Synthesis of Narrow Bandgap Polymers base on Benzobis(thiadiazole) and their Application to Organic Transistor Devices

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Two newly developed narrow bandgap polymers containing benzobis(thiadiazole) (BBT) have been synthesized using the Stille coupling reaction. The polymers showed absorption in the near infrared region due to strong charge-transfer interactions in the donor-acceptor (D-A) units, suggesting a rigid planarized structure. Although both the HOMO-LUMO levels of the polymers lie close to the work function of gold electrodes, a BBT-quaterthiophene polymer showed only p-type semiconducting behavior. In addition, the dominant charge-carrier type is holes even in BBT-thiazole-thiophene polymers, which consists mainly of acceptor units, and indicates that the thiophene ring in these polymers has a strong influence on the charge transport properties.

Keyword: Organic thin-film transistors, benzobis(thiadiazole), donor-acceptor, conjugated polymer

1. Introduction

Narrow bandgap polymers have been of interest to researchers for several decades because they exhibit interesting physical properties [1-3]. Recently, the development of such polymers has quickened to take advantage of their use as an organic semiconductor in electronic devices, such as organic thin-film transistors (OTFTs) [4-6] and organic photovoltaics (OPVs) [7-8]. One of strategies for obtaining narrow-band gap polymers is to use copolymerization of donor-accepter (D-A) units [9-10]. Most of semiconducting D-A polymers consist of thiophene units as the donor due to their ease of preparation, chemical stability, and good hole transport properties. However, there is a wide variety of choice for the acceptor units. We have focused on benz[1,2-c:4,5-c']bis-[1,2,5]thiadiazole (BBT), which is a quinoidal heterocycle with hypervalent sulfur atoms [11-19]. This system has a high electron affinity and forms a unique molecular network, resulting in excellent building blocks for n-type semiconductors. In previous work, we designed and synthesized copolymers of BBT with alkylated thiophene units (D-A system) or alkylated thiazole units (A-A system) (Figure 1, left) [20]. Although it is found that the thiazole rings enhance the intermolecular interactions and the polymer indeed showed n-type semiconductor characteristics, the substitutions of alkyl groups, which is required for solubilizing polymers, causes steric hindrance, resulting in lower levels of crystallinity and mobility.

To address this, we introduced additional spacer rings to minimize the steric hindrance between alkyl groups and a BBT ring (Figure 1, right). In addition, thiophene and thiazole rings are compared in terms of thermal
properties, quantum calculations, optical and electrochemical spectroscopies, crystallinity within thin films, and semiconducting properties.

2. Experimental

2.1. Materials

10-Dibromobenzo[1,2-c:4,5-c′]bis[1,2,5]thiadiazole (Br-BBT) [12, 21], 5,5′-dibromo-4,4′-dihexadecyl-2,2′-bithiophene [22], 2-(tributylstannyl)thiazole [23], and 5-(tributylstannyl)thiazole [23] were prepared according to the reported procedure. The compounds 1b–3b were synthesized by a Stille coupling reaction of 5,5′-dibromo-4,4′-dihexadecyl-2,2′-bithiophene with trialkylstannyl thiophene or thiazole units. Other chemicals were obtained commercially and used as received.

2.2. Synthesis of (1b–3b)  
1b: dark yellow solid. Yield: 56%. Mp: 77–79 °C. 1H-NMR: δ/ppm (500 MHz, CDCl 3, Me 4Si) = 7.30 (d, 2H, J = 3.3 Hz); 7.09 (s, 2H); 2.89 (t, 4H, J = 7.9 Hz); 1.75–1.69 (m, 4H); 1.47–1.41 (m, 4H); 1.37–1.32 (m, 4H); 0.88 (t, 6H, J = 6.9 Hz). 13C-NMR: δ/ppm (125 MHz, CDCl 3) = 141.9, 140.0, 138.3, 135.6, 134.9, 130.0, 126.9, 126.5, 32.08, 30.64, 29.87, 28.95, 29.84, 29.82, 29.76, 29.73, 29.60, 29.52, 22.85, 14.28. HRMS (FD-TOF) m/z Calcd. For C 48 H 74 S 4: 780.45783 [M ′], Found: 780.45859. Anal Calcd. For C 48 H 72 N 2 S 4: C, 73.97; H, 9.57; S, 16.46. Found: C, 74.11; H, 9.83; S, 16.52.

