Synthesis, Characterization, and Photovoltaic Properties of a Low Band Gap Polymer Based on Silole-Containing Polythiophenes and 2,1,3-Benzothiadiazole

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Polymer solar cells have been attracting considerable attention due to their unique advantages of being low in cost and lightweight, as well as their potential application in flexible large-area devices.[1] To realize high efficiencies, the active layer of polymer solar cells must have good absorption of sunlight. Since 54.3% of the sunlight energy is distributed in the visible region from 380 to 800 nm, an ideal active layer for a polymer solar cell should have a broad and strong absorption spectrum in this range. Fullerenes and their derivatives, such as [6,6]-phenyl-C61-butyric acid methyl ester (PCBM), are widely used as electron acceptor materials in polymer solar cells, but they exhibit weak absorption in the visible range. As a result, the absorption of polymer:PCBM based solar cells is mainly from the electron donor material. Hence, to improve harvesting of sunlight, some low band gap conjugated polymers were designed, synthesized, and used in polymer solar cells.[2] In several works, poly[(4,4-bis(2-ethylhexyl)-cyclopenta-[2,1-b;3,4-b']dithiophene)-2,6-diyl-*alt*-2,1,3-benzothiadiazole-4,7-diyl], PCP-DTBT,[3] has been proven to be one of the most efficient low band gap photovoltaic materials. For the PCPDTBT/PC$_{70}$BM based polymer solar cell, an efficiency of 3.2% was achieved,[3a] and by morphology control using octane-1,8-dithiol as an additive in the device fabrication process, the efficiency of the solar cell device reached 5.4%.[3b] As reported, the response of the solar cell based on PCPDTBT covers the range 380−900 nm; this wide response range is the main advantage of this material, and as a result, the short circuit voltage of the solar cell reaches 16 mA/cm.[2,3b]

To ensure effective charge carrier transport to the electrodes and reduce the photocurrent loss in solar cells, high carrier mobility is also needed for polymer solar cells.[4] Poly[(9,9-dialkylfluorene)-2,7-diyl-*alt*-(4, 7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5′-diyl] (PFDTBT) and its derivatives are a well-known class of photovoltaic materials, and the efficiency of this kind of material is ~2−3%.[5] When the carbon atoms on the 9-position of the fluorene units of PFDTBT were substituted with silicon atoms, the photovoltaic properties of the material improved significantly, and an efficiency of 5.4 % was reported by using poly[(2,7-dioctylsilafluorene)-2,7-diyl-*alt*-(4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5′-diyl], PSiFDT-BT, as shown in Scheme 1, as the active layer material.[6] As reported, although the absorption spectrum of PSiFDTBT is similar to that of PFDTBT, the substitution of silicon atoms significantly improves the hole transport property of the material. As a result, the fill factor (FF) and short circuit current (J$_{sc}$) of the PSiFDBT-based device is better than those of the PFDTBT-based device.[6]

Recently, dithieno[3,2-*b*:2′,3′-*d*]silole-containing polymers have attracted much attention due to their potential applications in the field of optoelectronic devices.[7−9] For instance, the hole mobility

Scheme 1. Structures of PCPDTBT, PSiFDBT, and PSBTBT
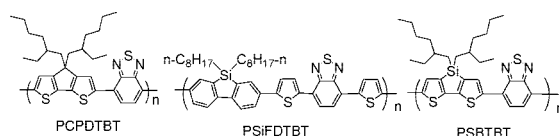
of the field effect transistor (FET) using a dithieno[3,2-*b*:2′,3′-*d*]silole-containing polymer as the active layer material reached 0.02 cm^2 V^{-1} s^{-1};[8] another dithieno[3,2-*b*:2′,3′-*d*]silole-containing polymer, poly[(4,4′-bis(2-ethylhexyl)dithieno[3,2-*b*:2′,3′-*d*]silole)-2,6-diyl-alt-(4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5′-diyl], was used in polymer solar cells and exhibited some interesting photovoltaic properties.[9] Therefore, to incorporate the broad absorption spectrum and good hole transport property of both the low band gap and silole-containing polymers, a new dithieno[3,2-*b*:2′,3′-*d*]silole polymer, poly[(4,4′-bis(2-ethylhexyl)dithieno[3,2-*b*:2′,3′-*d*]silole)-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl] (PSBTBT shown in Scheme 1), was designed and synthesized through a facile synthesis route.

