

Supporting Information

A water/alcohol soluble conjugated porphyrin small molecule as a cathode interfacial material for organic photovoltaics

Lin Zhang, Chang Liu, Tianqi Lai, Huadong Huang, Xiaobin Peng*, Fei Huang, Yong Cao

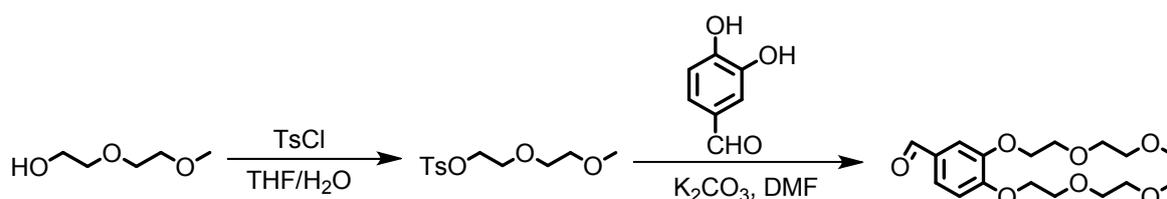
State Key Laboratory of Luminescent Materials and Devices, Institute of Polymer Optoelectronic Materials and Devices, South China University of Technology, 381 Wushan Road, Guangzhou 510640, China. *Email: chxbpeng@scut.edu.cn

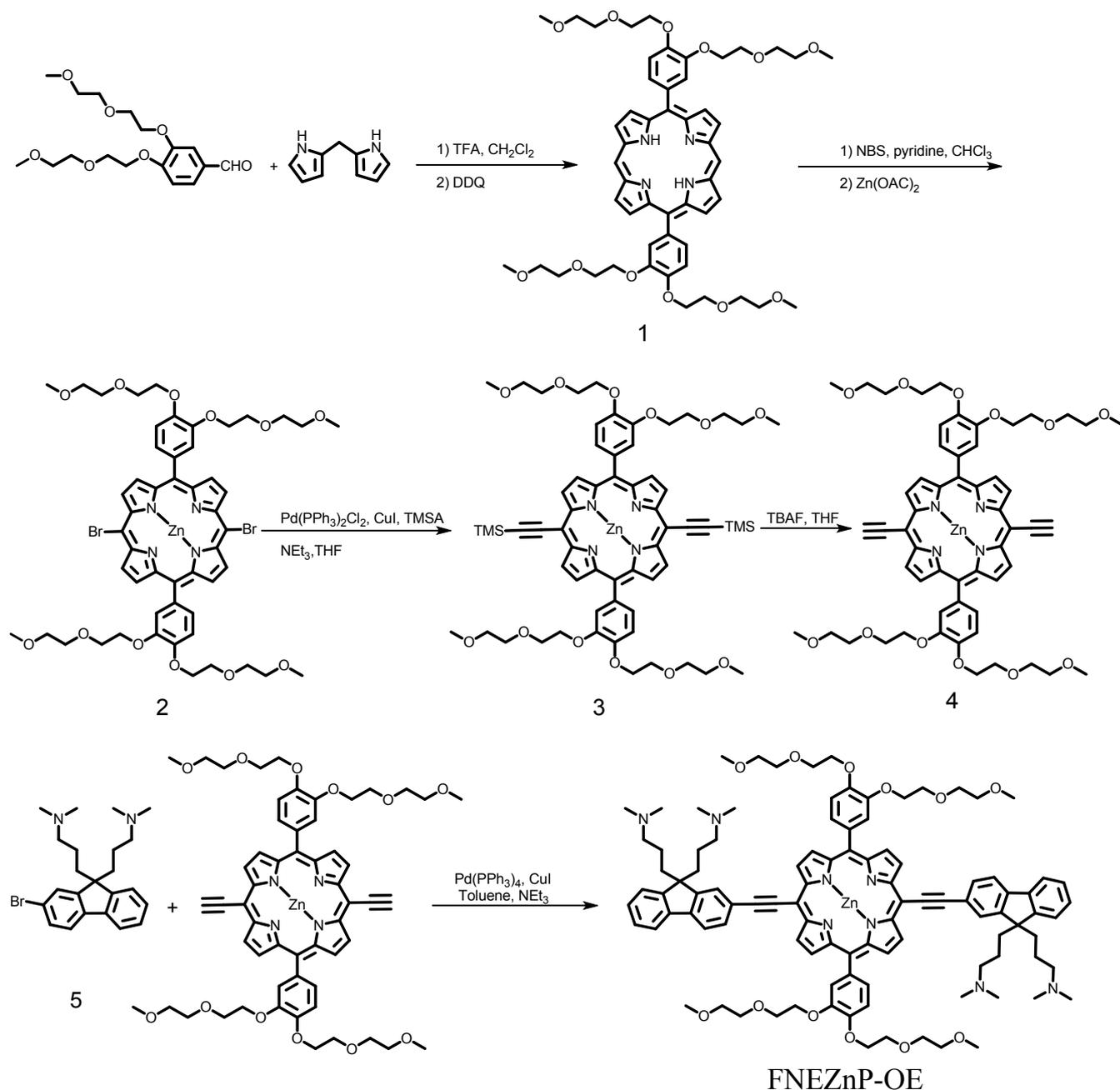
Experiment Details:

