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2,5-Bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4-(2H,5H)-dione-Based Donor-Acceptor Alternating Copolymer Bearing Benzothieno[3,2-b] benzothiophene as an Organic Semiconductor and Its Application to Thin Film Transistors

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New diketopyrrolopyrrole (DPP)-containing conjugated polymer such poly (benzothieno[3,2-b]benzothiophene-2,5-bis(2-octyldodecyl)-6-(thiophen-2-yl)pyrrolo [3,4-c]pyrrole-1,4(2H,5H)-dione) was successfully synthesized via *Horner-Emmons condensation. The polymer showed a low bandgap energy ($E_g = 1.56$ eV) in a film state. The polymer also exhibits good solubility in common organic solvents and good self-film-forming properties. The semiconducting properties of the polymer synthesized herein were evaluated in organic thin film transistors (OTFTs). The polymer exhibits charge carrier mobilities as high as 3.0×10^{-3} cm^{2}V^{-1}s^{-1} ($I_{on/off} = 10^5$) after thermal annealing at 200°C for 10 min, which is three times higher than that of thin film transistor made of the pristine film.*

Keywords Benzothienobenzothiophene; conjugated polymer; diketopyrrolopyrrole; mobility; organic thin film transistor; semiconductor

Introduction

In the past, a number of promising organic semiconducting materials have been developed; therefore, high-performance organic thin film transistors (OTFTs) with high carrier mobilities of the order of 1 cm^{2}V^{-1}s^{-1} have been obtained by vacuum processing method [1,2]. Moreover, OTFTs can be fabricated by using soluble semiconducting materials *via* conventional low-cost spin-coating or drop-casting techniques [3,4]. Compared to vacuum-processed TFT devices, solution-processed OTFTs usually have significantly worse device performance. The development of high-performance solution-processable semiconducting materials is therefore an important research goal in the future flexible display and electronics.

For solution processing of OTFTs, two kinds of semiconducting materials are available; small molar mass conjugated molecules and crystalline conjugated polymers. Recent achievements in the charge-carrier mobility and stability of TFT devices fabricated with

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*Address correspondence to Dong Hoon Choi, Department of Chemistry, Research Institute for Natural Sciences, Korea University, Seoul 136-701, South Korea. E-mail: dhchoi8803@korea.ac.kr crystalline semiconducting polymers have resulted in TFT characteristics comparable to those of vacuum-processed TFTs [5–8]. Thus far, conjugated polymers composed of donor (D) and acceptor (A) units in the repeating group have been reported to have an excellent carrier mobility of 0.94–3.3 $cm^2V^{-1}s^{-1}$, which is attributed to strong intermolecular interaction between the polymer chains [9]. In D-A conjugated polymers, proper selection of donor moiety is expected to govern the degree of crystallinity and chain orientation on the desired substrate. Among many donor moieties, the fused benzothieno[3,2-b]benzothiophene (BTBT) structure inherently showed rigid and flat π-conjugated molecular frameworks. Dialkyl substituted BTBTs were known to show good solubility and good TFT device performance due to their favorable anisotropic molecular arrangement [10–12]. Therefore, BTBT moiety with reactive groups can be employed to prepare the semiconducting D-A conjugated polymers.

In this study, we demonstrate the synthesis and application of the new conjugated polymer containing diketopyrrolopyrrole (DPP) and BTBT moieties to OTFTs. The device properties were characterized and explained by possible mechanisms.

Experimental Section

All commercially available starting materials and solvents were purchased from Aldrich, TCI, and Acros Co. Compounds 1 and 3 were synthesized by following the method in the literature and a slightly modified method [13,14].

5,5′-(2,5-bis(2-octyldodecyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl) dithiophene-2-carbaldehyde (2): Compound 1 (1.0 g, 1.16 mmol) was dissolved in THF (20 mL). At −78°C, LDA (2 M, 2.3 mL) was added dropwise into the mother solution. The mixture was stirred at −78°C for 2h and DMF (0.47 mL, 6 mmol) was added dropwise at that temperature. The mixture was warmed up and then stirred at room temperature for 1 h. Dichloromethane (100 mL) was added and the organic phase was washed with saturated NaCl aqueous solution (3 × 50 mL), dried over $MgSO_4$, and the solvent was evaporated. The crude product was purified by flash chromatography on silica, using dichloromethane/heptane as an eluent. Yield: 0.76 g (72%). ^{1}H-NMR (300 MHz, $CDCl_3$) d (ppm): 10.03 (s, 2H, -CO*H*), 9.04 (d, $J = 4.3$ Hz, 2H, Ar-*H*), 7.88 (d, $J = 4.1$ Hz, 2H, Ar-*H*), 4.05 (m, 4H), 1.84 (m, 2H), 1.43–1.18 (m, 64H), 0.94–0.81 (m, 12H).

