

Preparation of a D–A polymer with disilanobithiophene as a new donor component and application to high-voltage bulk heterojunction polymer solar cells†

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A low band gap polymer composed of alternating (tetrabutylidisilano)bithiophene-benzothiadiazole units, whose absorption edge reached approximately 760 nm as a film, was prepared. A bulk heterojunction polymer solar cell was fabricated using the present polymer to provide a power conversion efficiency of 6.38% with a high V_{oc} of 0.82 V.

The bulk heterojunction type polymer solar cell (BHJ-PSC) is of current interest because of its potential applications to low-cost, lightweight, and flexible modules. In this system, microphase-separated organic layers consisting of an electron-donating host polymer and an electron-accepting guest compound, such as PCBM derivatives, operate as the active components. Donor–acceptor (D–A) type polymers are often employed as the host polymers.¹ Their broad, red-shifted absorptions arising from a low band gap make it possible to utilize the wide range of sunlight wavelengths, and their polar structures facilitate photo-induced charge separation in these polymers. In addition, the host polymers should exhibit moderately strong interchain interactions in the solid state to form microphase separation, and possess a low-lying HOMO to elevate the open-circuit voltage (V_{oc}) that collates the energy gap between the polymer HOMO and PCBM LUMO levels, in order to realize a high-performance BHJ-PSC.

To obtain efficient host polymers for BHJ-PSCs, a variety of donor and acceptor components have been developed.¹ Of those, a great deal of attention has been focused on a silicon-bridged

bithiophene named dithienosilole (DTS) as the donor component of D–A type polymers that can be used as the host materials of BHJ-PSCs,^{1–4} since Yang *et al.* prepared a DTS-benzothiadiazole (BT) alternate polymer (**pDTS-BT** in Chart 1) and demonstrated its efficient photovoltaic properties with a high power conversion efficiency (PCE) of 5.1% (V_{oc} = 0.68 V, J_{sc} (short circuit current density) = 12.70 mA cm⁻², and FF (fill factor) = 0.55) as a blend film with PC₇₀BM in the BHJ-PSC system.³ In DTS, the bithiophene unit is sterically fixed to be highly planar by the silicon bridge to enhance π -conjugation. The in-phase interaction between the silicon σ^* orbital and the bithiophene π^* -orbital stabilizes the LUMO whereas the HOMO remains nearly intact, to further minimize the HOMO–LUMO energy gap.⁵ This is suitable for the BHJ-PSC host polymers that should have a low-band gap and low-lying HOMO. Among the PSCs that were based on these DTS-containing polymers, a PCE higher than 7% was recently achieved by employing the DTS-thienopyrrolodione alternate polymer.^{4g}

In an effort to tune the donor structure to manipulate the desired electronic state for BHJ-PSCs, we prepared for the first time a D–A polymer containing disilanobithiophene (DSBT) as the donor. Previously, we demonstrated that DSBT possessed a

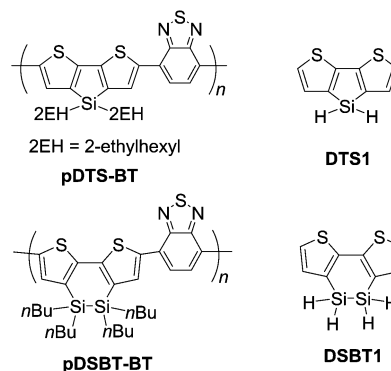


Chart 1 Structures of polymers **pDTS-BT** and **pDSBT-BT**, and model compounds.

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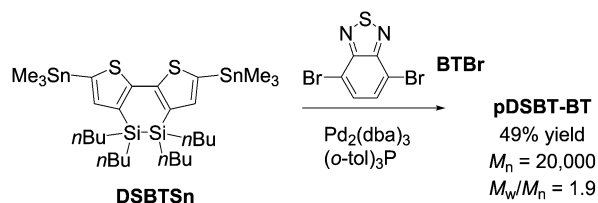
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lower-lying HOMO and LUMO than DTS and a similar band gap to DTS, based on UV absorption spectroscopy and quantum chemical calculations on their models.^{5a,6} For example, HF/6-31G calculations provided HOMO–LUMO energy levels to be $-8.04/1.65$ eV and $-7.88/1.75$ eV for non-substituted **DSBT1** and **DTS1**, respectively (Chart 1).^{5a} It is likely that the disilano σ^* -orbital efficiently interacts with the bithiophene π^* -orbital in LUMO to lower it, while the disilano σ -orbital does not contribute to the HOMO and a twisted bithiophene in DSBT is responsible for its lowered HOMO. The present DSBT polymer is therefore an exciting material for application to BHJ-PSCs with high V_{oc} .

