Development of n-Type Porphyrin Acceptors for Panchromatic Light-Harvesting Fullerene-Free Organic Solar Cells

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The development of n-type porphyrin acceptors is challenging in organic solar cells. In this work, we synthesized a novel n-type porphyrin acceptor, PZn-TNI, via the introduction of the electron withdrawing naphthalene imide (NI) moiety at the meso position of zinc porphyrin (PZn). PZn-TNI has excellent thermal stability and unique bimodal absorption with a strong Soret band (300–600 nm) and weak Q-band (600–800 nm). The weak long-wavelength absorption of PZn-TNI was completely covered by combining the low bandgap polymer donor, PTB7-Th, which realized the well-balanced panchromatic photon-to-current conversion in the range of 300–800 nm. Notably, the one-step reaction of the NI moiety from a commercially available source leads to the cheap and simple n-type porphyrin synthesis. The substitution of four NIs in PZn ring induced sufficient n-type characteristics with proper HOMO and LUMO energy levels for efficient charge transport with PTB7-Th. Fullerene-free organic solar cells based-on PTB7-Th:PZn-TNI were investigated and showed a promising PCE of 5.07% without any additive treatment. To the best of our knowledge, this is the highest PCE in the porphyrin-based acceptors without utilization of the perylene diimide accepting unit.

Keywords: porphyrin acceptors, n-type porphyrins, organic solar cells, non-fullerene acceptors, panchromatic absorption

INTRODUCTION

For decades, organic solar cells (OSCs) have been studied as a portable and low-cost power generator due to their unique advantages: light-weight, use of earth-abundant organic materials, solution-processability and flexibility. The power conversion efficiency (PCE) of OSCs, an important parameter to determine the performance of the OSCs, has been continuously improved by optimization of light-harvesting in active layers and hole/electron charge transport pathways (Zhan et al., 2015; Zhao J. et al., 2016; Lin et al., 2017; Che et al., 2018; Hou et al., 2018). In the 2000s, low-bandgap polymer donors and n-type fullerene acceptors blended OSCs were developed to make broad absorption in the active layer. Polymer donors showing a strong absorption coefficient were responsible for light-harvesting and exciton generation, while the n-type fullerenes effectively separate and transfer the electrons to the electrode (Kim et al., 2006; Liang et al., 2010; Li et al., 2012; Liao et al., 2013). However, this was not enough to cover all the visible band by blending polymer
donors and fullerene acceptors. In the 2010s, new types of OSCs replaced the fullerenes with strong light-harvesting organic non-fullerene acceptors (NFAs). The active layer was composed of organic donors and NFAs, called fullerene-free OSCs (Cheng et al., 2017; Lin et al., 2017; Tang et al., 2018; Yan et al., 2018). Due to the strong absorption of both NFAs and organic donors in the visible area, their complementary absorption is important to achieve panchromatic photon-to-current conversion in the active layer. There are several successful strategies for panchromatic absorption in the visible and near infra-red area. The most common approach is mixing wide-bandgap donors and low-bandgap small-molecule NFAs such as ITIC (Zhao W. et al., 2016, 2017; Lin et al., 2017; Yao et al., 2017; Zhao F. et al., 2016, 2017; Liang et al., 2017; Eom et al., 2018). Another approach is mixing low-bandgap donors and wide-bandgap NFAs (e.g., blending of PTB7-Th and perylene-diimide (PDI)-based acceptor) (Wu et al., 2016; Duan et al., 2017; Liang et al., 2017; Eom et al., 2018). The red-dye PDIs enable a strong absorption in the short-wavelength area of 400–600 nm, while showing effective n-type characteristics.

