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SUPPORTING INFORMATION

Solution-processable copper(II) phthalocyanine derivative as a dopant-free hole-transporting material for efficient and stable carbon counter electrode-based perovskite solar cells

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Contents

1. Synthesis of CuPc-TIPS

According to a previously reported method,[1] a mixture of CuI (0.121 g 0.64 mmol), (triisopropylsilyl)acetylene (3.91 mL, 17.4 mmol), 4-bromo-1,2-benzenedicarbonitrile (3.33 g, 16.1 mmol) and $PdCl_2(PPh_3)_2$ (0.446 g, 0.64 mmol) in diisopropylamine (80 mL) were stirred overnight at 90 °C. Then, CH_2Cl_2 and a saturated solution of NaCl were added to the mixture and the organic layer was separated, washed with water, dried over $MgSO_4$, and concentrated in vacuum to give a crude. The crude was purified by column chromatography on silica gel to afford 4-(triisopropylsilylethynyl)- phthalonitrile (4.21 g, 85%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.86 (s, 1H) , 7.77 (s, 2H), 1.15 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 156.50, 136.07, 133.41, 129.27, 116.23, 115.14, 114.71, 1141.44, 102.77, 100.50, 18.58, 11.23. EI: calcd for $[C_{19}H_{24}N_2Si]$ ($[M]^+$) m/z 308.1709, found, 308.1699.

CuPc-TIPS was obtained according to the method reported previously.[2] The mixture of compounds 4-(triisopropylsilylethynyl)- phthalonitrile (1322.4 mg, 4.29 mmol), urea (512.0 mg, 10.66 mmol), ammonium molybdate (20.3 mg, 0.10 mmol), and copper(I) chloride (102.4 mg, 1.03 mmol) in nitrobenzene (20 mL) was heated at 160 °C for 12 h. Solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using $CHCl_3/CH_3OH$ (100/1, v/v) as eluent to afford a blue-green powder (1.00 g, 72.0 % yield). Elemental analysis calcd (%) for $C_{76}H_{96}CuN_8Si_4$: C, 70.35; H, 7.46; and N, 8.64. Found: C, 71.06; H, 6.83; and N, 8.57. LD-TOF： calcd for $[C_{76}H_{96}CuN_8Si_4]$($[M]^+$) m/z 1295.6131, found, 1295.6113.

2. Device fabrication and characterization

The solar cell devices were fabricated and characterized by our previous work.[2] The mixed-ion perovskite precursor solution of $(FAPbI_3)_{1-x}(MAPbBr_3)_x$ (x = 0.15) was prepared by dissolving the FAI (1 M), MABr (0.2 M), PbI_2 (1.1 M) and $PbBr_2$ (0.2 M) in a mixed solvent of dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) (4 : 1, v/v). Fluorine–doped tin oxide (FTO) conducting glass (Pilkington TEC 15) was firstly patterned by etching with Zn powder and 2 M HCl. The etched substrate was sequentially cleaned by detergent, de-ionized water and ethanol. Remaining organic residues were removed by using oxygen plasma for 30 min. A compact TiO_2 layer (~30–40 nm) was deposited on the cleaned FTO glasses by spray pyrolysis of titanium diisopropoxide bis(acetylacetonate) diluted in anhydrous ethanol at a volumetric ratio of 1:10 and then heated at 500 °C for 30min. A mesoporous TiO_2 layer was deposited by spin-coating TiO_2 paste (18NR–T, Dyesol, Australia) diluted in anhydrous ethanol at ratio of 1:6 by weight at 5000 rpm for 30s. The substrates were then sintered in air at 500 °C for 30 min. The mixed-ion perovskite films were deposited onto the mesoporous TiO_2/compact TiO_2/FTO substrates from the precursor solution by a two-step spin-coating procedure, at 1000 rpm for 30s and then 5000 rpm for 20s. During the second step, 100 µL of chlorobenzene was dropped onto the substrates 10s prior to the end of the program. Afterwards, the HTM layer was coated by spin-coating HTM solution on top of the perovskite layer with a spin speed of 3000 rpm for 30s. The dopant-free HTM solution was prepared by dissolving 30 mg HTM in 1 mL chlorobenzene. For comparison purpose, doped spiro-OMeTAD HTM solution consisted of 60 mM spiro-OMeTAD, 30 mM Li-TFSI, 200 mM TBP. Finally, a commercially available carbon paste (CC, Shenzhen DongDaLai Chemical Co., Ltd.) was doctor-bladed on top of the HTM layer and then dried the whole device at 100 °C for 30 min. The size and thickness of the carbon electrode and its conductivity are 1.4 cm × 0.6 cm, 25 µm, 7.58 S/cm, respectively.

