

## A Thiophene, Benzothiadiazole, and Carbazole-Based Copolymer : Synthesis and Characterization

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Of the various types of polymerbased, photovoltaic devices designed to date, the most efficient photovoltaic devices, having power conversion efficiencies (PCEs) of 3-4%, were fabricated using a blend of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) as the electron-donor and electron-acceptor materials, respectively.<sup>1,2</sup> Soon after the initial reports, P3HT/PCBM-based photovoltaic devices were optimized to achieve PCEs approaching 5%.<sup>3-5</sup> New *p*-type polymers, which absorb light more broadly in the terrestrial solar radiation spectrum, were needed to increase the PCE of these photovoltaic devices. The HOMO/LUMO energy levels and the charge mobility of new *p*-type materials should also be optimized as these properties are intimately related to photovoltaic performance, as proposed by Scharber *et al.*<sup>6</sup>

Benzothiadiazole (BT) is a well-known electron-deficient molecule which can be conjugated with an electron-rich molecule to form oligomers or polymers with small band gap energies,<sup>7,8</sup> and several different polymers of this variety have been synthesized for applications in electronic devices.<sup>9,10</sup> Recently, Heeger and coworkers used a polymer of alternating cyclopentadithiophene and dibenzothiadiazole units in the fabrication of photovoltaic cells, yielding a PCE of 5%.<sup>11</sup> Carbazole derivatives have a planar conjugated structure and good hole transporting properties as well as electron-donating properties.<sup>12</sup> Blouin and coworkers have synthesized copolymers bearing carbazole units and employed them in the fabrication of photovoltaic devices with PCEs reaching to 3.6%.<sup>13</sup>

It appeared interesting to study polymers bearing thiophene-carbazole derivatives and BT as electron-releasing and electron-withdrawing units, respectively, in a polymer backbone. Thus, the goal of this report is to report the synthesis of a conjugated polymer consisting of 3HT, BT, and 2-ethylhexylcarbazol (CZ) (P3HT<sub>2</sub>BT<sub>2</sub>CZ) and describe the optical and electrochemical properties of the resulting polymer.

### Experimental Section

**Materials.** 3-Hexylthiophene (3HT), carbazole, 2,1,3-benzothiadiazole, *n*-butyllithium (2.5 M in hexane), 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, tributyltin chloride, tetrakis(triphenylphosphine) palladium(0), tetrahydrofuran (THF), *N*-bromosuccinimide (NBS), potassium carbonate, bromine, hydrogen bromide, toluene, and chloroform were

purchased from Aldrich and used without further purification.

**4,7-Bis(5-bromo-4-hexylthiophene-2-yl)benzo[c][1,2,5]-thiadiazole (1).** The synthetic procedure of compound **1** has been described elsewhere<sup>14</sup> (orange solid, 0.51 g, 85% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ/ppm): 7.97 (d, 2H), 7.83 (s, 2H), 2.66 (t, 4H), 1.66 (m, 4H), 1.35 (m, 12H), and 0.91 (t, 6H). IR (KBr) 2928, 2856, 1575, 1497, 1433, 1205, 827, 527 cm<sup>-1</sup>. Anal. Calcd: C, 49.84; H, 4.83; N, 4.47; S, 15.35. Found: C, 49.45; H, 4.71; N, 4.53; S, 14.97.

**3,6-Dibromocarbazole (2).** Using a modified version of a previously reported method,<sup>15</sup> carbazole (16.7 g, 100 mmol) was dissolved in DMF (150 mL) at 0 °C with stirring, followed by the addition of a solution of NBS (36.3 g, 200 mmol) in 100 mL of DMF. The resulting mixture was stirred at room temperature for 2 hr, and the solution then poured into 1 L of water, filtered, and washed with water. The crude product was recrystallized from ethanol (28.5 g, 88% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ/ppm): 8.14 (s, 2H), 8.11 (s, 1H), 7.53 (d, 2H), 7.33 (d, 2H). IR (KBr) 3420, 1600, 1570, 1470, 1430, 1290, 1240, 798, 677, 640 cm<sup>-1</sup>.

