

## Supporting Information

Highly efficient inverted perovskite solar cells incorporating  
P3CT-Rb as hole transport layer to achieve large open circuit  
voltage of 1.144 V

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## EXPERIMENTAL SECTION

### Materials Preparation:

P3CT-M was synthesized by the reaction of poly[3-(4-carboxylbutyl) thiophene (P3CT, Rieke Metals) with sodium hydroxide, potassium hydroxide, barium hydroxide, caesium hydroxide respectively (molar ratio 1:1) in H<sub>2</sub>O at room temperature under stirring for 2 day according to literature report. PbI<sub>2</sub> (*p*-OLED, >99.99%), MAI (*p*-OLED, 99.5%), PbCl<sub>2</sub> (*p*-OLED, >99.99%), C<sub>60</sub> (*p*-OLED), BCP

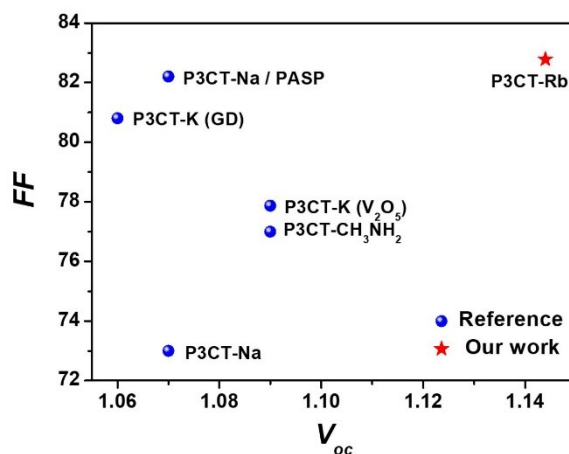
(*p*-OLED), Rhodamine 101 (Sigma-Aldrich), DMF (Sigma-Aldrich, 99.8%), DMSO (Sigma-Aldrich, 99.8%) and CB (Sigma-Aldrich, 99.8%) were used without further purification.

## Device Fabrication

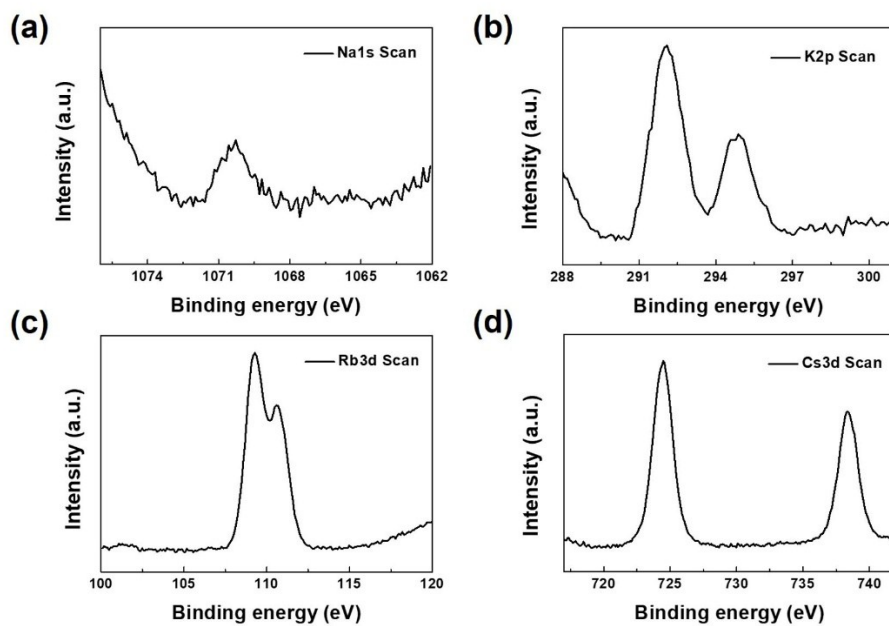
The indium tin oxide (ITO) glass substrates were sequentially washed by sonication using detergent, deionized water, and ethanol and dried by nitrogen flow. Then the dry ITO substrates were treated by O<sub>2</sub>-plasma for 180 s before using. The prepared HTL P3CT-M (1mg/mL in H<sub>2</sub>O) was spin-coated on the ITO substrates at 4000 rpm for 60 s followed by annealing at 140 °C for 30 min. After cooling down to room temperature, the substrates were transferred into glove box filled with N<sub>2</sub>. A CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub> precursor solution (1.26 M PbI<sub>2</sub>, 0.14 M PbCl<sub>2</sub> and 1.4 M MAI in DMF:DMSO mixed solution with a v/v of 9:1, stirred overnight at room temperature) was spin-coated on P3CT-M substrates at 400 rpm for 3 s and 4000 rpm for 30 s. During this spin coating process, the chlorobenzene (170 μL) was dripped directly on the substrates after spin-coated for 11 s, followed by annealing at 50 °C for 2 mins and 85°C for 25 mins. C<sub>60</sub> (40 nm) and BCP (6 nm) were evaporated under high vacuum on top of active layer served as electron transport layer and buffer layer respectively. At last, a 100 nm thick Ag electrode was deposited through a shadow mask.