The photocurrent–voltage (*J*–*V*) characteristics of the solar cells were accorded by using a Keithley 2400 Source-measure unit under illumination of a simulated sunlight (AM 1.5G, 100 mW cm^{-2}) provided by an Oriel Sol3A solar simulator (Newport USA, Model: 94023A) with an AM 1.5 filter in ambient air. Light intensity was calibrated by using a Newport calibrated standard Si reference cell (SER. No: 506/0358). A black mask with a circular aperture (0.09 cm^2) smaller than the active area of the square solar cell (0.20 cm^2) was applied on top of the cell. The *J*–*V* curves were achieved from forward bias to short-circuit at a scan rate of 10 mV S^{-1}. The measurement of the incident photon–to–current conversion efficiency (IPCE) spectra were obtained by a Hypermono−light (SM−25, Jasco Co. Ltd., Japan). A standard silicon solar cell was used as reference before the measurement.

3. Measurements

^1H NMR and ^{13}C NMR spectra were measured using a Varian INOVA 500NMR apparatus. Chemical shifts were calibrated against TMS as an internal standard. The differential pulsed voltammetry (DPV) measurements were carried out with a CHI 630 Electrochemistry Work station. Redox potentials of CuPc-TIPS were carried out in dichloromethane solution with 0.1 M $TBAPF_6$ as a supporting electrolyte. A glassy carbon electrode with a surface area of 0.785 cm^2 was used as working electrode. The counter electrode was a platinum wire. The reference electrode was an $Ag/AgNO_3$ electrode. The redox potential was calibrated against Fc/Fc^+ as an internal standard. The UV-visible absorption spectra were recorded by an Agilent 8453 spectrophotometer. SEM was obtained with FEI (Field Emission Instruments: Nova Nano SEM 450), USA.

