

Novel photovoltaic polymers constructed from alternative donor and acceptor units having one mother structure

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ABSTRACT

This work presents a new strategy for the preparation of donor–acceptor conjugated copolymers, in which both donor and acceptor units derive from one mother structure. Benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (BQDT) is an electron-deficient unit. From BQDT, benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) and benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione dioxime (BXDT) can be easily derived and serve as electron-donating and another electron-accepting unit, respectively. Based on these three units, poly(BDT-*alt*-BQDT) (**PBQ-C24**, with 2-decyltetradecyl side chains) and poly(BDT-*alt*-BXDT) (**PBX-C8**, with 2-ethylhexyl side chains) have been designed and synthesized. Their thermal, optical and electrochemical properties have been investigated. **PBQ-C24** has a broad absorption spectrum in the range of 300–700 nm, while **PBX-C8** can only harvest the light from 300 to 600 nm. However, the bulk heterojunction cell based on the blend of **PBX-C8** and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) displays a better performance with a power conversion efficiency of 0.51%.

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1. Introduction

As energy crisis and environment pollution go worse and worse, solar light, as a permanent green natural energy resource, has become an increasing significance for human sustainable development. Among a variety of light-to-electric conversion technologies, organic solar cells (OSCs) have attracted huge attention in terms of their ease of processing, low cost, flexibility, and light weight [1]. After the pioneering work of bilayer [2] and bulk heterojunction [3] device configurations, the active layer of OSCs is required to be composed of both p- and n-type organic semiconductors. In basic light-to-electric conversion mechanism, p-type materials play the roles of electron donors in photo-induced charge-separation process and conduct the separated positive charge carriers (holes) to anode. While, n-type materials behave as electron acceptors and transport the separated negative charge carriers (electrons) to cathode. Since it was first reported in 2000 [4], the bulk heterojunction composed of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) represents as a typical system having a top power conversion efficiency (PCE) of 4–5% [5]. The material innovation afterward for a long time is motivated to overcome the shortages of P3HT, which

are weak acquisition capability when light wavelength is longer than 650 nm and a little unmatched highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels relative to PC₆₁BM. Along this line, a variety of donor–acceptor (D–A) alternative conjugated copolymers have been designed and investigated [6], some of which have achieved PCE over 6% [7]. The incorporation of the alternative electron-deficient units (acceptor) in donor polymers can lower the band gap and the molecular energy level, which enables more efficient light absorption in the far visible and near infrared region and provides more matched HOMO and LUMO to fullerene acceptors.

Among the reported D–A copolymers, benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) has often been used as an electron-donating unit. The planar and rigid fused aromatic ring of BDT would be helpful to strengthen interactions among polymer chains, which is favourable for charge-transportation. In 2002, BDT was first applied for synthesis of conjugated polymers, including its homopolymers and copolymers [8]. Later, Ong et al. demonstrated that the copolymer of BDT and thiophene is a good field-effect transistor with hole mobility of $\sim 0.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [9]. In 2008, Hou, Yang and coworkers firstly used BDT to prepare D–A copolymers with benzothiadiazole, benzoselenadiazole, and thienopyrazine for photovoltaic application with PCE in the range of 0.1–0.9% [10]. The outstanding work was reported by Yu et al., who copolymerized BDT with thieno[3,4-*b*]thiophene, affording a family of promising photovoltaic materials (PTB) [11]. After structural optimization, this

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family frequently renewed the PCE record [12] and preserved the champion efficiency (9.2%) to date [13]. Recently, BDT was combined with thienopyrrolodione [14], 4,7-bis(2-thienyl)-2,1,3-benzothiadiazole [15], naphthobisthiadiazole [16], or fluorinated benzothiadiazole [17], producing a number of high performance photovoltaic copolymers with PCE of 6–7%. We notice that the precursor of BDT is benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione, a benzoquinone-fused dithiophene (BQDT, Scheme 1), which itself is an electron-deficient unit. From BQDT, another electron-deficient unit, benzoquinone dioxime-fused dithiophene (BXDT) can be easily derived (Scheme 1). We are curious about the D–A alternative copolymers, poly(BDT-*alt*-BQDT) (**PBQ**) and poly(BDT-*alt*-BXDT) (**PBX**), based on these units that derive from the same mother structure. The cost for producing such D–A alternative copolymers would be lower than those with D and A having different mother structures. Herein, we report their synthesis and photovoltaic properties.

2. Experimental

2.1. Measurements and characterization

^1H and ^{13}C NMR spectra were recorded in CDCl_3 or $\text{DMSO}-d_6$ on a Varian Mercury spectrometer operating at 300 and 75 MHz, respectively, using tetramethyl silane as an internal reference. Electron ionization (EI) mass spectra were tested on an Agilent 5973N Mass Spectrometer by an electron impact ionization procedure (70 eV). Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopy was carried out on a Shimadzu Biotech Axima Performance Mass Spectrometer using dithranol or α -cyano-4-hydroxycinnamic acid (CHCA) as a matrix. Gel permeation chromatography (GPC) was carried out on a Waters 1515 HPLC instrument equipped with a Waters 2489 UV detector, using tetrahydrofuran (THF) as eluent. The molecular weight and its polydispersity index (PDI) were calculated based on polystyrene standards. UV–vis absorption spectroscopy was performed on a Hitachi U-3310 spectrophotometer. Fluorescence spectroscopy was recorded in a Hitachi F4600 fluorophotometer. Cyclic voltammetric (CV) measurements were performed on a CHI 660C instrument using

a three-electrode cell with a glassy carbon as a working electrode, a platinum wire as a counter electrode, and Ag/AgNO_3 as a reference electrode. The samples were first casted on the glassy carbon electrode to form a film, and then measured in CH_3CN in the presence of 0.1 M Bu_4NPF_6 with a scan rate of 50 mV min^{-1} . Thermogravimetric analysis (TGA) was carried out by a TGA Q500 instrument under N_2 with a temperature rate of $10 \text{ }^\circ\text{C min}^{-1}$. Atomic force microscopy (AFM) was performed on a Veeco Instrument Nanoscope IIIa Multi-mode apparatus by tapping mode with a silicon tip.