1. Chemicals

All chemicals and solvents were purchased from commercial sources (Aldrich, Acros, or Alfa Aesar) and used as received unless otherwise indicated. THF and triethylamine were distilled over sodium, and toluene was dried by distillation over CaH₂ prior to use. 2-Bromo-9,9'-bis(3''-(*N,N*-dimethylamino)propyl)-fluorene (5) was synthesized according to reported procedures.¹ Poly[[2,6'-4,8-di(5-ethylhexylthienyl)benzo[1,2-b;3,3-b] dithiophene] [3-fluoro-2[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7-Th), and poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b'] dithiophene-2,6-diyl] [3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7) were obtained from 1-material Inc..

Synthesis of FNEZnP-OE:





Scheme S1. Synthetic routines of FNEZnP-OE.

Synthesis of (1)

A solution of 3,4-bis(2-(2-methoxyethoxy)ethoxy)benzaldehyde (1.19 g, 3.48 mmol) and dipyrromethane (508 mg, 3.48 mmol) in CH₂Cl₂ (350 mL) was purged with nitrogen for 30 min, and then trifluoroacetic acid (TFA) (0.035 mL) was added. The mixture was stirred for 12 h at room temperature, and then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (1.18 g) was added. After the mixture was stirred at room temperature for an additional 45 min, the reaction was quenched by triethylamine (5

mL). Then the solvent was removed, and the residue was purified by flash column chromatography on silica gel using dichloromethane as the eluent. Recrystallization from CHCl_3 /methanol gave **1** as a purple solid. Yield: 570 mg (35%). ^1H NMR (500 MHz, CDCl_3): δ 10.30 (s, 2H), 9.38 (d, $J = 4.6$ Hz, 4H), 9.11 (d, $J = 4.6$ Hz, 4H), 7.87 (t, $J = 1.7$ Hz, 2H), 7.79 (d, $J = 8.1$ Hz, 2H), 7.34 (d, $J = 8.1$ Hz, 2H), 4.51 (dd, $J = 5.7, 4.5$ Hz, 4H), 4.40 – 4.34 (m, 4H), 4.11 (dd, $J = 5.7, 4.5$ Hz, 4H), 3.99 – 3.94 (m, 4H), 3.93 – 3.88 (m, 4H), 3.80 – 3.74 (m, 4H), 3.72 – 3.66 (m, 4H), 3.57 – 3.51 (m, 4H), 3.49 (s, 6H), 3.29 (s, 6H), -3.10 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3): δ 148.89, 147.36, 134.66, 131.58, 131.03, 128.40, 121.56, 118.73, 112.92, 105.26, 72.17, 72.00, 70.99, 70.84, 70.03, 69.91, 69.16, 59.20, 59.02. Mass (MALDI-TOF): Obs. 935.3[M]⁺; Calcd. for $\text{C}_{52}\text{H}_{62}\text{N}_4\text{O}_{12}$, 934.4.

