

## **Supporting Information**

### **Additive engineering via multiple-anchoring enhances 2D perovskite solar cells performance**

Liangding Zheng<sup>a,#</sup>, Yuanju Zhao<sup>a,#</sup>, Rongjun Zhao<sup>\*b</sup>, Lin Xie<sup>\*a</sup> and Yong Hua<sup>\*a</sup>

## **Experimental Procedures**

### **Materials**

All the chemicals were used as received. TEMPIC(99%) was purchased from MACKLIN. Fluorine doped tin oxide (FTO) coated glass substrates, TiO<sub>2</sub> paste, Acetylacetone(99.8%), Titanium diisopropoxide bis(acetylacetonate) 75% in Isopropyl Alcohol, N-dimethylformamide(DMF, 99%), Dimethyl sulfoxide (DMSO, 99%), Chlorobenzene (CB, 99.8%,) were purchased from Sigma-Aldrich. Lead iodide(PbI<sub>2</sub>,>98%), Lead bromide(PbBr<sub>2</sub>,>98%,), Formamidinium iodide (FAI,99.0%), Cobalt(III) tris(bis(trifluoromethylsulfonyl)imide)) salt (Co(III) TFSI, FK209), 99%) were purchased from Greatcell solar. Methylammonium bromide (MABr,99.95%), Spiro-OMeTAD(99.8%), Bis(trifluoromethylsulfonyl)-imide lithium salt (Li-TFSI, 99%), 4-tert-Butylpyridine(tBP, 99%), Acetonitrile (ACN, >99.9%)were purchased from Advanced Election Technology Co. Ltd.

### **Device Fabrication**

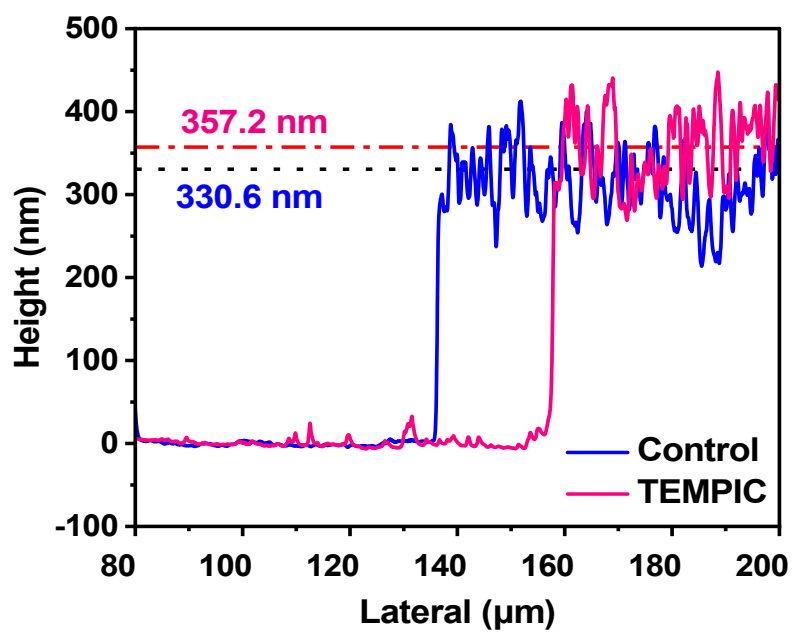
The quasi-2D PSCs prepared in this paper are formal mesoporous n-i-p structures, and the specific structures are as follows: FTO/cp-TiO<sub>2</sub>/mp-TiO<sub>2</sub>/perovskite with and without TEMPIC/Spiro-OMeTAD/Ag. First of all, TiO<sub>2</sub> and ethanol were mixed and stirred overnight at a mass ratio of 1:6. The FTO is cleaned and placed in an oven to dry. The dried glass is placed on a high-temperature heating table with the conductive side facing up and is shielded from a width of about 3 mm opposite the etched edge. The heating stage was then heated to 450 °C, and the prepared dense TiO<sub>2</sub> was evenly sprayed on the conductive glass by spray pyrolysis method, and annealed at 450 °C for

