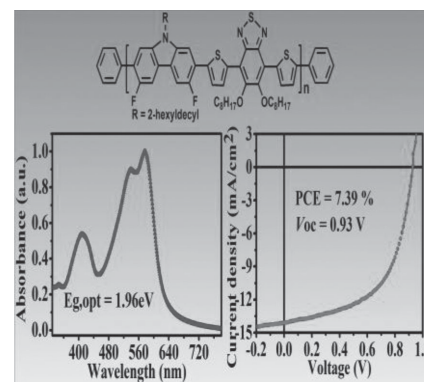


High-Efficiency Large-Bandgap Material for Polymer Solar Cells

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High-molecular-weight conjugated polymer HD-PDFC-DTBT with *N*-(2-hexyldecyl)-3,6-difluorocarbazole as the donor unit, 5,6-bis(octyloxy)benzothiadiazole as the acceptor unit, and thiophene as the spacer is synthesized by Suzuki polycondensation. HD-PDFC-DTBT shows a large bandgap of 1.96 eV and a high hole mobility of $0.16 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. HD-PDFC-DTBT:PC₇₁BM-based inverted polymer solar cells (PSCs) give a power conversion efficiency (PCE) of 7.39% with a V_{oc} of 0.93 V, a J_{sc} of 14.11 mA cm^{-2} , and an *FF* of 0.56.



1. Introduction

Polymer solar cells (PSCs) have had a fast growing development over the past decade because of their advantages such as low cost, light weight, and high-throughput manufacture.^[1–5] Bulk heterojunction (BHJ) PSCs composed of conjugated polymers and fullerene derivative such as (6,6)-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) or

(6,6)-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) have been proven to be the most efficient device structure.^[6–15] In order to improve the power conversion efficiency (PCE) of BHJ PSCs, great efforts have been focused on the optimization of polymer and device structures. Recently, PCE above 9% for BHJ PSCs has been reported.^[16–23] However, up to now, almost all high-efficiency (>7%) polymer donor materials are small-bandgap materials, whereas high-efficiency large-bandgap polymers are very rare. Both high-efficiency small-bandgap and large-bandgap materials are necessary for the fabrication of high-efficiency tandem solar cells.^[24] Poly(3-hexylthiophene) (P3HT) is the most sufficiently investigated large-bandgap polymer with an optical bandgap of 1.90 eV and a highest occupied molecular orbital (HOMO) level of -5.0 eV . PSCs with P3HT as the donor and PC₆₁BM as the acceptor gave a PCE of 4.2%.^[25] When indene-C₆₀ bisadduct (ICBA) was used as the acceptor instead of PC₆₁BM, the PCE was further enhanced to 6.6%.^[26,27] Poly[*N*-9'-hepta-decanyl-2,7-carbazole-alt-5,5'-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT), which was first reported by Leclerc and co-workers, is a typical representative of high-efficiency large-bandgap

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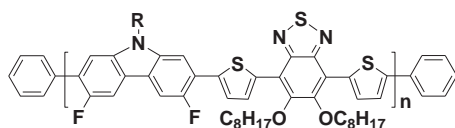
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HD-PDFC-DTBT: R = 2-hexyldecyl

O-PDFC-DTBT: R = octyl

■ Chart 1. Structures of HD-PDFC-DTBT and O-PDFC-DTBT.

conjugated polymers with an optical bandgap of 1.88 eV, and PSCs based on PCDTBT:PC₆₁BM gave a PCE of 3.6%.^[28] In 2009, the PCE was enhanced to 6.1% by incorporation of a TiO_x layer as the optical spacer.^[29] In inverted PSCs, PCDTBT also gave a PCE of about 6%. By using an antireflection coating, the PCE is further improved to 7.2%.^[30] Polymer PBnDT-FTAZ with an optical bandgap of 2.0 eV synthesized by You and co-workers^[31] gave the highest efficiency of 7.1% among the large-band polymers reported hitherto.

