# Synthesis of Diketopyrrolopyrrole Containing Copolymers: A Study of Their Optical and Photovoltaic Properties

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The diketopyrrolopyrrole-based copolymers **PDPP-BBT** and **TDPP-BBT** were synthesized and used as a donor for bulk heterojunction photovoltaic devices. The photophysical properties of these polymers showed absorption in the range 500–600 nm with a maximum peak around 563 nm, while TDPP-BBT showed broadband absorption in the range 620 – 800 nm with a peak around 656 nm. The power conversion efficiencies (PCE) of the polymer solar cells based on these copolymers and [6,6]-phenyl C61 butyric acid methyl ester (PCBM) were 0.68% (as cast PDPP-BBT:PCBM), 1.51% (annealed PDPP-BBT:PCBM), 1.57% (as cast TDPP-BBT:PCBM), and 2.78% (annealed TDPP-BBT:PCBM), under illumination of AM 1.5 (100 mW/cm<sup>2</sup>). The higher PCE for TDPP-BBT-based polymer solar cells has been attributed to the low band gap of this copolymer as compared to PDPP-BBT, which increases the numbers of photogenerated excitons and corresponding photocurrent of the device. These results indicate that **PDPP-BBT** and **TDPP-BBT** act as excellent electron donors for bulk heterojunction devices.

## Introduction

Solar cells based on the conjugated polymers have the virtue of being lightweight and flexible.<sup>1,2</sup> Hence, efforts were made in the recent past to enhance the efficiency of organic solar cells.<sup>3,4</sup> An additional attractive feature of organic solar cells is the compatibility with printing techniques which can be exploited for roll-to-roll processes.<sup>5,6</sup> The concept of polymerbased bulk heterojunction (BHJ) improved the performance of organic solar cells.<sup>7,8</sup> In a typical BHJ device, the blend of conjugated polymers as a donor and phenyl-C61-butyric acid methyl ester (PCBM) as an acceptor have been used as an active layer.<sup>9,10</sup> So far, the blend of two materials (P3HT:PCBM) with different electron affinities has provided a power conversion efficiency up to 4-5% under 1.5 a.m. (100 mW/cm<sup>2</sup>) illumination.<sup>11-13</sup> The efficiency of organic solar cells is limited due to several factors such as mismatch between the solar spectrum and absorption spectrum of the active layer, the low mobilities of charge carriers in organic materials, and the morphology of a thin film in the case of the P3HT:PCBM blend.<sup>14,15</sup> However, in the past few years, a large number of research groups have brought insights into the blend (P3HT: PCBM) morphology by altering the annealing temperature and the organic solvent and by adding a small amount of additives in the blend.<sup>4,16-18,21</sup> However, the relatively large band gap  $(\sim 2.0 \text{ eV})$  of P3HT limits the absorption of near-infrared light and thus lowers the light harvesting and efficiency of devices.

One of the fundamental features which limits the efficiency in organic solar cells is the band gap of conjugated polymers. The control over the band gap is necessary while designing the new materials. This band gap engineering allows one to design and synthesize new materials with maximum overlap of absorption spectrum with the solar emission spectrum. It is often found that the synthesis of low band gap polymer is not only the solution to address this problem but the position of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) limits the open-circuit voltage ( $V_{oc}$ ) of the photovoltaic cell.<sup>19,20</sup> These two properties of organic materials can be controlled by introducing alternative electronrich and electron-deficient units in the polymer backbone. By using a similar concept, various groups have synthesized low band gap diketopyrrolopyrrole (DPP)-based copolymers.<sup>22-26</sup> Many donor-acceptor (D-A) type copolymers have been used in polymer solar cells to achieve power conversion efficiencies above 5% with extensive device engineering efforts.<sup>27,28</sup> Recently. Yang and co-workers reported the family of alternating copolymers based on the DPP as a central core unit with an overall power conversion efficiency of 4.45%.29 Barbec et al. reported<sup>30</sup> a cyclopentabithiophene- and benzothiadiazole (donor-acceptor)-based low band gap polymer which shows a power conversion efficiency of  $\sim 3.3\%$  when blended with  $PC_{70}BM$  with  $J_{sc} = 10-11$  mA cm<sup>-2</sup> and EQE of 25%. These reports suggest that the structural manipulation is indeed necessary to optimize the performance of organic solar cells. In search of such novel materials, we have synthesized two copolymers with diketopyrrolopyrrole units by the palladiumcatalyzed Stille coupling reaction. Conceptually, the comonomers linked to the DPP unit were chosen on the basis of their high p-type mobility as reported in the literature.<sup>31a</sup> The photophysical properties of these copolymers in solution as well as in solid state have been investigated in detail. The DPP derivatives are known to exhibit distinct electronic properties in the solid state. The electronic properties of both of the polymers in the solid state have been discussed.

