Electronic Supplementary Information

Phenylene-bridged perylenediimide-porphyrin acceptors for non-fullerene organic solar cells

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Experimental Procedures

Device fabrication

Experimental devices with a structural configuration of ITO/ZnO/ZrAcac/PTB7-Th:acceptor/MoO_3/Ag were prepared as follows. Glass substrate with pre-patterned ITO (sheet resistance = 15 Ω sq^{-1}) was first ultra-sonicated in a detergent solution, then in deionized water, acetone, and isopropanol. After drying with high-pressure air flow, the substrate was subjected to UV-ozone treatment for 30 min. A ZnO precursor solution (2M diethylzinc solution in toluene, diluted with THF) was spin-coated on the substrate at 5000 rpm for 30 s in dry air, which was then baked on a hot plate at 180°C for about 30 min. After cooling to room temperature, the substrate was spin coated with a Zirconium acetylacetonate (ZrAacac) solution (0.5 mg/mL in methanol) in an argon-filled glove box, and dried on a hot plate at 80°C for 10 min. The resulting substrate was then spin coated with a solution of PTB7-Th and acceptor (1:1.3, w/w) in chlorobenzene(CB)/1,8-diiodoctane (DIO) (98.5:1.5, v/v) (total concentration: 25 mg mL^{-1}) at 1500 rpm for 60 s and dried. The optimal thickness of the active layer was typically 100 nm as measured using a Dektak 6 M surface profilometer. A thin layer (10 nm) of MoO_3 and Ag cathode (100 nm) was subsequently deposited by using thermal evaporation in a high vacuum chamber (~10^{-6} mbar). The device area was exactly fixed at 0.04 cm^2. The *J-V* characterization of the experimental devices was carried out on a computer-controlled Keithley 2400 Source Measurement system with a solar simulator (XES-70S1, SAN EI Co., Ltd.). The light intensity was monitored by using a standard Si solar cell

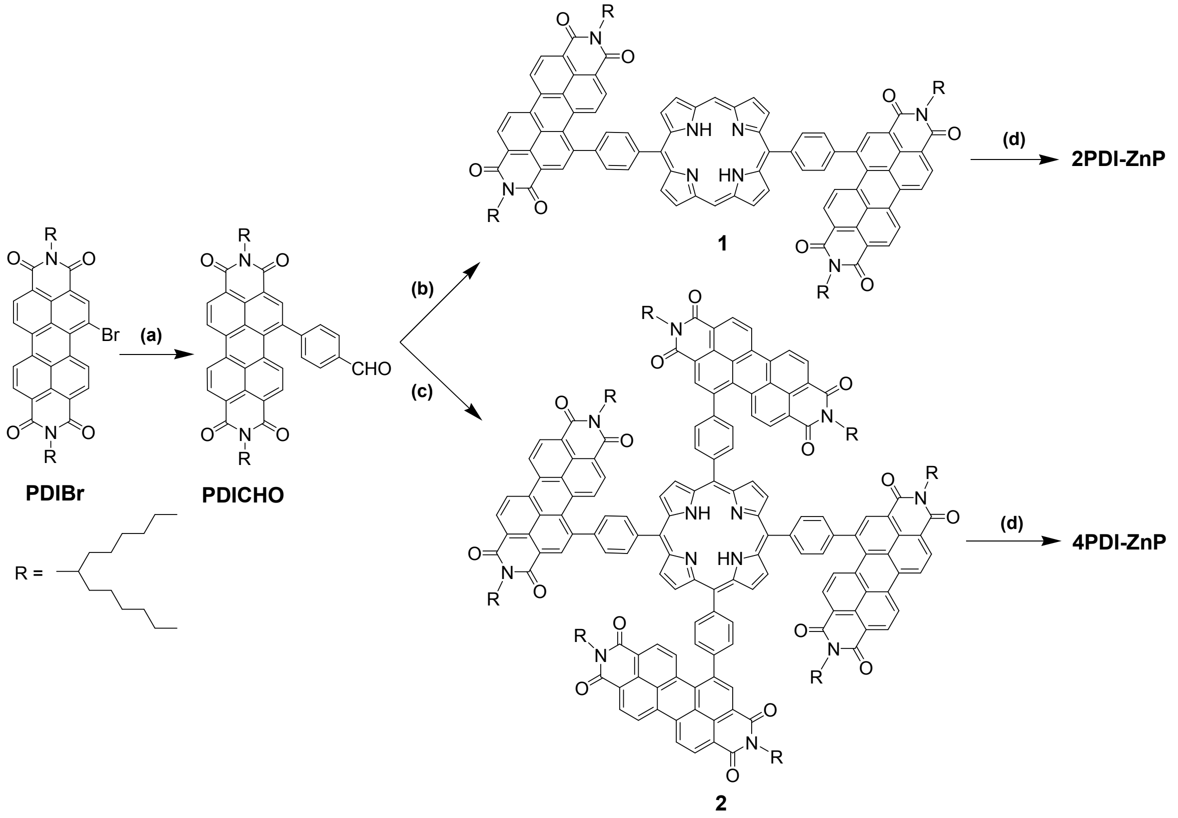
(KONICA MINOLTA, INC.). The EQE values were obtained on a Newport Model 77890 (Newport Co., Ltd.) during illumination with monochromatic light from a xenon lamp.

Characterization

^{1}H NMR spectra were recorded on a Bruker Ultrashield 400 Plus NMR spectrometer. UV-vis spectra of dilute solutions (1×10^{-5} M) of the samples in $CHCl_3$ were recorded at room temperature (ca. 25°C) using a Varian Cary 100 UV-vis spectrophotometer. Solid films for UV-vis spectroscopic analysis were prepared by spin-coating the solutions of the sample onto a quartz substrate and dried in vacuo. Cyclic voltammetry (CV) was performed on a Versastat II electrochemical workstation operated at a scan rate of 50 mV s^{-1} using anhydrous $CHCl_3$ as solvent with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte. The potentials were measured against a Ag/Ag^+ (0.01 M $AgNO_3$) reference electrode with ferrocene/ferrocenium ion (Fc/Fc^+) pair as the internal standard. The onset potentials were determined from the intersection of two tangents drawn at the rising and background currents of the cyclic voltammograms. HOMO and LUMO energy levels were estimated relative to the energy level of the ferrocene reference (4.8 eV below vacuum level). High-resolution matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Bruker Autoflex MALDI-TOF mass spectrometer. Topographic and phase images of the composite PTB7-Th:acceptor films (surface area: 5×5 μm^2) were obtained using a Digital Nanoscope III atomic force microscope operated in the tapping mode under ambient conditions.

