Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

High-efficiency and stable $Sb_2(S,Se)_3$ thin film solar cells with phthalocyanine as a hole transport layer

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1. Experimental section

1.1. Device fabrication

First, the FTO was ultrasonically cleaned with detergent, ultrapure water and ethanol for 30 min and treated with ozone for 15 min. A 60-nm film of CdS was then deposited on the FTO as an electron transfer layer using chemical bath deposition for 6 min. The coating was spun with $CdCl_2$ (20-mg mL^{-1} cadmium chloride methanol solution) for 30 s at 3000 rpm, followed by annealing at 400℃ for 10 min and a natural cooling process. Further, $Sb_2(S,Se)_3$ films were deposited on CdS substrates using a hydrothermal method with a modified formulation. The $Sb_2(S, Se)_3$ films were synthesised using $Na_2S_2O_3{\cdot}5H_2O$, $KSbC_4H_4O_7{\cdot}0.5H_2O$ and CH_4N_2Se as the S, Sb and Se sources, respectively. Briefly, 0.2671 g of $KSbC_4H_4O_7{\cdot}0.5H_2O$, 0.7942 g of $Na_2S_2O_3{\cdot}5H_2O$, 0.02 g of CH_4N_2Se, 0.04 g of EDTA and 0.25 g of NH_4F were added to a Teflon jar (50 ml) with 40 ml of ultrapure water and heated in a drying oven at 130℃ for 180 min to perform a hydrothermal reaction. Thereafter, the samples were washed with ultrapure water and the resulting $Sb_2(S,Se)_3$ films were placed under a nitrogen atmosphere and annealed at 350℃ for 15 min. Further, thin films of phthalocyanine were deposited on $Sb_2(S,Se)_3$ using a spin- coating method, the phthalocyanine solution was dispersed in a chlorobenzene solution. Finally, gold electrodes with an area of 0.07 cm^2 and a thickness of 60 nm were prepared through thermal evaporation.

1.2. Measurements and characterization

The surface and cross-sectional morphologies of phthalocyanine and $Sb_2(S,Se)_3$ films were characterised using scanning electron microscopy (SEM, SEM-S4800, Hitachi). The surface roughness values of the phthalocyanine and $Sb_2(S,Se)_3$ films were characterised using atomic force microscopy (AFM; Nano Man VS, Veeco). The optical properties of $Sb_2(S, Se)_3$ and phthalocyanine films were determined using UV–vis spectrophotometry (Shimadzu UV-2600). Ultraviolet photoelectron spectroscopy (UPS) was performed using a PHI 5000 VersaProbe III with a He I source (21.22 eV) under an applied negative bias of 9.0 V. Current density–voltage (*J–V*) curves of $Sb_2(S,Se)_3$ thin film solar cells were simulated using a source metre (ketley2400) under standard illumination (100 mW cm^{-2}). The dark *J–V* curves of the devices were measured from −1 to +2 V under dark conditions. The external quantum efficiency of the solar cells was obtained using a photovoltaic characterisation system (photovoltaic measurement system, QEXL). Electrochemical impedance spectroscopy (EIS) from 10 Hz to 4 MHz was performed under dark conditions at 0.60 V. Capacitive voltage (*C-V*) measurements were performed in the dark using a precision LCR metre (E4980AL) with a bias voltage from −1 V to +1 V. In the contact angle analysis, a contact angle goniometer and a high-resolution camera are used to capture an image of the drop sitting on the surface from the side view (JC2000D1).

