A new ambipolar copolymer for organic electronics

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ABSTRACT

The 5-(heptadecan-9-yl)dithieno[3,2-b:2′,3′-d]pyridine (NET) structure was designed as a new donor unit for copolymer synthesis. Benzothiadiazole (BT) was used as the electron acceptor unit. The new donor–acceptor copolymer was obtained through the Stille coupling reaction. The density functional theory analysis of the new copolymer showed that the highest occupied molecular orbital electron density was localized on the NET unit while the lowest unoccupied molecular orbital electron density was localized partially on the BT and partially on the pyridine group of the NET unit. The polymer presented good solubility and thermal stability, which are desirable properties for use in solution-processed devices. The new polymer is expected to show a potential for application in organic electronics, such as thin-film transistors.

1. Introduction

π-conjugated copolymer structures consist of planarized π-conjugated molecules, which provide excellent opto-electronic properties [1–5]. In the last decade, the development of specific copolymers had already led to a revolution in both material synthesis and device performance [6–11]. A crucial avenue for exploration is the synthesis of polymer-based organic thin-film transistors (OTFTs) with high efficiency, through a cheap and easy method [7–9]. As is known, the π-conjugation present in carbon double bonds increases the molecular stability; therefore, it is beneficial to obtain planarized molecular structures. Such polymer materials are an easy and cost-effective alternative to amorphous silicon-based transistors and are especially suitable for use in lightweight, large-area, and flexible devices. Many research groups concentrate their efforts on the synthesis of a target copolymer with high performance properties. Molecular order and the design of organic semiconducting molecules play key roles in determining the charge mobility in OTFTs. Among them, the donor–acceptor copolymers show high electron and charge transport properties due to the strong intermolecular interaction. Many organic semiconductors, based on triisopropyl-silylhexyl, pentacene, poly(3-hexylthiophene), poly(3-octylthiophene), poly(4,8-dialkyl-2,6-bis(3-alkylthiophene-2-yl)benzo[1,2-b:4,5-b′]dithiophene), poly(triarylamine), and dithothiophene, have been reported as suitable donor units for donor–acceptor polymers [12–17].

The development of new donor units for π-conjugated donor–acceptor copolymers, however, is still a challenge for further research [18–19]. In this paper, a new dithieno[3,2-b:2′,3′-]pyridine donor unit was designed for use in the preparation of a donor–acceptor copolymer. A new copolymer consisting of dithieno[3,2-b:2′,3′-]pyridine as the donor unit and benzo[2,1-b:3,4-b′]dithiophene as the acceptor unit was subsequently developed. Full synthesis and characterization of this copolymer were carried out.

2. Experiment section

2.1. Synthesis of 5,5′-dibromo-3-nitro-2,2′-bithiophene (1)

A mixture of 5,5′-dibromo-2,2′-bithiophene (61.7 mmol, 20.9 g), dichloromethane (250 ml), and acetic anhydride (0.124 mol, 3.53 ml) was added into a three-neck flask. The temperature was cooled to −40°C, and the mixture was stirred. A mixture of HNO3 (61.7 mol, 5.20 ml) and acetic acid (100 ml) was added dropwise into the flask. The reaction was left running overnight. Afterwards, the
reaction mixture was poured into an aqueous NaOH solution and was extracted with dichloromethane; the resulting organic layer was then collected. This organic layer was first dried with anhydrous magnesium sulfate, followed by filtration and evaporation. The solid residue was then dissolved in a small amount of dichloromethane and was then recrystallized from Et-OH. The proton nuclear magnetic resonance (1H NMR) (CDCl₃, 300 MHz) analysis showed the following peaks: δ 7.635 (s, 1H), 7.282–7.268 (d, 1H), and 7.112–7.098 (d, 1H).

2.2. Synthesis of 5,5′-dibromo-[2,2′-bithiophen]-3-amine (2)

A mixture of 5,5′-dibromo-3-nitro-2,2′-bithiophene (8.1 mmol, 3.0 g), iron powder (40.6 mmol, 2.27 g), and acetic acid (120 ml) was stirred and refluxed at 60°C overnight. Afterwards, the reaction mixture was poured into an aqueous NaOH solution, and extraction was performed with ether. The resulting organic layer was then collected. The organic layer was dried as described in Section 2.1. The solid residue was then purified by column (dichloromethane/hexane = 1/7). The 1H NMR (CDCl₃, 300 MHz) analysis showed the following peaks: δ 7.094–7.081 (d, 1H), 6.868–6.856 (d,1H), 2.122 (s, 1H), 1.727–1.703 (d, 2H), 1.699–1.698 (d, 2H), 1.343–1.338 (m, 20H), and 0.898–0.751 (t, 6H).