Synthesis of (2)

Porphyrin **1** (500 mg, 0.54 mmol) and pyridine (2.5 mL) were dissolved in 250 mL chloroform and then cooled to 0°C. To the cold solution, N-bromosuccinimide (211mg, 1.19mmol) was added and the mixture was stirred at 0 °C for 30 min. Then the reaction was quenched by acetone, and the mixture was washed with water and dried over anhydrous Na_2SO_4 . After the solvent was removed, the residue was dissolved in chloroform (50 mL), then added a solution of $\text{Zn}(\text{OAc})_2$ (273 mg, 1.35 mmol) in methanol (10 mL). The reaction mixture was refluxed for 2 h and then washed with water and dried over anhydrous Na_2SO_4 . After the solvent was removed, the residue was purified by flash column chromatography on silica gel using methanol /dichloromethane as the eluent, Recrystallization from CHCl_3 /methanol gave **2** as a purple solid. Yield: 446 mg (72%). ^1H NMR (500 MHz, CDCl_3): δ 9.69(d, $J = 4.5$ Hz, 4H), 8.95 (d, $J = 4.5$ Hz, 4H), 7.68 (d, $J = 5.9$ Hz, 2H), 7.63 (t, $J = 7.3$ Hz, 2H), 7.12 (dd, $J = 11.4, 8.0$ Hz, 2H), 4.24 (d, $J = 6.0$ Hz, 4H), 4.10 (d, $J = 21.8$ Hz, 4H), 3.76 (t, $J = 5.0$ Hz, 4H), 3.70 – 3.53 (m, 8H), 3.50 – 3.36 (m, 8H), 3.32 – 3.16 (m, 10H), 3.07 (d, $J = 21.6$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ 148.16, 147.62, 143.81, 133.01, 132.75, 128.21, 121.68, 112.37, 112.21,

104.97, 71.62, 71.55, 70.37, 70.33, 70.28, 70.25, 69.93, 69.43, 68.59, 58.76, 58.70, 58.65. Mass (MALDI-TOF): Obs. 1154.0; Calcd. for $C_{52}H_{58}Br_2N_4O_{12}Zn$, 1154.2.

Synthesis of (3)

Porphyrin **2** (400 mg, 0.346 mmol) was dissolved in THF (40 mL) and triethylamine (20 mL) was added. The mixture was purged with nitrogen for 30 min. Then $Pd(PPh_3)_2Cl_2$ (25 mg, 0.036 mmol), CuI (7.05 mg, 0.036 mmol), and trimethylsilylacetylene (169 mg, 1.73 mmol) were added. The mixture was stirred at room temperature for 36 h under nitrogen, the reaction was quenched with saturated brine. After the mixture was extracted with dichloromethane three times, the combined organic layer was dried with anhydrous Na_2SO_4 and concentrated. Finally, the residue was purified by column chromatography (silica gel, CH_2Cl_2 /methanol (30:1) to afford **3** as a green solid. Yield: 380 mg (95%). 1H NMR (500 MHz, $CDCl_3$): δ 9.69 (dd, $J = 4.6, 1.6$ Hz, 4H), 8.93 (dd, $J = 4.5, 1.5$ Hz, 4H), 7.70 (dd, $J = 6.5, 2.0$ Hz, 2H), 7.65 (m, 2H), 7.14 (dd, $J = 11.5, 8.0$ Hz, 2H), 4.32 – 4.22 (m, 4H), 4.15 (d, $J = 22.1$ Hz, 4H), 3.83 (d, $J = 6.6$ Hz, 4H), 3.71 (d, $J = 29.2$ Hz, 4H), 3.61-3.64 (m, 4H), 3.53 – 3.40 (m, 8H), 3.33 – 3.21 (m, 10H), 3.11 (d, $J = 20.1$ Hz, 6H), 0.62 (s, 18H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 149.95, 147.86, 132.28, 132.14, 131.11, 130.62, 127.50, 121.47, 111.93, 110.81, 71.44, 71.30, 70.25, 70.03, 69.17, 68.36, 67.83, 58.51, 58.40, 29.30. Mass (MALDI-TOF): Obs. 1188.2; Calcd. for $C_{62}H_{76}N_4O_{12}Si_2Zn$, 1188.4.

