

## Supplementary Information

### Small molecule incorporated SnO<sub>2</sub> layer for efficient perovskite solar cells

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### First-principles calculations

Electronic structure calculations were performed with the density functional theory as implemented in the *Vienna ab initio simulation package*,<sup>1,2</sup> employing the projected augmented wave potentials<sup>3</sup> to describe the atomic core electrons and the plane wave basis set to expand the Kohn–Sham electronic states. For the exchange and correlation function, the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) format was used.<sup>4</sup> The kinetic energy cutoff was set to 420 eV for all calculations in this work.

The bulk structure of sodium 3-oxo-3H-spiro[isobenzofuran-1,9'-xanthene]-3',6'-bis(olate) (SSB) was first optimized, the computational cell parameters are  $a = 10.5760 \text{ \AA}$ ,  $b = 7.4080 \text{ \AA}$ , and  $c = 6.5660 \text{ \AA}$  in this work. In the bulk structure relaxation, the Brillouin zone was sampled by a  $(2 \times 2 \times 1)$  k-points mesh with Gamma point centered. All the atoms and cell parameters were fully relaxed until the atomic forces are less than  $0.05 \text{ eV \AA}^{-1}$ .

To account for interactions between SnO<sub>2</sub> and SSB, the (110) surface of SnO<sub>2</sub> with dimensions of  $12.746 \text{ \AA} \times 13.4011 \text{ \AA}$  and with a thickness of  $37.9930 \text{ \AA}$  was constructed, and then it was combined with SSB. A vacuum thickness of  $30 \text{ \AA}$  was

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added along the z direction to avoid spurious interaction between slab images. The Brillouin zone was sampled by  $2 \times 2 \times 1$  gamma centered k-point mesh. During structural optimization, all the atoms were fully relaxed until the atomic forces are less than  $0.05 \text{ eV \AA}^{-1}$ .

To simulate the interface between SSB and perovskite, the (001) surface of  $\text{FAPbI}_3$  with dimensions of  $12.7225 \text{ \AA} \times 12.7225 \text{ \AA}$  and with a thickness of  $47.7225 \text{ \AA}$  was constructed, and then it was combined with SSB. A vacuum thickness of more than  $30 \text{ \AA}$  was added along the z direction to avoid spurious interaction between slab images. In the structural relaxation, the Brillouin zones were sampled by a  $2 \times 2 \times 1$  Monkhorst-Pack k-point mesh. All the atoms were fully relaxed until the atomic forces are less than  $0.05 \text{ eV \AA}^{-1}$ . The density of states was obtained in a denser k-point mesh of  $3 \times 3 \times 1$ . To consider the van der Waals interactions, the DFT-D3 method with Becke-Jonson damping<sup>5</sup> was used for all the calculations. The visualization of the crystal structure was by the VESTA code.<sup>6</sup>

## References:

1. G. Kresse, J. Hafne, *Phys Rev B*, 1996, **54**, 11169.
2. G. Kresse, J. Furthmüller, *Phys Rev B*, 1993, **47**, R558.
3. P. E. Blöchl, *Phys Rev B*, 1994, **50**, 17953.
4. J. P. Perdew, K. Burke, M. Ernzerhof, *Phys Rev Lett*, 1996, **77**, 3865.
5. S. Grimme, S. Ehrlich, L. Goerigk, *J. Comp. Chem*, 2011, **32**, 1456.
6. K. Momma, F. Izumi, *J. Appl. Crystallogr*, 2011, **44**, 1272.

