



Synthesis, characterization, and photovoltaic performance of the polymers based on thiophene-2,5-bis((2-ethylhexyl)oxy)benzene-thiophene

Rongyan Hou^a, Bin Zhao^{a,b,*}, Fen Wu^a, Guo Wang^a, Tianpei Shen^a, Huan Guo^a, Jian Zhang^c, Huajie Chen^b, Songting Tan^b

^a College of Chemistry and Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry, Xiangtan University, Xiangtan 411105, Hunan Province, PR China

^b Key Laboratory of Polymeric Materials & Application Technology of Hunan Province, Xiangtan University, Xiangtan 411105, PR China

^c Department of Material Science & Engineering, Guangxi Key Laboratory of Information Materials, Guilin University of Electrical Technology, Guilin 541004, PR China

ARTICLE INFO

Article history:

Received 13 January 2015

Received in revised form 7 February 2015

Accepted 7 February 2015

Available online 14 February 2015

Keywords:

Polymer solar cells

Conjugated polymer

Thiophene–benzene–thiophene

Isoidindigo

Diketopyrrolopyrrole

ABSTRACT

Three novel conjugated copolymers based on thiophene-2,5-bis((2-ethylhexyl)oxy)benzene-thiophene (TBT) as electron-donating units, either isoidindigo or both isoidindigo and diketopyrrolopyrrole (DPP) as electron-withdrawing units have been designed and synthesized by Stille-coupling reaction. All the polymers exhibit high thermal stability, broad absorption in the range of 300–800 nm, and the low-lying energy level of highest occupied molecular orbitals (HOMO) (−5.47 to −5.19 eV). After introduced with additional hexylthiophenes and further introduced with DPP units, the polymers **PTBT-HTID** and **PTBT-HTID-DPP** show smaller lamellar distance and π – π stacking distance, and the morphology of the corresponding photoactive layers possess more appropriate microphase separation and smaller domain size, which lead to high short circuit current densities (J_{sc}) and power conversion efficiency (PCE). The polymer photovoltaic devices based on **PTBT-HTID-DPP/PC₆₁BM** exhibit a high J_{sc} value of 11.13 mA cm^{−2}, a fill factor (FF) of 0.57, and the PCE of 4.2%.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Polymer solar cells (PSCs) are considered to be a promising candidate for future photovoltaic applications due to their use of potentially low-cost and flexible device, and their potential for solution processing such as inkjet printing and roll-to-roll coating [1–3]. In the past decade, tremendous progress in the performance of these devices has been achieved owing to the development of new materials, improved device geometries, and metal/organic interfaces [4,5]. Recently, the power conversion efficiencies (PCEs) of

the bulk heterojunction (BHJ) PSCs, consisting of conjugated polymers as donor and fullerene derivatives as acceptor, have achieved 10.8% for single-layer BHJ [6]. However, improvement in the PCE of OPVs is still required to push this technology toward commercial applications.

An efficient strategy to obtain high photovoltaic performance conjugated polymers has been carried out by combining electron-donating (D) and electron-withdrawing (A) conjugated moieties into their repeating units [7–10], and the band gap and energy levels of the conjugated polymers can be facilely tuned by choosing appropriate D and A moieties [11]. As a symmetric and planar conjugated unit, benzo[1,2-*b*:4,5-*b'*] dithiophene (BDT) has been proved to be one of the most effective D moieties recently used for polymeric photovoltaic materials because it can easily realize ordered π – π stacking in a large domain size [12]. Many

* Corresponding author at: College of Chemistry and Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry, Xiangtan University, Xiangtan 411105, Hunan Province, PR China.

E-mail address: xtuzb@163.com (B. Zhao).

BDT-based polymers possess high photovoltaic performance with a PCE over 7% in recent years [5,13,14]. In general, the BDT-based polymers exhibit high HOMO (highest occupied molecular orbital) energy level, which leads to a low open-circuit voltage (V_{oc}) [15]. For example, the PTB family polymers show high-lying HOMO energy levels between -4.9 to -5.12 eV, and the corresponding PSCs only exhibit low V_{oc} values between 0.58 V and 0.74 V [16]. In order to depress the HOMO energy levels of the BDT-based polymers, many groups tried to applied different substituent groups to replace alkoxy groups on BDT unit. You group applied alkyl groups to substitute alkoxy groups, and the polymer PBnDTDTBT achieved a deep HOMO energy level of -5.40 eV. [17] Subsequently, Ferraris and his coworkers applied thioalkoxy groups to replace alkoxy groups. The HOMO energy level of the polymer S-PBDT was reduced to -5.41 eV, and the corresponding PSC device achieved an enhanced V_{oc} (0.99 V) [18]. Hou group applied *meta*-alkoxy-phenyl and fluorothieryl groups to substitute alkylthienyl group, the HOMO energy levels of the polymers were reduced over 0.22 eV for PBT-OP [19], 0.25 eV for PTB-3F [20]. Certainly, many researchers always spent a lot in exploring promising methods to obtain low band-gap polymers with low-lying HOMO energy level.

An appropriate A unit is another key factor to obtain high-performance photovoltaic polymer besides an effective D unit. Recently, isoindigo (ID) has been considered as a remarkable A moiety because of its planar geometry, strong electron-deficient property and low-lying energy level of lowest unoccupied molecular orbital (LUMO) [1,7,21–23]. To further reduce the band gap and broaden the absorption spectra of the D–A conjugated polymers, terpolymers have been exploited by introducing complementary chromophores in the backbone [24–26]. Simultaneously, the frontier molecular orbital energy levels can be easily tuned by incorporating of different ratio of D or A moieties. Typically, diketopyrrolopyrrole (DPP) chromophore is widely applied for the terpolymers which usually exhibit an extended absorption spectra to 800 nm, high crystallinity and hole mobility [27,28].

