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# Benzobis(silolothiophene)-Based Low Bandgap Polymers for Efficient Polymer Solar Cells[†]

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Polymer solar cells (PSCs) have attracted great attention for applications in renewable energy due to their potential for low cost, light weight, and large-area processability.[1] To achieve high power conversion efficiency (PCE), bulk heterojunction devices containing polymer donors and fullerene-derived acceptors have been used and represent the most efficient PSC structure.[2] In the past decade, many low band gap conjugated polymers have been exploited to enhance light absorption.[3] Among them, benzodithiophene-based polymers have shown high PCE of over 7%, which shows great potential for commercialization.[4]

To achieve high performance PSC, conjugated polymers with broad and strong absorption, suitable HOMO−LUMO energy levels, good film-forming property, and high hole mobility in polymer blend are important prerequisites.[5] An extended rigid $\pi$-conjugation of the polymer backbone will facilitate intermolecular interaction between polymer chains and increase charge mobility of the polymers.[6] Previously, several ladder-type copolymers have been investigated for achieving efficient PSCs.[7] Poly(thiophene−phenylene−thiophene)s, a new type of donor, have demonstrated impressive hole mobilities up to $10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$.[8] Cyclopentadithiophene-based polymers represent another type of material for highly efficient OPVs.[9] When the carbon atoms in the 4-position of the cyclopentadithiophene unit are replaced by silicon atoms, enhanced interchain packing endows the polymer with a PCE as high as 5.9%.[10] Specifically, the introduction of silicon atoms into the polymer's backbone has been proven to be able to bring several desirable characteristics into polymers, such as lower HOMO and LUMO levels, improved packing ability, and higher charge mobility.[11]

Considering the above issues, we have designed and synthesized two new low bandgap copolymers that contain a thiophene−phenylene−thiophene fused ring in which the linked carbon atoms are replaced by silicon atoms.[12] A facile synthetic method was developed to synthesize the benzobis(silolothiophene) donor unit in high yield. The structures of the new copolymers are shown in Scheme 1. The introduction of silicon atoms was expected

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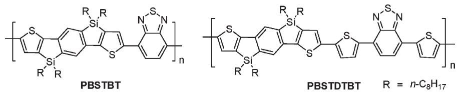
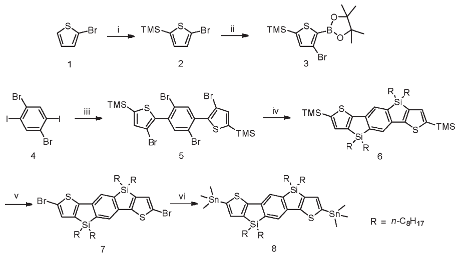
**Scheme 1. Structures of PBSTBT and PBSTDTBT**



**Scheme 2. Synthetic Route for Monomer 8**[a]



[a] (i) LDA, THF, −78 °C, 1 h, then TMSCl, −78 °C to rt, overnight; (ii) LDA, THF, −78 °C to rt, overnight, then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, −78 °C to rt, 6 h; (iii) **3**, $K_2CO_3$, $Pd(PPh_3)_4$, toluene/$H_2O$, reflux, 2 d; (iv) *n*-BuLi, THF, −78 °C to rt, 1 h, then dichlorodioctylsilane, −78 °C to rt, overnight; (v) NBS, THF, overnight; (vi) *n*-BuLi, THF, −78 °C to rt, 1 h, then trimethyltin chloride, −78 °C to r.t., overnight.

to enhance hole mobility and lower the HOMO level of the copolymers, which are important for obtaining high PCE. The hole mobilities measured by using the field effect transistor technique are $2.2 \times 10^{-3}$ and $1.1 \times 10^{-2}$ $cm^2 V^{-1} s^{-1}$ for PBSTBT and PBSTDTBT, respectively. PSCs using these two polymers blended with [6,6]-phenyl-C71-butyric acid methyl ester ($PC_{71}BM$) as acceptor showed PCE above 3.5%.

The synthetic route leading to the buliding blocks of low band gap polymers is shown in Scheme 2. 2-Bromothiophene was lithiated by LDA and subsequently quenched with trimethylsilyl chloride, yielding a colorless oil **2**. Further lithiation of **2** with LDA and then reaction with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane afforded **3** in 52% yield. **5** was obtained as a white solid in 40% yield through a Suzuki coupling reaction between 1,4-dibromo-2,5-diiodobenzene and **3**. After lithiation of **5** by *n*-BuLi, cyclization with dichlorodialkylsilane was performed to get the disilole **6** in 76% yield. The bromination of **6** with NBS and a successive reaction with *n*-BuLi quenched with trimethyltin chloride afforded **8** as a green oil which was directly used without further purification.

