Synthesis, characterization and photovoltaic properties of 2-fluor-derivatives of porphyrin as near-infrared dyes

Ashis K Sarker

Abstract

We designed and synthesized PznDPP-P-2F molecule, in which a porphyrin ring was linked to two diketopyrrolopyrrole units by ethynylene bridges. This new donor material is characterized by using NMR, MALDI-TOF-Mass, UV/Visible spectrophotometer and cyclic voltammetry. The resulted material exhibited a very low energy band gap of 1.49 eV and a broad light absorption to 830 nm. The photovoltaic performances of these donor materials were successfully evaluated in organic solar cells. PCBM was used as acceptor moiety in this work. Consequently, the OPV based on PznDPP-P-CF3 showed JSC of 11.32 mA/cm², Voc of 0.66 V, a FF of 0.62, the overall power conversion efficiency of (g) 4.65%. The easy synthetic route and purification technique provide the viability of this donor material as future OPV development.

Keywords: Diketopyrrolopyrrole, boronic acid, photovoltaics, cyclic voltammetry, efficiency

Introduction

Solution-processed small molecule (SM) bulk heterojunction organic solar cells (BHJ OSCs) have received intense study very recently because of the defined molecular structure and weight, high purity, and good batch-to-batch reproducibility in cell performance. These advantages make it easier to understand the relationships between the molecular structures and device performance and realize the ultimate performance limit of these materials and devices. Not surprisingly, dramatically increased PCEs up to 10% have been reported for single layer SM BHJ solar cells, comparable to the best of polymer solar cells. Inspired by the natural photosynthetic systems which utilize chlorophylls to absorb light and carry out photochemical charge separation to store light energy, porphyrins and their derivatives have been explored for a long time as the active materials in dye-sensitized solar cells with the highest efficiency of 13%, and in BHJ OSCs but with very low PCEs.

Recently, A-π-D-π-A structural design strategy to synthesize porphyrin-based donor materials has been studied, and successfully achieved high PCEs more than 4% employing PCBM as the acceptor units, demonstrating the potential of porphyrins for OSCs by their virtues of high molar absorption coefficients, easy chemical structure modification, and unique photophysical properties. To date, however, a very limited number of porphyrin-based materials have been developed with efficiencies higher than 4% in BHJ OSCs, since it is very challenging to achieve a balance between solubility and intermolecular interactions for porphyrin molecules, simultaneously targeting optically positioned energy levels (to ensure a high Voc) and an increased solar flux coverage and charge carrier mobility.

