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Graphical Abstract

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Synthesis and characterization of dithienobenzothiadiazole-based donor-acceptor conjugated polymers for organic solar cell applications

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ABSTRACT

New donor-acceptor conjugated polymers (**P1** and **P2**) containing a fused-ring dithienobenzothiadiazole (DT-BTD building block) were synthesized by using the Stille copolymerization method. The synthesized polymers were characterized by ¹H NMR, GPC, and elemental analysis. The optical band gaps of the polymers were found to be 1.86 and 1.9 eV, respectively, as calculated from their film onset absorption edge. Upon annealing both produced a distinct shoulder peak in their film absorption spectra. The electrochemical studies of **P1** and **P2** revealed that the HOMO and LUMO energy levels of the polymer were -5.3, -5.1 eV, and -3.4, -3.2 eV, respectively. The polymers are thermally stable up to 250-350 °C.

Since the discovery of conductive polymers in 1976 by Heeger, MacDiarmid and Shirakawa,¹ impressive advancements have been achieved in the synthesis of organic semiconductors and their applications for organic electronics devices. Organic semiconductors have special advantages over their inorganic counterparts on account of their light-weight, flexibility, and low-cost.²⁻⁸ Recent advances in the development of new semiconducting polymers have achieved impressive power conversion efficiencies (PCEs) surpassing 8% in polymer solar cells (PSCs),^{9,10} where a π -conjugated polymer as an electron donor and fullerene as an electron acceptor were blended in bulk-heterojunction (BHJ) configuration. Optimization of the performance of photovoltaic polymer materials necessitates the design and synthesis of conjugated polymers with ideal properties, such as low band gaps, a broad absorption range, high mobility, and relatively low highest occupied molecular orbital (HOMO) energy levels, because broad absorption and a higher hole mobility of the polymer donor lead to a larger short circuit current (J_{sc}),¹⁰ and a lower HOMO energy level of the polymer donor will result in a larger open circuit voltage (V_{oc}) of the PSCs.¹¹ Thus, the most popular and successful design strategy in achieving the aforementioned characteristics for a high performance polymer donor is through copolymerization of donor (electron-rich) and acceptor (electron-deficient) units. The D-A approach allows facile tuning of the frontier molecular orbital energies (HOMO and LUMO) and band gaps through intermolecular charge transfer (ICT) from a donor to an acceptor moiety within the repeat unit of the copolymers.

In the quest for designing a new polymer donor, the introduction of a thiadiazole unit as an electron-withdrawing

group to the backbone of conjugated polymers has attracted significant research interest. As a result a variety of D-A type conjugated polymers have been synthesized, a majority of them based on the 2,1,3- benzothiadiazole (BTz) moiety.¹²⁻¹⁵ In comparison to other acceptor moieties, BTz has been commonly utilized to construct D-A copolymers due to its high electron mobility and relatively low HOMO energy level, which gives a high V_{oc} in its PSCs.¹⁶⁻¹⁹ Also, BTz-based D-A copolymers have been exploited through substitution of the sulfur atom by oxygen,²⁰ nitrogen,²¹ and selenium,²² by replacement of the benzene ring with more electron-withdrawing rings such as pyridine²³ and pyridazine.²⁴ In addition, the introduction of heteroatoms such as fluorine or groups like alkyloxy, side chains have led to interesting developments in the PCEs of PSCs. In particular, the PCE of a BTz-based conjugated polymer as high as 7.2% was achieved by using a fluorinated BTz-based D-A conjugated polymer.²⁵ Another design strategy to modify BTz based D-A conjugated polymers is through fusion of the benzene ring with other aromatics moieties which can increase the π - π stacking and planarity of the resulting copolymer.²⁶

In this work, we report on the synthesis and characterization of two novel donor-acceptor type conjugated polymers based on a dithienobenzothiadiazole (DT-BTD) acceptor moiety for the application in PSCs. These two polymers are expected to have good π - π stacking for high mobility and reduced HOMO and LUMO energy levels. This is due to the improved planarity which arises from involvement of the fused acceptor moiety and also the introduction of an electron-deficient thiadiazole unit on the backbone of these two polymers, respectively.