Materials

The required chemicals and reagents for the synthesis were purchased from Dieckmann Chemical Ltd, China. 1-Hexylheptylamine, *N*,*N*’-bis(1-hexylheptyl)perylene-3,4,9,10-tetracarboxylbisimide (PDI) and 1-bromoperylene bisimide (PDIBr) were prepared according to the literature procedures and characterized by ^{1}H NMR by comparison with literature data.[1-4] Organic solvents used in this work were purified using standard processes.



Scheme S1. Syntheses of PDI-functionalized Zn(II)porphyrins, 2PDI-ZnP, 4PDI-ZnP. Reaction conditions: (a) 4-formylphenylboronic acid, $Pd(PPh_3)_4$, K_2CO_3, THF/H_2O (3:1 v/v), reflux; (b) dipyrromethane, TFA, DDQ, CH_2Cl_2, r.t.; (c) pyrrole, TFA, DDQ, CH_2Cl_2, r.t.; (d) $Zn(OAc)_2/CHCl_3$, reflux.

***Synthesis of N,N*'-Bis(1-hexylheptyl)-[1-(4-aldehyde-phenyl)perylene]-3,4,9,10-tetracarboxylbisimide (PDICHO):**

In a 100-mL round-bottom flask containing a well-stirred mixture of 1-bromoperylene bisimide (PDIBr; 1.00 g, 1.2 mmol), 4-formylphenylboronic acid (0.216 g, 1.44 mmol), K_2CO_3 (0.50 g, 3.6 mmol) and 30 mL THF/H_2O (3:1) was first purged with nitrogen. After addition of $Pd(PPh_3)_4$ (70 mg, 2 mol %), the reaction mixture was stirred and refluxed for 12 h. After the reaction, the reaction mixture was diluted with CH_2Cl_2 and water. The organic layer was separated, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography on silica gel using CH_2Cl_2/hexanes (1:1, v/v) as eluant, affording 0.9 g (yield: 88%).of PDICHO as a red solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 10.14 (s, 1H), 8.54-8.68 (m, 4H), 8.56 (d, *J* = 15.2 Hz, 1H), 8.06 (d, *J* = 8.8 Hz, 3H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 5.15-5.21 (m, 2H), 2.17-2.22 (m, 4H), 1.79-1.87 (m, 4H), 1.22-1.64 (m, 32H), 0.78-0.84 (m, 12H).

Synthesis of 2PDI-ZnP:

A solution of dipyrromethane (52 mg, 0.35 mmol) and PDICHO (300 mg, 0.35 mmol) in CH_2Cl_2 (50 mL) in a 100-mL round-bottomed flask was degassed by bubbling with nitrogen for 30 min. Three drops of TFA was then added and the solution was stirred for 12h at room temperature under nitrogen. Subsequently, 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (160 mg, 0.7 mmol) was added, and the reaction mixture was stirred for a further 2h. After the reaction, the solvent was evaporated and the crude product was purified by column chromatography on silica gel using CH_2Cl_2/n-hexane (1:1 v/v) as the eluent to give 122 mg (yield: 35%) of a purple porphyrin intermediate (**1**). A mixture of (**1**) (100 mg, 0.05 mmol) and zinc acetate (60 mg, 0.27 mmol) in $CHCl_3$ (30 mL) in a 100-mL round bottomed flask was stirred and refluxed for 12 h under nitrogen atmosphere. After solvent removal, the residue was purified by column chromatography on silica gel using CH_2Cl_2/hexanes (1:1, v/v) as eluant to give 99 mg (yield: 95%) of a red solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 10.34 (s, 2H) , 9.20-9.63 (m, 8H), 8.94 (s, 2H), 8.66 (s, 2H), 8.30–8.56 (m, 14H), 7.90 (s, 4H), 5.21–5.30 (m, 4H), 2.28–2.40 (m, 8H), 1.92-1.93 (m, 8H), 1.23-1.41 (m, 64H), 0.78–0.90 (m, 24H).

(MALDI–TOF, m/z) calculated for $C_{132}H_{140}N_8O_8Zn$: 2030.9828, found 2030.8839.

Synthesis of 4PDI-ZnP:

A solution of of pyrrole (24 μL, 0.35 mmol) and PDICHO (300 mg, 0.35 mmol) in CH_2Cl_2 (50 mL) in a 100-mL round-bottomed flask was degassed by bubbling with nitrogen for 30 min. Three drops of TFA was then added and the solution was stirred for 12h at room temperature under nitrogen. Subsequently, 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (160 mg, 0.7 mmol) was added, and the reaction mixture was stirred for a further 2h. After the reaction, the solvent was evaporated and the crude product was purified by column chromatography on silica gel using CH_2Cl_2/n-hexane (1:1, v/v) as the eluent to give 106 mg (yield: 28%) of a purple porphyrin intermediate (**2**). A mixture of (**2**) (100 mg, 0.03 mmol) and zinc acetate (30 mg, 0.14 mmol) in $CHCl_3$ (30 mL) in a 100-mL round bottomed flask was stirred and refluxed for 12 h under nitrogen atmosphere. After solvent removal, the residue was purified by column chromatography on silica gel using CH_2Cl_2/hexanes (1:1, v/v) as eluant to give 98 mg (yield: 95%) of a red solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.09-9.45 (m, 12H), 8.52-8.80 (m, 32H), 8.04 (s, 8H), 5.12-5.30 (m, 8H), 2.19-2.36 (m, 8H), 1.78-2.17 (m, 28H), 1.06-1.36 (m, 124H), 0.84-0.87 (m, 24H), 0.67-0.72 (m, 24H). (MALDI–TOF, m/z) calculated for $C_{244}H_{268}N_{12}O_{16}Zn$: 3689.9884, found 3689.9676.

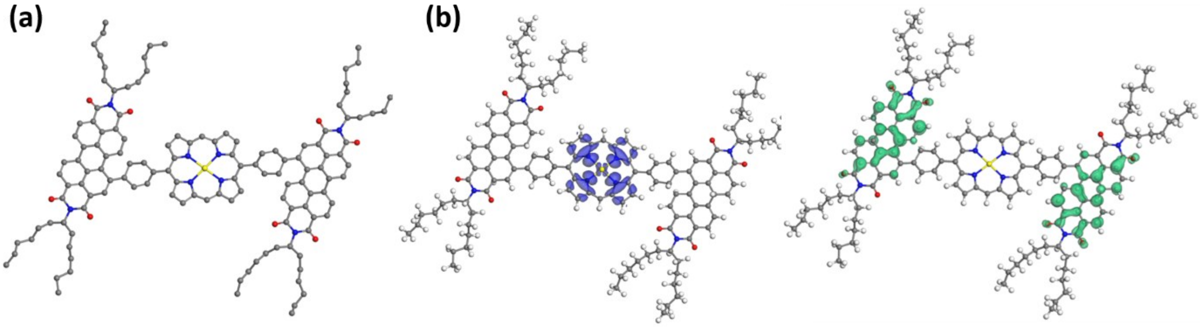


Figure S1. (a) Simulated side-view and partial front-view conformations and (b) HOMO/LUMO electron distribution of 2PDI-ZnP.

