

## Electronic Supplementary Information

### **Inverted Planar Perovskite Solar Cells based on CsI-Doped PEDOT:PSS with Efficiency beyond 20 % and Small Energy Loss**

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## 1. Experimental Section

**1.1 Materials:** In this work, all major materials were purchased from commercial suppliers and used without further purification, including PEDOT:PSS (Heraeus, Clevios PVP Al 4083), CsI (*p*-OLED, >99.99 %), PbI<sub>2</sub> (*p*-OLED, >99.99 %), MAI (*p*-OLED, ≥99.5 %), PC<sub>61</sub>BM (*p*-OLED, ≥99 %), Rhodamine 101 (Sigma-Aldrich), DMF (Sigma-Aldrich, 99.8 %), DMSO (Sigma-Aldrich, 99.8 %), isopropanol (Sigma-Aldrich, 99.5 %) and CB (Sigma-Aldrich, 99.8 %).

### 1.2 The relation between $EQE_{EL}$ and non-radiative recombination:

The open-circuit voltage ( $V_{OC}$ ) of any type of solar cells is determined by the ratio between short circuit current ( $J_{sc}$ ) and the dark saturation current ( $J_0$ ), following the expression: <sup>[1]</sup>

$$V_{OC} = \frac{kT}{q} \ln \left( \frac{J_{SC}}{J_0} + 1 \right)$$

With the Rau's reciprocity relation <sup>[2]</sup>, the expression of  $J_{sc}$  and  $J_0$  are given by:

$$J_{SC} = q \cdot \int_0^{\infty} EQE_{PV}(E) \cdot \phi_{AM1.5}(E) dE$$
$$J_0 = \frac{q}{EQE_{EL}} \cdot \int_0^{\infty} EQE_{PV}(E) \cdot \phi_{BB}(E) dE$$

Here,  $EQE_{PV}$  is the photovoltaic quantum efficiency, and  $EQE_{EL}$  is the electroluminescence (EL) quantum efficiency when we treat the solar cell as a light emitting diode. If we assume all the recombination are radiative and  $EQE_{EL}$  equals 1,  $J_0$  is minimized and  $V_{OC}$  is maximized.  $V_{oc}^{rad}$  is the open-circuit voltage under this assumption.

But due to the defects, trap states or other reasons, the  $EQE_{EL}$  can never get unitary, which will make  $V_{OC}$  smaller than  $V_{oc}^{rad}$ . The voltage loss due to non-radiative recombination, can be rewritten as:

$$\Delta V_{oc}^{non-rad} = V_{oc}^{rad} - V_{OC} = -\frac{kT}{q} \ln(EQE_{EL})$$

The non-radiative recombination loss is directly correlated to the  $EQE_{EL}$ . At room temperature, when the  $EQE_{EL}$  increases by one order of magnitude,  $\Delta V_{oc}^{non-rad}$  decreases by  $60meV$ .

### 1.3 EL and $EQE_{EL}$ measurement :

EL spectra were measured with an in-house-built system. The bias was applied on the OPV devices by a knob-style DC power supply (GW Instek GPC-3030). The voltage and current were recorded by two portable digital multimeters (a Thurlby 1905A and a Thurlby 1906) . The detector was as a Newton EM-CCD Si array detector (cool down to  $-65^{\circ}C$ ) with a spectrometer (Acton SpectraPro-500i). The device was aligned to the focal point of the spectrometer. The alignments of measurements for different samples were kept unchanged to make the collection efficiency stay the same.

### 1.4 Device fabrication

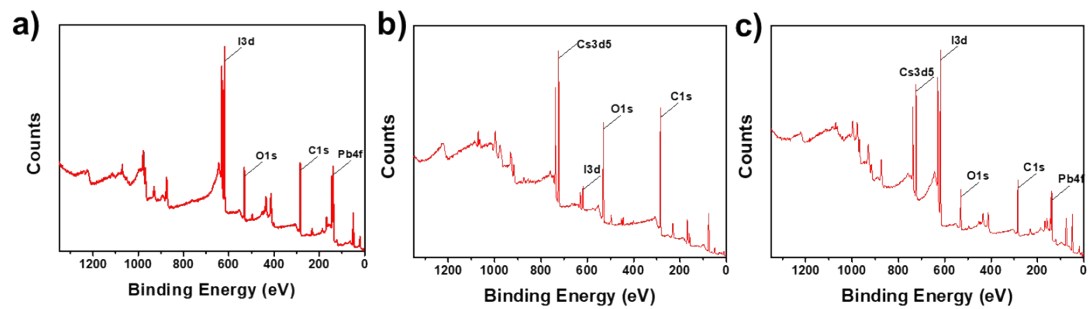
Patterned ITO glass was cleaned in an ultrasonic bath in detergent, deionized water, acetone, isopropanol sequentially and then treated with plasma for 3 min. CsI was dissolved into PEDOT:PSS solution to obtain different concentration CsI-PEDOT:PSS. The hole transporting layer PEDOT:PSS with or without CsI doping was formed on ITO substrates by spin coating at 6000 rpm for 60 s followed by annealing at  $120^{\circ}C$  for 30 min. Then the samples were transferred into an  $N_2$ -filled glovebox. A perovskite

