Study of Photoelectric Conversion in Benzothriothiophene-Based Conjugated Semiconducting Polymers

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Benzothriothiophene (BTT), where three thiophenes are fused to a central benzene, was polymerized with three kinds of electron accepting units, thiadiazolopyridine (TP), difluorobenzothiadiazole (FT), or naphthobisthiadiazole (NTz). These low bandgap polymers exhibited deep HOMO level (-5.4 ~ -5.6 eV) which can lead to increasing open circuit voltage ($V_{OC}$) of bulk heterojunction organic photovoltaics (OPV). One of the BTT polymers and methano[60]fullerene (PCBM) blend showed a high $V_{OC}$ of 0.99 V, owing to the deep HOMO level and low energy loss. The best power conversion efficiency (PCE) of 2.7% was obtained for the BTT-NTz polymer blended with methano[70]fullerene. We have intensively characterized optoelectronic and morphological features of the new polymers by atomic force microscopy, 2-dimensional X-ray diffraction, and time-resolved microwave conductivity. This work highlights the potential of BTT-based polymers for an increase of PCE, because there are extra rooms for further improvement.

keywords: low bandgap polymer, organic solar cell, time-resolved microwave conductivity

1. Introduction

Bulk heterojunction (BHI)-based organic photovoltaics (OPV) that typically consist of polymeric materials as electron donor with fullerene derivatives as electron acceptor are studied intensively. Polymers applied in OPVs are mostly made of two alternating monomers with different electron affinities. Hence, the polymer backbone has repeating units of electron donor (D) and electron acceptor (A) molecules, referred to as D-A copolymers. Utilizing D-A copolymers is an effective strategy to narrow optical bandgap via intramolecular charge transfer (CT) band.

The optical band gap of D-A copolymer is mainly dependent on the highest occupied molecular orbital (HOMO) of donor moieties and the lowest unoccupied molecular orbital (LUMO) of the acceptor moiety. Therefore, selection of D and A monomers has a direct impact on the device efficiency. High performing D-A copolymers have been synthesized using benzodithiophene (BDT), cyclopentadithiophene (CPDT), or naphthodithiophene (NDT) as donor moiety with benzothiadiazole (BT), thieno pyrroledione (TPD), or thiazolothiazole (TTz) as acceptor moiety. A successful example of D-A copolymer is poly(thieno[3,4-b]-thiophene-co-benzodithiophene) (PTB7) and its derivative whose power conversion efficiencies (PCE) approached 10% recently. Optimization of D-A polymers require matching of their HOMO–LUMO energy levels with that of the acceptor fullerene in order to enhance charge dissociation and minimize recombination. On the other hand, the difference between HOMO of the polymer and LUMO of fullerene needs to be maintained large in order to achieve high open circuit voltage ($V_{OC}$). In addition to the energy alignment, the morphology of the blend films plays a significant role in the device performance. Therefore, molecular weight, backbone planarity, and solubility are important factors need to be considered.
In this work, photovoltaic properties are investigated for three novel conjugated polymers incorporating benzotri thiophene unit as the D unit and thiadiazolo pyridine (TP), difluorobenzothi adiazole (FT) or naphthobisthiadiazole (NTz) as the A unit (Figure 1). BTT is a fused ter thiophene with planar and extended π-electron system that could bring the advantage of intermolecular hole transport and intramolecular CT absorption. An intrigued feature of BTT is the possibility to form seven structural isomers. Out of them, C5-symmetric benzo[1,2-b:3,4-b':5,6-c'] thiophene (bbc-BTT) and asymmetric benzo [1,2-b:3,4-b':5,6-b"] thiophene (BTT) have been often incorporated into backbone of π-conjugated polymers. The rare example of the former bbc-BTT is a BTT-BT polymer which has shown a high field-effect transistor (FET) hole mobility. On the other hand, the latter BTT has been polymerized with many kinds of electron accepting units for OPV applications, including TTz (PCE = 1.4%), BT (PCE = 2.2%), diketopyrrolo pyrrole (PCE = 5.1%), bisthiazole (PCE = 5.1%), benzo oxadiazole (PCE = 6.2%), and benzo thiadiazole-5,6- dicarboxylic imide (PCE = 8.3%). In addition to the asymmetry, the slightly bent structure of BTT molecule leads to backbone curvature which enhances the solubility of polymers.

