Synthesis and Photovoltaic Properties of a Novel Low Band Gap Polymer Based on N-Substituted Dithieno[3,2-*b*:2′,3′-*d*]pyrrole

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Received September 8, 2008
Revised Manuscript Received October 14, 2008

For the past few years, polymer solar cells (PSCs) have attracted considerable attention because of their unique advantages, such as low cost and easiness of fabrication, light weight, and the capability to fabricate flexible large-area devices.[1] The photoconversion process in such solar cells is accomplished by efficient light absorption of conjugated polymers, charge transfer between the conjugated polymers and acceptor materials, and subsequent charge collection at electrodes. Matching of the absorption of the conjugated polymer to the solar spectrum determines the ultimate performance of the solar cells. Among the conjugated polymers, poly(*p*-phenylenevinylene)s[2] and polythiophenes[3] are two kinds of typical materials that have been extensively studied. A bulk heterojunction[4] photovoltaic device combining regioregular poly(3-hexylthiophene) as the electron donor with [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM) as the electron acceptor achieves power conversion efficiencies (PCEs) of more than 4%.[5]

However, the performance of the photovoltaic cells with these polymers is considerably limited by their relatively large band gaps, which are not yet optimized with respect to the solar spectrum. Therefore, the development of low band gap polymers becomes very important for better harvesting of the solar spectrum, especially in the red and near-infrared ranges, which leads to a possible enhancement in the photocurrent of PSCs.[6]

It is widely accepted that the alternative copolymer structures with donor and acceptor functionalities are very effective in decreasing the band gap of the polymers. Numerous attempts to develop new donor/acceptor (D−A) combinations have shown that the 4,7-dithien-2-yl-2,1,3-benzothiadiazole (DTBT) unit is very effective as an acceptor, and it can copolymerize with many kinds of donor segments, such as fluorene,[7] silafluorene,[8] carbezole,[9] dithienosilole,[10] and cyclopenta[2,1-*b*:3,4-*b*]dithiophene.[11] When applied to PSCs, PCEs in the range of 0.18%−5.4% have been reported.

Although this approach is very promising and many donors have been developed as described above, the performances are still far from the level necessary for practical application. It is still an urgent issue to explore new types of donor functionalities to construct D−A type polymers for high-performance solar cells. Dithieno[3,2-*b*:2′,3′-*d*]pyrrole (DTP) has good planarity and stronger electron-donating ability of nitrogen atoms, which might lead to the development of a low band gap polymer when it is copolymerized with an acceptor such as DTBT. Koeckelberghs et al. synthesized many chiral polymers containing DTP and investigated their chiroptical properties.[12] Very recently, the copolymers of DTP and thiophene units have been synthesized and used for field effect transistors (FETs).[13] However, there have been no reports on the photovoltaic properties of DTP-containing D−A type polymers to date.

In this Communication, we report the synthesis and application of a novel D−A type low band gap polymer, where DTP and DTBT are adopted as the donor and acceptor segments, respectively. To improve the solubility of copolymer to fabricated photovoltaic devices in solution process, a bulky group of 1-(2′-ethylhexyl)-3-ethylheptanyl was introduced to the nitrogen atom in DTP to obtain a novel D−A polymer: poly{*N*-[1-(2′-ethylhexyl)-3-ethylheptanyl]dithieno[3,2-*b*:2′,3′-*d*]pyrrole-2,6-diyl-*alt*-4,7-di(2-thienyl)-2,1,3-benzothiadiazole-5′,5″-diyl} (PDTPDTBT).

Scheme 1 shows the synthetic routes of the monomers and polymer. The intermediate 1-(2′-ethylhexyl)-3-ethylheptylamine was prepared starting from 1-bromo-2-ethylhexane in three steps. *N*-Alkyl DTP was synthesized by the Buchwald−Hartwig reaction of the primary amine with 3,3′-dibromo-2,2′-bithiophene. The polymer was synthesized by the Stille reaction between 2,6-di(trimethyltin)dithieno[3,2-*b*:2′,3′-*d*]pyrrole and 4,7-di(2-bromothien-5-yl)-2,1,3-benzothiadiazole in the presence of a palladium catalyst.[12]

The polymer was obtained as a dark-green powder and can be easily dissolved in common organic solvents, such as chloroform, tetrahydrofuran (THF), toluene, and chlorobenzene. The good solubility can be attributed to the bulky side chain. The thermal property of the polymer was investigated by differential scanning calorimetry (DSC) (Figure S1). No obvious peak was detected in the trace, suggesting the amorphous nature of PDTPDTBT. An attempt to determine the molecular weight of the polymer using gel permeation chromatography with $CHCl_3$ eluent failed, possibly because the polymer adsorbed onto the polystyrene gels. Using THF containing 0.5% H_3PO_4 as eluent gave a reproducible chromatogram of PDTPDTBT to show a broad bimodal distribution ranging from ca. 100 000 to 1000 g mol^{-1} with a weight-average molecular weight (M_w) of 6000 g mol^{-1} and a polydispersity of 3.4.

