



Influence of the positions of thiophenes and side chains on diketopyrrolopyrrole based narrow band-gap small molecules for organic solar cells



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ABSTRACT

A series of low band-gap small molecules with multiple donor-acceptor type backbones, which contained diketopyrrolopyrrole as a bulk core, thiophene/benzene as donor moiety and isoindigo/thienoisoindigo as end acceptor moiety, were designed and synthesized. All the four compounds show broad absorption from 300 nm to 900 nm and the optical band gaps are all lower than 1.5 eV. The absorption spectra and the energy levels of the four compounds are finely tuned by changing the donor unit of benzene with thiophene. X-ray diffraction measurement indicated that there are differences between the crystallinity of the four materials. The effects of the positions of thiophenes and side chains on morphology, charge transport and photovoltaic properties of these narrow band-gap small molecules were also studied. The highest power conversion efficiency of these compounds is 2.01% after thermal annealing. Ternary solar cells were fabricated to investigate the effect of the second donor on the power conversion efficiency.

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1. Introduction

During the last decade, much attention has been paid to organic solar cells (OSC) due to their advantages of light weight, low cost and large area fabrication [1–4]. With continuous efforts, power conversion efficiency (PCE) of over 10% has been achieved for bulk heterojunction (BHJ) solar cells based on small molecules or polymers as donor and fullerene derivatives as acceptors [5–8]. Researchers have focused on designing and synthesizing ideal donors to improve PCE of organic solar cells [9]. Ideal donors must meet with the following requirements: (i) broad and strong absorption; (ii) suitable energy levels; (iii) high hole mobility [10–12]. In order to harvest the solar light of the visible and near-infrared regions, a commonly applied strategy is to design low band-gap donors by incorporating repeated electron-rich and electron-deficient moieties to the backbone of small molecules [13–17]. Meanwhile, increasing the intramolecular charge transfer by introducing strong

electron-deficient moieties into the conjugated backbone is also an important method to narrow the band-gap of small molecules [18,19].

Diketopyrrolopyrrole (DPP) has been widely used to construct high performance polymers and small molecules for organic solar cells and organic field-effect transistors due to its strong light absorption, good thermal and photochemical stability [20–22]. Wang et al. reported a narrow band gap small molecule based on DPP, showing an outstanding PCE of 7.00% [23]. In addition, Kim and co-workers synthesized a series of DPP-selenophene vinylene selenophene polymers with a maximum mobility of $17.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ by the side chain engineering [24].

Isoindigo based polymers exhibited wide absorption bands and appropriate highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) levels [25–28]. Xie and Geng developed a donor (D)-acceptor (A) type polymer with isoindigo and dithienocarbazole units, which showed an optical band-gap of 1.59 eV and strong absorption from 300 nm to 800 nm [29]. Meanwhile, charge delocalization would be enhanced with higher planarity for thienoisoindigo by replacing the benzene rings with thiophenes [30–32]. For example, poly(thienoisoindigo-alt-

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naphthalene) owned an ultra-high mobility of $14.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ due to its large coplanarity and favorable energy levels [33].

Based on the aforementioned observations, herein we designed and synthesized a family of small molecules (Scheme 1), namely DPPTTC6, DPPTTC8, IDPPTIC8 and IDPPTIEH for the OSC application as donors. These small molecules contain DPP as a bulk core, thiophene/benzene as donor moiety and isoindigo/thienoisindigo as end acceptor moiety. By introducing multiple acceptors into the molecules to form A-D-A-D-A type backbones, the optical absorption can be enhanced and the energy levels can be adjusted through enlarging the conjugation length. In addition, the interaction between donor moiety and acceptor moiety can be varied by changing the position of thiophene as well as side chains. The effects of the positions of thiophenes and side chains on charge transport, morphology and photovoltaic properties of the materials will be discussed.

2. Experimental section

2.1. Materials

Commercially available chemicals were purchased from commercial sources and used without further purification unless otherwise specified. All solvents were dried over sodium and freshly distilled prior to use. Compounds **1**, **2**, **3**, **4** were synthesized according to the same procedure as reported in the literature [30,34–36].