30 min. 40  $\mu\text{L}$  of mesoporous  $\text{TiO}_2$  was deposited on dense  $\text{TiO}_2$  at 5000 rpm, 20 s spin coating parameters, and annealed at 500  $^\circ\text{C}$  for 30 min. Successively, GAI, MAI and  $\text{PbI}_2$  were dissolved in the mixed solvent of DMF and DMSO at a molar ratio of 2:6:7, the concentration of  $\text{PbI}_2$  was 1 M, which was stirred overnight in the glove box and filtered with a 0.22  $\mu\text{m}$  filter membrane before use. 40  $\mu\text{L}$  of precursor solution was applied to  $\text{TiO}_2$  substrate, CB was added dropwise 10 s down to the spin coating program, annealed at 100  $^\circ\text{C}$  for 10 min, and then annealed at 150  $^\circ\text{C}$  for 10 min. The composition of perovskite material is  $\text{GA}_2\text{MA}_6\text{Pb}_7\text{I}_{22}$  as the light-harvesting layer. Next, 85 mg of Spiro-OMeTAD was dissolved in 951  $\mu\text{L}$  of CB, followed by 28.8  $\mu\text{L}$  of tBP, 17.8  $\mu\text{L}$  of Li-TFSI solution (520 mg/mL in acetonitrile), and 6.5  $\mu\text{L}$  of FK209 (300 mg/mL in acetonitrile) added to Spiro-OMeTAD solution with uniform shaking. 30  $\mu\text{L}$  of the filtered solution was applied to the surface of the perovskite layer, spin coated at 4500 rpm and 30 s, and then placed in a drying oven for oxidation overnight. Finally, 200 nm of the Ag layer was vaped at 0.2  $\text{\AA s}^{-1}$  in a vacuum evaporator.

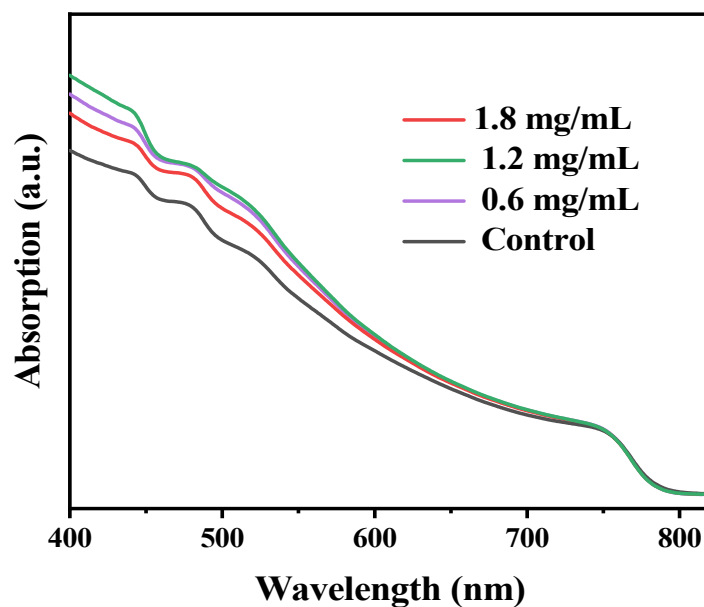
### **Characterization**

The Fourier Transform Infrared Spectrometer (FTIR) spectrum was obtained with the measuring instrument Thermo, Nicolet 6700 (The resolution of the instrument is 4  $\text{cm}^{-1}$ ). The samples for FTIR measurements were prepared by dripping the perovskite precursor solution on the KBr wafer, followed by annealing treatment at 100  $^\circ\text{C}$  for 40 minutes). The UV-Vis absorption spectra were measured by a U4100 spectrophotometer (Hitachi). X-ray diffraction (XRD) were performed in regular  $\theta$ -2 $\theta$  scanning mode using X-ray diffractometer (PANalytical,  $\text{CuK}\alpha 1$ :  $\lambda=0.154056$  nm) with scan rate 5 $^\circ\text{min}^{-1}$ . The steady-state photoluminescence (PL) spectra time-resolved photoluminescence (TRPL) spectra were measured by Perkin LS-55 fluorescence spectrometer excited at 450 nm. The time-resolved PL spectra were measured using a FLS1000 Edinburgh Instruments spectrofluorimeter equipped with the integrating sphere. Incident photon-to-current conversion efficiency (IPCE) spectra were obtained by a Newport QE measurement fit consisting of a Xenon light source (Spectral Products ASB-XE-175). The chemical states of ions were studied by X-ray photoelectron