As a new approach for panchromatic absorption in an active layer, utilization of a nature-inspired porphyrin dye has recently emerged in OSCs (Gao et al., 2015; Li et al., 2016; Hadmojo et al., 2018). The porphyrin dyes have peculiar bimodal absorption characteristics composed of Soret and Q bands; strong transition from ground state (S0) to second excited state (S2) yields the Soret band, while the weak transition from S0 to first excited state (S1) provides the Q-band. Thus, the strong Soret absorption of porphyrin dyes enables efficient short-wavelength absorption in the 400–600 nm, which can be blended with low-bandgap donors having a dominant absorption in the 600–800 nm for panchromatic absorption. In addition, the long-wavelength absorption of the Q-band intensifies the light harvesting in the low bandgap area where abundant solar flux exists. However, most of the developed artificial porphyrin derivatives are p-type materials and only a few porphyrin derivatives currently show n-type characteristics with a promising PCEs over 5% (Liang et al., 2017; Eom et al., 2018). The excessive ordering of PTB7-Th:PZn-TNI blend film without additive treatment, which resulted in the highest PCE of 5.07% (VOC = 0.72 V, JSC = 13.84 mA cm−2, and fill factor = 0.51) in the additive-free OSCs. The excessive ordering of PTB7-Th:PZn-TNI film via pyridine additive rather reduced the photovoltaic performances. Our successful utilization of NI moiety in the PZn core will broaden and diversify the synthetic approaches for developing high-efficiency porphyrin acceptors.

**EXPERIMENTAL**

**Synthesis**

5,10,15,20-tetrakis-ethyl porphyrin Zinc (II) (3): Macrocyclic porphyrin compound 1 was synthesized according to the reported general procedure (Yen et al., 2006). Compound 1 (0.90 g, 1.29 mmol) and zinc acetate (2.4 g, 13.1 mmol) were dissolved in the co-solvent (200 ml) of dichloromethanemethanol = 9:1 v/v%. The resulting mixture was refluxed at 65°C for 24 h. After removing the solvents, the remaining solid was rinsed with dichloromethane (300 ml) to give a purple solid compound 2 (0.65 g, yield: 62%). Without further purification, compound 2 was used directly to make compound 3. Compound 2 (2.06 g, 0.79 mmol) was dissolved in 100 mL anhydrous tetrahydrofuran (THF). Tetra-n-butylammonium fluoride solution 1.0 M in THF (3.6 ml, 3.6 mmol) was slowly added to the reaction mixture. The resulting mixture was stirred at room temperature for 4 h. After removing the solvents, the crude solid product was rinsed sequentially with methanol, dichloromethane, water and acetone. After drying the dark purple solid product 3 (180 mg, yield: 49%), it was immediately used in the next step to prevent the coupling reaction between the two terminal alkynes. 1H NMR (THF-d8, 400 MHz, ppm): δ 9.60 (s, 2H), 5.37 (s, 1H), 8.56 (d, J = 6.4 Hz, 1H), 8.40 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 7.6 Hz, 1H), 7.82 (m, 1H), 4.14 (t, J = 8.0 Hz, 2H), 1.70 (m, 1H), 1.24 (br, 27H), 0.87 (t, J = 7.2 Hz, 3H).

PZn-TNI: Compound 3 (100 mg, 0.212 mmol), compound 4 (1.06 g, 2.12 mmol), Pd2(dbta)3 (40 mg, 0.044 mmol) and AsPb3 (100 mg, 0.33 mmol) were dissolved in dry THF (15 mL) and triethylamine (15 mL). The reaction mixture was stirred at 65°C for 4 days under N2 atmosphere, and then quenched by distilled water. The organic layer was extracted using dichloromethane and water, and then the moisture in the organic solution was removed by Na2SO4. After evaporating the solvents, the solid residue was purified by column chromatography using an eluent of CH2Cl2:n-hexane = 4:1 to give a yellow solid compound 4 (3.0 g, 66%). 1H NMR (CDCl3, 400 MHz, ppm): δ 8.65 (d, J = 6.4 Hz, 1H), 8.56 (d, J = 7.6 Hz, 1H), 8.40 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 7.6 Hz, 1H), 7.82 (m, 1H), 4.14 (t, J = 8.0 Hz, 2H), 1.70 (m, 1H), 1.24 (br, 27H), 0.87 (t, J = 7.2 Hz, 3H).