Poly(benzothieno[3,2-b]benzothiophene-2,5-bis(2-octyldodecyl)-6-(thiophen-2-yl)pyrrolo [3,4-c]pyrrole-1,4(2H,5H)-dione), P(DPP-alt-BTBT) (4): 100 mL of oven-dried, magnetically stirred round bottom flask was charged with a powder of **2** (0.5 g, 0.545 mmol) and **3** (0.29 g, 0.545 mmol) in 20 mL of freshly distilled tetrahydrofuran (THF). The reaction mixture was allowed to stand for 0.5 h, and then, potassium *tert*-butoxide (70 mg, 0.60 mmol) was added to it. After the reaction was completed, the solution was poured into ethanol to collect the precipitates. The crude polymer was collected by filtration and then purified by Soxhlet extraction with methanol, acetone, hexane, and chloroform, successively. The final product was obtained by precipitation in methanol. Then, the product was dried under vacuum for 1 day. Yield: 59%, 380 mg of dark purple solid. ($M_n = 6683$, $M_w = 30819$, PDI = 4.61)

Instrumentation

X-ray diffraction (XRD) measurements were recorded with a Rigaku D/MAX Ultima III using nickel-filtered Cu Kα radiation ($\lambda = 1.5418$ Å) over a range of $2° < 2\theta < 40°$ and X'celerator detector operating at 40 kV and 30 mA.

In order to study absorption behavior, the polymer film was fabricated on quartz substrates as follows. The solution (1 wt%) in chloroform was filtered through an acrodisc syringe filter (Millipore 0.2 μm) and subsequently spin-cast on the quartz glass. The films were dried overnight at 70°C for 24 hours under vacuum. Absorption spectra of samples in a film and solution state (chloroform, conc. 1×10^{-5} mole/L) were obtained using a UV-VIS spectrometer (HP 8453, photodiode array type) in the wavelength range of 190–1100 nm.

Fabrication of OTFTs

For the characterization of TFT performance, bottom gate top contact device geometry was employed. On the heavily n-doped Si/SiO_2 substrate the spin-coated films (thickness ~40–50 nm) were prepared with chloroform as a solvent. Surface modification was carried out with n-octyltrichlorosilane (OTS) to make hydrophobic dielectric surface. Source and drain electrodes were then thermally evaporated (100 nm) through shadow mask with the channel width and length of 1500 μm and 150 μm, respectively. We followed the fabrication and measurement methods reported in our previous literature [15].

Results and Discussion

We outlined the synthesis route of new p-type DPP-based semiconducting conjugated polymer, **4**. (see Fig. 1) As solubilizing groups and crystallization promoting moieties, two octyldodecyl groups were substituted in the pyrroline ring of DPP. Horner-Emmons condensation of the monomers **2** and **3** yielded the conjugated-polymer, **4** in a high yield of 60%. The number-average molecular weight (M_n) of the polymer was determined by gel permeation chromatography (GPC) using a polystyrene standard and found to be 6,683 ($M_w/M_n = 4.61$).

The polymer was also found to have good self-film forming property and was readily soluble in various organic solvents such as chloroform, xylene, methylene chloride (MC), monochlorobenzene, and THF. In particular, more than 5 mg of polymer can be dissolved in 1 mL chloroform at room temperature.

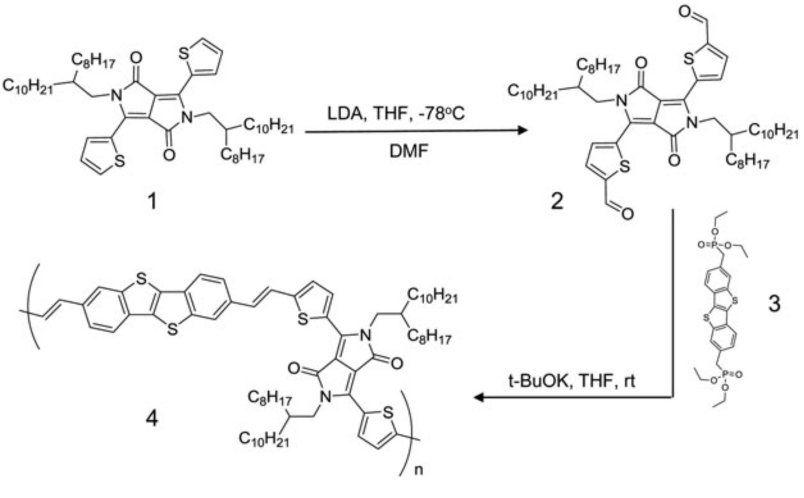

Figure 1. Synthetic procedure for the polymer, **4**.