spectroscopy (XPS) of model *K-Alpha*<sup>+</sup> that purchased from Thermo fisher Scientific. The X-ray light source is monochromatic Al K $\alpha$  source (Mono Al K $\alpha$ ) that energy is 1486.6eV, 6mA $\times$ 12KV and scan mode is fixed analyzer Energy (CAE). AFM was recorded from Bruker Innova atomic microscopy. An array of diodes (Molex 180081-4320) simulating 0.5 sun generated a white light bias to measure for transient photovoltage (TPV). The nanosecond transient absorption spectroscopy (ns-TAS) was recorded by the pulsed 532nm pump light source obtained by a frequency tripled Nd:YAG laser (a Spectra-Physics Quanta-Ray ProSeries, 10 Hz repetition rate, 10 ns pulse length) pumped an Optical Parametrical Oscillator (OPO). The sample was excited with 475 nm lase. The space charge limited current (SCLC) was obtained by Qinglang 150 W solar simulator with model Sirius-ss150A and Oriel IV Test Station software in a dark environment, under bias from 0 V to 10 V and current limit at 200mA. The current density-voltage (J-V) characteristics were measured by a Newport solar simulator (model 91160) and a Keithley 2400 source/meter under 100 mW cm<sup>-2</sup> (AM 1.5 G illumination). In this work, the mask area of the measured device is 0.0625 cm<sup>2</sup>.



**Fig. S1** The profilometry measurements of perovskite films without and with TEMPIC.



**Fig. S2** UV-vis absorption spectra of pristine and TEMPIC-treated perovskite films.

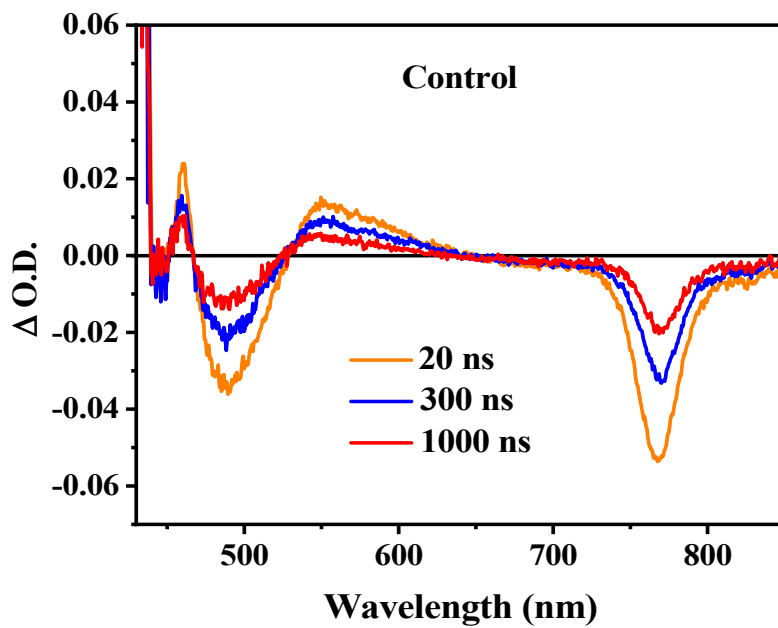


Fig. S3 ns-TA spectra at various delay times for perovskite films (Control).

