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Enhanced photovoltaic properties of the terpolymer containing diketopyrrolopyrrole and benzothiadiazole side chain

Min Zhang [a], Zhencai Cao [a], Fen Wu [a], Huajie Chen [a], Meiqi Zhang [a], He Qiao [a], Songting Tan [a,b,*]

[a] *College of Chemistry and Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, Xiangtan University, Xiangtan 411105, PR China*

[b] *Key Laboratory of Advanced Functional Polymeric Materials of College of Hunan Province, Xiangtan University, Xiangtan 411105, PR China*

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ABSTRACT

A new random terpolymer (**PBDTT–DPP–TDTBT**) based on alkylthienyl substituted benzodithiophene (BDTT), diketopyrrolopyrrole (DPP), and dialkylthienylbenzothiadiazole-thienyl vinylene (TDTBT) was designed and synthesized via the Stille coupling polymerization. The effects of DPP and TDTBT units on the thermal properties, photophysical and electrochemical properties of the polymer were investigated by thermogravimetric, UV–Vis–IR absorption spectra and cyclic voltammetry. By incorporating the TDTBT side-group into the random polymer main-chain, the absorption spectrum of **PBDTT–DPP–TDTBT** was broadened significantly. Moreover, the highest occupied molecular orbital (HOMO) energy level had been obviously lowered, consistent with the suitable backbone twists in main-chains. Therefore, the deep-lying HOMO energy level (ca. −5.5 eV) was achieved, which was beneficial for high open-circuit voltage (V_{oc}). Bulk heterojunction solar cells based on as-synthesized polymer as electron donor and (6,6)-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) as acceptor were fabricated. The results demonstrate that the terpolymer **PBDTT–DPP–TDTBT** exhibits an improved power conversion efficiency of 4.85%.

1. Introduction

Polymer solar cells (PSCs) have attracted an increasing attention in the photovoltaic research community due to their potential advantages in fabricating low cost and light weight productions compared to inorganic solar cells [1–9]. Over the past decades, significant progress has been made in this field. The power conversion efficiencies (PCEs) over 9% for single junction cells [10] and 10% for tandem devices [11] have been achieved by carefully designing the device structures. This remarkable advance in PCEs mainly resulted from the development of high-performance conjugated polymers [12,13] as well as novel device structures [14]. Although the progress is impressive, great efforts should be paid to further enhance photovoltaic efficiency and device stability before the realization of practical applications of PSCs.

In order to obtain high-performance photovoltaic polymer materials, it is necessary to design and synthesize conjugated polymers with ideal properties, including broad absorption range, low band gap, and appropriate molecular energy levels [15]. Recently, great interest has been focused on developing organic photovoltaic functional materials containing a diketopyrrolopyrrole (DPP) core. As a class of brilliant red pigments, DPP has been applied in paints, plastic ink, electroluminescent devices, thin-film transistors, and solar cells [16–19]. The DPP unit has a

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* Corresponding author at: College of Chemistry and Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, Xiangtan University, Xiangtan 411105, PR China.

E-mail address: tanst2008@163.com (S. Tan).

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highly coplanar structure, leading to strong π–π interaction [20]. Furthermore, the electron-deficient nature of DPP unit provides the possibility to design copolymers with strong intramolecular charge transfer (ICT) and broad absorption spectrum ranging from visible to near-IR region, especially in 600–900 nm. Currently, polymer solar cells fabricated by DPP-based copolymers exhibit the promising PCEs over 6.5% [21–23]. For DPP-based polymers, however, there are relatively weak absorption in 300–600 nm, thus limited the short-circuit current density (J_{sc}).

Our previous work had demonstrated that a new family of polymers with conjugated side chains had been successfully developed for PSCs [24–27]. Compared with the main-chain D–A polymers, the side-chain ones feature higher molecular weight, better solubility, excellent film-forming ability, and suitable phase separation with electron acceptor PCBM. Generally, side-chain polymers show the deep-lying energy levels of the highest occupied molecular orbital (HOMO), thus they demonstrate the prominent V_{oc} in PSCs. It turns out that a certain distortion of the polymer backbone resulting from the introduction of side chains is conducive to control the HOMO energy levels of the polymers [28]. In addition, most of these side-chain D–A conjugated polymers exhibited the relatively strong absorption bands in 300–600 nm, which could be complementary with the absorption range of the DPP-based polymers.

