



Synthesis and photovoltaic characterization of thiadiazole based low bandgap polymers



Jiefeng Hai^a, Wei Yu^b, Enwei Zhu^a, Linyi Bian^a, Jian Zhang^{b,*}, Weihua Tang^{a,*}

^a Key Laboratory of Soft Chemistry and Functional Materials, Ministry of Education of China, Nanjing University of Science and Technology, Nanjing 210094, People's Republic of China

^b State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, Zhongshan Road 457, Dalian 116023, People's Republic of China

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ABSTRACT

Two copolymers comprised of different fused thiadiazole electron withdrawing units and benzo[1,2-b:4,5-b']dithiophene electron donating unit have been synthesized by Stille reaction. The structural, optical, electrochemical and photovoltaic properties of the copolymers were investigated. Both copolymers in the film state exhibited broad absorption spectra with an extremely low bandgap of ~1.2 eV. Bulk heterojunction solar cells were further fabricated and the best device delivered a power conversion efficiency of 0.52% when thermal annealed at 90 °C.

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1. Introduction

During the past decade, polymers solar cells (PSCs) have attracted researchers' extensive attention in the field of renewable energy technologies due to their unparalleled features such as light-weight, low fabrication cost and great potential for the fabrication of large-area flexible devices with high speed [1–3]. PSCs based on bulk-heterojunction (BHJ) architecture are of particular interests since high performance devices with power conversion efficiencies (PCEs) that exceed 9% can be achieved [4–7] with the art of level of 10.6% [6]. Typical BHJ devices comprise a phase separated donor/acceptor blend layer with low bandgap conjugated polymers as the electron donor, and fullerene derivatives such as [6,6]-phenyl-C61-butyric acid methyl ester (PC₆₁BM) or [6,6]-phenyl-C71-butyric acid methyl ester (PC₇₁BM) as the electron acceptor. Nevertheless, the low PCE, dependable encapsulation technology to secure long-life working devices, and robust large-area processing for device making have become the most significant obstacle in the field of PSC commercial application [8–10].

To improve the PCE, an ideal donor polymer material requires the following ideal conditions: (i) optimal optical bandgap (E_g) with wide absorbance area and high extinction coefficient [11]; (ii) good solubility and appropriate compatibility with fullerene derivatives; (iii) highest occupied molecular orbital (HOMO) energy level for high open-circuit voltage (V_{oc}) [12]; and (iv) high hole mobility. To fulfill these criteria,

a large library of a so-called D–A copolymers designed by alternating electron-rich (D) and electron-deficient (A) units along the conjugated backbone have been developed for highly efficient PSCs more than 8% [4–7,13–16]. By incorporating a weakly electron donating donor unit and a strongly electron accepting unit in the copolymer backbone, the electrical and optical properties can be tuned. Furthermore, intramolecular charge transfer (ICT) from the donor to the acceptor unit can enhance the π – π stacking between copolymer chains and effectively reduce the bandgap [17]. To ensure suitable charge transport properties among the polymers, the close packing between polymers should be increased through the reduction of the energetic disorder of polymers, which is caused by the increase in the coplanarity and π – π stacking of polymers. The morphology of the BHJ blend of an electron donor (such as a conjugated polymer) and an electron acceptor (such as the derivative of fullerene, i.e., PC₆₁BM) is also of great importance to photovoltaic performance of PSCs [18].

Benzo[1,2-b:4,5-b']dithiophene (BDT) has been demonstrated to be one of the most excellent building blocks for the synthesis of highly efficient photovoltaic polymers [19–24]. The BDT units possess symmetric and rigid planar structures with extended π -conjugation. They facilitate π -electron delocalization in polymer chains and improve π – π interactions between polymer chains in solid states [24,25]. Therefore, BDT-based polymers usually have shown broad absorption properties, high charge carrier mobility and deep highest occupied molecular orbital (HOMO) energy position compared with the polymers based on other electron donor units [24].

In the past several years, 4,7-dithienyl-2,1,3-benzothiadiazole (DTBT) has emerged as a promising acceptor moiety for D–A polymers

* Corresponding authors. Fax: +86 25 84317311.