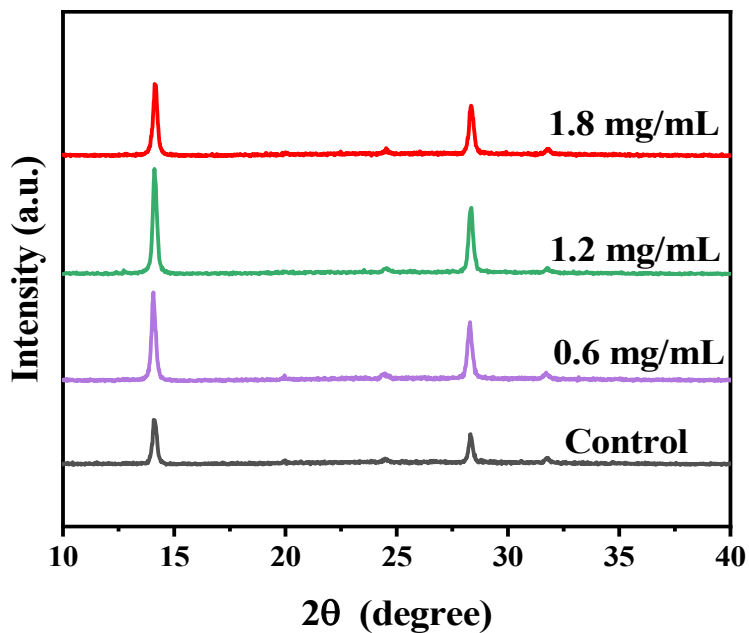


Fig. S4 XRD patterns of pristine and TEMPIC-treated perovskite films.

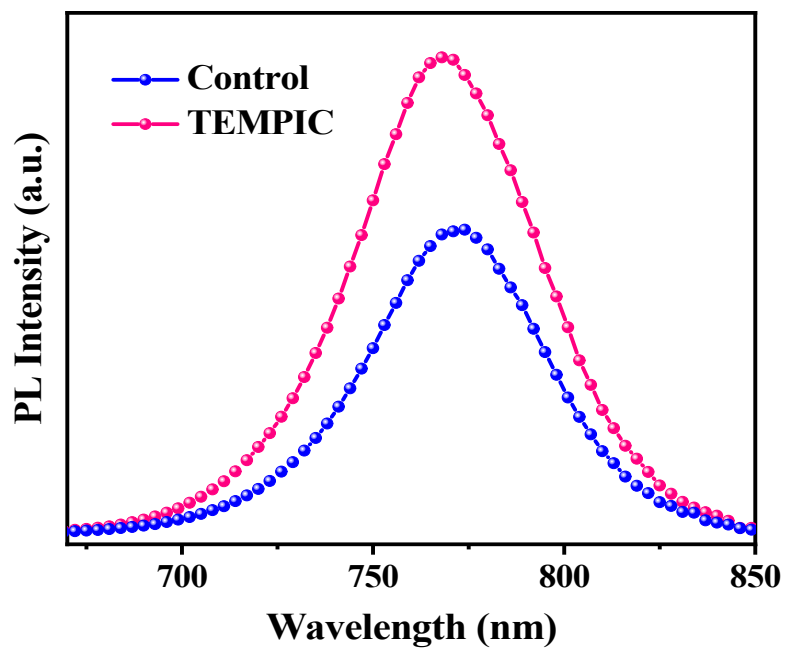


Fig. S5 Stable PL spectrum of perovskite films.

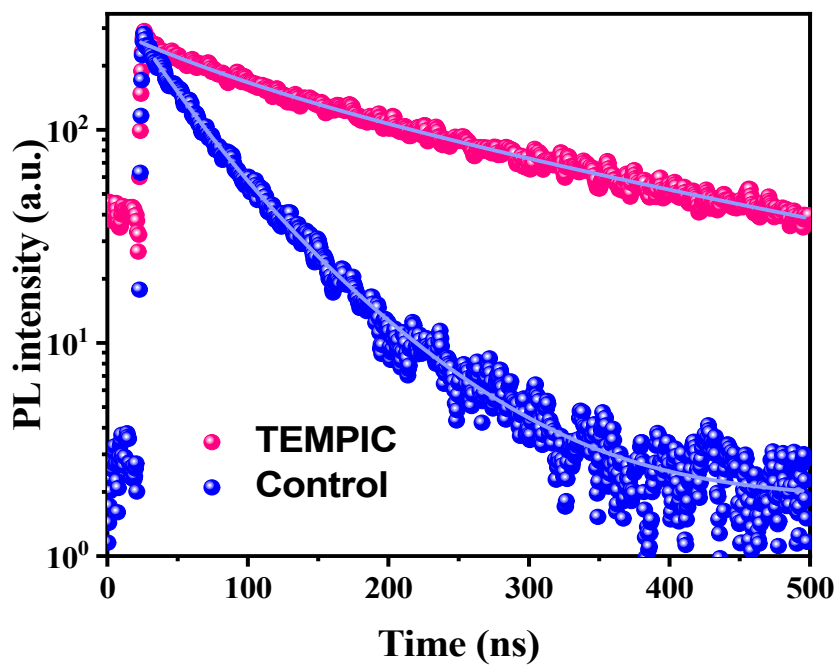


Fig. S6 TRPL spectrum of perovskite films.