A polymer with alternately arranged DSBT and BT units (**pDSBT-BT**, Chart 1) was prepared by the palladium-catalyzed Stille coupling reaction of bis(trimethylstannyl)disilano-bithiophene (**DSBTsn**) and dibromobenzothiadiazole (**BTBr**) as a dark purple solid that was soluble in THF, chloroform, and toluene, but insoluble in hexane, ethanol, and acetone (Scheme 1). The polymer molecular weight was determined by gel permeation chromatography (GPC) to be $M_n = 20\,000$ ($M_w/M_n = 1.9$). In THF, the polymer exhibited a broad absorption band at 633 nm with a shoulder at approximately 680 nm, as shown in Fig. 1. Measuring the spectrum of the polymer as a spin-coated film resulted in an enhancement and a red shift of the shoulder to become the major peak at 691 nm. This is indicative of a strong interchain interaction of the polymer in film. The enhanced planarity of the polymer by packing may also be responsible for the better conjugation. The peak at 633 nm in THF also shifted to the lower energy at 650 nm. These UV absorption bands of **pDSBT-BT** were at higher energies when compared to those of **pDTS-BT**, as reported by Yang *et al.*³ It was reported that **pDTS-BT** exhibited an absorption maximum and a shoulder at approximately 670 nm and 750 nm in solution, respectively, the latter of which was enhanced upon recording the spectrum of the polymer as a film. In contrast to **pDSBT-BT**, however, no remarkable shifts of the peaks were reported for **pDTS-BT**, regardless of the states (*i.e.*, in solution or film). This seems indicative of the higher degree of interchain interaction for **pDSBT-BT** than **pDTS-BT**. The cyclic voltammogram of the **pDSBT-BT** film was measured in acetonitrile containing tetrabutylammonium perchlorate as the supporting electrolyte to provide, as expected, the polymer HOMO energy level of -5.2 eV, which was lower than that reported for **pDTS-BT** (-5.1 eV),³ and thus the higher V_{oc} of **pDSBT-BT**-based cells than that of **pDTS-BT**-based ones by approximately 0.1 V was expected.



Scheme 1 Synthesis of disilano-bithiophene-benzothiadiazole polymer.

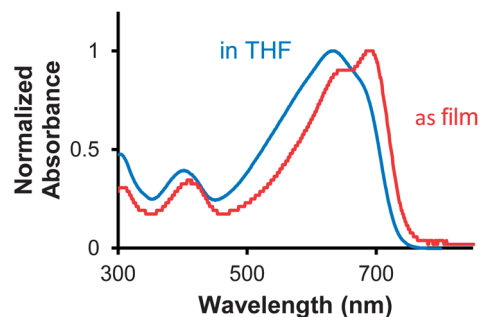


Fig. 1 UV-vis absorption spectra of **pDSBT-BT** in THF and as a film.

Then, BHJ-PSCs using **pDSBT-BT** as the host material were fabricated with the structure of ITO (150 nm)/PEDOT:PSS (30 nm)/**pDSBT-BT**:PC₇₀BM (85–90 nm)/LiF (0.5 nm)/Al (80 nm) and an active area of 0.25 cm². The active layers were prepared by spin coating *o*-chlorobenzene solutions of the blends of **pDSBT-BT** and PC₇₀BM containing 2.5 vol% diiodooctane. Annealing of the active layers as well as the devices did not affect the results. As expected, the cells exhibited distinct photovoltaic properties. The **pDSBT-BT**:PC₇₀BM ratio affected the cell current density significantly, although the voltage was nearly the same regardless of the

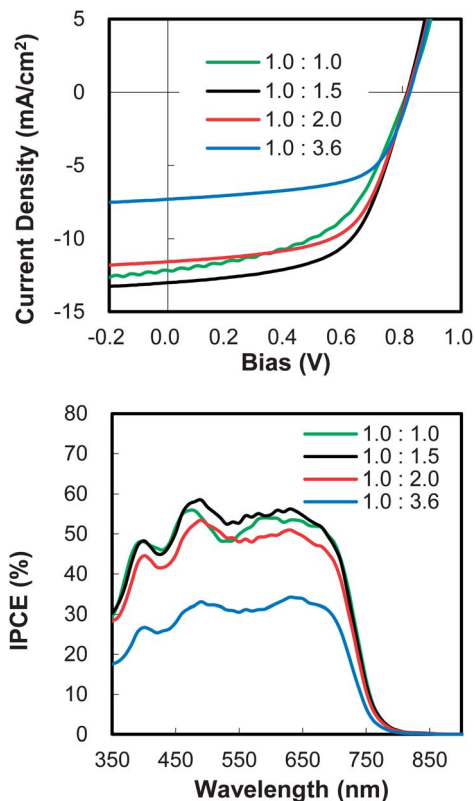


Fig. 2 *J*–*V* (current density–voltage) curves (top) and IPCE (incident photon-to-current conversion efficiency) spectra (bottom) of the cells based on **pDSBT-BT** with different **pDSBT-BT**:PC₇₀BM ratios. Data for the cell with the highest PCE among each of the four devices are presented.