Low band gap polymers PBSTBT and PBSTDTBT were obtained though a Stille reaction between monomer **8** and 4,7-dibromo-2,1,3-benzothiadiazole or 4,7-bis(2-bromo-5-thienyl)-2,1,3-benzothiadiazole, using $Pd(PPh_3)_4$ as catalyst in toluene. Both polymers possess good solubility in common organic solvents such as chloroform and dichlorobenzene, providing convenience for characterization and device processing. The number average molecular weights ($M_n$) of PBSTBT and PBSTDTBT are 38.5 kDa and 22.4 kDa with polydispersity indices (PDI) of 2.09 and 1.58, respectively. In addtion, the two polymers showed high thermal stability with no obvious thermal transition between 20 and 350 °C, which could be detected by differential scanning calorimetry (DSC).

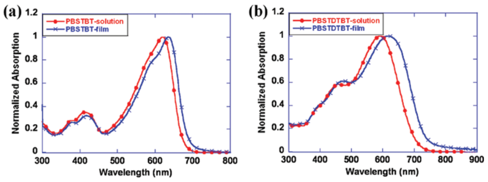


**Figure 1.** UV−vis spectra of (a) PBSTBT and (b) PBSTDTBT in $CHCl_3$ solution and film state.

Both PBSTBT and PBSTDTBT give rise to long-wavelength absorption which is attributed to charge transfer from the benzobis(silolothiophene) donor to the acceptor within the polymer chains. As shown in Figure 1a, the absorption maxima of PBSTBT in dilute chloroform solution was observed at 620 nm. This main absorption peak red shifts to 636 nm in cast film, indicating slight aggregation formed in the solid state. The optical band gap, obtained from the onset of the absorption spectrum in film, was estimated to be 1.80 eV. Similarly, the red shift of the maximum absorption from 590 nm in solution to 618 nm in a film indicates PBSTTBT also form aggregates in solid state, as shown in Figure 1b. A comparison of the polymers reveals that PBSTDTBT shows much broader and longer wavelength absorption than PBSTBT, which should be due to the introduction of two more thiophene units between the donor and the acceptor compared to PBSTBT. The optical band gap of PBSTDTBT calculated is 1.70 eV, which is 0.10 eV lower than PBSTBT. The HOMO and LUMO levels of PBSTBT determined electrochemically by cyclic voltammetry (CV) were −5.32 and −3.25 eV, respectively. The band gap obtained from CV is 2.07 eV which is slightly larger than that obtained from the absorption spectrum. Only the HOMO level of PBSTDTBT could be obtained from CV, which is −5.25 eV. With the optical band gap as 1.70 eV, the LUMO level was estimated to be −3.55 eV. In addition to optical and electrochemical methods, density functional theory (DFT) was also used to predict the HOMO and LUMO energy levels of the new polymers. The method used in this case, B3LYP/6-31G*, has been found to be an accurate formalism for predicting optical and structure properties of conjugated polymers.[13] HOMO and LUMO levels of PBSTBT were predicted to be −4.77 and −2.65 eV, respectively, while the corresponding levels for PBSTDTBT were −4.59 and −2.72 eV, respectively (see the Supporting Information).

Although the DFT predicted energy levels are overestimated, some useful correlations can still be made between experiment results and theory.[12] For instance, DFT accurately predicted a deeper lying HOMO level for PBSTBT (−4.77 eV) relative to PBSTDTBT (−4.59 eV), which is consistent with the trends in CV data (−5.32 eV vs −5.25 eV, respectively). Moreover, DFT predicted lower lying HOMO levels for both PBSTBT and PBSTDTBT, with a difference of 0.10 and 0.08 eV, respectively, relative to their analogues in which carbon replaces silicon. This provides theoretical confirmation that the silole containing

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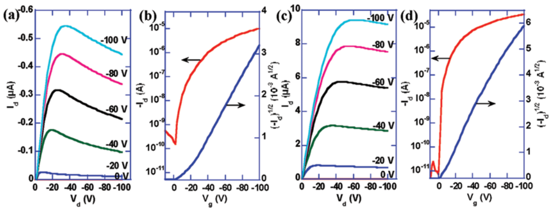

**Figure 2.** Output (a and c) and transfer (b and d) characteristics of FETs based on PBSTBT and PBSTDTBT.

donors have the potential to increase $V_{oc}$. The deeper HOMO levels of both PBSTBT and PBSTDTBT indicate the advantage of introducing silicon atoms into the donor part of polymer's backbone, which is critical for increasing the open circuit voltage ($V_{oc}$). In this case, there is no doubt that this family of silicon-containing low band gap polymers has good potential for organic photovoltaics.

To understand if the incorporation of silicon atoms into the fused rings can endow the copolymers with high hole mobility, field effect transistors with a bottom-gate, top-contact configuration were fabricated using PBSTBT and PBSTDTBT as the semiconductors. The detail of the device fabrication is described in the Supporting Information. The hole mobilities extracted from the saturation regime are $2.2 \times 10^{-3}$ and $1.1 \times 10^{-2}$ $cm^2$ $V^{-1}$ $s^{-1}$ based on the average taken from two batches of five devices each for PBSTBT (Figure 2a,b) and PBSTDTBT (Figure 2c,d), respectively. The on/off current ratios are around $10^5$ to $10^6$. The highest hole mobilities of PBSTBT and PBSTDTBT reached $2.5 \times 10^{-3}$ and $1.2 \times 10^{-2}$ $cm^2$ $V^{-1}$ $s^{-1}$, respectively. Such high hole mobilities, compared to other copolymers containing only large fused ring donors,[8] maybe arise from the silicon atoms that can enhance the intermolecular interaction and packing between polymer chains.[11d]