Figure 1 shows the UV−vis absorption spectra of PDTPDTBT. Both the solution in $CHCl_3$ and the film show two broad absorption bands with peaks at 450 and 671 nm and 451 and 697 nm, respectively. The second absorption peak in the film (697 nm) shows a red shift by 26 nm compared with that in the solution (671 nm), indicating strong intermolecular interaction in solid state. Compared with the absorption of the homopolymer of DTP (∼540 nm),[12] the red shift in this D−A copolymer clearly demonstrates the charge transfer absorption between DTBT and DTP functionalities, indicating that DTP is a new kind of effective donor segment for designing various D−A structure polymers.

The optical band gap of PDTPDTBT deduced from its absorption edge (850 nm) in solid state is 1.46 eV, which is the lowest compared with other D−A copolymers based on a DTBT acceptor segment with other donor segments (fluorene, silafluorene, carbezole, dithienosilole, and cyclopenta[2,1-*b*:3,4-*b*]dithiophene).[7,11]

The optimum geometry and electron-state-density distribution of the highest occupied molecular orbital (HOMO) and lowest

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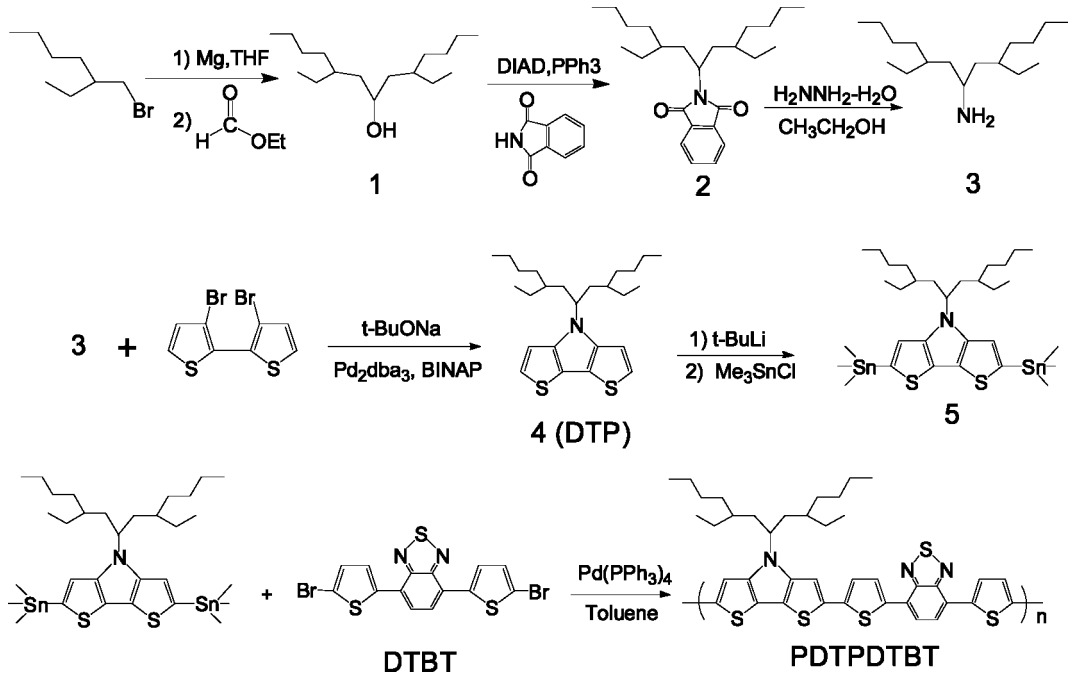
10.1021/ma802052w CCC: $40.75
Published on Web 10/31/2008

Scheme 1. Synthetic Routes of the Monomers and Polymer



unoccupied molecular orbital (LUMO) of the D−A model compound were also obtained at the DFT B3LYP/6-31G* level using the Gaussian 03 program suite[14] (Figure 2). Ab initio calculations on the model compound for PDTPDTBT show that it is a planar molecule, which enables the electrons to be delocalized within the molecule by conjugation. The HOMO state density was distributed entirely over conjugated molecules; however, the electron density of LUMO was mainly localized on the DTBT part. This result indicates that the decrease in the band gap of the copolymer is due to the introduction of the DTBT segment, in accordance with the change in the absorption spectrum.