ratio, as shown in Fig. 2. The best performance was achieved by employing the ratio of **pDSBT-BT**:PC₇₀BM = 1.0 : 1.5 with the average PCE being 6.24% for four devices prepared under the same conditions. The highest PCE of the cells was 6.38% (V_{oc} = 0.82 V, J_{sc} = 12.69 mA cm⁻², and FF = 0.60).

To understand the differences in electronic properties between **pDSBT-BT** and **pDTS-BT**, we carried out crystal orbital (CO) calculations on the polymer models simplified by the use of methyl groups as the substituents on the silicon atoms. Optimized geometries of the unit cells and the polymer band structures are depicted in Fig. 3. In accordance with the experimental observations, **pDSBT-BT** has a lower-lying HOCO than **pDTS-BT** (Table 1). However, the LUCO of **pDSBT-BT** is at a bit higher level than that of **pDTS-BT**, in contrast to **DSBT1** that was demonstrated to possess a lower-lying LUMO than **DTS1** (Chart 1).^{5a} This is most likely due to the largely twisted DSBT-BT bond when compared to that of DTS-BT, which is also responsible for rather flat HO and LU bands of **pDSBT-BT**. Although the twisting of **pDSBT-BT** would be decreased in the solid state as suggested by the red-shifted absorption bands, it seems essential that **pDSBT-BT** possesses a more twisted structure than **pDTS-BT**. The twisted structure, however, may stabilize the charge separated state by suppressing the

back charge transfer, thus enhancing the device current, although twisting usually suppresses the hole-conduction along the polymer chain and narrows the absorption window. In addition, the optical studies indicated that **pDSBT-BT** exhibited a stronger interchain interaction than **pDTS-BT** (*vide supra*), which enhances the hole-conduction by an interchain hopping process. Thus, somewhat serendipitously, the cells with **pDSBT-BT** and **pDTS-BT** exhibited nearly the same current density.

In summary, we prepared for the first time a D-A type polymer with DSBT as the donor and demonstrated its potential as a host polymer of BHJ-PSCs with high V_{oc} . Studies to prepare DSBT polymers with other acceptors are under way.

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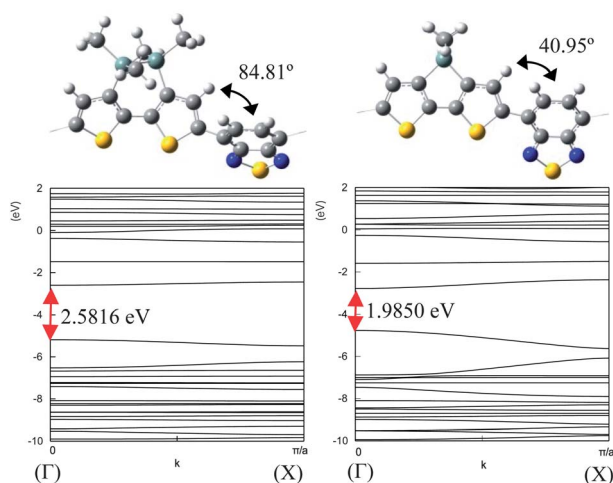


Fig. 3 Optimized geometries of repeating units of polymer models with S–C–C=C dihedral angles showing twisting between DSBT/DTS and BT rings and band structures (bottom).

Table 1 HO and LU energy levels^a

Polymer	HO (Γ)	LU (Γ)	HO (X)	LU (X)
pDSBT-BT	-5.1845	-2.6029	-5.4753	-2.4514
pDTS-BT	-4.7692	-2.7841	-5.6260	-2.3739

^a Highest occupied (HO) and lowest unoccupied (LU) orbital levels at Γ ($k=0$) and X ($k=\pi/a$), derived from simulation on polymer models with permethyl substitution on silicon atoms. The polymer structures were optimized by the one-dimensional crystal orbital calculations at the B3LYP/6-31G(d,p) level of theory. Note that the HOCO and the LUCO levels become the highest and the lowest, respectively, at Γ points for both the polymers. Energy levels are given in eV.

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