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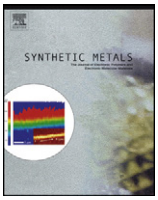

Synthesis and characterization of dithienothiophene/benzothiadiazole based low band gap donor–acceptor copolymers for bulk hetero junction photovoltaic cells

Abasaheb V. Patil[a], Woo-Hyung Lee[b], Kyuri Kim[a], Youn-Sik Lee[a], In-Nam Kang[b,*], Soo-Hyoung Lee[a,*]

[a] School of Semiconductor and Chemical Engineering, Chonbuk National University, Duckjin-dong 664-14, Jeonju 561-756, Republic of Korea
[b] Department of Chemistry, The Catholic University, 43-1, Yeokaok2-dong, Wonmi-gu, Buchen-si, Gyeonggi-do 420-743, Republic of Korea

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ABSTRACT

Two newly designed low band gap copolymers P2TDTT-BT and P2TDTT-DTBT, comprised of a substituted dithienyl-dithieno[3,2-*b*:2′,3′-*d*]thiophene derivative as a donor and a benzothiadiazole or dithienyl benzothiadiazole based acceptor, respectively, were synthesized by Stille polymerization. The UV–visible absorption of P2TDTT-BT and P2TDTT-DTBT films ranged from the UV to NIR regions. The HOMO/LUMO energy levels of P2TDTT-BT and P2TDTT-DTBT were estimated to be −5.41/−3.74 eV and −5.34/-3.65 eV, corresponding to energy band gaps of 1.67 and 1.69 eV, respectively. Bulk heterojunction photovoltaic cells were fabricated using a blend of P2TDTT-BT or P2TDTT-DTBT and $PC_{61}BM$ in a 1:1 ratio and delivered power conversion efficiencies of 0.31% and 0.92%, respectively.

1. Introduction

Polymer solar cells (PSCs) are a focus of worldwide research interest because of their potential utility as low-cost, lightweight, flexible, and easy to fabricate solar energy-to-electric power conversion devices [1–3]. Bulk hetero junction (BHJ) devices [1,3], in which a donor polymer (p-type) is blended with a fullerene derivative or other acceptor (n-type) material, have emerged as the most efficient polymer solar cells to date. Among donor polymers in fullerene-based BHJ solar cells, regioregular poly (3-hexylthiophene) (P3HT) has been the most widely investigated, and its use in solar cells has yielded some of the highest power conversion efficiencies (3–5%) [2–5]. However, P3HT only harvests photons with wavelengths below 650 nm, while a majority of solar photon energy is observed at much lower wavelengths (around 700 nm) [6]. Therefore, polymer materials with low band gaps are needed to harvest solar photons with longer wavelengths, particularly in the NIR region.

Various design strategies have been pursued to fulfill this requirement. One popular approach is to synthesize copolymers containing alternating monomer units with electron rich donor (D) and electron poor acceptor (A) character in the conjugated molecular backbone. Judiciously chosen D and A groups are particularly desirable for low-band gap polymers due to the significant enhancement of intra-molecular charge transfer (ICT) intensity and conjugation length, which lead to greater extended absorption and a higher absorption coefficient. An extended, rigid π-conjugation with quinoidal character in the polymer backbone facilitates intermolecular interactions between the polymer chains and increases the charge mobility of the polymer [7]. Fused thiophene ring systems stabilize the quinoidal structure, reduce the band gap, and enhance π–π stacking [8,9]. Recently, several D–A copolymer systems have achieved better efficiencies (up to approximately 5%) by tuning the HOMO energy of the polymer through modifications of the monomer structures based on known thienopyrazine or benzothiadiazole acceptor groups with electron-rich thiophene donor groups [10–12]. In these studies, considerable attention was focused on D–A conjugated polymers whose optical and electronic properties involving intra-molecular charge transfer (ICT) from the D to the A were tunable.

