Organic Electronics 48 (2017) 298–307

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Polymer with conjugated alkylthiophenylthienyl side chains for efficient photovoltaic cells

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A R T I C L E   I N F O

Article history:
Received 23 March 2017
Received in revised form
21 May 2017
Accepted 6 June 2017
Available online 9 June 2017

Keywords:
Polymer solar cells
Side-chain engineering
Alkylthiophenylthienyl side chains
Benzo[1,2-*b*:4,5-*b*']dithiophene
Structure-property relationship

A B S T R A C T

A donor-acceptor (D-A) conjugated copolymer **PSBT-FTT**, incorporating alkylthiophenylthienyl (**SBT**) side chains on benzo[1,2-*b*:4,5-*b*']dithiophene units (BDT), was designed and synthesized. Compared to the analogical polymer **PSB-FTT** with alkylthiophenyl (**SB**) side chains, **PSBT-FTT** exhibits stronger interchain π-π interaction, more redshifted absorption spectrum, stronger absorption coefficient, better compatibility with (7,7)-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$), more effective exciton dissociation and higher hole mobility. Therefore, the **PSBT-FTT**-based bulk heterojunction polymer solar cells (PSCs) achieved a PCE value of 7.06% that is almost 50% higher than 4.83% of the **PSB-FTT** based PSCs. The result indicates that the introducing **SBT** side chains is an excellent strategy for designing high performance photovoltaic polymers.

1. Introduction

In the last twenty years, polymer solar cells (PSCs) with bulk heterojunction structure (BHJ) have attracted considerable attention due to their potential application in making large area and flexible solar panels by roll-to-roll printing process [1–9]. As is well-known to all, photovoltaic performance of PSCs highly depends on the properties of conjugated polymers that are used in their BHJ active layers, so tremendous efforts have been devoted to molecular design of conjugated polymers for the applications in PSCs, and rapid progress has been achieved in the past decades [10–13]. So far, the single-junction PSC devices of which have been reported to reach 9–11% power conversion efficiencies (PCEs) by optimizing molecular structure to rationalize the energy levels and aggregation structure [14–16]. Donor-acceptor (D-A) conjugated polymers have been identified as highly promising donor materials for PSCs because the energy levels and band-gaps are easily tunable via intramolecular charge transfer (ICT) effects.

Over the last decade, benzo[1,2-*b*:4,5-*b*'] dithiophene (BDT) has been considered as the most famous D moiety, and the BDT-based polymers have been proved to be the most important polymer photovoltaic materials [17–24]. Among of them, the PTB family polymers based on thieno[3,4-*b*] thiophene and BDT firstly exceeded a PCE value of 7% [25,26]. To improve the photovoltaic performance of the polymers, side chain engineering has been widely focused and applied because it not only optimizes the highest occupied molecular orbital (HOMO) energy levels and bandgaps of the polymers, but also improves the molecular aggregation and charge carrier mobilities [27–31]. When alkoxy groups were substituted by alkyl groups [19] or alkylthio side chains [32–34], the polymers achieved a more deep-lying HOMO energy level, and the corresponding PSC device achieved an enhanced open-circuit voltage (V_{oc}). Moreover, the conjugated side chains have been introduced to the BDT-based polymers. When alkoxy groups on BDT unit were substituted by 2-alkylthienyl, *p*-alkylphenyl, 2-ethylhexylthiophenyl and 2-ethylhexylthiophenyl side chains, the polymers PBDTT-DPP [35], PBDTP-DPP [35], PBDTT-S-TT [33], and P3 [36] showed lower HOMO levels of −5.30 eV, −5.35 eV, −5.41 eV

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http://dx.doi.org/10.1016/j.orgel.2017.06.011

and −5.41 eV, respectively. Simultaneously, these polymers show more appropriate molecular aggregation, which leads to higher hole mobilities, short circuit current densities (J_{sc}) and PCE values [37,38].

The two-dimensional (2D) conjugated polymers with extended conjugated side chains were firstly reported by introducing vinyl side chains to polythiophene derivatives [39,40]. Afterwards, the concept of 2D-conjugated structure has been extensively accepted and applied for designing polymer photovoltaic materials. On the one hand, the conjugated side chains were introduced to D moieties, these polymers showed an amazing photovoltaic performance [41–47]. When tris(thienylenevinylene) [42], alkylthienylenevinylene-thiophene (TVT) [43], alkyl(trithienyl) [44], 5-(3,4,5-tris(octyloxy)-phenyl)thiophen-2-yl [45], and 5-(alkylthio)-thiophene-2-yl)vinyl)-thiophene-2-yl [46] groups were used as the side chains of BDT units, the polymers showed PCE values around 6.04–8.13%. On the other hand, the conjugated side chains were introduced to A moieties, which also showed a promising photovoltaic performance [48–52]. When dithienylbenzothiadiazole-vinylene [49], isoindigo [50], diketopyrrolopyrrole [51], and naphtha-bisthiadiazole [52], derivatives were used as the side chains, these polymers exhibited PCE values around 4.32–8.04%. These results indicate that the 2D-conjugated structure is a promising designing strategy to achieve high photovoltaic performance [53,54].