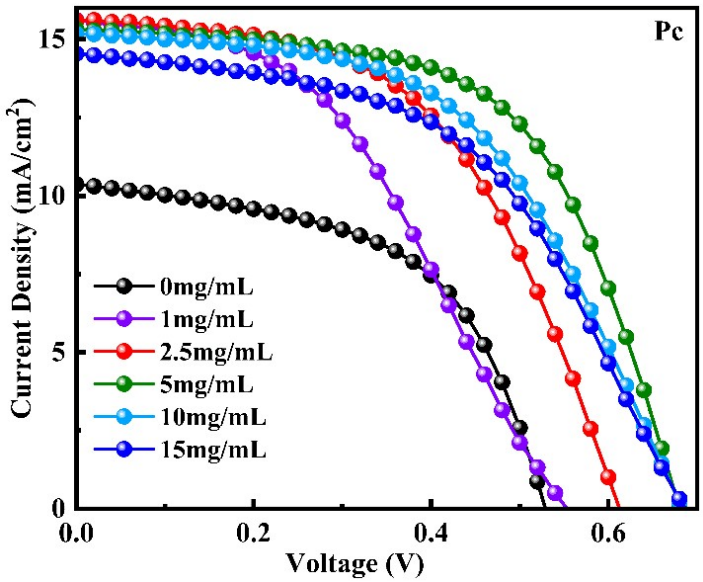

Fig. S1 The efficiency of $Sb_2(S,Se)_3$ solar cells with various concentration of pure phthalocyanine as hole transport layer.

Table S1 Photovoltaic parameters of the devices with different concentrations of phthalocyanine HTL

Sample	V_{OC} (mV)	J_{SC} (mA/cm^{-2})	*FF* (%)	*PCE* (%)	R_s (ohm)	R_{sh} (ohm)
0 mg mL^{-1}	0.5291	10.37	54.65	3.00	559.37	13902.77
1 mg mL^{-1}	0.5534	15.61	43.17	3.73	1106.26	12187.55
2.5 mg mL^{-1}	0.6126	15.60	52.60	5.03	564.97	34079.1
5 mg mL^{-1}	0.6802	15.32	59.00	6.15	471.51	42896.32
10 mg mL^{-1}	0.6832	15.17	52.72	5.46	719.56	36521.22
15 mg mL^{-1}	0.6869	14.54	51.14	5.11	856.01	18033.77

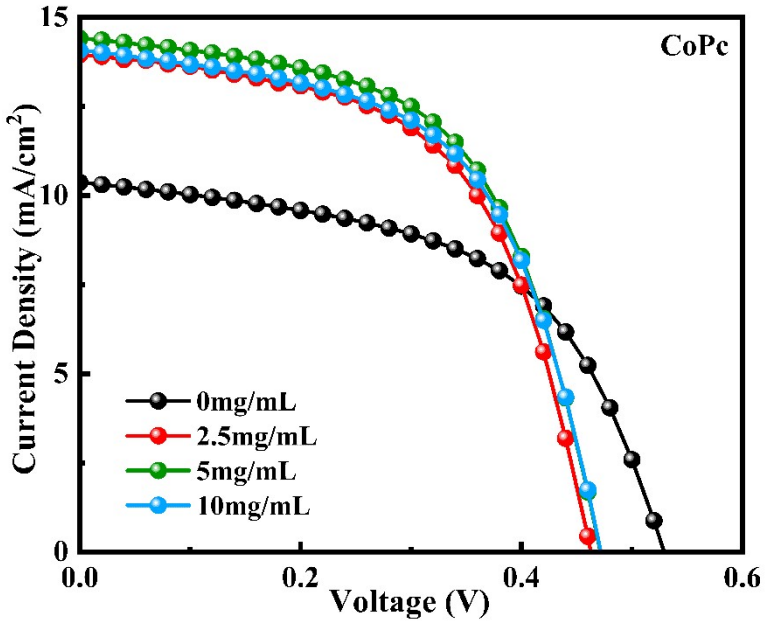

Fig S2 The efficiency of $Sb_2(Se,S)_3$ solar cell with different concentration of CoPc as hole transport layer

