Supporting Information

Doping ZnO with Water/Alcohol-Soluble Small Molecules as Electron Transport Layers for Inverted Polymer Solar Cells

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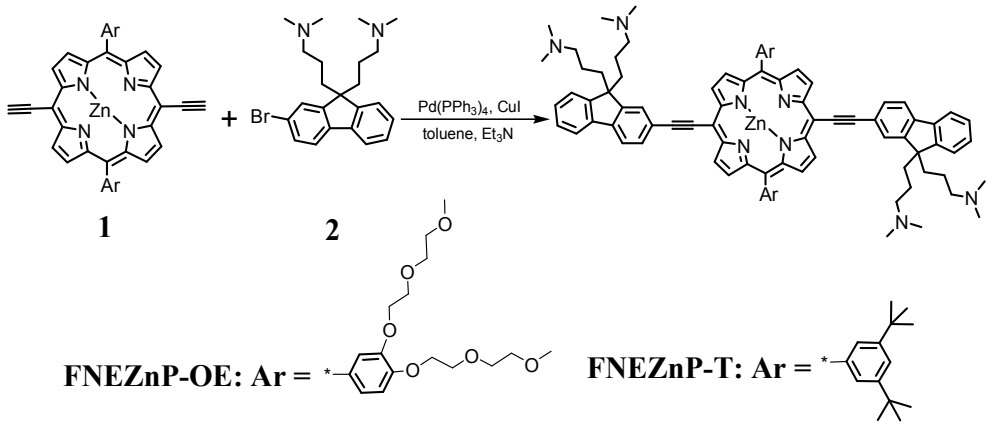
Experiment Details:

1. Synthesis of FNEZnP-T and FNEZnP-OE:

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 CaH_2 prior to use. FNEZnP-OE was synthesized according to reported procedures[1]. [10,20-Bis-(3,5-di-tert-butylphenyl)-5,15-bis-ethynylporphyrinato]zinc(II), 10,20-bis-(3,4-di-[2-(2-methoxy-ethoxy)-ethoxy]-phenyl)-5,15-bis-ethynylporphyrinato]zinc(II) (**1**) and 2-bromo-9,9′-bis(3″-(*N*,*N*-dimethylamino)propyl)-fluorene (**2**) were synthesized according to reported procedures.[2,3]



Scheme S1. Synthetic routines of FNEZnP-OE and FNEZnP-T.

To a 50 mL two necked round-bottom flask were added compound **1** (0.13 mmol), **2** (158 mg, 0.38 mmol), anhydrous toluene (20 mL) and triethylamine (10 mL), and the mixture was deoxygenated with N_2 for 30 min before Pd $(PPh_3)_4$ (14.6 mg, 0.01 mmol) and CuI (2.5 mg, 0.01 mmol) were added. Then the mixture was stirred at 80□ for 72 h under the protection of Ar. After cooled to room temperature, the mixture was washed with water and dried over anhydrous Na_2SO_4. Then the solvent was removed, and the residue was purified by column chromatography on silica gel to give a deep green solid of FNEZnP-T or FNEZnP-OE. Both FNEZnP-T and FNEZnP-OE do not show satisfied NMR spectra due to the expanded π structure.

Mass (MALDI-TOF) of FNEZnP-OE: Obs. 1713.6; Calcd. for $C_{102}H_{120}N_8O_{12}Zn$, 1713.8.

2. Instruments.

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. 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.The KP5050(by KP Technology) in a glove-box filled with nitrogen has been utilized for the working function.XPS data was obtained using a Kratos Axis Ultra DLD X-ray Photoelectron Spectroscopy/ESCA.

3. Dark Currents of Inverted Polymer Solar Cells.

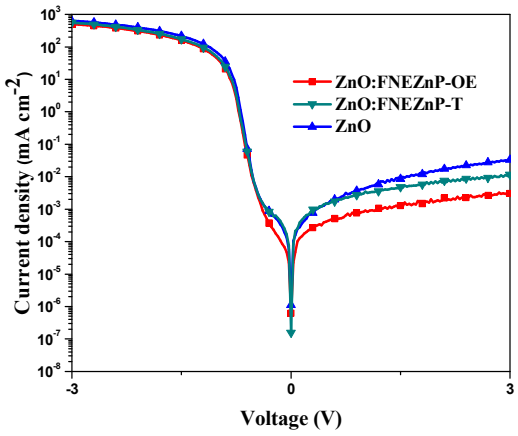


Figure S1. Dark currents of inverted PTB7:$PC_{71}BM$ based solar cells with ZnO, ZnO: FNEZnP-T and ZnO:FNEZnP-OE interlayers. Device configuration: ITO/ interlayer/ PTB7:$PC_{71}BM/MoO_3$/Al.

