Effect of end-groups on the photovoltaic property of diphenyl substituted diketopyrrolopyrrole derivatives

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ARTICLE INFO

ABSTRACT

In this work, a diphenyl substituted diketopyrrolopyrrole (DPP) and its two derivatives end-capped with fluorine and *n*-butyl respectively, namely PDPPP, FPDPPPF, and RPDPPPR, are designed and synthesized. The resulting molecules exhibit similar energy structures, i.e. both relatively narrow optical band gaps (1.75–1.79 eV) and deep highest occupied molecular orbital (HOMO) energy levels (−5.18 to −5.25 eV), implying that all of them are potentially good electron donors for organic solar cells (OSCs). However, three molecules show different photovoltaic performances when they are blended with [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) to fabricate OSCs: the RPDPPPR-based device gives the highest power conversion efficiency (PCE) of 1.59%, whereas the PCEs of PDPPP and FPDPPPF-based OSCs are 0.46% and 0.55%, respectively. Through atomic force microscopy (AFM), X-ray diffraction (XRD) and space charge limited current (SCLC) characterizations, the prominent role of end-groups in the photovoltaic properties of DPP derivatives is disclosed: terminal alkyl chains in RPDPPPR can promote molecular crystallization and lead to the formation of finer phase-separation domains in the blended film, which are in favor of charge generation and transportation in the photovoltaic devices. Thus, RPDPPPR provides the best photovoltaic property among three DPP molecules.

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1. Introduction

Diketopyrrolopyrrole (DPP) pigment was first reported by Farnum et al. in 1974 with a structure of diphenyl grafted DPP [1]. Since then, various DPP derivatives have been developed and become an important class of high-performance pigments with their applications in the coloration of plastics and in surface coating such as paints and inks [2]. Recently, the optical and electronic properties of DPP-based molecules and polymers have attracted significant attention because of π-conjugated molecular structure and exceptional stability. And their potential optoelectronic applications such as organic field-effect transistors (OFETs) and organic solar cells (OSCs) have been widely studied [3–10]. Usually, OSCs adopt a bulk-heterojunction (BHJ) structure based on a phase-separated mixture of an electron donor and an electron acceptor [which is normally a fullerene derivative, e.g. [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$)]. In the past decade, OSCs have made significant progresses, and the power conversion efficiencies (PCEs) of over 8% are achieved through combination of designing new donor materials and optimizing device structures [11–19].

The ideal donor materials should simultaneously possess strong absorption ability, suitable highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) energy levels, high hole mobility, and good film-forming properties which are necessary for the realization of efficient OSCs [20]. DPP is one of the most attractive building blocks to construct the excellent donor due to its unique planar conjugated bicyclic structure with polar carbonyl groups capable of hydrogen bonding [21]. The electron-deficient nature of DPP unit provides the possibility to get both a low band gap and a deep HOMO energy level of the resulting molecule via coupling with electron-rich aromatic moieties such as benzene, perylene, naphthalene, thieno[3,2-b]thiophene, etc. [5,22,23]. Besides, because of the self-organization property and strong π–π interaction, DPP-based molecules are endowed with high charge carrier mobility [24]. Therefore, these special properties make DPP derivatives promising photovoltaic materials.

The DPP-based compounds are not soluble in common organic solvents because of their strong intermolecular hydrogen bonds and π–π interactions [25]. Chemical modifications are normally employed for improving the solubility of DPP-based molecules and polymers by introducing alkyl side chains on the DPP core. Therefore, better film-forming property of DPP-based donors and their intimate mixing with fullerene acceptors can be obtained [26]. Beyond the film-forming property, nanoscale morphology in the