To extend the backbone conjugation and enhance intermolecular π-π interaction, we designed and prepared porphyrin small molecule Pzn-DPP-P-CF3 (Scheme 2) in which DPP was symmetrically conjugated to porphyrin core, then ended with alkyl chain terminal units. Detailed studies show that the appropriate alkyl chains on meso position and DPP conjugated backbone can not only enhance the directional intermolecular π-π stacking in films but also form the blend films with PCBM with characteristics of bicontinuous, interpenetrating networks required for efficient charge separation and transportation. The processing engineering for their blend films with PCBM afforded power conversion efficiencies of 4.56% in BHJ OSC based Pzn-DPP-P-2F.
Experimental Section  
Materials  All air and water-sensitive reaction were performed under nitrogen atmosphere. All of the chemicals were purchased from Sigma-Aldrich and Samchun South Korea. Organic solvents used in this work were purified using standard process. The other materials were of the common commercial level and used as received. Diketopyrrolopyrrole (DPP), N-bromosuccinimide (NBS), Pd(PPh₃)₄, phenylboronic acid, 2-fluorophenylboronic acid, were purchased from Sigma-Aldrich. Chloroform, Tetrahydrofuran (THF), Magnesium Sulfate (MgSO₄), Potassium carbonate (K₂CO₃) were purchased from Samchun chemicals.  
Methods  Column chromatography was performed using silica gel 230-300 mesh (purchased from Aldrich) as the solid support. All NMR spectra were recorded on a Bruker Advance DXP 400 MHz spectrometer at 25 °C in CDCl₃ and THF. ¹H NMR chemical shifts are reported in δ units, part per million (ppm) relative to the chemical shift of residual solvent. Deuterated solvents were used as received from Aldrich. Reference peaks for chloroform in ¹H NMR spectra were set at 7.18 ppm. Molecular masses were measured by Matrix-assisted laser desorption/ionization time-of-flight mass spectrometer (MALDI-TOF-MS). MALDI-TOF-MS was performed on Bruker Daltonics LR20 with diethanol (1,8,9-trihydroxyanthracene) and HCCA (α-Cyano-4-hydroxycinnamic acid) as the matrix. The absorption spectra were measured on a SHIMADZU/UV-2550 model UV-visible spectrophotometer. Recycling SEC was performed on JAI model LC9021 equipped with JAIGEL-1H, JAIGEL-2H and JAIGEL-3H columns using THF (DKUSAN) as the eluent. Cyclic voltammetry was performed on a BAS 100/B electrochemical analyzer with a three-electrode cell in 0.1 N Bu₄NBF₄ solution in acetonitrile at a scan rate of 50 mV/s.  
Synthesis of DPP-Br (2)  
To a stirred solution of 2,5-bis(2-ethylhexyl)-3,6-di(thiophen-2-yl) pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (5.00 g, 9.52 mmol) in dry chloroform (300 mL), N-bromosuccinimide (NBS, 1.69 g, 9.52 mmol) was slowly added at 0 °C. The mixture was allowed to warm up to room temperature and stirred overnight. The reaction mixture was poured into water and then extracted with chloroform. The combined organic layers were washed with water and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure and the mixture of products was separated using column chromatography (silica gel, eluent gradient 8:2 > 5:5 hexane:DCM). The target compound (2.59 g) was obtained as a red flaky powder (yield = 2.59 g, 45%). ¹H NMR (400 MHz, CDCl₃) δ: 8.93 (d, 1H), 8.90 (d, 1H), 7.67-7.70 (m, 4H), 7.40 (d, 1H), 7.15-7.10 (m, 2H), 4.07-4.02 (m, 4H).  
Synthesis of porphyrin derivatives 6  
To a degassed solution of dipyrromethane (0.5 g, 3.43 mmol) and corresponding aldehyde (1.24 g, 3.43 mmol) in DCM (500 mL) was added trifluoroacetic acid (0.23 mL, 37.3 mM). The solution was stirred under nitrogen atmosphere at 23 °C for 4 h, and charged with DDQ (1.17 g, 5.14 mmol). Then, the mixture was stirred for an additional 1 h. The mixture was basified with Et₃N (0.58 mL) and filtered through silica. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (silica gel) using DCM/hexane = 1/2 as eluent. The products were recrystallized from MeOH/DCM to give the product (1.02 g, 30%) as a purple powder. ¹H NMR (CDCl₃, 400 MHz) δ 10.13 (s, 2H), 9.26 (d, 4H), 8.96 (d, 4H), 7.51 (t, 2H), 6.92 (d, 4H), 2.65 (d, 4H), 1.76 (m, 2H), 1.33 (m, 12H), 1.25 (m, 20H), 0.89 (t, 12H) -3.12 (s, 2H). MS (MALDI-TOF): m/z 811.24 [M⁺]; C₃₂H₁₂F₁₀N₄ (812.2).  
Synthesis of 5,15-Dibromo-porphyrin derivatives 7  
To a stirred solution of compound 6 (0.35 g, 0.36 mmol) in DCM (150 mL) was slowly added a solution of NBS (0.13 g, 0.75 mmol) in DCM (50 mL) in a period of 6 h at 0 °C under inert condition. The reaction was quenched with adding acetone (30 mL). After the solvent was removed under reduced pressure, the residue was purified by column chromatography (silica gel) using DCM/hexane = 1/2 as eluent. Recrystallization from MeOH/DCM gave the product.
H$_2$d MeOH (25 mL) was stirred at 23 °C for 3 h. The green organic layer was removed with water (10 mL), and the mixture was extracted with DCM (3 x 10 mL). The combined extracts were washed with water and dried over anhydrous MgSO$_4$. The solvent was removed under reduced pressure to give the product (0.25 g, 96%). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 9.26 (d, 4H), 8.96 (d, 4H), 7.51 (t, 2H), 6.92 (d, 4H), 2.65 (d, 4H), 1.76 (m, 2H), 1.33 (m, 12H), 1.25 (m, 20H), 1.02 (t, 12H) 0.89 (t, 30H). MS (MALDI-TOF): m/z 1032.39 [M$^+$]; C$_{32}$H$_{32}$F$_{10}$N$_4$ (1033.15).

