Disilanobithiophene-dithienylbenzothiadiazole alternating polymer as donor material of bulk heterojunction polymer solar cells

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ABSTRACT

A donor-acceptor conjugated polymer composed of disilanobithiophene and dithienylbenzothiadiazole (**pDSBT-BHTBT**) was prepared and used as donor material of bulk heterojunction polymer solar cell with $PC_{71}BM$ as acceptor compound. We report herein the optimization of cell fabrication parameters, namely, the **pDSBT-BHTBT**:$PC_{71}BM$ ratio and the active layer film thickness, and the improvement of cell power conversion efficiency from 2.54% to 3.76%. Measurements of hole and electron mobilities of **pDSBT-BHTBT**:$PC_{71}BM$ films revealed relatively low electron mobility. Thin film transistors with a **pDSBT-BHTBT** film were also fabricated and p-type semiconducting properties were explored.

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1. Introduction

Bulk heterojunction polymer solar cells (BHJ-PSCs) have received much attention because of their potential application to low-cost, lightweight, and mechanically flexible modules. The ease of manufacture by the solution process is also an advantage of BHJ-PSCs. The active layer of BHJ-PSC consists of an electron-donating material and an electron-accepting compound, such as PCBM, which promote photo-induced charge separation. Recent studies include the introduction of donor-acceptor (D-A) alternating structures to the donor materials [1], which yield broad absorptions arising from the small band gaps to utilize a wide range of sunlight wavelengths. Si- and Ge-bridged 2,2′-bithiophenes, namely, dithienosilole (DTS) [2,3] and dithienogermole (DTG) [4], respectively, have been extensively studied as donor components of D-A polymers for BHJ-PSCs. In those bridged bithiophenes, the high planarity of the tricyclic systems enhances the π-conjugation. It is also found that a bonding interaction between Si or Ge σ* and the bithiophene π*-orbital stabilizes LUMO. On the other hand, HOMO is also lowered, but to a lesser extent, to further minimize the HOMO-LUMO energy gap; thus, the

bridged bithiophenes are expected to function as building units of low-band-gap conjugated polymers [5].

Previously, we prepared disilanobithiophene (DSBT) as a new silicon-bridged bithiophene. Both experimental and theoretical investigations of DSBT derivatives and their models showed HOMO and LUMO levels lower than, and HOMO-LUMO energy gaps similar to, those of DTS and DTG [6]. This was ascribed to the enhanced σ*-π* interaction that lowered LUMO and the twisting of the bithiophene π-system that lowered HOMO. The open-circuit voltage (V_{oc}) of BHJ-PSC is known to collate the energy gap between the polymer HOMO and the PCBM LUMO; thus, the low-lying HOMO of the donor polymer leads to the high V_{oc}. Therefore, DSBT with a low-lying HOMO and a small HOMO-LUMO energy gap seemed suitable as the building unit of donor materials of BHJ-PSCs. In fact, using DSBT as donor, we recently prepared a photovoltaic D-A polymer containing benzothiadiazole as the acceptor (**pDSBT-BT** in Chart 1) [7]. BHJ-PSC with **pDSBT-BT**:$PC_{71}BM$ (ITO/PEDOT:PSS/DSBT-polymer:$PC_{71}BM$/LiF/Al) as the active layer showed higher V_{oc} and thus higher power conversion efficiency (PCE) than similar devices with DTS-based polymer **pDTS-BT** (Chart 1) [2]. The high V_{oc} value was due to not only the twisted DSBT system but also the adequate twisting between the adjacent DSBT and BT units, although the σ*-π* interaction was not sufficiently operative in the polymer system contrary to our expectation.

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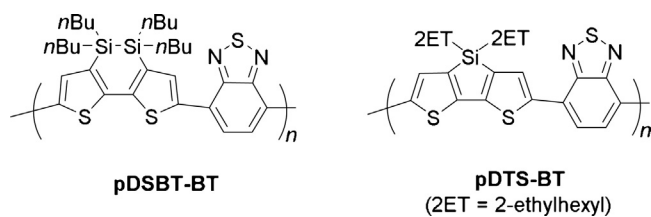
Chart 1. Structures of DSBT- and DTS-based polymers.

Scheme 1. Synthesis of **pDSBT-BHTBT**.

Very recently, we prepared DSBT-containing D-A polymers with dithienylbenzothiadiazole, thienopyrroledione, or diketopyrrolopyrrole as the acceptor. These DSBT-based polymers were preliminarily applied to BHJ-PSCs with the ITO/PEDOT:PSS/DSBT-polymer:$PC_{71}BM$/Ca/Al structure [8]. As expected, the devices based on those polymers showed rather high V_{oc}; the highest value of 0.76 V was obtained for the device with **pDSBT-BHTBT** (Scheme 1), which was even higher than that of the **pDSBT-BT**-based cell with the same structure (V_{oc} = 0.74 V). In order to explore further the scope of **pDSBT-BHTBT** as donor material with high voltage, we optimized the cell fabrication conditions to improve the performance. Measurements of hole and electron mobilities of **pDSBT-BHTBT**:$PC_{71}BM$ films were performed to obtain information for the further optimization of cell performance.

