



Polymer based on benzothiadiazole-bridged bis-isoindigo for organic field-effect transistor applications



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ABSTRACT

Two isoindigos were symmetrically connected by 2,1,3-benzothiadiazole core to form an acceptor2–acceptor1–acceptor2 monomer. The new monomer was used as electron acceptor unit in construction of a unique donor/acceptor polymer with donor–acceptor2–acceptor1–acceptor2 repeating units. The optical and electrochemical properties of the monomer and polymer were investigated. The optical band gap of monomer and polymer were about 1.86 and 1.65 eV, respectively. Both monomer and polymer showed relatively low-lying highest occupied molecular orbital energy levels and the corresponding values were –5.90 and –5.56 eV for monomer and polymer, respectively. The semiconducting properties of new materials were also studied. Organic field effect transistors based on solution processed thin films of the polymer displayed typical p-channel characteristics with a hole mobility of $0.02 \text{ cm}^2 (\text{V s})^{-1}$ in ambient conditions.

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1. Introduction

Organic semiconducting material for optoelectronic device application has been an intriguing research area over the last decade [1]. Conjugated polymers based on functional dyes as building blocks have received considerable attention recently because of their unique optical and electronic properties, and applications in various optoelectronic devices, such as organic light-emitting diodes (OLEDs) [2], organic solar cells (OSCs) [3], and organic field-effect transistors (OFETs) [4]. Most of high-performance conjugated polymers for OFET applications have a typical alternating D (donor, electron-rich)/A (acceptor, electron-deficient) structure in main chains (Fig. 1a) [4–11]. Intramolecular charge transfer interactions (ICT) can be utilized to tune the energies of frontier molecular orbits and band gaps of conjugated polymers. Introduction of electron-deficient dye units into polymer backbones has opened doors for developing high-performance OFET materials [5–7]. Many electron-deficient dyes or their core

components, such as benzothiadiazole (BT) [8], naphthalene diimide (NDI) [9], diketopyrrolopyrrole (DPP) [5], thieno-[3,4-c]pyrrole-4,6-dione (TPD) [10] and isoindigo (il) [11] have been extensively studied as the acceptor units for high-performance donor/acceptor conjugated polymers. Donor/Acceptor polymers based on two types of acceptor units randomly arranged in main-chains usually only show moderate performances in OFET device studies [12]. This could be caused by internal structural disorders in the materials [13]. However, some regioregular polymers with two types of acceptor units have shown high-performances in OFET device studies (Fig. 1a) [14–17]. The regioregular structures of alternating donor/acceptor units not only facilitate intramolecular charge transfer, but also benefit intermolecular chain packing order, and then enhance charge-carrier mobility. The donor–acceptor1–donor–acceptor2 (D-A1-D-A2) repeating structures are often used for D/A conjugated polymers with two acceptor units (Fig. 1b). Regioregular D/A conjugated polymers with donor–acceptor2–acceptor1–acceptor2 (D-A2-A1-A2) repeating structure has never been reported (Fig. 1c). The D-A2-A1-A2 repeating structure can also have typical intramolecular donor–acceptor interaction. Polymers based on this kind of repeating structures might have interesting properties. Isoindigo (il) and benzothiadiazole are frequently used as the building blocks

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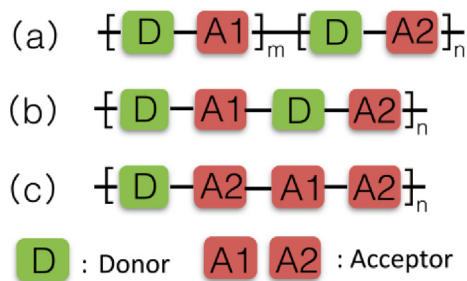


Fig. 1. The schematic of structures of polymers with two types of acceptor units in the main chain: (a) random polymers; (b) regioregular D-A1-D-A2 structural polymers; (c) regioregular D-A2-A1-A2 structural polymers.

for high performance optoelectronic materials recently [4,10,11]. Herein, we reported a new 2,1,3-benzothiadiazole-bridged bis-indigo monomer and a polymer with regioregular D-A2-A1-A2 repeating structure based on it. The optical, electrochemical and semiconducting properties of the new polymer were also investigated.

2. Experimental section

2.1. Materials

All chemicals and reagents were purchased from Sigma–Aldrich Chemical Co., Alfa Aesar Chemical Company and Sinopharm Chemical Reagent Co. Ltd. and were used without further purification unless stated otherwise. The compound **3** [18] and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene [19] were prepared according to reported procedures. All the reactions were carried out under nitrogen atmosphere.