The photovoltaic properties of PBSTBT and PBSTDTBT were studied in PSCs using a device structure of ITO/PEDOT:PSS/polymer:$PC_{71}BM$/Ca/Al with a device area of 16 $mm^2$. The device was annealed in an atmosphere of dichlorobenzene for 10 min before the deposition of the electrode. All the details of device fabrication and characterization were demonstrated in the Supporting Information. The effect of blending ratio between polymer and $PC_{71}BM$ was systematically investigated as well. As shown in Table 1, when implanted with three times $PC_{71}BM$ in weight ratio, both PBSTBT and PBSTDTBT achieve the highest PCE. Figure 3a shows the typical current density—voltage ($J-V$) characteristics and the external quantum efficiency (EQE) of solar cell devices based on PBSTBT and PBSTDTBT with a 1:3 weight ratio of polymer to $PC_{71}BM$. Under the AM 1.5 simulated solar illumination (100 $mW/cm^2$), the device with a PBSTBT:$PC_{71}BM$ weight ratio of 1:3 and an active-layer thickness around 80 nm demonstrated a short-circuit current density ($J_{sc}$) of 8.86 $mA/cm^2$, a $V_{oc}$ of 0.81 V, and a fill factor (FF) of 48.80%. The resulting PCE is 3.49%. The EQE curve of a PBSTBT based device, as shown in Figure 3b, indicates an efficient photoconversion efficiency from 400 to 700 nm, with EQE values of as high as 52%. For PBSTDTBT, a device with a PBSTDTBT:$PC_{71}BM$ 1:3 weight ratio and active-layer thickness around 90 nm shows a PCE up to 3.64%. A $J_{sc}$ of 8.80 $mA/cm^2$ with a $V_{oc}$ of 0.80 V and a FF of 51.60% was achieved. This device showed a higher photoconversion efficiency over the range of 600—700 nm. The $J_{sc}$ values calculated by integrating the EQE data compared with an AM 1.5 reference spectrum were 9.00 and 9.10 $mA/cm^2$ for PBSTBTand PBSTDTBT, respectively, which are similar to those obtained from the $J-V$ measurements. The AFM images of the blended films containing both polymer and $PC_{71}BM$ showed rather smooth morphology with small phase segregation (see the Supporting Information), which indicates good film-forming properties of these new silole-containing copolymers.

**Table 1. Performance of Photovoltaic Devices under the AM 1.5 Simulated Illumination (100 mW/cm$^2$)**

| ratio | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF | PCE (%) |
|---|---|---|---|---|
| 1:1[a] | 0.73 (±0.01) | 4.80 (±0.15) | 32.9 (±1.0) | 1.16 (±0.15) |
| 1:2[a] | 0.71 (±0.01) | 8.0 (±0.49) | 36.4 (±2.6) | 2.07 (±0.28) |
| 1:3[a] | 0.81 (±0.03) | 8.86 (±0.50) | 48.8 (±1.0) | 3.47 (±0.19) |
| 1:1[b] | 0.81 (±0.02) | 5.66 (±0.37) | 35.8 (±1.2) | 1.69 (±0.14) |
| 1:2[b] | 0.80 (±0.01) | 8.94 (±0.27) | 48.9 (±1.6) | 3.50 (±0.20) |
| 1:3[b] | 0.80 (±0.01) | 8.80 (±0.21) | 51.6 (±1.5) | 3.64 (±0.14) |

[a] PBSTBT:$PC_{71}BM$. [b] PBSTDTBT:$PC_{71}BM$.

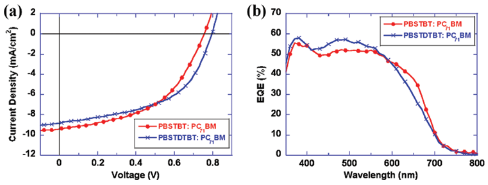

**Figure 3.** (a) $J-V$ curves of polymer solar cells under illumination of AM 1.5G, 100 $mW/cm^2$ at polymer:$PC_{71}BM$ ratio 1:3; (b) EQEs of polymer:$PC_{71}BM$ 1:3 solar cells.

In conclusion, we have developed a new type of benzobis(silolothiophene)-based low band gap copolymers using a facile method in high yield. The introduction of silicon atoms into the fused rings provides these new polymers with low HOMO levels and high hole mobilities up to 0.01 $cm^2$ $V^{-1}$ $s^{-1}$. Preliminary characterization of the bulk heterojuction solar cell devices shows PCE of around 3.5% for both of PBSTBT and PBSTDTBT. This work provides a new method for synthesizing silole-containing heteroarenes, which show great potential in the organic electronics applications, such as FETs and PSCs. Further structural functionalization and device optimazition based on PBSTBT and PBSTDTBT are ongoing.

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**Supporting Information Available:** Experimental details of the synthesis of the polymers, the fabrication and characterization of the devices, measurements, and instruments (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.