Density functional theory (DFT) calculations predicted that BTT unit has 0.19 eV deeper HOMO level than the well-known BDT (Figure 2), which may merit to $V_{OC}$ of the OPV devices, because the energy gap between HOMO of p-type material and LUMO of n-type material roughly scales with $V_{OC}$. However, the $V_{OC}$ of aforementioned BTT-based polymers are typically less than 0.8 V. In contrast, our BTT polymers (BTT-TP, BTT-F, and BTT-NTz) demonstrate the high $V_{OC}$ of 0.79–0.99 V, due to their deep HOMO levels. We have characterized the morphological, and optoelectronic properties of the polymers: fullerene blend films.

2. Experimental

Synthesis of monomers. BTT unit was synthesized according to the previous report followed by lithiation at the two α-positions with tert-butyllithium and quenching with trimethyltin chloride to afford the 2,8-distannylated BTT. Bis(5-bromo-4-(2-alkythienyl)) derivatives of TP, FT, and NTz were synthesized according to previous reports.

Synthesis of BTT-TP. 2,8-Bis(trimethyl stannyl)-5-(1-octynonyl)benzo[1,2-b:3,4-b':5,6-c']trithiophene (44 mg, 0.054 mmol) and 4,7-bis[5-bromo-4-(2-octyldodecyl)-2-thienyl]-2,1,3-thiadiazolepyridine (55.4 mg, 0.054 mmol) in anhydrous chlorobenzene (1 mL) was degassed via freeze-pump-thaw cycles. Tris(dibenzylideneacetone)dipalladium(0) (Pd2(dba)3) (1.24 mg, 1.35 μmol purchased from Sigma Aldrich) and tri(o-tolyl)phosphine (1.65 mg, 5.42 μmol) were added to the degassed solution under nitrogen gas flow. Then the reaction mixture was refluxed at 110°C for 3 hours. Followed end-capping by subsequent addition of bromobenzene (0.1 mL) and trimethyltinbenzene (0.1 mL) and refluxed for 1 hour after each addition. The resulted reaction mixture was diluted with chlorobenzene (10 mL) and precipitated in methanol. The precipitate was filtered and dried in a vacuum desiccator overnight. The precipitate was dissolved in chloroform and purified by column chromatography with alternatively packed acid, NH, and NH$_3$ silica gels. The obtained solution was filtered through celite filtration and concentrated by vacuum evaporators, and then precipitated in acetone. The obtained precipitate was dried to afford the product as dark blue solid (20 mg, yield: 27%).

Synthesis of BTT-FT. A solution of 2,8-Bis(trimethylstannyl)-5-(1-octynonyl)benzo[1,2-b:3,4-b':5,6-c']trithiophene (47.6 mg, 59 μmol) and 4,7-bis[5-bromo-4-(2-octyldodecyl)-thiophen-2-yl]-5,6-difluorobenzofuran[2,3-b]thia-

Figure 1. Chemical structures of BTT polymers.

Figure 2. Energy levels of the conjugated unit calculated by DFT (B3LYP/6-31G*) method.
diazole (63.5 mg, 60 μmol) in anhydrous chlorobenzene (1 mL) was degassed via “freeze-pump-thaw” cycles. Pd₂(dba)₃ (1.34 mg, 1.46 μmol) and tri(o-tolylyphosphine (1.79 mg, 5.88 μmol) were added to the degassed solution under nitrogen gas flow. Then the reaction mixture was refluxed at 110°C for 24 hours. End capping and purification processes were conducted as described above to afford the final product as dark green solid (60 mg, yield: 74%).