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Scheme 1: Synthesis of **Br₂-DT-BTD (5)** as an acceptor moiety. i) *n*-BuLi, -78 °C, CuBr/LiBr then oxalyl chloride, THF, 78%. ii) FeCl₃, CH₂Cl₂, r.t, 82%. iii) HONH₂·HCl, 10% Pd/C, 78 °C then N₂H₄·H₂O, ~ 60 °C, EtOH, 34%. iv) SOCl₂, CH₂Cl₂, reflux, 78%. v) Br₂, CHCl₃, reflux, 75%.

Scheme 2: Synthesis of donor moieties **M1** and **M2**. i) PCC, CH₂Cl₂, r.t, 90%. ii) *i*-PrMgCl·LiCl, THF, r.t. iii) LiAlH₄/AlCl₃, Et₂O, r.t, 50%. iv) NBS, DMF, r.t, 80%. v) Pd₂(dba)₃/P(*o*-Tolyl)₃, THF, reflux, 44% for **10** and 41% for **12**. vi) (Me)₃SnCl, THF, r.t, 88% for **M1** and 70% for **M2**.

Scheme 3: Synthesis of polymers **P1** (54%) and **P2** (27%).

The synthetic route for the acceptor moiety is shown in Scheme 1: diketone (**1**), which is an important intermediate was synthesized according to the reported procedure,²⁷ via the cross-coupling reaction between an organocuprate reagent of 3-bromothiophene and oxalyl chloride in the presence of LiBr. This was subjected to oxidative ring-closing by using FeCl₃ to provide **BDTD (2)**.²⁷ This aromatic diketone was further derivatized to **DT-BTD (4)** followed by bromination to give **Br₂-DT-BTD (5)**. The solubility of **Br₂-DT-BTD (5)** was found to be very poor in common organic solvents except dichlorobenzene, hot toluene, and hot chlorobenzene. Scheme 2 shows the synthetic routes for intermediates **M1** and **M2** which bear long-branched alkyl side chain groups to promote the solubility of the corresponding polymers. These polymers were synthesized via Stille cross-coupling between donor

moieties and π -spacer (**9**). The synthesis of the π -spacer group could not be accomplished by the usual Kumada cross-coupling reaction; this might be due to steric hindrance resulting from the branched alkyl group. To our delight, the π -spacer (**9**) was prepared through reaction of aldehyde **6** with a Grignard reagent; where the Grignard reaction precursor was prepared via the reaction of 3-bromothiophene with the turbo Grignard reagent (*i*-PrMgCl·LiCl complex). Dehydroxylation was achieved by reductive cleavage using AlH₃ which was generated *insitu* from a mixture of LiAlH₄-AlCl₃. Subsequent bromination of **8** gave π -spacer (**9**).²⁸ Finally, both polymers **P1** and **P2** were prepared through Pd(PPh₃)₄-catalyzed Stille copolymerization. The structures of all the products were confirmed by ¹H NMR spectroscopy and in addition, polymers were characterized by GPC and elemental analysis.

The thermal stability of polymers **P1** and **P2** was investigated by using thermogravimetric (TGA) analysis and differential scanning calorimeter (DSC) with a heating rate of

10 °C min⁻¹ under nitrogen. Figure 1(a) shows the TGA where the onset temperature with 5% weight loss (T_d) of **P1** is above 330 °C, indicating the polymer has sufficient stability for use in optoelectronic devices. That of **P2** is around 250 °C, which shows slight instability at high temperature compared to **P1**. Obviously, the thermal stability of these polymers was adequate for their applications in PSCs and other optoelectronic devices. In addition, DSC measurements were used to investigate the phase transition and crystallization properties of the polymers. As shown in Figure 1(b), neither the melting point (T_m) nor the glass transition temperature (T_g) was exhibited. This indicates that both **P1** and **P2** were amorphous.

The molecular weights and polydispersity indices (PDIs) of the copolymers were determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration and chloroform as the eluent. The two copolymers had relatively high weight-average molecular weights (M_w), especially **P1** and high PDIs for both **P1** and **P2**.