2b: orange solid. Yield: 40%. Mp: 73–75 °C. 1H-NMR: δ/ppm (500 MHz, CDCl 3, Me 4Si) = 7.82 (d, 2H, J = 3.3 Hz); 7.33 (d, 2H, J = 3.3 Hz); 7.09 (s, 2H); 2.89 (t, 4H, J = 7.9 Hz); 1.75–1.69 (m, 4H); 1.47–1.41 (m, 4H); 1.37–1.32 (m, 4H); 1.31–1.23 (m, 44H); 0.88 (t, 6H, J = 6.9 Hz). 13C-NMR: δ/ppm (125 MHz, CDCl 3) = 160.6, 143.1, 142.9, 137.2, 131.1, 127.4, 118.4, 32.08, 30.24, 29.86, 29.84, 29.82, 29.76, 29.73, 29.60, 29.52, 22.85, 14.28. HRMS (FD-TOF) m/z Calcd. For C 48 H 72 N 2 S 4: 780.45783 [M ′]. Found: 780.45835. Anal Calcd. For C 48 H 72 N 2 S 4: C, 70.71; H, 9.29; N, 3.59; S, 16.42. Found: C, 70.37; H, 9.46; N, 3.44; S, 16.44.

3b: dark yellow solid. Yield: 40%. Mp: 92–95 °C. 1H-NMR: δ/ppm (500 MHz, CDCl 3, Me 4Si) = 8.79 (s, 2H); 7.92 (s, 2H); 7.03 (s, 2H); 2.68 (t, 4H, J = 7.9 Hz); 1.67–1.60 (m, 4H); 1.39–1.33 (m, 4H); 1.32–1.21 (m, 4H); 0.88 (t, 6H, J = 6.9 Hz). 13C-NMR: δ/ppm (125 MHz, CDCl 3 ) = 152.7, 142.4, 141.4, 136.0, 130.9, 126.8, 125.5, 32.08, 30.63, 29.85, 29.84, 29.82, 29.79, 29.72, 29.64, 29.57, 29.54, 29.52, 22.85, 14.28. HRMS (FD-TOF) m/z Calcd. For C 48 H 72 N 2 S 4: 870.45783 [M ′], Found: 870.45789. Anal Calcd. For C 48 H 72 N 2 S 4: C, 70.71; H, 9.29; N, 3.59; S, 16.42. Found: C, 70.20; H, 9.02; N, 3.56; S, 16.38.

2.3. Synthesis of monomers (1a–3a)  
To a solution of 1b (0.85 g, 1.09 mmol), 2b (0.20 g, 0.256 mmol) or 3b (0.20 g, 2.56 mmol) in THF (10–50 mL) was added dropwise a 1.59 M solution of n-BuLi in hexane (2.1 mL, 3.27 mmol for 1b, 0.40 mL, 0.64 mmol for 2b, or 0.40 mL, 0.64 mmol for 3b) at −78 °C. The solution was stirred at −78 °C for 1 h and at room temperature for 30 min. Trimethyltin chloride (0.59 g, 2.96 mmol for 1b, 0.14 g, 0.691 mmol for 2b, or 0.14 g, 0.691 mmol for 3b) was added in one portion at −78 °C, the solution was allowed to stand at room temperature overnight. Water and ethyl acetate were added. The organic layer was washed with water, dried over magnesium sulfate and evaporated. The crude residue was purified by recrystallization from acetone to give the compound 1a (1.03 g, 88%) or 2a (0.154 g, 54%) as a solid. The compound 3a could not be successfully isolated due to the instability of the product.