Synthesis of [5,15-Dibromo-porphinato] zinc (II) derivatives 8
A suspension of the compound 7 (0.291 g, 0.243 mmol) and Zn(0Ac)$_2$ x 2H$_2$O (0.135 g, 0.615 mmol) in a mixture of DCM (110 mL) and MeOH (25 mL) was stirred at 23 °C for 3 h. The reaction was quenched with adding water (10 mL), and the mixture was extracted with DCM (3 x 10 mL). The combined extracts were washed with water and dried over anhydrous MgSO$_4$. The solvent was removed under reduced pressure to give the product (0.25 g, 96%). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 9.26 (d, 4H), 8.96 (d, 4H), 7.51 (t, 2H), 6.92 (d, 4H), 2.65 (d, 4H), 1.76 (m, 2H), 1.33 (m, 12H), 1.25 (m, 20H), 0.89 (t, 12H). MS (MALDI-TOF): m/z 969.03 [M$^+$]; C$_{32}$H$_{32}$F$_{10}$N$_4$ (969.57).

The compound 8 (50 mg, 42 μmol), anhydrous toluene (10 mL), (trisopropylisopropylacetylene (37 μL, 168 μmol), and copper(I)iodide (1.2 mg, 6.3 μmol) in a round-bottom flask were stirred under nitrogen. Triethylamine (1 mL) was then added into the mixture, which was then degassed by N$_2$ bubbling. After the addition of bis (triphenyl phosphine) palladium (II) dichloride (4.4 mg, 6.3 μmol), the solution was heated at 85 °C overnight. The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel) using CH$_2$Cl$_2$/CH$_3$OH (19/1) as eluent. Recrystallization from CH$_2$Cl$_2$/CH$_3$OH gave products 1 (29.7 mg, 30%). $^1$H NMR (400 MHz, THF-d$_8$, 25 °C) $\delta$ (ppm) $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 9.26 (d, 4H), 8.96 (d, 4H), 8.24 (d, 2H), 8.13 (d, 2H), 8.04 (d, 4H), 7.78 (d, 4H), 7.51 (t, 2H), 7.32 (d, 4H), 6.92 (d, 4H), 3.09 (m, 8H), 2.65 (d, 4H), 2.18 (m, 4H), 1.76 (m, 2H), 1.56 (m, 16H), 1.33 (m, 44H), 1.28 (m, 4H), 1.25 (m, 36H), 1.02 (t, 12H) 0.89 (t, 54H). MS (MALDI-TOF): m/z 2156.35 [M$^+$]; C$_{32}$H$_{32}$F$_{10}$N$_4$Zn (2156.24).

Results and Discussion

Synthesis

Pzn-DPP-P-2F containing meso substituent was synthesized as small molecule donor. The synthetic procedures of the porphyrin donor is outlined in Scheme 1 and summarized in the experimental part in detail. Briefly, monobromo-DPP was synthesized by controlled NBS bromination reaction of DPP at room temperature. DPP-P-F has been synthesized by Suzuki coupling reaction with DPP-Br and 4-fluorophenylboronic acid in basic condition. Br-DPP-P-2F has been synthesized by NBS bromination reaction with DPP-P-2F.

