

## Supporting Information

### **Down-converting ultraviolet light by a conductive passivator to enhance efficiency and stability of perovskite solar cells**

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## **Experimental sections:**

### **Materials:**

All of the chemicals and solvents were obtained commercially and were used without further purification. Methylammonium iodide (MAI), methylammonium bromide (MABr), methylammonium chloride (MACl), formamidinium iodide (FAI), lead iodide (PbI<sub>2</sub>, 99.99%), cesium iodide (CsI, 99.999%), 4-*tert*-butylpyridine (99.9%), acetonitrile (99.9%) were purchased from Xi'an Polymer Light Technology Corp. PbI<sub>2</sub> and Spiro-OMe TAD are purchased from Liao'ning advanced election Technology Corp. Dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF) and isopropanol (IPA) were purchased from Sigma-Aldrich. 4,4'-diaminostilbene-2,2'-disulfonic acid (DSDA) was purchased from TCI. Commercial tin (IV) oxide solution (SnO<sub>2</sub>, 15% in H<sub>2</sub>O colloidal dispersion) was purchased from Alfa Aesar.

### **Preparation of SnO<sub>2</sub> (DSDA) colloidal solution:**

Dilute the SnO<sub>2</sub> aqueous colloidal dispersion (15wt%) with deionized water to a concentration of 3.75 wt%. Subsequently, 0.5 mg of DSDA were dissolved in 1 mL of diluted SnO<sub>2</sub> aqueous colloidal dispersion. Mix SnO<sub>2</sub> (DSDA) solution in an ultrasonic cleaning machine for 2 hours to prepare SnO<sub>2</sub> (DSDA) precursor solution.

### **Device Fabrication:**

FTO substrate was sequentially ultrasonically cleaned by deionized water, acetone, ethanol, and isopropanol for 30 min, and then treated with UV/O<sub>3</sub> light for 60 min. SnO<sub>2</sub> colloidal solution solutions (3.75 wt%) doped with different concentrations of DSDA (0.5 mg mL<sup>-1</sup>) were spin coated on FTO substrate at 3000 rpm for 30 s to prepare SnO<sub>2</sub> layers, and then annealed at 150 °C in the environment for 30 minutes. The control device is based on a SnO<sub>2</sub> layer prepared from a SnO<sub>2</sub> colloidal solution (2.5 wt%) without SSS. Then, a 1.35 M PbI<sub>2</sub> and 0.0675 M CsI mixture solution (dissolved in DMF/DMSO (9:1, v/v) and stirred at 70 °C for 2 h) were spin-coated on the substrate at 3000 rpm for 30 s. Next, a mixed organic cation solution (600 mg of FAI, 75 mg of MAI, 30 mg of MABr, and 30 mg of MACl dissolved in 15 mL IPA) was spin-coated at 2800 rpm for 30 s and then annealed at 150 °C for 15 min in ambient environment. The hole transferer, Spiro-OMe TAD, was dissolved in chlorobenzene and LiTFSI and *tert*-butylpyridine (TBP) was used as the additive (167 mg Spiro-OMe TAD, 298 mg TBP, 10.3 mg in 1.00 mL chlorobenzene), and then the solution was deposited by spin-coating at 5000 rpm for 30 s. Finally, an Au electrode with a thickness

of 80 nm was evaporated with a vacuum evaporation apparatus. The active area of the electrode is controlled by the mask to 0.09 cm<sup>2</sup>.

### **Characterizations:**

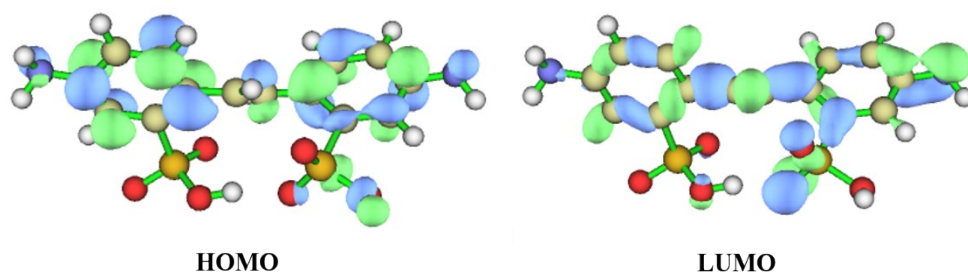
Current density versus voltage ( $J$ - $V$ ) testing was performed by measuring the solar cells under standard AM 1.5 sunlight with a solar simulator assembled with an electrochemical workstation (illumination 100 mW/cm<sup>2</sup>, WXS-90L2, Wacom). The light intensity was calibrated using a standard monocrystalline silicon photovoltaic cell, and a single mask sheet with an area of 0.09 cm<sup>2</sup> was used to control the active area of the device. Surface morphology was characterized by an atomic force microscope (AFM; Brook Multimode 8). The absorption spectra of the as-prepared films were recorded using a UV-Vis-NIR spectrophotometer (UV-3600i, Shimadzu). The surface morphology of the perovskite films was observed by field emission scanning electron microscopy (FE-SEM; Quanta 250 FEG) and atomic force microscopy (AFM; Brook Multimode 8). The Space Charge Limited Current (SCLC) test was measured by linear cyclic voltammetry with the SourceMeter with sweep rates from -1 V to 1 V. Steady-state photoluminescence (PL) curves were obtained by a steady-state lifetime spectrofluorometer (Varian Cary Eclipse) at room temperature. The time-resolved photoluminescence decay spectra of the as-prepared perovskite films were characterized using a Horiba Fluorolog-3 time-correlated single photon counting (TCSPC) system. Electrochemical impedance spectroscopy (EIS) were measured by an electrochemical station (CPE-2000) in the dark state.

