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# High-performance polymer heterojunction solar cells of a polysilafluorene derivative

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High-performance polymer heterojunction solar cells fabricated from an alternating copolymer of 2,7-silafluorene (SiF) and 4,7-di(2'-thienyl)-2,1,3-benzothiadiazole (DBT) (PSiF-DBT) as the electron donor blended with [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester as the electron acceptor were investigated. A power-conversion efficiency up to 5.4% with an open-circuit voltage of 0.90 V, a short-circuit current of 9.5 mA cm<sup>-2</sup>, and a fill factor of 50.7% was achieved under the illumination of AM 1.5 G from a calibrated solar simulator (800 W m<sup>-2</sup>). The field-effect transistors fabricated from PSiF-DBT showed a high hole mobility of  $\sim 1 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. © 2008 American Institute of Physics. [DOI: 10.1063/1.2836266]

With an increasing demand on cheap renewable energy sources, polymer-based heterojunction solar cells have been attracting considerable attention recently due to their unique advantages of low cost, light weight, and potential application in flexible large-area devices.<sup>1-4</sup> The bulk heterojunction (BHJ) of conjugated polymers (electron donor) blended with fullerene derivatives (electron acceptor) boosts the efficiency of polymer solar cells.<sup>1-7</sup> Power-conversion efficiency (PCE) up to 5% has been obtained from both the BHJ solar cells of poly(3-hexylthiophene) (P3HT) blended with [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC[60]BM) and the one of poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCP-DTBT) blended with [6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester (PC[70]BM).<sup>5-7</sup> The BHJ solar cells made from P3HT and PCPDTBT both have high fill factor (FF) and short-circuit current density ( $J_{sc}$ ), while PCE is still limited by lower open-circuit voltage ( $V_{oc}$ ) (0.60–0.65 V).<sup>5-7</sup> To improve PCE by means of increasing  $V_{oc}$  is a facile method.<sup>8-10</sup> Recently, the BHJ polymer solar cells using polyfluorene (PF)-based alternating copolymers (such as PFDTBT) as donor have demonstrated larger  $V_{oc}$  (0.95–1.04 V),<sup>11-13</sup> however, their PCE is still low owing to the lower  $J_{sc}$  than that of both P3HT and PCPDTBT based cells.<sup>5-7,11-13</sup> If the  $J_{sc}$  of this type of copolymer based solar cells can be further enhanced while maintaining their large  $V_{oc}$ , higher PCE can be expected.

Chan *et al.* and our group found that poly(2,7-silafluorene) (PSiF) was an excellent blue emitter, which shows similar photophysical properties to PFs, but higher electroluminescent efficiency and thermal stability.<sup>14-17</sup> The remarkable electronic properties of PSiF and the above-mentioned advantages of PF-based alternating copolymers (such as PFDTBT) (Ref. 11) as electron donor drive us to synthesize PSiF-based copolymers and to investigate their photovoltaic performance.

In this letter, we report the BHJ solar cells made by the alternating copolymer of 2,7-silafluorene (SiF) and

4,7-di(2'-thienyl)-2,1,3-benzothiadiazole (DBT) (PSiF-DBT) as the electron donor blended with PC[60]BM as the electron acceptor. A PCE of 5.4%, a  $V_{oc}$  of 0.90 V, a  $J_{sc}$  of 9.5 mA cm<sup>-2</sup>, and a FF of 50.7% were obtained from the single layer solar cells under Air Mass 1.5 Global (AM 1.5 G) illumination from a calibrated solar simulator with an irradiation intensity of 800 W m<sup>-2</sup>. A comparison study on the photovoltaic performance of PSiF-DBT and its analog, PF-based copolymer poly[2,7-(9-(2'-ethylhexyl)-9-hexyl-fluorene)-alt-5,5-(4',7',-di-2-thienyl-2',1',3'-benzothiadiazole)] (PFDTBT)<sup>11</sup> and poly[2,7-(9,9-dioctyl-fluorene)-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PFO-DBT)<sup>12</sup> was undertaken.