![Scheme 1: Synthetic route to Br-DPP-P-2F.](image)

Dipyromethane has been synthesized with pyrrole and aldehyde in an aqueous medium in the presence of an acid catalyst. 5,15-disubstituted cross-condensation and successive oxidation reactions of dipyromethane and substituted aldehyde. The Zn-incorporated porphyrin ring 8 was obtained via the metalation using zinc acetate and the meso-bromination reaction using bromosuccinimide (NBS). Trimethylsilyl acetylene was introduced to the Porphyrin...
derivative through the Sologashira coupling reaction, and this reaction was followed by the removal of the trimethylsilyl group to give ethynyl-bearing porphyrin 10. Porphyrin derivative X was synthesized according to the literature procedure. Finally, porphyrin donor 1 was synthesized using Br-DPP-P-2F and ethynyl-bearing prophyrin 10 by Sonogashira coupling. The molecular structures of the synthesized porphyrin small molecule was identified by $^1$H NMR and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS), which are recorded in the SI.

Optical properties
The UV/vis absorption spectra of Pzn-DPP-P-2F in CHCl$_3$ solution and film state are shown in Figure 1a and b, and corresponding spectroscopic data are summarized in Table 1. The absorption spectra of the porphyrin dyes exhibit a typical intense Soret band with 400-500 nm and less intense Q bands in a range of 550-700 nm. The Q bands of this molecule is higher intense than Soret band and red-shifted to 650-830 nm. For porphyrin moiety there is no absorption in the range of 500-600 nm. Highly conjugated DPP moiety connected with Acetylene Bridge covered the absorption in the range of 500-620 nm which is perfectly complementary absorption to the porphyrin ring. These DPP porphyrin can cover full visible range from 400 to 700 nm and extended to the NIR region up to 820 nm. DPP moiety attached with acetylene to the porphyrin will be the best choice for OPV application. Compared to the Pzn donor in a solution state, Q band absorption of the porphyrin derivative in a film state showed strong bathochromic shifts, indicating the formation of J-type aggregates. The full-width half-maximum (fwhm) of the Q-band absorption by the Pzn donor in film was ~100 nm higher than those in a solution state, implying that intermolecular interactions among the Pzn donors were very strong in a film state. Because DPP units and focal porphyrin are connected via ethyne bridges, Pzn donors possibly have planar backbone structures. Thus, high planarity would have contributed to strong molecular π-π interactions. We also choose the 2-(2-butyloctyl)thiophene molecule connected to the β-position of porphyrin to compare the optical properties of the molecule. Meso substituted 2-(2-butyloctyl)thiophene shown Q band at 750 nm. The main difference from porphyrin core is that this molecule contains two additional butyloctyl groups on the thiophene group which results in a 150 nm red shift of the Q-band, indicating that the butyloctyl groups are not only favorable for suppressing dye aggregation but also can extend the absorption to longer wavelengths and achieving a striking onset absorption wavelength of 830 nm.
**Electrochemical properties**

To evaluate the matching of energy levels between the porphyrin donor and PCBM, the highest occupied molecular orbital (HOMO) energy levels and the lowest unoccupied molecular orbital (LUMO) energy levels of porphyrin donor was determined using cyclic voltammetry (CV, Figure 2) and optical bandgap values. These results are summarized in Table 2. Electrochemical cyclic voltammetry of Pzn-DPP-P-CF₃ was carried out in acetonitrile solution (Figure 2) to measure the energy levels of Pzn-DPP-P-CF₃. The onset oxidation potential (E⁰ₒₓ) of Pzn-DPP-P-F was estimated to be 0.06 V vs. Ag/AgCl. The highest occupied molecular orbital (HOMO) energy level was determined to be -5.22 eV on the basis of the equation: E_{HOMO} = -e(E⁰ₒₓ) + 4.78 (eV). The LUMO energy levels of the three are determined by the reduction potential from cyclic voltammetry. And the lowest unoccupied molecular orbital (LUMO) energy level was calculated to be -3.67 eV from the equation E_{LUMO} = -e(E_{red}²) + 4.78 (eV). Figure 3 shows the energy level diagram and the energy level of Pzn-DPP-P-F is suitable of its application as a donor in bulk heterojunction solar cells. The electron donating meso-butylhexylthiophene groups raised the HOMO energy levels of the porphyrin donors. The electron donating meso-butylhexylthiophene groups decreased the HOMO energy levels of the porphyrin donors. Thus, the electrochemical bandgaps of porphyrin donor Pzn-DPP-P-CF₃ was determined as 1.55 eV, by the oxidation reduction values of the films. The energy levels of PCBM was measured using identical methods. The HOMO and LUMO energy levels of the porphyrin donor and PCMB are summarized in Table 2. The energy level of porphyrin donor was appropriate to collect holes from PCBM and to transfer electron to PCBM.

