### **Supporting information**

# Doping porphyrin-based bulk heterojunction solar cells with LITFSI and TFSA

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#### 1. Materials

Tetrahydrofuran (THF) and toluene were distilled from sodium-benzophenone under nitrogen prior to being used. Triethylamine (NEt<sub>3</sub>), dimethoxyethane,  $CH_2Cl_2$  and  $CHCl_3$  were distilled from  $CaH_2$  prior to use. All reagents, unless otherwise noted, were obtained from Aldrich, Acros, and TCI Chemical Co. and used without further purification. All manipulations involving air-sensitive reagents were performed under an atmosphere of argon or N<sub>2</sub>. 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (1) and 5,15-diethynyl-10,20-bis(5-(2-butyloctyl)benzo[b]thiophen-2-yl)porphyrin zinc (3) were synthesized according to reported procedures. <sup>[1,2]</sup> And the synthesis route of TDPPEZnP is shown in Scheme S1.



Scheme S1. The synthesis route of TDPPEZnP.

#### 2. Instruments and methods

The chemical structures of the as-prepared compounds were identified by <sup>1</sup>H-NMR spectra measured on a Bruker AVANCE Digital 600MHz spectrometer in deuterated chloroform/benzene. Matrix assisted laser desorption/ionization mass spectrometry (MALDI-TOF MS) was acquired on a Bruker Daltonics BIFLEX III MALDI-TOF Analyzer using MALDI mode. Elemental analysis was measured on an Elementar vario EL cube. UV-Vis absorption spectra was obtained using a Shimadzu UV-3600 spectrophotometer. Photoluminescence measurements were carried out in neat and blend films with a Fluorolog Max-4 spectrofluorometer. Cyclic voltammetry (CV) data was collected on a CHI660C electrochemical workstation at scan rate of 50 mV s<sup>-1</sup> in the nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) in acetonitrile (CH<sub>3</sub>CN). A glassycarbon electrode coated with a thin TDPPEZnP film, Pt wire and an Ag/AgCl (0.1 M) electrode were used as the working electrode, the counter electrode and the reference electrode, respectively. The atomic force microscopy (AFM) measurements were conducted on NanoScope NS3A system (Digital Instrument). The mobilities of the blend films of **TDPPEZnP** with  $PC_{61}BM$  were determined by fitting the dark current to the model of the space charge limited current (SCLC).



Figure S1. <sup>1</sup>H NMR spectrum of 2 in CDCl<sub>3</sub> at room temperature.



Figure S2. <sup>1</sup>H NMR spectrum of TDPPEZnP in CDCl<sub>3</sub> at room temperature.



**Figure S3.** <sup>13</sup>C NMR spectrum of **TDPPEZnP** in CDCl<sub>3</sub> (with 3% pyridine-d) at room temperature.



Figure S4. Cyclic voltammogram of TDPPEZnP film in CH3CN/0.1 M Bu<sub>4</sub>NPF<sub>6</sub>.

Material	HOMO <sup>a</sup> (eV)	LUMO <sup>a</sup> (eV)	Eg <sup>b</sup> (eV)	Eg <sup>opt</sup> (eV)	с
TDPPEZnP	-5.10	-3.41	1.69	1.34	

Table S1. Optical absorption properties and molecular energy levels of TDPPEZnP.

<sup>a</sup> Measured by cyclic voltammetry according to the empirical formulas  $E_{HOMO} = -e$  (Eox + 4.41 V) and  $E_{LUMO} = -e$  (Ere + 4.41 V). <sup>b</sup> Calculated from the equation  $E_g^{opt} = E_{LUMO} - E_{HOMO}$ . <sup>c</sup> Calculated from the onset of the absorption in film.



Figure S5. UV-Vis spectra of TDPPEZnP in CHCl<sub>3</sub> and pure films.



**Figure S6.** The UV-Vis-NIR absorption spectra of TDPPEZnP:PC<sub>61</sub>BM blend films without and with LITFSI and TFSA under optimal concentrations.



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**Figure S7.** AFM morphology height and phase images (a) and (d) of the control device, (b) and (e) of  $5 \times 10^{-4}$ % (w.t.) LITFSI doped device, (c) and (f) of  $5 \times 10^{-3}$ % (w.t.) TFSA doped device.



Figure S8. Dark current density versus voltage of the control and doped devices.



**Figure S9.** J–V characteristics and SCLC fit curves of the control and  $5 \times 10^{-4}$ % LITFSI and  $5 \times 10^{-3}$ % TFSA doped TDPPEZnP:PC<sub>61</sub>BM hole-only devices. The device structure is ITO/PEDOT:PSS/PCDTBT/MoO3/A1.



**Figure S10.** J–V characteristics and SCLC fit curve of control and  $5 \times 10^{-4}$ % LITFSI and  $5 \times 10^{-3}$ % TFSA doped TDPPEZnP:PC<sub>61</sub>BM hole-only devices. The devices structure is ITO/ZnO/active layer/PFN/Al.

The mobility was described by the following equation:

$$J = \frac{9\epsilon 0 \ \epsilon r \mu V \ 2}{8L^3}$$

Where J is the current density, L is the active-layer thickness,  $\varepsilon_0$  is the permittivity of free space,  $\varepsilon_r$  is the relative dielectric constant of the active layer,  $\mu$  is the zero-field mobility, and V is the voltage drop across the device.



**Figure S11.** Normalized TPC curve of (a)  $5 \times 10^{-4}$ % and  $5 \times 10^{-1}$ % LITFSI doped device and (b)  $5 \times 10^{-3}$ % and  $5 \times 10^{-1}$ % TFSA doped device.

## **References:**

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