

## Supplementary Information

### Nickel phthalocyanine as an excellent hole-transport material in the inverted planar perovskite solar cells

#### Experimental section

##### Materials

All the chemicals were directly used without further purification. Chemicals include Lead Iodide ( $\text{PbI}_2$ ) (99.999%, Sigma-Aldrich), Formamidinium Iodide (FAI) (Dyesol) Methylammonium bromide (MABr) (Dyesol), NiPc and CuPc (Sigma-Aldrich) dimethylformamide (DMF), Dimethyl sulfoxide (DMSO) (Sigma-Aldrich) 1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C 61 (PCBM) Xi'an Polymers, Poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS) Xi'an Polymers, acetone, isopropanol, ethanol and detergent.

##### The perovskite solar cell fabrication

The perovskite solar cells were fabricated on ITO glass substrates. Before fabrication, the ITO substrates were rinsed by sonication in detergent and deionized water, ethanol, acetone, and isopropyl alcohol in sequence each for 15 minutes. After drying in a  $\text{N}_2$  stream, the substrates were further cleaned with plasma treatment for 5 minutes to remove possible organic contaminants from surface. Then different hole-transporting layers (pristine NiPc and CuPc) were thermally deposited on the ITO substrates with different thickness, and then the samples were heated in ambient condition at 100 °C for 1 h. While the PEDOT:PSS was deposited by spin coating method with the spinning rate of 4000rpm for 30sec then the film was annealed for 120°C for 10min to form a homogenous film. Perovskite active layer was deposited by a two-step method, 599.3 mg  $\text{PbI}_2$  was dissolved in a mixed solvent of DMF (1ml) and DMSO (92.3 $\mu\text{l}$ ) by stirring at room temperature for overnight, then the  $\text{PbI}_2$  films were deposited on the substrates by spin-coating the precursor solution with a spinning rate of 3000 rpm for 30 s. The FAI and MABr<sub>2</sub> precursor solution (67.97 mg FAI and 12 mg MABr<sub>2</sub> were dissolved in 1 ml isopropanol) was spin coated atop the  $\text{PbI}_2$  films with a spinning rate of 3000 rpm for 30 s inside an Ar saturated glove box. After annealing at 150

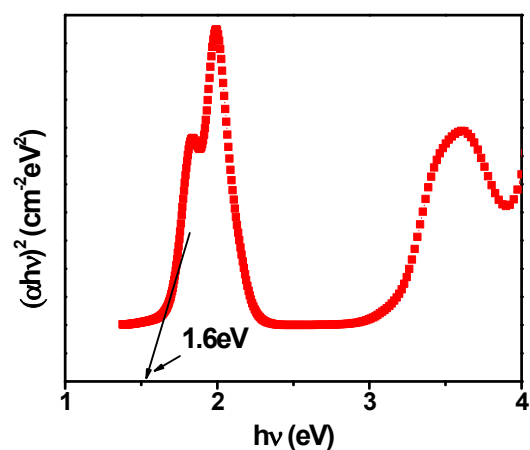
°C for 20 min in air (humidity 30%-40%), PCBM solution (20 mg/ml in chlorobenzene) was spin coated atop the perovskite films with a spinning rate of 1500 rpm for 45 s as the electron collector. Subsequently, 8 nm thick bathocuproine (BCP) layer and 100 nm thick silver layer were thermally evaporated in vacuum as the hole blocking layer and cathode, respectively.