## Characterization

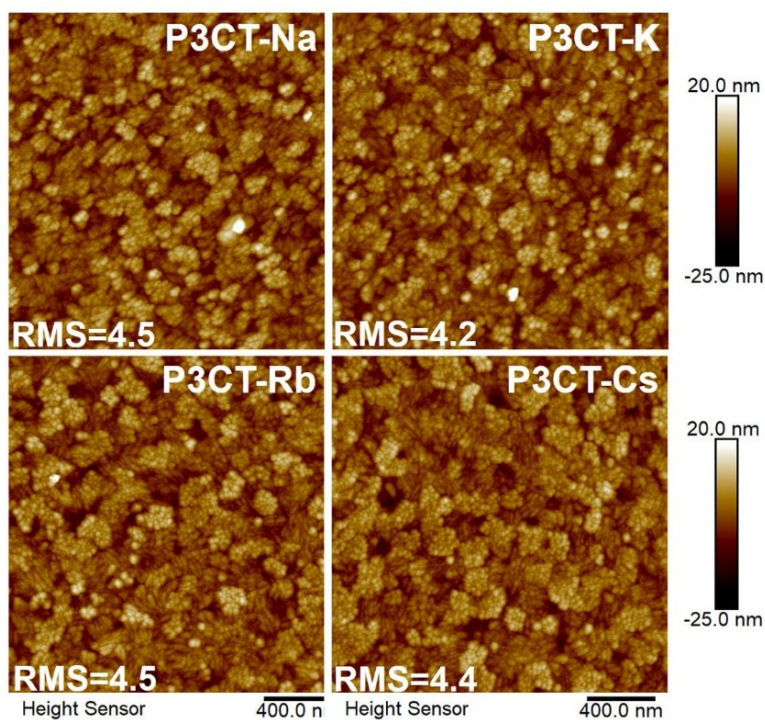
The current-voltage ( $J$ - $V$ ) curves were measured under 100 Mw/cm<sup>2</sup> (AM 1.5 G) simulated sunlight using Keithley 2400 in conjunction with a Newport solar simulator (94043A). The external quantum efficiency (EQE) was calculated from the photocurrent measurement under monochromatic illuminations at different wavelengths, using a lock-in amplifier (SR-830). UV-vis spectra was measured on a Shimadzu UV-2450 absorption spectrophotometer. XRD was performed on a Japan Shimadzu XRD-7000 diffractometer. The morphology of perovskite films were characterized by FE-SEM images (JSM-7800F). AFM images were collected in air on a Bruker. Steady-state PL spectra were recorded on HORIBA Scientific FluoroMax<sup>+</sup>. The EIS were measured with CHI in the dark at a bias of 0.94V. Film thickness was measured with Surfcoorder ET150.



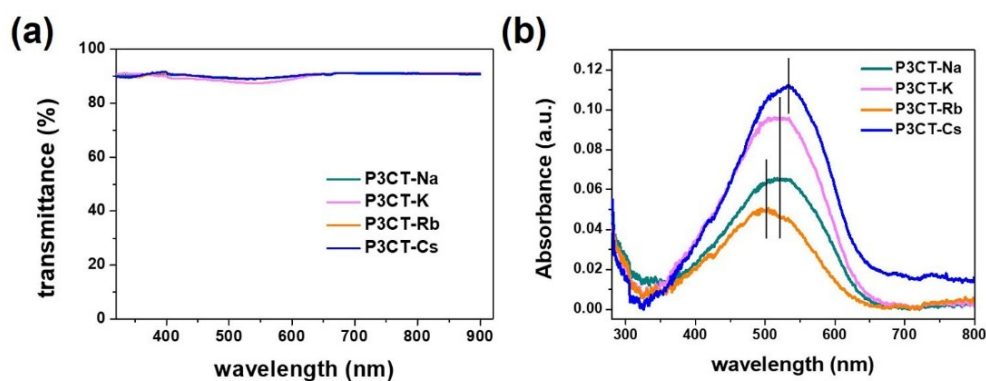
**Figure S1.** The  $FF$ - $V_{oc}$  scatter plot of inverted PSCs using P3CT as hole transport layer.