## Experimental Section

**Materials and Chemicals:** Indium tin oxide-coated glass slides ( $\text{ITO}$ ,  $\leq 15 \text{ \Omega square}^{-1}$ ) were cleaned before use. Sodium 3-oxo-3H-spiro[isobenzofuran-1,9'-xanthene]-3',6'-bis(olate) (cas: 518-47-8) and potassium chloride ( $\text{KCl}$ ) was purchased from J&K Scientific Ltd. N,N-dimethylformamide ( $\text{DMF}$ , 99%), bis(trifluoromethanesulfonyl)-imide lithium salt ( $\text{Li-TFSI}$ ), 4-tert-butylpyridine ( $\text{tBP}$ ), 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl) amino]-9,9'-spirobifluorene (spiro-OMeTAD), dimethyl sulfoxide

(DMSO,99%). Tin oxide (15% in H<sub>2</sub>O colloidal dispersion) (SnO<sub>2</sub>) was purchased from Alfa Aesar. Lead iodide (PbI<sub>2</sub>, Z99.9%), formamidine iodide (FAI, Z99.5%), methylammonium iodide (MAI, Z99.5%), methylammonium Chloride (MACl), and Phenylethylammonium Iodide (PEAI, Z99.5%) were all purchased from the Xi'an Polymer Light Technology Corp. Gold (Au, 99.995%) was purchased from China New Metal Materials Technology Co., Ltd. Ether absolute, isopropyl alcohol (IPA), and acetone were purchased from Tianjin Fuyu Fine Chemical Co., Ltd (China). None of the materials needed further purification.

**Device Fabrication:** The ITO substrate was ultrasonically cleaned with detergent, acetone, and isopropanol solution 45 min in advance and then dried with nitrogen. Then the SnO<sub>2</sub> solution was prepared by mixing 15% SnO<sub>2</sub> hydrocolloid solution with 5 mg mL<sup>-1</sup> KCl solution at a volume ratio of 2:1. 100 μL of the SnO<sub>2</sub> solution was spin coated on ITO to prepare the electron transport layer at a speed of 5500 rpm for 9 s. The resulting films were annealed at 150 °C for 10 min. In the case of SSB modification solutions, diluted SSB with a concentration of 0.1mg/ml into SnO<sub>2</sub> solution Then spin the solution onto the ITO substrate at a speed of 5500rpm for 9 s, and then anneal at 150 °C for 10 min UV–ozone chamber for 20 min. After that, the subsequent spin coating was carried out in a glove box with less than 1.0 ppm of water and oxygen. DMF: DMSO solution (9:1, v/v) containing 1.5 M PbI<sub>2</sub> was spin coated on SnO<sub>2</sub> films at 1500 rpm for 30 s to form yellow PbI<sub>2</sub> films and heated at 70 °C for 1 min. After the sample containing the PbI<sub>2</sub> film was cooled to room temperature. 90 mg FAI, 6.36 mg MAI, and 9 mg MACl were added to 1 mL isopropyl alcohol solution and stirred with magnetons until clear. 50 μL of the above mixed solution was rotated onto the upper layer of film at 2000 rpm for 30 s. Subsequently, the perovskite film was taken out from the nitrogen glove box to ambient air for thermal annealing at 150 °C for 15min in humidity conditions (30–40% humidity). After cooling, 80 μL of PEAi/isopropanol solution at a concentration of 5 mg mL<sup>-1</sup> was deposited on the perovskite layer by spinning, followed by dropping at 5000 rpm for 30 s. After cooling to room temperature, the hole transport layer was prepared. 28 μL spiro-OMeTAD solution was applied to the upper layer of PEAi film at 4500 rpm for 20 s. The solution contained

72.5 mg spiro-OMeTAD powder, 28.5  $\mu\text{L}$  tBP, 18  $\mu\text{L}$  Li-TFSI/acetonitrile (520 mg  $\text{mL}^{-1}$ ), and 1 mL chlorobenzene. Finally, gold electrodes (80 nm) were evaporated on the HTLs under vacuum.