4. Supplementary Figures

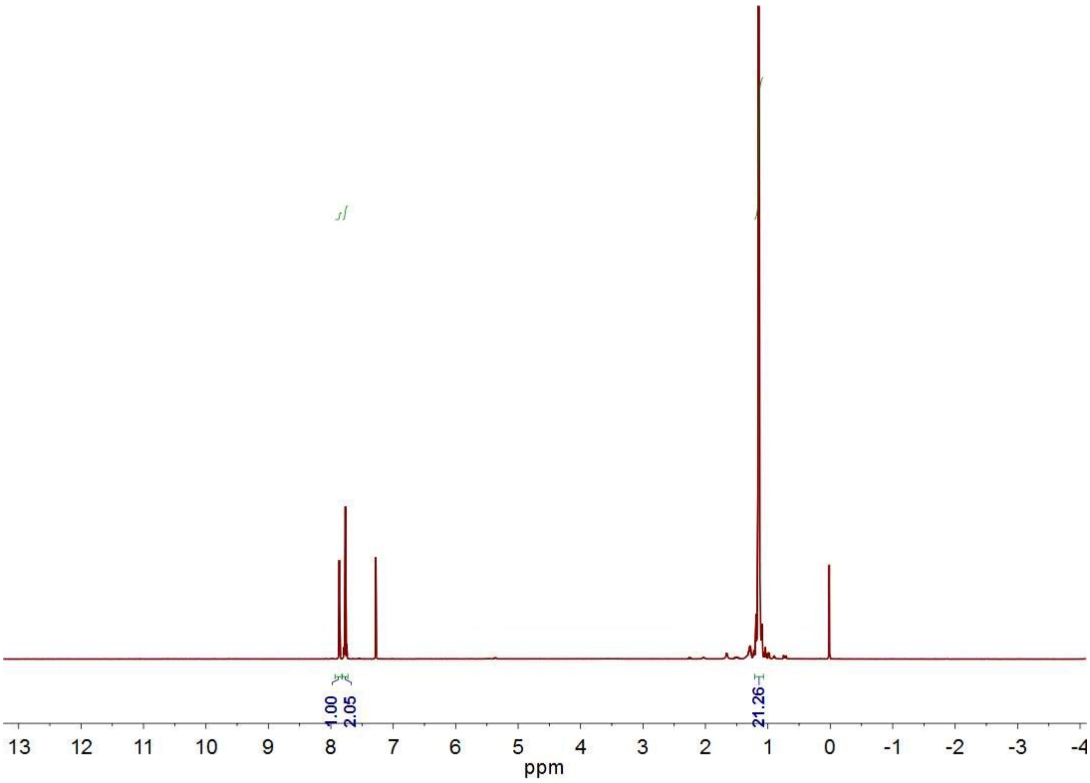

Fig. S1 ^1H NMR spectrum of compound 1

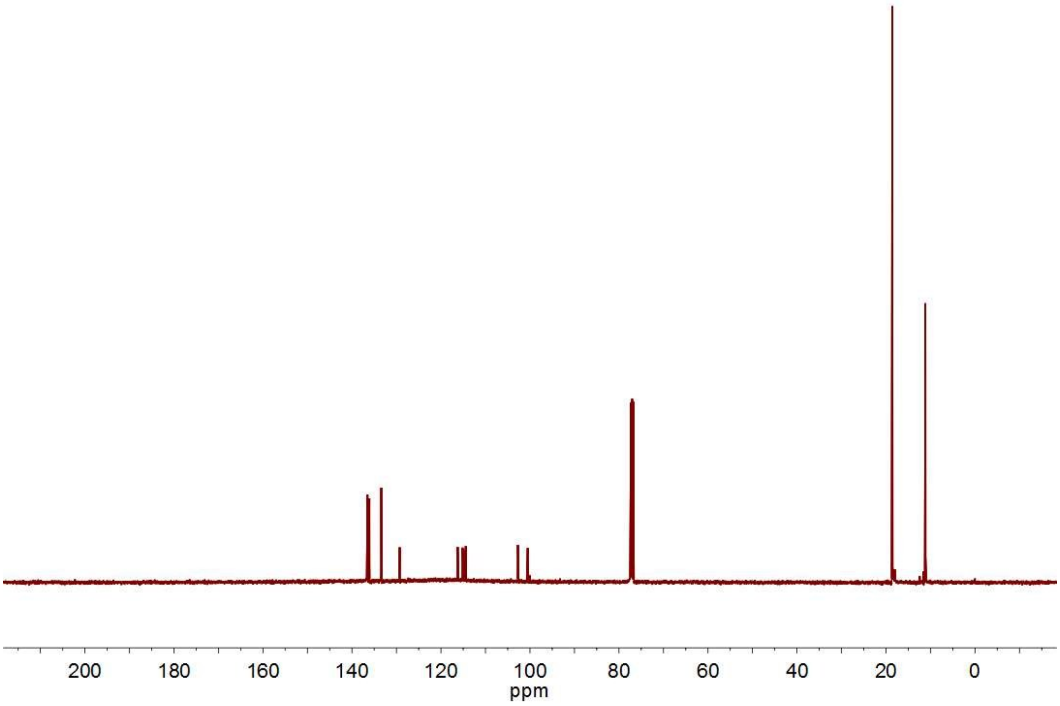

Fig. S2 ^{13}C NMR spectrum of compound 1

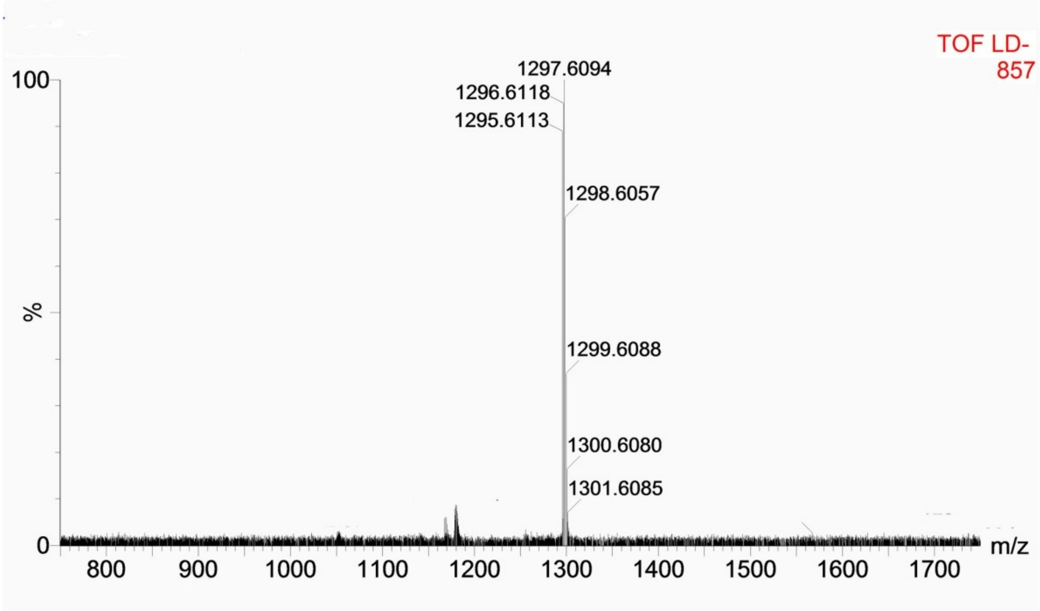

Fig. S3 LD-TOF spectrum of **CuPc-TIPS**.