**3,6-Dibromo-9-(2-ethylhexyl)carbazole (3).** Compound **2** (6.5 g, 20 mmol) was dissolved in 50 mL of acetone, followed by the addition of (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NHSO<sub>4</sub> (0.41 g, 1.21 mmol), 2-ethylhexyl bromide (5.79 g, 30 mmol), and NaOH (1.6 g, 40 mmol), then refluxed for 4 hr. The solvent was removed, and then 300 mL of toluene was added. The mixture was washed 3 times with 200 mL of brine, dried over anhydrous magnesium sulfate, and concentrated by rotary evaporation. The residue was purified by silica gel column chromatography (petroleum ether) to give compound **3** as a colorless liquid (8.13 g, 93% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ/ppm): 8.13 (s, 2H), 7.55 (d, 2H), 7.23 (d, 2H), 4.11 (d, 2H), 2.01 (m, 1H), 1.31 (m, 8H), 0.91 (t, 6H). IR (KBr) 2930, 2860, 1589, 1430, 1290, 1220, 799, 640 cm<sup>-1</sup>.

**3,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan)-9-(2-ethylhexyl)carbazole (4).** *n*-Buthyllithium (2.5 M, 8.63 mL, 20.2 mmol) in hexane was added to a solution of 3,6-dibromo-9-(2-ethylhexyl)carbazole (2.73 g, 6.23 mmol) in 160 mL of THF at -78 °C with stirring for 1 hr, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.2 mL, 20.4 mmol) was added with stirring at -78 °C for 1 hr, and stirred overnight at room temperature. One hundred mL each of water and ether were then added and the mixture washed 3 times with 40 mL of brine, dried over MgSO<sub>4</sub>, and the solvent rotary evaporated. The residue was purified using column chromatography over

silica gel (hexane/ethyl acetate, 10/1, v/v) to produce compound **4** as a white solid (1.3 g, 39% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 8.66 (s, 2H), 7.89 (d, 2H), 7.36 (d, 2H), 4.16 (d, 2H), 2.05 (m, 1H), 1.45–1.22 (m, 32H), 0.90 (t, 6H). IR (KBr) 2970, 2920, 2858, 1589, 1460, 1260, 1148, 1083, 962, 863, 677  $\text{cm}^{-1}$ . Anal. Calcd: C, 72.33; H, 8.91; N, 2.64. Found: C, 71.97; H, 8.76; N, 2.37.

**P3HT<sub>2</sub>BTCZ**. Compounds **1** (0.625 g, 1.0 mmol), **4** (0.531 g, 1.0 mmol), and  $\text{Pd}(\text{PPh}_3)_4$  (69 mg, 6 mol%) were dissolved in 30 mL of toluene followed by the addition of aqueous potassium carbonate (2 M, 30 mL) and vigorously stirred at 90 °C for 48 hr under nitrogen. For end-capping, 2-bromo-3-hexylthiophene (0.05 g, 0.20 mmol) was added, reacted for 6 hr, followed by the addition of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-4-hexylthiophene (0.12 g, 0.41 mmol). The resulting solution was allowed to react for 6 hr, cooled, poured slowly into methanol, collected by filtration, dissolved in chloroform, and precipitated again in methanol (0.51 g, 69% yield). IR (KBr) 2957, 2930, 2858, 1711, 1475, 1440, 1362, 1276, 1220, 1148, 1090, 1027, 799  $\text{cm}^{-1}$ .