To ensure good solubility, 2-ethylhexyl side chains were employed in the polymer. As shown in Scheme 2, dichlorobis(2-ethylhexyl)silane was synthesized through a two-step reaction route from tetrachlorosilane with a total yield of 40−45% (~65% for the first step and ~70% for the second step). As reported, 4,4′-dialkyldithieno[3,2-*b*:2′,3′-*d*]silole was commonly synthesized by a coupling reaction between dichlorodialkylsilane and 3,3′-dilithium-2,2′-bithiophene,[8b] but in our experiments, inconsistent yields, from 20 % to 60 %, were obtained in four batches of the reaction. Another method to synthesize 4,4′-dialkyldithieno[3,2-*b*:2′,3′-*d*]silole has been reported by Ohshita et al.,[10] and by using **3** as the starting material, this reaction can be carried out easily with a constant yield of ~70 %. The monomer, **6**, was synthesized by the commonly used method, and PDTSBT was prepared by a Stille coupling reaction. The number average molecular weight (M$_n$) of the polymer is 18.0 K, with a polydispersity index (PDI) of 1.2. Thermogravimetric analysis shows that the polymer exhibits good stability below 250 °C without the protection of an inert atmosphere.

The HOMO and LUMO levels of PSBTBT were measured by electrochemical cyclic voltammetry (CV). As shown in Figure 1a, both the n- and p-doping processes of this polymer are reversible. The onset points of the n- and p-doping processes are 0.25 and −1.52 V, and the HOMO and LUMO levels of the polymer were calculated to be −5.05 and −3.27 eV, respectively. Absorption spectra of the polymer PSBTBT in solution and in solid state are shown in Figure 2b. The optical band gap is 1.45 eV, which is very similar to the polymer PCPDTBT.[2d] The hole mobility value 3 × 10^{-3} cm^2/(V s) determined for the polymer from the field effect transistor is 3 times higher than that for PCPDTBT.[2d] All

Scheme 2. Synthesis Route of the Polymer PSBTBT[a]
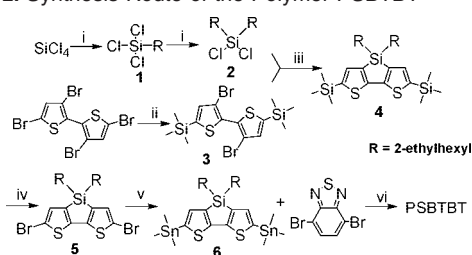
[a] (i) iso-C_8H_{17}MgBr, THF, 0 °C, 1 h, then ambient temp 4 h; (ii) n-butyllithium, THF, −90 °C, 10 min, then TMSCl, ambient temp 15 min; (iii) butyllithium, THF, −78 °C, 15 min; then compound **2**, ambient temp 1 h; (iv) NBS, THF, ambient temp 2 h; (v) butyllithium, −78 °C, 10 min; then trimethyltin chloride, 1 h; (vi) Pd(PPh$_3$)$_4$, toluene, reflux, 24 h.
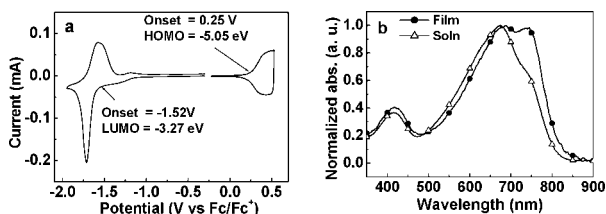