2.2. General measurement and characterization

Nuclear magnetic resonance (NMR) spectra were collected on a Bruker AV-500 (500 MHz) in deuterated chloroform with tetramethylsilane as a reference. MALDI-TOF mass spectrometric measurements were carried out on Bruker Biflex III MALDI TOF. Elemental analyses were performed with a Harrios elemental analysis instrument. Thermo-gravimetric analysis (TGA) were analyzed on a TA Instrument Model SDT Q600 simultaneous TGA/DSC analyzer with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ and a N_2 flow rate of 90 ml min^{-1} . UV–vis absorption spectra were obtained using a Shimadzu UV-3600 UV–vis–NIR spectrometer. Cyclic voltammetry (CV) data were collected on a CHI630E electrochemical workstation equipped with a saturated calomel electrode as the reference electrode, a platinum wire counter electrode, and a glassy carbon working electrode. The measurements were carried out with anhydrous acetonitrile tetrabutylammoniumhexafluorophosphate (0.1 M) as the supporting electrolyte at a scan rate of 100 mV s^{-1} under an argon atmosphere. Potentials were referenced to the ferrocene/ferrocenium couple by using ferrocene as the standard. The oxidation potential of ferrocene was set at -4.80 eV with respect to zero vacuum level. The HOMO and LUMO energy levels were calculated according to the equation of $E_{\text{HOMO}} = -[4.8 + (E_{\text{ox}} - E_{\text{Fc}/\text{Fc}^+})]$ (eV) and $E_{\text{LUMO}} = -[4.8 + (E_{\text{red}} - E_{\text{Fc}/\text{Fc}^+})]$ (eV). Atomic force microscopy (AFM) images were obtained by using

Oxford atomic microscope at tapping mode. X-ray diffraction (XRD) patterns of the polymers were recorded on a Rigaku X-ray diffractometer operated in reflection geometry at 30 mA, 40 kV with Cu $K\alpha$ radiation. Space charge limited current (SCLC) is described by $J = 9\epsilon_0\epsilon_r\mu V^2/8L^3$, where J is the current density, ϵ_r is the relative dielectric constant of the transport medium, ϵ_0 is the permittivity of free space ($8.85 \times 10^{-12} \text{ F m}^{-1}$), μ is the hole or electron mobility, L is the film thickness of active layer, V is the internal voltage in the device and $V = V_{\text{appl}} - V_{\text{bi}} - V_{\text{a}}$, where V_{appl} is the applied voltage to the device, V_{bi} is the built-in voltage due to the relative work function difference of the two electrodes and V_{a} is the voltage drop due to contact resistance and series resistance across the electrodes.

2.3. Device fabrication and characterization

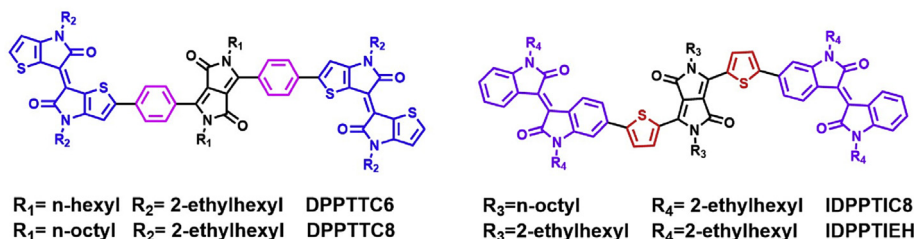
The conventional devices were fabricated with the configurations of indium tin oxide (ITO)/poly(3,4-ethyl-enedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/active layer/PFN/Al. Prior to use, ITO glass was cleaned by sequential sonication in detergent, ultra pure water, acetone, and isopropyl alcohol for 20 min and finally UV/ozone treatment for 30 min. After that, a thin layer (30 nm) of PEDOT:PSS (Baytron PVP Al 4083, Germany) was spin-coated onto the ITO glass with a spin-coating speed of 2500 rpm and baked at $150 \text{ }^\circ\text{C}$ for 10 min. For optimal performance, active layer solutions were prepared with different weight ratios or additives. Active layer solutions were spin-coated in a nitrogen filled glovebox to obtain a photosensitive layer. Then the PFN solution in methanol was spin-coated on the surface of the obtained active layer at 2500 rpm for 30 s to obtain a thin interlayer of 5 nm. At last, thin layer of 100 nm of Al was evaporated through a shadow mask at $2 \times 10^{-6} \text{ mbar}$. As for the device structure of ITO/ZnO/active layer/ MoO_3 /Ag, the ZnO cathode buffer layer (20 nm) was spin-coated on an ITO substrate at 3000 rpm for 30 s and annealed at $250 \text{ }^\circ\text{C}$. The substrates were then transferred to a nitrogen filled glove box for spin casting the active layer. Finally, a bilayer anode structure of MoO_3 layer (10 nm)/Ag (100 nm) was deposited atop the active layer by thermal evaporation in a vacuum of $2 \times 10^{-6} \text{ mbar}$.

The thicknesses of the active layers were measured using Veeco Dektak 150 surface profiler meter. The active area of the devices were 0.045 cm^2 defined by shadow mask. The current density–voltage (J - V) characteristics were measured with Keithley 2400 source measurement unit under AM 1.5G (100 mW cm^{-2}) irradiation from Newport solar simulator. Light intensity was calibrated with a standard silicon solar cell. External quantum efficiencies (EQE) of solar cells were analyzed by certified Newport incident photon conversion efficiency (IPCE) measurement system.

2.4. Synthesis of compounds

2.4.1. Synthesis of DPPTTC6

To a mixture of **1** (60 mg, 0.085 mmol), **2** (196 mg, 0.339 mmol),



Scheme 1. The chemical structures of these small molecules.

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