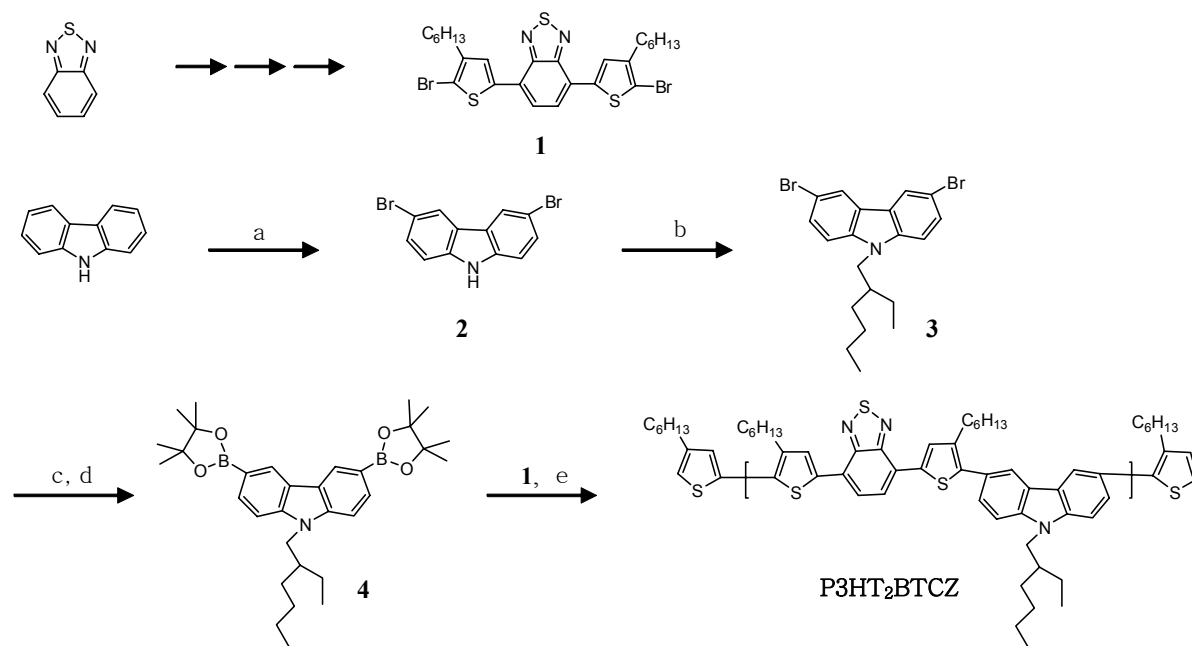
**Measurements.**  $^1\text{H}$ -NMR spectra were recorded using a JEOL FT-NMR (400 MHz) spectrometer. FT-IR spectra were recorded using an FT-IR spectrophotometer (JASCO-4100). UV-visible spectra were obtained using a Shimadzu UV-2550 spectrophotometer, and cyclic voltammetric (CV) measurements performed on a Bioanalytical System 100B, using a solution of tetrabutylammonium tetrafluoroborate ( $n\text{Bu}_4\text{NBF}_4$ ) (0.10 M) in chloroform under argon at a scan rate of 50 mV/s at room temperature. A Pt wire and  $\text{Ag}/\text{Ag}^+$  were used as the counter and reference electrodes, respectively. Photoluminescence (PL) emission spectra of solutions or films were obtained in chloroform using a photon counting spectrometer (ISS Inc.).

## Results and Discussion

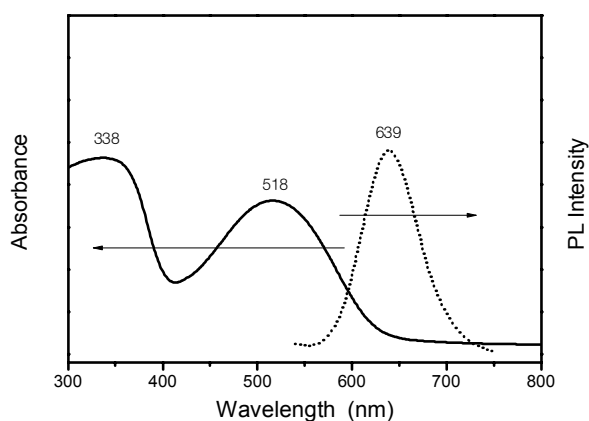
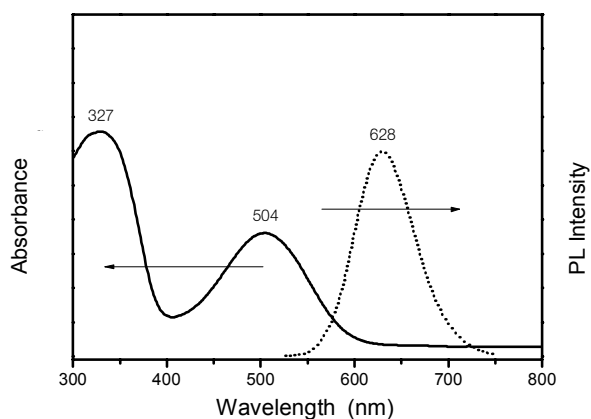
The synthesis of P3HT<sub>2</sub>BTCZ is outlined in Scheme 1. Compound **4** was prepared from carbazole in three steps by following a published procedure,<sup>15</sup> and was Suzuki coupled with compound **1** to give the corresponding polymer, which was end-capped as described above to produce P3HT<sub>2</sub>BTCZ. All reactions were straight-forward and gave moderate to high yields. The number-average molecular weight of P3HT<sub>2</sub>BTCZ was estimated to be 12,000 g/mol, by comparison of the proton NMR peak integrals of the polymers with those of a 4-dinitrobenzaldehyde NMR sample internal reference as the aldehyde proton peak was located in a region which did not interfere with the polymer proton peaks.

