Supporting Information

Study of Arylamine-Substituted Porphyrins as Hole-Transporting Materials in High-Performance Perovskite Solar Cells

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Experimental Section

Characterization

^{1}H NMR spectra were recorded using a Bruker Ultrashield 400 Plus NMR spectrometer. High-resolution matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained with a Bruker Autoflex MALDI-TOF mass spectrometer. UV-vis spectra of dilute solutions (1×10^{-5} M) of samples in $CHCl_3$ were recorded at room temperature (ca. 25℃) using a Shimadzu UV-3600 spectrophotometer. SEM images were obtained from JEOL JSM-7401F operating at 2 kV. The excitation of the sample was carried out with a picosecond diode laser (Edinburgh Instrument, EPL470) at 470 nm. The optimum geometries of **CuP** and **ZnP** and their electron-state-density distributions of HOMOs and LUMOs were investigated by performing density functional theory (DFT) calculations using the cam-B3LYP3 and the 6-31G** basis set for all atoms, without any symmetry constraints. All reported calculations were carried out by means of Gaussian 09.[1, 2]

Electrochemical Measurements

Electrochemical experiments were performed with a CH Instruments electrochemical workstation (model 660A) using a conventional three-electrode electrochemical cell. A glassy carbon electrode (diameter 3mm) was used as the working electrode, a platinum wire as the counter electrode, an $Ag/AgNO_3$ electrode as the reference electrode and 0.1 M of tetrabutylammoniunhexafluorophosphate (n-Bu_4NPF_6) in dichloromethane solution as supporting electrolyte. The cyclovoltammetric scan rate was 50 mV/s. Each measurement was calibrated with Fc. $E_{1/2}^{Fc}$ = 0.20 V. E_{HOMO} = $-5.1-(E_{1/2}-E_{1/2}^{Fc})$.

Conductivity Measurement

The electrical conductivities of the HTMs films were determined by using two-probe electrical conductivity measurements, which were performed by following published procedure.[3] Conductivity devices structure was shown in **Fig. S1**, and the electrical conductivity (σ) was calculated by using the following equation (1):

$$\sigma = \frac{W}{R\,L\,D} \quad (1)$$

where L is the channel length 10 mm, W is the channel width 2 mm, D is the film thickness of the TiO_2 and HTM, and R is the film resistance calculated from the gradients of the curves.

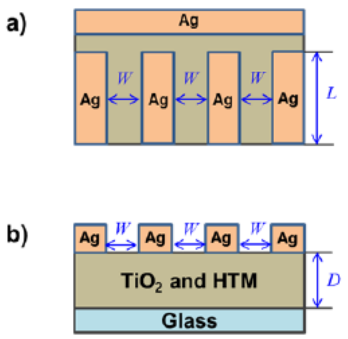

Figure S1. Schematic illustrations of the conductivity device: (a) top-sectional view; (b) cross-sectional view.

The conductivity devices were fabricated as following. Glass substrates without conductive layer were carefully cleaned in ultrasonic baths of detergents, deionized water, acetone and ethanol successively. A thin layer of nanoporous TiO_2 was coated on the glass substrates by spin-coating with a diluted TiO_2 paste (Dyesol DSL 18NR-T) with terpineol (1:3, mass ratio). The thickness of the film is ca. 500 nm, as measured with a DekTakprofilometer. After sintering the TiO_2 film on a hotplate at 500 °C for 30 min, the film was cooled to room temperature. A solution of HTMs in chlorobenzene was subsequently deposited by spin-coating. Here the concentration of **CuP** or **ZnP** is 20 mg mL^{-1} in chlorobenzene. The doped Spiro-OMeTAD/chlorobenzene (80 mg/mL) solution was prepared with addition of 20 μL Li-TFSI (520 mg Li-TFSI in 1 mL acetonitrile), and 30 μL tert-butylpyridine (tBP). Subsequently, a 200 nm thick Ag back contact was deposited onto the organic semiconductor by thermal evaporation in a vacuum chamber with a base pressure of about 10^{-6} bar, to complete the device fabrication. *J-V* characteristics were recorded on a Keithley 2400 semiconductor characterization system.

Mobility Measurements

Due to the low mobility of charge carriers in organic semiconductors, the injected carrier forms a space charge. This space charge creates a field that opposes the applied bias and thus decreases the voltage drop across junction; as a result, space charge limited currents (SCLCs) have been proposed as the dominant conduction mechanism in organic semiconductors by researchers. Mobility devices structure was shown in **Fig. S-2**, andohmic conduction can be described by equations (2):

$$J = \frac{9}{8}\mu\varepsilon_0\varepsilon_\gamma \frac{V^2}{d^3} (2)$$

where J is the current density, μ is the hole mobility, ε_o is the vacuum permittivity (8.85×10^{-12} F/m), ε_r is the dielectric constant of the material (normally taken to approach 3 for OSs), V is the applied bias, and d is the film thickness.