In our previous work, we have reported a D–A alternating conjugated polymer (O-PDFC-DTBT) with 3,6-difluorocarbazole as the donor unit and 5,6-bis(octyloxy) benzothiadiazole as the acceptor unit (Chart 1).^[32] As expected, the fluorinated polymer O-PDFC-DTBT exhibits markedly lower HOMO and LUMO (lowest unoccupied molecular orbital) energy levels, forms close packing in solid state, and shows higher thermal and electrochemical stability. However, a PCE of only 4.8% was obtained for PSCs based on O-PDFC-DTBT. It is well known that the molecular weight of conjugated polymers plays a pivotal role in the performance of devices.^[33–36] O-PDFC-DTBT has a number-average molecular weight (\bar{M}_n) of 9.1 kg mol^{−1}. The low molecular weight of O-PDFC-DTBT is due to its limited solubility in the reaction media used for polymerization. In this work, to achieve high-molecular-weight polymers, we replace the octyl chain on the 9-position of 3,6-difluorocarbazole unit with a 2-hexyldecyl chain to increase the solubility of the resulting polymers. High-molecular-weight polymers (HD-PDFC-DTBT) have been synthesized and used for the fabrication of PSCs. Inverted devices have also been fabricated and applied to investigate the photovoltaic performance. A PCE of 7.39% with a V_{oc} of 0.93 V, a J_{sc} of 14.11 mA cm^{−2}, and an FF of 0.56 and hole mobility (μ) up to 0.16 cm² V^{−1} s^{−1} have been obtained for HD-PDFC-DTBT. Considering the relatively large bandgap of 1.96 eV, HD-PDFC-DTBT is a very promising large-bandgap material for the fabrication of tandem solar cells.^[19,23,24] To the best of our knowledge, a PCE of 7.39% is the highest efficiency for large-bandgap materials reported up to now.

2. Results and Discussion

The synthesis of O-PDFC-DTBT has been reported in our previous work.^[32] To achieve high-molecular-weight

polymers, we synthesized 3,6-difluoro-9-(2-hexyldecyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (M1), which bears a branched alkyl chain on the 9-position of carbazole unit. Suzuki-Miyaura polycondensation of M1 with 4,7-bis(5-bromothiophen-2-yl)-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole (M2) with freshly prepared Pd(PPh₃)₄ as the catalyst precursor afforded HD-PDFC-DTBT in a yield of 96%. HD-PDFC-DTBT exhibited limited solubility in normal organic solvents at room temperature, but could be fully dissolved in chlorobenzene (CB), 1,2-dichlorobenzene (DCB), and 1,2,4-trichlorobenzene (TCB) at elevated temperature. Molecular weight and molecular weight distribution of HD-PDFC-DTBT was therefore characterized by gel permeation chromatography (GPC) at elevated temperature (150 °C) using TCB as an eluent and narrowly distributed polystyrenes as calibration standards. Number-average molecular weight of HD-PDFC-DTBT has reached 38.3 kg mol^{−1} with a polydispersity index (PDI) of 2.56. Thermogravimetric analysis (TGA) indicated that HD-PDFC-DTBT was of good thermal stability with the decomposition temperature up to 320 °C (5% weight loss) under a nitrogen atmosphere. The slightly lower degradation temperature than O-PDFC-DTBT (328 °C) can be attributed to the incorporation of branched side chains. The data are summarized in Table S1 (Supporting Information). X-ray diffraction (XRD) was used to investigate the packing of polymer chains in the solid state, and diffraction patterns of powdery polymer samples are shown in Figure S1 (Supporting Information). The spacing corresponding to the π – π stacking distance between polymer backbones is about 4.4 Å.