The chemical structure of PC[60]BM, PFDTBT, PFO-DBT, and PSiF-DBT are shown in Scheme 1. PC[60]BM was purchased from America Dyes Sources (ADS). The synthesis and characteristics of PFO-DBT were reported elsewhere.<sup>12</sup> The monomers 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylsilafluorene and 4,7-bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole were synthesized following the literatures.<sup>14-18</sup> The copolymer PSiF-

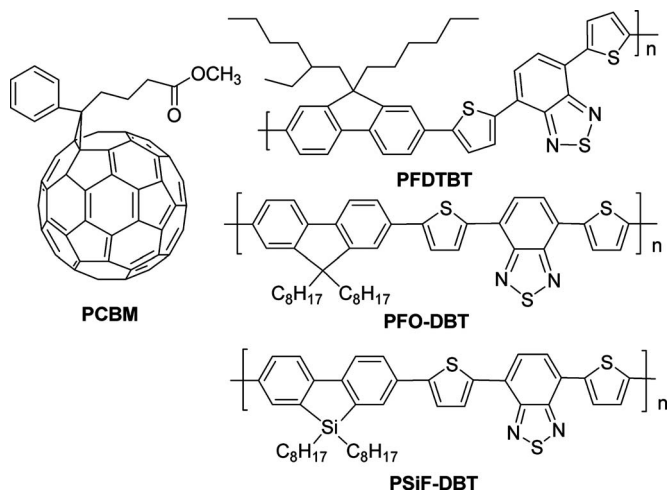


FIG. Scheme 1. Chemical structures of PC[60]BM, PSiF-DBT, PFDTBT, and PFO-DBT.

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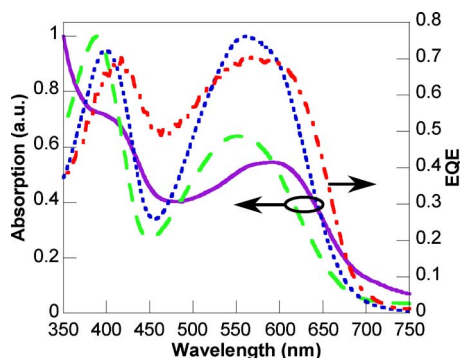


FIG. 1. (Color online) The normalized absorption spectrum of PSiF-DBT in films (dot line), in toluene solution (dashed line), the absorption of the blends of PSiF-DBT:PC[60]BM (1:2, *w/w*) spin coated from chlorobenzene (solid line), and the EQE of the device illuminated by monochromatic light.

DBT was synthesized via a modified Suzuki coupling reaction.<sup>17</sup> The number-average molecular weight ( $M_n$ ) of the polymer determined by gel permeation chromatography with polystyrene standards is 79 000 with a polydispersity index of 4.2. PSiF-DBT exhibited an excellent thermal stability determined by thermal gravimetric analysis with a decomposition temperature under nitrogen of 430 °C (5% weight loss).

As shown in Fig. 1, two absorption bands were observed from PSiF-DBT both in films (70 nm in thickness) and in toluene solution. The absorption peak of PSiF-DBT in films redshifts 14 nm as compared with that in toluene solution, indicating that a strong intermolecular interaction occurred in solid state. The optical band gap of PSiF-DBT deduced from its absorption edge in solid state is 1.82 eV, which is 0.1 eV lower than that of PFDTBT (1.92 eV).<sup>11,12</sup> It was also found that the absorption peaked at 565 nm redshifted approximately 20 nm compared with that of its analogous PFDTBT (peaked at 545 nm).<sup>11</sup> This redshift is beneficial for the polymer to absorb more solar radiation at long wavelength region and, consequently, a higher PCE can be expected from the BHJ solar cells made from PSiF-DBT.