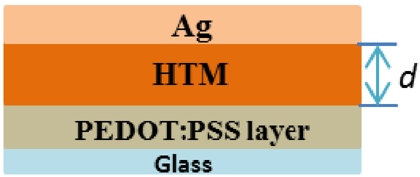

Figure S2. Schematic illustration of the mobility device

Fluorine-doped tin-oxide (FTO) coated glass substrates (Pilkington TEC15) were patterned by etching with zinc powder and 2 M hydrochloric acid. The substrates were carefully cleaned in ultrasonic baths of detergents, deionized water, acetone and ethanol successively. The remaining organic residues were removed with 10 min by airbrush. A 40 nm thick PEDOT: PSS layer was spin-coated onto the substrates, which were then annealed at 120 °C for 30 min in air. The substrates were then transferred into a glove box for further fabrication steps. The HTMs were dissolved in anhydrous chlorobenzene. Here the concentration of **CuP** or **ZnP** is 20 mg mL^{-1} in chlorobenzene. The doped Spiro-OMeTAD/chlorobenzene (80 mg/mL) solution was prepared with addition of 20 µL Li-TFSI (520 mg Li-TFSI in 1 mL acetonitrile), and 30 µL tert-butylpyridine (tBP). This HTMs solution was spin-coated at 3000 rpm to yield films. The thicknesses of the films are measured by using a Dektak 6M profilometer. 200 nm of silver was then evaporated onto the active layer under high vacuum(less than 10^{-6} mbar). *J-V* characteristics of the devices have been measured with a Keithley2400 Source-Measure unit, interfaced with a computer. Device characterization was carried out in air.

Fabrication of perovskite solar cells

Fluorine-doped tin-oxide (FTO) coated glass substrates (Pilkington TEC15) were etched with zinc powder and 2 M hydrochloric acid. The substrates were carefully cleaned in ultrasonic baths of detergents, deionized water, acetone and ethanol subsequently. A thin compact TiO_2 blocking layer was deposited onto the FTO substrate by spray pyrolysis on a hotplate at 450 °C. A mesoporous TiO_2 film was deposited on the compact TiO_2 blocking layer by spin-coating at 6000 rpm for 45 s, using a commercial 20 nm TiO_2 paste (Dyesol 18NRT, Dyesol) diluted in 2-proponal (1:3, weight ratio), followed by annealing at 525 °C for 30 min, then cooling down to room temperature. PbI_2 in N,N-dimethylformamide solution (510 mg mL^{-1}) was stirred at 70 °C overnight. The PbI_2 solution was spin-coated on the mesoporous TiO_2 at 6000 rpm for 15 s and then dried at 100 °C for 15 min. After cooling down to the room temperature, the PbI_2 coated film was then dipped in the CH_3NH_3I solution (8.5 mg mL^{-1} in 2-proponal) for 20 s. After the formation of the $CH_3NH_3PbI_3$, the film was rinsed at 70 °C for further manipulation. After cooling down to the room temperature, the doped HTMs solution was deposited by spin-coating at 3000 rpm for 30 s. Here the concentration of **CuP** or **ZnP** is 20 mg mL^{-1} in chlorobenzene. The doped Spiro-OMeTAD/chlorobenzene (80 mg/mL) solution was prepared with addition of 20μL Li-TFSI (520 mg Li-TFSI in 1 mL acetonitrile), and 30 μL tert-butylpyridine (tBP). Finally, 200 nm of gold was thermally evaporated on top of the device to form the counter-electrode. The prepared PSCs samples were masked during the measurement with an aperture area of 0.126 cm^2 (diameter 4 mm) exposed under illumination.

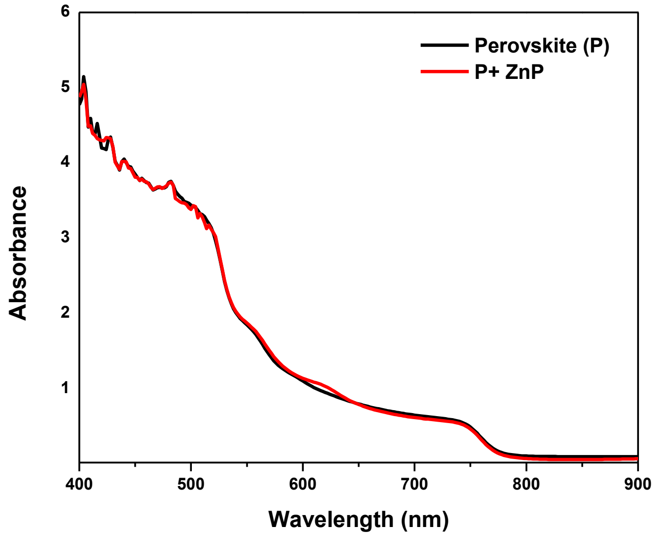

Figure S3. Absorption spectra of perovskite films with and without **ZnP**.