Furthermore, the copolymers were incorporated as an electron donor in bulk heterojunction solar cells with  $PC_{60}BM$  as an electron acceptor. In the present contribution, we describe the

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synthesis and photovoltaic properties of DPP-based copolymers with different donor segments. The structure—property correlation and its performance in the bulk heterojunction organic solar cells were also evaluated.

#### **Experimental Section**

**Materials.** 1-Bromo hexane, 4-bromo benzonitrile, thiophene 3-carboxylicacid, *n*-butyllithium (1.6 M solution in hexane), tetrakis(triphenylphosphine)palladium(0) (Pd(PPh<sub>3</sub>)<sub>4</sub>), and tetrabutylammonium hexafluorophosphate ((TBA)PF<sub>6</sub>) were obtained from Aldrich and used without further purification. *N*-Bromosuccinimide (NBS) was crystallized prior to use. THF, CHCl<sub>3</sub>, and NMP have been dried by Na/benzophenone, P<sub>2</sub>O<sub>5</sub>, and calcium hydride, respectively.

**Instrumentation.** <sup>1</sup>H NMR and <sup>13</sup>C NMR were recorded using a Bruker 400 MHz instrument. Chemical shifts were recorded with respect to TMS and given in parts per million. Molecular weights were measured by gel permeation chromatography in THF. Thermal gravimetric analysis (TGA) was conducted on a Mettler Toledo TGA/SDTA 851 instrument. Absorption spectra of monomers and polymers were recorded by using a Perkin-Elmer UV—vis spectrometer for both solid and solution. Solution spectra's were recorded in chloroform. Electrochemical properties of both of the polymers were examined by using cyclic voltammetry (CH instrument). Polymers were coated on a platinum disk and immersed in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> acetonitrile solution. CVs were recorded using a platinum disk as a working electrode and Ag/Ag<sup>+</sup> as the reference electrode at a scan rate of 20 mV s<sup>-1</sup>.

**Synthesis of Monomers.** Thiophene-3-carbonyl Chloride, *N*,*N*-diethylthiophene-3-carboxamide, and 4,8-dihydrobenzo[1,2b:4,5-b']dithiophen-4,8-dione (**4**) have been synthesized by a previously reported procedure.<sup>31b</sup> 3,6-Dithiophen-2-yl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione, 1,4-diketo-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole,1,4-diketo-2,5dihexyl-3,6-bis(4bromophenyl)pyrrolo[3,4-c]pyrrole<sup>25</sup> (**1**), and 2,5-di-*n*-hexyl-3,6dithiophen-2-yl-pyrrolo[3,4-c]pyrrole-1,4-dione<sup>32</sup> (**2**) were synthesized by a previously reported procedure.

3,6-Bis-(5-bromo-thiophen-2-yl)-2,5-di-n-hexyl-pyrrolo[3,4-c]pyrrole-1,4-dione (3).<sup>32</sup> A 0.50 g (1.07 mmol) portion of TDPP was taken in dry chloroform. Under an argon atmosphere, 0.418 g (2.35 mmol) of *N*-bromosuccinimide was added portionwise at 0 °C. It was stirred at room temperature for 48 h. This mixture was poured into an excess of MeOH and stirred for 2 h. Solid was vacuum filtered and washed with MeOH and H<sub>2</sub>O to remove excess *N*-bromo succinimide and polar impurities. The crude solid was purified through column chromatography using DCM as a solvent. Dibrominated DPP (BrDPP) was obtained as a dark purple flaky solid (0.430 g). Yield: 65%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$  (ppm): 8.66 (d, 2H), 7.24 (d, 2H), 3.98 (t, 4H), 1.71 (m, 4H), 1.31–1.43 (m, 12H), 0.89 (t, 6H). IR (KBr) 2951.56 (m), 2924.71 (m), 1655.27 (s).