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**Table 1: Optoelectronic properties of Pzn-DPP-P-2F in solution and film state**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Band λ_{ab} (nm) (log ε)×10⁵</th>
<th>Onset λ_{ab} (nm)</th>
<th>E_{g,opt} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pzn-DPP-P-2F (soln)</td>
<td>330 (0.54), 465 (0.1.15), 580 (1.00), 750 (1.30)</td>
<td>825</td>
<td>1.50</td>
</tr>
<tr>
<td>Pzn-DPP-P-2F (film)</td>
<td>350, 475, 600, 750, 810</td>
<td>1000</td>
<td>1.24</td>
</tr>
</tbody>
</table>

**Table 2: Electrochemical properties of molecule Pzn-DPP-P-2F**

<table>
<thead>
<tr>
<th>Donor</th>
<th>E_{HOMO} (eV)</th>
<th>E_{LUMO} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pzn-DPP-P-2F</td>
<td>-5.27</td>
<td>-3.27</td>
</tr>
<tr>
<td>PCBM</td>
<td>-6.00</td>
<td>-3.95</td>
</tr>
</tbody>
</table>

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Fig 1: Absorption spectra (a) in solution (chloroform) and (b) solid film of Pzn-DPP-P-2F

**Fig 2:** Cyclic voltammetry of Pzn-DPP-P-2F (a) Oxidation and (b) Reduction

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Table 2: Electrochemical properties of molecule Pzn-DPP-P-2F
Photovoltaic properties.
Solution-processed BHJ OSCs were fabricated using porphyrin Pzn-DPP-P-2F as the electron donor material and PCBM as the electron acceptor materials with an inverted device structure of ITO/ZnO/BHJ/MoOx/Ag. ZnO (30 nm) acts as an electron transport layer. Bulk heterojunctions as active layers were achieved by mixing porphyrin Pzn-DPP-P-2F as electron donor and PCBM (1:1.2 w/w) with DIO (0.8 v/v %) and pyridine (0.5 v/v %) as additives. The active materials were dissolved in chloroform and stirred for 2 h in an ambient environment. The donor concentration was 7.5 mg/mL. The thickness of the active layer was 100 nm. MoOx (8 nm) as the hole transport layer and Ag (100 nm) as the electrode were deposited using thermal evaporation at low pressure ($10^{-6}$ bar). The active area was measured to be 0.707 cm$^2$. The current density-voltage (J-V) characteristics of the porphyrin donor:PCBM-based SM-OPV devices are shown in Figure 4, and the results are summarized in Table 3. The Pzn-DPP-P-2F-OPV devices fabricated from Meso substituted 2-(2-butylhexyl)thiophene donor Pzn-DPP-P-2F showed higher PCEs with improved Voc and FF values. Thus, the porphyrin donor Pzn-DPP-P-2F:PCBM device attained the highest PCE of 4.65%, Jsc of 11.32 mA/cm$^2$, Voc of 0.66 V and FF of 0.62.

Conclusion
In conclusion, the new porphyrin small molecules of Pzn-DPP-P-2F has been developed for BHJ OSCs. The structural engineering with the horizontal conjugation of DPP to porphyrin-core with the vertical Pzn-DPP-P-2F peripheral substitutions can not only effectively increase the solar flux coverage in the visible and near-infrared region, but also optimize molecular packing through polymorphism associated with the long alkyl chain appended. At the same time their blend film with PCBM demonstrated efficient photogenerated exciton dissociation and charge collection when processed by DIO additive. As a result, the excellent device performances with PCEs of 4.65% were achieved for Pzn-DPP-P-2F based OSC.

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References