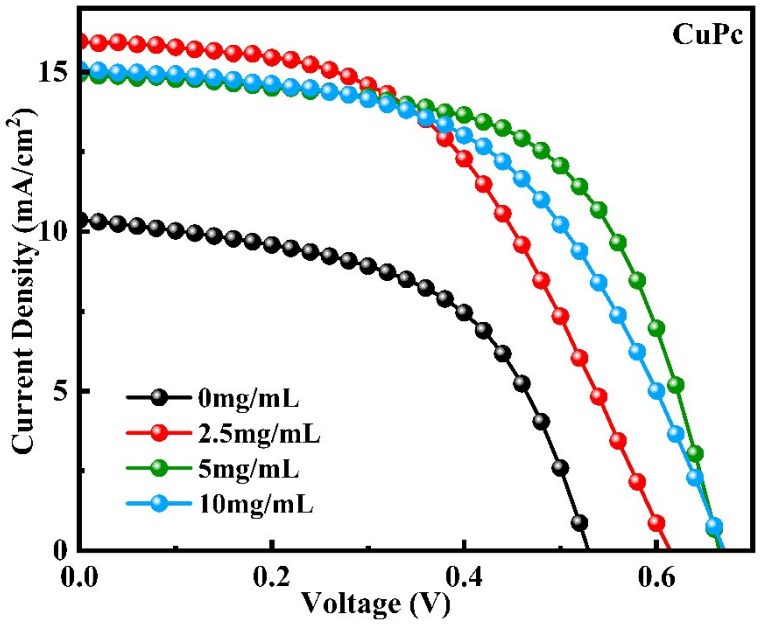

Fig S3 The efficiency of $Sb_2(Se,S)_3$ solar cell with different concentration of CuPc as hole transport layer

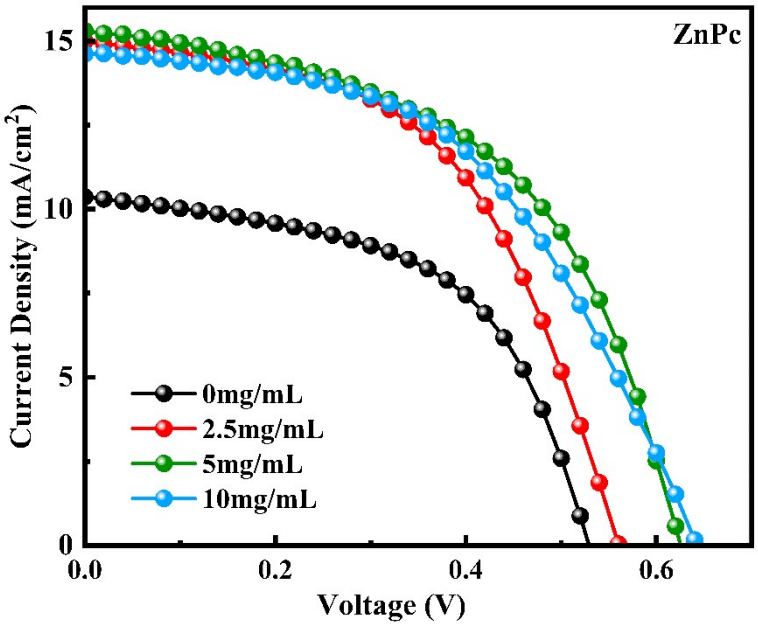

Fig S4 The efficiency of $Sb_2(Se,S)_3$ solar cell with different concentration of ZnPc as hole transport layer

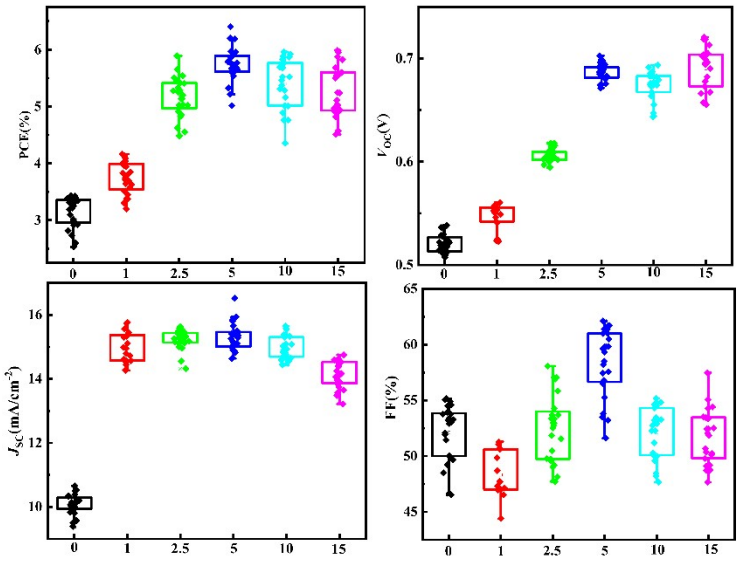

Fig S5 The statistical deviation of the device with various concentration of Pc solution