E-mail addresses: jianzhang@dicp.ac.cn (J. Zhang), whtang@mail.njust.edu.cn (W. Tang).

due to its strong electron-drawing ability, which lowers the bandgap through ICT [26]. As is known, DTBT and its derivatives have been broadly used as building blocks in photovoltaic materials. Several important polymers have been developed with PCEs reaching 4–7% in PSCs [27–30]. Fused heteroaromatic units with extended π -conjugation and rigid coplanar structure can enhance π -conjugation within polymer chains and promote interaction and stacking between polymer chains. Conjugated polymers based on fused heteroaromatic repeating units frequently show improved absorption properties and high charge mobilities [31,32]. So we tried to enlarge the conjugated framework of benzothiadiazole via fusing quinoxaline or phenazine and developed accepting units called thiadiazolo[3,4-g]quinoxaline (DTBTQx) and thiadiazolo[3,4-i]phenazine (DTBTBPz). DTBTQx has been a promising building block for the synthesis of low bandgap polymers because of the strong electron-withdrawing property of four imine nitrogen in the DTBTQx unit. However, most of the alternating copolymers composed of DTBTQx derivatives as electron acceptor and thiophene [33], fluorene [34], phenylene [35] or carbazole [36] as electron donor have shown poor photovoltaic performance with the PCE lower than 2% [37,38]. This low PCE is mainly attributed to the low molecular weights ($M_n < 10$ kDa) of the copolymers because of the lack of solubility. DTBTBPz derivatives have been developed for optoelectronic applications, but no report on PSC application [39,40].

In this study, two alternating copolymers of BDT with DTBTQx or DTBTBPz were designed and synthesized two narrow bandgap copolymers, i.e., poly[4-(5-(4,8-bis(dodecyloxy)-4,8-dihydrobenzo[1,2-b:4,5-b']dithiophen-2-yl)-alt-5,8-bis-(thiophen-2-yl)-6,7-bis(3,4-bis(dodecyloxy)phenyl)-[1,2,5]-thiadiazolo[3,4-g]quinoxaline) (PBDDTBTQx) and poly[4-(5-(4,8-bis(dodecyloxy)-4,8-dihydrobenzo[1,2-b:4,5-b']dithiophen-2-yl)-alt-10,14-bis(4-(2-ethylhexyl)thiophen-2-yl)dibenzo[a,c][1,2,5]thiadiazolo[3,4-i]phenazine) (PBDDTBTBPz). The correlation of optical, electrochemical and PSC device performance of the resulted polymers with different fused accepting units was investigated. PBDDTBTQx exhibits good solubility with introduced peripheral tetradodecyloxybenzyl side chains of DTBTQx unit. A recent publication discussed the photovoltaic performance with the DTBTQx derivative as acceptor unit and BDT as donor unit just when we were preparing this paper [41]. The device of bulk heterojunction solar cells by blending PBDDTBTQx with PC₆₁BM exhibits a maximum power conversion efficiency of 0.52%, with a short circuit current of 1.44 mA/cm², an open-circuit voltage of 0.69 V and a fill factor of 0.40. Our results indicate that these copolymers show promising photovoltaic properties after careful structure design.

2. Experimental section

2.1. Materials

All chemicals and solvents were reagent grade and purchased from Aldrich, Acros or TCI companies and used without further purification. Toluene, tetrahydrofuran (THF) and diethyl ether were freshly distilled before use. Unless otherwise specified, all reactions were conducted under a nitrogen atmosphere. The alternating polymers of BDT with DTBTQx or DTBTBPz were synthesized according to the procedure outlined in Scheme 1. The synthesis detail of monomers and targeted polymers are described as follows.

2.1.1. 4,7-Dibromobenzo[c][1,2,5]thiadiazole (1) [42]

2,3,1-Benzothiadiazole (5.00 g, 36.72 mmol) was dissolved in HBr aqueous solution (100 mL, 47%). Bromine (17.60 g, 110.15 mmol) in HBr aqueous solution (50 mL of 47%) was slowly added to the solution. The mixture was refluxed overnight. After the mixture was cooled to room temperature, an aqueous solution of Na₂S₂O₃·5H₂O was added and the product was extracted with CH₂Cl₂. The organic layer was washed with water and brine, dried with MgSO₄, filtered, concentrated via rotary evaporation and

purified by column chromatography on silica gel eluting with CH₂Cl₂ to give pure compound **1** as pale yellow needles (8.50 g, 79%). ¹H NMR (500 MHz, CDCl₃) δ 7.73 (s, 2H).