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RESULTS AND DISCUSSION

The synthetic procedure of P_{Zn}-TNI was recorded in Scheme 1 and in the Supporting Information (SI) in detail. The porphyrin ring 1 was synthesized from pyrrole and 3-(trimethylsilyl)propionaldehyde in the presence of BF$_3$·Et$_2$O followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). The zinc porphyrin (P$_{Zn}$) compound 2 was obtained using Zn(OAc)$_2$. The deprotection of TMS group by tetra-n-butylammonium fluoride (TBAF) was performed immediately before synthesizing the final acceptor, P$_{Zn}$-TNI. 4-Bromo-1,8-naphthalic anhydride purchased from Sigma-Aldrich was alkylated with 2-hexyldexylamine to give a compound 4. This one-step reaction to prepare the electron withdrawing NI unit is highly beneficial in terms of time and cost for achieving the n-type porphyrins. The final porphyrin acceptor, P$_{Zn}$-TNI, was achieved via Sonogashira coupling with P$_{Zn}$ compound 3 and excess of NI compound 4, which was identified by $^1$H-NMR and matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) (Figures S1–S4). The synthesized P$_{Zn}$-TNI showed excellent solubility in common organic solvents such as tetrahydrofuran (THF), dichloromethane (DCM), and chloroform (CF). In addition, it has excellent thermal stability, which was determined by thermal gravimetric analysis (TGA), with a 5% weight loss temperature (T$_{5d}$) of 412°C under an N$_2$ atmosphere (Figure S5).

Absorption spectra of P$_{Zn}$-TNI were measured in solution and the film state, as shown in Figure 1. P$_{Zn}$-TNI exhibited clear bimodal absorption composed of the Soret band (300–600 nm) and Q-bands (600–800 nm); the maximum absorption peaks of P$_{Zn}$-TNI were 479 and 713 nm in solution, and 478 and 719 nm in the film. The absorption of P$_{Zn}$-TNI was complementary to that of the low-bandgap donor polymer, PTB7-Th, which induced a well-balanced short- and long-wavelength absorption in the entire wavelength of 300–800 nm (Figure 2B). Notably, the film of P$_{Zn}$-TNI showed broadened
and red-shifted Q-band absorption spectra compared to that in solution, indicating the enhanced intermolecular $\pi-\pi$ stacking in the film state. Since the planar NIs and $\text{PZn}$ are connected by an sp-hybridized ethyne $\pi$-bridge, $\text{PZn-TNI}$ possesses a highly planar conjugated backbone for efficient intermolecular stacking. The optical bandgap ($E_{\text{pt}}$) of $\text{PZn-TNI}$ was 1.63 eV, which was calculated from the absorption onset wavelength of 761 nm in the film. We previously reported the pyridine additive effect on the molecular ordering of porphyrin derivatives; pyridine enhances the intermolecular ordering of porphyrin derivatives via coordination to the zinc (Hadmojo et al., 2017). As shown in Figure 1B, the absorption of $\text{PZn-TNI}$ was significantly broadened and red-shifted compared to that without pyridine treatment, resulting in the bathochromic shift of 42 nm in the Soret band and 15 nm in the Q-band. This supports our previous hypothesis for the pyridine effect on the molecular ordering and confirms that pyridine enhances the intermolecular ordering of $\text{PZn-TNI}$ in the film states.

To evaluate the energy levels of $\text{PZn-TNI}$, the highest occupied molecular orbital (HOMO) energy levels and the lowest unoccupied molecular orbital (LUMO) energy levels were measured using cyclic voltammetry. The oxidation and reduction onset potentials of $\text{PZn-TNI}$ were 1.07 and $-0.80$ V, respectively, which corresponds to HOMO levels ($E_{\text{HOMO,CV}}$) and LUMO levels ($E_{\text{LUMO,CV}}$) of $-5.50$ and $-3.62$ eV, respectively. The optical LUMO energy level ($E_{\text{LUMO,UV}}$) was calculated to be $-3.87$ eV from $E_{\text{HOMO,CV}}$ and $E_{\text{pt}}$ of $\text{PZn-TNI}$. The energy diagram of the PTB7-Th and $\text{PZn-TNI}$ was shown in Figure 1D, and the $E_{\text{HOMO,CV}}$, $E_{\text{LUMO,CV}}$, and $E_{\text{LUMO,UV}}$ of polymer donor (PTB7-Th) were taken from our previous measurement (Zhang et al., 2015; Hadmojo et al., 2016). The LUMO energy level of $\text{PZn-TNI}$ is suitable for electron transport from PTB7-Th to $\text{PZn-TNI}$, while the HOMO of $\text{PZn-TNI}$ is appropriate for hole transport from $\text{PZn-TNI}$ to PTB7-Th (Marcus, 1963; Clarke and Durrant, 2010). The optical and electrochemical properties of $\text{PZn-TNI}$ are summarized in Table 1.