precursor solution (1.26 M  $\text{PbI}_2$  and 1.54 M MAI in DMF:DMSO mixed solution with a v/v of 4:1) was spin-coated in a two-step program at 400 and 5000 rpm for 3 and 30 s, respectively. During the second step, 200  $\mu\text{L}$  of chlorobenzene was dropped on the spinning substrate at 10 s after the start-up. Next, the as-spun perovskite layer was annealed on a hot plate at 60  $^\circ\text{C}$  for 1 min and at 85  $^\circ\text{C}$  for 25 min to drive off the solvent and form the perovskite phase.  $\text{PC}_{61}\text{BM}$  (20 mg/mL in chlorobenzene) was deposited on the top of the perovskite layer by spin coating at 5000 rpm for 30 s. After that, Rhodamine 101 was deposited by spin coating Rhodamine 101 solution (0.05 wt% in isopropanol) at 1000 rpm for 40 s onto the ITO/PEDOT:PSS (w or w/o CsI)/Perovskite/ $\text{PC}_{61}\text{BM}$  substrate. Afterward, 1 nm thick LiF was then thermally evaporated, and an approximately 100 nm thick Ag counter electrode was deposited on top to finish the device fabrication. The Rhodamine 101 and LiF layers are the double interlayers (buffer layer) between  $\text{PC}_{61}\text{BM}$  and Ag electrode. The active area of our device is 0.09  $\text{cm}^2$ . The current-voltage (J-V) curves were measured under 100  $\text{mW cm}^{-2}$  (AM 1.5 G) simulated sunlight using Keithley 2400 in conjunction with a Newport solar simulator (94043A). The external quantum efficiency (EQE) was calculated from the photocurrent measurement under monochromatic illuminations at different wavelengths, using a 150 W xenon lamp and a monochromator.

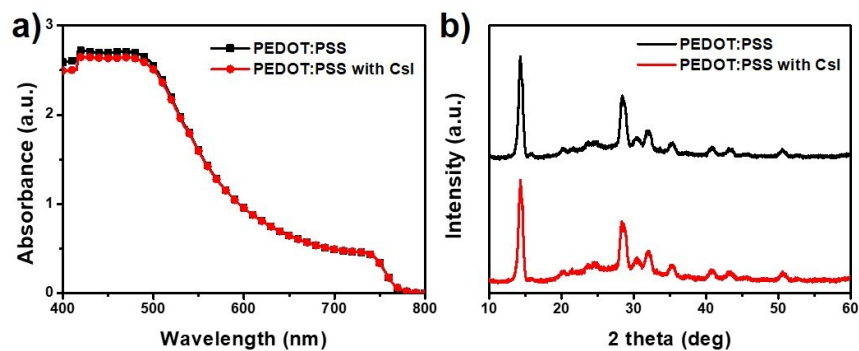
### **1.5 Characterization**

The UV-vis absorption spectra were measured on a Shimadzu UV-2450 absorption spectrophotometer. XRD was performed on a Japan Shimadzu XRD-7000 diffractometer. X-ray photoelectron spectroscopy (XPS) was recorded on ESCALAB