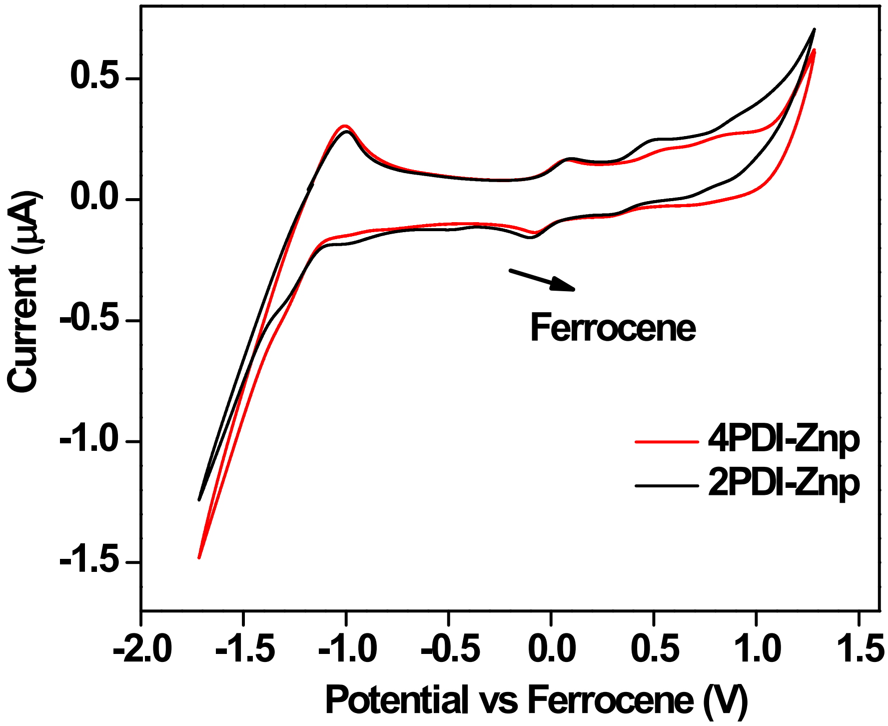
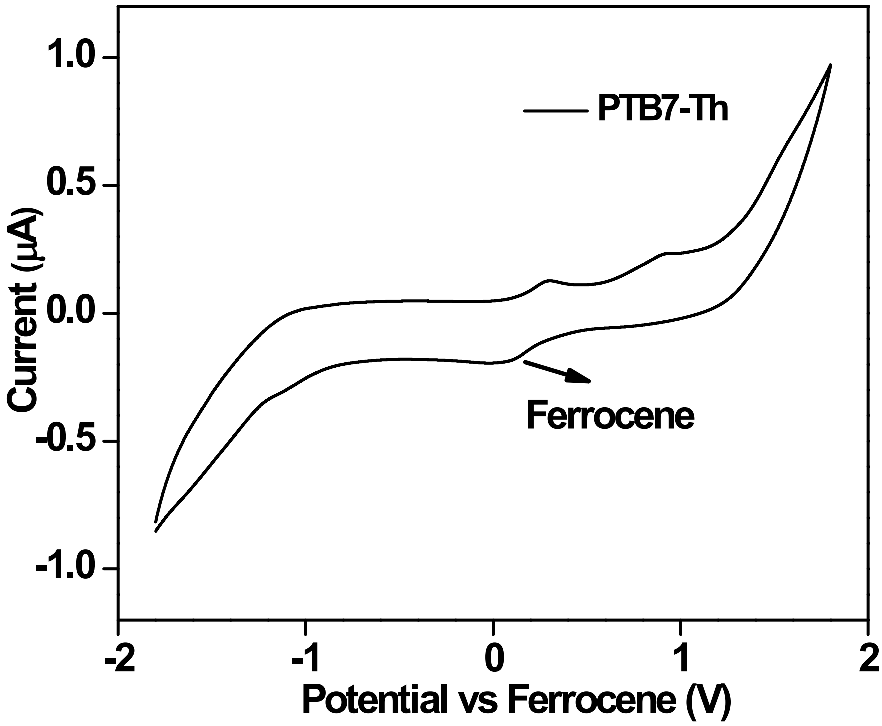


Figure S2. Cyclic voltammograms of 2PDI-ZnP and 4PDI-ZnP recorded in chloroform solution.



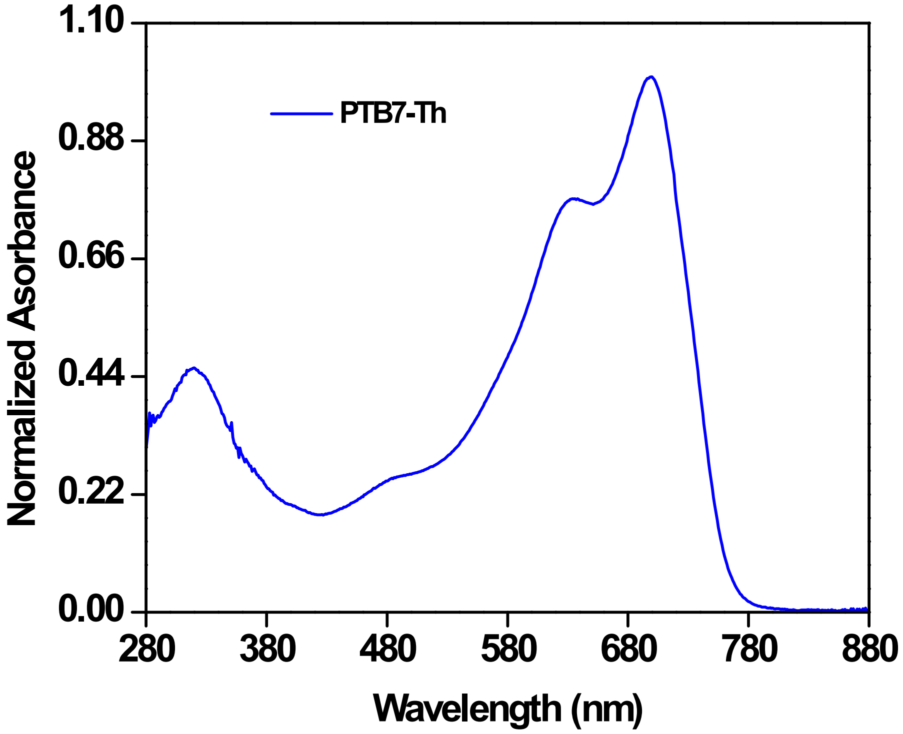
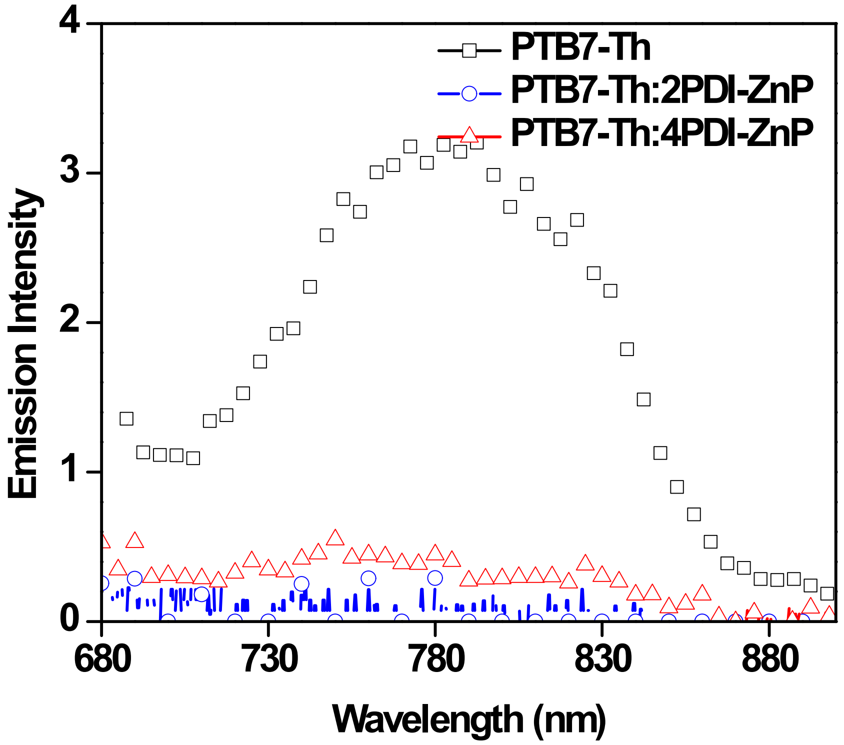


