Benzodithiophenedione and diketopyrrolopyrrole based conjugated copolymers for organic thin-film transistors by structure modulation

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ABSTRACT

Three copolymers (**P1**, **P2**, and **P3**) based on benzodithiophenedione and diketopyrrolopyrrole units were synthesized by Suzuki reaction. The thermal, optical, electrochemical, microstructure, charge transport and phototransistor properties of the copolymers were also investigated. The field-effect performances of the copolymers were optimized by tailoring their structure and using thermal annealing. The three copolymers exhibited ambipolar transport under vacuum, but hole characteristics in air. The optimized copolymer **P3** exhibited a balanced hole and electron mobility of 0.022 and 0.028 cm^2 V^{-1} s^{-1}, respectively, under vacuum conditions, but hole transport in air with a hole mobility of as high as 0.034 cm^2 V^{-1} s^{-1}. Phototransistors based on **P3** showed a photocurrent/dark current ratio of 6.4×10^3 under near-infrared light illumination (808 nm). This is the first investigation on the field-effect and phototransistor performances of benzodithiophenedione-based copolymers.

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1. Introduction

Solution-processable conjugated polymers have attracted tremendous attention in the field of organic thin-film transistors (OTFTs) owing to many advantages such as light weight, low cost, and high flexibility [1]. Recently, rapid progress has been made in the charge-carrier mobilities of OTFTs. Various p-channel, n-channel, and ambipolar polymers with remarkably high mobility have been successfully synthesized by tailoring their structural characteristics, and the devices have been optimized [2]. In the past few years, polymer-based OTFTs exhibited a high hole mobility of up to 10 cm^2 V^{-1} s^{-1} and electron mobility of more than 1 cm^2 V^{-1} s^{-1} [3]. In general, the high performance of polymer-based OTFTs can be attributed to some of their features as follows: First, the copolymer should possess suitable highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels for hole and electron injection [4]. Second, the copolymer should possess a high-level planarity in its conjugated backbone to achieve a high charge-carrier mobility [5]. Third, the copolymer should possess a close $\pi-\pi$ stacking distance and long-range-ordered lamellar crystalline structure, leading to an excellent charge transport. Moreover, the close $\pi-\pi$ stacking distance is also beneficial to prevent the diffusion of water and oxygen [6]. Finally, a high molecular weight is also beneficial for satisfactory OTFT performance. Copolymer semiconductors with a high molecular weight usually exhibit a high field-effect performance than those with a low molecular weight [7]. Diketopyrrolopyrrole (DPP) is one of the promising building blocks for high-performance semiconducting polymers. In the past five years, conjugated polymers based on DPP have emerged as an active material for OTFTs because of their planar structure, capability to form a close $\pi-\pi$ stacking and good crystalline structure in the solid state, leading to efficient charge transport [8].

As for the other building block in conjugated copolymers, benzodithiophenedione (BDD) has attracted much interest owing to its

inherent advantages as follows: BDD is easy to synthesize and has a relatively simple planar structure, which may be beneficial for electron delocalization when it is incorporated into conjugated polymers [9]. Moreover, its relatively strong electron-withdrawing ability leads to conjugated polymers with lower HOMO and LUMO energy levels. Usually, a lower HOMO energy level is beneficial to obtain polymer solar cells with a higher open-circuit voltage [10]. In 2011, BDD was synthesized and successfully applied in producing highly efficient photovoltaic polymers [11]. Copolymers containing BDD usually show strong π−π stacking interactions and thus provide highly ordered crystalline structures in solid state [12]. BDD-based polymers exhibited excellent photovoltaic performance. Huo and coworkers reported a copolymer containing BDD with a high power conversion efficiency of 9.7% and a high fill factor of 75% [13]. However, to the best of our knowledge, the field-effect properties of BDD-based copolymers have not been investigated. BDD-based copolymers have a great potential to achieve excellent charge-carrier mobility in OTFTs.

In this study, the polymer backbone was tailored to synthesize three new copolymers (**P1**, **P2**, and **P3**) using BDD and DPP units, and their thermal, optical, electrochemical properties, microstructures were evaluated. When Au metal was used as the electrode and the devices were tested under vacuum conditions, the three copolymers exhibited ambipolar transport. The optimized polymer **P3**-based OTFTs exhibited balanced hole and electron mobilities of 0.022 and 0.028 cm^{-1} V^{-1} s^{-1}, respectively. Moreover, the OTFTs were also used as efficient near-infrared (NIR) photosensitive sensors. The phototransistors showed a high photocurrent/dark-current ratio of 6.4×10^3 under NIR light at a wavelength of 808 nm.

2. Experimental

2.1. Instrumentation

The ^1H NMR spectra were recorded using a VNMRS600 MHz spectrometer. The molecular weights of the polymers were measured by GPC using a Waters Series 1525 gel using 1,2,4-trichlorobenzene as the eluent and polystyrene as the standard. The thermal analyses were performed using a TA instrument QS000IR in a nitrogen atmosphere and a heating rate of 10 °C/min. DSC measurements were conducted under nitrogen using a TA Instruments Q2000. The samples were heated at a rate of 10 °C/min. The UV−Vis−NIR absorption spectra were obtained using a Perkin Elmer model k 20 UV−Vis−NIR spectrophotometer. For solid state measurements, a chloroform solution of the polymer was spin-coated onto quartz plates. The CV was performed using a CHI 660D electrochemical workstation equipped with a three-electrode system in an acetonitrile solution of 0.1 M Bu_4NPF_6 and at a scan rate of 100 mV/s. Ferrocene was used as the standard, and the polymer thin films were coated on a platinum disc electrode, which was used as the working electrode. A platinum wire was used as the auxiliary electrode, and an Ag/Ag^+ electrode was used as the reference electrode. The morphology of the polymer films was investigated using a Veeco Multimode V AFM in tapping mode equipped with a 1 μm scanner.