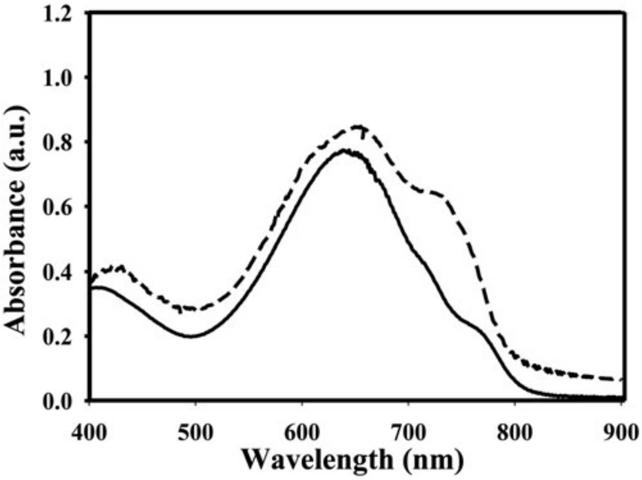

Figure 2. Optical absorption spectra of polymer **4**. *Solid line: solution, short-dashed line: film.

Figure 2 shows the UV-Vis absorption spectra of the polymer samples both in solution and in film states. The polymer exhibited absorption maxima at 644 nm and 655 (730) nm in the solution and film, respectively. The solution spectrum showed a broad absorbance, extending from 500 nm to 800 nm; it is attributed to the $\pi-\pi$ transition as well as the donor-acceptor (D-A) interaction between the DPP and BTBT moieties.

This implies that DPP/BTBT-containing repeating groups are highly interactive, forming self-assembled molecular domains through strong electronic coupling both in solution and film states. The optical bandgap of the polymer was determined from the absorption onset in the film state, which was 1.56 eV.

Figure 3 shows the electron-state-density distribution of the highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO) of geometrically optimized structures (DFT B3LYP/6–31G) of the repeating group in the structure of the polymer **4**, using the Spartan program ('10). Electron delocalization could be observed in the HOMO and LUMO states of the repeating group. In LUMO state, electrons are mainly localized in DPP moiety. In HOMO state, the electrons were delocalized from DPP unit to benzothiophene in BTBT moiety slightly. As a result, it can be thought that BTBT moiety did a little contribution for absorption spectrum. Theoretical HOMO, LUMO energies, and bandgap were calculated to be −4.99, −2.64, and 2.35 eV, respectively.

From the XRD patterns presented in Figure 4, the crystalline nature of P(DPP-*alt*-BTBT) was found to be evident and the variation of the diffraction patterns indicates the

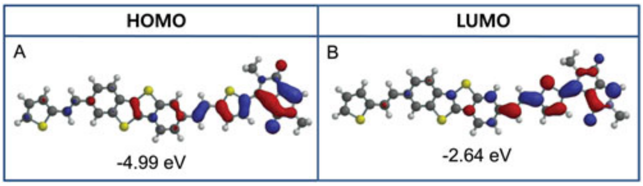

Figure 3. Molecular simulation results of the simplified repeating unit in the polymer **4**, showing HOMO and LUMO distribution.

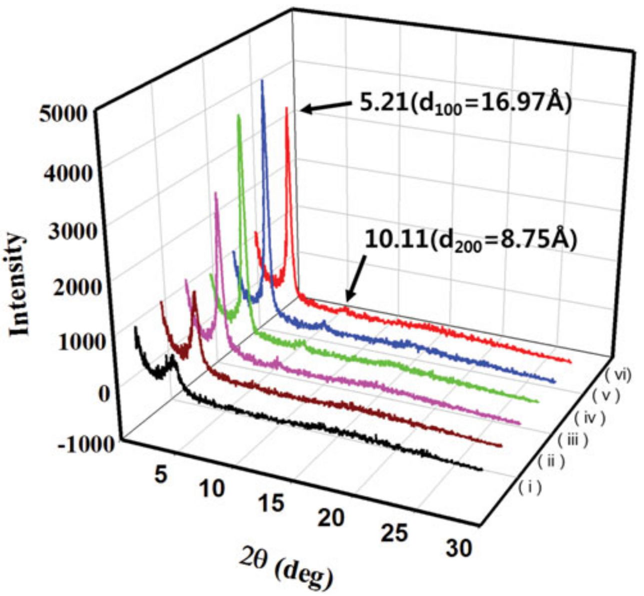

Figure 4. X-ray diffraction (XRD) patterns of P(DPP-*alt*-BTBT). as-spun film (i), annealed film at 120°C (ii), 150°C (iii), 180°C (iv), 200°C (v), and 220°C (vi).

formation of well-grown polycrystallites in the spin-coated film on n-octyltrichlorosilane (OTS)-modified SiO_2/Si substrate. As shown in the diffractogram of the as-spun film (Fig. 4(i)) there is a clear diffraction peak arising from the interlamella spacing; when annealing the sample at 180°C ~ 220°C, we could observe the 2nd-order diffraction peaks. Two highly resolved diffraction peaks were observed at $2\theta = 5.21°$ and 10.11°, which indicates that the polymer chains exhibit well-organized intermolecular lamella ordering, resulting in the enhanced crystallinity. Based on literature reports [16], the polymer film was found to form a lamellar crystalline structure in the film with an interlayer distance of ~16.97 Å (100).

