

Electronic Supplementary Information (ESI) for

**Efficiency improvement of planar perovskite solar cells by  
phenol additive**

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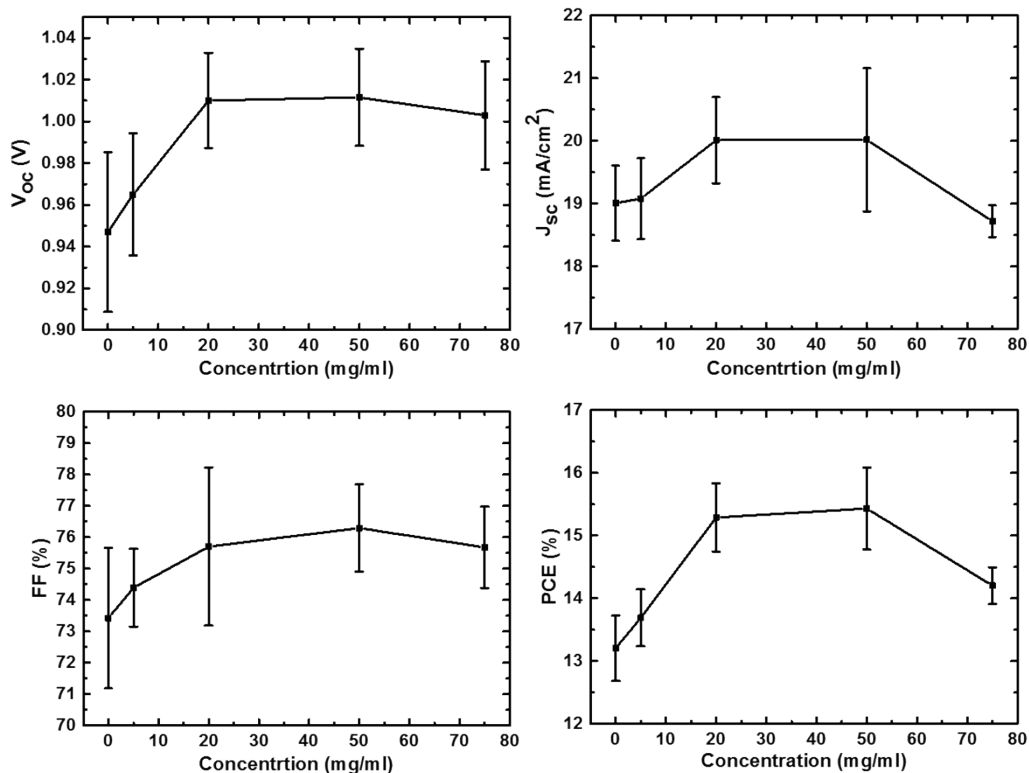
## Experimental section

**Materials:** Phenol (99% purity) was obtained from Admas. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) aqueous solution (Clevios PVP Al 4083) was purchased from Heraeus. Methylammonium iodide (MAI, >99.5% purity) was obtained from Dyesol Ltd. Phenyl-C61-butyric acid methyl ester (PCBM, 99.5% purity) were acquired from 1-Material Inc. Lithium fluoride (LiF) (99.99% purity) was supplied by Alfa Aesar Inc. Isopropanol (IPA, anhydrous, 99.5% purity) and  $\gamma$ -butyrolactone (GBL, anhydrous, 99% purity) were bought from J&K Scientific Ltd. All other chemicals, including lead (II) iodide (PbI<sub>2</sub>, beads, 99.999% purity), lead (II) chloride (PbCl<sub>2</sub>, beads, 99.999% purity), dimethyl sulfoxide (DMSO, anhydrous,  $\geq$ 99.9% purity), rhodamine 101 inner salt were supplied by Sigma-Aldrich. All of materials were used directly without further purification.