In order to investigate the potential application of PSiF-DBT in solar cells, the devices with a sandwich structure of indium tin oxide (ITO)/poly (3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/PSiF-DBT:PC[60]BM (1:2, *w/w*)/Al were fabricated. The ITO-coated glass substrates were cleaned by ultrasonic treatment in de-ionized water, acetone, detergent, and isopropyl alcohol sequentially, followed by spin coating of a 40 nm thin layer of PEDOT:PSS (Baytron PH 500 from H. C. Starck). After drying PEDOT:PSS at 120 °C for 20 min, a 70 nm layer of PSiF-DBT:PC[60]BM (1:2, *w/w*) was spin coated from chlorobenzene solution onto the top of PEDOT:PSS. The film thickness was verified by a surface profilometer (Tencor, Alpha-500). A 140 nm thick of aluminum as cathode was thermally evaporated in vacuum at a pressure below  $3 \times 10^{-4}$  Pa through a shadow mask. The active area of the device was 0.15 cm<sup>2</sup>. The PCEs were measured under the illumination of AM 1.5 G from a solar simulator (Oriel model 91192) (800 W m<sup>-2</sup>). The current density-voltage (*J-V*) characteristics were recorded with a Keithley 236 source unit. The spectral response was measured with a commercial photomodulation spectroscopic setup (model Merlin, Oriel).

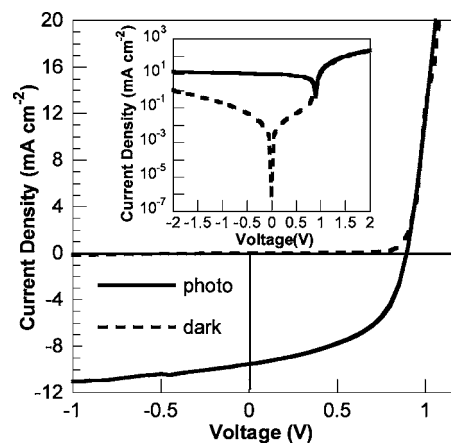


FIG. 2. *J-V* characteristics of a device with the structure of ITO/PEDOT:PSS/PSiF-DBT:PC[60]BM (1:2, *w/w*)/Al in the dark and under the illumination of AM 1.5 G from a solar simulator (800 W m<sup>-2</sup>).

The *J-V* characteristics of the devices measured both in dark and under the illumination of AM 1.5 G (800 W m<sup>-2</sup>) from a solar simulator are shown in Fig. 2. The dark *J-V* curve shows a typical diode characteristic (inset in Fig. 2). The PCE up to 5.4% was observed from the solar cells made by PSiF-DBT:PC[60]BM with a  $V_{oc}$  of 0.90 V, a  $J_{sc}$  of 9.5 mA cm<sup>-2</sup>, and a FF of 50.7%, which is one of the highest PCEs for single active layer polymer solar cells. It is worth noting that all these good values (high PCE, high  $V_{oc}$ , large  $J_{sc}$ , and acceptable FF) were obtained from the solar cells without additional postannealing treatment and without adding any additive into the active layer to control film morphology. This is a remarkable advantage over the high PCE observed from either P3HT or PCPDTBT based solar cells because additional processing involved in the fabrication procedure of polymer solar cells will definitely increase the costs of solar cells.<sup>5-7</sup>

The absorption spectrum of PSiF-DBT:PC[60]BM (1:2, *w/w*) spin coated from chlorobenzene solution and the external quantum efficiency (EQE) of the device illuminated by monochromatic light are shown in Fig. 1. Both the absorption spectrum and EQE profiles ranged from 350 to 750 nm, which are broader than those of PFDTBT:PC[60]BM.<sup>11</sup> In addition, a maximum EQE of  $\sim 70\%$  is achieved from the device made by PSiF-DBT:PC[60]BM, which is also higher than that of PFDTBT:PC[60]BM.<sup>11,12</sup> The broader profile and higher values of EQE from PSiF-DBT:PC[60]BM are consistent with the higher  $J_{sc}$  measured in the solar cells [4.66 mA cm<sup>-2</sup> for PFDTBT (Ref. 11) and 9.5 mA cm<sup>-2</sup> for PSiF-DBT].