Synthesis of (4)

Tetrabutylammonium fluoride (0.3 mL, 1M in THF) was added to a stirred solution of porphyrin **3** (165 mg, 0.14 mmol) in THF (20 mL). After the mixture was stirred for 5 min, water was added to quench the reaction. Then the solution was extracted with chloroform, washed with water and dried over anhydrous Na_2SO_4 . After evaporation of the solvent, the

residue was purified by GPC to give **4** as a deep green crystals. The molecule was not stable and directly used for next step without further purification. Yield: 133 mg (89%).

Synthesis of (**5**)

Compound **5** was synthesized according to the procedures reported previously.¹ ¹H NMR (500 MHz, DMSO-*d*₆): δ 7.67 – 7.63 (m, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.48 (d, *J* = 1.8 Hz, 1H), 7.44 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.36 – 7.28 (m, 3H), 2.08 – 1.92 (m, 20H), 0.84 – 0.68 (m, 4H). ¹³C NMR (126 MHz, CDCl₃) δ: 152.35, 149.69, 140.17, 140.05, 130.11, 127.63, 127.16, 126.10, 122.81, 121.12, 121.10, 119.86, 59.68, 54.99, 45.28, 37.68, 21.96. HRMS (EI) *m/z* calcd. for C₂₃H₃₁BrN₂ [M]⁺ 414.1671, found 414.1407.

Synthesis of FNEZnP-OE

To a 50 mL two necked round-bottom flask were added Compound **4** (133 mg, 0.13 mmol), **5** (158 mg, 0.38 mmol), anhydrous toluene (20 mL) and triethylamine (10 mL), and the mixture was deoxygenated with Ar for 30 min before Pd (PPh₃)₄ (14.6 mg, 0.01 mmol) and CuI (2.5 mg, 0.01 mmol) were added. Then the mixture was stirred at 80°C for 72 h under the protection of Ar. After cooled to room temperature, the mixture was washed with water and dried over anhydrous Na₂SO₄. Then the solvent was removed, and the residue was purified first by column chromatography on silica gel and then by GPC to give a deep green solid **FNEZnP-OE**. Yield: 76 mg (35%). **FNEZnP-OE** does not show satisfied NMR spectra due to its expanded π structure. Mass (MALDI-TOF): Obs. 1713.6; Calcd. for C₁₀₂H₁₂₀N₈O₁₂Zn, 1713.8.

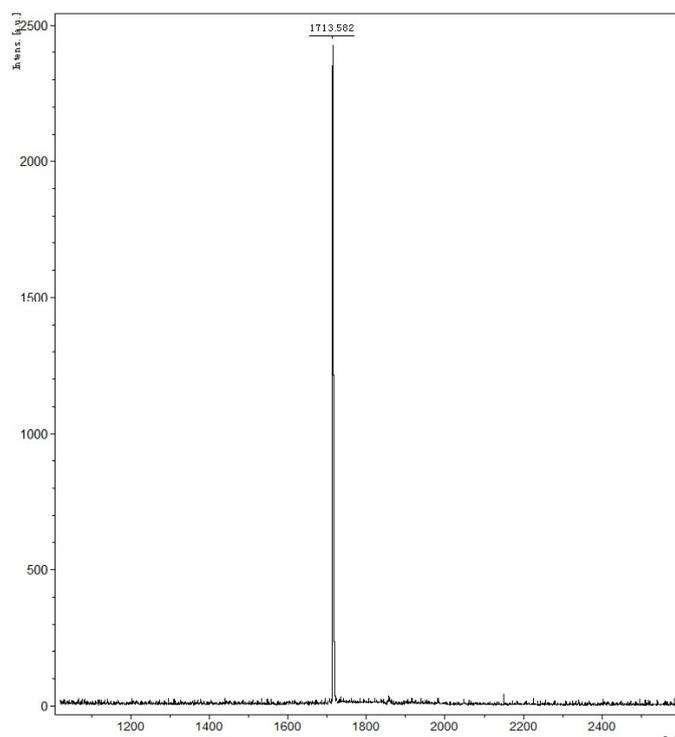


Figure S1. Mass (MALDI-TOF) spectrum of FNEZnP-OE.

