



# Synthesis and photovoltaic property of polymer semiconductor with phthalimide derivative as a promising electron withdrawing material

Jang Yong Lee, Seung Min Lee, Kwan Wook Song, Doo Kyung Moon \*

Department of Materials Chemistry and Engineering, Konkuk University, 1 Hwayang-dong, Gwangjin-gu, Seoul 143-701, Republic of Korea

## ARTICLE INFO

### Article history:

Received 15 September 2011

Received in revised form 2 November 2011

Accepted 6 December 2011

Available online 14 December 2011

### Keywords:

Photovoltaic materials

Phthalimide

Conjugated polymers

Donor materials

## ABSTRACT

Donor–acceptor type (DA-type) polymeric photovoltaic material with a dicarboxylic imide-substituted benzene (phthalimide) derivative as electron-withdrawing units, poly[4,4'-didodecyl-2,2'-(bithiophene-co-5,5'-(3,6-bis(thieno-2-yl)-N-octyl-phthalimide)] (PDBTTPT), was synthesized by a Stille coupling reaction. It had an optical band gap of 1.96 eV and a relatively low HOMO energy level of  $-5.34$  eV in spite of it being a thiophene-based polymer. Photovoltaic devices with PDBTTPT/PC<sub>71</sub>BM active layers were fabricated under a variety of conditions for optimizing device performance. PDBTTPT exhibited the best power conversion efficiency (PCE) of 1.5% in the device where 80 wt.% of the PC<sub>71</sub>BM was contained in the active layer (PDBTTPT:PC<sub>71</sub>BM = 1:4, w/w) and which was pre-annealed at 120 °C for 10 min. In addition, a device which was pre-annealed at 140 °C for 10 min and a device which was post-annealed at 120 °C for 10 min showed analogous PCE values of 1.5% as well, although small differences were exhibited between various parameters, such as  $V_{OC}$ ,  $J_{SC}$ , and FF.

© 2011 Elsevier Ltd. All rights reserved.

## 1. Introduction

Organic photovoltaic devices based on polymer semiconductors are clean and efficient electronic devices that directly generate usable electricity by reactions between photons from solar irradiation and semiconductor materials in their active layers. In this respect, in order to develop a high performance organic photovoltaic device, the key technology is the design and synthesis of polymer semiconductor materials. Photovoltaic polymer materials have gained considerable attention for two decades due to their various advantages, such as low-cost, flexibility, eco-friendly use, etc. Recently, developments of several high-performance organic photovoltaic materials [1–9] and researches for photochemical stability of  $\pi$ -conjugated polymers have increased the potential for organic photovoltaic applications [10,11]. Moreover, fabrication technologies of flexible and large area devices, such as ink-jet

printing and roll-to-roll through solution processing [12–16], have increased the practical potential of these materials towards next generation energy converting devices.

Since organic photovoltaic devices had been investigated, a variety of strategies have been used for developing high efficiency polymeric photovoltaic materials [17–21]. Among them, the synthesis of copolymers that alternate electron donating materials with electron withdrawing materials in polymer backbones has been regarded as the most efficient strategy for synthesizing photovoltaic materials since the polymer band gap was effectively controlled by the intra-chain charge transfer [22,23]. In order to develop outstanding donor–acceptor (DA) type copolymers, the most important consideration is the choice of electron-donating and electron-withdrawing materials that had various favorable properties, such as good solubility, appropriate energy level, structural planarity, etc.

In this respect, phthalimide is a promising electron-withdrawing material for organic photovoltaics. The solubility and the energy levels of phthalimide can be easily controlled by introducing various functional groups at its

\* Corresponding author. Tel.: +82 2 450 3498; fax: +82 2 444 0765.

E-mail address: [dkmoon@konkuk.ac.kr](mailto:dkmoon@konkuk.ac.kr) (D.K. Moon).

nitrogen site. Moreover, the highest occupied molecular orbital (HOMO) energy level of a polymer with phthalimide in its polymer backbone could also be easily lowered because of the low HOMO energy level of phthalimide, which leads to improved open circuit voltage ( $V_{OC}$ ) values of final devices. Nevertheless, there are almost no investigations concerning polymeric materials with phthalimide for OPVs, except for a few studies [24,25].

In this study, a DA-type polymer semiconductor that had a phthalimide as an electron-withdrawing moiety, PDBTTPT, was synthesized through a Stille coupling reaction for organic photovoltaic materials. Bulk heterojunction-type devices with 1-(3-methoxycarbonyl)propyl-1-phenyl-6,6-C-71 (PC<sub>71</sub>BM) as acceptors were fabricated in order to investigate the photovoltaic properties of PDBTTPT. Additionally, in order to optimize device performance, photovoltaic devices were fabricated under a variety of conditions, according to different weight ratios between PDBTTPT and PC<sub>71</sub>BM or various annealing temperatures and times.

## 2. Experimental section

### 2.1. Materials

All reagents were purchased from Aldrich and were used without further purification. 4,4'-Didodecyl-5,5'-trimethylstannyl-2,2'-bithiophene [26] were prepared as described in the literature.