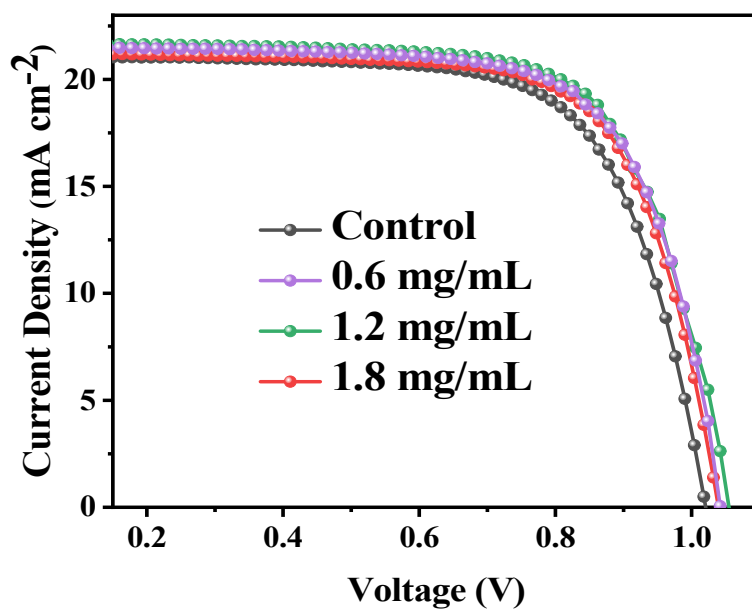


Fig. S7 J-V curve of devices with different concentrations of TEMPIC.

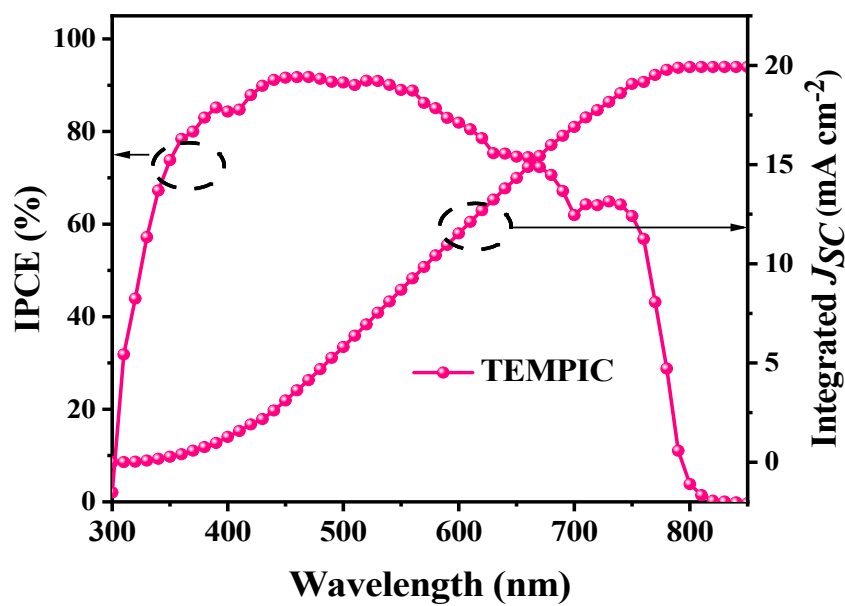


Fig. S8 IPCE curve of devices with TEMPIC.

