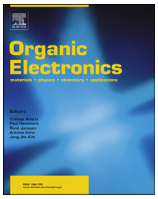
Organic Electronics 41 (2017) 1–8

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel



Benzothiadiazole-pyrrolo[3,4-*b*]dithieno[2,3-*f*:3′,2′-*h*]quinoxalindione-based random terpolymer incorporating strong and weak electron accepting [1,2,5]thiadiazolo[3,4g]quinoxalinefor polymer solar cells

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ARTICLE INFO

Article history:
Received 12 October 2016
Received in revised form
4 November 2016
Accepted 23 November 2016

Keywords:
D-A random copolymers
Bulk heterojunction
Polymer solar cells
Solvent additives
Power conversion efficiency

ABSTRACT

We report the synthesis of a D-A random terpolymer denoted as **P2** consists of one thiophene donor unit and three acceptor benzothiadiazole (BT), pyrrolodithienoquinoxalinedione (PDQD) and thiadiazoloquinoxaline (TDQ) units by Stille-coupling reaction and investigated its optical and electrochemical properties. We have compared its properties with the parent copolymer **P1**. The **P2** exhibits bandgap of about 1.18 eV which is lower than that of **P1** (1.50 eV), indicating strength of accepting units controls both the optical and electrochemical bandgap. We have used terpolymer **P2** as electron donor along with [6,6]-phenyl C_{71} butyric acid methyl ester ($PC_{71}BM$) as electron acceptor for the fabrication of solution processed bulk heterojunction polymer solar cells (PSCs). PSC based on an optimized **P2**:$PC_{71}BM$ (1:2 by weight) active layer processed with 3v % DIO/DCB solution, displayed a power conversion efficiency (PCE) of 7.22%, which is higher than that for **P1** based polymer solar cell (PCE = 6.56%) processed under same conditions. The higher value of PCE for **P2**:$PC_{71}BM$ may be related to more favorable phase separated morphology of active layer as compared to **P1**:$PC_{71}BM$, beneficial for the exciton dissociation and charge transport, as evidenced from the larger hole mobility.

1. Introduction

Polymer solar cells (PSCs) based on bulk heterojunction (BHJ) active layer that consist of a blended film of a conjugated polymer donor and fullerene derivatives acceptor have attracted lot of attention as a promising renewable energy resource due to their unique advantages for achieving light weight, low cost, large area and flexible devices through inject printing and roll to roll solution processes [1]. Significant progress in the field of PSCs has been made in past few years and has shown power conversion efficiencies (PCEs) over 10% using conjugated polymers as donor and fullerene derivatives as acceptor in single BHJ junction devices, particularly due to the optimization of bandgap, charge carrier mobility and energy levels of conjugated polymers, and the nanoscale morphology of the active layer [2]. However, further development of conjugated polymers is necessary to achieve high performance PSCs for commercialization [3]. One promising approach toward the broadening of absorption profile of polymers is to develop random terpolymers based on the copolymerization of two different electron rich units and one electron deficient unit [4] or one electron rich unit and two different electron withdrawing units [5]. Moreover, the energy levels, absorption profile, molecular ordering and charge carrier mobility can be adjusted by controlling the selection of different monomers or the ratio of composition [6]. Moreover, the choice of co-monomers with planar molecular structure can also enhance the π-π interaction between copolymer chain backbones. Ternary copolymerization is an easy and effective method used to tune the optical and electronic properties of the conjugated copolymers and the PCE of the resultant devices can be

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http://dx.doi.org/10.1016/j.orgel.2016.11.034
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enhanced as compared to D-A copolymer counterpart. Tajima and coworker reported a terpolymer based on BDT, TPD and thiophene and the thiophene unit has a tris-(thienylenevinylene) conjugated side chain and achieved PCE of 6.46%, higher than that for D-A copolymer [7]. Recently Jo et al. synthesized a conjugated random copolymer composed of bithiophene (electron donating unit) with thiophene-capped diketopyrrolopyrrole (TDPP) and pyridine-capped diketopyrrolopyrrole (PyDPP) (co-electron accepting units) and employed it as electron donor along with $PC_{71}BM$ as electron acceptor for BHJ PSC, achieved overall PCE of 8.11% [8]. Na et al. have reported a new random terpolymer based on (2,5-difluorophenylene) dithiophene and dialkoxybenzothiadiazole with thiophene as the third conjugated bridge having sulfur and fluorine (S/F) and/or oxygen (S/O) non-covalent intramolecular interaction and reported overall PCE of 7.71% and 8.50% for conventional and inverted PSCs, respectively [9]. These observations indicate that a rational selection of the three components and detail characterization of the molecular structure with multiple components is crucial for the designing of new terpolymers for efficient PSCs.