2.2. Measurement and characterization

Nuclear magnetic resonance (NMR) spectra were recorded on a Mercury plus 400 MHz machine. Gel permeation chromatography (GPC) analyses were carried out on a Shimadzu SIL-20A liquid chromatography instrument using tetrahydrofuran as eluent with polystyrenes as standards. Thermo-gravimetric analyses (TGA) were taken on a TA instrument Q5000IR at a heating rate of $20\text{ }^\circ\text{C min}^{-1}$ under nitrogen gas flow. Differential scan calorimetry (DSC) studies were carried out with a Perkin Elmer Pyris 1 under nitrogen flow. Samples (about 5.0 mg in weight) were first heated up to $300\text{ }^\circ\text{C}$ and were held for 2 min to remove thermal history, followed by the cooling at a rate of $10\text{ }^\circ\text{C min}^{-1}$ to $0\text{ }^\circ\text{C}$ and then heating at a rate of $10\text{ }^\circ\text{C min}^{-1}$ to $300\text{ }^\circ\text{C}$. UV–vis spectra were recorded on a Perkin Elmer Lambda 20 UV–vis spectrophotometer. Cyclic voltammetry (CV) measurements were conducted on a CHI 600 electrochemical analyzer with a three-electrode cell under nitrogen atmosphere in a deoxygenated anhydrous acetonitrile solution of tetra-*n*-butylammoniumhexafluorophosphate (0.1 M) at a scan rate of 100 mV/s. A platinum disk electrode was used as a working electrode, a platinum-wire was used as a counter electrode, and an Ag/Ag⁺ (0.01 M AgNO₃ in acetonitrile) electrode was used as a reference electrode. The sample thin films were coated on the surface of platinum disk electrode. The CV curves were calibrated with ferrocene/ferrocenium (Fc/Fc⁺) redox couple as an external standard, which was measured under same condition before and after the measurement of samples. Atomic force microscope (AFM) images were obtained using a MultiMode V microscope. Matrix assisted laser desorption ionization time-of-flight

(MALDI-TOF) mass spectrometry (MS) analyses were performed on a Bruker Autoflex.

2.3. Synthesis of monomer and polymer

2.3.1. Synthesis of compound **1**

9-(Bromomethyl)-nonadecane (10.84 g, 30 mmol) was added dropwise under nitrogen atmosphere to a suspension of 6-bromoindoline-2,3-dione (4.52 g, 20 mmol), potassium carbonate (11.06 g, 80 mmol) in anhydrous *N,N*-dimethylformamide (80 mL). The mixture was stirred at room temperature for 1 h, and then stirred at $70\text{ }^\circ\text{C}$ for 20 h. The mixture was poured into water. It was extracted with dichloromethane. The organic layer was washed with water, brine and dried over sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (1:2, v/v) as eluent to give an orange colored oil (7.20 g, 71%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.45 (d, $J = 7.9$ Hz, 1H), 7.27 (d, $J = 7.7$ Hz, 1H), 7.04 (s, 1H), 3.58 ($J = 7.5$ Hz, 2H), 1.86 (br, 1H), 1.17–1.42 (m, 32H), 0.84–0.89 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 182.50, 158.49, 152.49, 133.68, 126.97, 126.51, 116.45, 114.20, 45.10, 36.15, 32.12, 32.08, 31.60, 30.15, 29.83, 29.79, 29.74, 29.55, 29.50, 26.48, 22.89, 14.34.

2.3.2. Synthesis of compound **2**

4,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,1,3-benzothiadiazole (1.98 g, 5.1 mmol), compound **1** (5.66 g, 11.2 mmol), aliquat 336 (1 drop), potassium phosphate (2.80 g, 13.2 mmol), tris-(dibenzylideneacetone)dipalladium (0.050 g, 0.055 mmol), tri(*o*-tolyl)-phosphine (0.100 g, 0.328 mmol) were dissolved in a mixture solvent of toluene (24 mL) and water (3 mL). The solution was degassed for 30 min and was heated at $110\text{ }^\circ\text{C}$ for 24 h. After cooling to room temperature, water (50 mL) was added. The mixture was extracted with ethyl acetate for three times. The combined organic layer was dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (4:1, v/v) as eluent to obtain a reddish-brown solid (3.78 g, 75%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.96 (s, 2H), 7.78 (d, $J = 7.8$ Hz, 2H), 7.70 (s, 2H), 7.64 (dd, $J = 7.8, 1.3$ Hz, 2H), 3.71 (d, $J = 7.3$ Hz, 4H), 1.98 (s, 2H), 1.15–1.40 (m, 80H), 0.89–0.84 (m, 12H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 183.10, 158.72, 151.68, 146.44, 133.25, 124.15, 117.31, 111.76, 44.86, 36.15, 31.89, 31.86, 31.64, 29.97, 29.64, 29.62, 29.60, 29.57, 29.33, 29.29, 26.52, 22.67, 22.65, 14.11, 14.09; HRMS-MALDI (m/z): [M + Na]⁺ calcd for C₆₂H₉₀N₄O₄Na 1009.6575, found 1009.6513.

2.3.3. Synthesis of monomer **M**

To a suspension of 6-bromooxindole (933 mg, 4.4 mmol) and compound **2** (1.98 g, 2 mmol) in acetic acid (25 mL), conc. hydrochloric acid solution (2 drops) was added. The mixture was heated under reflux for 24 h. It was allowed to cool to room temperature and was filtered. The residue was washed with water and small amount of ethanol. After drying under vacuum, compound **4** was obtained as a black solid (2.17 g, 79%). This product was used in the next step without further purification. To a solution of **4** (0.688 g, 0.5 mmol) and potassium carbonate (0.346 g, 2.5 mmol) in *N,N*-dimethylformamide (20 mL), 9-(bromomethyl)-nonadecane (0.433 g, 1.2 mmol) was added dropwise under nitrogen. The mixture was stirred for 20 h at $100\text{ }^\circ\text{C}$ and then was poured into water. The mixture was extracted by dichloromethane. The organic layer was washed with water, brine and dried over sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using

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