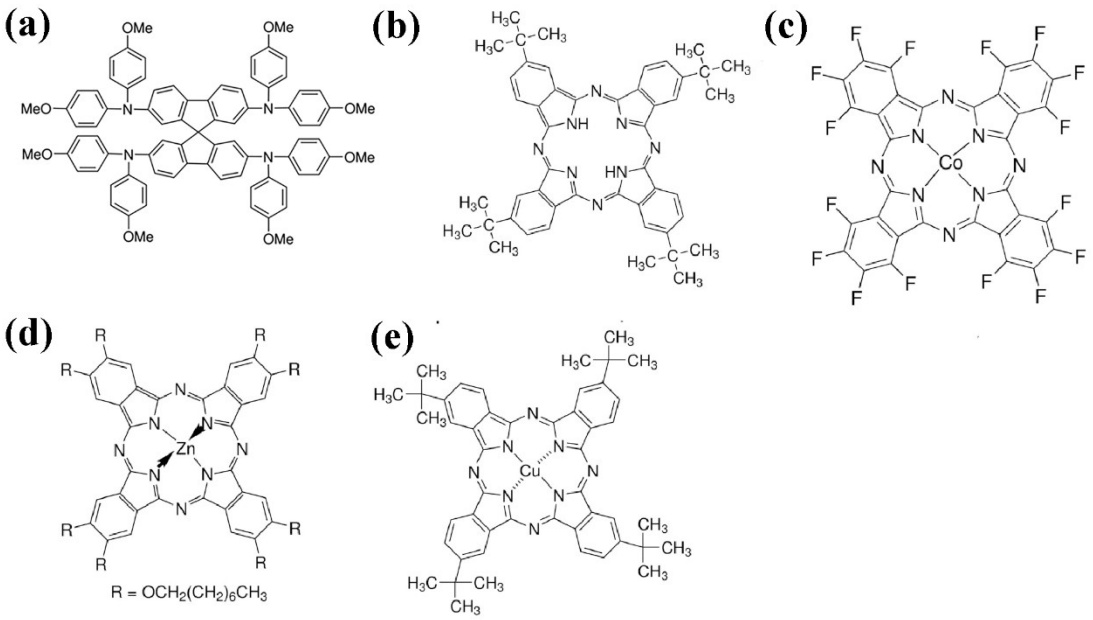

Fig S6 The chemical molecular structure diagram of (a) Spiro, (b) Pc, (c) CoPc, (d) ZnPc and (e) CuPc