Optical properties of HD-PDFC-DTBT were characterized by UV–vis absorption spectroscopy. As shown in Figure 1, the solution spectrum at room temperature displays three absorption peaks located at 406, 534, and 573 nm, respectively. When the polymer solution was heated to 80 °C, the absorption spectrum was markedly blue-shifted, and the two well-resolved peaks in the low-energy region

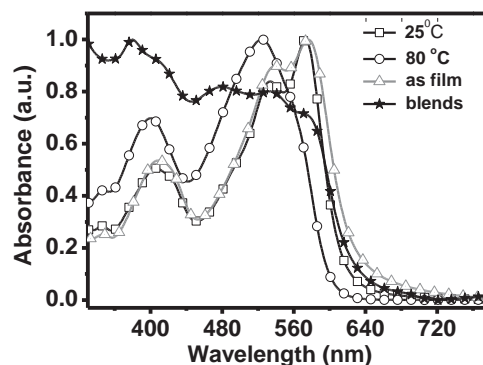


Figure 1. Normalized absorption spectra of HD-PDFC-DTBT in CB solutions at 25 °C, 80 °C, and in thin films, and the blend of HD-PDFC-DTBT:PC₇₁BM (1:3 by weight).

disappeared and a new featureless broad absorption peak appeared 524 nm. In the solution spectrum at elevated temperature, the absorption peak at 401 nm is due to the π - π^* transition of the 3,6-difluorocarbazole unit and the peak at 524 nm is attributed to the intramolecular charge transfer from the donor unit to the acceptor unit. The film absorption spectrum of HD-PDFC-DTBT is similar to its solution spectrum at room temperature. The above results indicated that the polymer chains of HD-PDFC-DTBT formed a strong aggregation in solution at room temperature, and the aggregation could be disassembled to form real solution at elevated temperature. Clearly, the absorption spectrum of HD-PDFC-DTBT in DCB solution at 80 °C is similar to that of O-PDFC-DTBT and HXS-1 in DCB solutions.^[15,32] Compared with the film absorption spectrum of O-PDFC-DTBT (Figure S2, Supporting Information), the intensity of the long-wavelength absorption peak of HD-PDFC-DTBT in film absorption spectrum is markedly enhanced, indicating that more ordered aggregation was formed due to the improved molecular weight. From the film absorption onset, the optical bandgap of HD-PDFC-DTBT was calculated to be 1.96 eV. The data have been summarized in Table S2 (Supporting Information).

Electrochemical properties of HD-PDFC-DTBT as thin films were investigated by electrochemical method, since they are crucial to the photovoltaic performance of PSCs. HOMO and LUMO energy levels of polymers were determined by cyclic voltammetry (CV). As shown in Figure S3 (Supporting Information), the onset oxidation potential (E_{ox}) of HD-PDFC-DTBT is 0.61 V, versus Ag/AgCl reference electrode. According to the equation $E_{HOMO} = -(E_{ox} + 4.71)$ (eV), HOMO energy level of HD-PDFC-DTBT was calculated to be -5.32 eV, which is deeper than the low-molecular-weight polymer O-PDFC-DTBT due to its longer side chains. LUMO energy level of HD-PDFC-DTBT was calculated to be -3.30 eV by using the equation $E_{LUMO} = E_{HOMO} + E_{g, opt}$. The data are also summarized in Table S2 (Supporting Information). It is apparent that the fluoro-substituted polymers are of deeper HOMO and LUMO energy levels than the corresponding nonfluoro-substituted polymers, which is beneficial to achieving high V_{oc} for devices.

The hole mobility of pristine HD-PDFC-DTBT film is investigated by the fabrication of field effect transistors (FETs). Figure 2 shows transfer characteristics of FETs fabricated using HD-PDFC-DTBT as the material in the channel. And output characteristics are shown in Figure S4 (Supporting Information). HD-PDFC-DTBT film exhibited a very promising p-type transistor performance, with saturated charge carrier mobilities up to $0.16 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ observed, a factor of 50 larger than the mobility obtained from O-PDFC-DTBT film ($3.1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). As expected, high-molecular-weight HD-PDFC-DTBT furnished high hole mobility.