**Characterization:** The current–voltage (J–V) characteristics of the prepared solar cells were measured under simulated air mass (AM) 1.5 G illumination using a Keithley 2410 source meter (Cleveland, OH, USA). The solar cells were sealed in a glovebox ( $\text{O}_2 < 1.0$  ppm,  $\text{H}_2\text{O} < 1.0$  ppm) and measured in the forward (from -1.2 to 0.1 V) and reverse (from 0.1 to -1.2 V) modes at a scan rate of  $0.1 \text{ V s}^{-1}$ . The light intensity was calibrated with a NIST-certified silicon reference solar cell (Newport 532 ISO1599). XRD patterns of ETL/perovskite film were measured by an X-ray diffractometer (D8 ADVANCE, Bruker, Germany). Observation of  $\text{PbI}_2$  film morphology, the surface morphology of perovskite films, and elemental scanning of the hole transport layer was done using SEM (JEOL JSM-7610 F Plus, Nippon Electronics Co., Ltd., Japan). SSB powder and the samples glass/different ETL/perovskite were detected by FTIR spectrometer (VERTEX 70, Bruker Spectrum Instruments, Germany). XPS and UPS of  $\text{SnO}_2$  and  $\text{SnO}_2$ :SSB film, and ETL film on ITO substrates were determined using an X-ray photoelectron-ultraviolet electron spectrometer (AXIS SUPRAp, Kratos, UK). (He I $\alpha$  photon source,  $h\nu \frac{1}{4} 21.21 \text{ eV}$ ). The EIS was recorded with a CHI660E (Chenhua Device Company, Shanghai, China) electrochemical measurement system under illumination of  $100 \text{ mW cm}^{-2}$ . The frequency range was  $1\text{-}10^6 \text{ Hz}$  and the results were fit using Z-view software. The SCLC measurements were carried out on dual-hole devices (ITO/ETL/perovskite/PCBM/Au) in the dark. AFM was tested with scanning probe microscopy (Multimode 8, Bruker, USA). Mott–Schottky (M–S) data for PSCs were derived using an electrochemical workstation (CHI660E, Chenhua Device Company, China) in the dark, with a frequency range of  $10^4 \text{ Hz}$ . Steady-state PL spectra and TRPL decay dynamics were measured on a HORIBA Jobin Yvon Fluorolog-3 spectrofluorometer system and an FLS 980 PL spectrometer (Edinburgh Instrument, England) with Xe 900 (450 W xenon arc lamp) as the light source, respectively. IPCE was tested with the Solar Cell Quantum Efficiency Test System (Qtest Station 500ADX, United States Dawn Technology Co., Ltd., USA). Contact angle testing of

different ETL/perovskite film were done on glass substrates using a fiber optic contact angle tensiometer (LAUDA OSA100, AUDA Scientific GmbH, China). The UV–vis absorption spectra were measured with a UV–vis–NIR spectrophotometer (PE Lambda 950, PerkinElmer, USA).

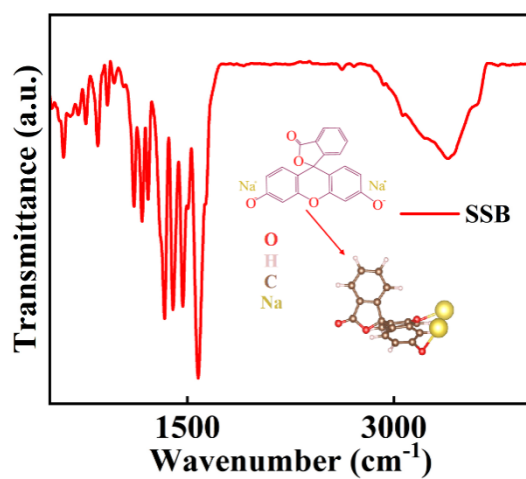


Figure S1 FT-IR spectra of SSB powder.