Table1. Molecular Weights and Thermal Properties of the Synthesized Copolymers

Copolymer	Yield (%)	M_n	M_w	PDI	T_d (°C)
P1	55	9941	83686	8.42	330
P2	27	3694	28268	7.65	250

Figure 1. TGA plots at a heating rate of 10 °C min⁻¹ under nitrogen (a), DSC traces (b)

Figure 2 shows the absorption spectra of the polymers in chloroform solution and as thin films. Table 2 summarizes the optical data, including the maximum absorption peak wavelengths (λ_{max}), absorption edge wavelengths (λ_{onset}), maximum absorption wavelength of the shoulder peak ($\lambda_{shoulder}$) and the optical band gap (E_g^{opt}). The entire absorption spectra feature broad absorption bands from ca. 360 to ca. 700 nm in the long wavelength region, which was attributed to intermolecular charge transfer (ICT) between the donor and acceptor units for both **P1** and **P2**. The absorption maximum (λ_{max}) for **P1** in solution is ca. 503 nm, and in the thin film exhibits a red-shift of ca. 39 nm and a small shoulder peak at ca. 591 nm, whereas for **P2** its λ_{max} in solution is ca. 502 nm, and in thin film exhibits a red-shift of ca. 46 nm with a vague

shoulder peak at ca. 590 nm. Upon annealing (150 °C) for 15 minutes both polymers have produced distinct shoulder peaks at ca. 594 nm, which indicates the presence of strong π - π stacking among the polymer backbones and formation of ordered arrangements in their solid films. In comparison, both polymers show almost similar optical properties, but upon annealing, **P2** gives a clearer and more pronounced shoulder peak than **P1**. This might be due to the flexibility of **P2** involving bithiophene (**BT**) on its backbone, which is usually inferred as enhanced molecular aggregate formation. Finally, the optical band gaps (E_g^{opt}) for **P1** and **P2** determined from their film absorption edges (λ_{onset}) were about 1.86 and 1.90 eV, respectively.

Table 2. Optical Data of the Polymers

UV-Vis absorption spectra								Cyclic Voltammetry			
Solution			Film					E_g^{opt} ^c (eV)	E_{ox}^{onset} (V)	HOMO (eV)	LUMO (eV)
λ_{max}^a [nm]	λ_{onset}^b [nm]	λ_{max}^a [nm]	λ_{onset}^b [nm]	Annealed @150 °C							
					λ_{max}	$\lambda_{shoulder}$	λ_{onset}				
P1	503	652	542	664	550	591	667	1.86	0.938	-5.338	-3.478
P2	502	654	548	655	553	593	661	1.90	0.738	-5.138	-3.238

^a Absorption maxima. ^b The onset edge absorption. ^c Estimated from the onset edge of absorption in films.

Figure 2. UV-Vis spectra of the polymers **P1** and **P2** in chloroform solution and as thin films (at room temperature and annealed at 150 °C for 15 min).

The electrochemical properties were obtained from thin-film cyclic voltammetry analysis of **P1** and **P2** (Figure 3). The HOMO levels were estimated from the onsets of their corresponding oxidative peaks, $\text{HOMO} = - (E_{\text{ox}}^{\text{onset}} + 4.4) \text{ eV}$, and $\text{LUMO} = E_{\text{g}}^{\text{opt}} + \text{HOMO}$; the LUMO levels were then calculated from the differences between the HOMO energy levels and the optical band gaps. Compared to **P2** (HOMO =

−5.138 eV), **P1** shows a deeper HOMO energy level of −5.338 eV. Accordingly, a higher V_{oc} can be expected for **P1**-based BHJ-PSCs. The calculated LUMO levels for **P1** and **P2** were −3.478 and −3.238 eV, respectively, matching the LUMO energy level differences (> 0.3 eV) with **PC₇₁BM/PC₆₁BM** might lead to efficient exciton dissociation and charge separation.

Figure 3. The cyclic voltammograms of **P1** and **P2** films on a platinum electrode measured in 0.1 mol/L Bu_4NPF_6 acetonitrile solutions at a scan rate of 50 mV s^{-1} .

In summary, we have designed, synthesized, and characterized two novel donor-acceptor type conjugated polymers based on the electron-deficient, fused-ring building block, dithienobenzothiadiazole (**DT-BDT**) and electron-rich thienothiophene (**TT**) and bithiophene (**BT**) units. Both polymers are highly soluble in common organic solvents, have high molecular weights, and good thermal stabilities. In comparison with the absorption spectra of both polymers in solution, both polymers exhibit red-shifted film absorption spectra, and after annealing, produce distinct shoulder peaks. **P1** exhibited a lower HOMO energy level of −5.33 eV than **P2** −5.13 eV and both polymers have relatively low band gaps.

Based on these results, it was shown that both the polymers could be used as potential candidates for PSC applications.

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