2. Instruments.

^1H NMR spectra was conducted on a Bruker AVANCE Digital 500MHz spectrometer in deuterated chloroform using tetramethylsilane as an internal standard. Mass Spectrometry (MS) data was obtained on a Bruker Daltonics BIFLEX MALDI-TOF Analyzer using MALDI mode. UV-Vis-NIR absorption spectra of the films on quartz substrates were measured using a Shimadzu UV-3600 spectrophotometer.

Cyclic voltammetry (CV) measurements were carried out on a CHI660A electrochemical workstation with platinum electrodes at a scan rate of 50 mV s^{-1} and against an Ag/AgCl reference electrode with argon-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile (CH_3CN). A glass carbon electrode was used as the working electrode. The ferrocene/ferrocenium system (Fc/Fc^+ , 4.8 eV below vacuum level) was used as an internal standard. Under the same experimental conditions, the onset potential of Fc/Fc^+ was measured to be 0.36 V with respect to the Ag/AgCl reference electrode.

The J - V characteristics were measured under AM 1.5 solar simulator (Japan, SAN-EI, XES-40S1) at 100 mW cm^{-2} calibrated with a

standard Si solar cell, and data were collected using a Keithley 2400 digital source meter. External quantum efficiency (EQE) values of the encapsulated devices were measured by using an integrated system (Enlitech, Taiwan, China) and a lock-in amplifier with a current preamplifier under short-circuit conditions.