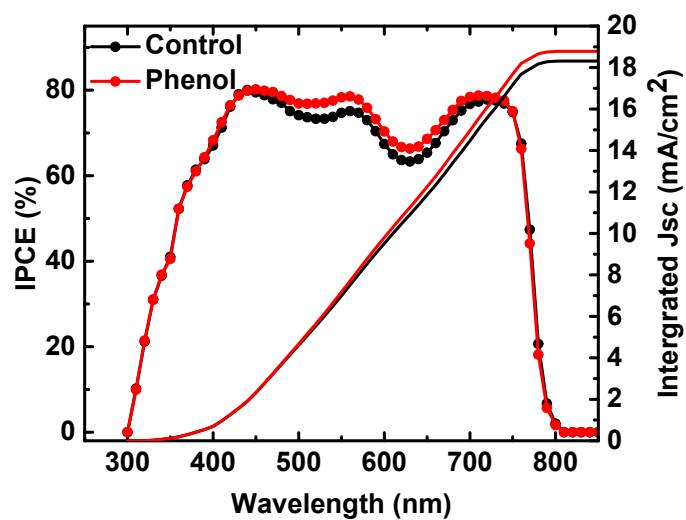
**Fabrication of devices:** Inverted PSCs were manufactured on patterned indium tin oxide (ITO)-coated glass substrates (15  $\Omega$ /sq, AE Tech.). At first, these substrates were cleaned sequentially with detergent, de-ionized water, acetone, and isopropyl alcohol for 20 min under sonication. Then they were dried in nitrogen flow and treated with UV ozone for 30 min. After that, 50  $\mu$ L PEDOT:PSS aqueous solution was spin-coated on ITO substrate at 8000 rpm for 40 s, followed by thermal annealing on a hot plate at 120  $^{\circ}$ C for 20 min to form the hole transport layer (HTL). Then, the substrates were transferred into a glovebox filled with nitrogen (O<sub>2</sub> < 10 ppm; H<sub>2</sub>O < 1 ppm). A perovskite precursor solution with a composition of 0.14 M PbCl<sub>2</sub>, 1.26 M PbI<sub>2</sub>, and 1.3 M MAI dissolved in 1 mL mixture solvent of DMSO and GBL (3:7 volume ratio) was spin-coated on the PEDOT: PSS layer. Before coating process, the substrate and the precursor with or without phenol were maintained at 70  $^{\circ}$ C, active layer was spin coated at 1000 rpm for 20 s and then 3500 rpm for 40 s. To form uniform perovskite film, at 17 s before the end of the spin-coating program, the spinning film was quenched by dripping 900  $\mu$ L toluene. Subsequently, the obtained perovskite films were put in vacuum (0.2 bar) for 20 s and then annealed at 100  $^{\circ}$ C for 20 min. PC<sub>61</sub>BM with a concentration of 23 mg/mL dissolved in chlorobenzene was deposited on top of the perovskite layer by spin coating at 2500 rpm for 40 s. After that, 0.6 mg/mL rhodamine 101 dissolved in IPA was spin coated onto the PCBM layer at 1500 rpm for 40 s. Before evaporation process, all semi-finished devices were transferred into a drying tower (35 %RH) for 15 min. Finally, these films were moved to a thermal evaporation chamber with a base pressure of approximately  $7.5 \times 10^{-4}$  Pa, where 1.5 nm LiF and 100 nm Ag were deposited through a shadow mask with the active area of 0.11 cm<sup>2</sup>.

**Characterization:** The J-V curves were measured by a solar simulator (XES-50S1, SAN-EI) illuminated at 100 mW/cm<sup>2</sup> (AM 1.5G) and Keithley 2450 source meter. The scanning electron microscopy (SEM) images were performed on JSM-7800F. UV-Vis absorption spectra were recorded using Shimadzu UV-1800. X-ray diffractions (XRD) of the perovskite films were analyzed using PANalytical X'Pert