Porphyrin acceptor-based fullerene-free OSCs were fabricated by blending PTB7-Th and $\text{PZn-TNI}$ (Figure 2A). The current density-voltage ($J-V$) characteristic of PTB7-Th:$\text{PZn-TNI}$ devices was investigated via changing the weight ratio between PTB7-Th and $\text{PZn-TNI}$, and the photovoltaic performance was optimized at the weight ratio of 1:1.5 w/w. The photovoltaic properties are summarized in Figure 2C, Figure S6, and Table 2. The best PCE of 5.07% was achieved with a $V_{\text{OC}}$ of 0.72 V, a $J_{\text{SC}}$ of 13.84 mA cm$^{-2}$, and FF of 0.51 (Figure 2C). As shown in Figure 2D, the external quantum efficiency (EQE) spectra of PTB7-Th:$\text{PZn-TNI}$ devices cover the entire visible area of 300–800 nm and
showed the panchromatic photon-to-current conversion due to the complementary solar flux absorption between PTB7-Th and PZn-TNI. Notably, the additive-free film-formation process provided superior photovoltaic performance compared to the pyridine-assisted one as shown in Figure 2C. As shown in Figure 2D, the EQE was increased in the entire wavelength, which indicates that hole/electron transport properties of both PTB7-Th and PZn-TNI are improved in the additive-free devices.

To understand the charge recombination mechanisms of PTB7-Th:PZn-TNI devices in the presence and absence of pyridine additive, the J-V characteristics were investigated as a function of the illumination intensity. The power law dependence of $J_{SC}$ on the illumination intensity is generally expressed as $J_{SC} \propto I^\alpha$, where $I$ is the light intensity and $\alpha$ is an exponential factor (Figure 3A) (Blom et al., 2007; Azmi et al., 2016). The $\alpha$ value of the PTB7-Th:PZn-TNI devices was close to unity regardless of additive treatment, indicating the negligible bimolecular recombination in PTB7-Th:PZn-TNI devices. However, the $V_{OC}$ vs. illumination intensity was highly affected by the pyridine treatment. Assuming there is no trap-assisted recombination under an open-circuit condition, the slope of $V_{OC}$ vs. the illumination intensity produces $1.00 \frac{kT}{q}$ (Mihailetchi et al., 2006). The higher value of $kT/q$ indicates the more probability of trap-assisted recombination under an open-circuit condition (Mandoc et al., 2007; Azmi et al., 2016). As shown in Figure 3B,
TABLE 2 | Photovoltaic properties of PTB7-Th:PZn-TNI devices.

| PTB7-Th:PZn-TNI | $\mu_h$ (cm$^2$ V$^{-1}$s$^{-1}$) | $\mu_e$ (cm$^2$ V$^{-1}$s$^{-1}$) | $V_{OC}$ (V) | $J_{SC}$ (mA cm$^{-2}$) | FF | PCE (PCEave)$^a$(%) |
|----------------|-----------------|-----------------|----------|-----------------|---|-----------------|
| No additives   | 1:1             | –               | –        | 0.73             | 11.25 | 0.52           | 4.29 (3.97) |
| 1:1.5          | $2.9 \times 10^{-4}$ | $2.5 \times 10^{-6}$ | 0.72     | 13.84            | 0.51 | 5.07 (4.85)   |
| 1:2            | –               | –               | 0.71     | 13.81            | 0.49 | 4.82 (4.59)   |
| 1% (v/v) pyridine | 1:1.5          | $2.4 \times 10^{-4}$ | $1.3 \times 10^{-6}$ | 0.78 | 6.76 | 0.34 | 1.82 (1.61) |

$^a$Average PCEs more than 10 devices.