4. Characteristics of the i-PSCs with different concentration of FNEZnP-OE doped in ZnO.

Table S1. Photovoltaic performances of inverted PSCs with various FNEZnP-OE ratios to ZnO.

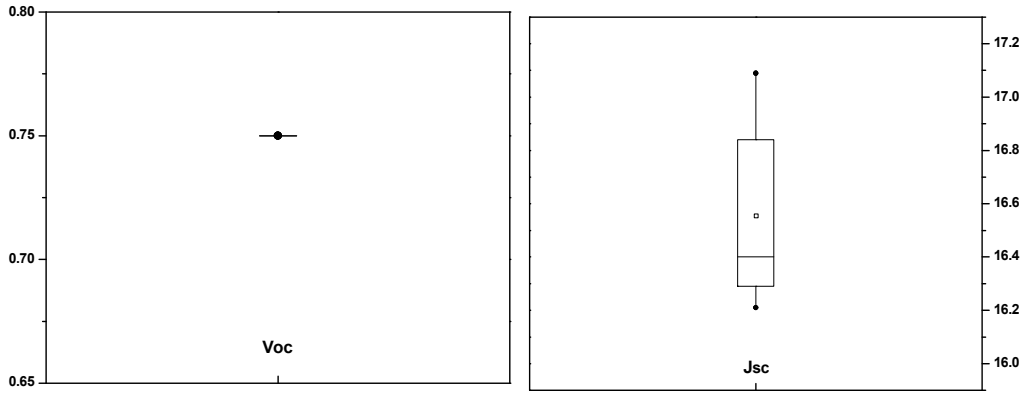
Ratio	J_{SC}(mAcm^{-2})	V_{OC}(V)	*FF*(%)	*PCE*(%)
100:0.5	16.24	0.75	73.11	8.90
100:1.0	17.09	0.75	72.13	9.24
100:1.5	15.89	0.74	66.67	7.84

5. Characteristics of the i-PSCs with PTB7-Th as active layer.

Table S2. Photovoltaic performances of PTB7-Th:$PC_{71}BM$ based solar cells with different cathode interlayer.

Cathode interlayer	Ratio	J_{SC}(mAcm^{-2})	V_{OC}(V)	*FF*(%)	*PCE*(%)
ZnO	-	17.20	0.80	61.98	8.53
ZnO: FNEZnP-OE	100:1.0	17.52	0.80	68.87	9.65

6. Variation 10 samples of V_{oc}, J_{sc} and FF.



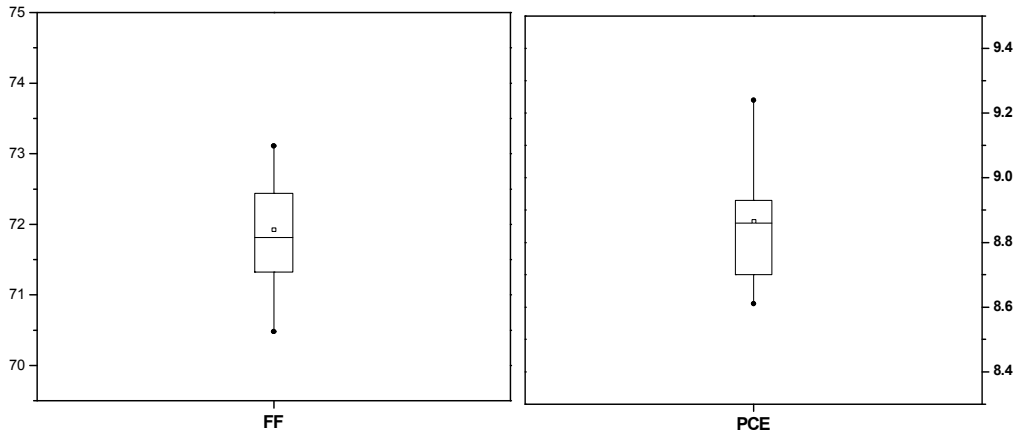


Figure S2. Open circuit voltage (V_{oc}), current density (J_{sc}), fill factor (*FF*), power conversion efficiency (PCE) variation of 10 samples of ITO/ZnO:FNEZnP-OE /PTB7:$PC_{71}BM$ /MoO_3/Al.