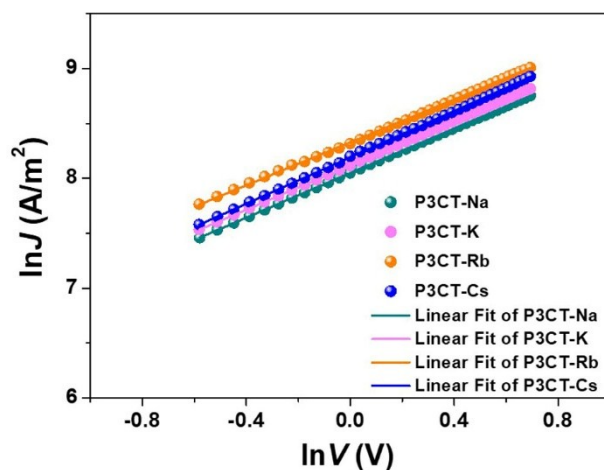
**Figure S2.** XPS spectra of elements (a) Na, (b) K, (c) Rb and (d) Cs of P3CT-Na, P3CT-K, P3CT-Rb, and P3CT-Cs films on ITO substrates, respectively.



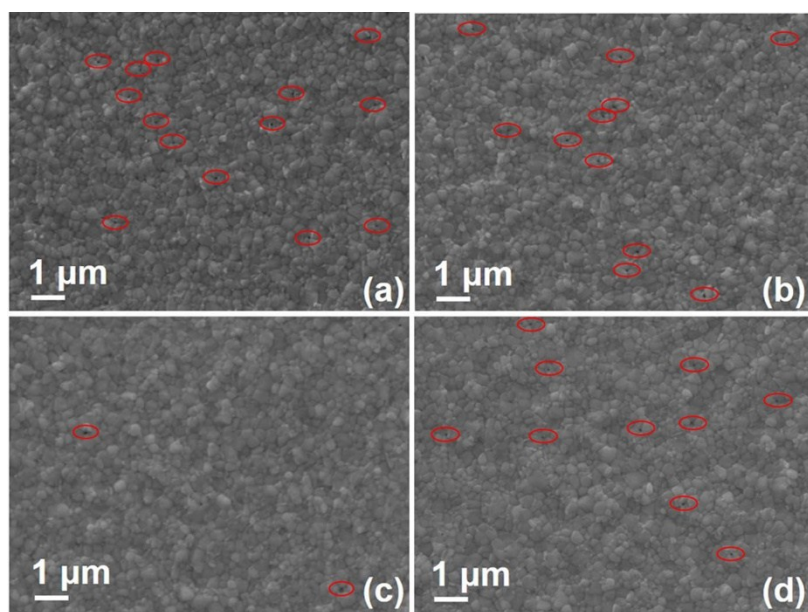
**Figure S3.** AFM images of (a) P3CT-Na, (b) P3CT-K, (c) P3CT-Rb, (d) P3CT-Cs films.