Taking these results into account, in our survey of electron-rich monomers, we became interested in the dithieno[3,2-*b*:2′,3′-*d*]thiophene (DTT) unit [13], an important building block for a wide variety of functional organic materials. The planarity and S–S interactions of fused DTT structures promote highly ordered π-stacking [14,15] and elevated hole mobility [15], which are predictors of pronounced charge transport in devices [16]. Several groups have reported the synthesis of DTT derivatives for applications in organic thin film transistors (OTFTs) [14,17–22]. It is interesting to note that despite all of these promising features, to the best of our knowledge, there have been only a few reports on the photovoltaic properties of DTT-containing D–A type copolymers [23–25,20]. Zhan and co-workers reported DTT-based donor–acceptor polymers consisting

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* Corresponding authors. Tel.: +82 632 702 435; fax: +82 632 702 306.
E-mail addresses: inamkang@catholic.ac.kr (I.-N. Kang), shlee66@jbnu.ac.kr, shlee66@chonbuk.ac.kr (S.-H. Lee).

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of alternating perylenediimides (PDI)–dithienothiophen unit as an acceptor and bis(thienylvinylene)-substituted polythiophene as a donor with high electron mobility and power conversion efficiency (PCE) up to 1% under simulated AM 1.5, 100 mW/cm^2 conditions [23,20]. Moreover, this group also reported porphyrene based DTT-π-conjugated alternating copolymers [24] and substituted-DTT alternating with thiophene copolymers [25] for photovoltaic applications. However the device performance of these two examples was poor. Recently, we rationally designed a copolymer, PTDTTTQX based on DTT and adopted a simple D–π–A structure with thiophenes as a shorter conjugated spacer between the electron donor and electron acceptor to facilitate the electronic coupling, wavelength tuning, and absorption capability between the donor and acceptor, resulting in a red-shifted absorption with good power conversion efficiency (PCE) [26]. Encouraged by these results, herein we report the synthesis and application of novel DTT-containing D–π–A conjugated low band gap copolymers P2TDTT-BT and P2TDTT-DTBT comprised of (2,6-bis(thiophen-2-yl))-3,5-didecanyl dithieno[3,2-*b*:2′,3′-*d*]thiophene (2TDTT) donor and 4,7-dibromo-2,1,3-benzothiadiazole (BT) or 4,7-bis(2-bromo-5-thienyl)-2,1,3-benzothiadiazole (DTBT) acceptor units, respectively. The introduction of thiophene units as a shorter conjugated spacer at the 2- and 6-positions of the DTT core can reduce steric hindrance, extend conjugation, enhance absorption, and improve charge transport properties, whereas incorporation of linear long chain alkyl (decanyl) groups at the 3- and 5-positions of the DTT core improve the solubility and processability of the resulting copolymers. It is widely accepted that BT and DTBT units are very effective as acceptors and can polymerize with many different kinds of donor units. The design of materials containing DTT derivatives and BT or DTBT has led to a novel family of polymeric semiconductors with the potential for polymer backbones with substantial π–π stacking.