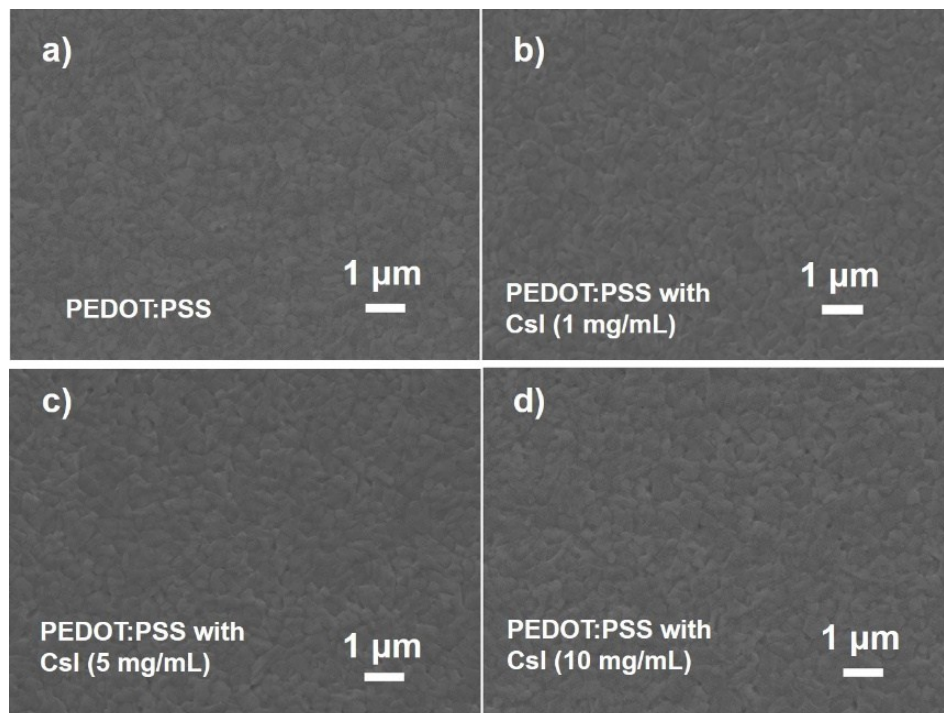
250 Xi device. UPS (ESCALAB 250Xi) measurements were performed in an ultrahigh vacuum system at base pressures  $10^{-7}$  Pa. He-UPS measurements with an excitation energy of 21.22 eV were conducted to determine the ionization potentials, and the energy resolution is  $\sim 50$  meV. The work function was determined by fitting a Boltzmann sigmoid function to the secondary electron cut off. The morphology of perovskite films was characterized by FE-SEM images (JSM-7800F). AFM images were collected in air on a scanning probe microscope (Being Nano-Instruments, Ltd., CSPM5500) using a tapping mode. Steady-state PL spectra were recorded on FS5 fluorescence spectrometer. Time-resolved PL decay curves were measured by a single photon counting spectrometer from Edinburgh Instruments (FS5). The transient photovoltage or photocurrent (TPV or TPC) decay measurements were obtained by using a pulsed double frequency Nd:YAG laser (Brio, 1000 Hz), at 635 nm with an ultra-low light intensity and a sub-nanosecond resolved digital oscilloscope (Tektronix DPO 7104) with input impedances of 1 MW and 50 W, respectively. The dynamics curves were recorded on a digital oscilloscope at a 50- $\Omega$  (short-circuit condition for TPC) resistor and a mega  $\Omega$  (open-circuit condition for TPV).



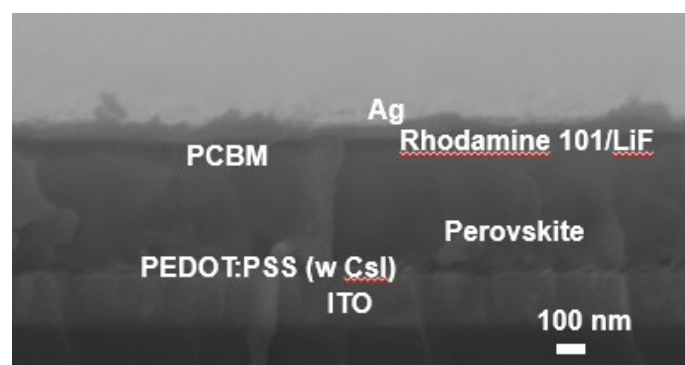
**Figure S1.** XPS measurements for a)  $\text{PbI}_2$  spin-coated on PEDOT:PSS without CsI, b) PEDOT:PSS containing CsI, and c)  $\text{PbI}_2$  spin-coated on PEDOT:PSS containing CsI.



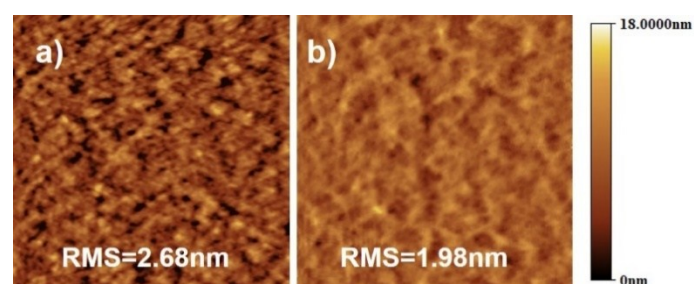
**Figure S2.** a) UV-vis absorption spectra and b) XRD of perovskite film prepared on PEDOT:PSS (with and without CsI) substrate.