The UV-visible absorption of P3HT<sub>2</sub>BTCZ in chloroform showed an absorption range from UV to near 600 nm with two absorption peaks at 338 and 518 nm (Fig. 1). The absorption peaks of free BT and CZ were observed at 308 and 288 nm, respectively, suggesting that the polymer absorption bands were not due to free HT (244 nm), BT, or CZ units, but from the  $\pi$ -conjugated system of the polymer. The PL emission peaks of P3HT<sub>2</sub>BTCZ in solution and solid film were observed at 628 and 639 nm, respectively, indicating a slight red-shift in the solid, as compared to the solution sample, due to closer solid intermolecular interactions.<sup>16</sup>

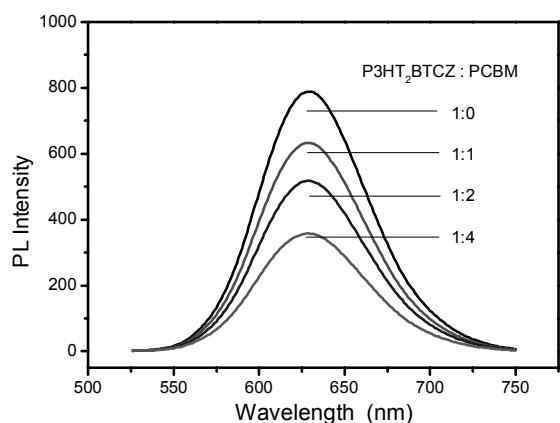
PL spectra for various weight blends of P3HT<sub>2</sub>BTCZ/PCBM in chloroform revealed that the PL intensity of P3HT<sub>2</sub>BTCZ decreased with the increasing proportions of PCBM from 1:0 to 1:4 (P3HT<sub>2</sub>BTCZ/PCBM, w/w) (Fig. 2). This observation indicates that the electron transfer efficiency from the photo-excited P3HT<sub>2</sub>BTCZ to PCBM increases with the PCBM content and, thus, the quenching efficiency of the PL emissions of the polymer also increases with the PCBM



**Scheme 1.** Synthetic route to P3HT<sub>2</sub>BTCZ: (a) NBS,  $\text{CHCl}_3$ , 0–20 °C, and 2 hr; (b) 2-ethylhexylbromide and NaOH; (c)  $n\text{-BuLi}$ , THF, –78 °C, and 2 hr; (d) 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, –78 °C, 1 hr and RT, 12 hr; (e)  $\text{Pd}(\text{PPh}_3)_4$ , toluene,  $\text{K}_2\text{CO}_3$ , and 24–48 hr.



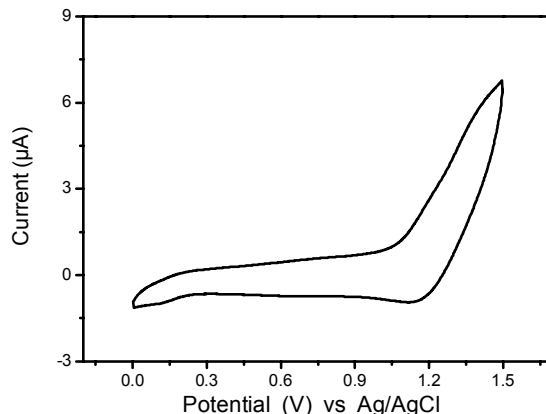
**Figure 1.** UV-visible absorption (solid lines) and PL emission spectra (dotted lines) of P3HT<sub>2</sub>BTCZ: (top) chloroform solution and (bottom) film.



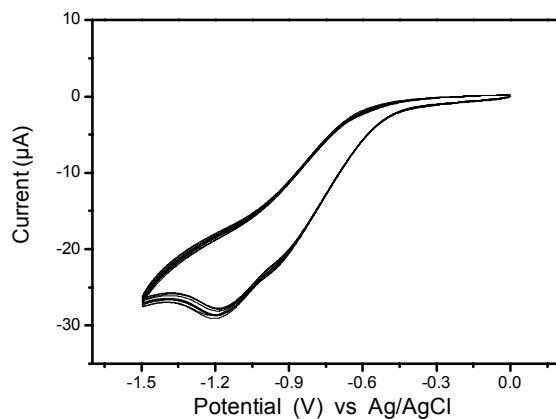
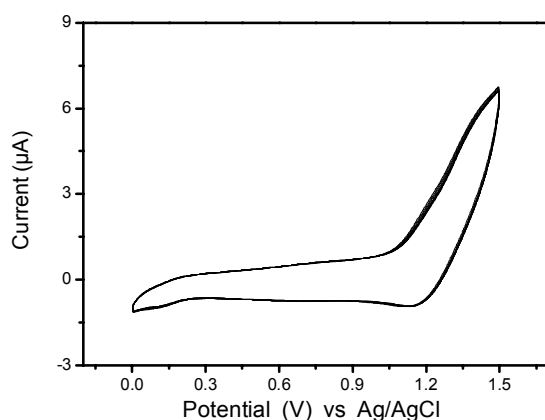
**Figure 2.** PL emission spectra for blends of P3HT<sub>2</sub>BTCZ/PCBM in chloroform.

content in the blend solutions. This leads to the speculation that the photoexcited electron transfer from P3HT<sub>2</sub>BTCZ to PCBM may be much more efficient in their corresponding solid films, due to the closer proximity between the solid state P3HT<sub>2</sub>BTCZ and PCBM.