BHJ active layer, such as bicontinuous donor and acceptor domains, phase-separation size and crystallinity, plays a key role in the device performance. Recent works have suggested that different alkyl substituents (linear and branched) in conjugated polymers would afford distinct π–π stacking distances and orientations, and thus influence crystallinity, morphology, and the resultant photovoltaic performances [12,27,28]. Additionally, introduction of fluorine atom as substituent into conjugated polymers can not only lower their HOMO energy level, which is favorable for providing higher open-circuit voltage (V_{oc}) of OSCs, but also affect lamellar spacings in polymer films [29]. However, researches on the effect of different substituents on the aggregation structure and photovoltaic property of DPP-based small molecules, especially substituents as end-groups instead of side-groups, are few. Taking these into consideration, in this work, we designed and synthesized a diphenyl substituted diketopyrrolopyrrole (DPP) molecule and its two derivatives end-capped with fluorine and *n*-butyl respectively, namely PDPPP, FPDPPPF, and RPDPPPR. Their optical properties, electrochemical behaviors, and the morphologies of the blended films with PC$_{61}$BM are fully investigated, in order to clarify how the end-groups influence the photovoltaic property of DPP derivatives.

2. Experimental

2.1. Instrument

^{1}H NMR and ^{13}C NMR spectra of the synthesized molecules were collected on a Bruker Advance DMX-300 (300 MHz) nuclear magnetic resonance spectrometer. UV–vis absorption spectra of the solutions and films were recorded over the range 300–900 nm on a Shimadzu UV-2450 spectrophotometer. Elemental analyses were carried out using a LECO 932 CHNS elemental analyzer. Thermogravimetric analyses (TGA) were performed on a WCT-2 thermal balance under N$_2$ atmosphere at a heating rate of 20 °C/min. Cyclic voltammetry (CV) was carried out on a CHI600A electrochemical workstation with Pt disk, Pt plate, and standard calomel electrode (SCE) as working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) CH$_2$Cl$_2$ solution. The CV curves were recorded versus the potential of SCE, which was calibrated by the ferrocene–ferrocenium (Fc/Fc$^+$) redox couple (4.8 eV below the vacuum level). X-ray diffraction (XRD) patterns were collected on a Rigaku D/max 2550PC X-ray diffractometer with Cu K$_\alpha$ radiation (λ = 1.5406 Å) operated at the voltage of 40 keV and the current of 40 mA. Topographic images of the thin films were studied using a Veeco MultiMode atomic force microscopy (AFM) under the tapping mode with an etched silicon cantilever at a nominal load of ~2 nN, and the scanning rate for a 10 μm × 10 μm image size was 1.5 Hz.

2.2. Materials

All reagents, unless otherwise specified, were obtained from Aldrich, Acros and TCI Chemical Co., and used as received. All the solvents were freshly distilled prior to use. 3,6-Bis(5-bromothiophene-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrolo-1,4-dione (**1**) was synthesized according to the reported procedure [20]. Phenylboronic acid (**2a**), 4-fluorophenylboronic acid (**2b**), and 4-*n*-butylphenylboronic acid (**2c**) were purchased from Aladdin Co.

2.3. Synthesis

The general synthetic route toward three small molecules is illustrated in Scheme 1. PDPPP, FPDPPPF, and RPDPPPR were synthesized by one-step traditional palladium-catalyzed Suzuki coupling reaction. The detailed synthetic processes are as follows:

2.3.1. Synthesis of 3,6-bis(5-phenylthiophene-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrolo-1,4-dione (PDPPP)

Compound **1** (0.60 g, 0.88 mmol), phenylboronic acid (0.43 g, 3.5 mmol), 2.0 M aqueous K$_2$CO$_3$ solution (9 mL), ethanol (4 mL), and toluene (70 mL) were mixed thoroughly in a 250 mL two-neck flask, which was purged with nitrogen for 20 min ahead to start the reaction. Then, 0.062 g tetrakis(triphenylphosphine)palladium [Pd(PPh$_3$)$_4$] was added, and the mixture was refluxed at 80 °C for 48 h. After being cooled to room temperature, the mixture was extracted with CH$_2$Cl$_2$, washed with brine, and dried over anhydrous MgSO$_4$, then the solvent was evaporated under vacuum. The crude product was purified by chromatography on silica gel (eluent: CH$_2$Cl$_2$/petroleum ether, 2:1, v/v) to provide dark purple powder (0.50 g, 84%). ^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm): 8.98 (d, 2H), 7.67 (d, 4H), 7.48 (d, 2H), 7.43 (t, 4H), 7.37 (d, 2H), 4.21–3.96 (m, 4H), 2.03–1.86 (m, 2H), 1.48–1.20 (m, 16H), 0.97–0.81 (m, 12H). ^{13}C NMR (300 MHz, CDCl$_3$), δ (ppm): 161.79, 149.72, 139.94, 137.00, 133.27, 129.27, 128.93, 126.21, 124.57, 108.24, 46.07, 39.35, 30.46, 28.69, 23.79, 23.26, 14.24, 10.72. Anal. Calcd for C$_{42}$H$_{48}$N$_2$O$_2$S$_2$: C, 74.32; H, 7.24; N, 4.02. Found: C, 74.52; H, 7.15; N, 4.14.

