

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 PC₇₁BM as acceptor compound. We report herein the optimization of cell fabrication parameters, namely, the **pDSBT-BHTBT**:PC₇₁BM 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**:PC₇₁BM 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**:PC₇₁BM (ITO/PEDOT:PSS/DSBT-polymer:PC₇₁BM/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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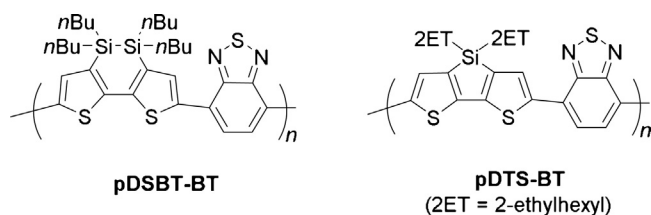


Chart 1. Structures of DSBT- and DTS-based polymers.

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:PC₇₁BM/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**:PC₇₁BM films were performed to obtain information for the further optimization of cell performance.

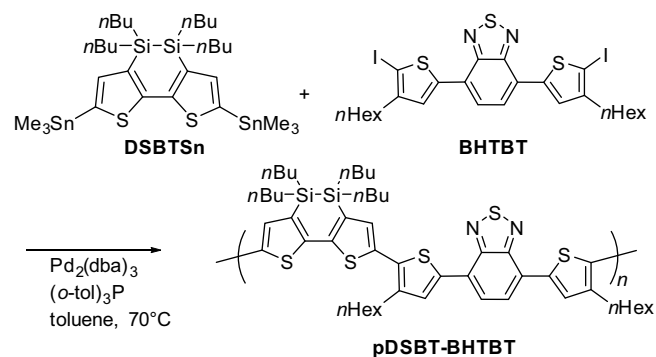
2. Experimental

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 $\text{Pd}_2(\text{dba})_3$, 70.8 mg (0.233 mmol) of (*o*-tolyl)₃P, 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



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

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. ¹H NMR (in C₆D₅Cl) 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). ¹³C NMR (in C₆D₅Cl) 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 Al 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]		M_n (M_w/M_n) ^a	E_g ^b [eV]	HOMO ^c [eV]	LUMO ^d [eV]
in C ₆ H ₅ Cl	film				
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 .

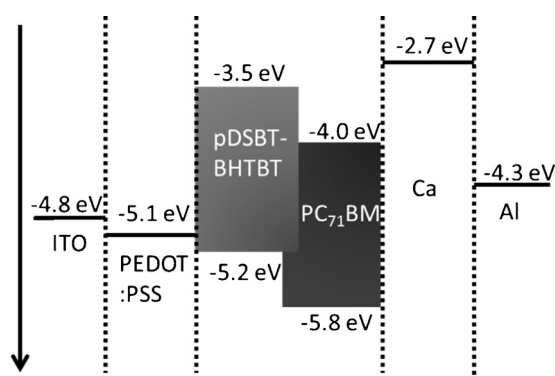


Fig. 1. Energy diagram of the cell.

Table 2

Performance of pDSBT-BHTBT-based BHJ-PSC.

V_{oc} [V]	J_{sc} [mA/cm ²]	FF	PCE [%]	Reference
0.76	8.64	0.38	2.49	[7]
0.89	8.64	0.49	3.76	this work

ratio of $x=3.5$, the influence of organic layer thickness on cell performance was investigated, as shown in Fig. 2b. Both V_{oc} and FF were not affected by the thickness, but J_{sc} reached a maximum at the thickness of 50 nm, and its value was approximately 5% higher than those at 40 nm and 60 nm, leading to a maximum PCE of 3.76% at the thickness of 50 nm. Fig. 3 shows the J - V plot and the IPCE (incident photon-to-current efficiency) spectrum, and Table 2 summarizes the photovoltaic parameters of the optimized BHJ-PSC. The calculated J_{sc} value based on the IPCE spectrum was 8.69 mA/cm², consistent with the measured value of 8.64 mA/cm². Compared with previously reported values ($V_{oc}=0.76$ V, $J_{sc}=8.64$ mA/cm², FF=0.38, PCE=2.49%), the optimized cell showed higher V_{oc} and FF, resulting in an approximately 50% improvement of PCE. Annealing the device or the organic layer suppressed the performance.

