



Research paper

A triazoloquinoxaline and benzodithiophene bearing low band gap copolymer for electrochromic and organic photovoltaic applications



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ABSTRACT

A new triazoloquinoxaline and benzodithiophene based copolymer was synthesized to investigate its electrochemical, optical and photovoltaic behaviors. According to the polymer design, combination of two acceptor units (benzotriazole and quinoxaline) which contribute imine bonds to the structure and a triazoloquinoxaline unit for enhancing electron accepting ability was pursued. As a result of electrochemical studies, the copolymer PTQBDT has a low lying HOMO energy level as -5.23 eV which increases the chemical stability of the resulting polymer and leads to a higher V_{oc} . In addition, the copolymer has an ambipolar character with two well-defined redox couples in the n -doped state and multichromic behavior. In the context of optical studies, PTQBDT has wide absorption range in the visible region with a tail in the NIR region, which yields a low band gap of 1.20 eV. Organic photovoltaic devices were designed using PTQBDT (the electron donor) and PC₇₁BM (the electron acceptor) for the preliminary studies. The resulting device exhibits a power conversion efficiency of 2.0% with a current density of 8.07 mA cm⁻², an open-circuit voltage of 0.45 V, and a fill factor of 55%. The carrier mobility of the PTQBDT was calculated as 3.00×10^{-3} cm² V⁻¹ s⁻¹ via space-charge-limited current (SCLC) method.

1. Introduction

Conjugated polymers are of high interest due to a variety of fields like light emitting diodes, photovoltaic diodes, field effect transistors and electrochromic devices [1–4]. They have diverse advantages such as low cost, light weight, ease of fabrication in large-scale, feasibility of flexible devices and tunability of physicochemical properties [5–7]. Most of the physicochemical properties of such polymers are affected by their band gap. Among all band gap-engineering strategies, use of donor-acceptor (D-A) is the most effective strategy to alter the band gap of conjugated polymers. In this approach, such units are alternated along the polymer backbone. It is a fact that the choice of different units for the development of D-A type conjugated polymers affects all physicochemical properties by controlling the degree of aromaticity, the planarity of the backbone, and the electron density of polymers [8].

For electrochromic devices, the use of D-A conjugated polymers as

an active layer became more popular since a variety of achievable colors can be achieved via structural alternations. Synthesis of D-A type conjugated polymers is crucial not only for color tuning but also for processability, fast switching time, high optical contrast and stability of conjugated polymers for electrochromic applications [9].

Synthesis of novel donor-acceptor (DA) conjugated polymers with suitable physicochemical properties is also important to control photovoltaic properties for efficient organic solar cells. Conjugated polymers must have: (1) a broad absorption in visible and near-infrared regions to harvest sun light efficiently to increase J_{sc} , (2) suitable alignment of HOMO and LUMO for efficient charge separation and higher V_{oc} , (3) good charge mobility to overcome recombination process and facilitate the charge transport efficiency for high FF and J_{sc} , (4) processability in the fabrication of OSCs and suitable morphology, and (5) nanoscale phase separation for effective charge separation and extraction [10]. Therefore selection of suitable donor-acceptor combination is impor-

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tant for the synthesis of p-type conjugated polymers.

Recently, an electron-rich benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) unit has been utilized as the attractive building block due to its symmetric and coplanar structure. These properties increase intermolecular π - π^* interaction [11]. Therefore, in this study we coupled BDT with triazoloquinoxaline for the synthesis of low band gap copolymers (PTQBDT) with suitable energy levels for both electrochromic and organic solar cell applications. Two acceptor units i.e. benzotriazole and quinoxaline, were combined for the synthesis of triazolequinoxaline. This combination not only increases the imine moieties and the coplanarity of the polymer backbone but also decreases optical band gap to harvest more photons [12,13].

This study emphasizes optoelectronic and photovoltaic properties of copolymer i.e. PTQBDT. Optical and electrochemical studies of PTQBDT showed a low optical band gap with a suitable HOMO level. Therefore, BHJ OSCs were fabricated using PTQBDT and PC₇₁BM. The preliminary results showed a power conversion efficiency of 2.0% with a current density of 8.07 mA cm⁻², an open-circuit voltage of 0.45 V, and a fill factor of 55%. The hole mobility of the PTQBDT was calculated as 3.00×10^{-3} cm² V⁻¹ s⁻¹ via SCLC method.

2. Experimental

2.1. Materials

¹H-benzotriazole, potassium *tert*-butoxide, 1-bromododecane, bromine, hydrobromic acid, sulfuric acid, nitric acid, thiophene, tributyltin chloride, bis(triphenylphosphine)-palladium(II) dichloride, ammonium chloride N-bromosuccinimide (NBS), acetic acid, ethanol magnesium sulfate, dichloromethane, hexane, chloroform, 2,6-bis(trimethylstannyl)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene, toluene, NBS, *p*-toluenesulfonic acid, bis(dibenzylideneacetone)palladium(0) and tri(*o*-tolyl)phosphine were purchased from Sigma Aldrich Chemical Co. Ltd and used without further purification. Tetrahydrofuran (THF) and toluene were dried over Na/benzophenone ketyl and distilled before use. Air sensitive reactions were conducted under argon atmosphere. 2-Dodecyl-2H-benzo[d][1,2,3]triazole, 4,7-dibromo-2-dodecyl-2H-benzo[d][1,2,3]triazole, 4,7-dibromo-2-dodecyl-5,6-dinitro-2H-benzo[d][1,2,3]triazole, 2-dodecyl-5,6-dinitro-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole, 2-dodecyl-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole-5,6-diamine and 2-dodecyl-6,7-diphenyl-4,9-di(thiophen-2-yl)-2H-[1,2,3]triazolo[4,5-*g*]quinoxaline were synthesized according to previously described methods [14].