Figure S3. (a) Differential pulse voltammogram (b) UV-vis absorption spectra of PT7-Th recorded in chloroform solution.



Figurer S4. Photoluminescence of spin coated films of PTB7-Th and PTB7-Th:2PDI-ZnP, and PTB7-Th:4PDI-ZnP recorded at the excitation wavelength of 650 nm.

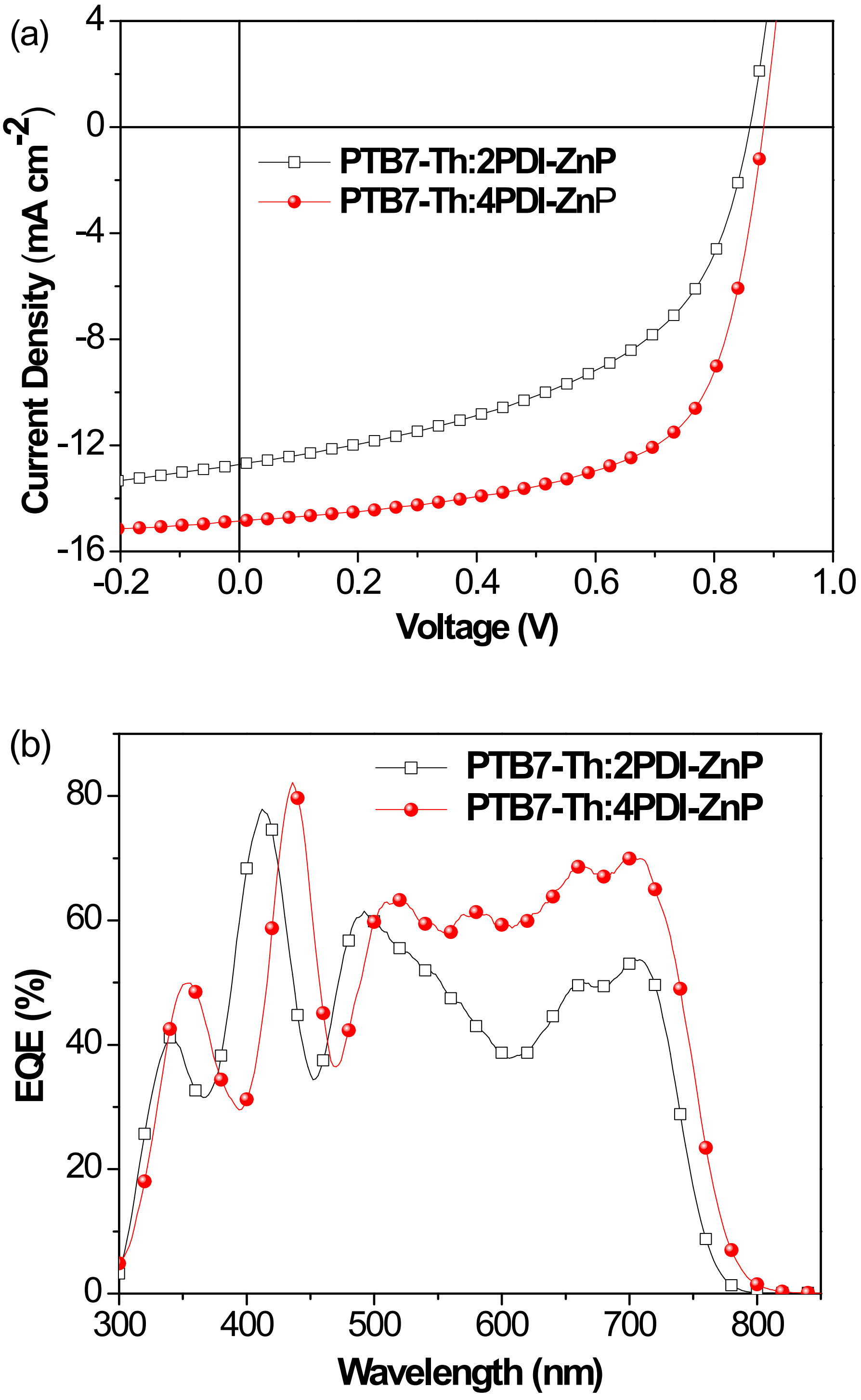


Figure S5. (a) *J-V* and (b) EQE curves of BHJ OSCs based on device of ITO/ZnO/Zirconium acetylacetonate(ZrAcac) /PTB7-Th:Acceptor/MoO_3/Ag under AM 1.5G illumination at 100 mW cm^{-2}.