**Synthesis of BTT-NTz.** A solution of 2,8-Bis(5-trimethylstanyl-3-dodecylthiophen-2-yl)-5-(1-octylnonyl) benzo[1,2-b:3,4-b':6,5-b"] tri thiophene (46 mg, 35 μmol) and 4,7-bis[5-bromo-4-(2-dodecyltetradecyl)-2-thienyl]naphtho[1,2-c:5,6-c'] -bis[1,2,5] thiadiazole (43 mg, 35 μmol) in anhydrous chlorobenzene (2 mL) was degassed via “freeze-pump-thaw” cycles. The mixture transferred to a microwave reactor vail and tetrakis-(triphenylphosphine)palladium(0) (Pd(PPh₃)₄, 2.00 mg, 1.73 μmol) in chlorobenzene (1 mL) was degassed via “freeze-pump-thaw” cycles. Pd2(dba)₃ (1.34 mg, 1.46 μmol) and tri(o-tolylyphosphine (1.79 mg, 5.88 μmol) were added to the degassed solution under argon gas flow. Then in the microwave reactor the solution was heated to 180°C for 70 min. After end capping the product was purified as described above to afford the final product as dark green solid (60 mg, yield: 84%).

**General measurements.** Weight and number-averaged molecular weights for the three polymers were measured by gel permeation chromatography (GPC) using tetrahydrofuran eluent and polystyrene standard. Photoelectron chromatography (GPC) using tetrahydrofuran as an eluent and polystyrene standard. Photoelectron spectroscopy (PYS) measurements of polymer films on an ITO glass were performed by a Sumitomo Heavy Industry Co. PCR-202. Atomic force microscopy (AFM) observations were performed by a Seiko Instruments Inc. model Nanocute OP and Nanonavi II. Xe-flash time-resolved microwave conductivity (Xe-TRMC, 9 GHz)²⁷ experiment using a pseudo-sunlight white light pulse (0.3 mJ cm⁻² pulse⁻¹) as an excitation was conducted in order to study the photovoltaic performance of polymer: [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM, purchased from Frontier Carbon Inc.) blends prior to device fabrication.²⁴,²⁸,³¹ The blend samples were prepared by drop-casting chlorobenzene (CB) solution of polymer:PC₆₁BM onto quartz plate and dried under vacuum. The photoconductivity Δσ was obtained by ΔP / AP, where ΔP, A, and P, are the transient power change of reflected microwave power, sensitivity factor, and reflected microwave power, respectively. All TRMC measurements were conducted at ambient conditions. The 2-dimensional grazing-incidence X-ray diffraction (2D-GIXRD) experiments were conducted at the SPring-8 (Japan Synchrotron Radiation Research Institute, JASRI) on the beam line BL19B2 or BL46XU using 12.39 keV (λ = 1 Å) X-ray. The GIXRD patterns were recorded with a 2-D image detector (Pilatus 300K).

**OPV device fabrication.** OPV devices were fabricated according to the previous report.³² The device configuration was ITO (120–160 nm)/ZnO (30 nm)/ BHJ active layer/MoO₃ (10 nm)/ Ag (100 nm) with an active area of 7.1 mm². Polymers and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) were purchased from Frontier Carbon Inc. and used as the n-type materials. Current-voltage (J-V) curves were measured using a source-measure unit (ADCMT Corp., 6241A) under AM 1.5 G solar illumination at 100 mW cm⁻² (1 sun, monitored by a calibrated standard cell, Bunko Keiki SM-250KD) using a 300 W solar simulator (SAN-EI Corp., XES-301S). The EQE spectra were measured by a Bunko Keiki model BS-520BK equipped with a Keithley model 2401 source meter. The monochromatic light power was calibrated by a silicon photovoltaic cell, Bunko Keiki model S1337–1010BQ.