Herein, we reported a series of conjugated polymers based on thiophene-2,5-bis((2-ethylhexyl)oxy)benzene-thiophene (TBT) as a D unit and ID as A unit for efficient PSC. Compared with BDT, the TBT unit is a relatively tortile conjugated block because of steric hindrance, which would lead to a deeper HOMO energy level of **PTBT-ID** (Fig. 1) and a higher V_{oc} of the PSC. To improve the aggregation structure and the morphology of the polymer with the fullerene derivative, the polymer **PTBT-HTID** was synthesized by introducing hexylthiophene between the ID and TBT units. Subsequently, the terpolymer copolymer **PTBT-HTID-DPP** was also prepared to extend the light absorption range and further tune the aggregation and the morphology. In addition, the effects of the different structure units on the energy levels, absorption spectra, the aggregation structure and the morphology of the active layer were prudentially studied. The structures of the three polymers are shown in Fig. 1.

2. Experimental

2.1. Materials and chemicals

n-BuLi, Pd(PPh₃)₄, and (C₄H₉)₃SnCl and 1,2-dichlorobenzene (DCB) were obtained from Alfa Aesar and used as

received. Other reagents and solvents were purchased commercially as analytical-grade quality and used without further purification. Tetrahydrofuran (THF) and toluene were dried over Na/benzophenone ketyl and freshly distilled prior to use. 2,5-Dibromobenzene-1,4-diol [29], 2-(tributylstannyl)thiophene, 6,6'-di(4-hexylthien-2-yl)-*N,N'*-(2-ethylhexyl)-isoindigo (**3**) [7], 6,6'-dibromo-*N,N'*-(2-hexyldecyl)-isoindigo (**M2**) [21], and 2,5-diethylhexyl-3,6-bis(5-bromothiophene-2-yl)pyrrolo-[3,4-*c*]-pyrrole-1,4-dione (**M4**) [30] were synthesized according to the literature procedures.

2.2. Characterization

Nuclear magnetic resonance (NMR) spectra were measured with Bruker AVANCE 400 spectrometer. The elemental analysis was performed with an Elementar Vario EL III element analyzer for C, H, N, and S. MALDI-TOF mass spectrometric measurements were performed on Bruker Autoflex III. UV-Visible-Near Infrared absorption spectra (UV-vis-NIR) of the polymers were conducted on a Perkin-Elmer Lamada 25 UV-vis-NIR spectrometer. The average molecular weight and polydispersity index (PDI) of the polymers were determined using Waters 1515 gel permeation chromatography (GPC) analysis with THF as eluent and polystyrene as standard. Thermogravimetric analysis (TGA) measurement was conducted on a Netzsch TG 209 analyzer under nitrogen at a heating rate of 20 °C min⁻¹. Electrochemical redox potentials were obtained by cyclic voltammetry (CV) using a three-electrode configuration and an electrochemistry workstation (ZAHNER ZENNIUM) at a scan rate of 100 mV s⁻¹. CV was conducted on an electrochemistry workstation with the thin film on a Pt plate as the working electrode, Pt slice as the counter electrode, and Ag/AgCl (saturated KCl) electrode as the reference electrode. The supporting electrolyte is 0.1 M *tetra-n*-butylammoniumhexafluorophosphate (Bu₄NPF₆) in anhydrous acetonitrile solution. AFM measurements were performed on a Digital Instruments Enviro Scope in a tapping mode.

2.3. Synthetic procedures

The synthetic routes of the monomers and polymers are shown in Scheme 1.

2.3.1. 1,4-Dibromo-2,5-bis((2-ethylhexyl)oxy)benzene (**1**)

To a solution of compound 2,5-dibromobenzene-1,4-diol (2.0 g, 7.46 mmol) in *N,N*-dimethyl formamide (DMF) (50 mL), K₂CO₃ (2.6 g, 18.65 mmol) was added quickly. The mixture was stirred at 80 °C for 30 min, then the solution of 2-ethylhexyl bromide (3.17 g, 16.41 mmol) in DMF (10 mL) was added under nitrogen. The mixture was refluxed overnight. After cooling to room temperature, it was filtered, and the filtrate was extracted by ethyl acetate and washed with brine. The organic layer was dried over anhydrous magnesium sulfate, and then filtered. After removed the solvent by a rotary evaporator, the crude product was obtained, and it was further purified by column chromatography using petroleum ether as an eluent to yield a colorless liquid (1.47 g, 40%). ¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.08 (s, 2H), 3.84 (d, *J* = 5.22 Hz, 4H), 1.75 (t, *J* = 5.76, 2H), 1.52–1.33 (m, 16H), 0.95–0.92 (m, 12H). ¹³C NMR (100 MHz, CDCl₃, δ/ppm): 150.17, 118.14, 111.05, 72.48, 39.44, 30.47, 29.07, 23.89, 23.08, 14.15, 11.21.

Download English Version:

<https://daneshyari.com/en/article/1263740>

Download Persian Version:

<https://daneshyari.com/article/1263740>

[Daneshyari.com](https://daneshyari.com)