### **Theoretical calculations:**

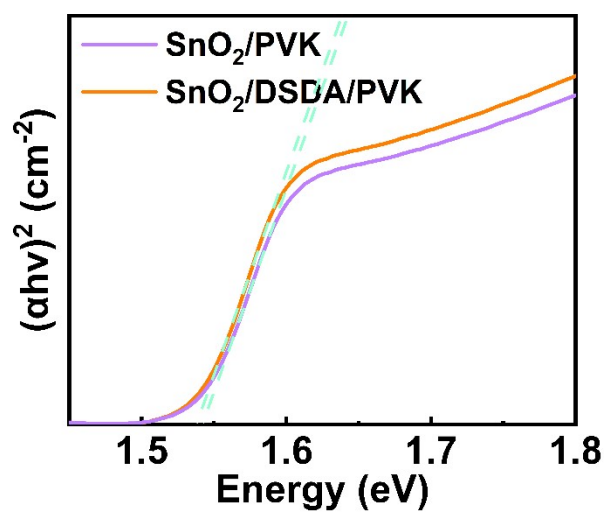
Time-dependent density functional theory (DFT) theoretical calculations were performed using the Gaussian 16 package to calculate and visualize electrostatic potential (ESP) maps for SSS using the 6-311G(d) level and to optimize DSDA and Pb possible coordination modes. The corresponding frequency analysis was carried out, and the minimum vibration frequency was greater than zero, which proved that all the optimized structures are stable. Density functional theory (DFT) calculations were performed using the Gaussian 16 suite of programs, and geometry optimization was performed at the B3LYP/6-31G(d) theoretical level.<sup>[1,2]</sup> Binding energy  $\Delta E$  is calculated according to equation: <sup>[3,4]</sup>  $\Delta E = E_{\text{Pb}^{2+}/\text{m}} - E_{\text{m}} - E_{\text{Pb}^{2+}}$

Among them,  $E_{\text{Pb}^{2+}/\text{m}}$ ,  $E_{\text{m}}$ , and  $E_{\text{Pb}^{2+}}$  represent the energy of Pb<sup>2+</sup> binding to molecules, the energy of molecules, and the energy of Pb<sup>2+</sup>, respectively. M is H<sub>2</sub>O or DSDA.

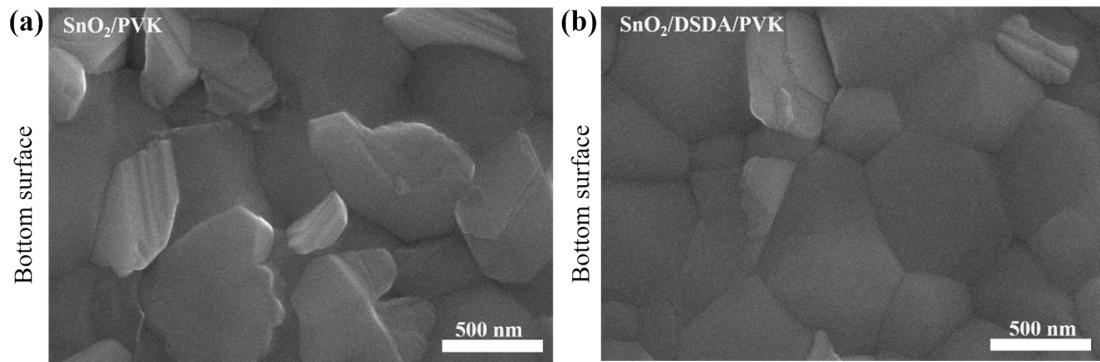
**Figures:**



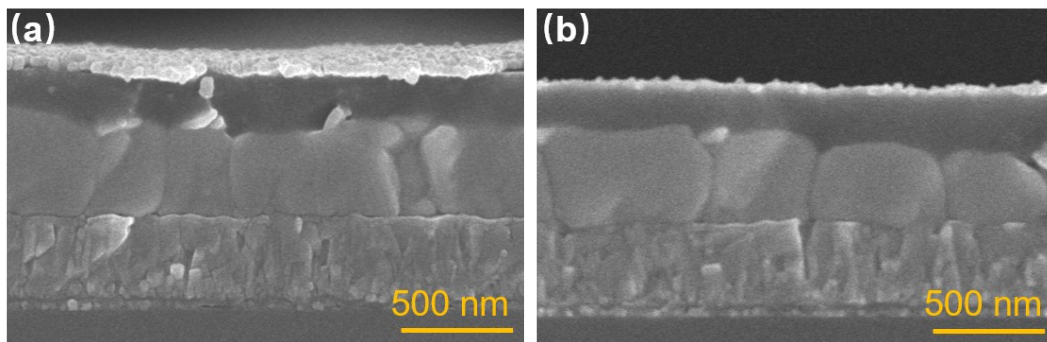
**Figure S1.** Frontier orbitals of DSDA molecule.