**4,8-Dihexyl Benzo[1,2-b;3,4-b]dithiophene** (5).<sup>31b</sup> A 0.50 g (2.27 mmol) portion of compound **4** and 0.44 g of Zn (6.81 mmol) were taken in 50 mL of water. NaOH (0.44 g × 4) was added and refluxed until it was dissolved. After 2 h, 1.12 g (6.82 mmol) of hexyl bromide and a catalytic amount of tetrabutylammoniumbromide were added to this mixture and refluxed for 12 h. This mixture was poured into cold water and extracted with DCM. The DCM layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic layer was concentrated and purified by column chromatography using ethyl acetate:hexane (1:99) as the eluent. Compound **5** was obtained as a white crystalline solid (1.33 g). Yield: 75%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$ 

(ppm): 7.46 (d, 2H), 7.33 (d, 2H), 4.26 (t, 4H), 1.87 (m, 4H), 1.561 (m, 4H), 1.37 (m, 8H), 0.91(m, 6H). IR (KBr) 2934.41(m), 1018.11(s).

2,6-Bis(tributyltin)-4,8-dihexylloxybenzo[1,2-b;3,4b]dithiophene (BBT) (6).<sup>31b</sup> A 0.50 g (1.28 mmol) portion of compound **5** was taken in dry THF. A 0.34 g (3.33 mmol) (1.6 M) portion of *n*-BuLi was slowly added to this mixture at 0 °C and stirred at room temperature for 1 h. After 1 h, 1.25 g (3.85 mmol) of tertiarybutyltinchloride was added at 0 °C and allowed to stir at room temperature overnight. Then, the reaction mixture was quenched with H<sub>2</sub>O and extracted with DCM. The DCM layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic layer was concentrated and used for the next step without purification.

General Procedure for the Synthesis of Polymers PDPP-BBT and TDPP-BBT. Equal amounts of both of the monomers were taken in dry toluene and DMF (4:1). This mixture was purged with argon for 15 min. It was evacuated and flushed with argon three times. A catalytic amount of Pd(PPh<sub>3</sub>)<sub>4</sub> was added under an argon atmosphere and refluxed for 16 h. After polymerization, solvent was removed under reduced pressure and the solid was dissolved in CHCl<sub>3</sub> and precipitated in MeOH. This precipitate was washed several times with MeOH, and the crude solid was washed on a Soxhlet apparatus with MeOH, hexane, and acetone to remove low molecular weight impurities. The solid was dried under a vacuum for 2 h. PDPP-BBT was obtained as a dark brown solid, and TDPP-BBT was obtained as a dark blue solid.

Bulk Heterojunction Photovoltaic Device Fabrication and Characterization. Indium tin oxide coated glass substrates were cleaned in acetone and in an ultrasonic bath. The blends of copolymer PDPP-BBT or TDPP-BBT and PCBM in 1:1 ratio in chloroform solution were coated over ITO glass substrates by the spin coating method under a nitrogen atmosphere in a glovebox. The top aluminum electrode was evaporated by thermal evaporation under a vacuum of  $10^{-6}$  Torr. The blended active layers were thermally annealed at 100 °C for 1 min before the deposition of the top Al electrode. The thickness of the active layers and effective area of the devices were about 80 nm and 0.25 cm<sup>2</sup>, respectively. The J-V characteristics of the devices in the dark and under illumination were measured by a semiconductor parameter analyzer (Keithley 4200-SCS). A xenon light source (Oriel, USA) was used to give a simulated irradiance of 100 mW/cm<sup>2</sup> (equivalent to AM1.5 irradiation) at the surface of the device. The photoaction spectrum of the devices was measured using a monochromator (Spex 500 M, USA), and the resulting photocurrent was measured with a Keithley electrometer (model 6514), which is interfaced to the computer by LABVIEW software.