To know more about the cell characteristics, we prepared organic thin-film transistors (TFTs) with the active layer composed of pDSBT-BHTBT:PC₇₁BM, as shown in Fig. 4a, and investigated p- and n-type carrier transport properties. The p- and n-type transfer characteristics of TFTs that showed the highest hole and electron mobilities ($\mu_h = 1.3 \times 10^{-2}$ cm²/Vs and $\mu_e = 2.7 \times 10^{-3}$ cm²/Vs) are depicted in Fig. 4b and c. The average hole and electron mobilities of the TFTs were 4.8×10^{-3} cm²/Vs and 2.8×10^{-4} cm²/Vs, respectively; the hole mobility was approximately 20 times higher than the electron mobility. The relatively low electron mobility of the blend film seems to be responsible for the rather low PCE [9].

We also examined the TFT activity of pure pDSBT-BHTBT films. Bottom contact type TFTs based on pDSBT-BHTBT were fabricated on doped Si wafers with a 230 nm thermally grown SiO₂. The drain-

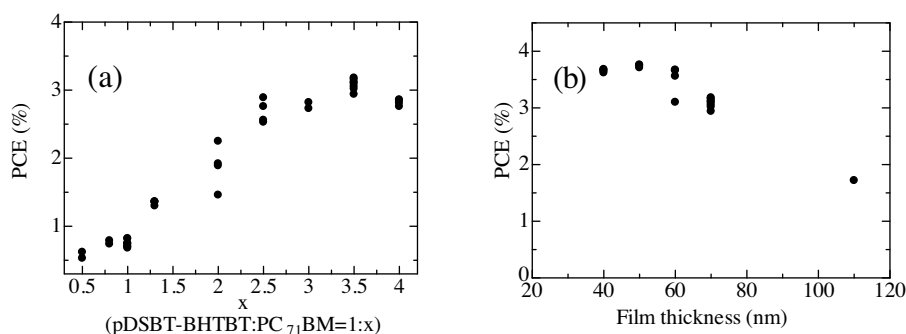


Fig. 2. Dependence of PCE of pDSBT-BHTBT-based cell on (a) pDSBT-BHTBT:PC₇₁BM ratio and (b) pDSBT-BHTBT:PC₇₁BM film thickness.

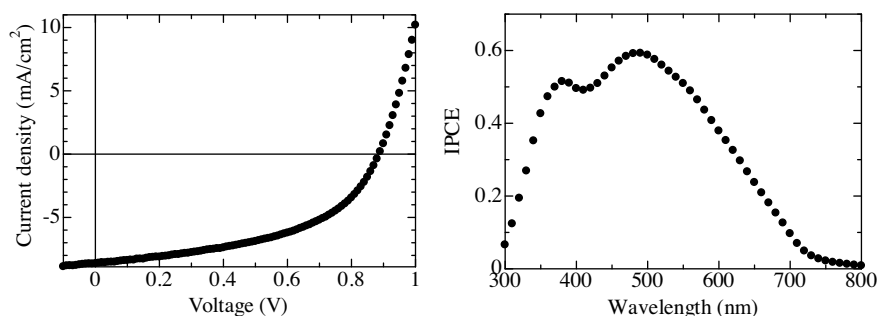


Fig. 3. J - V plot and IPCE spectrum of BHJ-PSC with pDSBT-BHTBT, after optimization.