The electrochemical properties of PDTPDTBT were also investigated by cyclic voltammetry (CV) (Figure S2). The HOMO and the LUMO energy levels of PDTPDTBT were estimated from the onset oxidation and reduction potentials as −5.00 and −3.43 eV, respectively, relative to the vacuum level. The electrochemical band gap (1.57 eV) is somewhat higher than the corresponding optical band gap (1.46 eV).

It is believed that the mixing morphology of the polymer and PCBM composite film will largely affect the photovoltaic properties of PSCs.[5,6c,15] The morphology of the blend films with PDTPDTBT and PCBM was observed by atomic force microscopy (AFM) (Figure S3). The film shows small roughness with an R_a of 0.42 nm, and no significant aggregation, suggesting that the polymer is highly compatible with PCBM molecules.

The bulk heterojunction PSCs were fabricated with a device structure of ITO/PEDOT:PSS/polymer:PCBM (1:1 wt %)/Al. Figure 3 shows the $I-V$ curve of the device and the corresponding open-circuit voltage (V_{OC}), short-circuit current (I_{SC}), fill factor, and power conversion efficiency (PCE) of the devices under the illumination of AM 1.5, 100 mW/cm^2, with an irradiation area defined by a photomask as 2 × 3 mm^2. The V_{OC} of the device based on PDTPDTBT/PCBM was 0.52 V,

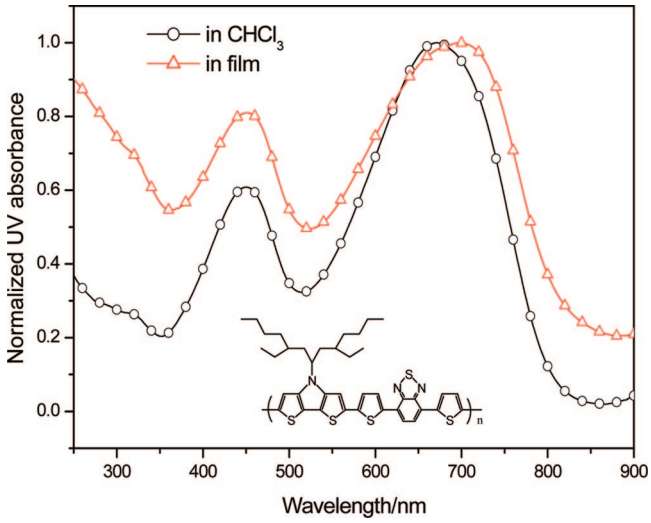


Figure 1. UV−vis absorption spectra of solutions in $CHCl_3$ and films on a quartz plate.

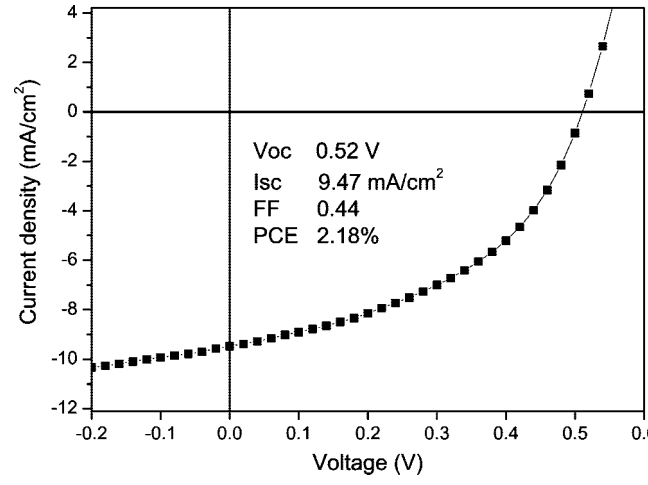


Figure 2. Molecular orbital surfaces of the HOMO and LUMO of the model compound for PDTPDTBT, obtained at the DFT B3LYP/6-31G* level.