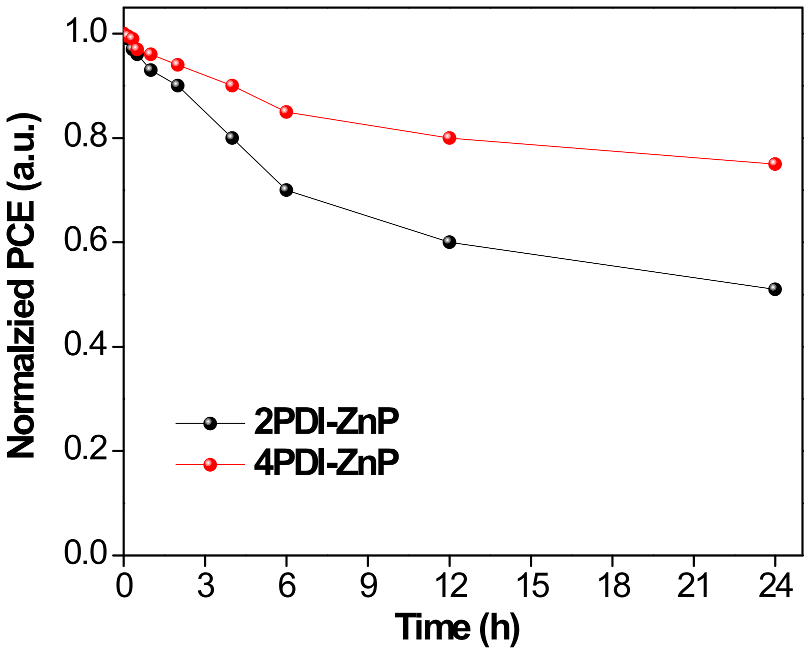
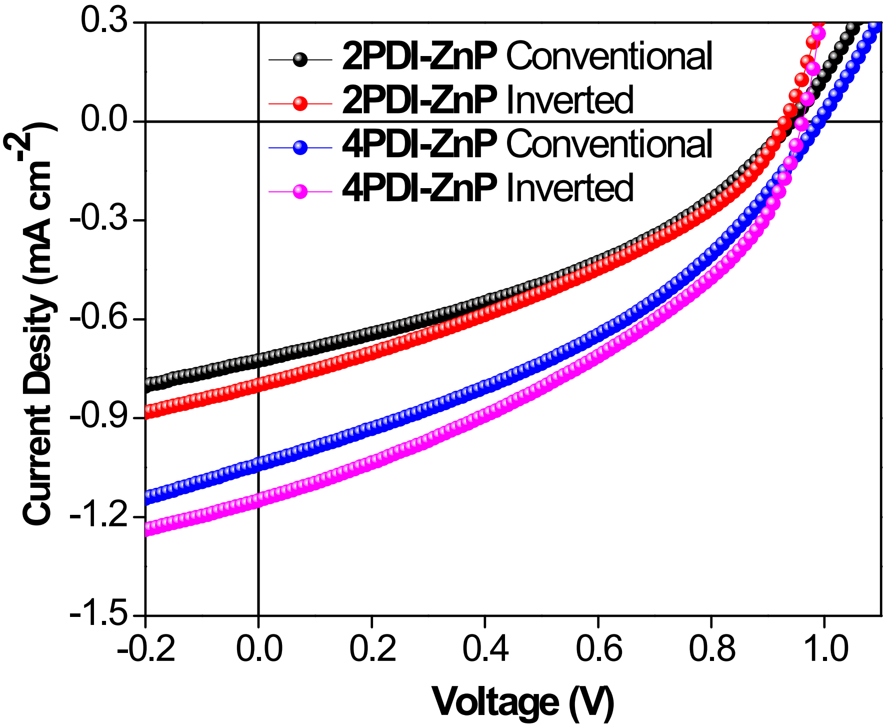


Figure S6. Normalized PCEs of the devices under heating at 100 °C for 24 hours.



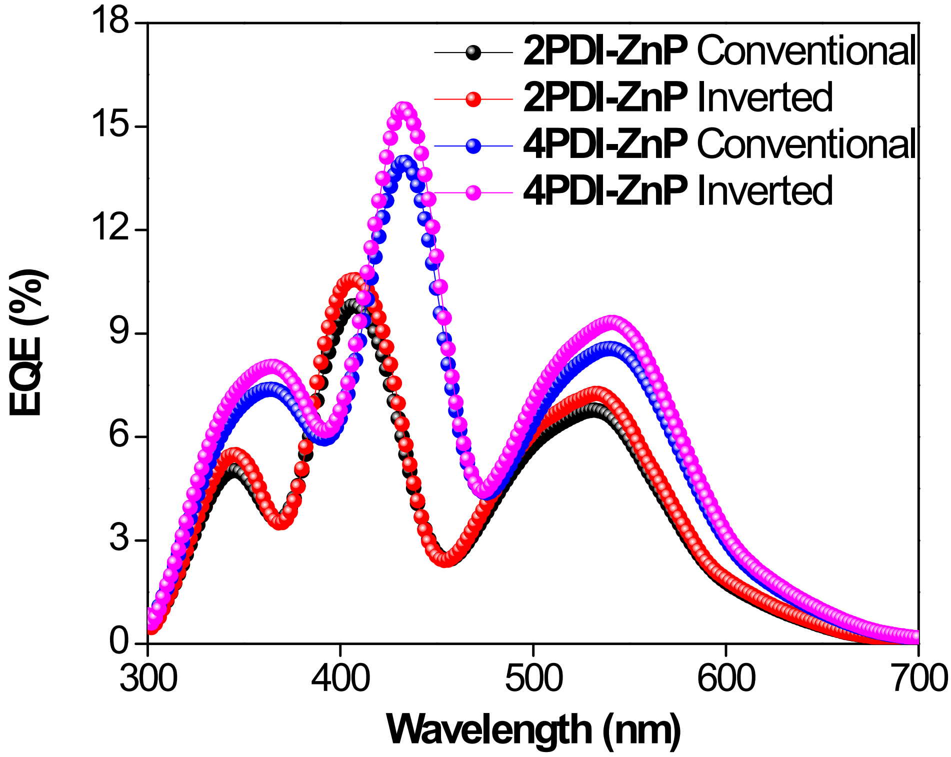


Figure S7. *J*-*V* and EQE curves of single-component BHJ OSCs based on device of ITO/ZnO/PNDIT-F3N-Br/Acceptor/MoO_3/Ag (or ITO/PEDOT:PSS/Acceptor/PFN/Al) under AM 1.5G illumination at 100 mW cm^{-2}.

Table S1. Device Parameters of single-component BHJ OSCs based on device of ITO/ZnO/PNDIT-F3N-Br/Acceptor/MoO_3/Ag (or ITO/PEDOT:PSS/Acceptor/PFN/Al) under AM 1.5G illumination at 100 mW cm^{-2}.

