



Synthesis and characterization of the conjugated polymers tethered with dipolar side chains containing a benzothiadiazole entity for bulk heterojunction solar cells

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ABSTRACT

New conjugated copolymers (**P1–P3**) containing dipolar side chains connected to the main chain via triphenylamine donors have been synthesized and characterized. The side chains of these polymers have an electron deficient benzothiadiazole moiety in the spacer, but with different acceptors at the end. By changing the acceptor moieties of the side chain, the absorption spectra and HOMO/LUMO gaps of the polymers can be fine-tuned, ranging from 1.86 to 1.59 eV. Solution processed bulk heterojunction (BHJ) solar cells using these polymers as the donor and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) as the acceptor were fabricated and measured under 100 mW cm⁻² of AM 1.5 illumination. The cell based on the blend of **P1**/PCBM (1:1, w/w) exhibited the highest power conversion efficiency of 1.78%, with open circuit voltage (V_{oc}) = 0.79 V, short circuit current (J_{sc}) = 6.63 mA cm⁻² and fill factor (FF) = 0.34, respectively.

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1. Introduction

Owing to the increasing energy consumption and limited energy resources such as fossil fuel, renewable energy sources, especially solar cells, have attracted considerable interests in both academic and industrial communities [1–3]. Polymeric solar cells (PSCs) are considered as a promising candidate due to their unique advantages of low cost, light weight and flexible large area devices [2a–f,4]. Solution processed PSCs can adopt either heterojunction (HJ) or bulk heterojunction (BHJ) architecture, with the latter less confined by exciton diffusion length (normally 10–20 nm). BHJ systems normally consist of fullerene derivative, [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM), as the electron acceptor and conjugated polymers as the donor counterpart. Poly(3-hexylthiophene) (P3HT) is one of the most popularly used donor polymers for organic photovoltaics (OPVs). Though it is not uncommon

for the power conversion efficiency (PCE) of a P3HT-based OPV to reach ~4–5% [5], mismatch of the electronic absorption with the solar spectrum prevents the cell from achieving ideal efficiency. To optimize the light-harvesting of the materials, one practical approach towards lowering the absorption band gap is to design copolymers with push–pull alternating units in the main chain (Fig. 1). High PCEs of >7% have been reported for some OPVs due to the combined efforts devoted by both materials and devices fabrication scientists [6]. Alternatingly, the band gap of conjugated copolymers can be conveniently tuned by conjugated dipolar side chains tethered via their donor residing at the electron-rich backbone (Fig. 1) [7]. For this kind of polymers, the absorption spectra and band gaps of the polymers can be fine-tuned without significant raising the HOMO level, by changing the conjugated spacer and/or the acceptor. In addition, the two-dimensional like conjugated structures may improve the isotropic charge transport abilities of the polymer, which is extremely important for PSCs [8]. Indeed, a side chain system has been reported to have a very promising PCE of 4.74% [7a]. With the use of different acceptors in the side chains,

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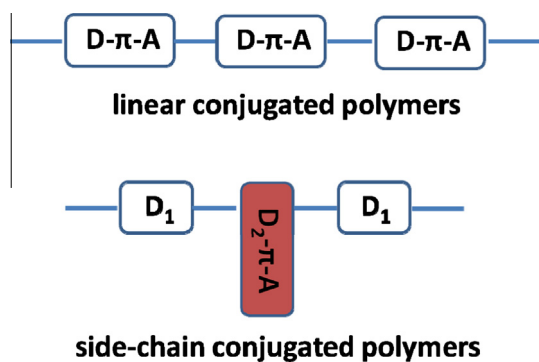


Fig. 1. The structure of the linear and side chain conjugated polymers.

improved photo flux is expected due to complementary absorption [7i].

Electron deficient “benzothiadiazole” entity was popularly used for construction of polymers absorbing in the longer wavelength region [8,9]. Accordingly, benzothiadiazole-based polymers or small molecules have been widely employed for photovoltaic applications [2g,10]. The conjugated polymer, poly[(4,4-bis(2-ethylhexyl)-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene)-2,6-diyl-*alt*-2,1,3-benzothiadiazole-4,7-diyl], **PCPDTBT**, has been proven to be one of the most efficient low band gap polymers for solar cells [11], with PCEs exceeding 6% [11c]. We also demonstrated that incorporation of a benzothiadiazole unit in the conjugated spacer between the donor and the acceptor resulted in efficient intramolecular charge-transfer and effectively red shifted the absorption band ($\lambda_{\max} > 500$ nm in solution) in dipolar sensitizers [12]. The best conversion efficiency of dye-sensitized solar cells (DSSCs) from these dyes reached ~92% of the N719-based standard cell fabricated and measured under similar conditions [12b].

