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Effect of substituent groups on quinoxaline-based random copolymers on the optoelectronic and photovoltaic properties

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ABSTRACT

In this study, three low band gap donor-acceptor (D-A) type quinoxaline-based random copolymers were synthesized. The effect of varying substituent groups on quinoxaline groups on optoelectronic properties and the performance of bulk-heterojunction polymer solar cells was investigated. Electrochemical and optical studies indicate that these copolymers are promising materials for both electrochromic and polymer solar cells applications. Two random polymers were found as excellent candidates for NIR electrochromic devices owing to their 60% and 94% optical contrast values respectively in NIR region with less than 1 s switching times. Polymer solar cells were constructed using the copolymers as the donor components together with $PC_{71}BM$ as the acceptor in the active layer. Among all, the highest PCE was reported as 2.13%.

1. Introduction

Polymer solar cells (PSCs) based on semiconducting polymers have drawn great attention both in academia and industry due to their low cost, flexibility, light weight, ease of fabrication and fine tuning of polymer structure [1–5]. However, low power conversion efficiency (PCE) of PSCs has been the greatest obstacle [6]. One possible way to increase efficiency is to introduce bulk-heterojunction as photoactive layer where donor conjugated polymers and acceptor fullerene derivatives are blended [1–7]. In PSCs, absorbed incident photons generate tightly bounded electron-hole pairs, namely excitons, which then dissociate into free charges only at the donor-acceptor (D-A) interface [8–10]. Therefore, bulk heterojunction takes the leading part in effective charge separation owing to bicontinuous interpenetrating network with large donor-acceptor interfacial area. In this manner, bicontinuous-interpenetrating area creates two channels to transport separated free charges into corresponding domains resulting in enhanced efficiency in bulk heterojunction PSCs [3,9,11,12]. PCEs have significantly improved up to 11% with the advances in device fabrication and versatility of organic chemistry [13,14].

Another way to increase the efficiency of PSCs is to develop novel low band gap polymers with D-A approach [15]. Combination of D-A units has become an attractive methodology to tune optical and electrochemical properties of desired polymers and to extend absorption spectra to longer wavelengths [5,7,12,16]. Among a wide range of acceptor units, quinoxaline unit is shown as conspicuous moiety to attain low band gap conjugated polymers owing to two electron-withdrawing imine nitrogens in quinoxaline unit. They can be easily structurally diversified via introducing substituent groups on the two and three positions [4,6,16,17]. E. Wand and coworkers reported that 5,8-dithien-2-yl-2,3-diphenylquinoxaline based polymers revealed up to 6% PCE [18]. Later on Jen group reported a quinoxaline derivative containing fused-phenyl rings and 6.24% PCE was achieved [19]. It was proven that fused-phenyl rings reduce the energetic disorder of the polymer backbone after facilitating polymer coplanarity and interchain π-π^* interactions which

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enable high FF and PCE in PCSs [6,20].

Benzotriazole (BTz) containing polymers revealed superior properties in electrochromic and photovoltaic applications. Most of the BTz derivatives showed multichromic character with highly transmissive states which are very essential for electrochromic devices [21]. Due to the diamine unit, BTz was used as the moderately electron-deficient unit in D-A type conjugated polymers [22]. Low electron accepting property of BTz leads to high LUMO energy level and high band gap consequently [21]. BTz is not accepted as a strong acceptor as benzothidiazole for polymer solar cell structures [23]. However, it can be easily modified with alkyl groups at one of the nitrogen atoms on the triazole unit to achieve high solubility [24]. Hence, in this study different substituents on quinoxaline unit were selected to combine with BTz to improve electrochemical and photovoltaic cell properties of conjugated polymers in terms of optical contrast, switching times, processability, low band gap and high power conversion efficiency. Two absorption peaks in the visible region located at around 400 nm and 600 nm result in green color. In literature, copolymers of quinoxaline and thiophene derivatives showed such property [25–28]. Moreover, Yongfang Li and coworkers reported quinoxaline and thiophene based alternating copolymer (PT-QX(0F)) which has dual absorption peaks at red and blue regions [29]. The aim of this study was to obtain polymers which have broad absorption peak covering red, blue and green regions. To compensate the lack of absorption maxima at green region, benzotriazole and thiophene based polymers can be incorporated into polymer backbone [30]. Optical properties of resulting polymers can be tuned via rational design strategies to harvest more sunlight. In this study, regarding these information, random copolymers of quinoxaline, thiophene and benzotriazole moieties were synthesized.

2. Experimental part

2.1. Materials

All chemicals used in the synthesis of monomers and polymers were purchased from Sigma-Aldrich Chemical Co. Ltd. $PC_{71}BM$ was purchased from Solenne. 9-(Bromomethyl)nonadecane (**1**) [21], 4,7-dibromo-1H-benzo[d][1,2,3]triazole (**4**) [31], 4,7-dibromo-2-(2-octyldodecyl)-2H- benzo[d][1,2,3]triazole (**5**) [21], 2,5-bis(trimethylstannyl)thiophene (**6**) [32], 5,8-dibromo-2,3-di(thiophen-2-yl)quinoxaline (**7**) [33] 5,8-dibromo-2,3-diphenylquinoxaline (**8**) [33], 10,13-dibromodibenzo[*a*,*c*]phenazine (**9**) [33] with some modifications were synthesized according to literature reports. Tetrahydrofuran (THF) and toluene were dried over sodium and benzophenone and freshly used in the reactions. Other solvents were used as received without any further drying operation. Reactions were performed under argon atmosphere unless otherwise mentioned.