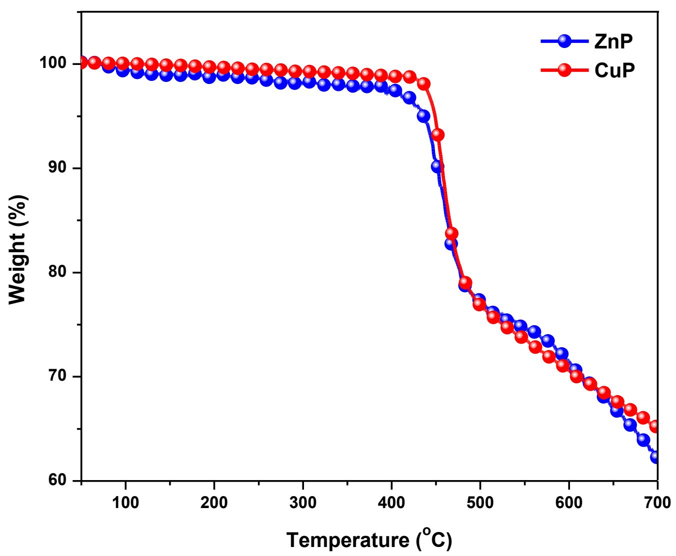

Figure S4. Thermogravimetric analysis of these two new HTMs

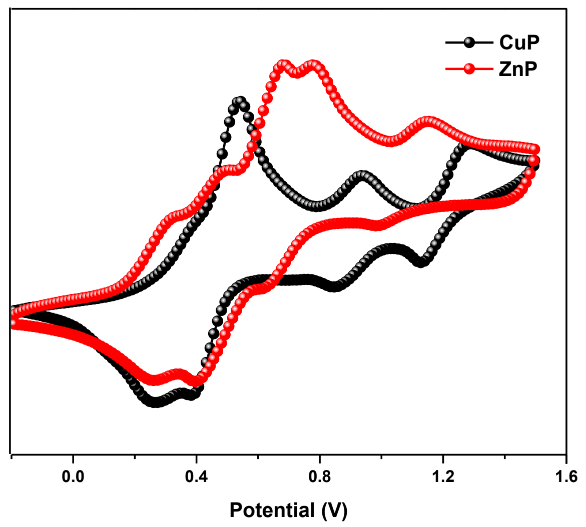

Figure S5. Cyclic voltammograms of **CuP** and **ZnP**.