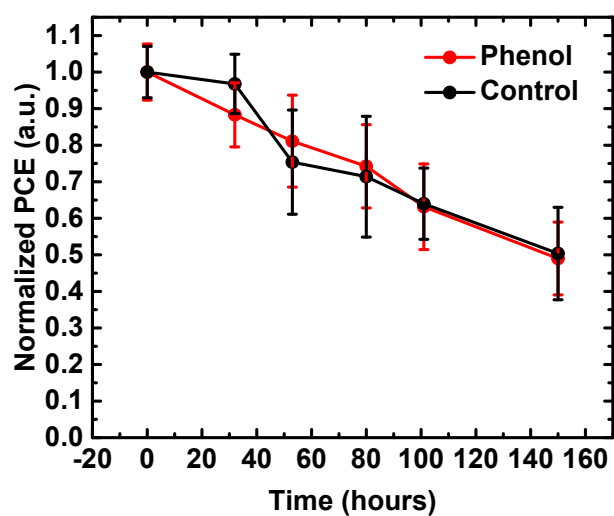
Powder X-ray diffractometer equipped with Cu K $\alpha_1$  radiation (60 kV, 60 mA). The samples for SEM, and XRD measurements were deposited on ITO/PEDOT:PSS substrate. Steady-state photoluminescence (PL) spectra were recorded by PL Spectrometer Agilent Cary Eclipse G9800A, excited at 530 nm and detected in the wavelength range of 600 nm and 900 nm. Time-resolved photoluminescence (TRPL) spectra at the peak emission wavelength of 760 nm were derived from Edinburgh FS5 Fluorescence Spectrometer, and the excitation was provided by a picosecond pulsed diode laser (EPL-510, Edinburgh Instruments Ltd.) at the wavelength of 510 nm with a pulse width of 129.8 ps, a repetition frequency of 0.5 MHz, maximum average power of 5 mW. The samples for PL measurements were deposited on plain glass.  $^1\text{H}$  Nuclear Magnetic Resonance (NMR) spectra was determined by Agilent 600 MR, and  $^1\text{H}$  NMR spectra of dimethyl sulfoxide (DMSO) (peak of  $\delta = 2.50$  ppm) was selected as internal reference to evaluate chemical shifts. The phenol sample was obtained by dissolving 5 mg phenol in 1 mL DMSO-d $_6$  solution to serve as a reference. Meanwhile, several mixtures of phenol and  $\text{PbI}_2$  with different weight ratio were stirred in DMSO-d $_6$  solution to prepare the phenol- $\text{PbI}_2$  samples, and it has to note that the concentration of phenol always keep at 5 mg/ml. Liquid Chromatography with Mass Spectrometer (LC-MS) was performed by using Agilent 1290-6530 and running in negative ionization mode. Phenol was dissolved in methanol to serve as control sample, while perovskite powder doped by phenol was peeled off from substrate and then dissolved in methanol solution under sonication, finally the turbid liquid was filtered by a 0.45  $\mu\text{m}$  Millipore filter before test.



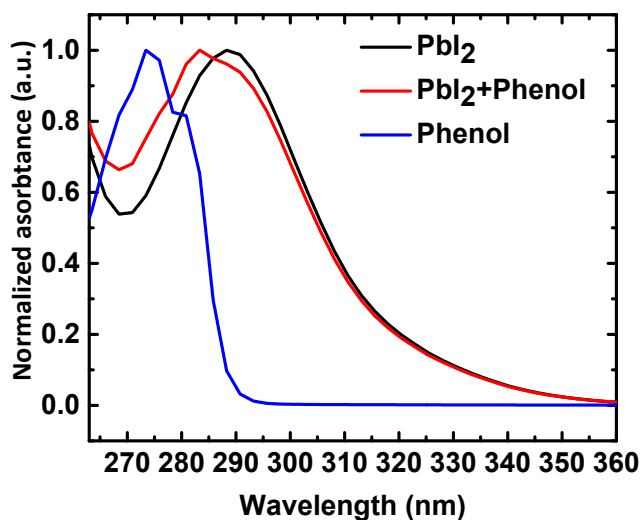
**Fig. S1** Open circuit voltage ( $V_{oc}$ ), short circuit current density ( $J_{sc}$ ), fill factor (FF) and power conversion efficiency (PCE) line charts for cells with different doping concentration.