## **Results and Discussion**

Synthesis of Monomers. The synthetic approach to monomers (TDPP and PDPP) is outlined in Scheme 1. The diketopyrroloprrrole moiety was prepared by a pseudo stobbe condensation between isopropyl succinicester and *p*-bromobenzonitrile (or) thiophene carbonitrile as reported in the literature.<sup>25</sup>

This DPP core consists of two fused lactam rings. Inter- and intramolecular H-bonding due to the lactam hydrogen atoms is responsible for insolubility of DPP in common organic solvents such as chloroform, dichloromethane, and tetrahydrofuran. The solubility of this product was enhanced by alkylation on lactam nitrogen atoms of DPP which was subsequently converted into a dibromo derivative by using *N*-bromosuccinimide in dry SCHEME 1: (a) KBuO<sup>t</sup>, Dry DMF, 60°C, Hexyl Bromide, 10 h; (b) *N*-Bromo Succinimide, Chloroform, 2 Days; (c) Zn/NaOH, H<sub>2</sub>O, Hexyl Bromide, Reflux, 12 h; (d) Butyl Lithium, 0 °C, 1 h, Tributyl Tin Chloride, Overnight



SCHEME 2: Synthesis of DPP Copolymers by Stille Coupling by Using Pd (PPh<sub>3</sub>)<sub>4</sub>, Toluene:DMF (4:1) at 110°C for 24 h



CHCl<sub>3</sub>. The other comonomer **6** was prepared by stannylation of compound **5** and used for polymerization without further purification.

Synthesis of Polymers. The synthetic protocol for the polymerization of DPP copolymers from the relevant monomers (1 or 3 + 6) is depicted in Scheme 2. Polymerization via Stille coupling was carried out between dibrominated DPP monomers (1 or 3) and compound 6 in the presence of tetrakis (triphenylphosphine) palladium (0). Stille coupling gave PDPP-BBT as a dark brown solid with a molecular weight of 9700 g/mol and a polydispersity (PDI) of 2.06. A similar experimental protocol has been used to obtain TDPP-BBT as a dark blue solid with a molecular weight of 19 000 g/mol and a PDI of 1.64.

The molecular weights of these two copolymers were measured by gel permeation chromatography (GPC) using tetrahydrofuran as an eluent. The average values and polydispersity index (PDI) of PDPP-BBT and TDPP-BBT are given in Table 1. These two polymers show very good solubility in

 TABLE 1: Molecular Weight and Thermal Properties of the

 Polymers

polymer	$M_{ m w}{}^a$	M <sub>n</sub>	$\text{PDIM}_{\text{w}}/M_{\text{n}}$	$T_{\rm d}^{\ b}$ (°C)
PDPP-BBT	9700	4700	2.06	355
TDPP-BBT	19000	11560	1.64	318

 $^{a}$   $M_{n},~M_{w},$  and PDI of the polymers were determined by gel permeation chromatography using polystyrene standards in tetrahydrofuran.  $^{b}$  The 5% weight-loss temperatures in N<sub>2</sub> atm. The heating rate is 10 °C/min.

chloroform dichloromethane, and tetrahydrofuran. The chemical structural characterization of PDPP-BBT and TDPP-BBT was carried out by <sup>1</sup>H NMR, as shown in Figure 1. The copolymers of DPP show broad peaks due to their coil-like nature unlike their monomers, whose signals are sharp. Aromatic signals appear between 7.27 and 9.02 ppm. In the polymer PDPP-BBT, the aromatic signals get split compared to its monomer which shows a singlet for all eight aromatic protons (not shown). Protons of the hexyl group appeared between 0.71 and 1.97 ppm, the methylene group attached to nitrogen appears between 3.72 and 4.16 ppm, and the methylene group attached to oxygen appears between 4.32 and 4.48 ppm.

**Thermal Properties.** The thermal stability of organic material is a very important parameter in organic solar cells. High thermal stability is required to prevent the degradation of polymers in photovoltaic devices upon annealing. We have investigated the thermal properties of these two polymers by thermo gravimetric analysis. These two polymers show a very good thermal stability. PDPP-BBT is stable up to 355 °C and TDPP-BBT is stable up to 318 °C, as shown in Figure 2.

**Optical Properties of Copolymers.** Figure 3 shows the UV-visible spectra of **PDPP-BBT** and **TDPP-BBT** in chloroform solution and in the thin film. Both of the polymers show well-defined vibronic features in solution at room temperature with  $\lambda_{\text{max}}$  at 539 nm for **PDPP-BBT** and  $\lambda_{\text{max}}$  at 638 nm for **TDPP-BBT**. The peak between 280 and 400 nm corresponds to  $\pi - \pi^*$  transition and between 470 and 660 nm corresponds to the intramolecular charge transfer (ICT)<sup>33,34</sup> from the donor



Figure 1. 400 MHz <sup>1</sup>H NMR spectra of the two polymers (left) PDPP-BBT and (right) TDPP-BBT.



Figure 2. TGA of the PDPP-BBT and TDP-BBT.