### **Characterization**

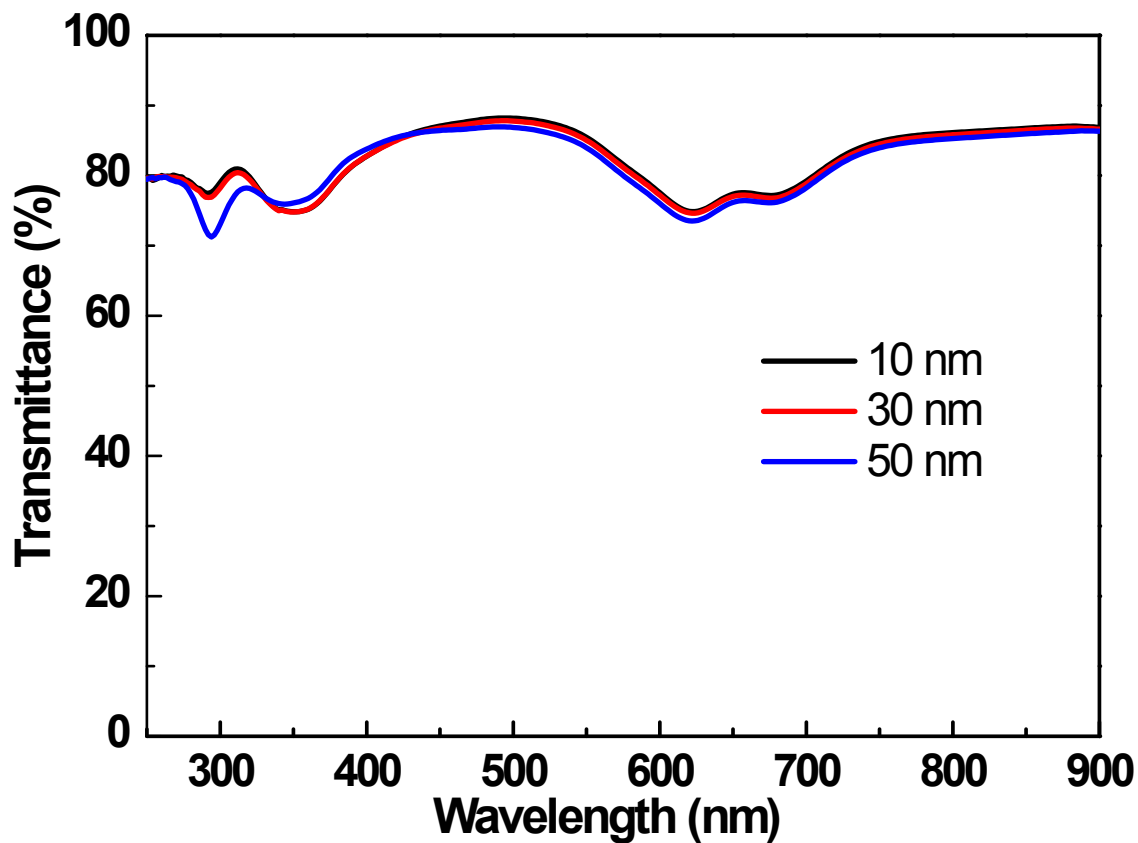
UV–vis absorption and transmittance of the different substrates were measured with a UV–vis spectrophotometer (JASCO-770). Atomic force microscopy (AFM, Bruker MultiMode 8) was used to characterize the surface roughness of the substrate with a scanasyst mode. Steady-state and time-resolved photoluminescence spectra measurements were performed with fluorescence spectrophotometer (Edinburgh Instruments, FLSP-920). The excitation was performed with pump pulse at 471 nm provided by a nanosecond tunable OPOlett-355II laser. The data were fitted with bi-exponential function of  $A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$ . XRD patterns were recorded on a Rigaku diffractometer using Cu K $\alpha$  irradiation. SEM images were performed with Field Emission Instruments: Nova Nano SEM 450 (FEI).