In our recent work [10] we prepared D-A copolymer **P1** (chemical structure shown in Scheme 1), which exhibited promising optical and electrochemical properties. In order to further improve the characteristics of the parent polymer **P1** we developed new random terpolymer **P2** comprising additional electron acceptors with different electron withdrawing ability, units **M3** (strong acceptor). Our study clearly shows that introduction of additional strong acceptor unit **M3** leads to broaden and red-shifted absorption spectrum of **P2** compared to parent copolymer **P1**. Random terpolymer **P2** was used as electron donor along with the $PC_{71}BM$ as electron acceptor for the fabrication of solution processed BHJ PSCs. After the optimization of donor to acceptor ratio and solvent additive concentration, the device based on **P2**:$PC_{71}BM$ showed overall PCE of 7.22%, higher than that for **P1** based solar cells processed under same fabrication conditions [10]. The higher value of PCE for **P2**:$PC_{71}BM$ may be related to more favorable phase separated morphology of active layer as compared to **P1**:$PC_{71}BM$, beneficial for the exciton dissociation and charge transport, as evidenced from the larger hole mobility. Moreover, a high PCE of 7.22% is achieved with low energy loss (0.46 eV) with a low bandgap random terpolymer **P2** (1.18 eV), which may be the highest PCE with our best of knowledge.

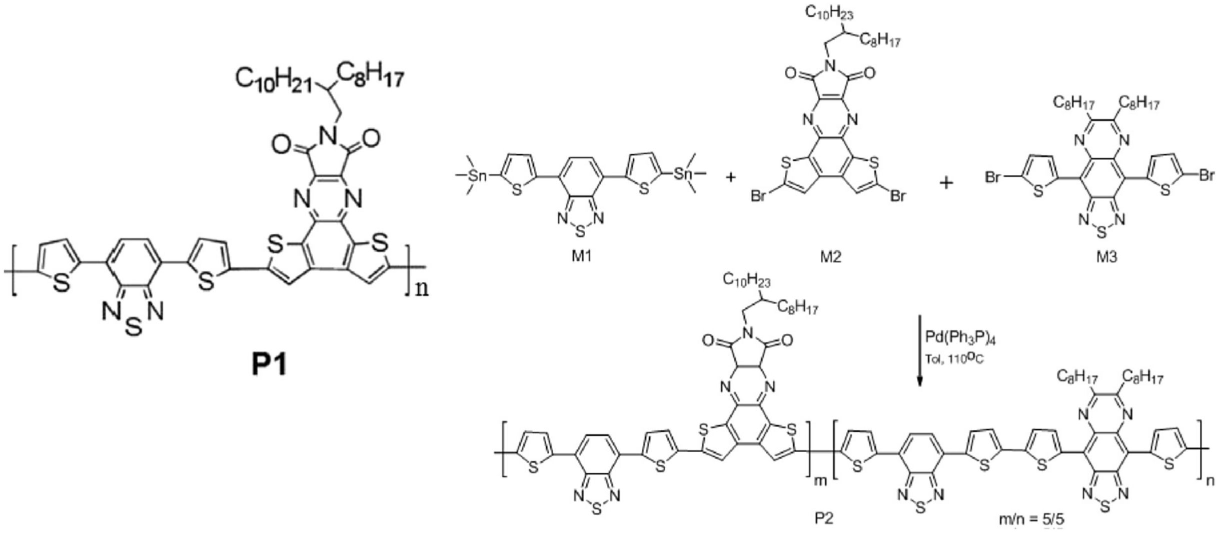
2. Experimental details

^1H NMR and ^{13}C NMR spectra were measured with Bruker AVANCE 400 spectrometer. UV–vis spectra were measured on Perkin Elmer Lamada-25 spectrometer. The elemental analysis was performed with an Elementar Vario EL III element analyzer for C, H, N and S determination. Thermal gravimetric analysis (TGA) analysis was performed on "Perkin-Elmer TGA-7″ with heating rate 20 deg/min. The average molecular weight and poly-dispersity index (PDI) of the copolymers was performed on Waters gel permeation chromatography GPC instrument, consisting of a M-600 pump, two U-Styragel Linear Columns, M-484 spectrophotometric detector and maxima data acquisition and processing system with $CHCl_3$ as eluent and polystyrene as standard. Electrochemical redox potentials were obtained by cyclic voltammetry (CV) using a three-electrode cell and an electrochemistry work station (CHI830B, Chenhua Shanghai). The working electrode was a Pt ring electrode; the auxiliary electrode was a Pt wire, and Ag/AgCl was used as reference electrode. The *tetra*-butylammoniumhexafluorophosphate 0.1 M was used as supporting electrolyte in dry acetonitrile. Transmission electron microscopy (TEM) images were recorded with a Tecnai G2F30 transmission electron microscope (FEI Inc.; accelerating voltage = 300 kV).

3. Synthesis of random terpolymers P2

Toluene was dried and distilled over sodium/benzophenone. $CHCl_3$ and CH_3CN were dried with CaH_2 and distilled prior to use. All other solvents and chemicals used in this work were analytical grade and used without further purification. All chromatographic separations were carried out on silica gel (200–300 mesh).

The polymerization was performed by a Stille coupling reaction. In a 50 mL flask, monomers **M1** (0.3130 g, 0.5 mmol), **M2** (0.1874 g, 0.25 mmol) and **M3** (0.1836 g, 0.25 mmol) were dissolved in 15 mL of toluene, and the solution was flushed with argon for 15 min, then 27 mg of $Pd(PPh_3)_4$ was added into the solution. The mixture was again flushed with argon for 20 min. The reaction mixture was heated to reflux for 48 h. The reaction mixture was cooled to room temperature and added drop-wise to 400 mL methanol. The precipitate was collected and further purified by Soxhlet extraction with methanol, hexane, and chloroform in sequence. The chloroform fraction was concentrated and added drop-wise into



Scheme 1. Synthesis routes of **P2** and chemical structure of **P1** is also shown.