(thiophene or phenyl) to the central core acceptor unit.<sup>35,36</sup> We also found that the absorption peaks of **TDPP-BBT** are bathochromically shifted. This can be attributed to enhanced intramolecular charge transfer due to incorporation of the thiophene unit as a strong donor. Both of the copolymers show unusual features in the absorption spectrum upon thin film formation. The absorption peaks correspond to  $\pi - \pi^*$  transition and ICT significantly red-shifted and show a broad extended absorption edge toward the near-infrared region. This indicates that these materials have strong electronic coupling and  $\pi - \pi$  interactions in the solid state.<sup>37,38</sup> The absorption spectrum of both of the polymers covers the maximum photon flux in the solar spectrum. PDPP-BBT and TDPP-BBT also exhibit an intramolecular charge transfer (ICT) band at 539 nm (solution), 563 nm (film), 638 nm (solution), and 656 nm (film), respec-



tively. Both of the polymers show a broad absorption spectra with an extended absorption edge in the solid state. The detailed optical data of PDPP-BBT and TDPP-BBT are summarized in Table 2. The optical band gap of these polymers has been calculated from the absorption edge of the film using  $E_{g}^{opt} = 1240/\lambda_{onset}$ , with  $\lambda_{onset}$  being the onset wavelength of the materials.

The absorption band maximum of TDPP-BBT is more redshifted as compared to PDPP-BBT, which indicates that there is an excited state delocalization in TDPP-BBT polymer relative to PDPP-BBT and more exciton interaction between adjacent  $\pi$ -conjugated chromophores in TDPP-BBT. The presence of a strong TDPP donor lowers the band gap, resulting a substantial red shift in the absorption maximum band.



Figure 3. UV-vis absorption spectra of polymers (PDPP-BBT and TDPP-BBT) in chloroform and thin film on a quartz plate.

**TABLE 2: Optical Properties of the Polymers** 

	$\lambda_{\rm max.abs}$ (nm)		$\lambda_{\text{onset}}$ (nm)	
polymer	solution	film	film	$E_{\rm g}^{{ m opt}\;a}~({ m eV})$
PDPP-BBT	539	563	728	1.70
TDPP-BBT	638	656	866	1.43

<sup>*a*</sup> Band gap ( $E_{g}^{opt}$ ) measured at the onset of electronic absorption of the polymer film ( $E_{opt} = 1240/\lambda_{onset} \text{ eV}$ ).

Electrochemical Properties. Cyclic voltammetry is employed to calculate the oxidation and reduction potential of polymers and the HOMO-LUMO energy levels of the polymers. The cyclic voltammograms of TDPP-BBT and PDPP-BBT are shown in Figure 4. Both of the polymers show reversible oxidation (p-doping /rereduction) and irreversible reduction (n-doping/reoxidation) waves. All of these electrochemical values are given in Table 3. Potentials have been measured with respect to the Ag/Ag<sup>+</sup> electrode. HOMO and LUMO levels were calculated from the following equation  $HOMO = -e(E_{ox} + 4.7)LUMO = -e(E_{red} + 4.7)$ . Electrochemical band gaps have been calculated from  $E_{g}^{Elc} = e(E_{onset}^{ox})$  $- E_{\text{onset}}^{\text{red}}$ ). PDPP-BBT has an onset reduction potential and oxidation potential at -0.96 and 0.77 V vs Ag/Ag<sup>+</sup>, respectively. The calculated values are HOMO = 5.47 eV and LUMO = 3.74 eV. TDPP-BBT has reduction and oxidation potentials at -1.01 and 0.45 V, respectively. It has a HOMO level at 5.15 eV and a LUMO level at 3.69 eV. The electrochemical band gap is 1.73 eV for PDPP-BBT and 1.46 eV for TDPP-BBT. Band gaps estimated from cyclic voltammetry data are comparable with the optical band gaps estimated from the optical absorption data. Similar kinds of CV plots were reported in the literature for DPP copolymers.<sup>24,29</sup> TDPP-BBT exhibits a smaller band gap (1.46 eV) compared to PDPP-BBT (1.73 eV). This difference reflects the strong donor property of TDPP moieties, which increases the HOMO level more than the LUMO level, leading to a decrease in the band gap.