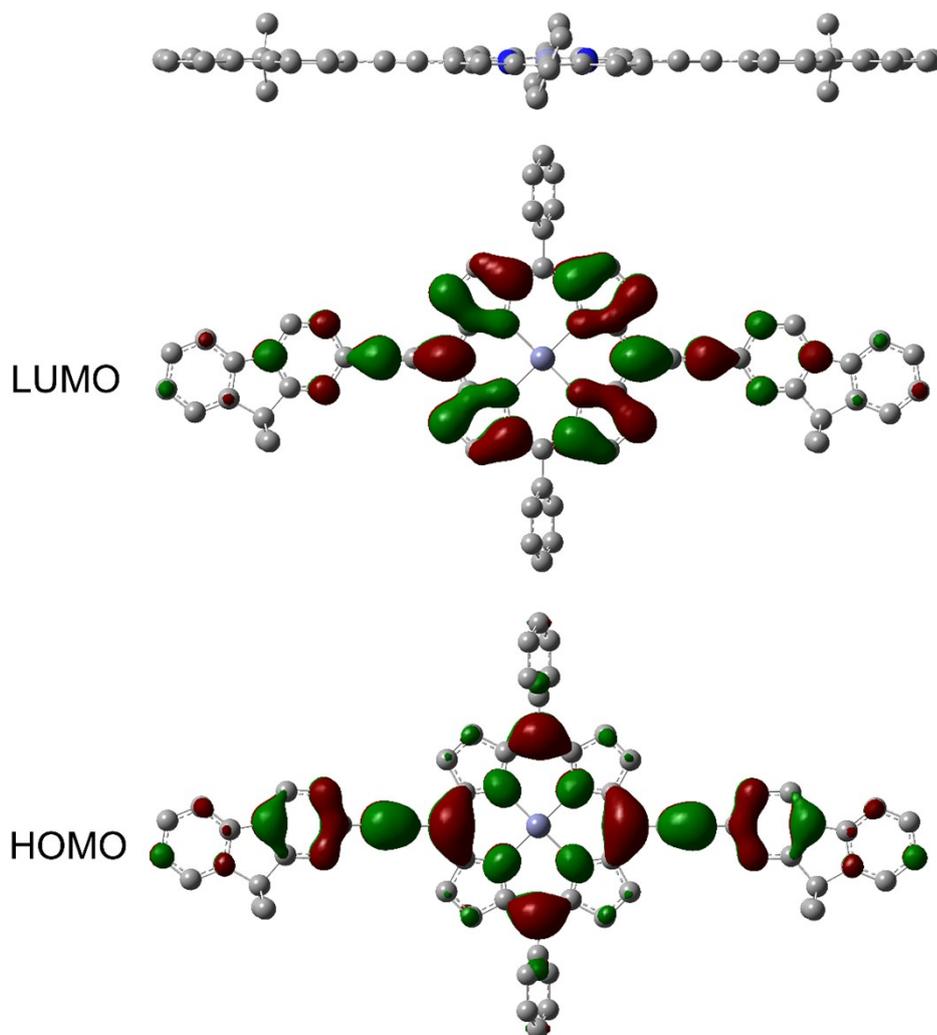


Figure S2. The optimum geometry and electron-state-density distribution of FNEZnP-OE at HOMO and LUMO (side chains were not calculated for the simplification of calculations).

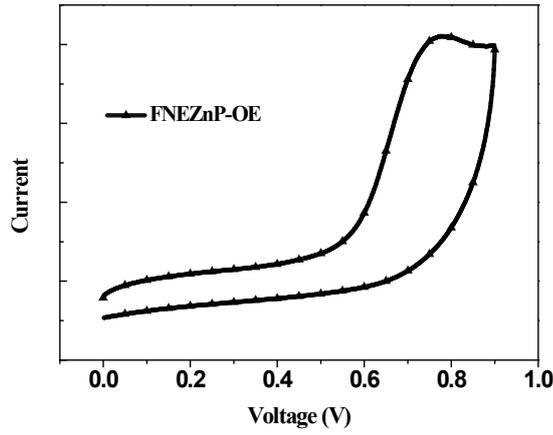


Figure S3. Cyclic voltammogram of FNEZnP-OE.

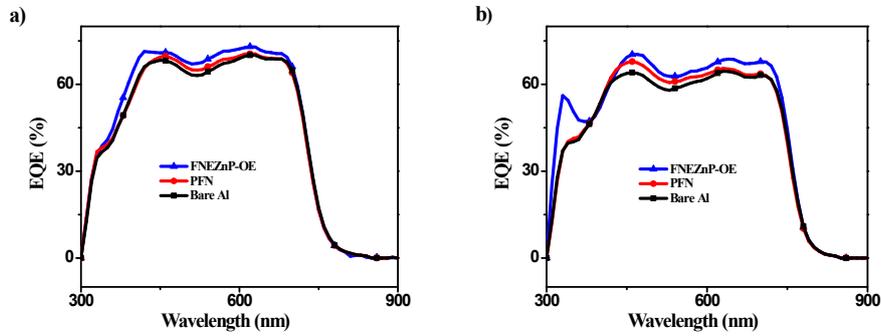


Figure S4. EQE curves of the devices using (a) PTB7:PC₇₁BM and (b) PTB7-Th: PC₇₁BM as the active layers with/without ETLs.

3. Electron-only devices fabrication

The mobility was described by the following equation:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu V^2}{8L^3}$$

Where J is the current density, L is the active-layer thickness, ε_0 is the permittivity of free space (8.85×10^{-12} F m⁻¹), ε_r is the relative dielectric constant of the active layer, μ is the zero-field mobility, V is the voltage drop across the device. The electron mobility of the whole devices was calculated from the SCLC curves shown in **Table S1**.

Table S1. Electron mobilities of the devices of ITO/ ZnO/PTB7:PC₇₁BM/interlayer/Al with no, PFN and FNEZnP-OE ETLs.

ETL	Bare Al	PFN	FNEZnP-OE
μ_e cm ² V ⁻¹ S ⁻¹	1.92×10^{-5}	2.30×10^{-4}	3.05×10^{-4}

Table S2. W_F values of Al cathode with no, PFN and FNEZnP-OE ETLs measured by a Kelvin probe under N₂.

