovskite film.

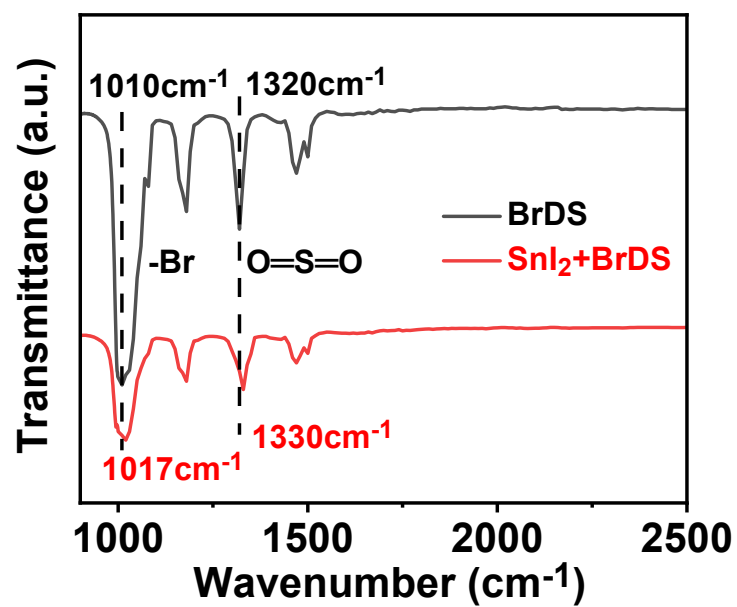


Figure S6. FT-IR spectra of Halogen group(-Br), O=S=O group for BrDS and BrDS with SnI<sub>2</sub>.

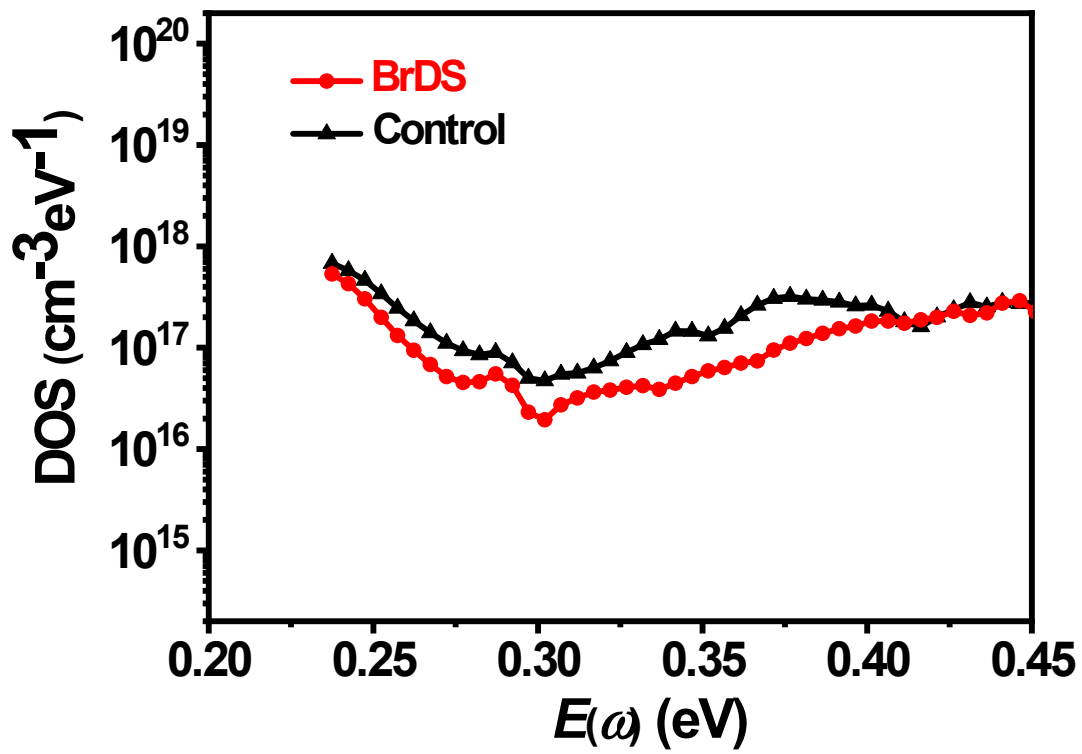


Figure S7. The trap density of states (tDOS) of the control and BrDS-doped perovskite film-based devices.