**Electrical and Photovoltaic Properties.** The focus of the paper is on the performance of the copolymers in BHJ solar cells; therefore, we have measured the current–voltage (J-V) characteristics of the devices having configuration ITO/PDPP-BBT or TDPP-BBT/Au to estimate the hole mobility. The J-V data were analyzed using nonlinear square fitting to the modified Mott Gurney equation, described as<sup>39</sup>

$$J = \frac{9}{8} \varepsilon \varepsilon_0 u \frac{V^2}{L^3} \exp\left(\frac{0.89\beta}{\sqrt{L}}\sqrt{V}\right) \tag{1}$$

where J is the current density, V is the applied voltage, L is the thickness of the active layer,  $\mu$  is the zero field mobility,  $\varepsilon$  is the dielectric constant,  $\varepsilon_0$  is the permittivity of free space (8.85 × 10<sup>-12</sup> F/M), and  $\beta$  is the field activation factor. From the analysis of the *J*-*V* current in the dark and using eq 1, the zero field hole mobilities of PDPP-BBT and TDPP-BBT were determined to be 3.2 (±0.4) × 10<sup>-5</sup> and 6.3 (±0.5) × 10<sup>-5</sup> cm<sup>2</sup>/(V s), respectively. The hole mobilities in both of the



Figure 4. Cyclic voltammograms of the polymers PDPP-BBT and TDPP-BBT. The scan rate is 20 mV s<sup>-1</sup>. T = 30 °C.

TABLE 3: Electrochemical Properties of the Polymers<sup>a</sup>

polymer	E <sup>ox</sup> onset	E <sup>red</sup>	HOMO	LUMO	$E_{\rm g}^{\rm elc}$	$E_{\rm g}^{ m opt}$
(V)	(V)	(eV)	(eV)	(eV)	(eV)	(eV)
PDPP-BBT TDPP-BBT	0.77 0.45	-0.96 -1.01	-5.47 -5.15	-3.74 -3.69	1.73 1.46	1.70 1.43

<sup>*a*</sup> The HOMO–LUMO gap was calculated according to the equations  $-E_{\text{LUMO}} = E_{\text{onset(red)}} + 4.7 \text{ eV}$  and  $-E_{\text{HOMO}} = E_{\text{onset(ox)}} + 4.7 \text{ eV}$ , where  $E_{\text{onset(ox)}}$  and  $E_{\text{onset(red)}}$  are the onset potentials for the oxidation and reduction processes of polymer thin films vs the Ag/Ag<sup>+</sup> electrode.

polymers are comparatively higher than other copolymers reported in the literature.<sup>40,41</sup>

We have investigated both copolymers PDPP-BBT and TDPP-BBT for their utility as light absorbing and electron donating materials with the PCBM as an electron acceptor for BHJ photovoltaic devices. The J-V characteristics of the devices in the dark and under AM 1.5 irradiation (100 mW/cm<sup>2</sup>) are shown in Figure 6. The optimized photovoltaic parameters for each device are compiled in Table 4. The open circuit voltage of the photovoltaic device based on TDPP-BBT is slightly lower than the device based on PDPP-BBT. This difference of  $V_{\rm oc}$ could result from the upward shift of the HOMO energy level of TDPP-BBT because the  $V_{oc}$  is related to the energy difference between the LUMO of the acceptor (PCBM) and the HOMO of the donor (the conjugated polymer).<sup>41,42</sup> The energy offset between the HOMO of PDPP-BBT (-5.47 eV) or TDPP-BBT (-5.15 eV) and the LUMO of PCBM (3.9 eV) is estimated to be 1.57 and 1.25 eV for PDPP-BBT:PCBM and TDPP-BBT: PCBM active layers, respectively, which are the theoretical limit for  $V_{\rm oc}$  for devices using a blend layer. Similar results have been reported for P3HT/fullerene solar cells.11,15,43 The experimentally measured lower value of  $V_{oc}$  as compared to the theoretical value may be attributed to charge carrier losses at the electrodes,<sup>44</sup> energy level alignment of the polymer at the polymer/electrode interface,45 and lowered effective band gap of the blends due to the formation of the charge transfer complexes.<sup>46</sup> Since the HOMO levels of both polymers are not aligned to the work function of ITO, it causes a band bending at the interface between ITO and polymer and results in a voltage loss that is responsible for the lower value of  $V_{oc}$  as expected theoretically. The short circuit photocurrent and overall power conversion



Figure 5. Energy band diagram of ITO/copolymer: PCBM/Al electrode.



