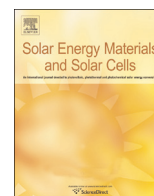




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Improved open-circuit voltage of benzodithiophene based polymer solar cells using bulky terthiophene side group

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ABSTRACT

Terthiophene, including one α - α and one branching α - β connection of the thiophene units, is introduced as benzodithiophene (BDT) side chain to build a novel two-dimensional (2D) conjugated BDT block. By copolymerizing this BDT block with three electron acceptors (DTTz (bis(thiophene-2-yl)-tetrazine), DPP (diketopyrrolopyrrole), DTffBT (4,7-bis(4-hexylthienyl)-5,6-difluoro-2,1,3-benzothiadiazole)) and one electron donor (TTT (2,5-Di(2-thienyl)thiophene)), four terthiophene side-chained benzodithiophene based copolymers were synthesized. Due to the difference in electron affinity among DTTz, DPP, DTffBT and TTT, these four polymers show different UV-vis absorption spectra and optical band gaps (1.3–2.0 eV), while fortunately they all remain deep highest occupied molecular orbital (HOMO) energy levels (–5.3 to 5.6 eV) which is very favorable to high open-circuit voltage (V_{oc}) polymer solar cells (PSCs). By comparing the photovoltaic properties with polymers which have same backbone but do not have the bulky 2D side group in the literatures, our polymer solar cells devices show higher V_{oc} . Especially for PQ3 (a copolymer of benzodithiophene and diketopyrrolopyrrole), the donor photon energy loss ($E_g - eV_{oc}$) is 0.51 eV which is almost the lowest value achieved by the researchers. It can be concluded that: the bulky terthiophene side group helps to improve V_{oc} of the PSCs devices. The overall performance of solar cells devices is correlated with the molecule conformation, polymer hole mobility and polymer/PCBM blend film morphology.

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1. Introduction

Polymer solar cells (PSCs) have attracted considerable interests due to their unique advantages in the development of renewable energy resources, such as low cost, light weight, flexibility and easy processability [1]. Bulk heterojunction (BHJ) polymer solar cells device architecture, based on a variety of blends of electron-donating semiconductor polymers and electron-accepting fullerene derivatives, has been proved to be the most efficient devices structure [2–5]. Among various types of semiconducting polymers, the benzo [1,2-*b*:4,5-*b'*]dithiophene (BDT) based polymers exhibited promising photovoltaic properties, since BDT unit possesses its special merits. Firstly, BDT has a large planar conjugated structure and easily forms π - π stacking, which improves polymer mobility [6,7]. Secondly, there

is small steric hindrance between BDT and adjacent units, as 4,9-bis-substituted-BDT has no substituent on 1,3,5 and 7 positions, which makes BDT an ideal conjugated unit for photovoltaic material. Thirdly, starting from 4,8-dihydrobenzo [1,2-*b*:4,5-*b'*] dithiophene-4,8-dione, it is very easy to attach different substituents to the central benzene core of BDT by nucleophilic addition which can tune the optical-electronic properties of resultant polymers.

In 2008, Hou et al. synthesized the 4,8-bisalkoxy-BDT monomer and prepared eight photovoltaic polymers by copolymerizing this BDT monomer with different units [8]. After that, lots of new alkoxy-BDT based polymers have been designed, synthesized and applied for PSCs within the past five years [9–12]. Many milestone PCE achievements in recent years are also based on BDT polymers [13–17]. According to the reported works, efficient photovoltaic materials can be obtained by copolymerizing BDT units with other types of conjugated building blocks [18]. For example, 8–9% PCEs have been achieved by the BDT with thieno[3,4-*b*]thiophene (TT) copolymers [13–16], the BDT with TPD copolymers [17], etc.

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Therefore, how to further improve photovoltaic properties of the BDT-based polymers is a very important topic for molecular engineering.

Li's group developed the concept of two-dimensional conjugated polythiophenes (2D-PTs) [19]. Recently, Li et al. summarized the progress of the 2D-PTs in a review paper [20]. They found that, it is a very effective method to enhance the open-circuit voltage (V_{oc}) by using the 2D-structure. On this basis, Yang and Hou et al. introduced 2,4-dioctylthienyl substituent onto BDT unit and constructed the first 2D-conjugated BDT polymer [21], named as PBDTTBT-T. Although the steric hindrance caused by the alkyls at 4-position of the thiophene unit is too strong to get effective conjugated effect of the side groups, PBDTTBT-T showed a high V_{oc} of 0.92 V, thus resulting in one of the outstanding photovoltaic data. Then, many pairs of BDT polymers, which are substituted by alkoxy or conjugated side groups, were designed and synthesized [22–28]. By comparing the photovoltaic properties of each pair of polymers, the conclusion is drawn that once the substituents on BDT are changed from alkoxy chains to conjugated side groups, their HOMO levels are reduced and thus the V_{oc} of corresponding PSCs device is increased. So far, we can say that, for all the materials based on BDT, it is a certain thing to increase their V_{oc} by introducing the conjugated side chain substituent [29].

Terthiophene, including one α - α and one branching α - β connection of the thiophene units, can be used to directly allow selective reactions at the inner free α -position, and the other two outer α -positions can connect different functional groups by electrophilic reactions. Janssen et al. designed and synthesized two series of oligothiophene dendrimers based on terthiophene unit with silylated and nonsubstituted two outer α -positions [30]. Solution-processed bulk heterojunction photovoltaic cells based on these two materials exhibited a high V_{oc} of 1.0 V which showed that terthiophene unit is an excellent group for organic electronics.