1a: dark yellow solid. Mp: 65–68 °C. 1H-NMR: δ/ppm (500 MHz, CDCl 3, Me 4Si) = 7.23 (d, 2H, J = 3.4 Hz); 7.14 (d, 2H, J = 3.4 Hz); 6.98 (s, 2H); 2.73 (t, 4H, J = 7.9 Hz); 1.69–1.63 (m, 4H); 1.41–1.36 (m, 4H); 1.32–1.22 (m, 48H); 0.88 (t, 6H, J = 6.9 Hz); 0.40 (s, 18H). 13C-NMR: δ/ppm (125 MHz, CDCl 3) = 141.9, 140.0, 138.3, 135.6, 134.9, 130.0, 126.9, 126.5, 32.08, 30.64, 29.87, 29.85, 29.84, 29.82, 29.77, 29.70, 29.62, 29.56, 29.52, 22.85, 14.28, 8.04. MS (FD-TOF) m/z: 1104 [100%, M ′], 1106, 1102, 1105, 1103, 1107, 1101. Anal Calcd. For C 54 H 90 S 4Sn 2: C, 58.70; H, 8.21; N, 3.59; S, 16.42. Found: C, 58.70; H, 8.21; S, 16.42; N, 3.59; S, 16.38.
A suspension of Br-BDT (47.9 mg, 0.136 mmol), Pd(PPh3)4 (6.3 mg, 0.0054 mmol) and 1a (150 mg, 0.136 mmol) in anhydrous DMF (23 mL) or Br-BDT (31.7 mg, 0.090 mmol), Pd(PPh3)4 (4.2 mg, 0.0036 mmol) and 2a (100 mg, 0.090 mmol) in anhydrous DMF (17 mL) was stirred at 110 °C for 3h under N2 atmosphere. After cooling to room temperature, the reaction mixture was poured into a mixture of methanol (30 mL) and water (10 mL) and stirred for 2 h. The suspension was filtered to give the polymer, which was purified by soxhlet extraction with methanol, acetone, and hexane to remove low molecular weight fractions. The residue was extracted with o-dichlorobenzene, and then precipitated in methanol to give the polymer P1 (103 mg, 79%) or P2 (75 mg, 86%) as a black solid.

P1: 1H-NMR could not be taken due to the low solubility. Anal Calcd. For C54H72N4S6: C, 66.89; H, 7.48; N, 5.78; S, 19.84. Found: C, 67.00; H, 7.83; N, 5.11; S, 19.05.

P2: 1H-NMR could not be taken due to the low solubility. Anal Calcd. For C52H70N6S6: C, 64.29; H, 7.26; N, 8.65; S, 19.80. Found: C, 63.51; H, 7.37; N, 7.53; S, 18.75.

2.5. Device Fabrication

The HMDS (hexamethyldisilazane) treatment was carried out by immersing the substrate in HMDS at room temperature for >10 h. OFETs were constructed on heavily doped n-type silicon wafers covered with thermally grown silicon dioxide (200 nm) which was cleaned by piranha solution. The silicon dioxide acts as a gate dielectric layer, and the silicon wafer serves as a gate electrode. Polymers were spin-coated from 0.12 wt% solution in o-dichlorobenzene (prepared at 100 °C) with 2000 rpm for 60 sec, followed by thermal heating at 150 °C under nitrogen atmosphere. Gold was used as source and drain electrodes (50 nm) and deposited on the organic semiconductor layer through a shadow mask with L/W = 75/2000 μm. The FET measurements were carried out at room temperature in a glovebox without exposure to air with a semiconductor parameter analyzer (4200-SCS, KEITHLEY). Mobilities (μ) were calculated in the saturation regime by the relationship: μsat = (2I0D/L)/[Cox(VG-Vth)2] where I0 is the source-drain saturation current; Cox (4 F) is the oxide capacitance; VG is the gate voltage and Vth is the threshold voltage. The latter can be estimated as the intercept of the linear section of the plot of VG (I0)1/2.