**Figure 6.** (a) Current–voltage (J-V) characteristics of the ITO/PDPP-BBT:PCBM/Al device in the dark, under light. (b) Current–voltage (J-V) characteristics of the ITO/TDPP-BBT:PCBM/Al device in the dark, under light.

 TABLE 4: Photovoltaic Parameters of the Devices Based on

 Different Active Layers Sandwiched between ITO and Al

 Electrodes

active layer	short circuit current $(J_{sc})$ $(mA/cm^2)$	open circuit voltage (V <sub>oc</sub> ) (V)	fill factor (FF)	power conversion efficiency (η) (%)
PDPP-BBT:PCBM (as cast)	1.77	0.84	0.46	0.68
PDPP-BBT:PCBM (annealed)	3.73	0.78	0.52	1.51
TDPP-BBT:PCBM (as cast)	3.8	0.78	0.53	1.57
TDPP-BBT:PCBM (annealed)	6.72	0.74	0.56	2.78

efficiency for the device based on the TDPP-BBT:PCBM blend is higher than that for PDPP-BBT:PCBM under similar conditions. This can be attributed to the larger difference in the LUMO of the donor and acceptor in TDPP-BBT:PCBM than PDPP-BBT:PCBM, leading to more efficient photoinduced charge transfer in the device based on the TDPP-BBT:PCBM blend.

The devices were also tested for their incident photon to current efficiency (IPCE) and shown in Figure 7. Both of the



**Figure 7.** IPCE spectra of the ITO/PDPP-BBT:PCBM/Al and ITO/ TDPP-BBT:PCBM/Al devices using as cast and annealed films.

devices show the IPCE peak, which corresponds to the peak in the absorption spectra of the polymers. The similarity of the absorption spectrum with IPCE response demonstrates that the excitons produced by the absorption in the polymers are dissociated into free charge carriers at the interfaces between PDPP-BBT or TDPP-BBT and PCBM in the active layer and subsequently collected at the electrodes.

We have also investigated the effect of thermal annealing on the photovoltaic response of the BHJ devices. The J-Vcharacteristics under illumination and IPCE spectra of the devices are shown in Figures 6 and 7, respectively. The overall PCE for the devices based on thermally annealed PDPP-BBT: PCBM and TDPP-BBT:PCBM are 1.51 and 2.78%, respectively. The increase in the IPCE and short circuit current in the devices based on annealed blends was attributed to the increase in the crystallinity of the blend and hole mobility upon thermal annealing and discussed in the following part of the paper.

After the photoinduced electron transfer at the donor/acceptor interfaces present in the bulk of the photoactive layer in BHJ photovoltaic devices and subsequent dissociation, the electrons are localized in the PCBM phase and holes remain in the copolymer phase, i.e., PDPP-BBT or TDPP-BBT in the present case. Subsequently, the free electrons and holes must be transported via percolated PCBM and copolymer pathways toward Al and ITO electrodes, respectively, to produce the photocurrent. Therefore, the electron transport in PCBM and hole transport in copolymer are crucial for understanding the photogeneration process in the BHJ device. We have also investigated the effect of thermal annealing on the performance of the photovoltaic active layer in terms of charge carrier mobility as reported earlier in the literature for P3HT:PCBM blends.<sup>47</sup> To measure the space charge limited current (SCLC) of only one type of the charge carrier in the blend, the other one must be suppressed by a large injection barrier, resulting in an electron or hole only device. We have measured the dark current density-voltage curves of TDPP-BBT:PCBM blends for hole only and electron only devices for both devices using annealed and as cast blend thin films. To fabricate the hole only device, gold (Au) was evaporated as the top electrode having a structure of ITO/TDPP-BBT:PCBM/Au. The work function of ITO (-4.9 eV) is very close to the HOMO level of TDPP-BBT, forming Ohmic contact for hole injection, whereas the Au strongly suppress the electron injection into the LUMO of PCBM owing to the large mismatch between its work function



**Figure 8.** (a) Current-voltage characteristics of devices based on TDPP-BBT:PCBM for a hole only device using as cast and annealed blends. (b) Current-voltage characteristics of devices based on TDPP-BBT:PCBM for an electron only device using as cast and annealed blends.