2. Experimental

2.1. Analytical information

NMR spectra were measured on a Varian System 500 spectrometer. UV–vis absorption spectra were measured on a Shimadzu UV-3150 spectrometer. GPC was carried out on serially connected Shodex KF2001 and KF2002 columns using THF as the eluent, and monitoring was conducted with a UV absorption detector at 240 nm. The cyclic voltammogram (CV) of the polymer cast film containing 10-fold weight excess of tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte on platinum electrodes was measured in acetonitrile with 100 mM TBAP.

2.2. Preparation of **pDSBT-BHTBT**

A mixture of 901 mg (1.16 mmol) of **DSBTSn**, 838 mg (1.16 mmol) of **BHTBT**, 53.2 mg (5.81×10^{-2} mmol) of $Pd_2(dba)_3$, 70.8 mg (0.233 mmol) of $(o$-tolyl$)_3$P, and 30 mL of toluene (distilled from CaH_2) was stirred at 70 °C for 3 days in a dry argon atmosphere (Scheme 1). The mixture was allowed to cool to room temperature and the resulting precipitate was filtered. The precipitate was placed in a Soxhlet apparatus and extracted with hot toluene. The filtrate and the extract were combined and the solvent was removed. Then, the residue was dissolved in chlorobenzene. To remove palladium species, the polymer solution was stirred with 30 mL of an aqueous solution of sodium N,N-diethyldithiocarbamate trihydrate (10%) at 85 °C for 2 h. The organic layer was separated and washed with water, 3 vol% acetic
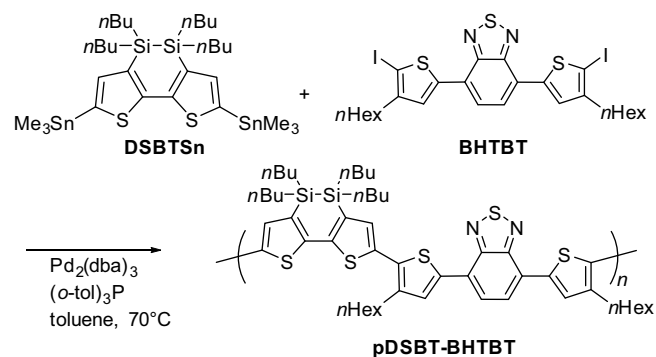
acid (aq), and water again. The organic layer was separated and dried over anhydrous potassium carbonate. After the solvent was evaporated, the residue was subjected to repeated reprecipitation from chlorobenzene/ethanol, chlorobenzene/ethyl acetate, and chlorobenzene/hexane in this order to provide 674 mg (63% yield) of **pDSBT-BHTBT** as a dark purple solid: mp > 300 °C. ^{1}H NMR (in C_6D_5Cl) δ 0.88–0.95 (br m, 18H, Bu Hex), 1.03–1.19 (br m, 8H, Bu Hex), 1.28–1.61 (br m, 28H, Bu Hex), 1.78–1.86 (br m, 4H, Hex), 2.95–2.99 (br m, 4H, Hex), 7.58 (br s, 2H, thiophene), 7.67 (br s, 2H, thiophene), 8.17 (br s, 2H, benzothiadiazole). ^{13}C NMR (in C_6D_5Cl) δ 12.95, 13.94, 14.39, 23.07, 27.00, 27.53, 29.77, 30.25, 30.94, 32.08, 125.17, 125.57, 131.35, 132.50, 134.96, 135.13, 137.45, 141.03, 145.73, 152.72. Other data of the polymer are summarized in Table 1.

3. Results and discussion

We carried out the Stille-coupling polymerization of **DSBTSn** and **BHTBT** on a larger scale than that used in the previously reported synthesis (Scheme 1) [8]. Reprecipitation of the resulting polymer provided **pDSBT-BHTBT** as a dark purple solid in 63% yield with molecular weight M_n = 9200 (M_w/M_n = 1.6), which was slightly higher than that of the previously prepared polymer (M_n = 7600 (M_w/M_n = 1.6)). It is known that molecular weights of donor polymers affect the cell performance [4e]. The low molecular weight, however, was likely due to the low solubility of the polymer. An attempt to increase further the molecular weight by elevating the reaction temperature in chlorobenzene at the reflux temperature failed and gave the polymer with smaller molecular weight. The UV absorption bands of the present polymer in solution and as film, and the CV cathodic peak of the film appeared at nearly the same energies as those of the previously prepared polymer sample (Table 1) [8]. Fig. 1 presents the energy diagram of the cell based on **pDSBT-BHTBT**, indicating the adequate matching of the energy levels in the cell.

For the fabrication of BHJ-PSCs, patterned ITO glasses were washed sequentially by acetone and 2-propanol in an ultrasonication bath and UV/ozone-treated. PEDOT-PSS (Clevios P VP AI 4083) was spin-coated at 3000 rpm on the ITO glasses and then baked at 130 °C for 10 min in air. The substrates were transferred to a glove box filled with dried nitrogen (dew point: −80 °C), where a

Table 1
Properties of **pDSBT-BHTBT**.

UV-vis abs λ_{max} [nm]					
in C_6H_5Cl	film	M_n (M_w/M_n)[a]	E_g[b] [eV]	HOMO[c] [eV]	LUMO[d] [eV]
576	625	9200 (1.6)	1.8	−5.2	−3.4

[a] Determined by GPC relative to polystyrene standards.
[b] Based on absorption edge.
[c] Based on CV anodic onset.
[d] HOMO + E_g.