Figure 1. (a) Cyclic voltammograms of PSBTBT films on a platinum electrode in 0.1 mol/L Bu$_4$NPF$_6$, CH$_3$CN solution; (b) absorption spectra of PSBTBT solution in chloroform and as a film.
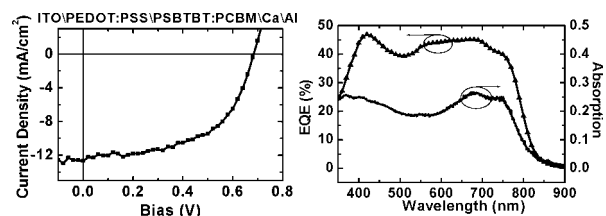

Figure 2. (a) I−V curve of a PSBTBT-based solar cell device under illumination of AM 1.5G, 100 mW/cm^2; (b) input photon-to-converted current efficiency curve of the device.

these characteristics indicate that PSBTBT is an ideal polymer for organic photovoltaic applications.

We fabricated the photovoltaic device with a structure of ITO/PEDOT-PSS/PSBTBT:PCBM/Ca/Al. After spin-coating a 30 nm layer of poly(3,4-ethylene dioxythiophene):poly(styrenesulfonate) onto a precleaned indium−tin oxide (ITO) coated glass substrate, the polymer/PC$_{70}$BM (1:1, w/w) solution in chlorobenzene was spin-coated, and then the substrate was subsequently annealed at 140 °C for 5 min. The devices were completed by evaporating Ca/Al metal electrodes with an area of 12 mm^2, which were defined by masks. To ensure accuracy of the device measurement, the testing method reported in our previous work[11] was used, and the detailed conditions of the device fabrication and characterization are provided in the Supporting Information. The average power conversion efficiency (PCE) of 100 devices reached 4.7 %, and for the best device, a PCE of 5.1% was observed. Figure 2a shows the typical I−V curve under illumination of AM 1.5G (100 mW/cm^2) of the devices with V_{oc} 0.68V, J_{sc} 12.7 mA/cm^2, and FF 55%. After measuring the I−V curve, the device was encapsulated in a nitrogen filled glovebox, and the EQEs of the devices were measured in air. As shown in Figure 2b, the device exhibits a very broad response range covering 350 to 800 nm, and within the whole range, the external quantum efficiency (EQE) is ∼43%, with the maximum EQE being 47% at 420 nm. A 10% difference between

the J_{sc} and the integral of the EQE is observed. Since the EQE was tested in the air, this discrepancy should be mainly ascribed to the degradation caused by the oxidation of the Ca electrode.

Although the absorbance of the active layer at 670 nm is ∼0.2 only, the EQE of the device reached 45%, meaning that 78% of the photons that were absorbed by the active layer were converted to electrons. Therefore, by optimizing the interpenetrating network morphology of PSBTBT-based devices, higher J_{sc} and FF, and hence better PCE, can be expected. This portion of work is being carried out to explore the full potential of this new material.

On the other hand, since the active layer exhibits an almost flat absorption spectrum in the visible range, it has little influence on the color of the transmitted light. These properties make the polymer PSBTBT a promising candidate for applications of translucent polymer solar cells.

In conclusion, a new low band gap silole-containing conjugated polymer, PSBTBT, was designed and prepared. Photovoltaic properties of the material were initially investigated, and a PCE of up to 5.1 % was observed under AM 1.5G, 100 mW/cm^2 illumination, and the response range of the device covers the whole visible range from 380 to 800 nm. These results indicate that PSBTBT is a promising polymer material for application in polymer solar cells.

Supporting Information Available: Experimental details of the synthesis of the polymer, the fabrication and characterization of the polymer solar cells, measurements, and instruments. This material is available free of charge via the Internet at http://pubs.acs.org.

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