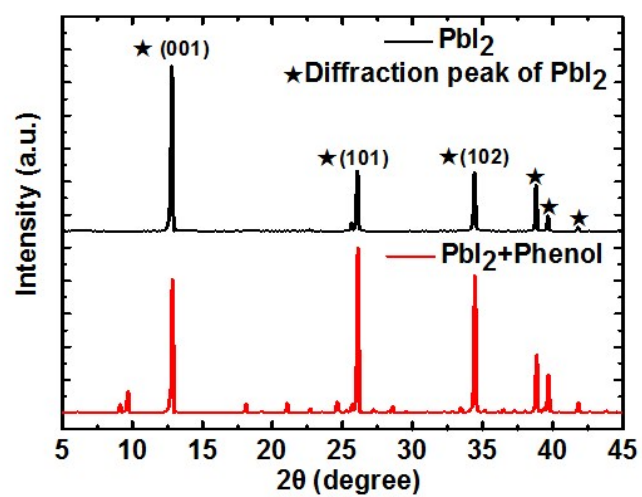
**Fig. S2** IPCE spectra and integrated  $J_{sc}$  from 300 to 800 nm of devices with or without phenol additive.



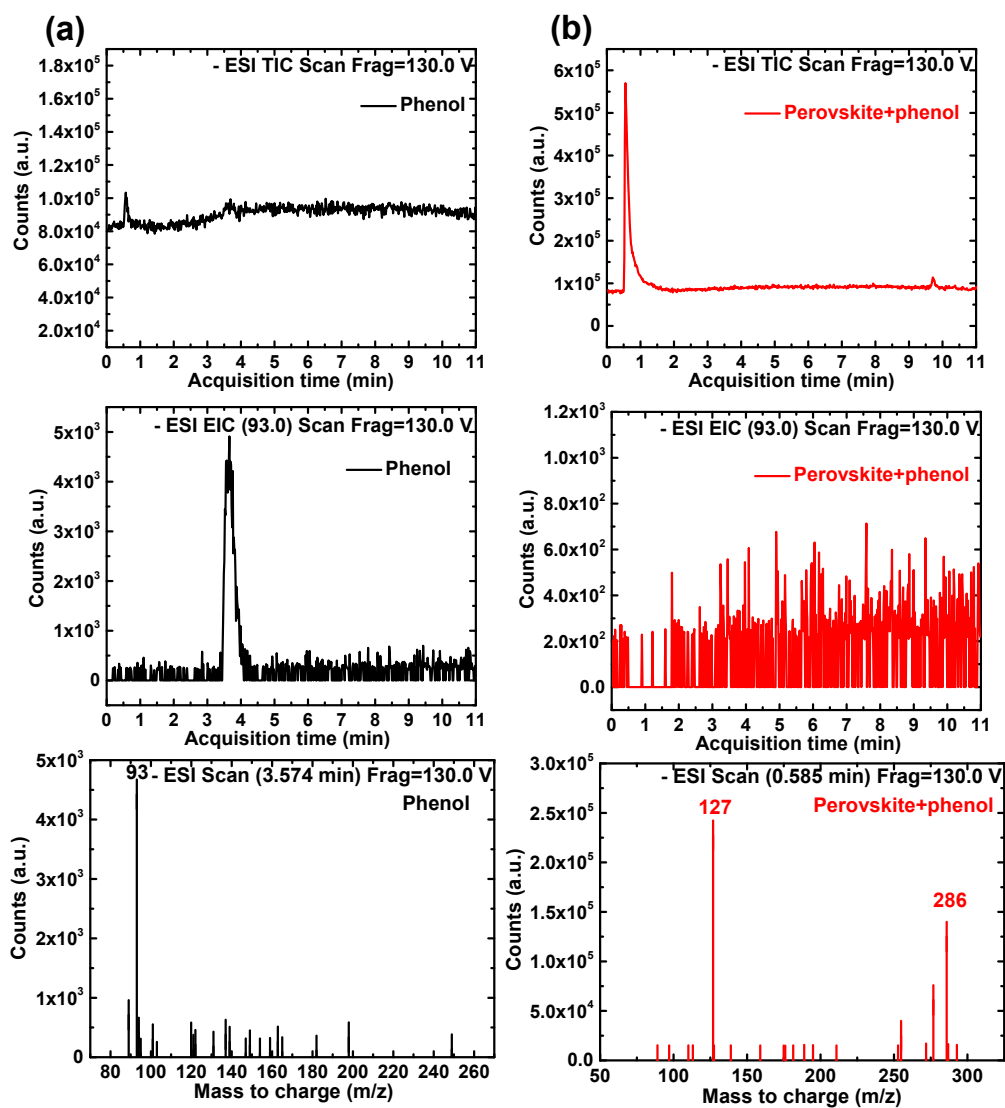
**Fig. S3** Normalized PCE of devices with and without phenol additive as a function of storage time in ambient environment ( $45\pm 5$  RH%,  $30\pm 2$  °C), statistic data from 10 devices without encapsulation.