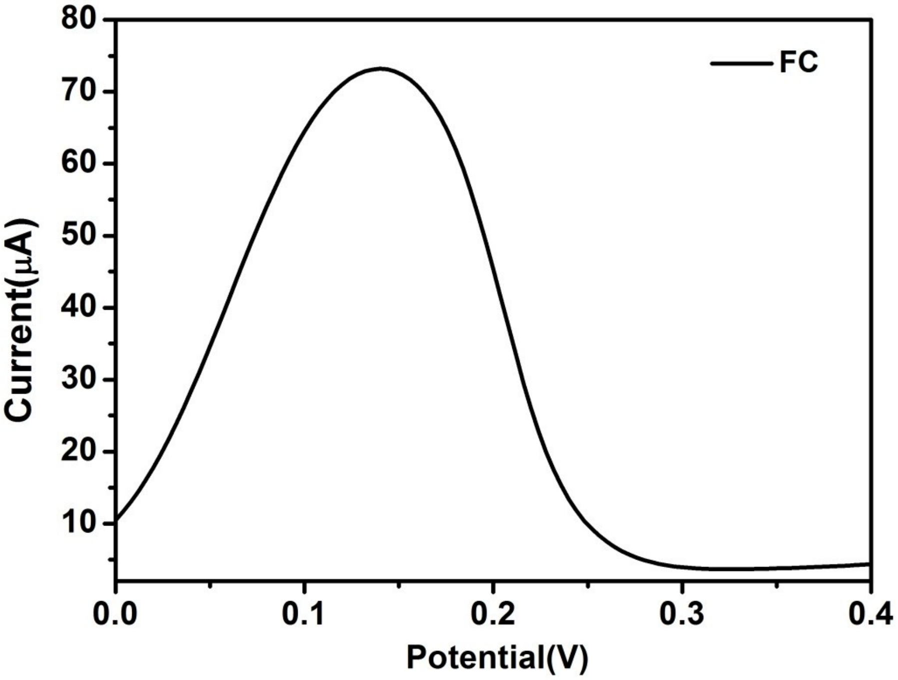

Fig. S4 Differential pulsed voltammetry (DPV) of Ferrocene(Fc) in a dichloromethane solution, potential vs. Ag/$AgNO_3$.

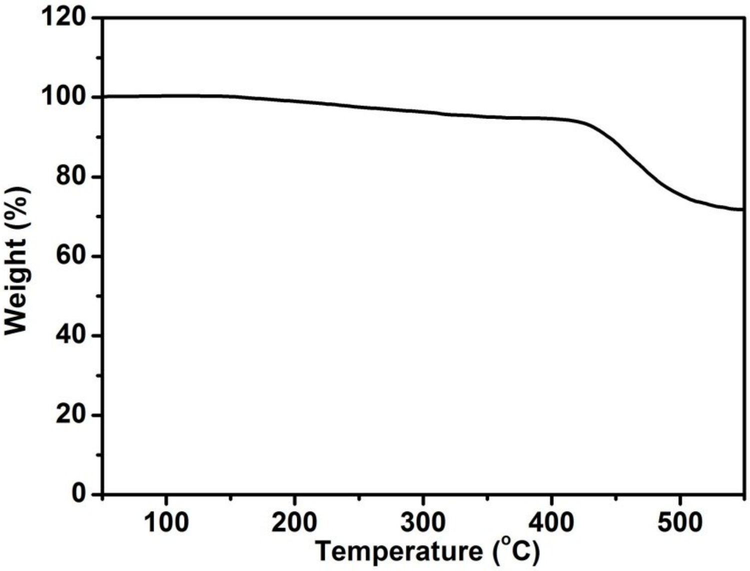

Fig. S5 Thermal gravimetric analysis of **CuPc-TIPS**.