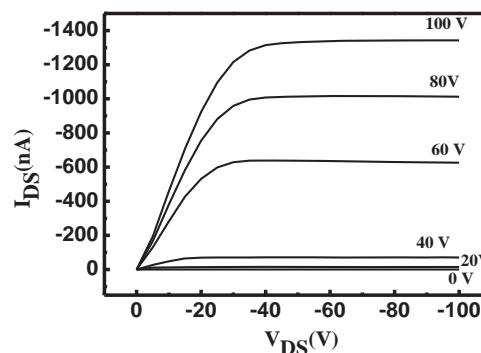


Figure 2. Transfer characteristics of the OFET from a pristine HD-PDFC-DTBT film.

Photovoltaic performance of HD-PDFC-DTBT was investigated in bulk heterojunction devices with an inverted device configuration of ITO/ZnO (40 nm)/interfacial layer/active layer/MoO₃ (7.5 nm)/Ag (100 nm). The active layer is a blend of HD-PDFC-DTBT and PC₇₁BM. Different processing solvents, different ratios of HD-PDFC-DTBT to PC₇₁BM, different polymer concentrations, different spin-coating speeds, and with or without the interfacial layer were used to optimize the device performance. Figure 3 shows the best device performance with a blend film of HD-PDFC-DTBT:PC₇₁BM in an optimal weight ratio of 1:3 spin-coated from DCB solution as the active layer. The optimum thickness of the active layer was found to be around 90 nm. Under the illumination of AM 1.5G, the devices furnished a PCE of 6.95% with a V_{oc} of 0.92 V, a J_{sc} of 12.98 mA cm^{-2} , and an FF of 0.58. It is worth noting that the good performance was achieved without using any processing additive. Inverted PSCs based on O-PDFC-DTBT:PC₇₁BM were also fabricated, a PCE of 5.32% with a V_{oc} of 0.91 V, a J_{sc} of 10.10 mA cm^{-2} , and an FF of 0.58 was obtained. Obviously, the high efficiency of HD-PDFC-DTBT:PC₇₁BM-based PSCs is mainly due to their high J_{sc} , which is usually related to the hole mobility of polymers (vide supra). C-PCBSD is a cross-linked fullerene derivative developed by Hsu et al.^[37–41] In situ cross-linking of

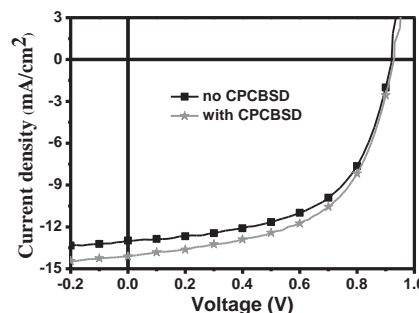


Figure 3. J - V curves of BHJ solar cells fabricated from the blend of HD-PDFC-DTBT:PC₇₁BM (1:3 by weight) in DCB. The device structure is ITO/ZnO (40 nm)/interfacial layer/active layer/MoO₃ (7.5 nm)/Ag (100 nm).

Table 1. Parameters of HD-PDFC-DTBT:PC₇₁BM-based devices fabricated from DCB solutions. The device structure is ITO/ZnO (40 nm)/interfacial layer/HD-PDFC-DTBT:PC₇₁BM (1:3)/MoO₃ (7.5 nm)/Ag (100 nm).

Interfacial layer	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF	PCE [%]
No	0.91	10.10	57.90	5.32 (5.22)
No	0.92	12.98	58.16	6.95 (6.83)
C-PCBSD	0.93	14.11	56.33	7.39 (7.10)