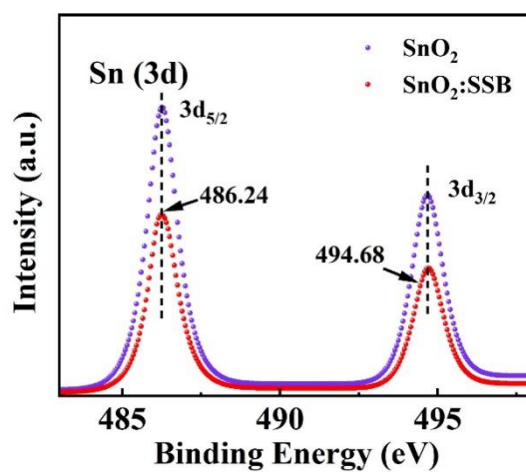
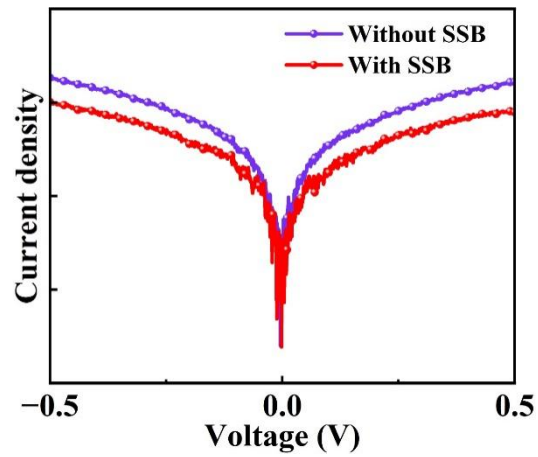
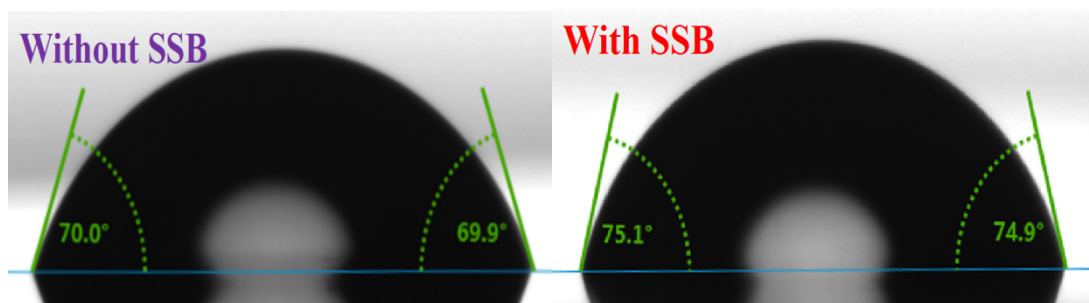


Figure S2 XPS spectra of Sn 3d for pristine  $\text{SnO}_2$  and  $\text{SnO}_2$ :SSB.



**Figure S3**  $J$ - $V$  characteristics of undoped and doped SSB devices in ETL scanning from -0.5 V to 0.5 V in the dark.



**Figure S4** Contact angle test of different devices.

**Table S1** Fitted results of TRPL curves of the perovskite films deposited on SnO<sub>2</sub> and

SnO<sub>2</sub>:SSB.

Devices	$\tau_1$ (ns)	$A_1$ (%)	$\tau_2$ (ns)	$A_2$ (%)	$\tau_{ave}$ (ns)
Without SSB	19.44	0.977	170.35	0.023	45.27
With SSB	14.43	0.995	138.92	0.005	30.42

**Table S2** The parameter data table of the equivalent circuit diagram.

Devices	$R_s$ [ $\Omega$ cm <sup>2</sup> ]	$R_{CT1}$ [ $\Omega$ cm <sup>-2</sup> ]	$R_{CT2}$ [ $\Omega$ cm <sup>-2</sup> ]
Without SSB	140	230	1333
With SSB	90	201	1083

**Table S3** Photovoltaic parameters of champion PSCs with and without SSB.

Devices	Voc [V]	Jsc [mA cm <sup>-2</sup> ]	FF [%]	PCE [%]
Without SSB Forward	1.10	25.18	70.25	19.49
Without SSB Reverse	1.10	25.26	72.06	20.01
With SSB Forward	1.13	26.22	76.30	22.64
With SSB Reverse	1.12	26.23	74.70	21.90