====Measurement Results====

	Forward Scan (Isc to Voc)		Reverse Scan (Voc to Isc)	
Area	6.78 mm <sup>2</sup>			
Isc	1.594	mA	1.604	mA
Voc	0.780	V	0.781	V
Pmax	0.882	mW	0.974	mW
Ipm	1.375	mA	1.518	mA
Vpm	0.642	V	0.641	V
FF	70.96	%	77.73	%
Eff	13.02	%	14.36	%

- Spectral Mismatch Factor: SMM=0.9924.
- Designated illumination area defined by a thin metal mask was measured by the measuring microscope.
- Test results listed in this measurement report refer exclusively to the mentioned measured sample.
- The results apply only at the time of the test, and do not imply future performance.

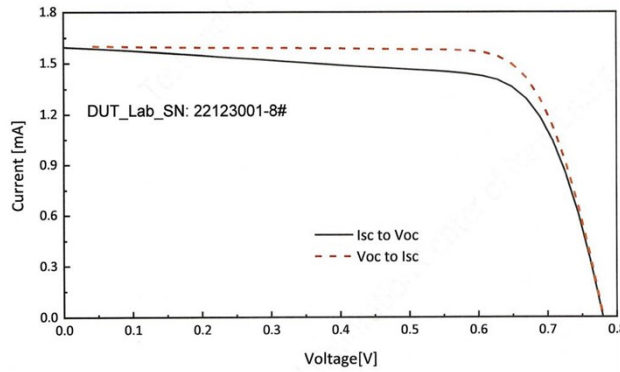


Fig.1 I-V curves of the measured sample

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Figure S8. Independent PCE testing report of a tin-based device by an accredited PV Metrology Laboratory of SIMIT (Shanghai Institute of Microsystem and Information Technology, China) verified a PCE of 14.36%. The device was tested in air without encapsulation during the test process.

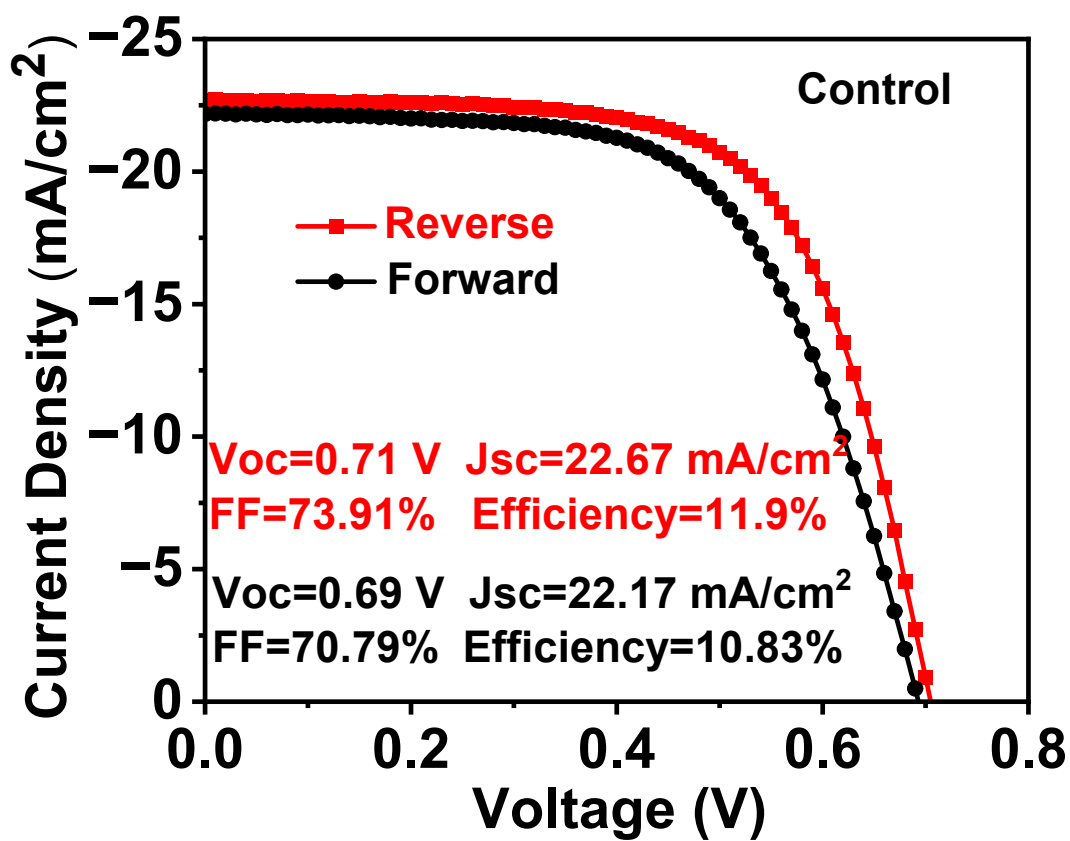


Figure. S9. The forward and reverse scan direction  $J$ - $V$  curves of control device under AM 1.5G solar 100  $\text{mW cm}^{-2}$  simulator illumination.