2.2. Measurements

¹H and ¹³C NMR spectra were recorded on a Bruker Spectrospin Avance DPX-400 Spectrometer using trimethyl silane (TMS) as the internal reference and the chemical shifts were reported in ppm. For all electrochemical studies, the polymer was dissolved in CHCl₃ (5 mg mL⁻¹) and spray processed on an ITO coated glass substrate. Cyclic voltammetry studies were carried out using a Gamry Reference 600 potentiostat/galvanostat in a three-electrode cell bearing an ITO-coated glass slide (the working electrode), a Pt wire (the counter electrode), and a Ag wire calibrated against Fc/Fc⁺. 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in anhydrous acetonitrile (ACN) was used for electrochemical studies. Corresponding HOMO and LUMO energy levels were calculated from the onset of oxidation and reduction potentials. For optical and spectroelectrochemical studies, Varian Cary 5000 UV-vis-NIR spectrophotometer was used and UV-vis-NIR spectra were recorded under ambient conditions. Average molecular weight of the polymer was determined by gel permeation chromatography (GPC) on a Polymer Laboratories GPC 220 using polystyrene as the standard and THF as the solvent.

2.3. Synthesis of monomer and polymer

2.3.1. Synthesis of 4,9-bis(5-bromothiophen-2-yl)-2-dodecyl-6,7-diphenyl-2H-[1,2,3]triazolo[4,5-*g*]quinoxaline

2-Dodecyl-6,7-diphenyl-4,9-di(thiophen-2-yl)-2H-[1,2,3]triazolo[4,5-*g*]quinoxaline (70 mg, 0.107 mmol) was dissolved in 30 mL chloroform. The reaction medium was filled with argon and the temperature was set up at 0 °C using an ice bath. At the same time, 2 equivalents of NBS (38 mg, 0.213 mmol) were dissolved in 15 mL chloroform under an inert atmosphere and added to the reaction medium drop wise. After addition of NBS, the reaction was warmed to room temperature and stirred for 18 h. The reaction was controlled with TLC and after reaction was completed, the product was extracted with saturated sodium thiosulfate solution. The collected organic layer was washed with water and dried with anhydrous magnesium sulfate. The residue was purified by flash column chromatography (silica gel, CHCl₃-hexane, 1:1) to yield a purple solid (45 mg, 52%).

¹H NMR (400 MHz, CDCl₃) δ 8.50 (d, *J* = 4.2 Hz, 2H), 7.61-7.58 (m, 4H), 7.40-7.33 (m, 6H), 7.07 (d, *J* = 4.2 Hz, 2H), 4.62 (t, *J* = 7.4 Hz, 2H), 1.30 (m, 2H), 1.25-1.15 (m, 18H), 0.80 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 151, 140.5, 136.9, 136.1, 130.8, 129.8, 128.3, 128.2, 127, 125.7, 118.5, 61.9, 56.6, 30.8, 30.2, 28.8, 28.6, 28.5, 28.4, 28.3, 27.9, 25.6, 21.7, 13.1.

2.3.2. Synthesis of PTQBDT

4,9-Bis(5-bromothiophen-2-yl)-2-dodecyl-6,7-diphenyl-2H-[1,2,3]triazolo[4,5-*g*]quinoxaline (76 mg, 0.0942 mmol) and 2,6-bis(trimethylstannyl)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene (76.4 mg, 0.0989 mmol) were dissolved in anhydrous toluene (4 mL) under inert atmosphere. After the mixture was purged with argon to remove O₂, tris(dibenzylideneacetone)dipalladium(0) (4.5 mg, 0.005 mmol) as the catalyst and tri(*o*-tolyl)phosphine (12 mg, 0.04 mmol) as the ligand were added to reaction mixture and the mixture was refluxed for 2 days under argon. After polymerization reaction was completed, the end cappers 2-bromothiophene and tributyl(thiophen-2-yl)stannane were added to the reaction medium. Then the solvent was removed under reduced pressure and the crude product was washed with methanol, acetone, and hexane using a Soxhlet extractor to remove oligomers. Finally the polymer was precipitated into methanol to afford a green solid (57 mg, 40%).

GPC: Mn: 23000 gmol⁻¹, Mw: 31000 gmol⁻¹, PDI: 1.35. ¹H NMR (400 MHz, CDCl₃) δ 8.70 (triazoloquinoxaline), 7.75 (BDT), 7.45 (thiophene), 5.23 (O-CH₂), 3.40 (N-C), 2.10 (CH), 0.90-1.60 (CH₂, CH₃)

2.4. Organic solar cell (OSC) fabrication and characterization

The ITO electrodes were cleaned with detergent (Hellmanex, 2%), deionized water and isopropyl alcohol for 15 min by sonication. After ultrasonic cleaning oxygen plasma cleaning was carried out. PEDOT:PSS was filtered through 0.45 μ m pore sized filter and spin coated on the ITO substrate. Then ITO coated substrates were placed on hot plate at 135 °C to remove water for 15 min. Polymer:PCBM blends were prepared and stirred overnight and filtered with 0.2 μ m PTFE. Filtered solution was spin-coated in a nitrogen filled glove box. Finally, lithium fluoride (0.6 nm) and aluminum (100 nm) were evaporated onto the active layer with an average rate of 0.1 Å/s and 1 Å/s in a glove box (H₂O < 0.1 ppm and O₂ < 0.1 ppm) under high vacuum (1×10^{-6} mbar), respectively. The active area of the cells was determined as 0.06 cm². The current density-voltage (J-V) characteristics were measured with a Keithley 2400 source measurement unit under AM 1.5 solar simulator. The incident photon to current efficiencies (IPCE) of organic solar cells were recorded using a Newport quantum efficiency measurement.

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