In order to investigate the semiconducting properties of P(DPP-*alt*-BTBT), we fabricated OTFT devices and characterized their performances. Bottom-gate top-contact OTFT devices were fabricated using gold source and drain electrodes that were thermally evaporated using the conventional method. A p-doped polycrystalline silicon was used as the gate electrode, with an OTS-treated SiO_2 surface layer used as the gate dielectric insulator. A 50–65 nm thin film of the semiconductor was deposited by spin-coating a 1 wt% solution of the polymer in chloroform. After spin-coating the polymer solution onto the insulator surface, gold was deposited *via* thermal evaporation.

The output characteristics showed very good saturation behaviors and clear saturation currents that were quadratic to the gate bias (see Figure 5). The saturated field-effect mobilities, μ_{FET} can be calculated from the amplification characteristics, by using the classical equations describing FETs.

According to the results shown in Fig. 5**,** the hole mobility of the pristine film of P(DPP-*alt*-BTBT) was measured to be 1.0×10^{-3} $cm^2V^{-1}s^{-1}$ ($I_{\text{on/off}} = 10^4$, $V_{th} = -20$ V). However, when annealing the film at 200°C for 10 min., the mobility value increased to 3.0×10^{-3} $cm^2V^{-1}s^{-1}$ maintaining a high on-off current ratio of 10^5 ($I_{\text{on/off}} = 10^5$, $V_{th} = -42$ V). It was observed that the threshold voltage was shifted by 22V in thermally annealed

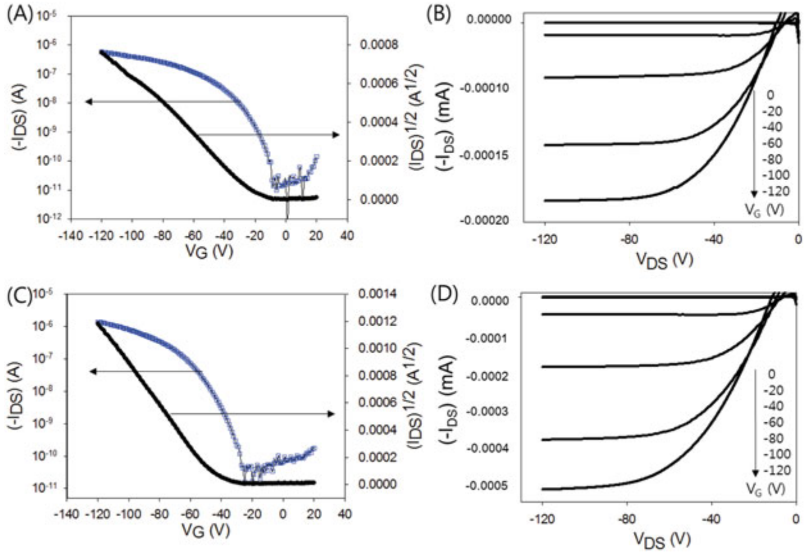

Figure 5. Transfer (A) and output (B) curves of the OTFT device fabricated with pristine P(DPP-*alt*-BTBT) film. Transfer (C) and output (D) curves of the TFT device fabricated with thermally annealed P(DPP-*alt*-BTBT) film ($T_{\text{ann}}. = 200°\text{C}$, for 10 min).

film. It might be attributed to variation of interfacial contact between the active layer and the gate insulator, resulted from the increase of crystallite size in the active polymer layer. In brief, thermally annealed film exhibited higher crystallinity and more efficient charge transport properties in TFT devices.

Conclusions

We have successfully synthesized and characterized new DPP-based conjugated polymer bearing BTBT moiety as a p-type semiconducting material. The polymer showed good film forming property and a high degree of crystallinity in the solid state after thermal annealing. The thin-film transistor device made of the thermally annealed film provided a field effect mobility of 3.0×10^{-3} cm^{2}V^{-1}s^{-1}, together with a high current on/off ratio ($>10^5$) and a threshold voltage ($V_{th} = -42$ V). Our study unambiguously demonstrates that DPP-based conjugated polymer with planar BTBT moiety can be utilized for fabricating and much improving OTFT devices.

Acknowledgments

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