Based on the considerations above, a dialkylthienylbenzothiadiazole-thienyl vinylene (TDTBT) side chain was introduced into the DPP-based copolymer main-chain (**PBDTT–DPP–TDTBT**, see Fig. 1) to tune its HOMO energy level and absorption spectrum. To establish structure–property correlations within the as-synthesized polymers, the binary copolymer PBDPP-2, similar structure reported by Hou group previously, was also synthesized [29]. The results indicated that the random terpolymer **PBDTT–DPP–TDTBT** exhibited obviously enhanced optical absorption in 300–850 nm as well as a deep-lying HOMO energy level (−5.5 eV) compared with PBDPP-2 [29]. Bulk heterojunction solar cells based on **PBDTT–DPP–TDTBT** as electron donor and (6,6)-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) as acceptor were fabricated. An improved power conversion efficiency of 4.85% was obtained.

2. Experimental

2.1. Measurements and characterization

^{1}H NMR spectra were recorded on Bruker AVANCE 400 spectrometer. UV–Vis spectra of the polymer were obtained on Perkin–Elmer Lamada 25 spectrometer. FT-IR spectra were measured on Perkin–Elmer Spectra One spectrometer. Molecular mass of the compounds were determined by matrix assisted laser desorption–ionization time-of-flight mass spectrometry (MALDI-TOF MS) using a Bruker Aupoflex-III mass spectrometer. The average molecular weight and polydispersity index (PDI) of the polymer were determined using Waters 1515 gel permeation chromatography (GPC) analysis with THF as eluent and polystyrene as standard. Thermal analyses were performed on Netzsch TG 209 analyzer under N_2 atmosphere with a heating and cooling rate of 20 °C/min. Cyclic Voltammetry (CV) was conducted on an electrochemistry workstation (ZAHNER ZENNIUM) with the polymer film on Pt plate as the working electrode, Pt slice as the counter electrode, and saturated calomel electrode (SCE) as the reference electrode in 0.1 M tetra-*n*-butylammonium hexafluorophosphate acetonitrile solution. The scan rate is 50 mV/s. Atomic force microscopy (AFM) measurements were performed using a Digital Instruments EnviroScope in tapping mode.

2.2. Materials

Tetrakis(triphenylphosphine)palladium(0) [Pd(PPh_3)$_4$], *n*-butyllithium (*n*-BuLi), and Tri-*n*-butyltin chloride

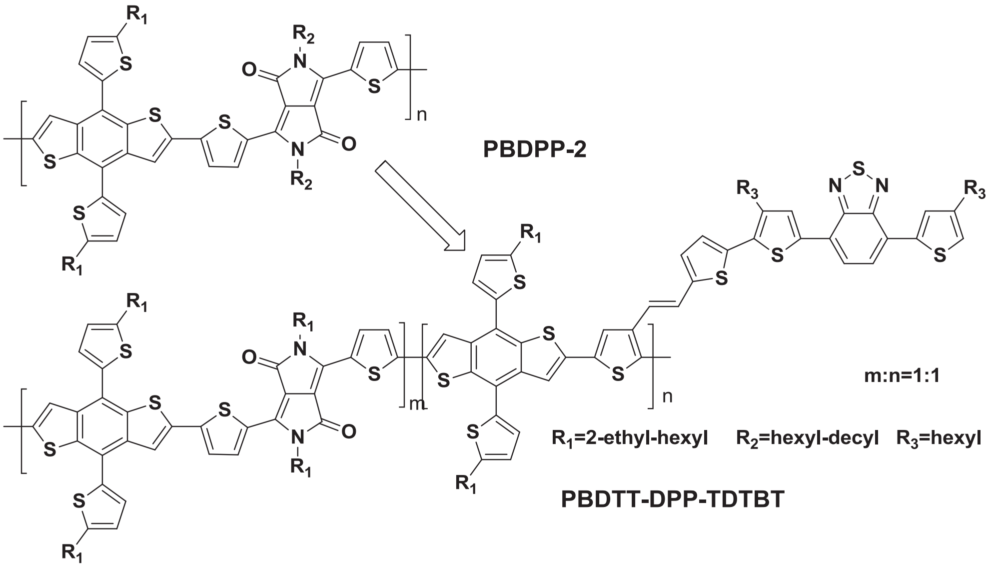

Fig. 1. Molecular structure of the polymer.