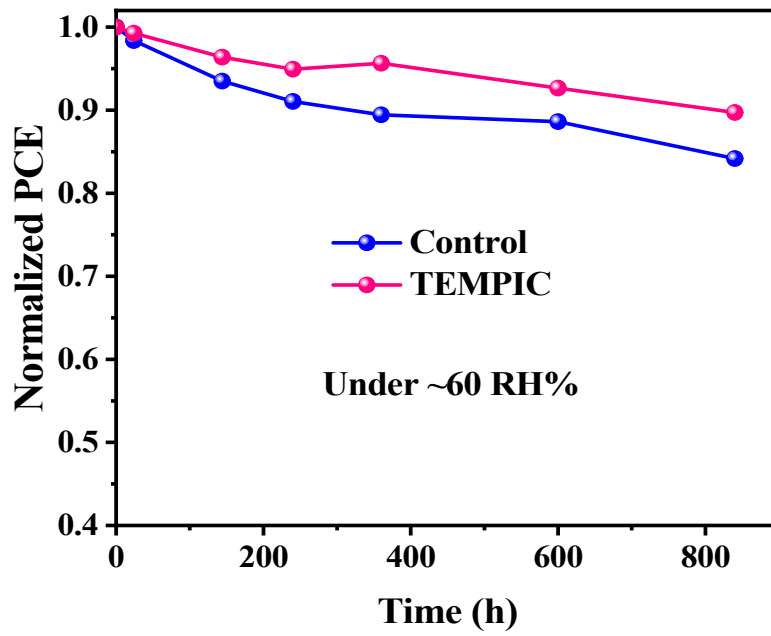


Fig. S9 The long-term stabilities of devices under 60 RH%.

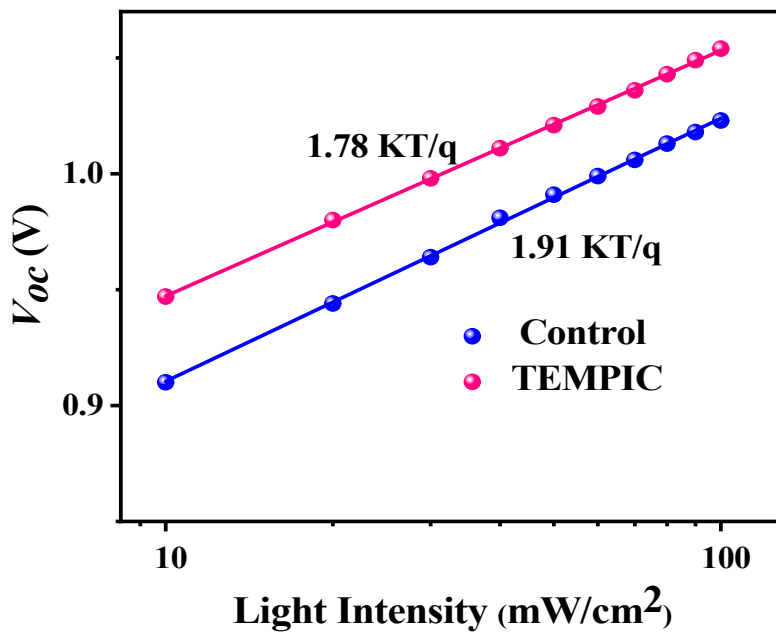


Fig. S10  $V_{oc}$  as a function of different light intensity.



**Table S1.** TRPL fitting parameters of perovskite film with different TEMPIC.

Device	$A_1$ (%)	$\tau_1$ (ns)	$A_2$ (%)	$\tau_1$ (ns)	$\tau_{\text{avg}}$ (ns)
Control	36.3	24.4	63.7	62.8	55.8
TEMPIC	10.2	63.2	89.8	183.6	178.8

**Table S2.** Photovoltaic parameters of devices at different TEMPIC concentrations.

Concentration	$J_{SC}$ (mA cm <sup>-2</sup> )	$V_{OC}$ (V)	FF (%)	PCE (%)
0 mg/mL	21.09	1.020	68.9	14.82
0.6 mg/mL	21.56	1.042	70.7	15.88
1.2 mg/mL	21.69	1.054	71.2	16.28
1.8 mg/mL	21.21	1.040	70.3	15.51

**Table S3.** Photovoltaic parameters of devices under both forward and reverse scans.

Sample	Scans	$J_{SC}$ (mA cm <sup>-2</sup> )	$V_{OC}$ (V)	FF (%)	PCE (%)	HI
Control	Reverse	21.09	1.020	68.9	14.82	0.055
	Forward	20.81	1.013	66.5	14.01	
TEMPIC	Reverse	21.69	1.054	71.2	16.28	0.047
	Forward	21.72	1.029	70.3	15.51	

$$\text{HI} = (\text{PCE}_{\text{reverse}} - \text{PCE}_{\text{forward}}) / \text{PCE}_{\text{reverse}}.$$