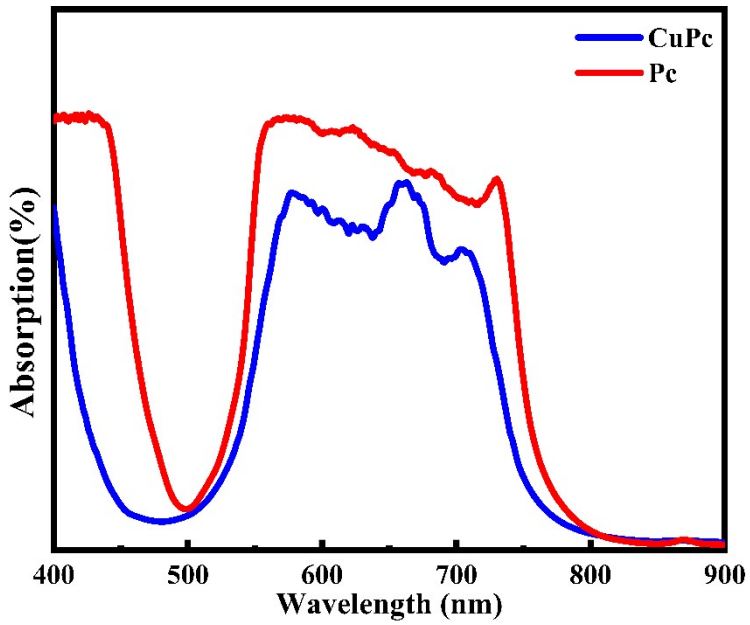

Fig S7 The UV-Vis absorption spectrum of

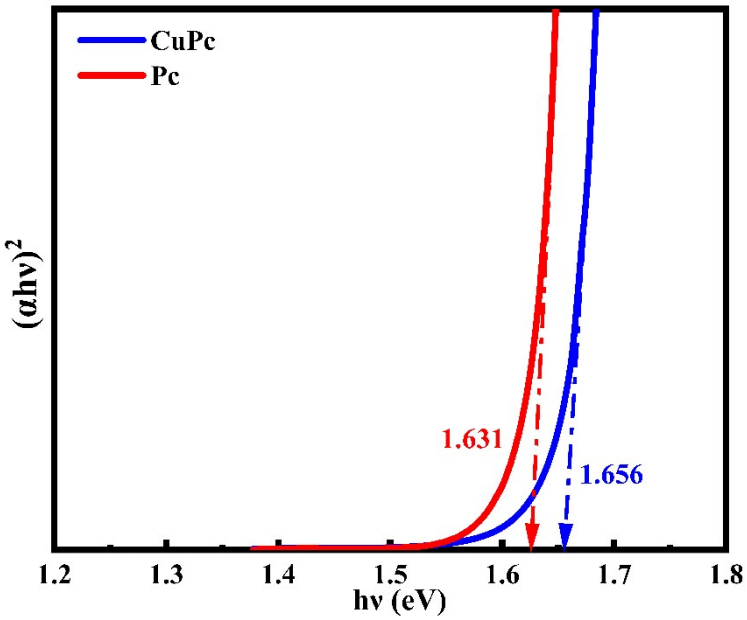

Fig S8 The band gap of CuPc and Pc hole transport layer

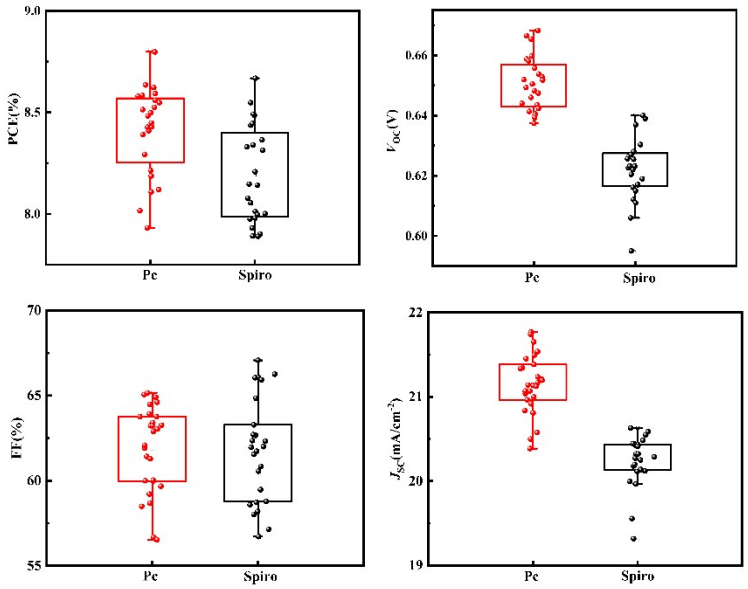

Fig S9 The statistical deviation of the device with Pc and Spiro as the hole transport layer