### **Solar cell characterization**

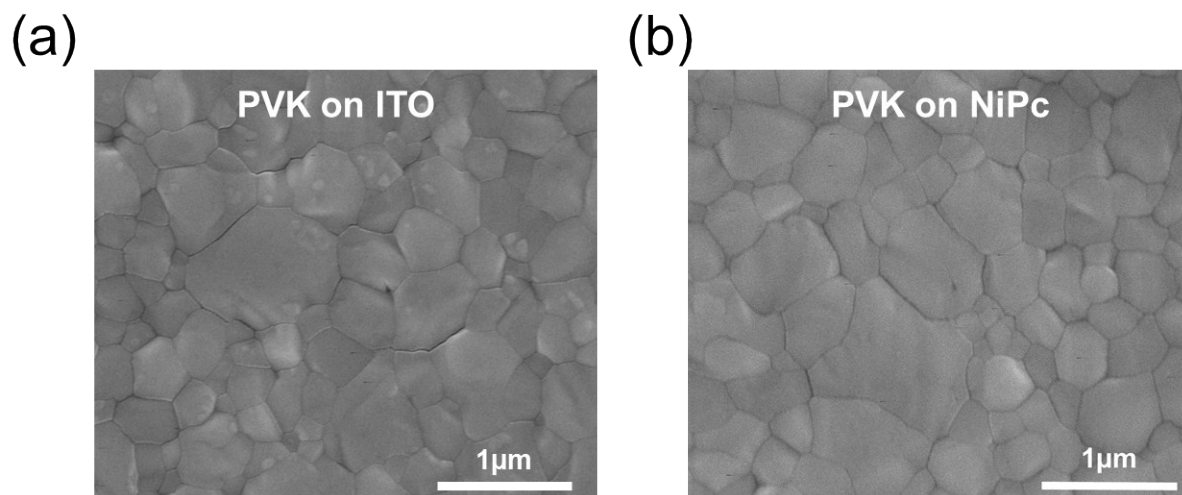
The photocurrent–voltage (J-V) characteristics of solar cells were measured by using an electrochemical station (biologic, VSP300) under illumination of a simulated sunlight (AM 1.5G, 100 mW cm<sup>-2</sup>) provided by Oriel Sol3A solar simulator (Newport USA, Model: 94023A) with an AM 1.5 filter in ambient air. Light intensity was calibrated with a Newport calibrated standard Si reference cell (SER. No: 506/0358). The measurement of the incident photo–to–current conversion efficiency was obtained by QTest Station 1000AD (CROWNTECH). Prior to measurement, a standard silicon solar cell was used as reference.



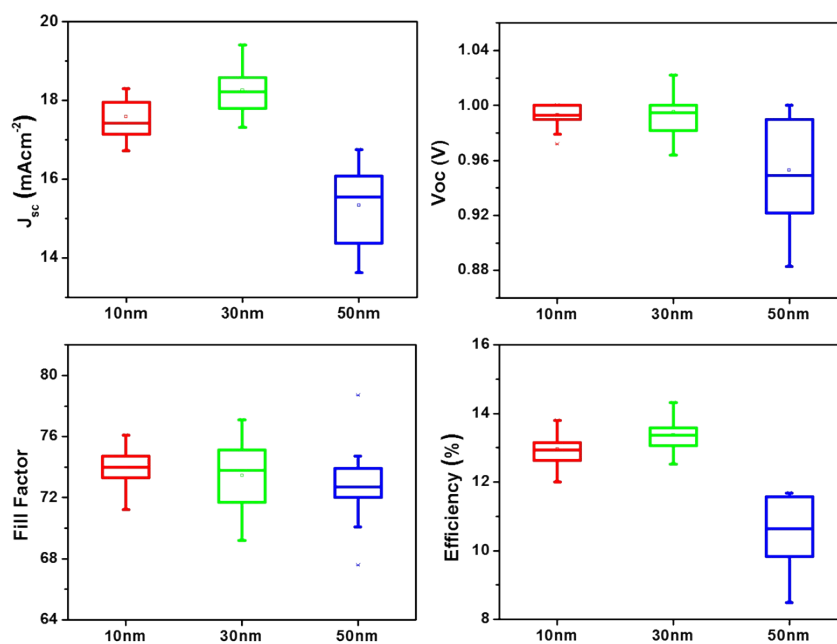
**Fig. S1.** The Kubelka- Munk function curve transformed from the absorption spectrum of NiPc film.



