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COMMUNICATION TO THE EDITOR

Dialkyl-Substituted Dithienothiophene Copolymers as Polymer Semiconductors for Thin-Film Transistors and Bulk Heterojunction Solar Cells

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Organic semiconducting polymers have attracted intense interest for a variety of applications such as, for example, organic light-emitting diodes (OLEDs), organic photovoltaic (OPV), and organic thin-film transistors (OTFTs) by virtue of a number of enablers, including good solution processability, which permits a low-cost fabrication process via printing, and robust mechanical properties for producing compact, lightweight, and flexible electronic devices.[1−4]

The dithieno[3,2-*b*:2′,3′-*d*]thiophene (DTT) structure had earlier been utilized in the synthesis of a wide variety of electronically active or semiconducting small molecular compounds for electroluminescence, two-photon absorption and excited fluorescence, nonlinear optical chromophores, photochromism, OTFT, and OPV applications.[5,6] However, not many DTT-based semiconducting polymers have been reported, primarily due their inherently poor solubility and processability.[7,8] The introduction of long alkyl side chains to the β-positions of DTT unit would be an excellent solution in creating soluble DTT-based semiconducting polymers. Thus, several β,β'-dialkyl-substituted DTT-based polymer semiconductors have been synthesized,[9] but their performance characteristics in OTFT and OPV are poor; i.e., their field-effect transistor (FET) mobility and OPV power conversion efficiency have been relatively low (i.e., 7×10^{-3} cm^2/(V s)[9c] and 0.71%,[9b] respectively). These poor device performance data have unfortunately left the impression that β,β'-dialkyl-substituted DTT polymers are not suitable polymer semiconductors for electronic applications.

In this Communication, we report our independent studies on the synthesis of a DTT-based copolymer, poly(2,6-bis(thiophene-2-yl)-3,5-dipentadecyl-dithieno[3,2-*b*;2′,3′-*d*]thiophene) (PBTDTT-15), and its characterization as a polymer semiconductor in OTFT and OPV devices. The applicability of a polymer semiconductor in printed electronics depends not only on its functional performance but also on its processability, which greatly affects the manufacturing cost of electronics. The semiconducting polymer PBTDTT-15, which we synthesized, possessed a relatively high molecular weight as well as good solubility. When evaluated as a solution-processed channel semiconductor in OTFTs under ambient conditions, it displayed a FET mobility of 0.06 cm^2/(V s) and a current on/off ratio more than 10^6, which are significantly much better than those earlier reported for analogous polymers. More importantly, its performance as a hole-transport polymer in combination with the electron-transporting PC$_{71}$BM in bulk heterojunction (BHJ) photovoltaic devices was quite remarkable. Specifically, the power conversion efficiency (PCE) was over 3%, which is competitive with the performance characteristics of some of the best polymer semiconductors for OPV devices. These results clearly demonstrate the potential of judicially functionalized DTT polymers as efficient polymer semiconductors for OTFT and OPV applications.

A general synthesis of PBTDTT-15 is schematically depicted in Scheme 1 with the detailed synthetic procedures described in the Supporting Information. PBTDTT-15 was chosen for its solution processability by virtue of the presence of two long pentadecyl side chains on the DTT repeating units. The greater solubility characteristics of the resulting polymer also ensured that a reasonably high molecular weight could be achieved before its precipitation during synthesis. PBTDTT-15 was prepared by Stille coupling polycondensation of 3,5-dipentadecyldithienothiophene (**7**) and 5,5′-bis(trimethylstannyl)-2,2′-bithiophene (**8**). Specifically, the intermediate **7** was synthesized from 6-bromo-3-pentadecylthieno[3,2-*b*]thiophene (**1**)[10] by treatment with LDA followed by hexadecanal to yield the corresponding alcohol **2** with excellent regioselectivity at the carbon atom adjacent to that bearing the bromine substituent. The alcohol **2** was readily oxidized to the corresponding ketone **3** with the Jones reagent. The dipentadecyl-substituted DTT **6** was obtained from **3** in reasonably good yields following the normal ring closure procedure used for **1**. Our attempt to prepare compound **6** via the procedure of He et al.[11] involving a dual-ring closure reaction failed in our case when a hexadecanal derivative was used. Stille coupling copolymerization of **7** and **8** in chlorobenzene using tris(dibenzylideneacetone)dipalladium and tri(*o*-toyl)phosphine as the catalyst system[8b] afforded PBTDTT-15. The preparation of an analogous polymer with a shorter side chain (ca. decyl group) in toluene using tetrakis(triphenylphosphine)palladium(0) as the catalyst[9c] gave a relatively low molecular weight. The use of chlorobenzene polymerization medium and a more efficient tris(dibenzylideneacetone)dipalladium/tri(*o*-toyl)phosphine catalyst system[12] had largely contributed to the ability in achieving a much higher molecular weight for the polymer product. Sequential Soxhlet extractions with methanol, hexane, and chloroform afforded pure PBTDTT-15 as a purple-red solid in 86% yield. The number-average molecular weight (M_n) of PBTDTT-15 was estimated by gel-permeation chromatography (GPC) analysis to be 8.0×10^4 against polystyrene standards with a polydispersity index (M_w/M_n) of 5 from a bimodal distribution.