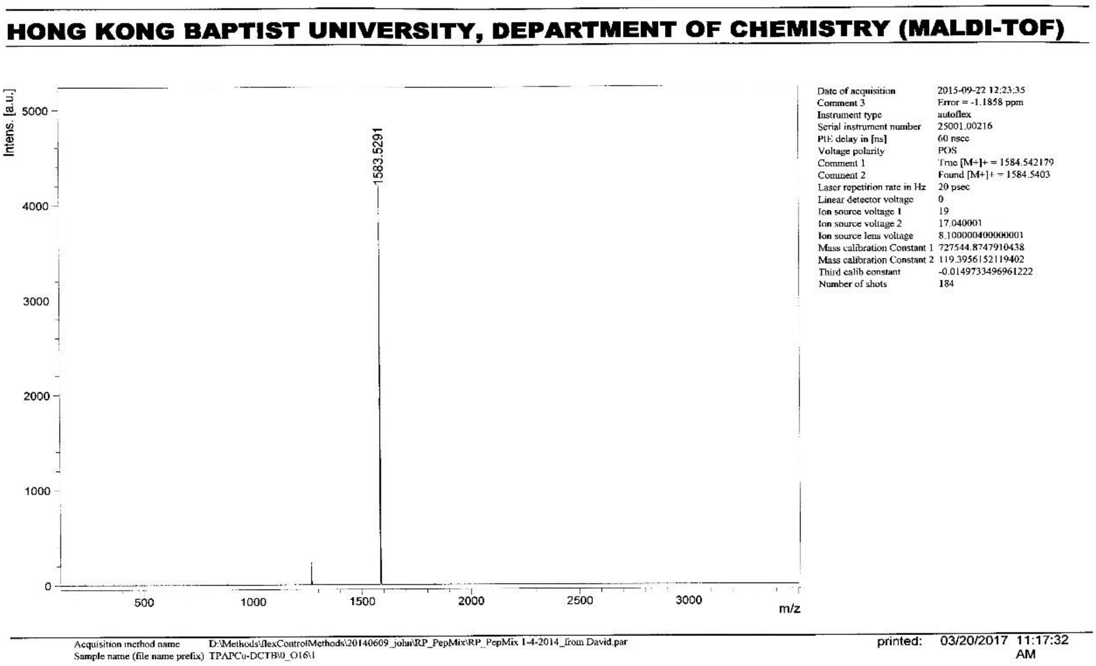

Figure S6. The MALDI-TOF mass spectrum of **CuP**.

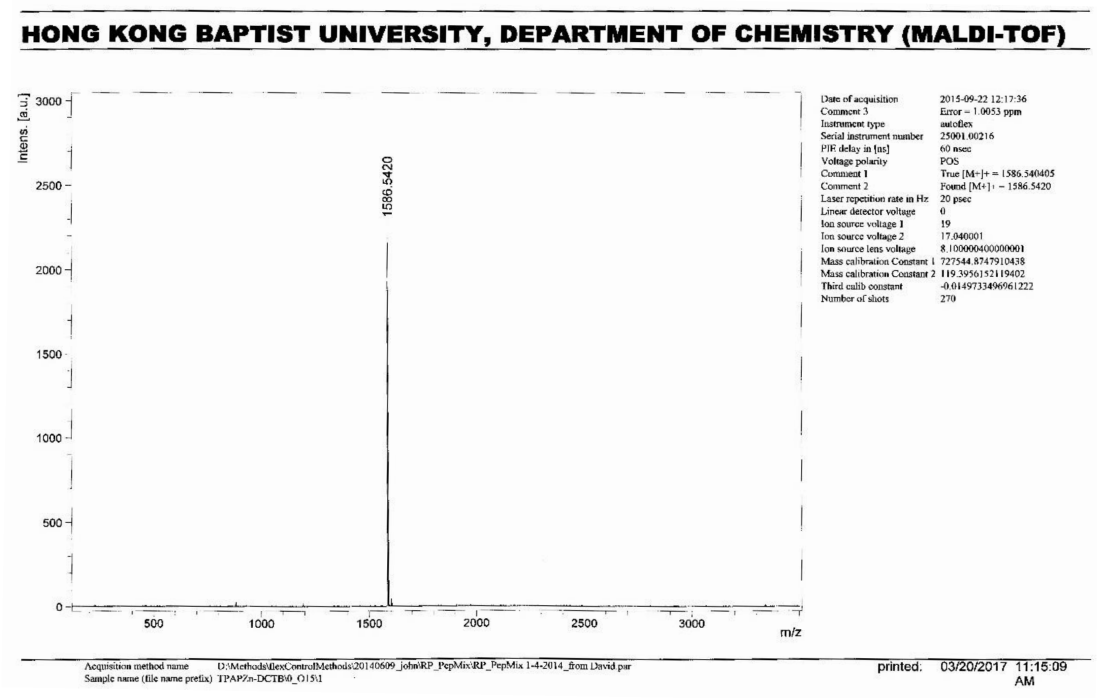

Figure S7. The MALDI-TOF mass spectrum of **ZnP**.

References

[1] Xu, B.; Sheibani, E.; Liu, P.; Zhang, J.; Tian, H.; Vlachopoulos, N.; Boschloo, G.; Kloo, L.; Hagfeldt, A.; Sun, L. Carbazole-Based Hole-Transport Materials for Efficient Solid-State Dye-Sensitized Solar Cells and Perovskite Solar Cells. *Adv. Mater.* **2014,** *26*, 6629-6634.

[2] Xu, B.; Tian, H.; Bi, D.; Gabrielsson, E.; Johansson, E. M.; Boschloo, G.; Hagfeldt, A.; Sun, L. Efficient Solid State Dye-Sensitized Solar Cells Based on an Oligomer Hole Transport Material and an Organic Dye. *J. Mater. Chem. A* **2013,** *1*, 14467-14470.

[3] Snaith, H. J.; Grätzel, M. Enhanced Charge Mobility in a Molecular Hole Transporter via Addition of Redox Inactive Ionic Dopant: Implication to Dye-Sensitized Solar Cells. *Appl. Phys. Lett.* **2006,** *89*, 262114-262116.