To understand the origin of the high  $V_{oc}$  obtained from the device made by PSiF-DBT:PC[60]BM, electrochemical study was conducted. The highest occupied molecular orbital (HOMO) level of PSiF-DBT, calculated from the empirical formula  $E_{HOMO} = -(E_{ox} + 4.40)$  (eV),<sup>19</sup> was  $-5.39$  eV. The  $E_{ox}$  (oxidation potential) was determined by cyclic voltammetry, which was performed on a potentiostat/galvanostat model 283 (Princeton Applied Research) electrochemical workstation with platinum working electrodes at a scan rate of 50 mV s<sup>-1</sup> against a saturated calomel reference electrode with a nitrogen-saturated anhydrous solution of 0.1 mol L<sup>-1</sup> tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) in acetonitrile. Scharber *et al.* reported that  $V_{oc}$  is linearly correlated with the difference of the HOMO level of electron do-



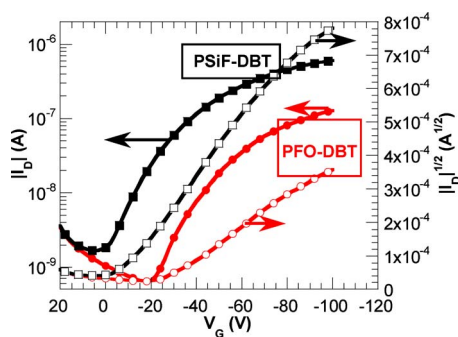


FIG. 3. (Color online) Transfer curves in the saturated regime at a constant source-drain voltage of  $-100$  V and the square root of the absolute values of the current as a function of the gate voltage from the FETs made by PSiF-DBT and PFO-DBT.

nor with the lowest unoccupied molecular orbital level of electron acceptor.<sup>10</sup> In comparison with other common low band gap donor polymers, the higher  $V_{oc}$  of the solar cells made by PSiF-DBT:PC[60]BM can be attributed to the lower HOMO level of PSiF-DBT.<sup>5-7,10,20</sup>

Hole transport properties of polymer donors has a significant influence on the performance of BHJ solar cells.<sup>20</sup> To further explore the reason for the high performance of the solar cells made by PSiF-DBT:PC[60]BM, the hole mobility of the field-effect transistors (FETs) from PSiF-DBT were investigated. For comparison, the FETs fabricated from PFO-DBT (Ref. 21) were also investigated in the same condition. A bottom gate structure was used to fabricate the FETs. The substrates consisted of highly *n*-doped silicon wafers with a 300 nm thick layer of SiO<sub>2</sub> as the gate dielectric insulator. The measured capacitance of the SiO<sub>2</sub> was  $\sim 10.4$  nF cm<sup>-2</sup>. A 60 nm thick polymer film was spin coated from toluene solution onto the substrates. A 40 nm thick layer of Au as the source and drain electrodes was deposited by thermal evaporation onto the semiconductor films through a shadow mask under high vacuum. The transistors have a channel length ( $L$ ) of 100  $\mu$ m and a channel width ( $W$ ) of 2 mm. The FET characteristics were performed using a probe station and an Agilent 4155C semiconductor parameter analyzer. The FETs were measured under ambient conditions without any encapsulation, which indicated a good stability of PSiF-DBT to oxygen and moisture. According to the transfer characteristics ( $I_D$  versus  $V_G$ ) of the FETs (Fig. 3), the hole mobility of PSiF-DBT was calculated to be  $\sim 1 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, which is nearly ten times higher than that of PFO-DBT ( $\sim 3 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>). High mobility can ensure effective charge carrier transport to the electrode and reduce photocurrent loss in solar cells.<sup>6,22</sup> Therefore, a high  $J_{sc}$  and an acceptable FF observed from the device made by PSiF-DBT:PC[60]BM can be attributed to its higher hole mobility. Taken together, the higher performance of the solar cells made by PSiF-DBT:PC[60]BM is attributed to the broader absorption spectrum and good hole transport properties of PSiF-DBT compared with its analogous PFDTBT and PFO-DBT.

In conclusion, the PCE up to 5.4% was observed from the BHJ polymer solar cells made by PSiF-DBT:PC[60]BM. A comparison study between PSiF-DBT and PFDTBT was investigated. The high  $V_{oc}$  from PSiF-DBT based solar cells originated from its lower HOMO level and the higher  $J_{sc}$  is due to its broader absorption spectrum and higher hole mobility. Our results demonstrated that PSiF derivatives are a promising class of electron donor materials for high-performance BHJ polymer solar cells.<sup>23</sup>

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