2.1.2. 4,7-Dibromo-5,6-dinitrobenzo[c][1,2,5]thiadiazole (2) [42]

Trifluoromethanesulfonic acid (7.5 mL) and HNO₃ (8 mL) were added dropwise to concentrated H₂SO₄ (10 mL) at 0 °C. Compound **1** (2.00 g, 6.85 mmol) was added to the acid mixture at 0 °C. The mixture was kept at room temperature for 4 h before being poured into ice-water (100 mL) and then extracted with CH₂Cl₂. The organic layer was washed with water and brine, dried with MgSO₄, filtered, concentrated via rotary evaporation and purified by column chromatography on silica gel with ethyl acetate:petroleum ether (1:10, v/v) as eluent to give pure compound **2** as a pale yellow solid (1.58 g, 40%). mp: 190–195 °C.

2.1.3. 5,6-Dinitro-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (3) [43]

PdCl₂(PPh₃)₂ (78.2 mg, 0.11 mmol) was added to a solution of 2-tributylstannylthiophene (2.40 g, 6.41 mmol) and **2** (1.07 g, 2.79 mmol) in anhydrous THF (40 mL). The reaction mixture was then heated at 80 °C for 20 h. After cooling to room temperature, the solvent was evaporated and the crude product was washed with hexane and dried to give pure compound **3** as an orange solid (0.72 g, 67%). ¹H NMR (500 MHz, CDCl₃) δ 7.74 (d, $J = 4.9$ Hz, 2H), 7.52 (d, $J = 3.5$ Hz, 2H), 7.24 (dd, $J = 5.0$ Hz, 3.9 Hz, 2H).

2.1.4. 4,7-Bis(4-(2-ethylhexyl)thiophen-2-yl)-5,6-dinitrobenzo[c][1,2,5]thiadiazole (4) [43]

PdCl₂(PPh₃)₂ (144 mg, 0.21 mmol) was added to a solution of tributyl(4-(2-ethylhexyl)thiophen-2-yl)stannane (4.59 g, 9.46 mmol) and **2** (1.58 g, 4.11 mmol) in anhydrous THF (40 mL). The reaction mixture was then heated at 80 °C for 20 h. After cooling to room temperature, the solvent was evaporated and the crude product was washed with hexane and dried to give pure compound **4** as an orange solid (2.04 g, 81%). ¹H NMR (500 MHz, CDCl₃) δ 7.30 (s, 2H), 7.29 (s, 2H), 2.61 (d, $J = 6.8$ Hz, 4H), 1.60–1.56 (m, 2H), 1.29 (m, 16H), 0.90 (t, $J = 7.4$ Hz, 12H).

2.1.5. 4,7-Di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole-5,6-diamine (5) [44]

Iron dust (1.23 g, 20.01 mmol) was added to a solution of compound **3** (0.72 g, 1.83 mmol) in acetic acid (50 mL). The mixture was heated at 80 °C for 5 h before being cooled to room temperature, poured into the water, and extracted with ether. The organic layer was washed with water and brine, dried with MgSO₄, filtered, concentrated via rotary evaporation to yield compound **5** as a brown solid (0.51 g, 84%). ¹H NMR (500 MHz, CDCl₃) δ 7.56 (dd, $J = 5.2, 1.0$ Hz, 2H), 7.37 (dd, $J = 3.5, 1.0$ Hz, 2H), 7.26 (m, 2H), 4.40 (s, 4H).

2.1.6. 4,7-Bis(4-(2-ethylhexyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole-5,6-diamine (6) [44]

Iron dust (1.85 g, 33.15 mmol) was added to a solution of compound **4** (1.70 g, 2.76 mmol) in acetic acid (50 mL). The mixture was heated at 80 °C for 5 h before being cooled to room temperature, poured into the water, and extracted with ether. The organic layer was washed with water and brine, dried with MgSO₄, filtered, concentrated via rotary evaporation to yield compound **6** as an orange liquid (1.17 g, 76%). ¹H NMR (500 MHz, CDCl₃) δ 7.17 (s, 2H), 7.11 (s, 2H), 4.40 (s, 4H), 2.64 (d, $J = 6.8$ Hz, 4H), 1.63 (m, 2H), 1.39–1.25 (m, 16H), 0.92–0.87 (m, 12H).

2.1.7. 6,7-Bis(3,4-bis(dodecyloxy)phenyl)-4,9-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-g]quinoxaline (7) [45]

Compound **5** (510 mg, 1.54 mmol) and 1,2-bis(3,4-bis(dodecyloxy)phenyl)ethane-1,2-dione [39] (1.61 g, 1.70 mmol) were dissolved in acetic acid (80 mL). The reaction mixture was purged with nitrogen and heated at 90 °C for 12 h. After cooling to room temperature, the

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