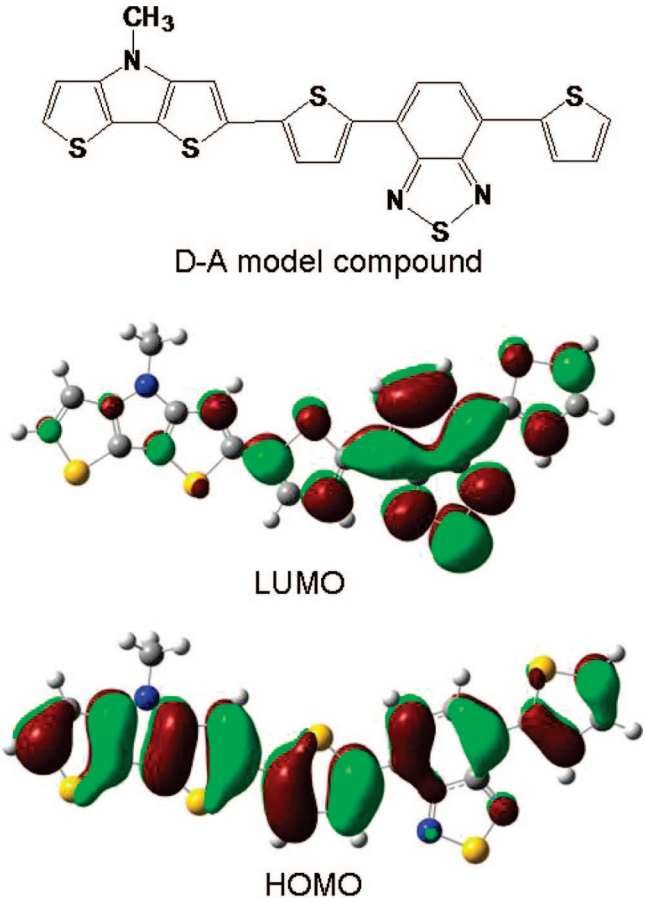


Figure 3. $I-V$ curves of the polymer solar cells based on PDTPDTBT under the illumination of AM 1.5, 100 mW/cm^2.

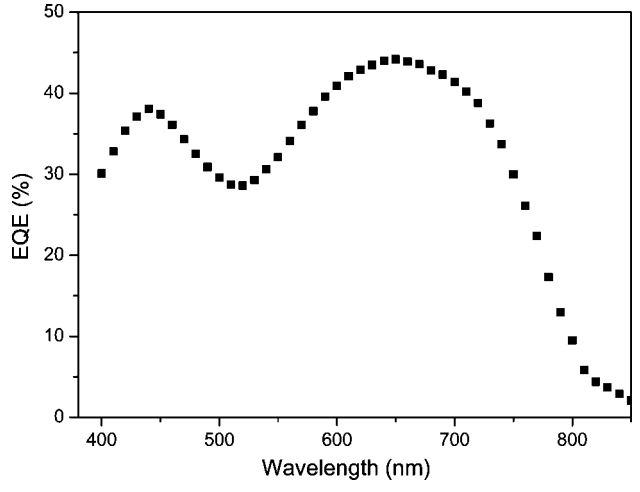


Figure 4. EQE of the polymer solar cells based on PDTPDTBT.

lower than that of other D−A structure polymers such as DTBT copolymerized with fluorine (~1 V),[7] silafluorene (~0.9 V),[8] or carbezole (~0.9 V).[9] The I_{SC} was 9.47 mA/cm^2, significantly high in the PSCs, which can be attributed to the broad absorption of PDTPDTBT. As a result, a PCE of 2.18% was achieved, suggesting that DTP is a good candidate for the building block applicable to efficient PSCs.

The external quantum efficiency (EQE) of the device illuminated by monochromatic light is shown in Figure 4. The shape of the EQE curves of the device is very similar to the absorption spectra, indicating that all the absorption of the polymers contributed to the photovoltaic conversion. The broader profile and higher values of EQE are consistent with the higher I_{SC} measured in the solar cells.

It is likely that the photovoltaic performance of this kind of copolymer can be further improved from two aspects. One is from the material aspect, such as optimizing the polymerization conditions to improve polymer purity, or optimizing the energy level to increase the V_{OC} of the device. The other is device fabrication conditions, such as optimizing the ratio of the polymer to PCBM, and/or controlling the phase morphology by processing additives[6c,11,16] or solvent annealing.[15b] Presently, all work on optimization is underway.

In summary, we have synthesized an alternating copolymer of 2,6-dithieno[3,2-*b*:2′,3′-*d*]pyrrole (DTP) and 4,7-di(2′-thienyl)-2,1,3-benzothiadiazole (DTBT). This novel D−A structure polymer has a low band gap and good solubility. The preliminary investigation on the photovoltaic device based on a PDTPDTBT:PCBM bulk heterojunction gives a power conversion efficiency of 2.18%, indicating that DTP could be a promising building block for the materials in photovoltaic application. Detailed investigations on PDTPDTBT properties and further synthesis of new DTP-containing copolymers are currently in progress and will be reported in due course.

Supporting Information Available: Details of the synthesis, DSC, CV, AFM, fabrication details, and characterization of the PSC devices and instruments. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA802052W