2.3.2. Synthesis of 3,6-bis(5-(4-fluorophenyl)thiophene-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrolo-1,4-dione (FPDPPPF)

This compound was synthesized by the same procedure as the compound PDPPP, with 1 molar equivalent of compound **1** and 4 molar equivalents of 4-fluorophenylboronic acid, to yield dark purple powder (0.81 g, 77%). ^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm): 8.95 (d, 2H), 7.66 (d, 4H), 7.40 (d, 2H), 7.13 (t, 4H), 4.21–3.96 (m, 4H), 2.03–1.86 (m, 2H), 1.48–1.20 (m, 16H), 0.97–0.81 (m, 12H). ^{13}C NMR (300 MHz, CDCl$_3$), δ (ppm): 164.01, 162.42, 148.59, 140.00, 136.93, 129.63, 129.00, 128.10, 124.60, 116.48, 108.39, 46.14, 39.42, 30.52, 28.73, 23.88, 23.26, 14.22, 10.76. Anal. Calcd for C$_{42}$H$_{46}$F$_2$N$_2$O$_2$S$_2$: C, 70.70; H, 6.55; N, 3.81. Found: C, 70.75; H, 6.50; N, 3.93.

2.3.3. Synthesis of 3,6-bis(5-(4-n-butylphenyl)thiophene-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c] pyrrolo-1,4-dione (RPDPPPR)

This compound was synthesized by the same procedure as the compound PDPPP, with 1 molar equivalent of compound **1** and 4 molar equivalents of 4-*n*-butylphenylboronic acid, to yield dark purple powder (0.44 g, 76%). ^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm): 8.98 (d, 2H), 7.59 (d, 4H), 7.42 (d, 2H), 7.32 (d, 4H), 4.22–3.96 (m, 4H), 2.83–2.50 (m, 4H), 2.05–1.86 (m, 2H), 1.64 (p, 4H), 1.48–1.20 (m, 20H), 0.99–0.83 (m, 18H). ^{13}C NMR (300 MHz, CDCl$_3$), δ (ppm): 161.83, 150.01, 144.12, 139.89, 137.03, 130.71, 129.31, 128.44, 126.12, 124.13, 108.10, 46.05, 39.35, 35.57, 33.62, 30.45, 28.69, 23.77, 23.28, 22.48, 14.25, 14.10, 10.71. Anal. Calcd for C$_{50}$H$_{64}$N$_2$O$_2$S$_2$: C, 75.86; H, 8.17; N, 3.54. Found: C, 76.10; H, 8.17; N, 3.55.

2.4. Device fabrication and characterization

OSCs were fabricated with indium tin oxide (ITO) glass as the anode, Al as the cathode, and a blended film of DPP derivative (PDPPP, FPDPPPF, or RPDPPPR):PC$_{61}$BM between the two electrodes as the photoactive layer. At first, the ITO glass was pre-cleaned and PEDOT:PSS [poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)] (Baytron P 4083, Germany) was spin-coated for 60 s on the ITO substrate. The thickness of the PEDOT:PSS layer was about 30 nm. Followed by the deposition of PEDOT:PSS, the photoactive layer was spin-cast at varying spinning speeds from a solution of DPP derivative and PC$_{61}$BM in chlorobenzene at a total solid concentration of