7. Thermal stability of FNEZnP-OE.

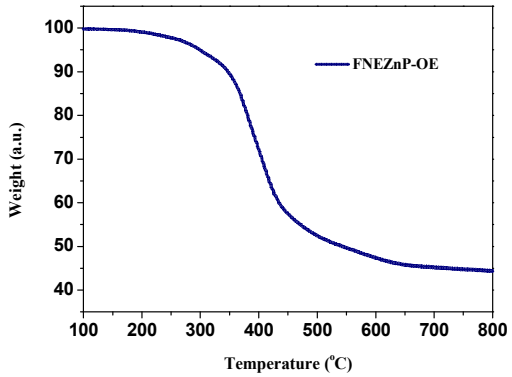


Figure S3. Thermalgravimetric analysis of FNEZnP-OE in a nitrogen atmosphere.

8. X-Ray Photoelectron Spectroscopy (XPS) of ZnO, ZnO:FNEZnP-OE.

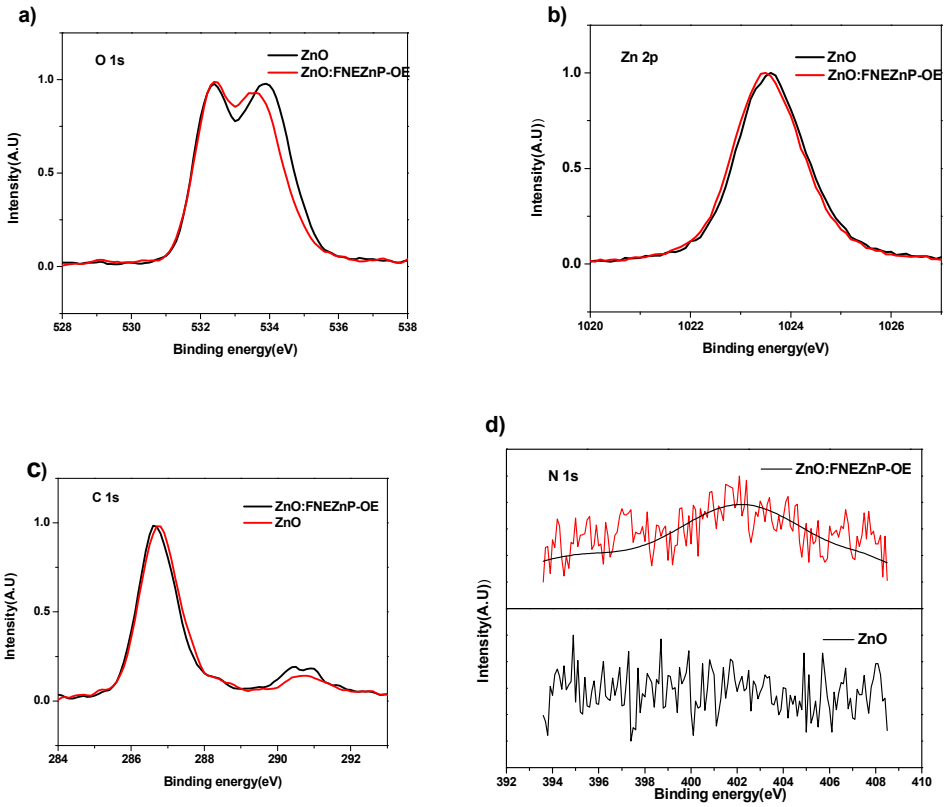


Figure S4. XPS analysis on Si/ZnO and Si/ZnO:FNEZnP-OE for (a) oxygen O 1s, (b) Zn 2p, (c) carbon C 1s and (d) nitrogen N 1s.

References

(1) Zhang, L.; Liu, C.; Lai, T.; Huang, H.; Peng, X.; Huang, F.; Cao, Y. A Water/alcohol Soluble Conjugated Porphyrin Small Molecule as a Cathode Interfacial Layer for Efficient Organic Photovoltaics. *J. Mater. Chem. A* **2016,** DOI: 10.1039/C6TA05726H.

(2) Zhang, W.; Wu, Y.; Bao, Q.; Gao, F.; Fang, J. Morphological Control for Highly Efficient Inverted Polymer Solar Cells Via the Backbone Design of Cathode Interlayer Materials. *Adv. Energy Mater.* **2014,** *4*, 1400359.

(3) Huang, Y.; Li, L.; Peng, X.; Peng, J.; Cao, Y. Solution Processed Small Molecule Bulk Heterojunction Organic Photovoltaics Based on a Conjugated Donor–Acceptor Porphyrin. *J. Mater. Chem.* **2012,** *22*, 21841-21844.