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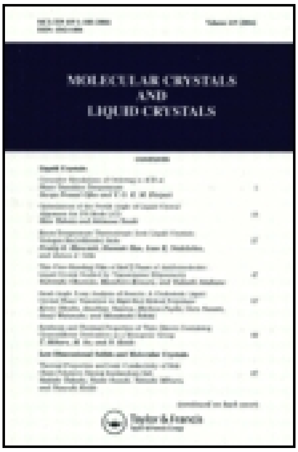

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The Effect of Side-Chain Structure on Copolymer-Based Bulk Heterojunction Solar Cells

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The Effect of Side-Chain Structure on Copolymer-Based Bulk Heterojunction Solar Cells

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This paper describes the synthesis and photovoltaic studies of copolymer based on benzo[1,2-b:4,5-b′]dithiophene and 2,1,3-benzothiadiazole. Bulk-heterojunction solar cells were fabricated by using chlorobenzene, and 2% chloronapthalene as a solvent additive in chlorobenzene. The copolymers as the electron donor were blended with [6,6]-phenyl-C61-butyric acid methyl ester ($PC_{61}BM$) as the electron acceptor. The effect of side–chain on BDT was compared between 4,8-bis(1-pentylhexyl)benzo[1,2-b:4,5-b′]dithiophene (C11BDT) and 4,8-bis(1-butylhexyl)benzo[1,2-b:4,5-b′]dithiophene (C9BDT). The power conversion efficiency (PCE) was improved with the shorter side–chain. The highest PCE was found in PC9BDTBT with 2.29%.

Keywords Bulk heterojunction solar cells; conjugated polymer; side–chain

Introduction

Bulk heterojunction (BHJ) polymer solar cells based on polymer:fullerene are envisioned to exhibit advantages such as a low–cost, printable, light weight and flexible potential sources of renewable electrical energy [1]. In the last eighteen years, the power–conversion efficiency (PCE) of BHJ solar cells has evolved from the poly(phenylene vinylene) [2] to poly(3–hexylthiophene) [3] to copolymer as reported recently [4]. The copolymers based on benzo[1,2-*b*:4,5- *b*′]dithiophene (BDT) were reports with high PCE [5–6]. Several low band gap copolymers have been reported, one is BDT-*co*-BT (benzothiadiazole) that was reported by Hou *et al*. [6]. The high molecular weight (M_w) and solubility can improve the PCE. However, Coffin *et al*. [7]. reported that M_w and solubility can be improved by altering the side–chains on the polymer. In this work we studied the synthesis, characterization and

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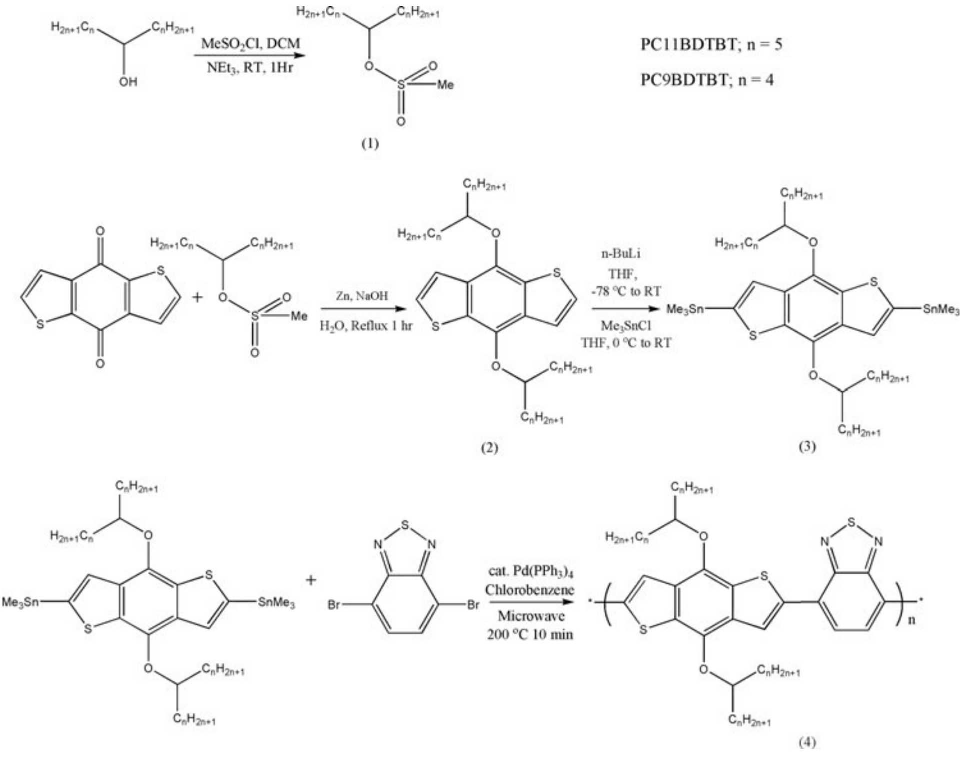
photovoltaic properties of copolymer BDT-*co*-BT with different length of side–chain at BDT structure.