	Al	Al/FNEZnP-OE	Al/PFN
W_F [eV]	3.9	3.4	3.5

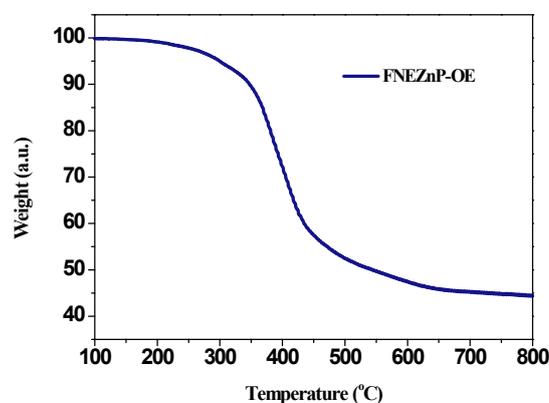


Figure S5. Thermalgravimetric analysis of FNEZnP-OE in a nitrogen atmosphere.

The electron-only devices with the architectures of ITO/ZnO/ETL/Al and ITO/ZnO/PC₇₁BM/ETL/Al are prepared and the electron mobilities are determined to be 8.92×10^{-5} and 1.23×10^{-3} cm² V⁻¹ s⁻¹, respectively, by fitting the J-V curves shown in Figure S6 above using the SCLC model.

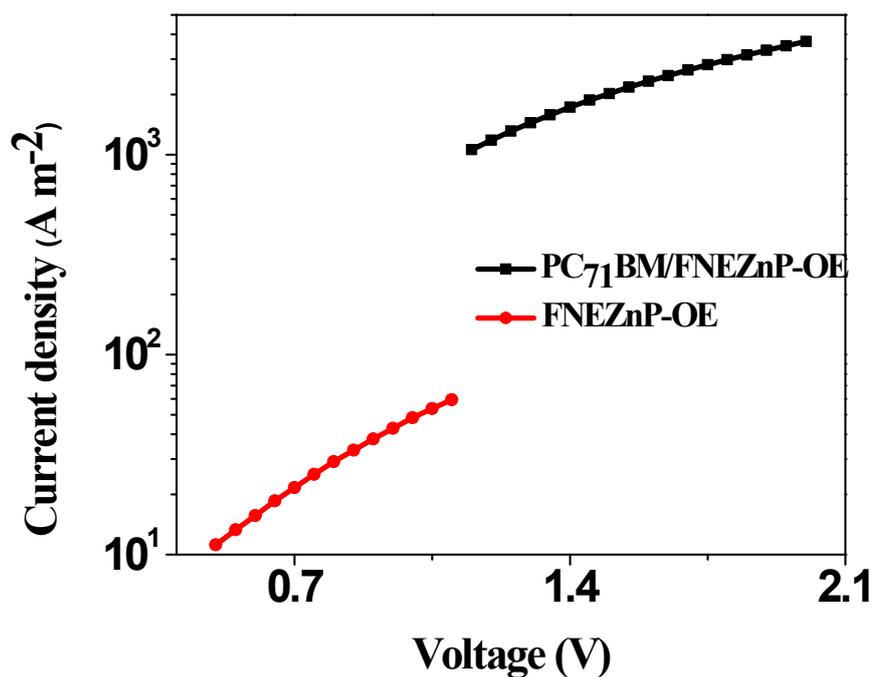


Figure S6. J-V curves of electron only devices with the device structure of ITO/ZnO/ETL/Al and ITO/ZnO/PC₇₁BM/ETL/Al.

Table S3. Photovoltaic characteristics of the PSC devices of ITO/PEDOT:PSS/PTB7:PC₇₁BM/ FNEZnP-OE/Al under the illumination of AM 1.5G 100 mW/cm² with different thicknesses of ETLs by spin-casted varied FNEZnP-OE concentrations but at same speed of 2000 rpm.

FNEZnP-OE Concentration	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)
0.2mg/mL	13.70	0.74	58.45	5.92
0.4mg/mL	16.38	0.74	70.31	8.52
0.5mg/mL	15.82	0.76	67.25	8.08
0.7mg/mL	15.62	0.76	62.31	7.40

1. W. Zhang, Y. Wu, Q. Bao, F. Gao and J. Fang, *Advanced Energy Materials*, 2014, **4**, 1400359.