2.6. Measurement

1H-NMR and 13C-NMR spectra were recorded on a JEOL 500 MHz JNM-ECX instrument. Thermogravimetry-differential thermal analysis (TG-DTA) and differential scanning calorimeter (DSC) were performed on a TA Instruments DSC Q2000 and SDT Q600 unit under a N2 atmosphere with a heating rate of 10 °C per minute. The UV-Vis-NIR spectra were measured using a Hitachi High-Tech. U-4100 UV-Vis-NIR spectrometer. Differential pulse voltammetry (DPV) were performed on BAS 660E Electrochemical system. Tetrabutylammonium perchlorate (TBAP) (0.1 M) in acetonitrile was used as the supporting electrolyte. The conventional three-electrode configuration consisted of an ITO working electrode, a platinum wire auxiliary electrode, and an Ag/AgNO3 reference electrode. Each measurement was calibrated using ferrocenium-ferrocene (Fc/Fc+) as a standard. Photoelectron yield spectroscopy (PYS) was performed on a Riken Keiki AC-3. X-ray diffraction (XRD) analysis was conducted on a Rigaku Smart Lab Diffractometer operated at 45 kV and 200 mA using CuKα radiation. Mass spectra were collected on JEOL JMS-T100GC instrument equipped with a direct probe ionization. The elemental analyses were performed with Perkin Elmer 2400 series II CHNS/O elemental analyzer.

3. Results and Discussion

3.1. Synthesis of BBT-based Polymers

The BBT-based polymers P1 and P2 were synthesized via the Stille coupling reaction with good yields by modifying reported procedures [20], as shown in Scheme 1.
Although the synthesis of an isomer of P2, which has the different nitrogen position in thiazole rings, was attempted, it could not be obtained due to the instability of the stannyl reagent of monomer unit 3a. This is the similar to the failure in the stannylation of 5,5’-bithiazole. The obtained P1 and P2 have a very low solubility. Thus, both of them undergo Soxhlet extraction with o-dichlorobenzene after using chloroform to eliminate low molecular weight fractions. Unfortunately, we could not determine the molecular weight of the polymers due to their low solubility at room temperature.

3.2 Thermal Properties

Thermogravimetric (TG) and differential scanning calorimetric (DSC) analyses of P1 and P2 were carried out to examine thermal stability and phase transitions. The TG measurements showed 5% weight loss at temperatures of 363 °C for P1 and 312 °C for P2, respectively, which is good enough for use as semiconductors. The DSC curves for polymers did not exhibit any melting or glass transition behavior under 300 °C.

3.3 Computational Chemistry

Density functional theory (DFT) and time-dependent (TD)-DFT calculations were carried out on the model oligomers (BBT-TTTT)_n and (BBT-TzTTTz)_n with n = 1–5 (Figure 2 insets) at the B3LYP/6-31G(d,p) level [24]. The highest occupied molecular orbitals (HOMOs) of the polymers were delocalized within the entire range of molecules and the lowest unoccupied molecular orbitals (LUMOs) were localized primarily on the acceptor units, as seen in similar D-A polymers [18, 25]. The estimated energies for polymers were obtained by extrapolation to n = ∞, as shown in Figure 2. The HOMO-LUMO levels and the lowest excited-state energy are −4.24 eV, −3.69 eV and 0.42 eV for P1, and −4.58 eV, −3.86 eV and 0.55 eV for P2, respectively.

3.4 Optical and Electrochemical Properties

The UV-Vis-NIR spectra and the cyclic voltammograms (CVs) for polymers P1 and P2 were obtained in thin film layers. As seen in Figure 3, the both polymers exhibited a wide absorption band in the NIR region caused by a large quinoidal contribution of the BBT units. The absorption band of P1 appeared at a longer wavelength region up to 2000 nm compared to that of P2, suggesting strong donor-acceptor interactions between thiophene rings and the BBT units. The λ_max were found at 1125 nm for P1 and 1027 nm for P2. The absorption onsets at 2043 nm and 1513 nm correspond to optical band gaps (E_g) of 0.61 eV and 0.82 eV for P1 and P2, respectively, which are consistent with the computationally estimated HOMO-LUMO gaps. The CVs of polymers are shown in Figure 4. The polymers were spin-coated on glass with ITO layer, which was used as working electrode. The polymers P1 and P2 exhibited nearly the same reversible reduction peaks. The first reduction potentials of P1 and P2 were −1.07 V and −1.01 V vs Fe/Fe^+. Therefore, the electron accepting thiazole rings in P2 only slightly affected LUMO levels. However, the oxidation peaks in P1 and P2 were clearly different, whereby P1 showed a smaller oxidation potential. The electrochemically-derived values for the HOMO-LUMO levels are summarized in Table 1. In addition, the ionization potentials (IP) were also measured in film form by photoelectron yield spectroscopy (PYS) in air. The IP values were 4.84 eV for P1 and 5.23
eV for P2. While the estimated HOMO-LUMO energies resulted in slightly different values in DFT calculations, CVs and PYS, there is tendency to have similar LUMO levels for P1 and P2 and deeper HOMO level for P2. Those HOMO-LUMO levels are suitable for a charge injection from gold electrodes in OFET devices.