Methods

Chemicals are purchased from Aldrich and Acros. Benzo[1,2-*b*:4,5-*b*′]dithiophene-4, 8-dione [8] was synthesized according to the procedures reported in the literature. The synthesis routes for poly[4,8-bis(1-pentylhexyl)benzo[1,2-*b*:4,5-*b*′]dithiophene-2,6-diyl-alt-2,1,3-benzothiadiazole-4,7-diyl] (PC11BDTBT) and poly[4,8-bis(1-butylhexyl) benzo[1,2-*b*:4,5-*b*′]dithiophene-2,6-diyl-alt-2,1,3-benzothiadiazole-4,7-diyl](PC9BDTBT) were prepared using a procedure similar to Nie *et al.* [5] as shown in Scheme 1.



Scheme 1. Synthesis routes for PC11BDTBT and PC9BDTBT.

Nonan-5-yl methanesulfonate (1) The flask containing dichloromethane, nonan-5-ol, triethylamine, and methanesulfonyl chloride was added. Stirring for 1 h at RT, the residue was extracted with diethyl ether and washed with water. The organic layer was dried, filtered and evaporated. The yellow oil was purified by column chromatography (9:1 hexane:dichloromethene). ^{1}H NMR ($CDCl_3$), δ (ppm): 4.57 (q, $J = 5.9$ Hz, 1H), 2.99 (s, 3H), 1.74–1.67 (m, 4H), 1.54–1.41 (m, 4H), 1.37–1.25 (m, 4H), 0.90 (t, $J = 6$H, 7.2 Hz).

4,8-bis(1-butylhexyl)benzo[1,2-*b*:4,5-*b*′]dithiophene-2,6-diyl (2) were prepared using a procedure similar to Hou *et al.* [9] Benzo[1,2-*b*:4,5-*b*′]dithiophene-4,8-dione, zinc powder, NaOH and water were placed in a flask. The mixture was stirred and reflux for 1 h, then nonan-5-yl methanesulfonate and tetrabutylammonium bromide were added. The

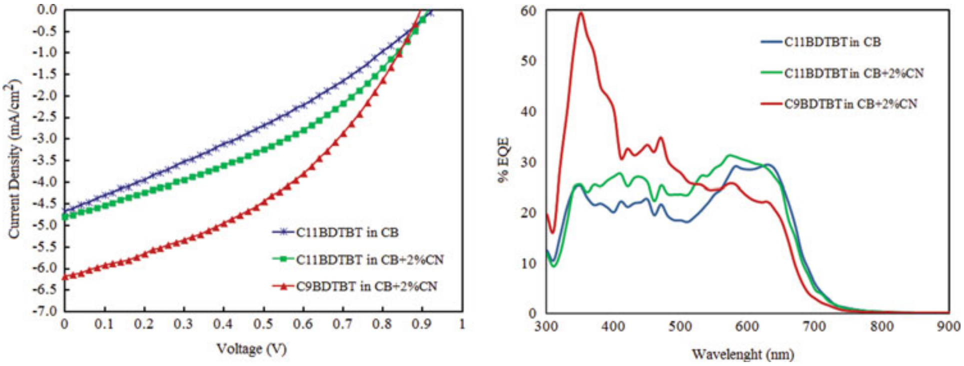


Figure 1. *I-V* characteristics and EQE spectra of 8 mg 1:1.5 polymer:$PC_{61}BM$ BHJ solar cells with CB, and additive solvent.

reaction was refluxed overnight. The mixture was poured into water and extracted with ether, filtered and evaporated. The yellow oil was purified by column chromatography (8:2 hexane:dichloromethene). ^{1}H NMR ($CDCl_3$), δ (ppm): 7.46 (d, 2H, $J = 5.6$ Hz), 7.32 (d, 2H, $J = 5.6$ Hz), 4.57 (q, 2H, $J = 5.9$ Hz), 1.74–1.67 (m, 8H), 1.54–1.41 (m, 8H), 1.37–1.25 (m, 16H), 0.90 (t, 12H, $J = 6.3$ Hz)

2,6-bis(trimethylstannyl)-4,8-bis(1-butylhexyl)benzo[1,2-*b*:4,5-*b′*]dithiophene (Sn-C9BDT) (3) A solution of C9BDT in dry THF at −78°C was added 1.6 M *n*-BuLi in hexane. This mixture was stirred for 15 min then warmed to RT. The solution was subsequently cooled to 0°C, and a solution of trimethyltin chloride in THF was added. The solution was warmed to RT and stirred overnight. The mixture was poured into a separatory funnel containing DI water. The diethyl ether was added. The organic layer was separated. The organic layer was washed with water, then dried, filtered and evaporated. A waxy pale yellow solid was obtained. ^{1}H NMR ($CDCl_3$), δ (ppm): 7.51 (s, 2H), 4.62 (q, 2H, $J = 5.8$ Hz), 1.75–1.68 (m, 8H), 1.56–1.46 (m, 8H), 1.37–1.42 (m, 8H), 0.90 (t, 12H, $J = 7.2$ Hz), 0.43 (t, 18H, $J = 28.8$ Hz).