Previously, our research group has reported one new 2D BDT building block, bulky terthiophene-substituted BDT (3TC12BDT). Polymer based on this building block and 4,7-di(thiophen-2-yl)-benzo[c] [1, 2, 5] thiadiazole showed a PCE of 3.57% [31]. In this work, we selected three other acceptors and one donor unit, DTTz [32], DPP [33], DTffBT [34] and TTT [35] to copolymerize with 3TC12BDT forming four novel polymers. The PSCs devices based on these four polymers with our new bulky side chain (terthiophene) show high V_{oc} compared with those polymers without 2D side chain or even those with typically 2D side chain (alkylthienyl).

2. Experimental section

2.1. Materials

All reagents and chemicals were purchased from commercial sources (Acros, Aldrich, Alfa, J&K) and used as received without further purification unless otherwise noted. 3TC12BDTBr was synthesized according to our previously published procedures [31]. DTTz [32], DPP [33] and TTT [35] have been reported in the corresponding literatures. DTffBT was bought from Derthon Optoelectronic Materials Sciences & Technology Co., LTD. All reactions were conducted under purified argon atmosphere. Tetrahydrofuran (THF) and toluene were distilled from sodium/benzophenone. *N,N*-Dimethylformamide (DMF) was distilled from calcium hydride.

2.2. Instrumentation

^1H and ^{13}C NMR spectra were recorded using the Bruker Avance-III 600MHz spectrometer at 25 °C in CDCl_3 . The number-average (M_n) and weight-average (M_w) molecular weights of polymers were determined by gel permeation chromatography (GPC) on a HLC-8320

instrument, using THF as eluting solvent and polystyrene as standard. The thermal gravimetric analysis (TGA) was made using a SDT Q600 instrument and operated under a nitrogen atmosphere. The Ultra-violet-visible (UV-vis) absorption spectra were measured by a Hitachi U-4100 spectrometer. Cyclic voltammetry (CV) was performed on a CHI660D electrochemical workstation with a glassy carbon working electrode, a platinum wire counter electrode and Ag/AgCl reference electrode in a solution of Bu_4NPF_6 (0.1 M) in acetonitrile at a scan rate of 50 mV/s. The XRD samples of the polymer only and blend films with PCBM were prepared by casting the corresponding solutions in *o*-DCB (ortho-dichlorobenzene) in a concentration of 24 mg/ml. AFM studies were carried out on a VEECO-dimension 5000 scanning probe microscope.

2.3. Preparation of solar cell devices

Solar cells devices were fabricated with the structure of ITO/PEDOT:PSS/Polymer:PCBM/Ca/Al. Glass substrates coated with ITO (170 nm) were patterned using standard photolithography. The substrates were cleaned by ITO lotion (commercially available), distilled water, acetone and isopropyl alcohol in ultrasonication bath for 30 min. The substrates were subjected to oxygen plasma treatment for 3 min twice prior to use. After that, poly(3,4-ethyl-enedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was spin coated on the substrates (4000 rpm, 20 s). The thickness of the PEDOT:PSS layer was ~ 30 nm, as determined by a Dektak 150 surface profilometer. The substrates were annealing at 160 °C for 30 min under a nitrogen atmosphere. Polymer:PCBM blends (1:1 to 1:4) were in *o*-DCB with a total blend concentration of 24 mg/ml which were spin coated on to the PEDOT:PSS treated substrates. Films of 20 nm Ca and 100 nm Al were thermally evaporated onto the substrates through a shadow mask to obtain the solar cell devices. J - V testing was carried out under a controlled nitrogen atmosphere using a Keithley 2420 source measurement unit under simulated 100 mW/cm² (AM 1.5G) irradiation from a Newport solar simulator. The active area of the devices was 0.1 cm².

2.4. Space Charge Limited Current (SCLC)

ITO/PEDOT:PSS/Polymer:PCBM substrate was prepared as solar cells devices and then Au (100 nm thickness) was thermally evaporated on the substrates through a shadow mask to obtain the devices. J - V testing was carried out under a controlled nitrogen atmosphere using a Keithley 2420 source measurement unit. The active area of the devices was 0.1 cm². The active layer film thickness was measured using a Dektak 150 surface profilometer. The SCLC mobilities μ were extracted using the standard trap-free SCLC transport equation:

$$J = \frac{9}{8} \epsilon_r \epsilon_0 \mu \frac{U^2}{d^3}$$

where ϵ_r is the relative dielectric constant, ϵ_0 is the vacuum permeability, U is the applied voltage, and d is the device thickness.

2.5. Synthesis of the monomer and polymers

The monomer 3TC12BDTBr was synthesized according to our reported procedures [31].

2.5.1. Synthesis of 3TC12BDTSn

3TC12BDTBr (3.03 g, 2.0 mmol) and 80 mL of THF were added into a 200 mL flask under an inert atmosphere. The solution was cooled down to 0 °C by an ice-water bath, and 5.0 mmol of *n*-butyllithium (3.13 mL, 1.6 M in *n*-hexane) was added dropwise. After being stirred

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