the C-PCBSD film on ZnO could be achieved by annealing the film at 160 °C for 30 min to generate a robust, adhesive, and solvent resistant film. The cross-linking C-PCBSD film can be used as an interfacial material as an electron-transfer layer between the active layer and ZnO, which can significantly improve the performance of PSCs. When C-PCBSD was used as the interfacial layer, the PCE was further enhanced to 7.39% with a V_{oc} of 0.93 V, a J_{sc} of 14.11 mA cm⁻², and an FF of 0.56. The data are summarized in Table 1. The morphology of polymer:PC₇₁BM blend films was investigated by atomic force microscopy (AFM) in tapping mode. As shown in Figure S5 (Supporting Information), the blend film showed nanoscale phase separation and a small RMS value of 0.294 nm. As a comparison, AFM images of the corresponding low-molecular-weight polymer and PC₇₁BM blends showed much rougher surface morphology. XRD measurements also indicated that low-molecular-weight polymers formed more ordered packing in the solid state than the corresponding high-molecular-weight polymers. The poorer solubility and higher crystallinity of low-molecular-weight O-PDFC-DTBT may prohibit its miscibility with PC₇₁BM and result in large phase separation. The nanomorphology of blend films fabricated under optimized conditions was also investigated by transmission electron microscopy (TEM). As shown in Figure S6 (Supporting Information), HD-PDFC-DTBT:PC₇₁BM blend films are uniform without large-scale phase separation. TEM image suggests that interpenetrated networks for electron and hole transport have been formed. Such ideal interpenetrating network would provide a suitable interface between the polymer and the PC₇₁BM and ensure efficient exciton dissociation. Meanwhile, a bicontinuous network that would enhance charge transport with a low recombination.^[42–45] To verify the J_{sc} values obtained by J – V measurement, external quantum efficiencies (EQEs) of PSCs fabricated with and without the C-PCBSD interfacial layer were measured and the EQE curves are shown in Figure 4. For PSCs fabricated with the C-PCBSD interfacial layer, the EQE values are over 80% in the range of 400 to 600 nm. The J_{sc} value obtained by the integration of EQE curves agreed well with the J_{sc} obtained by J – V

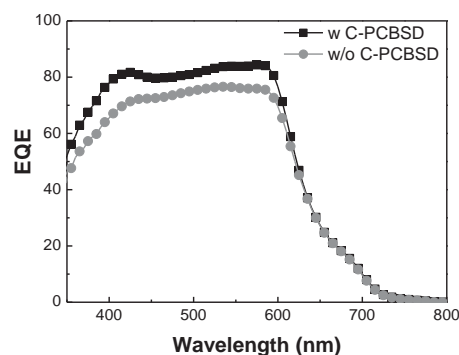


Figure 4. EQE curves of PSCs fabricated with and without the cross-linked C-PCBSD interfacial layer.

measurement. With C-PCBSD interlayer, the J_{sc} obtained by the integration of EQE curve is 13.08 mA cm⁻², which is fit well with the J_{sc} of 14.02 mA cm⁻² obtained by J – V measurement under the illumination of AM1.5. A deviation of 6.8% was observed. For PSCs fabricated without the C-PCBSD interlayer, a J_{sc} of 12.91 mA cm⁻² (AM1.5) was obtained by J – V measurement; whereas the J_{sc} obtained by the integration of EQE curve is 12.11 mA cm⁻². A deviation of 6.2% is obtained. A deviation smaller 20% is considered within the discrepancy threshold.^[46] The EQE results confirmed that the J_{sc} obtained by J – V measurement is believable.

3. Conclusion

In conclusion, high-molecular-weight HD-PDFC-DTBT has been synthesized and used for FETs and PSCs. HD-PDFC-DTBT films exhibited a high hole mobility of 0.16 cm² V⁻¹ s⁻¹. A PCE of 7.39% with a V_{oc} of 0.93 V, a J_{sc} of 14.11 mA cm⁻², and an FF of 0.56 has been obtained with inverted PSCs. Improved photovoltaic performance and increased hole mobility have been observed for high-molecular-weight polymer.