**Figure S2.** UPS of perovskite films on different  $\text{SnO}_2$  ETLs.



**Figure S3.** Top-view SEM images of perovskite surface exfoliated from (a) SnO<sub>2</sub> and (b) SnO<sub>2</sub>/DSDA.



**Figure S4.** Cross-sectional SEM images of PSCs based on different ETLs (a) SnO<sub>2</sub> and (b) SnO<sub>2</sub>/DSDA.

**Tables:****Table S1. Hall effect measurement of devices based SnO<sub>2</sub> ETL without and with DSDA.**

Name	t [nm]	Lp [mm]	Hall mobility [cm <sup>2</sup> /V·s]	Carrier type	Resistivity [Ω·cm]
Control	20	40	33.36	N	2.28 E-5
With DSDA	20	40	35.22	N	2.16 E-5

**Table S2. The fitting parameter of TRPL spectra.**

Name	A <sub>1</sub>	τ <sub>1</sub> [ns]	A <sub>2</sub>	τ <sub>2</sub> [ns]	τ <sub>ave</sub> [ns] <sup>a)</sup>
SnO <sub>2</sub> /PVK	0.68629	29.41103	0.68344	88.10453	58.69671
SnO <sub>2</sub> /DSDA/PVK	0.69537	13.83971	0.909503	19.976	17.31723
Glass/PVK	0.59892	70.26661	0.33844	500.4003	225.5692
Glass/DSDA/PVK	0.3496	78.72561	0.58597	758.0764	504.2193

b)  $\tau_{ave} = \frac{A_1\tau_1 + A_2\tau_2}{A_1 + A_2}$

**Table S3. The parameters of the SCLC for sample with different ETLs.**

Sample	V <sub>TFL</sub> (V)	N <sub>trap</sub> (cm <sup>-3</sup> )
PVK	0.36	5.10×10 <sup>15</sup>
SnO <sub>2</sub> (DSDA)/PVK	0.17	2.41×10 <sup>15</sup>

The density of trap states can be calculated using the following formula:  $N_{trap} =$

$$2\varepsilon_r\varepsilon_0V_{TFL}/eL^2$$

**Table S4.** The detailed photovoltaic parameters of PSCs based on SnO<sub>2</sub> ETL incorporating different DSDA concentrations.

concentration [mg/ml]	Scan direction	$J_{sc}$ [mA cm <sup>-2</sup> ]	$V_{oc}$ [V]	FF [%]	PCE [%]
0	Reverse	24.47	1.15	81.73	22.95
	Forward	24.3	1.12	81.47	22.27
0.2	Reverse	24.71	1.17	81.29	23.51
	Forward	24.53	1.16	80.64	22.06
0.5	Reverse	25.61	1.17	83.76	25.09
	Forward	25.4	1.16	83.67	24.71
1.0	Reverse	24.48	1.12	78.03	21.12
	Forward	24.02	1.08	77.19	19.86

**Table S5.** Fitted  $R_{tr}$  and  $R_{rec}$  of EIS parameters of PSCs based on pristine SnO<sub>2</sub> and SnO<sub>2</sub> (DSDA)

Name	$R_{ct}$	$R_{rec}$
SnO <sub>2</sub> /PVK	1.68E+05 <sup>a)</sup>	1.26E+06
SnO <sub>2</sub> (DSDA)/PVK	1.37E+05	2.03E+06

a) E+01:  $\times 10^1$

**Table S6.** The parameter calculated by DFT.

Sample	Energy (a.u.)
Pb <sup>2+</sup>	-192.7293
H <sub>2</sub> O	-76.4089
the smallest unit of DSDA	-1899.3091
Pb <sup>2+</sup> /H <sub>2</sub> O	-269.1651
Pb <sup>2+</sup> / the smallest unit of DSDA	-2092.1046

Binding energy  $\Delta E$  is calculated according to equation:  $\Delta E = E_{\text{Pb}^{2+}/\text{m}} - E_{\text{m}} - E_{\text{Pb}^{2+}}$ .

Among them,  $E_{\text{Pb}^{2+}/\text{m}}$ ,  $E_{\text{m}}$ , and  $E_{\text{Pb}^{2+}}$  represent the energy of Pb<sup>2+</sup> binding to molecules, the energy of molecules, and the energy of Pb<sup>2+</sup>, respectively. M is H<sub>2</sub>O or DSDA.