**3. Results and discussion**

The UV/Vis photoabsorption spectra for BTT-TP, BTT-FT, and BTT-NTz in dilute chloroform solution and in thin films are shown in Figure 3. The absorption peaks in solution appeared at 560, 570 and 613 nm for BTT-TP, BTT-FT, and BTT-NTz, respectively. Whereas, the absorption peaks showed slight red shift in thin film samples, indicating the ordering of polymer backbone. The optical bandgap (Eg) was estimated from the absorption onset in the film state, which displayed a clear narrowing in BTT-NTz (1.68 eV) compared with BTT-TP (1.75 eV) and BTT-FT (1.78 eV). The HOMO levels were determined by PYS experiments and found to be -5.60, -5.52, and -5.41 eV for BTT-TP, BTT-FT, and BTT-NTz, respectively. Accordingly, LUMO levels were calculated to be -3.85, -3.74, and -3.73 eV for these polymers, respectively. The optical, electrochemical, and polymeric properties are summarized in Table 1.

Figure 3. Normalized photoabsorption spectra for BTT-TP, BTT-FT, and BTT-NTz (a) in chloroform solution and (b) in thin films.
The photoconductivity transient maxima ($\Delta \sigma_{\text{max}}$) obtained from TRMC experiments provide information about the charge carrier lifetime, mobility, and density, all of which impact the device performance.27) The TRMC results of all polymers showed an increase in $\Delta \sigma_{\text{max}}$ when blended with PC61BM. The peaks are located at ~75% PC61BM for BTT-TP (Figure 4a), ~50% for BTT-FT (Figure 4b) and BTT-NTz (Figure 4c). The high PC61BM loading of 70-80% is sometimes required to maximize PCE and $\Delta \sigma_{\text{max}}$ in amorphous or semi-crystalline low bandgap polymers (LBPs). This is assumed due to an essential role of electron delocalization in PCBM aggregates for efficient charge separation. In the case of crystalline polymers such as poly(3-hexylthiophene)33,34) and high performing LBPs,35) the 1:1 blend ratio (50 wt%) is often optimal, because self-assembling nature of polymer concurrently promotes the growth of PCBM aggregates. In the present case, BTT-TP is amorphous, while BTT-FT and BTT-NTz are more crystalline, as evidenced by X-ray diffraction (vide infra). Therefore, the trend in p/n blend ratio of these polymers is consistent with the previous OPV polymers.

The photovoltaic performance of BTT-TP, BTT-FT, and BTT-NTz blended with PC61(71)BM were investigated at around the optimized blend ratios from the observed maximum $\Delta \sigma_{\text{max}}$. Inverted OPV devices were fabricated from CB solution of the polymer:PCBM blend in the presence of 3 vol% solvent additive (1,8-diodooctane, DIO). Table 2 lists the photovoltaic performance of the three polymers. As seen in the J-V curves in Figure 5a, the devices showed the high $V_{\text{OC}}$ of 0.99, 0.92 and 0.78 V for BTT-TP, BTT-FT and BTT-NTz respectively. The increase of $V_{\text{OC}}$ is in proportion to the deepening of HOMO levels (Table 1) with relatively small energy loss. For example, poly[N-9”-hepta-decanyl-2,7-carbazole-alt-5,5-(4 ’,7’-di-2-thienyl-2’,1’,3’-benzothiadiazole)], PCDTBT ($V_{\text{OC}} = 0.88$ V, HOMO = -5.5 eV)36) showed almost similar to $V_{\text{OC}}$ of BTT-FT (0.92 V, HOMO = -5.52 eV).

Although BTT-TP showed the highest $V_{\text{OC}}$ yet it exhibited a very low PCE of about 0.35%. On the other hand, BTT-FT showed higher PCE of 1.0%. Increased molecular weight as well as enhanced polymer packing due to fluorine modification in BTT-FT results in enhanced intra- and intermolecular charge transport as predicted.
by TRMC measurements. The order of external quantum efficiency (EQE) is consistent with the observed short circuit current density ($J_{SC}$). BTT-NTz > BTT-FT > BTT-TP (Figure 5b). At wavelengths from 550 nm to 800 nm, the EQE spectrum for BTT-NTz device drops to lower than 20% which can be attributed to the low efficiency of charge carrier generation from the polymer exciton. A small exciton diffusion length which becomes pronounced in the case of short exciton lifetime and/or large polymer domain is noted as one of the causes.