(-5.0 eV) and the LUMO of PCBM (-4.0 eV). A schematic diagram of the hole only device is shown in the inset of Figure 8a. To suppress the hole injection into TDPP-BBT, the bottom electrode must have a low work function. Therefore, we have fabricated an electron only device by sandwiching the TDPP-BBT:PCBM blend between two Al electrodes, as shown in the inset of Figure 8b. Similar results have been observed for the devices based on PDPP-BBT:PCBM blends.

The charge carrier mobilities of the TDPP-BBT:PCBM blend films were evaluated by space charge-limited current (SCLC) measurements using eq 1. Figure 8 shows the relationship between dark current density (*J*) and voltage (*V*) in the hole only devices of TDPP-BBT:PCBM blends. The solid lines in the figure represent the fitting curves using this eq 1. The dielectric constant was assumed to be 3 in the calculation.<sup>48</sup> The zero field mobilities of the hole for PDPP:PCBM and TDPP-BBT:PCBM are quite comparable with the value measured for pristine polymers. However, the values of hole mobilities are about  $2.8 \times 10^{-4}$  and  $5.2 \times 10^{-4}$  cm<sup>2</sup>/(V s) for annealed PDPP-BBT:PCBM and TDPP-BBT:PCBM blends, respectively. The electron mobility for as cast and annealed TDPP-BBT:PCBM are in the range  $10^{-3}$  cm<sup>2</sup>/(V s) similar to that reported for P3HT:PCBM blends.<sup>47</sup>

The increase in hole mobility upon thermal annealing leads to better balanced charge transport and reduces the charge recombination during their transportation toward the electrodes. The increase in the photovoltaic performance with the annealed blends is likely due to a better charge transport collection as a result of the formation of crystalline domains that is ideal for both charge carrier separation and their collection at the electrodes. It has been shown in polymer-based BHJ solar cells that the degree of phase separation and surface roughness in blended films significantly affect the efficiency of electron transfer, charge transport, and carrier collection.<sup>49,50</sup> Therefore, it is assumed that similar processes are taking place in our devices.

The fill factor (FF) of the device is determined by the series resistance ( $R_s$ ) and shunt resistance ( $R_{sh}$ ).<sup>51,52</sup>  $R_s$  can be calculated from the inverse of the slope of the J-V curves of the device in the first quadrant and closely related to the intrinsic resistance, morphology, and thickness of the active layer used in the device. On the other hand,  $R_{\rm sh}$  is correlated with the impurities and defects in the active organic layer because impurities and defects cause recombination and leakage current. We have estimated the value of  $R_s$  from the J-V curves (Figure 6) under illumination and found that  $R_s$  is lowered for the thermally annealed blend (decreases from 8.9 to 5.6  $\Omega$  cm<sup>2</sup> for PDPP-BBT:PCBM and 7.5 to 5.1  $\Omega$  cm<sup>2</sup> for TDPP-BBT:PCBM). This decrease in  $R_s$  is attributed to the fact that the thermally induced intermolecular packing and crystallization allow more efficient intra- and intermolecular charge transport through the conjugated polymer in the blend layer.<sup>51–53</sup> Since the backbones of the conjugated polymer pack densely upon thermal annealing, that provides more efficient intermolecular charge hopping as well. The J-V curves in Figure 6 show almost the same value of  $R_{\rm sh}$ . The enhanced short circuit current with devices based on the thermally annealed blend can be attributed to not only the increased absorption efficiency but also the reduced resistivity of the blend layer.

### Conclusions

The diketopyrrolopyrrole-based copolymers PDPP-BBT and TDPP-BBT, containing donor-acceptor structural units, have been synthesized by using the Stille coupling reaction. Both of the polymers are soluble in common organic solvent and reveal a significant red shift in absorption properties in the solid state. Furthermore, TDPP-BBT has shown very promising photovoltaic performance in bulk heterojunction devices. A maximum power conversion efficiency of 2.78% was achieved after annealing the device at 100 °C. These results suggest that the structural manipulation of active material influences the efficiency of organic solar cells. Furthermore, the excellent properties of DPP-based copolymers make them a predominant choice of a material for bulk heterojunction solar cells.

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**Supporting Information Available:** <sup>1</sup>H NMR of compounds **1**, **2**, **3**, and **5**; FTIR of compounds **1**, **3**, **5**, PDPP-BBT, and TDPP-BBT; and absorption coefficients of PDPP-BBT and TDPP-BBT. This material is available free of charge via the Internet at http://pubs.acs.org.

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