The thermal properties of PBTDTT-15 were evaluated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The DSC of PBTDTT-15 did not show any phase transition behaviors at up to about 300 °C before a broad endothermic peak showed up at 306 °C during heating, and a corresponding exothermic peak appeared at 296 °C when cooled (Figure S1 in Supporting Information). These were respectively attributed to the melting and crystallization of the polymer backbone. Excellent thermal stability of PBTDTT-15 was manifested in its TGA profile (Figure S2 in Supporting Information) showing a decomposition temperature of 425 °C (5% weight loss).

The UV−vis absorption spectra of a dilute PBTDTT-15 solution in chloroform and drop-cast thin film are shown in Figure 1. The dilute solution showed a poorly resolved vibronic splitting absorption with λ_{max} at 537 nm, while the drop-cast film exhibited a slight red shift relative to that of the solution with λ_{max} at 546 nm and a weak absorption shoulder at 577 nm, most likely

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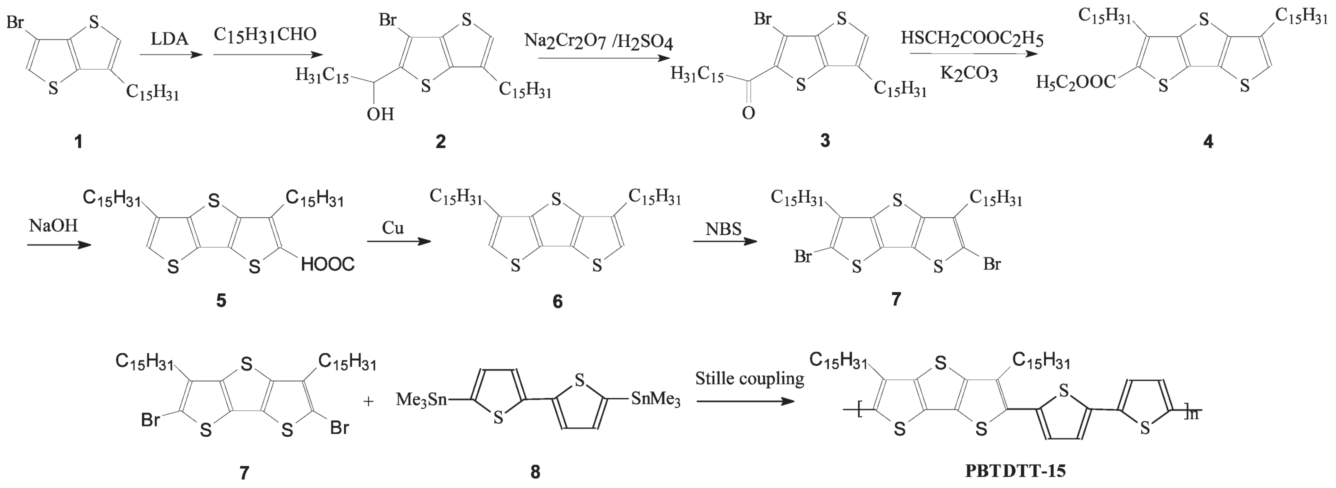
Scheme 1. Synthesis of PBTDTT-15



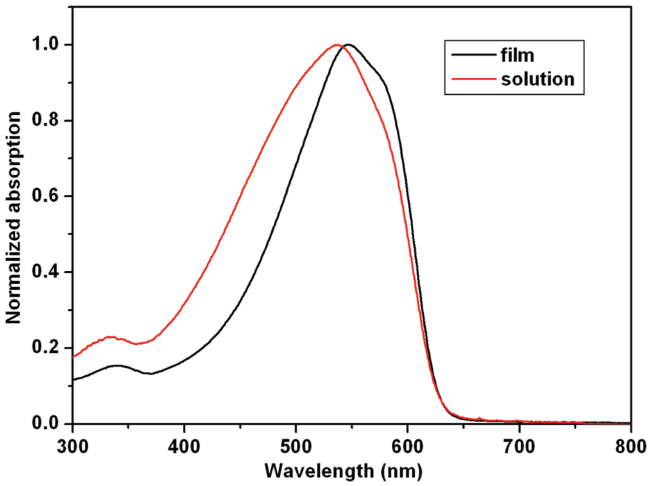


Figure 1. UV−vis absorption spectra of PBTDTT-15 in chloroform solution (red line) and as a thin film (black line).