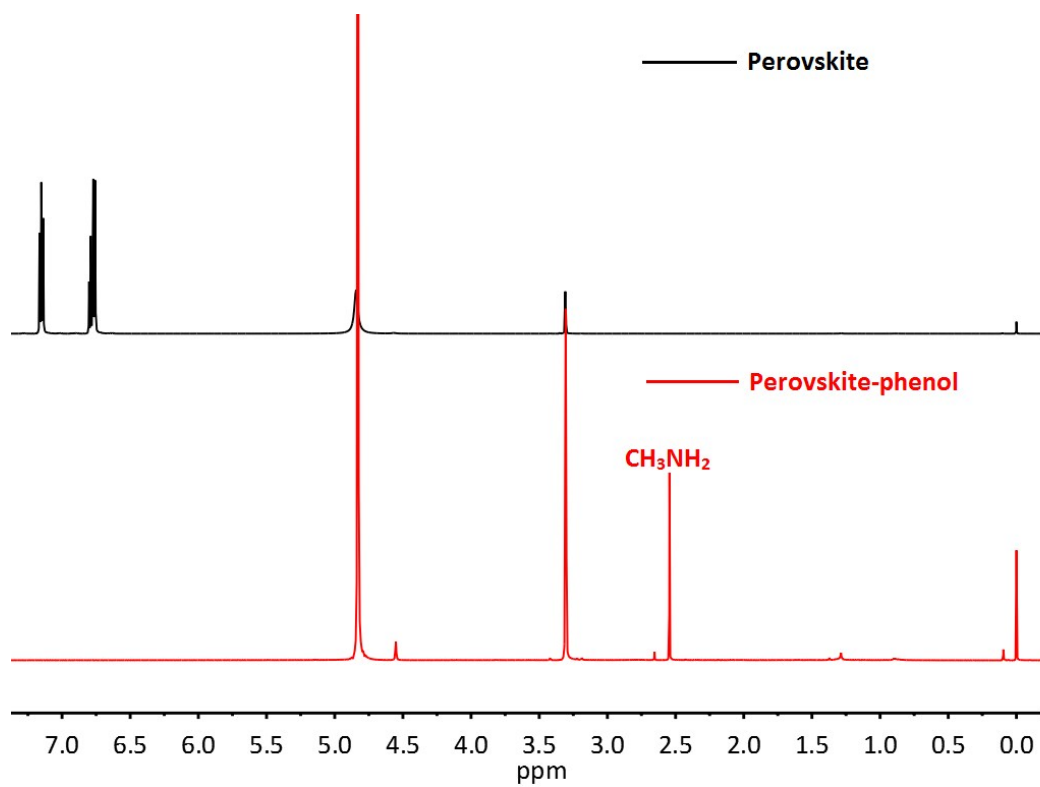
**Fig. S4** UV-vis spectra for PbI<sub>2</sub>, PbI<sub>2</sub>-phenol, and phenol dissolved in mixture solution of DMSO and GBL.



**Fig. S5** XRD spectra collected from  $\text{PbI}_2$  and  $\text{PbI}_2$ -phenol powders.



**Fig. S6** LC-MS chromatograms and full scan mass spectra of a) phenol and b) doped perovskite film.



**Fig. S7** <sup>1</sup>H NMR spectra of phenol and doped perovskite film in deuterated methanol. The signals of phenol were detected at about  $\delta = 6.8$  and 7.2 ppm.