Acceptor	J_{SC} (mA cm^{-2})	J_{EQE} (mA cm^{-2})	V_{OC} (V)	FF (%)	PCE (%)
2PDI-ZnP	0.80 (0.73)	0.75 (0.70)	0.93 (0.94)	36.1 (36.9)	0.27 (0.25)
4PDI-ZnP	1.15 (1.04)	1.11 (1.02)	0.96 (0.99)	38.8 (37.9)	0.43 (0.39)

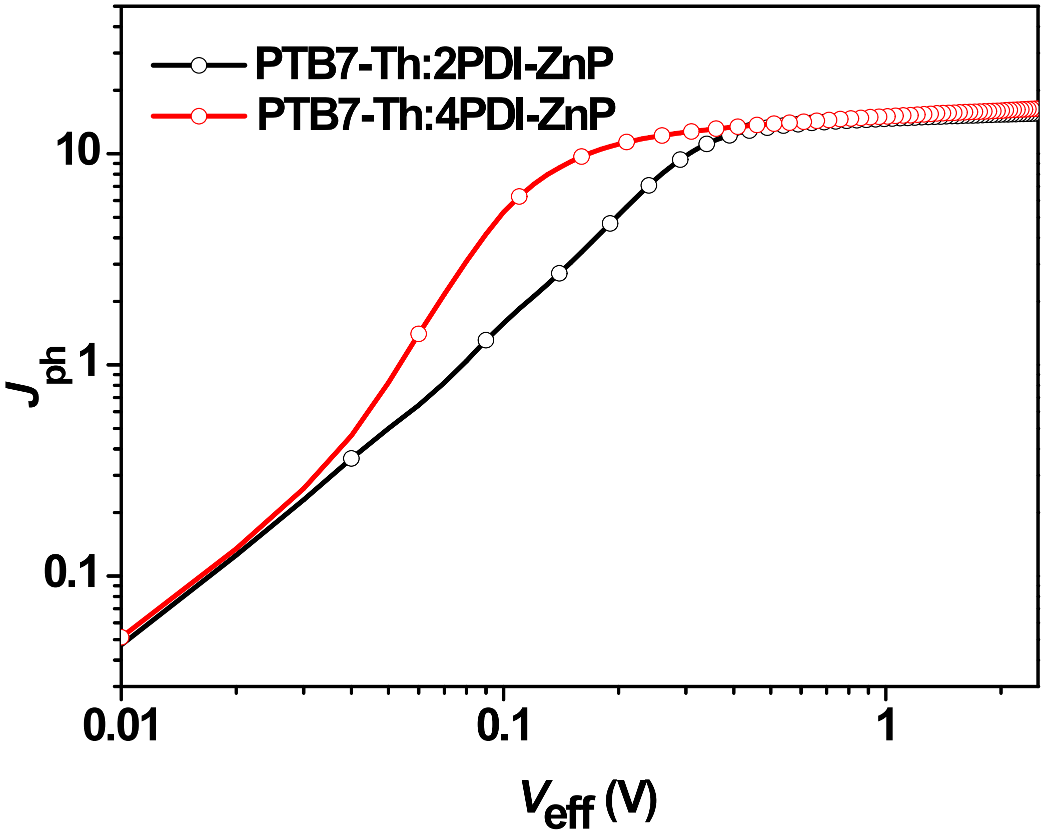


Figure S8. J_{ph} of the optimal devices versus V_{eff}.

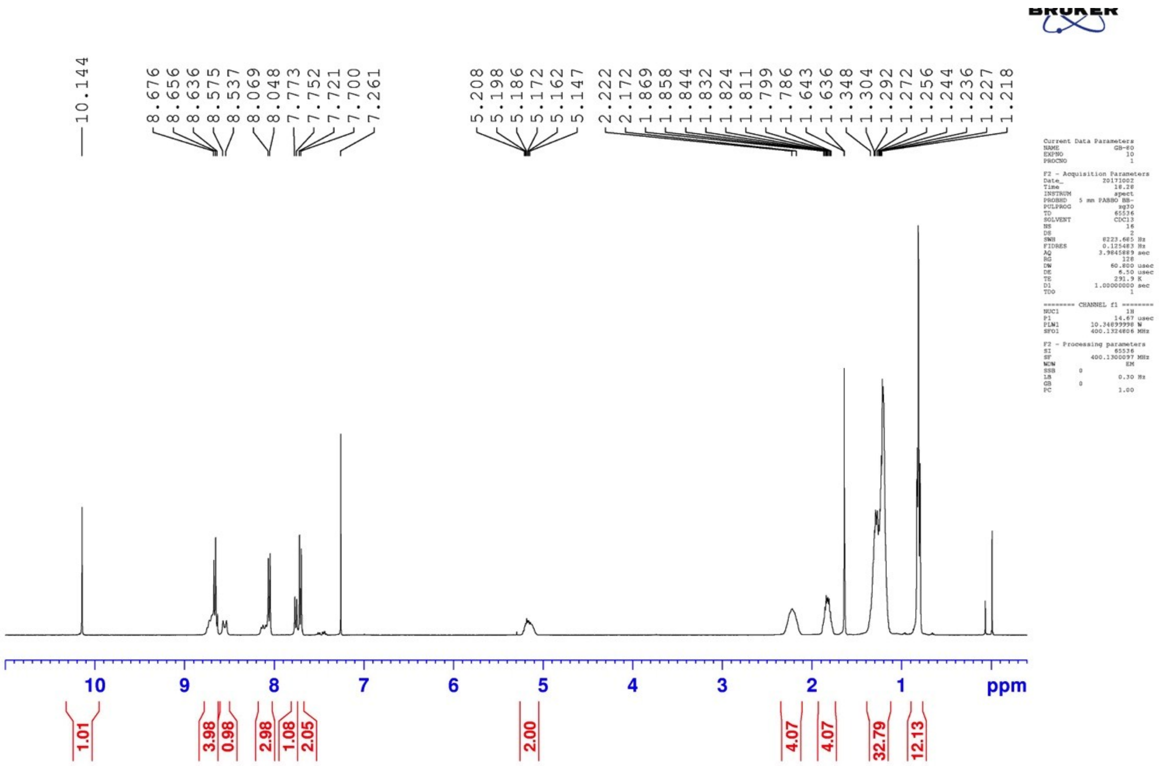


Figure S9. ^{1}H NMR spectrum of PDICHO recorded in $CDCl_3$.