**Fig. S2.** UV-vis transmittance spectra of the NiPc thin films with different thicknesses (10, 30, and 50 nm).



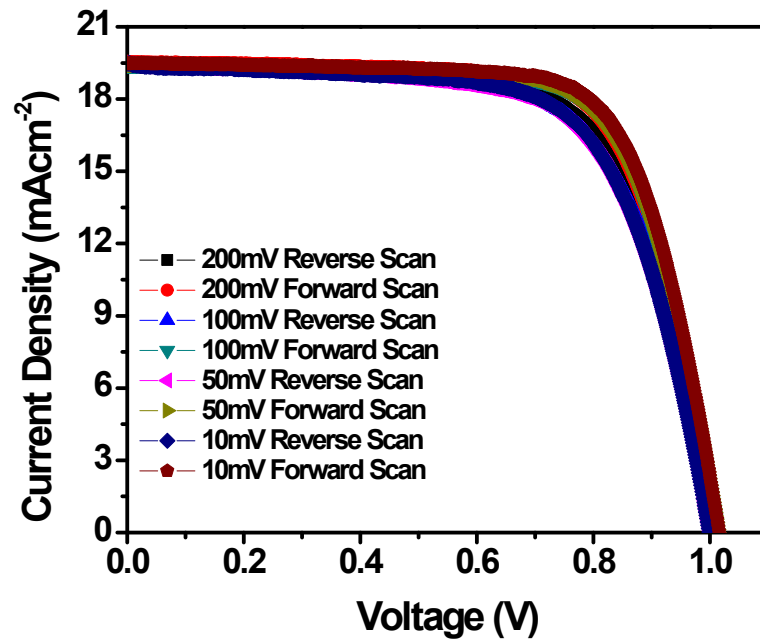
**Fig. S3.** SEM images of the perovskite films deposited on (a) bare ITO and NiPc coated ITO substrates.



**Fig. S4.** Photovoltaic parameter histograms of the devices with different thicknesses of NiPc films.

**Table S1.** Photovoltaic parameters of the champion p-i-n PSCs with different thicknesses of NiPc films.

Thickness	Scan Direction	Jsc (mAcm <sup>-2</sup> )	Voc (V)	FF	Efficiency
10nm	Forward	18.24	1	75.6	13.7
30nm	Forward	19.45	1	73.6	14.31
50nm	Forward	16.50	0.98	72	11.64



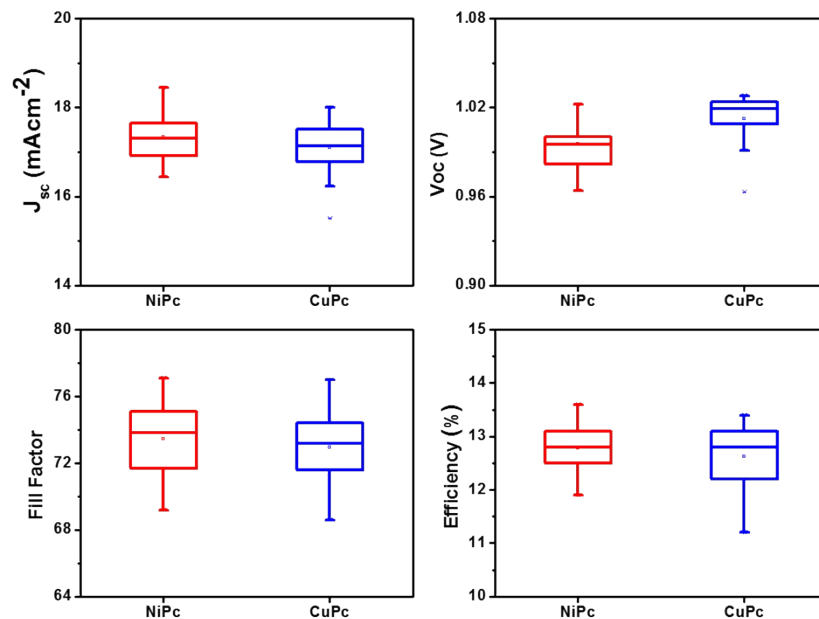
**Fig. S5.** Comparison of J-V curves under different scan rates for a NiPc based device.