The electrochemical properties of P3HT<sub>2</sub>BTCZ were examined by CV experiments in a three-electrode cell, set up with 0.10 M *n*-Bu<sub>4</sub>NBF<sub>4</sub> supporting electrolyte in chloroform



**Figure 3.** Cyclic voltammograms of P3HT<sub>2</sub>BTCZ in chloroform containing 0.10 M Bu<sub>4</sub>NBF<sub>4</sub>.



**Figure 4.** Cyclic voltammograms of P3HT<sub>2</sub>BTCZ in chloroform containing 0.10 M Bu<sub>4</sub>NBF<sub>4</sub> for 10 cycles: (top) oxidation and (bottom) reduction.

(Fig. 3). In the anodic scan, the onset of oxidation potential ( $E_{\text{ox, onset}}$ ) of P3HT<sub>2</sub>BTCZ occurred at 0.99 V and the CV curve remained essentially unchanged over 10 oxidation-reduction cycles (Fig. 4), indicating that P3HT<sub>2</sub>BTCZ was electrochemically stable under these conditions.

The highest occupied molecular orbital (HOMO) energy level of P3HT<sub>2</sub>BTCZ was estimated to be -5.70 eV, according to the empirical formula,  $\text{HOMO} = -(E_{\text{ox, onset}} + 4.71)$  (eV),<sup>15</sup> suggesting that P3HT<sub>2</sub>BTCZ may be air stable and easily handled under atmospheric conditions as it had a HOMO energy below -5.2 eV.<sup>17</sup> The optical band gap energy ( $E_g$ ) of

**Table 1.** Summary of the optical and electrochemical data of P3HT<sub>2</sub>BTCZ

	$\lambda_{\text{ab, onset}}$ Film (nm)	$\lambda_{\text{PL, max}}$ Film (nm)	$E_{\text{ox, onset}}$ (V)	$E_{\text{g}}^a$ (eV)	HOMO (eV)	LUMO (eV)
P3HT <sub>2</sub> BTCZ	628	639	0.99	1.97	-5.70	-3.73

$$^a E_{\text{g}} (\text{eV}) = 1240/\lambda_{\text{ab, onset}}$$

P3HT<sub>2</sub>BTCZ was estimated to be 1.97 eV, based on the UV-visible absorption spectrum (in solution), and was very close to that of P3HT (~2.0 eV).<sup>18-20</sup> From the correlation between the HOMO energy level and  $E_{\text{g}}$ , the lowest unoccupied molecular orbital (LUMO) energy level of PHT<sub>2</sub>BTCZ was calculated to be -3.73 eV. The lower energy edge of the UV-visible absorption range ( $\lambda_{\text{ab, onset}}$ ),  $E_{\text{ox, onset}}$ ,  $E_{\text{g}}$ , and the HOMO and LUMO energies of P3HT<sub>2</sub>BTCZ in solution are listed in Table 1.

The energy difference of the LUMOs of two materials should be at least equal to or slightly larger than the exciton binding energy (0.4-0.5 eV) for efficient electron transfer.<sup>17</sup> The difference in the LUMO energy levels of P3HT<sub>2</sub>BTCZ and PCBM was close to 0.6 eV, suggesting that the photoexcited electron transfer from P3HT<sub>2</sub>BTCZ to PCBM may be sufficiently efficient for the polymer to be useful as an electron-donor material in photovoltaic devices.

In conclusion, P3HT<sub>2</sub>BTCZ was successfully synthesized via a multi-step procedure. The polymer absorbed in a spectral range from the UV region to near 600 nm and had a band gap energy estimated to be 1.97 eV. The polymer appeared exhibited reversible oxidation-reduction cycles under the experimental conditions and the polymer's PL emissions in organic solution were quenched in the presence of PCBM. The present results suggested that polymer blends with PCBM can be employed in fabrication of bulk, heterojunction, photovoltaic devices.

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