From the above description, we decided to tether conjugated copolymers with dipolar side chains containing a benzothiadiazole unit in the spacer for PSCs application. Herein, we report new conjugated polymers (**P1–P3**) with conjugated backbones consisting of alternating fluorene and triphenylamine units. The nitrogen atom of the triphenylamine is tethered with a conjugated side chain consisting of a benzothiadiazole moiety and different acceptors. Their relevant physical properties will be discussed. Photovoltaic properties of these polymers were also investigated by fabricating BHJ type photovoltaic cells using these polymers as the electron donor and PCBM as the electron acceptor.

2. Experimental section

2.1. General information

^1H NMR and ^{13}C NMR spectra were taken on a Bruker AV-400 or a Bruker AV-500 spectrometer using CDCl_3 as the solvent. Fast atom bombardment mass spectrometry (FABMS) analysis was performed on a JEOL Tokyo Japan JMS-700 mass spectrometer equipped with the standard FAB source. Elemental analyses were performed on a

Perkin–Elmer Model 2400 analyzer. Absorption spectra were recorded on a Dynamica DB-20 UV–Vis spectrophotometer. Low-energy photoelectron spectra were taken from a photoelectron spectrometer (AC-2, Riken-Keiki PT5-0210). Gel permeation chromatography (GPC) was performed with a Waters apparatus equipped with Waters Stygel columns and a refractive index (RI) detector using tetrahydrofuran (THF) as the eluent (polystyrene calibration). Glass transition temperature (T_g) and thermal decomposition temperature (T_d) of the copolymers were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) using Seiko DSC 6220 SII Extra 6000 and Thermo Cahn Versa Therm analyzer systems, respectively. The morphology of the thin films was analyzed by atomic force microscopy (AFM) (AFM, Digital instrument NS 3a controller with D3100 stage). The photoelectrochemical characterizations of the solar cells were carried out by using an Oriel Class A solar simulator (Oriel 91195A, Newport Corp.). The photocurrent–voltage (J – V) curves were recorded under a light intensity of 1.0 sun calibrated by an Oriel reference solar cell (Oriel 91150, Newport Corp.). The light power was 100 mW cm^{-2} and was calibrated by a mono-silicon photodiode with KG-5 color filter (Hamamatsu, Inc.). The external quantum efficiency (EQE) was measured by a monochromator (Oriel 74100) at short circuit condition and recorded at short-circuit by a CHI 650B electrochemical system.

2.2. Materials

All chemical reagents, unless otherwise specified, were used as received. All the solvents such as dichloromethane (DCM), tetrahydrofuran (THF), and dimethylformamide (DMF), and toluene were freshly distilled over appropriate drying agents prior to use and stored under nitrogen. 5-[7-(4-Diphenylamino-phenyl)-benzo[1,2,5]thiadiazol-4-yl]-thiophene-2-carbaldehyde (**1'**) was prepared according to the literature [12a].

2.2.1. Synthesis of 5-(7-{4-[bis-(4-bromo-phenyl)-amino]-phenyl}-benzo[1,2,5]thiadiazol-4-yl)-thiophene-2-carbaldehyde (**1**)

A 100 mL of round-bottom flask containing 5-[7-(4-diphenylamino-phenyl)-benzo[1,2,5]thiadiazol-4-yl]-thiophene-2-carbaldehyde (0.50 g, 1.02 mmol) was added DMF (15 mL). NBS (0.40 g, 2.24 mmol dissolved in 10 mL of DMF) was added and the solution was stirred at room temperature for overnight. After the reaction was complete, the reaction mixture was poured into water and then extracted with CH_2Cl_2 . The organic extract was dried over anhydrous MgSO_4 and was further purified by column chromatography using a hexanes/dichloromethane (1:4) mixture as the eluent. Compound **1** was isolated as a bright red powder in 77% yield. (0.51 g). ^1H NMR (500 MHz, CDCl_3 , δ , ppm): 9.97 (s, 1H), 8.21 (d, $J = 4.0$ Hz, 1H), 8.04 (d, $J = 7.5$ Hz, 1H), 7.89 (d, $J = 8.5$ Hz, 2H), 7.84 (d, $J = 4.0$ Hz, 1H), 7.73 (d, $J = 7.5$ Hz, 1H), 7.38 (d, $J = 9.0$ Hz, 4H), 7.17 (d, $J = 9.0$ Hz, 2H), 7.02 (d, $J = 8.5$ Hz, 4H). ^{13}C NMR (125 MHz, CDCl_3 , δ , ppm): 182.88, 153.74, 152.65, 148.69, 147.52, 146.01, 143.43, 136.64, 134.18, 132.54,

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