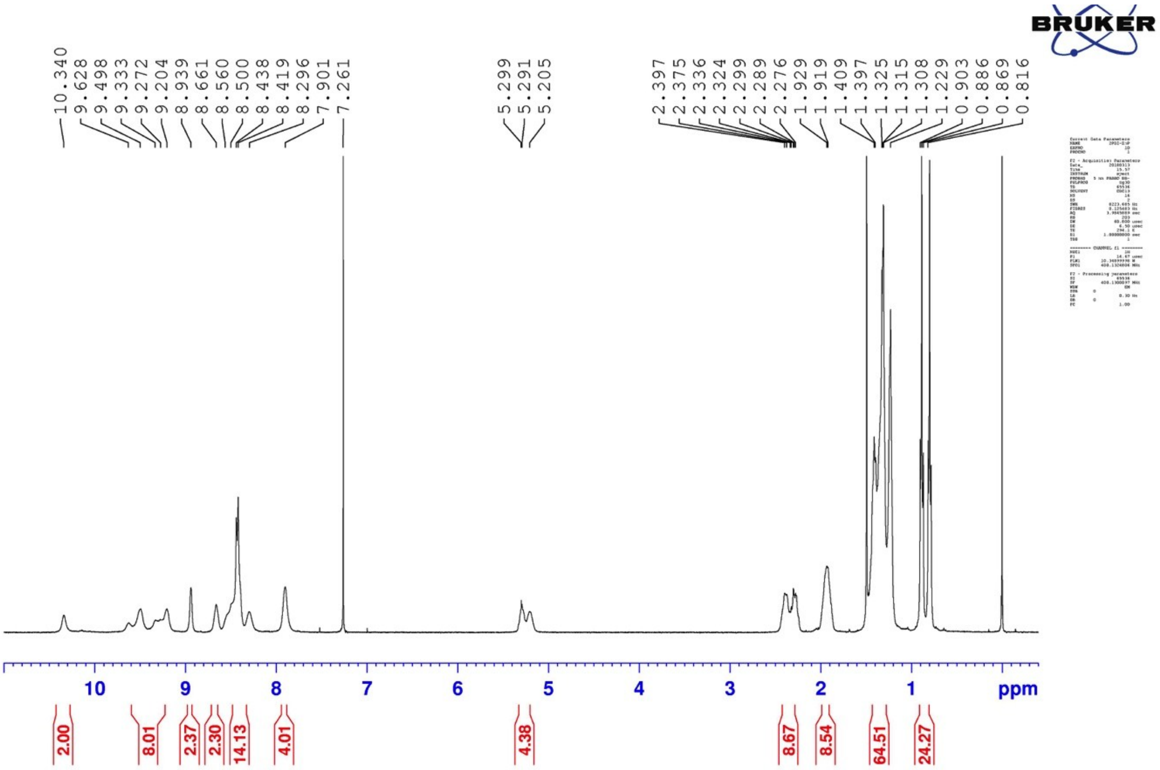


Figure S10. ^{1}H NMR spectrum of 2PDI-ZnP recorded in $CDCl_3$.

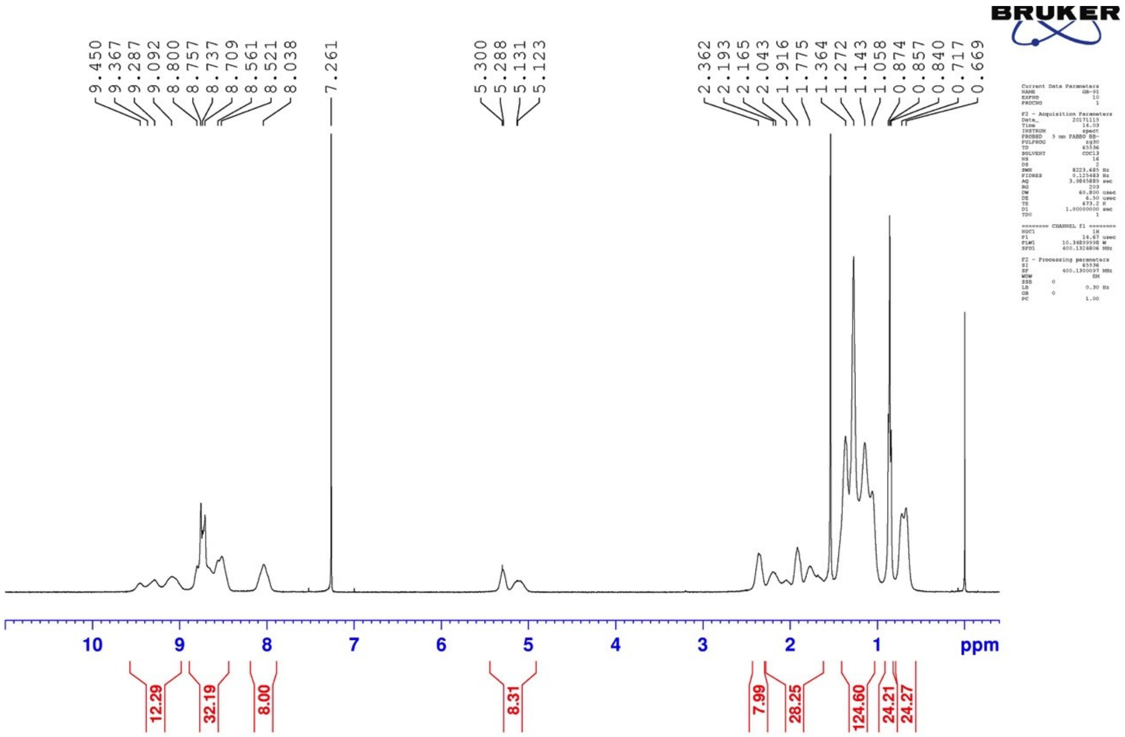


Figure S11. ^{1}H NMR spectrum 4PDI-ZnP recorded in $CDCl_3$.