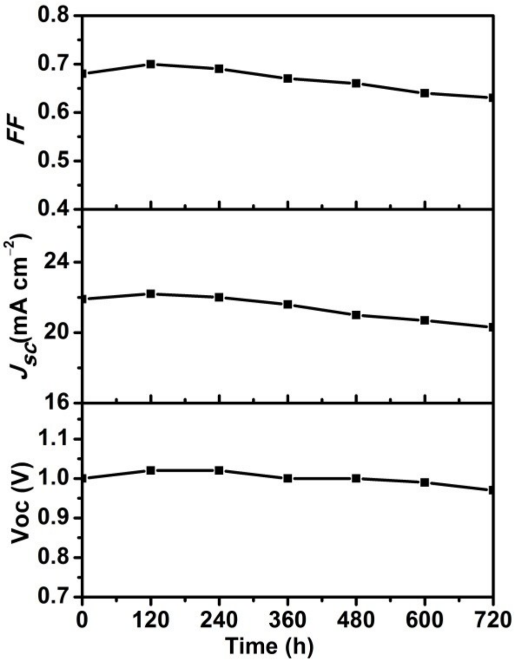

Fig. S6 Changes of photovoltaic parameters of V_{oc}, J_{sc}, and FF based on PSCs with doped spiro-OMeTAD.

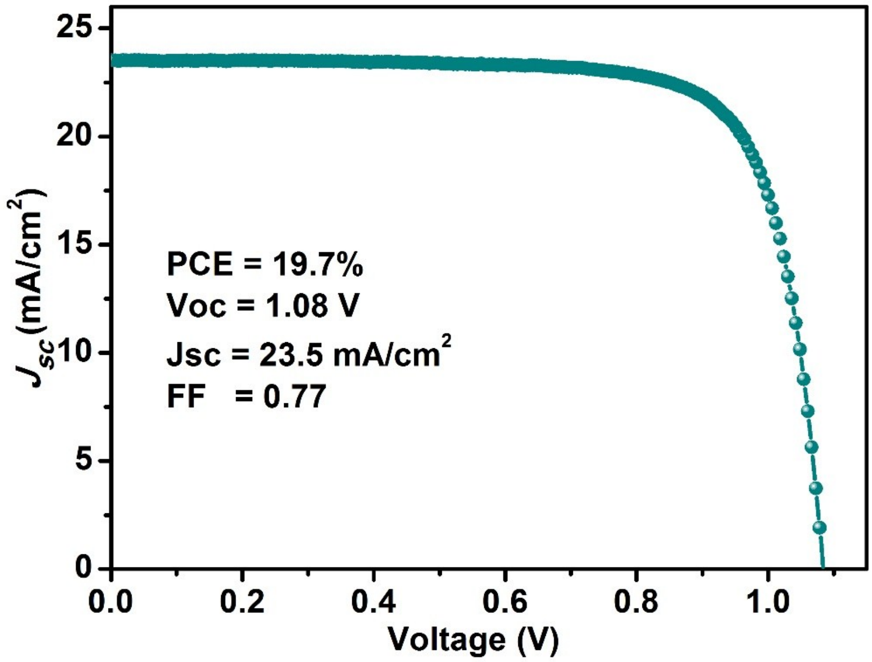

Fig. S7 *J–V* curve of the best PSCs based on spiro-OMeTAD as a HTM and gold as a cathode.

References:

1. Y. Nakano, K. Ishizuka, K. Muraoka, H. Ohtani, Y. Takayama and F. Sato, *Org. lett.*, 2004, **6**, 2373.
2. X. Jiang, Z. Yu, J. Lai, Y. Zhang, M. Hu, N. Lei, D. Wang, X. Yang and L. Sun, *ChemSusChem*, 2017, **10**, 1838-.