originated from the polymer backbone $\pi-\pi$ stacking. The observed spectral red shift of PBTDTT-15 relative to that of the DTT polymer with a shorter decyl side chain λ_{max} at 511 nm[9c] indicated that a high molecular weight led to a greatly extended π-conjugation along the polymer backbone. Furthermore, this λ_{max} is significantly red-shifted (~80−160 nm) compared to those of earlier reported didecyl-substituted DTT based polymers,[9a] suggesting a more extensive π-conjugation among the DTT and bithienylene moieties along the backbone of our polymer. This may likely due to significantly reduced steric interference of the alkyl side chains in the present polymer structure. The optical band gap of PBTDTT-15 was 1.93 eV as estimated by the onset point of the absorption band (ca. 640 nm). The similarity of the solution and solid-state absorption spectra of PBTDTT-15 appears to suggest that its solution contained some degree of aggregation. X-ray diffraction (XRD) analysis of a PBTDTT-15 thin film cast from chloroform solution onto a OTS-treated silicon wafer surface revealed the amorphous nature of the film as no Bragg refraction peaks were detected even after thermal annealing at 160 °C (Figure S3 in Supporting Information). Cyclic voltammetric (CV) characterization of PBTDTT-15 with a three-electrode cell in 0.1 M solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in CH_3CN showed quasi-reversible oxidation and reduction peaks (Figure S4 in Supporting Information). The highest occupied molecular orbital (HOMO) level, estimated from the onset of oxidation potential from CV curve,[13] was 5.05 eV. This was about 0.15 eV larger than that of regioregular P3HT (4.9 eV) measured at the same condition, thus demonstrating the greater oxidative stability of PBTDTT-15.

The FET properties of a solution-processed PBTDTT-15 semiconductor thin film were evaluated using a bottom-gate, top-contact TFT configuration built on an n-doped silicon wafer with evaporated gold source/drain electrodes and octyltrichlorosilane (OTS)-modified 200 nm SiO_2 gate dielectric on silicon wafer surface. Figure 2a,b shows the typical output curve and transfer characteristics of a representative as-prepared TFT device (W/L = 1000/175) with no postdeposition thermal annealing. The output behaviors followed closely the gradual channel model employed in metal oxide semiconductor FETs with very good saturation and no observable contact resistance. The transfer characteristics showed a near-zero turn-on voltage, which signified negligible charge carrier traps in the dielectric/semiconductor interface, a threshold voltage of −3.8 V, and a subthreshold slope of 1.47 V/decade. The mobility estimated at the saturated regime was 0.05−0.06 $cm^2/(V\ s)$ with a current on/off ratio of more than 10^6 when measured in ambient conditions. Thermal annealing of TFT devices at temperatures up to 160 °C did not lead to improved performance as expected on the basis of the amorphous semiconductor film. For comparison, the charge mobility in a thick polymer film (4.45 μm) at room temperature obtained via time-of-flight (TOF) photoconductivity technique was 2.7×10^{-4} $cm^2/(V\ s)$ at an applied electric field of 1.5×10^4 V/cm and increased to 6×10^{-4} $cm^2/(V\ s)$ at a field of 6.7×10^4 V/cm.[14] These values are much lower than the FET mobility. The moderate FET mobility and other excellent TFT characteristics, coupled with the ease of solution processing without the need for the time-consuming, energy-intensive postdeposition thermal annealing, have rendered PBTDTT-15 an ideal TFT channel semiconductor for fabricating backplane electronics for large-area displays (e-paper, e-book, signage, etc.) which do not require fast video rates.