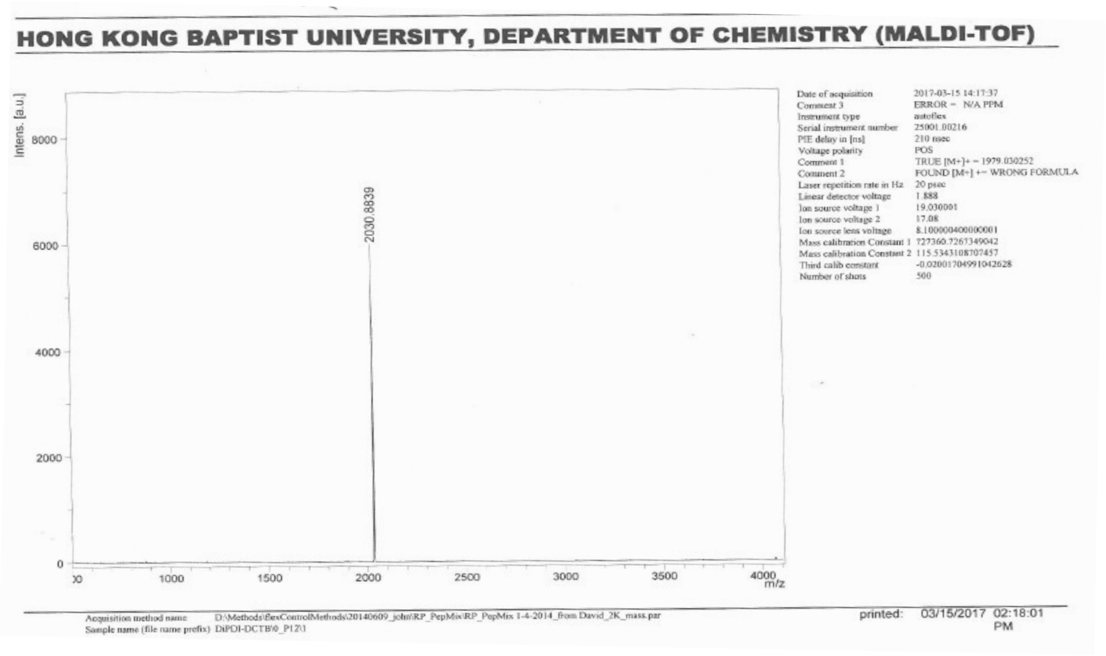


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Figure S12. The MALDI-TOF mass spectrum of 2PDI-ZnP.

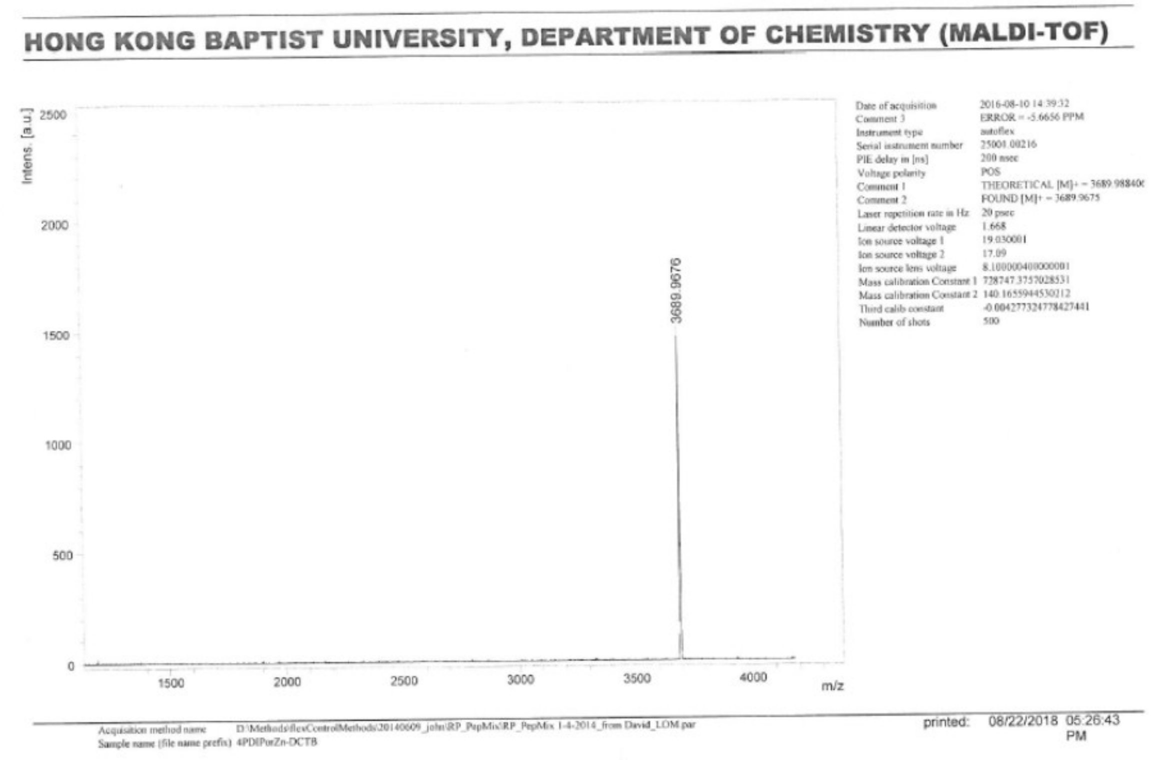

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Figure S13. The MALDI-TOF mass spectrum of 4PDI-ZnP.

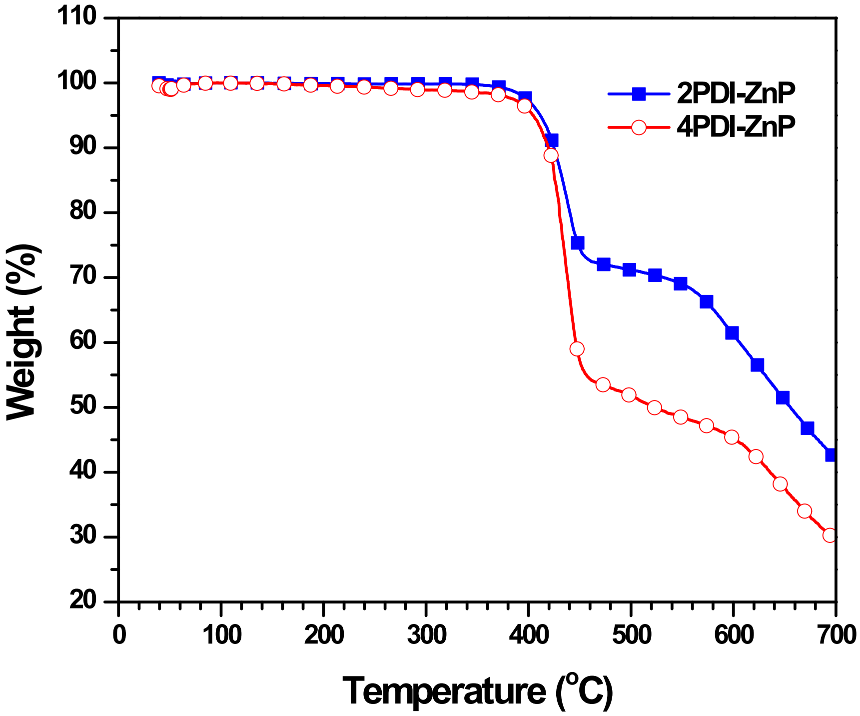

Figure S14. Thermogravimetric analysis of 2PDI-ZnP and 4PDI-ZnP.

References:

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3. Y. Huang, J. Hu, W. Kuang, Z. Wei, C. F. Faul, *Chem. Commun.* **2011**, *47*, 5554–5556.
4. W. Jiang, L. Ye, X. Li, C. Xiao, F. Tan, W. Zhao, J. Hou, Z. Wang, *Chem. Commun.* **2014**, *50*, 1024–1026.