2.3. Synthesis of N-(5,5′-dibromo-[2,2′-bithiophen]-3-yl)-2-hexyldecanamide (3)

A mixture of triethylamine (5ml) and 2-hexyldecanoyl amine (2) (36.2 mmol, 5.2 g) was dissolved into freshly distilled POCl₃ (160 ml). This mixture was stirred and refluxed for 2h. The reaction mixture was then collected. The resulting organic layer was then dried with anhydrous magnesium sulfate, and was then recrystallized from Et-OH. The product was washed with ether and was dried with MgSO₄. After the solvent was removed, the product was purified through recrystallization. The 1H NMR (CDCl₃, 300 MHz) analysis showed the following peaks: δ 7.759 (s, 1H), 7.645 (s, 1H), 3.463 (m, 1H), 2.018–1.897 (m, 2H), 1.802–1.687 (m, 2H), 1.274–1.194 (m, 20H), 0.875–0.831 (t, 6H), and 0.592–0.376 (m, 18H).

2.4. Synthesis of 2,7-dibromo-5-(pentadecan-7-yl)dithieno[3,2-b:2′,3′-d]pyridine (4)

A mixture of N-(5,5′-dibromo-[2,2′-bithiophen]-3-yl)-2-hexyldecanamide (5.1 mmol, 3.1 g) and P₂O₅ (36.2 mmol, 5.2 g) was dissolved into freshly distilled POCl₃ (160 ml). This mixture was stirred and refluxed for 24 h. Afterwards, the mixture was poured into ethyl acetate (60 ml) and water (60 ml), then 5 M NaOH was added until the mixture pH became equal to 10. An extraction was performed with ethyl acetate, and the resulting organic layer was collected. This organic layer was dried as described above. The residue was purified by column (ethyl acetate/hexane = 1/4). The 1H NMR (CDCl₃, 300 MHz) analysis showed the following peaks: δ 7.625 (s, 1H), 7.578 (s, 1H), 3.198 (s, 1H), 1.930–1.741 (m, 2H), 1.210–1.204 (t, 2H) 1.076–1.049 (m, 20H), and 0.898–0.751 (t, 6H).

2.5. Synthesis of 5-(pentadecan-7-yl)-2,7-bis(trimethylstannyl)dithieno[3,2-b:2′,3′-d]pyridine (5)

n-Butyl lithium (0.98 ml, 2.5 M in hexane, 0.0025 mol) was added dropwise at −78°C to 2,7-dibromo-5-(pentadecan-7-yl)dithieno[3,2-b:2′,3′-d]pyridine (0.5 g, 0.0011 mol) in 50 ml dry THF, and the mixture was stirred for 1 h at −78°C. Trimethyltin chloride (0.49 g, 0.0025 mol) was added in one step. After 10 min, the mixture was warmed to room temperature and was stirred for 2 h. The reaction mixture was extracted with diethyl ether and was dried with MgSO₄. After the solvent was removed, the product was purified through recrystallization. The 1H NMR (CDCl₃, 300 MHz) analysis showed the following peaks: δ 7.759 (s, 1H), 7.645 (s, 1H), 3.463 (m, 1H), 2.018–1.897 (m, 2H), 1.802–1.687 (m, 2H), 1.274–1.194 (m, 20H), 0.875–0.831 (t, 6H), and 0.592–0.376 (m, 18H).

2.6. Synthesis of poly 2-methyl-7-(7-methylbenzo[c][1,2,5]thiadiazol-4-yl)-5-(pentadecan-7-yl)dithieno[3,2-b:2′,3′-d]pyridine (PNET-BT)

The 5-(pentadecan-7-yl)-2,7-bis (trimethylstannyl) dithieno[3,2-b:2′,3′-d]pyridine and 4,7-dibromo-2,1,3-benzothiadiazole were dissolved in chlorobenzene and were bubbled with nitrogen for 0.5 h. Then Pd(dba)₃ and p(o-tol)₃ were added into the mixture, and the reaction was maintained at 100°C for 40 h. The reaction mixture was transferred into a mixture of methanol (200 ml) and 2M hydrochloric acid (30 ml), and was stirred for 1 h. The precipitate was then filtered. The product was washed via Soxhlet extraction with methanol, acetone, hexanes, tetrahydrofuran, and chloroform. Then, the chloroform solution was precipitated into methanol and was dried under vacuum.