4. Experimental Section

Synthesis of HD-PDFC-DTBT: A mixture of M1 (157 mg, 0.23 mmol), M2 (165 mg, 0.23 mmol), THF (40 mL), toluene (13 mL), H₂O (4 mL), and NaHCO₃ (0.4 g, 4.8 mmol) was carefully degassed before and after Pd(PPh₃)₄ (3.5 mg, 2.98 μmol) was added. The mixture was stirred and refluxed under nitrogen for 3 d. Phenylboronic acid and Pd(PPh₃)₄ were added and refluxed for 4 h; after that bromobenzene and Pd(PPh₃)₄ were added, and the mixture was refluxed overnight to complete the end-capping reaction. After being cooled to room temperature, water and CB were added, and the organic layer was separated and washed three times with water. And then, the solution was heated to 100 °C to dissolve the polymers and filtered. After the removal of most solvent, the residue was poured into a large amount of acetone,

and the resulting precipitates were collected by filtration and washed with acetone. The crude product was redissolved in a minimum amount of CB and precipitated into a large amount of acetone. The formed precipitates were collected by filtration and dried under high vacuum to afford HD-PDFC-DTBT as a dark red solid (222 mg, 96%). ^1H NMR (400 MHz, 1,2-dichlorobenzene- D_4): δ 8.88–8.70 (br, 2H), 8.59–8.56 (br, 2H), 4.74–4.45 (br, 6H), 2.39–0.95 (br, 61H); GPC (PS standards): $\bar{M}_w = 98.1 \text{ kg mol}^{-1}$, $\bar{M}_n = 38.3 \text{ kg mol}^{-1}$, and PDI = 2.56.

Fabrication and Characterization of PSCs: Photovoltaic performance of HD-PDFC-DTBT was investigated in bulk heterojunction devices with an inverted device configuration of ITO/ZnO (40 nm)/interfacial layer/active layer/ MoO_3 (7.5 nm)/Ag (100 nm). The ZnO sol was prepared using a sol–gel procedure by dissolving zinc acetate dihydrate (99.9%, 2.0 g) and 2-aminoethanol (99%, 0.28 g) in anhydrous methanol (>99.8%, 9.1 mL) under vigorous stirring for 24 h for hydrolysis reaction and aging. Nano-sized ZnO thin films were prepared by spin-coating the sol–gel precursor solution at 4000 rpm on top of the indium tin oxide (ITO)-coated glass substrates with a sheet resistance of 10Ω . The films were heated at 200°C for 5 min in air. During this process, the precursor was converted to solid-state ZnO (i.e., Gel of ZnO), forming a transparent nanoparticle ZnO thin film with a thickness of ca. 40 nm. For devices fabricated with C-PCBSD interlayer, PCBSD was spin-cast from DCB onto the ZnO layer to form a thin film with a thickness of ca. 5 nm. Subsequently, the as-cast film was heated at 180°C for 10 min for thermal cross-linking in the glove box. For BHJ solar cells, the HD-PDFC-DTBT:PC71BM in an optimal weight ratio of 1:3 spin-coated from DCB solution on ZnO (no interfacial layer) or on C-PCBSD (with interfacial layer), PEDOT:PSS (Clevios P, purchase from H.C. Starck GmbH) was then spin-cast at 6000 rpm on top of the aforementioned layer using X-triton 100 (1 wt%) as the processing additive to form a smooth layer with a thickness of ca. 50–60 nm and then soft-baked at 120°C in the glove box. Finally, to complete the devices, the top electrode, made of 100 nm Ag film, was evaporated thermally at a base pressure below 10^{-6} torr. The top electrode was thermally evaporated, with a 7.5 nm MoO_3 layer, then followed by 100 nm of Ag at a pressure of 10^{-4} Pa through a shadow mask. Five cells were fabricated on one substrate with an effective area of 0.04 cm^2 . The measurement of devices was conducted in air without encapsulation. Current–voltage characteristics were recorded using a Keithley 2400 SMU under the irradiation of a 300 W solar simulator (San-Ei electric, XES-301S) as the white light source and the intensity was calibrated with a standard single-crystal Si photovoltaic cell. The temperature while measuring the J – V curves was approximately 25°C . The characteristics of the solar cells were optimized by testing approximately 10 cells.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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