PTB7-Th:PZn-TNI devices with and without additives show the slope of 2.63 and 1.93 kT/q, respectively. This implies that PTB7-Th:PZn-TNI devices in the absence of additives have the lowest trap-assisted recombination in an open-circuit condition. The hole and electron transport properties of PTB7-Th:PZn-TNI devices were measured by a space-charge-limited-current (SCLC) analysis (Figures 3C,D) (Mihailetchi et al., 2005). The electron- and hole-only devices were fabricated with a structure of ITO/ZnO/PTB7-Th:PZn-TNI/ZnO/Al and ITO/PEDOT:PSS/PTB7-Th:PZn-TNI/MoO$_x$/Ag, respectively. In the presence of pyridine additive, the hole and electron mobilities of PTB7-Th:PZn-TNI were $2.4 \times 10^{-4}$ and $1.3 \times 10^{-6}$ cm$^2$ V$^{-1}$s$^{-1}$, respectively, whereas, in the absence of additives, the hole and electron mobilities were increased to $2.9 \times 10^{-4}$ and $2.5 \times 10^{-6}$ cm$^2$ V$^{-1}$s$^{-1}$, respectively. Thus, it is expected that the pyridine additive worsens the nanomorphology of PTB7-Th:PZn-TNI devices via excessive intermolecular aggregation.

The morphology of the PTB7-Th:PZn-TNI active layer was investigated by atomic force microscopy (AFM) (Figure 4) and two-dimensional grazing incidence X-ray diffraction (2D-GIXD) analyses (Figure 5). In AFM images, PTB7-Th:PZn-TNI blended film possesses bicontinuous crystalline domains in the absence of additives (Figures 4A,B), whereas the addition of pyridine additive intensifies the intermolecular ordering of PZn-TNI domains, leading to severe phase segregation between PTB7-Th and PZn-TNI (Figures 4C,D). The 2D-GIXD results also support the AFM analysis. Additive-free PTB7-Th:PZn-TNI film showed clear $\pi$-$\pi$ stacking orientation (010) peak at $\sim 1.6$ Å along the $q_z$ axis, which indicates the face-on orientation with a $d$-spacing of $\sim 3.9$ Å (Figures 5B,C). However, the pyridine-treated PTB7-Th:PZn-TNI film showed the increased $\pi$-$\pi$ stacking...
interaction and induced the phase aggregation (Figure 5C). The (010) peak in the blend film is assigned to the orientation of PTB7-Th domains (Figure 5A), which implies that the decrease in the photovoltaic performances in presence of pyridine is probably due to the aggregation of the PTB7-Th domains in the PTB7-Th:PZn-TNI blend film. As a result, the PZn-TNI having highly planar molecular structure possesses the sizable π-π intermolecular stacking and crystalline nanomorphology in the additive-free solvent system, which means that no more post-treatment is required in PTB7-Th:PZn-TNI blend system. In addition, the additive-free system can prevent undesirable morphological change and photo-oxidation degradation by additives in the active layer (Li et al., 2017).

CONCLUSIONS

We have synthesized a novel porphyrin acceptor, PZn-TNI, by incorporating four naphthalene imide (NI) units at the meso position of the PZn core. PZn-TNI showed unique bimodal absorption with a strong Soret band and a weak Q-band. The insufficient long-wavelength absorption of PZn-TNI was covered by a low-bandgap donor, PTB7-Th. As a result, bulk heterojunction fullerene-free OSCs composed of PZn-TNI and PTB7-Th showed panchromatic photon-to-current conversion covering entire area of 300–800 nm. The PTB7-Th:PZn-TNI devices exhibited a promising PCE of 5.07%, which is the highest and the first promising PCE in the porphyrin-based acceptors except for those utilizing the PDI units. Notably, the additive-free solution process provided the best photovoltaic performance, whereas the pyridine additive had a negative effect on the nanomorphology by the excessive molecular aggregation of the PTB7-Th:PZn-TNI film. The planar backbone structure of PZn-TNI assists the sizable molecular ordering in the PTB7-Th:PZn-TNI film without additive treatment, which is favorable for practical applications.

AUTHOR CONTRIBUTIONS

IJ and SY conceived the ideas and designed the PZn-TNI. U-HL synthesized all the materials and JK assisted the characterization of all the materials. S-YJ supervised all the device fabrication and optimization. WH fabricated all the OSC devices and SE assisted the device characterization.

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SUPPLEMENTARY MATERIAL

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