2.2. Measurements

Chemical structures of the monomers and polymers were proven by ^1H and ^{13}C NMR spectra in $CDCl_3$. They were recorded on a Bruker Spectrospin Avance DPX-400 Spectrometer with respect to trimethylsilane (TMS) as the internal reference. Average molecular weights of the polymers were determined by gel permeation chromatography (GPC) with respect to polystyrene standards in chloroform ($CHCl_3$). Thermal analysis of the polymers were studied by thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC). Perkin Elmer Pyris 1 TGA was used under nitrogen (N_2) atmosphere with a 10 °C/min heating rate up to 950 °C. In order to clarify melting point (T_m) and glass transition temperature (T_g), Perkin Elmer DSC Diamond was used under N_2 atmosphere with a 10 °C/min heating rate up to 300 °C. For cyclic voltammetry studies polymers were dissolved in $CHCl_3$ (5 mg/mL) and spray coated onto an ITO coated glass substrate. Cyclic voltammetry studies were carried out in a solution of 0.1 M of tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile (ACN) solution at a scan rate of 100 mV/s. A Gamry 600 potentiostat was used with a three-electrode cell consisting of an ITO-coated glass substrate as the working electrode, Pt wire as the counter electrode, and Ag wire as the reference electrode.

2.3. Fabrication and characterization of polymer solar cell

The BHJ polymer solar cell device was fabricated with the structure of ITO/PEDOT:PSS/Polymer:$PC_{71}BM$/LiF/Al. ITO coated glass substrates were cleaned with toluene, detergent, water and isopropyl alcohol in ultrasonic bath for 15 min and dried with N_2 gun. After the plasma cleaning (Harrick Plasma Cleaner), PEDOT:PSS was filtered through 0.45 μm PVDF syringe filter. PEDOT:PSS was coated onto the ITO surface at 4000 rpm for 1 min by spin coating. To evaporate the water substrates were dried at 135 °C for 15 min polymer:$PC_{71}BM$ mixtures with different ratios were prepared and filtered with 0.2 μm PTFE syringe filter. Filtered mixtures were coated on PEDOT:PSS layer in the glove-box system filled with nitrogen (O_2 concentration <0.1 ppm and H_2O concentration <0.1 ppm). LiF (0.6 nm) and Al layer (100 nm) were evaporated through a shadow mask in sequence under a vacuum of 10^{-6} mbar. The active area was determined as 6 mm^2. Current density-voltage (J-V) characteristics were measured using a Keithley 2400 source meter under AM 1.5G irradiation.

2.4. Synthesis

2.4.1. Synthesis of 9-(bromomethyl)nonadecane (**1**)

2-Octyl-1-dodecanol (10 g, 33.5 mmol) and triphenylphosphine (PPh_3) (9.22 g, 35.15 mmol) were dissolved in 75 mL dichloromethane (DCM) and reaction mixture was cooled down to 0 °C (Scheme 1). Bromine (1.8 mL, 35 mmol) was added to reaction mixture and mixture was stirred for 30 min at 0 °C. Then, reaction was warmed to room temperature and stirred for additional 30 min. $NaHSO_3$ solution was added to the reaction mixture to compensate for excess Br_2. Via addition of $NaHSO_3$ the dark yellow solution turns into faint yellow. Organic phase was washed with DCM, water and brine. After the extraction, organic phase was dried over $MgSO_4$ and evaporated to obtain a white solid. Purification of crude product was performed with column chromatography on silica gel by using hexane and 9-(bromomethyl)nonadecane was obtained as a colorless oil (12 g, 94%) ^1H NMR (400 MHz, $CDCl_3$), δ (ppm): 3.37 (d, $J = 4.7$ Hz, 2H), 1.52 (m, 1.46–1.57, 1H), 1.20 (m, 1.15–1.32, 32 H), 0.81 (t, $J = 6.58$ Hz, 6H).^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 39.6, 39.5, 32.59, 31.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 26.6, 22.7, 14.1.

2.4.2. Synthesis of 4,7-dibromobenzo[c][1,2,5]thiadiazole (**2**)

Benzo-1,2,5-thiadiazole (5.0 g, 36.7 mmol) was dissolved in 40 mL HBr (47%) in room temperature. Later, a solution of Br_2 (17.6 g, 110 mmol) in 30 mL HBr was added drop wise to reaction mixture. After the addition of Br_2, the reaction mixture was heated to 135 °C and refluxed for overnight. Then the mixture was cooled down to room temperature and $NaHSO_3$ solution was added to get rid of excess Br_2. The mixture was filtered and orange solid was washed with cold diethyl ether and water several times to obtain 4,7-dibromobenzo[c][1,2,5]thiadiazole (9.53 g, yield 88%) as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.66 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 152.9, 132.3, 113.9.