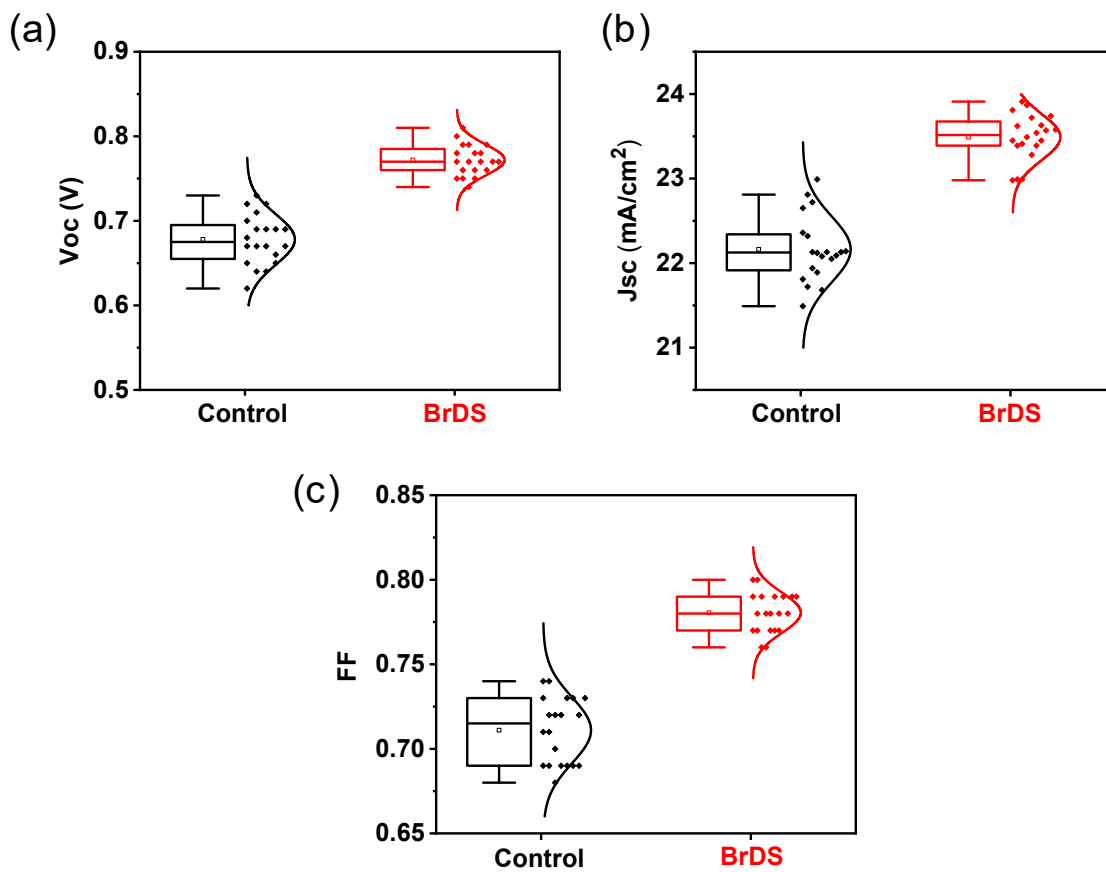


Figure S10. The statistical photovoltaic parameters ( $V_{oc}$ ,  $J_{sc}$ ,  $FF$ ) distribution for 20 independent control and BrDS-doped devices obtained from reverse scan  $J$ - $V$  curves.

### Time-resolved photoluminescence

TRPL (the time-resolved photoluminescence) spectra were fitted with a two-component exponential decay model based on the following equation according to the literature,<sup>[2]</sup>

$$I(t) = A_1 \exp\left(-t/\tau_1\right) + A_2 \exp\left(-t/\tau_2\right)$$

and the average time constant is calculated with the following equation,

$$\tau_a = A_1 \tau_1 + A_2 \tau_2$$

**Table S1.** Time constants extracted from the fitted TRPL.

film	$\tau_1$ [ns]	$A_1$ [%]	$\tau_2$ [ns]	$A_2$ [%]	$\tau_a$ [ns]
control	6.78	4.32	13.24	95.68	12.7
BrDS	9.24	9.87	20.76	90.13	18.8

**Table S2.** The optimization for the BrDS doping concentration in the tin-based perovskite film-based perovskite solar cells (statistical data including average values and standard deviations are calculated from at least 10 separate devices.)