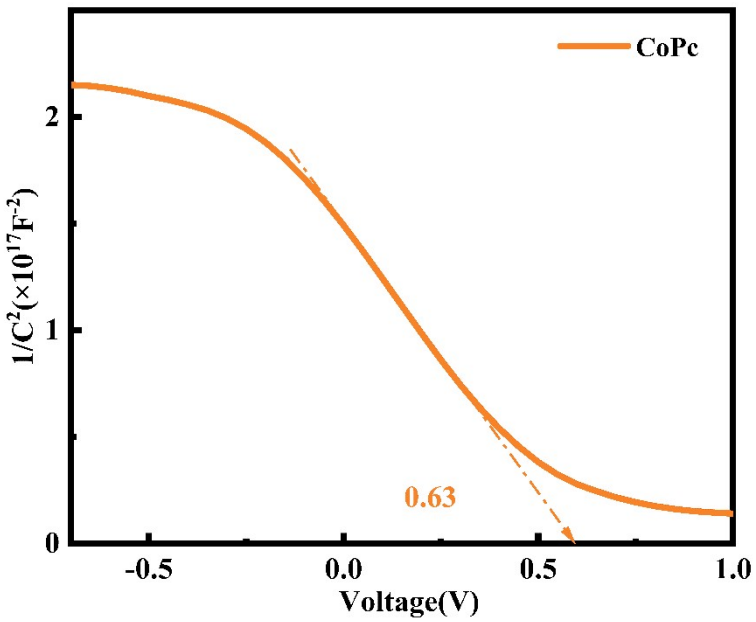

Fig S10 The *C–V* characteristics of $Sb_2(S,Se)_3$ solar cell with CoPc HTLs

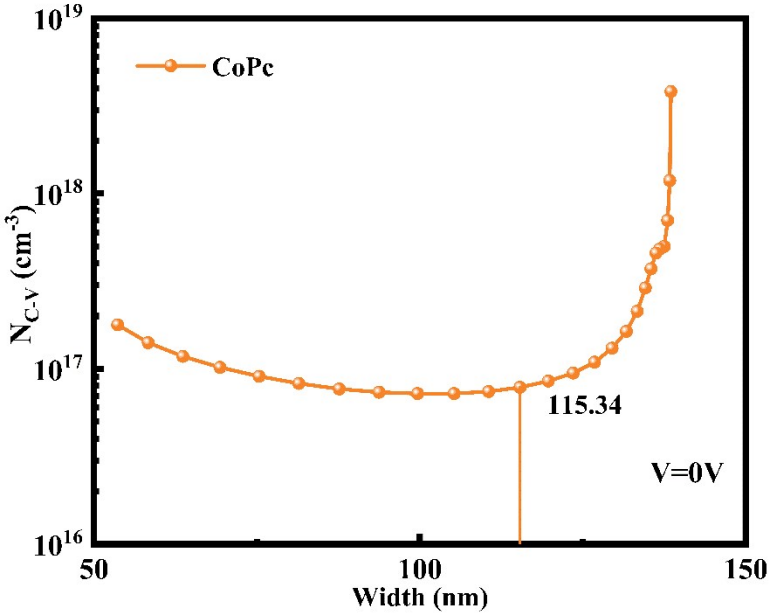

Fig S11 The N_{C-V} characteristics of $Sb_2(S,Se)_3$ solar cell with CoPc HTLs

Table S2 The ideal factor and J_0 of all the devices calculated from the Dark IV result

Sample	***A***	J_0
CoPc	3.12	1.98×10^{-3}
ZnPc	1.80	6.40×10^{-5}
CuPc	1.76	5.07×10^{-5}
Pc	1.54	8.61×10^{-6}
Spiro	1.67	2.00×10^{-5}

Table S3 The R_s and R_{rec} of all the devices calculated from the EIS result

Sample	R_s **(ohm)**	R_{rec} **(ohm)**
CoPc	3.59	57.95
ZnPc	2.36	263.2
CuPc	1.37	275.6
Pc	1.21	302.8
Spiro	1.28	285.4

Table S4 the Wd and NC-V result of all the devices calculated from the C-V result

Sample	**Wd**	$N_{C\text{-}V}$
ZnPc	300	2.54E16
CuPc	307	3.56E16
Pc	328	5.08E16
Spiro	310	3.82E16