2.2. Device fabrication and characterization

The solar cell devices were fabricated with a structure of ITO/PEDOT:PSS/active layer/Ca/Al. A layer of PEDOT:PSS (Heraeus Clevious P VP, Al 4083) with a thickness around 30 nm was spin-coated on top of well cleaned ITO glass at 4000 rpm and baked at $150 \text{ }^\circ\text{C}$ for 20 min. After transfer into a N_2 -filled glove box, the active layer was spin-coated from a chlorobenzene solution of polymer and PC_{61}BM (Lumitec LT-8905) at 3000 rpm. For **PBX**-based cells, the plates were annealed at $100 \text{ }^\circ\text{C}$ for 25 min, while the **PBQ**-based cells were annealed at $120 \text{ }^\circ\text{C}$ for 10 min. Finally, a 10 nm-thick Ca layer and a 100 nm-thick Al layer were subsequently thermally deposited on the top of the active layer under a high vacuum (10^{-5} mbar) through a shadow mask. The active cell area is 7 mm^2 . Layer thickness was measured on a Veeco Dektak 150 profilometer. Current density–voltage (J – V) curves were recorded on a Keithley 2420 source meter. Photocurrent was acquired upon irradiation using an AAA solar simulator (Oriel 94043A, 450 W) with AM 1.5G filter. The intensity was adjusted to be 100 mW cm^{-2} under the calibration with an NREL-certified standard silicon cell (Oriel reference cell 91150). External quantum efficiency (EQE) was detected with a 75 W Xe lamp, Oriel monochromator 74125, optical chopper, lock-in amplifier and an NREL-calibrated crystalline silicon cell.

2.3. Materials

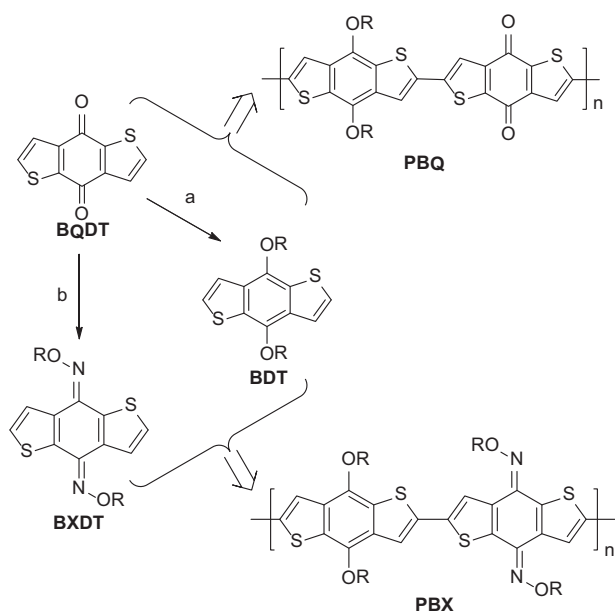
Unless indicated, all commercial reagents were used as received. Tetrahydrofuran (THF), ether, and toluene were refluxed over a mixture of sodium and benzophenone, while chlorobenzene was dried over CaH_2 under argon, and freshly distilled prior to use. BQDT [10], *N,N*-dimethylthiophene-3-carboxamide [18], and monomers **3a** [19] and **3b** [20] were synthesized according to literature procedures.

2.3.1. 2,5-Dibromo-thiophene-3-carboxylic acid dimethylamide (**1**)

N,N-dimethylthiophene-3-carboxamide (16.3 g, 105.0 mmol) and *N*-bromosuccinimide (NBS, 41.1 g, 231.1 mmol) were added into 150 mL DMF. The solution was shielded from light and stirred for 2 h at room temperature. Afterward, the reaction mixture was poured into 600 mL water, and extracted with ethyl acetate. The organic phase was washed with water, dehydrated with MgSO_4 , filtered, concentrated under reduced pressure. The residue was subjected to silica gel column chromatography using hexane/ethyl acetate (6:1, v/v) as eluent, affording compound **1** (28.0 g) as yellow oil with a yield of 85.2%. ^1H NMR (300 MHz, CDCl_3 , δ): 6.92 (s, 2H), 3.10 (s, 3H), 2.99 (s, 3H).

2.3.2. 2,6-Dibromo-benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (**2**)

BuLi (15.3 mmol, 2.5 M in hexane) was added dropwise into an Et_2O solution of compound **1** (4.9 g, 15.4 mmol, 40 mL) under dry-ice/acetone bath. After slowly warming to room temperature, the mixture was added with saturated NH_4Cl aqueous solution (30 mL). Then, the precipitate was collected and subjected to silica gel column chromatography using CHCl_3 as eluent, affording compound **2** (1.3 g) as an orange solid with a yield of 43.6%. ^1H NMR (300 MHz,



Scheme 1. Molecular structures of BDT, BQDT, BXDT, and their alternative copolymers, **PBQ** and **PBX**. Conditions: a) Zn , NaOH , R-Br , H_2O , reflux; b) i. $\text{NH}_2\text{OH}\cdot\text{HCl}$, pyridine, reflux; ii. CH_3ONa , CH_3OH , reflux; iii. R-Br , DMSO .

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