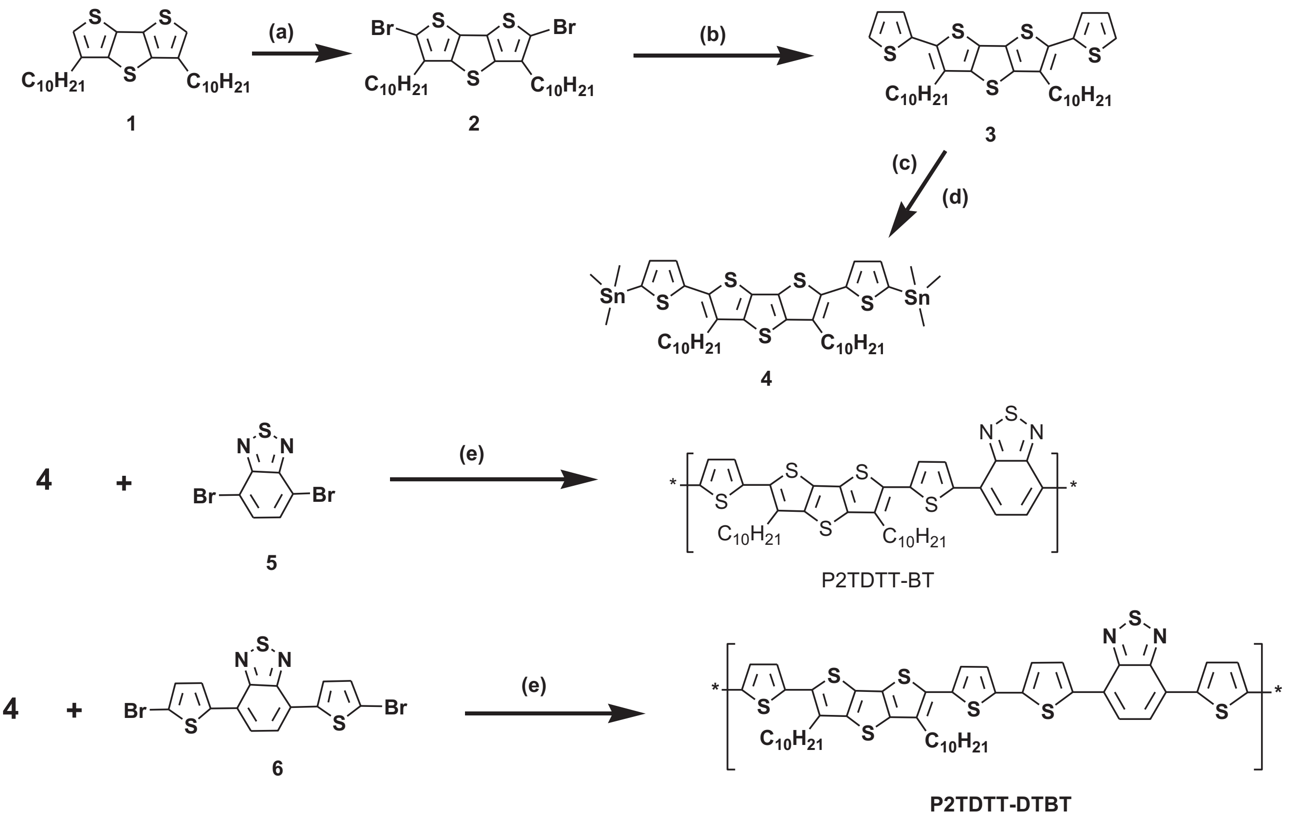
2. Experimental

2.1. Materials

All of the chemicals and solvents used to synthesize the copolymers P2TDTT-BT and P2TDTT-DTBT, shown in Scheme 1, were purchased from Aldrich and were used without further purification. 3,5-Didecanyldithieno[3,2-*b*:2′,3′-*d*]thiophene [27] (**1**), 4,7-dibromo-2,1,3-benzothiadiazole (BT) (**5**), and 4,7-bis(2-bromo-5-thienyl)-2,1,3-benzothiadiazole (DTBT) (**6**) were prepared according to previously described procedures [28]. *N*-Bromosuccinimide (NBS) was recrystallized from water prior to use. Reaction solvents were distilled prior to use; other solvents were used as received. Column chromatography was carried out on silica gel (size: 300–400 mesh).

2.1.1. Synthesis of 2,6-dibromo-3,5-didecanyl dithieno[3,2-b:2′3′-d]thiophene (2)

Dithieno[3,2-*b*:2′,3′-*d*]thiophene (**1**) was synthesized according to previously described procedures [26]. We added a solution of NBS in THF (2.14 g, 12.0 mmol) drop-wise to a stirred solution of **1** (2.0 g, 5.48 mmol) in THF at room temperature. The reaction was stirred for 2 h and monitored by TLC. After completion of the reaction (TLC), the reaction mixture was poured into water, extracted with chloroform, and then dried over $MgSO_4$. After evaporation of the solvent, the crude product was chromatographed on silica gel with hexane as eluent to yield **2** as a pale white, low melting solid (2.74 g, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm, Fig. S1 in supporting information): 2.70 (t, 4H), 1.65–1.59 (m, 4H), 1.27–1.18 (m, 28 H), 0.82 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 138.81, 135.23, 129.04, 108.71, 31.87, 29.57, 29.51, 29.32, 29.25, 29.020, 28.065, 22.66, 14.10. Elemental analysis: Calculated for



Scheme 1. Synthetic route to the copolymers: (a) NBS, THF, 2 h, RT; (b) thienyl-2-boronic acid, $Pd(PPh_3)_4$, 2 M aq. K_2CO_3, THF, reflux, 24 h; (c) 1.6 M n-BuLi, TMEDA, −78 °C, reflux 3 h; (d) 1.0 M trimethyltin chloride in THF, −78 °C, rt, 6 h; (e) Pd_2dba_3, P(*o*-tolyl)$_3$, chlorobenzene, 110 °C, 24 h.