![Figure 3](image)

Figure 3. Normalized absorption spectra of polymers P1 and P2 in film form.

![Figure 4](image)

Figure 4. Cyclic voltammograms of polymers P1 and P2 films on ITO electrode in acetonitrile vs Fe/Fe⁺.

Table 1. Physical properties for polymers P1 and P2

<table>
<thead>
<tr>
<th>Polym.</th>
<th>λ_{abs} (nm)</th>
<th>IP (eV)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>523, 1125</td>
<td>4.84</td>
<td>-4.56</td>
<td>-3.73</td>
</tr>
<tr>
<td>P2</td>
<td>513, 1027</td>
<td>5.23</td>
<td>-5.20</td>
<td>-3.79</td>
</tr>
</tbody>
</table>

*Spincoated on a glass plate. *Measured by PYS. *Estimated by CV.

3.5 XRD Measurement

The X-ray diffraction for thin films of polymers P1 and P2 revealed that the polymers have a crystalline morphology (Figure 5), whereby both polymers showed nearly the same diffraction peaks. The out-of-plane XRD determined a typical edge-on orientation with lattice spacings of 2.1 nm. This value is nearly the same as a crystalline polymer with C16 alkyl chains [26]. The in-plane XRD with a diffraction peak of around 24.8° indicates π-π stacking interactions of 3.6 Å between the polymer chains. These results are favorable for charge transport.

![Figure 5](image)

Figure 5. Out-of-plane and in-plane (insets) X-ray diffractograms of (a) P1 and (b) P2 on HMDS-treated Si/SiO₂ substrate.

3.6 OFET Device Characteristics

OFET devices using the polymers were fabricated on HMDS-treated Si/SiO₂ substrate by spin-coating (Figure 6). Although the polymer contains BBT rings that acts as strong acceptor units, the devices for P1 showed predominantly p-type characteristics with good carrier mobilities of 0.02 cm² V⁻¹ s⁻¹, threshold voltages of −9 and on/off ratios of 10⁴. These results are consistent with exclusive p-type behavior in similar polymers [14]. Since the donor unit proportions are decreased in P2, it is expected that the charge carrier type would change in P2. In fact, P2 showed bipolar behavior with a hole mobility of 8 × 10⁻³ cm² V⁻¹ s⁻¹ and an electron mobility of 1 × 10⁻³ cm² V⁻¹ s⁻¹. However, the dominant charge carrier was still holes and OFET device performance was relatively poor. These results indicate that thiophene rings in polymers strongly affect charge carrier transport and cause a decrease in electron mobility. Thus, the donor properties for the building blocks in polymers have a relatively large impact on overall charge transport properties.

![Figure 6](image)

Figure 6. Transfer characteristics of P1 and P2 on (a) p-type and (b) n-type operations.
4. Conclusion

We have synthesized two novel narrow bandgap polymers with BBT units. Since the BBT rings are known to act as strong acceptor units, the polymers showed deep LUMO levels and shallow HOMO levels due to strong D-A interactions. The OFET devices of P1 showed p-type charge transport with good hole mobility. On the other hand, P2-based devices showed bipolar properties. Therefore, the combination of donor and acceptor building blocks can modulate the charge carrier types and transport properties in OFET devices.

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References

24. DFT calculations were carried out with Gaussian 09 program package: Frisch, M. J. et al. Gaussian 09, revision C.01; Gaussian, Inc.: Wallingford, CT, 2010.