Concentration (mg/mL)	Jsc (mA cm <sup>-2</sup> )	Voc (V)	FF	PCE (%)
1	23.3 ± 0.6	0.71 ± 0.04	0.72 ± 0.03	12.76 ± 1.4
2	23.5 ± 0.5	0.77 ± 0.03	0.78 ± 0.03	14.08 ± 0.9
3	23.4 ± 0.5	0.75 ± 0.04	0.74 ± 0.04	13.67 ± 1.2



**Table S3.** Comparison of the photovoltaic performance of the reported high-efficiency Tin-based PSCs (our results are included for comparison).

Device configuration	Jsc (mA cm <sup>-2</sup> )	Voc (V)	FF (%)	PCE (%)	Publish year	Ref
FTO/c-TiO <sub>2</sub> / m-TiO <sub>2</sub> /FASnI <sub>3</sub> /SpirO-OMeTAD/Au	24.00	0.28	60.0	4.03	2016	[6]
ITO/NiO <sub>x</sub> /FASnI <sub>3</sub> /PCBM/Ag	14.44	0.59	69.0	5.88	2017	[7]
ITO/PEDOT:PSS/FASnI <sub>3</sub> /PCBM/Ag	18.50	0.48	57.2	5.08	2018	[8]
ITO/PEDOT:PSS/FASnI <sub>3</sub> /C <sub>60</sub> /BCP/Ag	21.60	0.63	74.70	10.17	2019	[9]
ITO/PEDOT:PSS/Cs <sub>0.2</sub> FA <sub>0.8</sub> SnI <sub>3</sub> /PCBM/C <sub>60</sub> /BCP/Ag	21.60	0.64	75.2	10.40	2020	[10]
ITO/PEDOT:PSS/FASnI <sub>3</sub> /C <sub>60</sub> /BCP/Ag	23.50	0.76	64.0	11.40	2020	[11]
ITO/PEDOT:PSS/FA <sub>0.75</sub> MA <sub>0.25</sub> SnI <sub>3</sub> /PCBM/C <sub>60</sub> /BCP/Ag	22.00	0.76	69.0	11.50	2020	[12]
ITO/PEDOT:PSS/(FA <sub>0.9</sub> EA <sub>0.1</sub> ) <sub>0.98</sub> EDA <sub>0.01</sub> SnI <sub>3</sub> /C <sub>60</sub> /BCP/Ag	20.32	0.84	78.0	13.24	2020	[13]
ITO/PEDOT:PSS/FASnI <sub>2.9</sub> Br <sub>0.1</sub> /PCBM/C <sub>60</sub> /BCP/Ag	23.02	0.81	72.0	13.40	2021	[14]
ITO/PEDOT:PSS/FASnI <sub>3</sub> -EDABr <sub>2</sub> /C <sub>60</sub> /BCP/Ag	22.49	0.82	77.4	14.23	2022	[15]
ITO/PEDOT:PSS/PEA <sub>0.15</sub> FA <sub>0.85</sub> SnI <sub>3</sub> /trans-3/BCP/Ag	21.39	0.90	75.7	14.58	2023	[16]
ITO/PEDOT:PSS/PEA <sub>0.15</sub> FA <sub>0.85</sub> SnI <sub>2.85</sub> Br <sub>0.15</sub> /ICBA/BCP/Ag	20.60	0.91	77.1	14.63	2021	[17]
ITO/PEDOT:PSS/FA <sub>0.75</sub> MA <sub>0.25</sub> SnI <sub>3</sub> /C <sub>60</sub> /BCP/Ag	24.90	0.77	76.7	14.70	2021	[18]
ITO/PEDOT:PSS/FPEA <sub>0.1</sub> FA <sub>0.9</sub> SnI <sub>2.9</sub> Br <sub>0.1</sub> /ICBA/BCP/Ag	24.91	0.84	70.8	14.81	2021	[19]
<b>ITO/PEDOT:PSS/FASnI<sub>3</sub>-BrDS/ICBA/C<sub>60</sub>/BCP/Cu</b>	<b>23.86</b>	<b>0.79</b>	<b>79.5</b>	<b>14.98</b>		<b>This work</b>

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