The 2D-GIXRD images of the blend films are shown in Figure 6a-c, which highlights the amorphous nature and isotropic orientation of BTT-TP, while BTT-FT displayed more intense diffraction band at low q region along with the appearance of π-stacking diffraction ($d = 3.68 \text{ Å}$) in the out-of-plane direction. This resulted in the increase of $J_{SC}$ from 0.76 mA cm$^{-2}$ for BTT-TP to 2.04 mA cm$^{-2}$ for BTT-FT. However, the orientation of crystalline BTT-FT was random and the fraction of preferred face-on orientation is likely less than half, which is necessary for vertical hole transport in OPV device.

Among the polymers, BTT-NTz showed the highest PCE of 1.87% with PC$_{61}$BM and it further improved to 2.73% with PC$_{71}$BM, thanks to the increased $J_{SC}$ via enhanced photoabsorption of PC$_{71}$BM in the visible region. The increased efficiency of BTT-NTz can be attributed to the highest molecular weight, lowest bandgap, and improved polymer face-on orientation. The 2D-GIXRD pattern of BTT-NTz film in Figure 6c shows more distinct but slightly extended π-stacking diffraction at $d = 3.74 \text{ Å}$. However, the polymer orientation is still isotropic, which hampers the further boost of PCE.

The morphologies of the active layers of the best performing devices were examined by atomic force microscopy (AFM). The AFM images of BTT-TP:PC$_{61}$BM blend showed large spherical aggregates of ~ 600 nm size with surface roughness of 12 nm (Figure 6d). Compared to BTT-TP:PC$_{61}$BM blend, the BTT-FT:PC$_{61}$BM blend showed very less surface roughness of 2 nm with fibrous structures which must result in higher $J_{SC}$ (Figure 6e). On the other hand, AFM images of BTT-NTz:PC$_{61}$BM showed ~260 nm-sized large aggregates with comparably high surface roughness of ~ 25 nm (Figure 6f). Such phase separation is a typical example of coarse morphology without nano-scaled interpenetrating BHJ network. We have examined the effect of DIO concentration (1, 3, and 5 vol%) for BTT-NTz:PC$_{61}$BM; however, the phase separation could not be mitigated (3 vol% is optimal). Since the solvent mixture (CF and CB or o-dichlorobenzene) sometimes improves the device efficiency, we further examined solvent mixture of CF/CB with/without DIO additive. However, a large phase separation still persisted (PEC was also lower than CB+DIO). Despite the formation of relatively large aggregates, the BTT-NTz showed PCE of 1.87% for PC$_{61}$BM and 2.73% for PC$_{71}$BM. This indicates that further improvement in device efficiency may be possible by controlling the morphology via alkyl side-chain and/or by changing the molecular weight.

4. Conclusion

We designed and synthesized three BTT-based copolymers (BTT-TP, BTT-FT, BTT-NTz). They showed deep HOMO and LUMO levels of -5.4 ~ -5.6 eV and -3.7 ~ -3.9 eV, respectively. Owing to these electrochemical properties, high $V_{OC}$ of 0.79~0.99 V were obtained. However, the PCEs were constrained to stay at low values (0.4~1.8%), mainly due to the low $J_{SC}$. The low $J_{SC}$ is readily explained by the extremely coarse BHJ morphology with several hundred nanometer-sized aggregates. The
BTT-NTz showed the best PCE of 2.73% by the use of visible light absorbing PC_{71}BM. The higher molecular weight, lower bandgap, and slightly-improved face-on orientation are responsible for the higher PCE of BTT-NTz. We should note that the large phase separation in BTT-NTz:PCBM was unable to be alleviated by either solvent mixture or additive concentration. In light of observed high $V_{OC}$, there is a great possibility for BTT-based polymers to improve the efficiency by controlling morphology via alkyl side-chain and/or molecular weight.

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