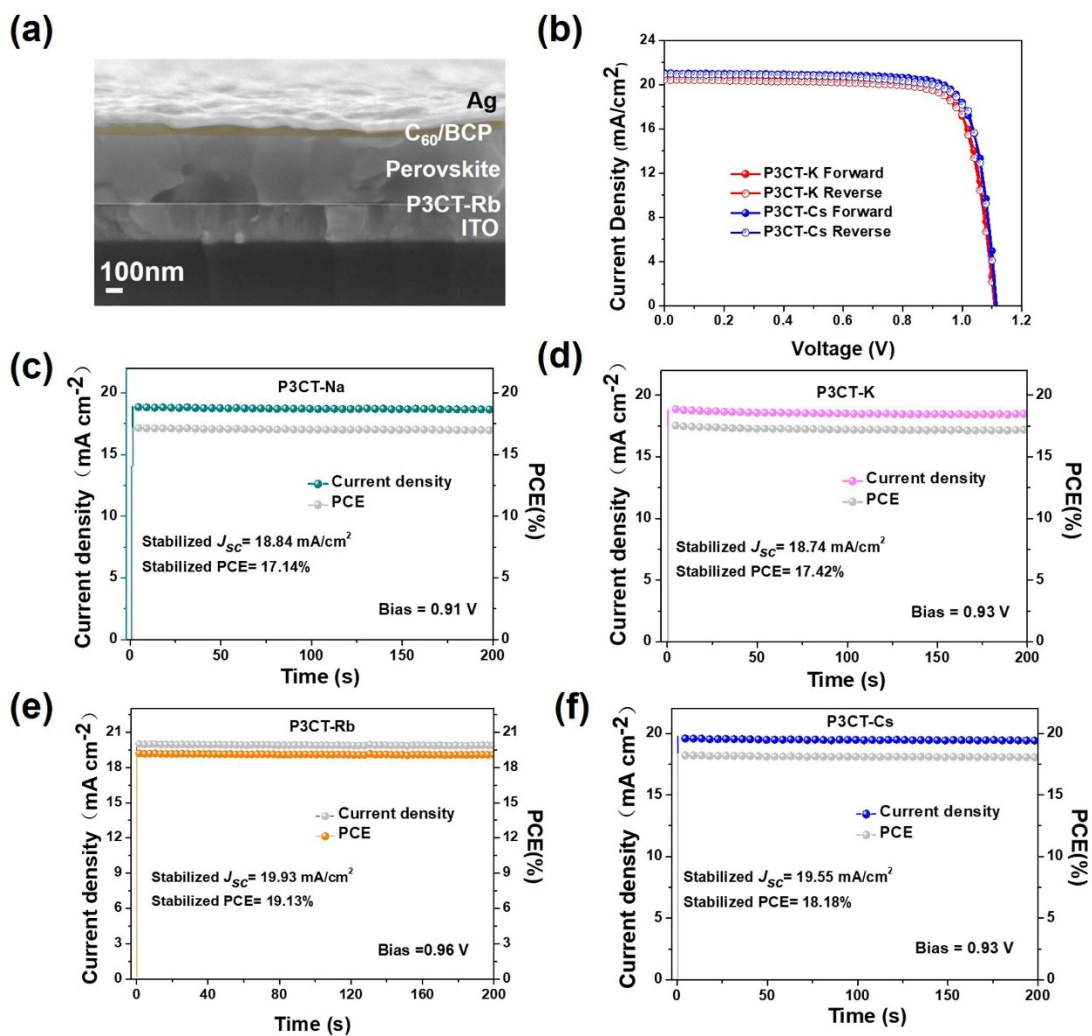
**Figure S4.** (a) UV-Vis transmission spectra of P3CT-M films (b) UV-Vis absorption spectra of P3CT-M films



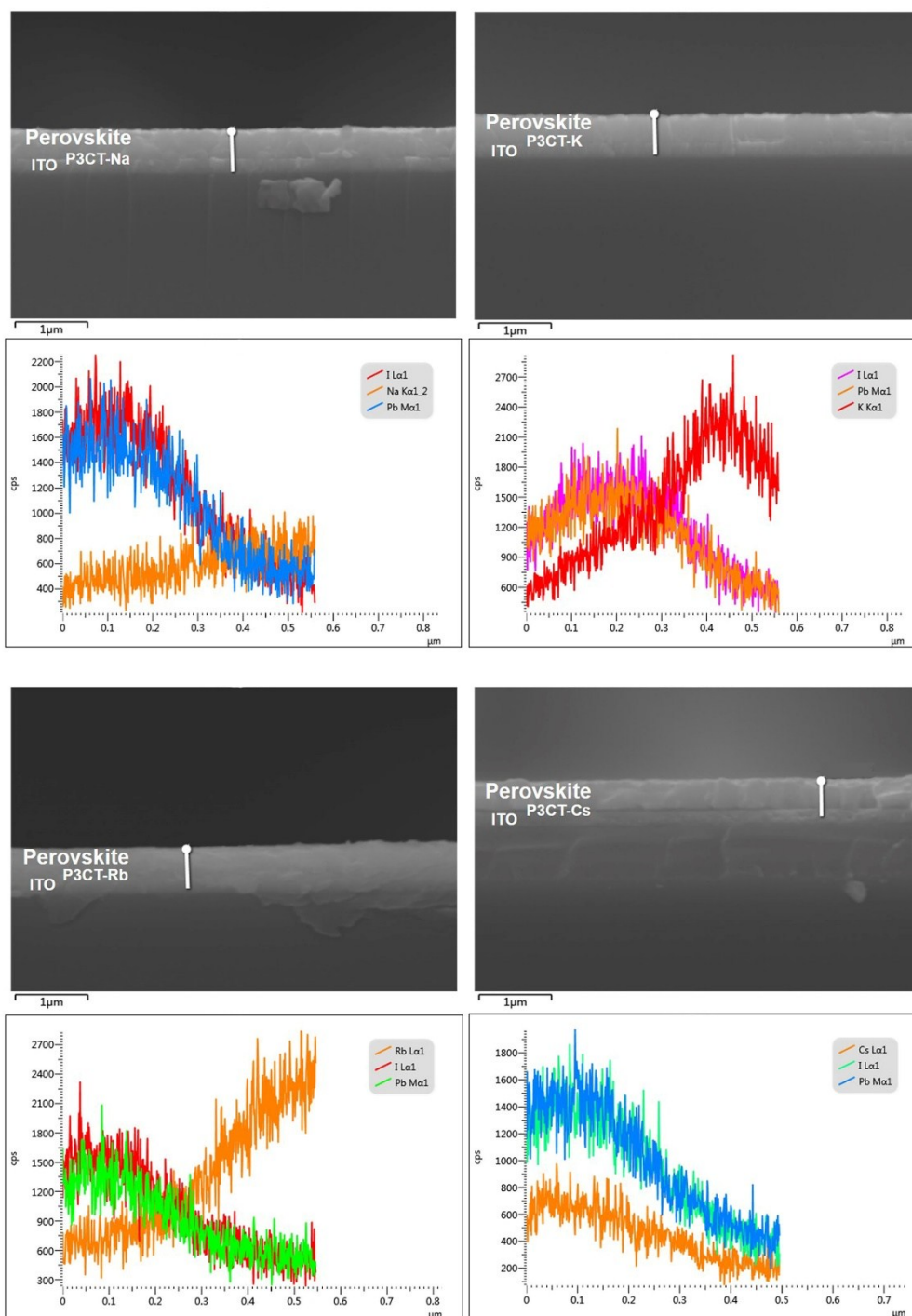
**Figure S5.** The hole mobility of different P3CT HTLs measured using space charge limited current (SCLC) method (ITO/P3CT-M (M=Na, K, Rb or Cs) /MoO<sub>3</sub>/Ag).