2.2. Fabrication and characterization of field-effect transistors

The electrical properties of the three polymers were investigated using a bottom-gated/top-contact OTFT configuration, with a 300-nm-thick SiO_2 dielectric on a heavily N-type-doped silicon substrate as the gate electrode. A fluoropolymer Cytop was spin-coated to reduce the number of hydroxyl groups present on the SiO_2 surface. The organic semiconductor thin films were prepared by spin-coating of a 5 mg/mL chloroform solution at 8000 rpm. The polymer films were subsequently annealed at 150 and 180 °C for 30 min in a nitrogen-filled glove box. Then, the Au source/drain electrodes were evaporated on top of these semiconductor layers (40 nm). The OTFT devices had a channel length (L) of 100 μm and a channel width (W) of 800 μm. The OTFT measurements were carried out in vacuum (3×10^{-4} mbar) and ambient environment using a Keithley 4200-SCS semiconductor parametric analyzer on the probe stage. The mobilities of electrons (μ_e) and holes (μ_h) were obtained using the following equation at the saturation regime: $I_d = (W/2L)C_i\mu(V_g-V_{th})^2$, where W/L is the channel width/length, I_d is the drain current in the saturated regime, C_i is the capacitance of the Cytop gate dielectric, and V_{th} is the threshold voltage. A light-emitting diode (LED) lamp (808 nm) was used as the illumination source. The optical power was measured using a calibrated silicon photodiode. Photoresponsivity (R) and photocurrent/dark-current ratio (P) are crucial parameters for assessing the performance of phototransistors equations: $R = I_i - I_{dark}/P_{ill} \times S$, and $P = I_i - I_{dark}/I_{dark}$, where P_{ill} is the incident illumination intensity, S is the area of the channel region exposed to illumination, I_i is the drain current under illumination, and I_{dark} is the drain current in dark.

2.3. Materials

The monomers (1, 4, 5, M1, and M3) were synthesized according to the previous literatures [9,10,12]. 3,6-Bis-(5-(4,4,5,5-tetramethyl-1,3,3-dioxaborolan-thiophene-2-yl))-N,N′-bis(octyl-dodecyl)-1,4-dioxo-pyrrolo[3,4-c]pyrrole was obtained from Derthon Optoelectronic Materials Science Technology Co. Ltd, China. Other chemicals used in this work were purchased from Sigma−Aldrich Chemical Company, Alfa Aesar Chemical Company and Sinopharm Chemical Reagent Co. Ltd, China. All reagents were purchased from commercial sources and used without purification. (THF) and toluene were freshly distilled over a sodium wire. All reactions were carried out under a nitrogen atmosphere.

2.4. Synthesis of monomers and copolymers

2.4.1. 5,7-Dibromo-2-(2-hexyldecyl)benzo[1,2-b:4,5-c′]dithiophene-4,8-dione (2)

2,5-Dibromothiophene-3,4-dicarboxylic acid 1 (4.21 g, 12.69 mmol) and dimethylformamide (DMF) (two drop) was dissolved in toluene (110 mL), then oxalylchloride (4.6 mL, 50.3 mmol) was slowly added. The mixture was refluxed for 1 h, and then cooled to room temperature. After removal of the solvent under vacuum, the 2,5-dibromothiophene-3,4-dicarboxylic acid chloride (3.93 g, 10.71 mmol) was used directly. A solution of the monomer in dry dichloromethane was added to a suspension of anhydrous $AlCl_3$ (6.21 g, 46.57 mmol) in 10 mL dichloromethane at 0 °C. The mixture was stirred at 0 °C for 10 min. Then 2-(2- hexyldecyl)thiophene (3.01 g, 9.74 mmol) was added dropwise, the mixture was stirred overnight at room temperature and poured into ice water, then was extracted with dichloromethane and the organic layer was washed with brine and dried over anhydrous sodium sulfate. The resulting solvent was concentrated by evaporation. The crude product was purified through the silica gel column with petroleum ether/dichloromethane/diethyl ether (60:1:1 by volume) as eluent to give compound **2** as a yellow solid (0.96 g, yield 16.4%). ^1H NMR (600 MHz, $CDCl_3$, ppm: δ = 7.31 (s, 1H), 2.83−2.80 (d, 2H), 1.69 (s, 1H), 1.53−1.12 (m, 24H), 0.86−0.80 (m, 6H).

2.4.2. 2-(2-Hexyldecyl)-5,7-bis(thiophen-2-yl)benzo[1,2-b:4,5-c′]dithiophene-4,8- dione (3)

Compound **2** (0.76 g, 1.26 mmol) and tributyl(thiophen-2-yl)stannane (1.32 g, 3.54 mmol) were dissolved in THF (25 mL) in a pressure tube. The solution was degassed by nitrogen flow for