**Table S2.** Photovoltaic parameters of a NiPc based device under different scanning rates.

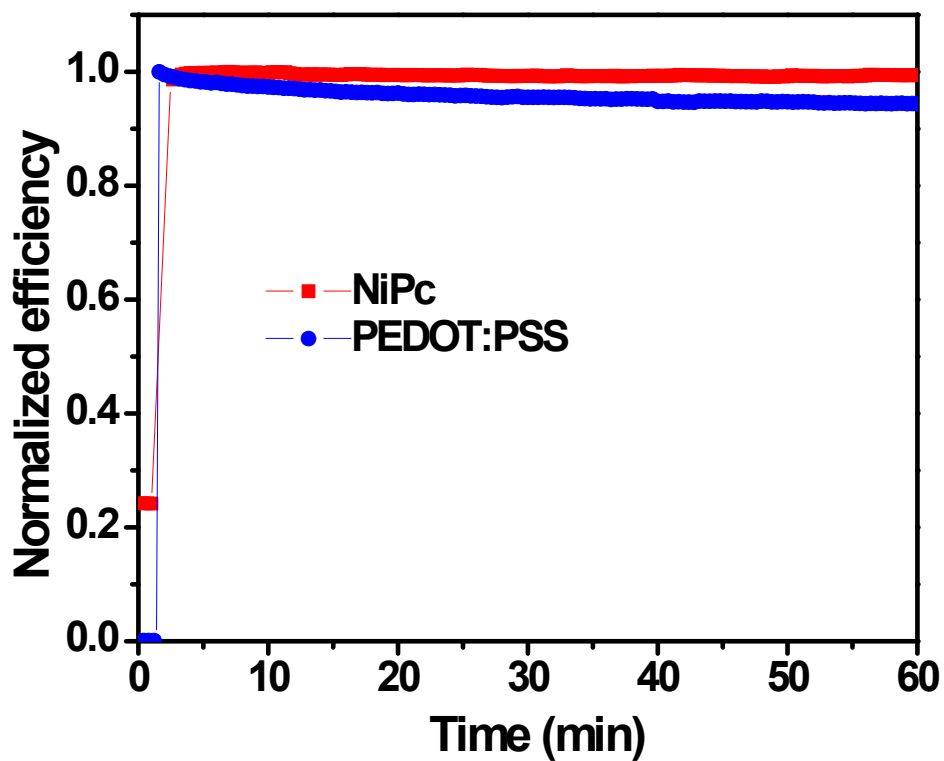
<b>Scan Rate</b>	<b>Scan Direction</b>	<b>Jsc (mAcm<sup>-2</sup>)</b>	<b>Voc (V)</b>	<b>FF</b>	<b>Efficiency</b>
<b>200mV</b>	Reverse	19.54	1	67.6	13.2
	Forward	19.54	1	70.9	13.85
<b>100mV</b>	Reverse	19.41	1	67.2	13.04
	Forward	19.41	1	72.1	13.99
<b>50mV</b>	Reverse	19.42	1	66.9	12.99
	Forward	19.42	1	72.5	14.04
<b>10mV</b>	Reverse	19.45	0.99	67.3	12.95
	Forward	19.45	1	73.6	14.3

**Table S3.** Photovoltaic parameters of the champion devices with different HTMs.

<b>HTMs</b>	<b>Scan Direction</b>	<b>Jsc (mAcm<sup>-2</sup>)</b>	<b>Voc (V)</b>	<b>FF</b>	<b>Efficiency</b>
<b>NiPc</b>	Forward	19.45	1	73.6	14.31
<b>CuPc</b>	Forward	18.94	0.99	75.1	14.1



**Fig. S6.** Photovoltaic parameter histograms of devices with different HTMs.



**Fig. S7.** The efficiency decay curves of the devices based on the NiPc (red line) and PEDOT:PSS, respectively (blue line).