



Benzodithiophene and benzotrithiophene-based conjugated polymers for organic thin-film transistors application: Impact of conjugated- and acyl-side chain

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ABSTRACT

A series of benzodithiophene (BDT) and benzotrithiophene (BTT)-based conjugated polymers (**P1–P4**), with/without conjugated- and acyl-side chain, have been synthesized by Stille cross-coupling reaction. Their thermal, photophysical, electrochemical properties, devices performances, and microstructure have been investigated. Conjugated-side chain can significantly raise the thermal stability and acyl-side chain can lower HOMO/LUMO energy levels. Organic thin-film transistors (OTFTs) based on conjugated polymers were fabricated and the transistor electrical characterization showed the device performance was sensitive to the conjugated- and acyl-side chain substituent of polymers. A maximum hole mobility of $1.70 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was obtained for **P1**-based devices, which is an order of magnitude higher than those of **P3** and **P4**-based devices. The corresponding microstructures were investigated by grazing-incidence X-ray diffraction (GIXD) to correlate with conjugated- and acyl-side chain dependent carrier mobility of **P1–P4**. The results showed that the conjugated- and acyl-side chain have an impact on the polymer packing models and device performances.

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1. Introduction

Organic thin-film transistors (OTFTs) based on conjugated polymers have undergone significant progress due to many advantages such as light weight, low-cost, and good compatibility with solution-processes that are promising for the fabrication of flexible large-area devices [1–3].

To pursue high mobility, many new conjugated polymers have been designed and synthesized, and encouraging progress has been made with hole mobility of OTFTs up to $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and electron mobilities over $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the past few years [4–8]. Solution processable conjugated polymers generally contain two parts: π -conjugated backbone and flexible solubilizing side chains. π -Conjugated backbone determine the optoelectronic properties of the conjugated polymers [9–11]. However, the side chains are as important as the conjugated backbones when designing conjugated polymers. Side chains play an important role not only in improving the solubility of the conjugated polymers but also in impacting the intermolecular interactions, thin-film packing orders and charge

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carrier transport [12]. Most of related research has been focused on conjugated backbone, while the side chain engineering has not been fully exploited and have begun to attract attention in recent years [13–15].

Benzodithiophene (BDT) was a famous monomer for constructing high performance conjugated polymers used in polymer solar cells and OTFTs. BDT has a symmetric and planar conjugated structure, and hence tight and regular stacking is expected for the BDT-based conjugated polymers [16]. In 2007, a BDT-thiophene-based polymer was reported and exhibited a hole mobility of $0.25 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [17]. Benzotrithiophene (BTT) was another construction unit for conjugated polymers which was designed with inspiration from BDT by fusing three thiophene units to a central benzene core instead of two [18,19]. BTT possesses high co-planarity and extended π -conjugation which are beneficial for promoting intermolecular π -stacking and charge transport. The BTT-based polymers exhibited hole mobilities as high as $0.24 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [20]. Recently, some of us reported the synthesis of BDT and BTT-based polymers (**P3** and **P4**), which have deep highest occupied molecular orbitals (HOMO). Furthermore, polymer-based photovoltaic devices obtained a PCE of 4.20% with a Voc as high as 0.96 V [21], clearly suggesting the investigation as OTFTs materials.

In this paper, we report the use of the BDT and BTT-based polymer as semiconductors in OTFTs. In order to investigate the side effect, BDT and BTT-based polymers **P1–P2** (Scheme 1) with different side chains were also strategically designed and successfully synthesized for OTFTs applications. We introduce the conjugated side chain (electron-donating side chain) on BDT unit and acyl-side chain (electron-withdrawing side chain) on the BTT unit used in conjugated polymers (Scheme 1). The impact on thermal, optical, electrochemical, electrical properties and microstructure of the polymers film (with and without side chains) were also investigated.