Synthesis of PC11BDTBT and PC9BDTBT (4) The following contents were added into a microwave tube equipped with a stir bar: Sn-C11BDT or Sn-C9BDT, 4,7-dibromo-2,1,3-benzothiadiazole (BT), tetrakis(triphenylphosphine) palladium(0), and chlorobenzene (CB). The tube was sealed and heated in a microwave reactor for 10 min at 200°C. After the reaction completion, the polymer was dissolved in CB and filtered through celite. The filtrate was precipitated in methanol, filtered and dried to give PC11BDTBT 82% yield, PC9BDTBT 90% yield of a dark blue solid.

Fabrication of BHJ Solar Cells Devices

The PC11BDTBT solution were prepared by blending 8 mg/mL of PC11BDTBT with $PC_{61}BM$ in the ratio of 1:1.5 polymer to $PC_{61}BM$ by weight in CB, and CB with 2% v/v 1-chloronapthlene (1-CN). The PC9BDTBT solution were prepared by blending 8 mg/mL of PC9BDTBT with $PC_{61}BM$ in the ratio of 1:1.5 polymer to $PC_{61}BM$ by weight in CB with 2% v/v 1-CN. The solutions were stirred for 24 h. The BHJ solar cells devices were fabricated as follows: The ITO substrates were cleaned in an ultra-sonication bath, DI water, acetone and isopropanol. The ITO substrates were exposed to an ultraviolet ozone plasma. Then the ITO substrates was spin-coated with a PEDOT:PSS film on top, and

Table 1. Solar cells characteristics of 8 mg 1:1.5 polymer:$PC_{61}BM$ with CB, and additive solvent.

Polymer	V_{oc}(V)	I_{sc}(mA/cm^2)	FF	η(%)
PC11BDTBT in CB	0.930 ± 0.005	4.96 ± 0.28	0.320 ± 0.009	1.47 ± 0.11
PC11BDTBT in CB + 2% CN	0.913 ± 0.004	4.44 ± 0.25	0.384 ± 0.002	1.56 ± 0.08
PC9BDTBT in CB + 2% CN	0.887 ± 0.006	6.18 ± 0.08	0.408 ± 0.006	2.24 ± 0.03

dried. The substrates were spin-coated by the active layer. The content was transferred to a vacuum chamber to evaporate, 0.25 nm of lithium fluoride and 100 nm of aluminum as top electrode. The active area of these devices is 0.28 +/− .04 cm^2.

Characterization

^{1}H-NMR spectra were recorded using a Bruker 300 UltraShield (300 MHz). The Current–Voltage (*I*–*V*) characteristics of the produced devices were tested in air with a calibrated solar simulator with an intensity of 100 mW/cm^2. The external quantum efficiency (EQE) was measured on a Newport Merlin lock-in amplifier.

Results and Discussion

The *I*–*V* curve, and the EQE of PC11BDTBT, and PC9BDTBT with $PC_{61}BM$-blend were observed from the best device, as shown in Fig. 1. The EQE measurements show an increase in photon collection, and thus photocurrent, across all wavelengths absorbed. The absorption maxima of PC11BDTBT, and PC9BDTBT and $PC_{61}BM$ were approximately 330–690, 320–690 nm and 570 nm respectively.

Table 1 shows the solar cells characteristics of PC11BDTBT, and PC9BDTBT blending with $PC_{61}BM$ BHJ solar cells. For PC11BDTBT:$PC_{61}BM$ BHJ solar cells, it was found that the power conversion efficiency was improved by adding solvent additive (CN) into CB. The solvent additive (CN) could prevent polymer aggregation and decrease phase separation [5]. The result between PC11BDTBT, and PC9BDTBT blending with $PC_{61}BM$ in CB adding 2% v/v CN BHJ solar cells was shown, that PC9BDTBT had the better performance with the best short-circuit current density $I_{sc} = 6.18$ mA/cm^2, a fill factor $FF = 0.414$, an open-circuit voltage $V_{oc} = 0.896$ V and a resulting efficiency of 2.29%. The length of the side-chain has an effect on power conversion efficiency of the polymer. For PC9BDTBT has a shorter side-chain than PC11BDTBT therefore leading I_{sc}, FF, and power conversion efficiency to increase as shown in the Table 1.

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