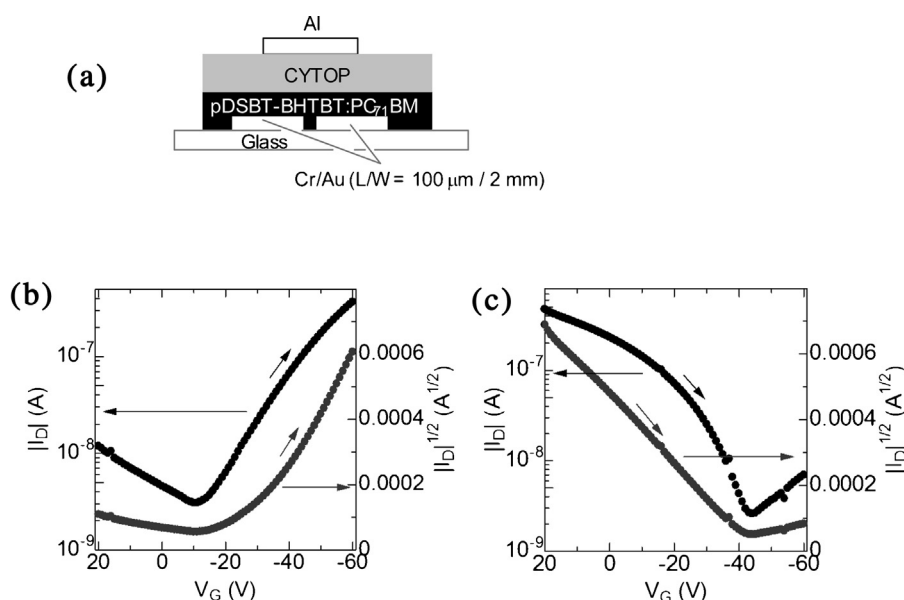


Fig. 4. (a) Device structure, and (b) p-type and (c) n-type transfer characteristics of TFT with **pDSTBT-BHTBT:PC₇₁BM** as active layer.

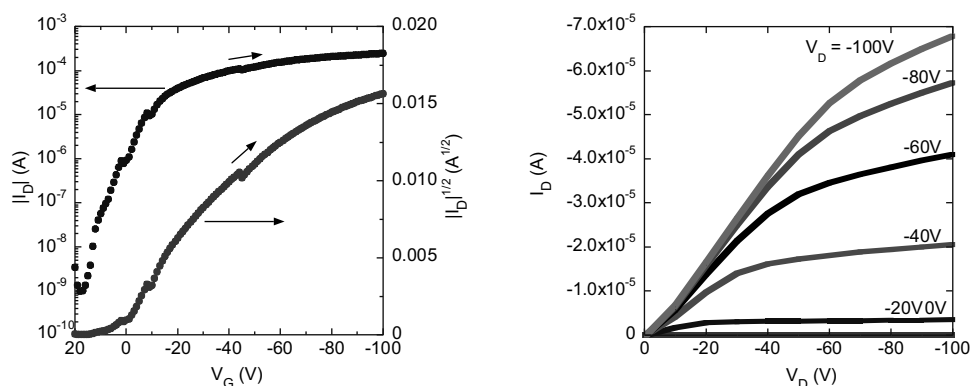


Fig. 5. TFT characteristics of **pDSTBT-BHTBT** film.

source channel length and width are 10 μm and 20 mm, respectively. The active layers were prepared by spin-coating from *o*-dichlorobenzene solutions of **pDSTBT-BHTBT** (0.4 wt% in chloroform) at 2000 rpm. Field-effect characteristics of the devices were measured under vacuum at room temperature, and the results appear in Fig. 5. The device parameters were $\mu_h = 4.0 \times 10^{-3} \text{ cm}^2/\text{Vs}$ and on/off current ratio ($I_{\text{on}}/I_{\text{off}}$) = 10^5 . The mobility was as high as that of the **pDSTBT-BHTBT:PC₇₁BM** blend film described above, suggesting that the hole conduction path based on **pDSTBT-BHTBT** was effectively generated in the blend film. The **pDSTBT-BHTBT** film was amorphous and no clear peaks were observed by XRD analysis. Annealing the film did not significantly affect the results, and the TFT annealed at 60 $^\circ\text{C}$ led to an approximately 10% increase in mobility, whereas annealing at 100 $^\circ\text{C}$ and 140 $^\circ\text{C}$ lowered the mobility to $2.4 \times 10^{-3} \text{ cm}^2/\text{Vs}$ and $1.5 \times 10^{-3} \text{ cm}^2/\text{Vs}$, respectively. Using chlorobenzene as solvent in place of *o*-dichlorobenzene suppressed TFT activity to $\mu_h = 3.6 \times 10^{-4} \text{ cm}^2/\text{Vs}$ and $I_{\text{on}}/I_{\text{off}} = 10^3$.

In summary, we examined **pDSTBT-BHTBT** as donor material of BHJ-PSC. Optimization of **pDSTBT-BHTBT:PC₇₁BM** ratio and film thickness improved performance, and a maximum PCE of 3.76%

was realized. Although the performance is still unsatisfactory, the results suggest that the performance could be further improved by employing an acceptor material whose electron mobility is higher than that of PC₇₁BM [10]. Studies geared toward the further optimization of cell fabrication parameters are underway.

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