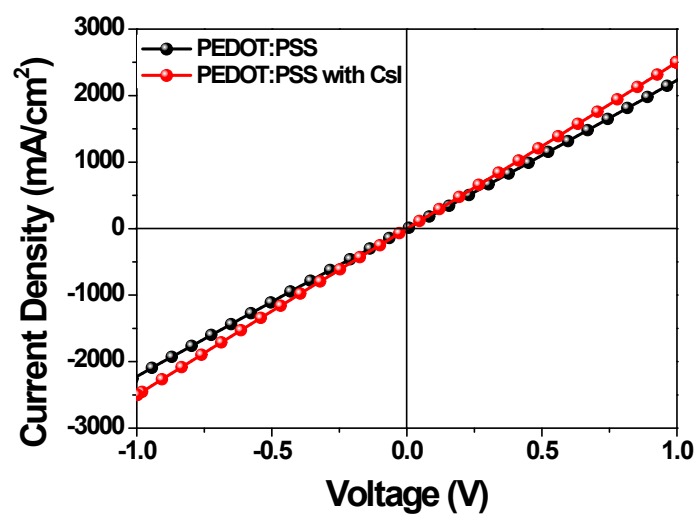
**Figure S3.** Surface FE-SEM images of perovskite films deposited on a) neat PEDOT:PSS, and b-d) PEDOT:PSS doped with CsI in different concentrations.



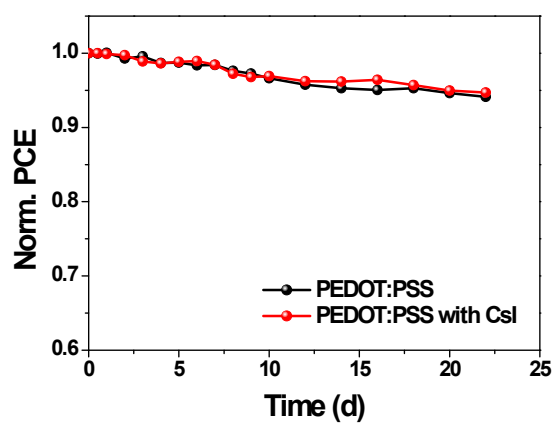
**Figure S4.** Cross-sectional SEM image of inverted PSCs using CsI-modified PEDOT:PSS HTL.



**Figure S5.** AFM images of PEDOT:PSS film a) without CsI and b) with CsI.

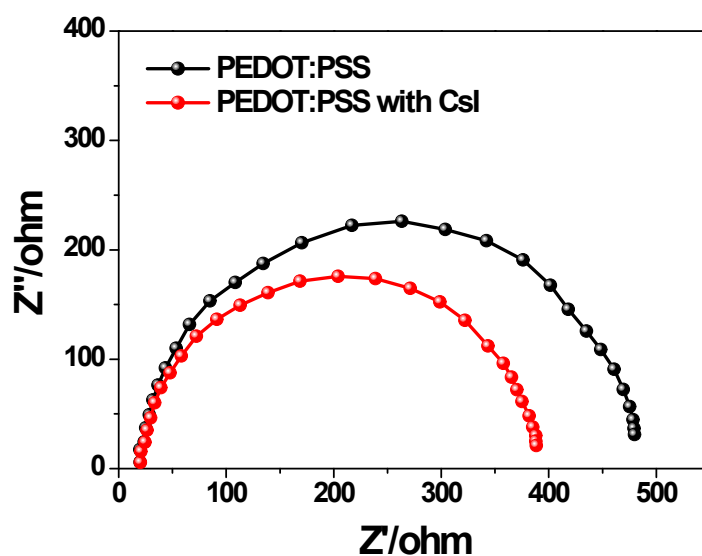


**Figure S6.** Hole transport property measurement of PEDOT:PSS film with and without CsI



**Figure S7.** Stability of the inverted PSCs based on PEDOT:PSS (with and without CsI) measured in 25 days. The devices are not encapsulated and stored in the ambient condition.





**Figure S8.** Nyquist plots of perovskite solar cells based PEDOT:PSS with (red) and without (black) CsI in the dark with a bias of  $0.9 V V_{oc}$ .

**Table S1.** Forward and reverse scanning of PSCs using different HTLs. Pristine stands for PEDOT:PSS without CsI, PEDOT:PSS with CsI in different concentrations are denoted as CsI 1 mg/mL, 5 mg/mL and 10 mg/mL.

HTLs		$V_{oc}$ (mV)	$J_{sc}$ (mA cm <sup>-2</sup> )	$FF$	PCE (%)
Pristine	Forward	998	20.61	0.80	16.45
	Reverse	1003	20.62	0.80	16.57
CsI 1 mg/mL	Forward	1019	21.31	0.80	17.47
	Reverse	1033	21.31	0.80	17.54
CsI 5 mg/mL	Forward	1080	22.57	0.82	19.97
	Reverse	1084	22.58	0.83	20.22
CsI 10 mg/mL	Forward	1048	21.54	0.78	17.70
	Reverse	1051	21.61	0.79	18.03

## References:

- [1] K. Vandewal, K. Tvingstedt, A. Gadisa, O. Inganäs, and J. V. Manca. Nature Materials Volume 8 November (2009)
- [2] U.Rau. Physical Review B 76, 085303 (2007)