3. Results and discussion

3.1. Synthesis and characteristics

The monomers and polymer were synthesized according to scheme 1 (Figure 1). The new N-(5,5′-dibromo
[2,2'-bithiophen]-3-yl)-2-hexyl decanamide was obtained through the nitration of dibromobithiophene following reduction and amidization. Finally, the new 2,7-dibromo-5-(pentadecan-7-yl)dithieno[3,2-b:2',3'-d]pyridine copolymer was synthesized through cyclic dehydration. PNET-BT was obtained through the Stille coupling reaction. The synthesized polymer presented good solubility in various common organic solvents, such as chloroform and chlorobenzene, which facilitates its use in solution-processed organic electronics. The number average molecular weight of the polymer was determined through gel permeation chromatography as 9000 g/mol, with a polydispersity index of 1.42.

The density function calculation of the donor–acceptor moiety was carried out by the Gaussian 08 program (Figure 2). The electron density of the highest occupied molecular orbital (HOMO) was localized on the 5-(pentadecan-7-yl)dithieno[3,2-b:2',3'-d]pyridine unit while that of the lowest unoccupied molecular orbital (LUMO) was localized partially on pyridine and partially on the benzothiadiazole (BT) unit. A planar backbone was observed.

3.2. Thermal properties

Figures 3 and 4 show the thermal stability of the polymer, as found through thermogravimetric analysis and differential scanning calorimetry (DSC) under a nitrogen atmosphere. The polymer exhibited 5% weight loss at 376°C. In the DSC measurements over 200°C, thermal transitions were not observed. Therefore, it was deduced that the new synthesized polymer has good thermal stability for application in organic electronics.

3.3. Optical and electrochemical properties

The polymer showed a maximum chloroform solution absorption of 545 nm. In the film states, the maximum absorption spectra were observed at 545 and 604 nm. In the film state, the absorption spectra showed a dual-band absorption profile, where the high-energy band originates from the charge transfer band and the low-energy band can be attributed to the intermolecular interaction band. After annealing, the film maximum absorption spectra of PNET-BT were red-shifted to 565 and 610 nm. This may have been due to the enhanced
charge transfer and intermolecular interaction occurring after annealing. The optical band gap of the polymer was calculated to be 1.75 eV from the absorption edge. The results are comparable with the 5H-dithieno[3,2-b:2′,3′-d]pyran-based copolymer (PDTP-DFBT), which has oxygen instead of nitrogen of the 5-(pentadecan-7-yl)dithieno[3,2-b:2′,3′-d]pyridine-based copolymer. The newly developed PNET-BT showed more blue-shifted absorption because the pyridine unit had a slightly electron-withdrawing property compared with the pyran unit [20] (Figure 5).

3.4. Electrochemical property

As shown in Figure 6, cyclic voltammetry (CV) was used to measure the energetic properties of the polymer. The CV measurements exhibited ferrocene onset at 0.43 eV. From the oxidation onset, the HOMO level was −5.67 eV. The LUMO level was calculated to be −3.92 eV from the optical band gap and HOMO energy level. As was expected in the UV absorption, the HOMO and LUMO energy levels were deeper than those of the 5H-dithieno[3,2-b:2′,3′-d]pyran-based copolymer (PDTP-DFBT) with a −5.26 eV HOMO and a −3.64 eV LUMO. The new polymer is expected to show a potential for various organic electronics applications.

4. Conclusion

A new donor unit was developed, and a new polymer, PNET-BT, was polymerized with the newly prepared donor unit and a BT acceptor. The resulting copolymer, PNET-BT, presented good thermal stability. The film’s UV absorption maxima were observed at 545 and 604 nm, resulting from the charge transfer band and intermolecular interaction. The new polymer was expected to show a potential for various organic electronics applications.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by National Research Foundation of Korea (NRF) [Grant Number 2012M3A7B4049647].

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