2. Experimental section

2.1. Instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded on a VNMR600 MHz machine. Gel permeation chromatography (GPC) analyses were performed on a Waters Series 1525 gel coupled with UV–vis detector using tetrahydrofuran as eluent with polystyrene as standards. Thermogravimetric analysis (TGA) analyses were conducted with a TA instrument Q5000IR at a heating rate of $20 \text{ }^\circ\text{C min}^{-1}$ under nitrogen gas flow. UV–vis absorption spectra were recorded on a Perkin Elmer model λ 20 UV–vis spectrophotometer. Electrochemical measurements were conducted under nitrogen in a deoxygenated anhydrous acetonitrile solution of tetra-*n*-butylammonium hexafluorophosphate (0.1 M), using a CHI 660D electrochemical analyzer. A platinum-disc electrode was used as a working electrode, a platinum-wire was used as an auxiliary electrode, and an Ag/Ag⁺ electrode was used as a reference electrode. Polymer thin film was coated on the platinum-disc electrode and ferrocene was used as a reference. The grazing-incidence X-ray diffraction (GIXD)

studies were performed using 3C beamlines at the Pohang Accelerator Laboratory (PLA) in Korea.

Tapping atomic force microscopy (AFM) was obtained using a Veeco Multimode V instrument.

2.2. Fabrication and characterization of field-effect transistors

Top-contact and bottom-gate OTFTs devices were fabricated in this work. Octadecyltrichlorosilane (OTS) was spin-coated onto SiO₂/Si substrate, hence OTS/SiO₂ and Si work as gate-dielectric and gate-electrode, respectively. A chloroform solution containing semiconductor polymer was dropped onto the OTS thin film and spin-coated. The polymer films were subsequently annealed (100–200 °C) in nitrogen. Then Au source-drain electrodes were prepared by thermal evaporation. The OTFTs devices had a channel length (*L*) of 100 μm and channel width (*W*) of 1 mm. The evaluations of the OTFTs were performed in glovebox using a Keithley 4200 parameter on probe stage. The mobilities for hole (μ_h) were obtained by the following equation used at saturation regime: $I_d = (W/2L)C_i\mu_h(V_g - V_{th})^2$, where *W/L* is the channel width/length, *I_d* is the drain current in the saturated regime, *C_i* is the capacitance of OTS/SiO₂ gate-dielectric, and *V_{th}* is the threshold voltage.

2.3. Materials

All the chemicals used in this work were purchased from Sinopharm Chemical Reagent Co., Ltd., Sigma–Aldrich Chemical Company and Alfa Aesar Chemical Company, China. Toluene and tetrahydrofuran (THF) were freshly distilled over sodium wire under nitrogen prior to use.

2.4. Synthesis of polymers

2.4.1. Synthesis of **P1**

Tris(dibenzylideneacetone)dipalladium (Pd₂(dba)₃, 0.0077 g, 0.0084 mmol), tri(*o*-tolyl)phosphine (P(*o*-tol)₃, 0.010 g, 0.034 mmol) were added to a solution of (4,8-bis((2-hexyldecyl)thiophene)benzodithiophene-2,6-diyl)bis(trimethylstannane) (0.23 g, 0.21 mmol) and 2,8-dibromo-5-(2-hexyldecyl)benzotrithiophene (0.13 g, 0.21 mmol) in toluene (6 mL) under nitrogen. The solution was subjected to three cycles of evacuation and admission of nitrogen, the mixture was heated to 110 °C for 48 h. After cooled to room temperature, the mixture was poured into methanol and stirred for 2 h. A red precipitate was collected by filtration. The product was purified by washing with methanol and petroleum ether in a Soxhlet extractor for 24 each. It was extracted with hot chloroform in an extractor for 24 h. After removing solvent, a red solid was collected (0.19 g, 73.1%). ¹H NMR (400 MHz, CDCl₃), σ (ppm): 7.3–7.6 (br, 6H), 6.9–7.1 (br, 3H) 4.0–4.5 (br, 6H), 1.8–2.0 (br, 3H), 1.1–1.7 (br, 72H), 0.7–1.0 (br, 18H). GPC: *M_n* = 26.1 kDa, PDI = 2.28.

2.4.2. Synthesis of **P2**

P2 was synthesized according to the same procedure for **P1**. Compound used were Pd₂(dba)₃ (0.0073 g, 0.008 mmol), P(*o*-tol)₃ (0.0097 g, 0.032 mmol), (4,8-bis(2-hexyldecyl)thiophene)benzodithiophene-2,6-diyl)bis(trimethylstannane) (0.27 g, 0.24 mmol), 2,8-dibromo-5-(2-hexyldecyl)ben-

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