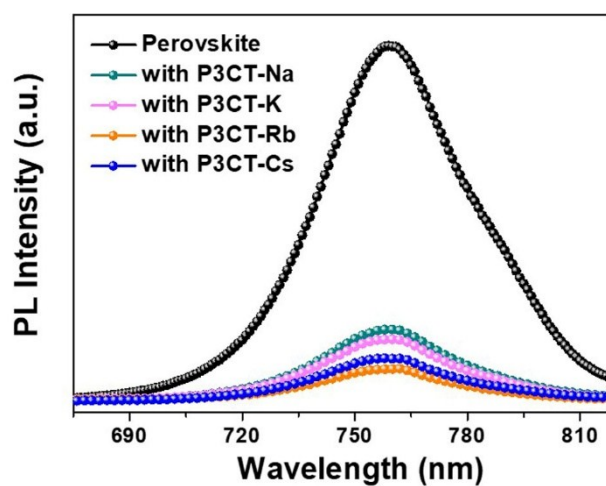
**Figure S6.** Magnified SEM images of perovskite films coated on (a) P3CT-Na, (b) P3CT-K, (c) P3CT-Rb, (d) P3CT-Cs films. (The red circle represents pin-hole on perovskite film)



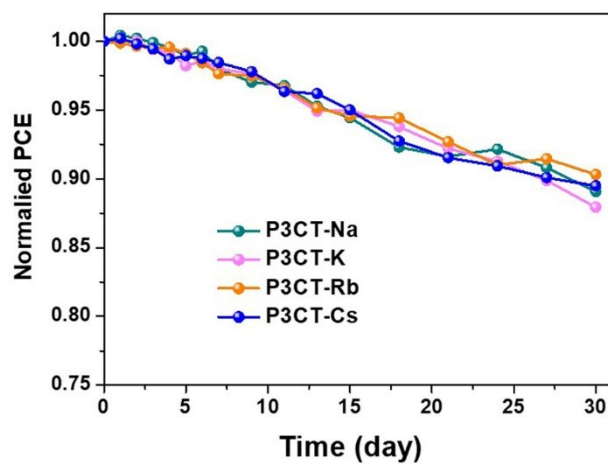
**Figure S7.** (a) Cross-sectional SEM image of the device (b)  $J$ - $V$  curve hysteresis of the P3CT-K, P3CT-Cs cells. (c-f) The output current density and PCE of the devices fabricated on different P3CT-M HTLs at the maximum power output point voltage.



**Figure S8.** The Energy Dispersive Spectrometer (EDS) of the sections on P3CT-M HTLs deposited on perovskite.



**Figure S9.** PL spectra of perovskite films coated on different P3CT-M layers.



**Figure S10.** The stability test of the unencapsulated devices based on different P3CT-M HTL in  $N_2$  environment.