In our earlier study, the BDT-based polymers based on 2-hexyldecylthiophenyl side chains were reported, and the polymer **PSB-FTT** only showed a low PCE value of 4.45% because of the large bandgap (1.81 eV) and narrow absorption band. Herein, a novel BDT-based copolymer **PSBT-FTT** based on the BDT unit with 2-hexyldecylthiophenylthienyl (**SBT**) side chains as electron-donating moiety and 2-ethylhexyl-3-fluorothieno[3,4-*b*]thiophene-2-carboxylate as electron-withdrawing moiety was designed and synthesized (Fig. 1). To study the effect of the side chains with different conjugated length on the photovoltaic performance, the polymer **PSB-FTT** with 2-hexyldecylthiophenyl (**SB**) side chains was synthesized again. Finally, the effects of the side chains with different conjugated length on molecular aggregation, absorption spectra, bandgaps, compatibility with fullerene derivative, hole mobilities and photovoltaic performance have been fully investigated.

2. Experimental section

2.1. Materials and chemicals

Benzo[1,2-*b*:4,5-*b*']dithiophene-4,8-dione, and 2-ethylhexyl 4,6-dibromo-3-fluorothieno[3,4-*b*]thiophene-2-carboxylate (**M2**) were purchased from SunaTech Inc. 1-Bromo-4-(2-hexyldecyl)thiobenzene, 2-(tri-*n*-butylstannyl)thiophene and **PSB-FTT** were synthesized according to already published procedures [55,56]. Tetrahydrofuran (THF) and toluene were refluxed over sodium and benzophenone, and distilled prior to use. All the other chemicals were purchased from commercial suppliers (Aldrich, Energy Chemical, Alfa, *etc.*) and used as received unless noted otherwise. Column chromatography was carried out on silica gel (Qingdao Banke Separation Materials Co., LTD., 200–300 mesh).

2.2. Characterization

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 spectrometer. Molecular mass was determined by matrix assisted laser desorption/ionization time-of-light mass spectrometry (MALDI-TOF MS) using a Bruker Aupoflex-III mass spectrometer. The high resolution mass spectrum was measured using a Solarix FF-ICR-MS Analyzer in the MALDI mode. The elemental analysis result was characterized by Eementar VarioEL CHNS. UV–Visible-Near Infrared absorption spectra (UV–vis–NIR) spectra of the polymers were recorded on a Perkin-Elmer Lambda 25 spectrometer. Thermogravimetric analyses (TGA) were performed by using a Netzsch TG 209 analyzer under nitrogen atmosphere at a heating rate of 20 °C min^{-1}. Differential scanning calorimetric measurement (DSC) was performed on a TA DSC Q10 instrument at a heating rate of 10 °C min^{-1}. The average molecular weight and polydispersity index (PDI) of the polymers were determined by Waters 1515 gel permeation chromatography (GPC) analysis with $CHCl_3$ as the eluent and polystyrene as the standard. Cyclic voltammetry (CV) was conducted on an electrochemistry workstation (ZAHNER ZENNIUM) with the polymer thin film on ITO (indium tin oxide) glass as the working electrode, Pt wire as the counter electrode, and Ag/Ag$^+$ electrode as the reference electrode in a 0.1 M *tetra*-*n*-butylammonium hexafluorophosphate acetonitrile solution at a scan rate of 100 mV s^{-1}. Atomic force microscopy

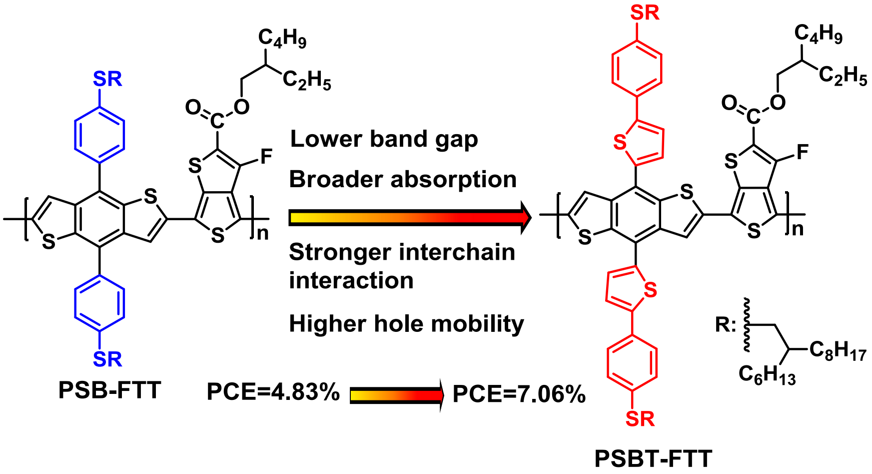

Fig. 1. Chemical structure of the polymers.