More importantly, the performance of PBTDTT-15 as a hole transport semiconductor in combination with the electron-transporting $PC_{70}BM$ in BHJ solar cell devices had been respectrably competitive.[14] The experimental solar cell devices were fabricated using a blend of PBTDTT-15 and $PC_{70}BM$ with a device structure of ITO/PEDOT:PSS/semiconductor blend/Al and were evaluated using air mass 1.5G at an intensity of 100 mW/cm^2 in an inert glovebox environment (Figure 3). The devices with the 1:3 ratio by weight of PBTDTT-15:$PC_{71}BM$ had provided most promising results. The devices exhibited an open circuit voltage (V_{oc}) of 0.63, a short-circuit current density (J_{sc}) of 8.5 mA/cm^2,

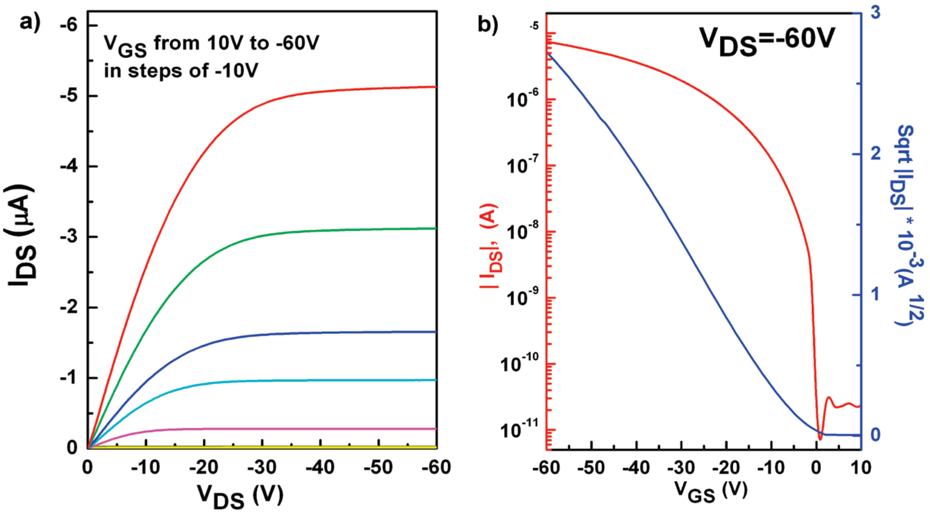


Figure 2. Current−voltage characteristics of a representative OTFT device with PBTDTT-15 as a channel semiconductor: (a) output curves at different gate voltages; (b) transfer curve in saturated regime at constant source-drain voltage of −60 V and square root of the absolute value of the drain current as a function of gate voltage.

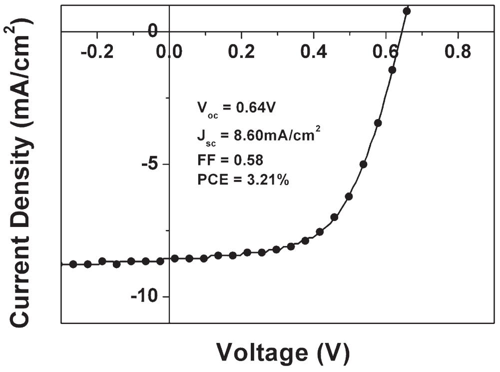


Figure 3. Current density−voltage measurements under AM 1.5G illumination (100 mW/cm^2) of a PBTDTT-15:PC$_{70}$BM BHJ OPV device.

and a fill factor (FF) of 0.6 with a power conversion efficiency of 3.2%. This is the best device performance reported to date for OPV devices based on DTT-containing polymer semiconductors.[8d,e,9] Considering the relatively narrow absorption window of PBTDTT-15 for solar light spectrum, we believe that β,β′-dialkyl-substituted DTT is a promising build block for photovoltaic cells. Ongoing work is exploring the synthesis of various β,β′-dialkyl-substituted DTT-based donor−acceptor copolymers for organic electronics.

In conclusion, we have demonstrated that β,β′-dialkyl-substituted DTT unit is an excellent building block for creating solution processable high-performance polymer semiconductors for printed electronic applications. These polymer semiconductors can be readily synthesized and structurally optimized for functional performance. The easy solution processability coupled with the ability to use as-deposited semiconductor thin films without the need for postdeposition thermal annealing would potentially lead to a low-cost manufacturing. The OTFT performance characteristics of PBTDTT-15 are sufficiently good for display backplane electronics that do not require fast switching video rates. Its performance in BHJ solar cells is impressive considering the mismatch between its relatively narrow light absorption (ca. onset wavelength at 640 nm) and the energy distribution of the solar spectrum would lead to insufficient light absorption. We are confident that the performance can be further improved through structural optimization.

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Supporting Information Available: Experimental procedures; TGA, DSC, and CV curves; detailed information about the fabrication and measurement of TFTs and OPVs. This material is available free of charge via the Internet at http://pubs.acs.org.

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