#### 2.1.1. 3,6-Dibromophthalic anhydride (**1**)

A mixture of phthalic anhydride (5.9 g, 40 mmol), oleum (20% free SO<sub>3</sub>, 75 ml), bromine (13.4 g, 84 mmol) and silver sulfate (25 g, 80.2 mmol) was stirred at 70 °C for 24 h. After cooling to room temperature, precipitations were filtered off and washed by dichloromethane. The solution was washed with water and extracted with chloroform. The organic layer was concentrated via rotary evaporation to a brown solid. This brown solid was recrystallized twice from acetic acid to provide colorless crystals (1.4 g, 4.6 mmol). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 7.85 (s, 2H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 159.15, 141.55, 131.10, 120.16.

#### 2.1.2. N-Octyl-3,6-dibromophthalimide (**2**)

Compound **1** (1.4 g, 4.6 mmol) was dissolved in glacial acetic acid (25 ml) followed by dropwise of octyl amine (0.78 g, 6.0 mmol). The mixture was refluxed under nitrogen for 2 h. After most of the acetic acid was removed under reduced pressure, the crude product was purified using column chromatography using dichloromethane/hexane (1:3, v/v) as the eluent. Colorless crystals were obtained after recrystallization from hexanes (1.6 g, 3.9 mmol). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 7.62 (d, 2H), 3.66 (d, 2H), 1.65 (m, 2H), 1.37–1.24 (m, 10H), 0.87 (t, 3H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 165.05, 139.68, 131.51, 117.69, 38.05, 31.33, 28.97 (2C), 28.05, 26.88, 22.87, 13.98.

#### 2.1.3. 3,6-Bis(thieno-2-yl)-N-octyl-phthalimide (**3**)

Compound **2** (1.6 g, 3.9 mmol), 2-tributylstannylthiophene (3.7 g, 9.8 mmol) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (5 mol%) were

dissolved in a mixture of THF (40 ml). The mixture was refluxed for 24 h. After cooling to room temperature, the organic layer was dried with Na<sub>2</sub>SO<sub>4</sub> and was concentrated via rotary evaporation. The product was purified using column chromatography using dichloromethane/hexane (1:3, v/v) as the eluent. The product was obtained as bright yellow solid (1.15 g, 2.7 mmol). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 7.77 (d, 2H), 7.76 (s, 2H), 7.47 (d, 2H), 7.17 (t, 2H), 3.66 (d, 2H), 1.65 (m, 2H), 1.37–1.24 (m, 10H), 0.87 (t, 3H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): δ 167.02, 137.24, 135.87, 132.31, 130.00, 127.95, 127.72, 127.54, 38.27, 31.64, 29.05 (2C), 28.18, 26.96, 22.96, 14.04.

#### 2.1.4. 5,5'-Dibromo-3,6-bis(thieno-2-yl)-N-octyl-phthalimide (**4**)

Compound **3** (1.15 g, 2.7 mmol) were dissolved to mixture of chloroform/acetic acid (1:1, v/v) at room temperature. NBS (1.0 g, 5.9 mmol) was added to the mixture. After 24 h, the mixture was poured to water and organic layer was extracted with chloroform. The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub> and was concentrated via rotary evaporation. The product was purified using column chromatography using dichloromethane/hexane (1:3, v/v) as the eluent. The product was obtained as bright yellow solid (0.87 g, 1.5 mmol). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 7.70 (s, 2H), 7.52 (d, 2H), 7.12 (d, 2H), 3.66 (d, 2H), 1.66 (m, 2H), 1.33–1.20 (m, 10H), 0.86 (t, 3H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 167.27, 138.48, 135.27, 131.43, 130.55, 130.38, 127.88, 115.10, 38.35, 31.79, 29.16 (2C), 28.46, 26.97, 22.64, 14.12.

#### 2.1.5. PDBTTPT

4,4'-Didodecyl-5,5'-trimethylstannyl-2,2'-bithiophene (0.41 g, 0.5 mmol), compound **4** (0.30 g, 0.5 mmol) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (1.5 mol%) were dissolved in THF/DMF (1/1, v/v). The solution was refluxed for 48 h with vigorous stirring in nitrogen atmosphere, and then the excess amount of bromothiophene and 2-tributylstannylthiophene were added and stirring continued for 3 h, respectively. The whole mixture was poured into methanol. The precipitate was filtered off, purified with methanol, acetone and hexane in a Soxhlet apparatus for 24 h, respectively. The chloroform soluble fraction was recovered and dried under a reduced pressure at 80 °C. The product was obtained as dark red powder (0.13 g, 27%). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 7.86 (d, 2H), 7.80 (s, 2H), 7.19 (d, 2H), 7.05 (s, 2H), 3.70 (t, 2H), 2.81 (t, 4H), 1.71 (m, 4H), 1.61 (m, 2H), 1.5–1.2 (br, 8H), 0.87 (t, 3H). Elem. Anal. for C<sub>56</sub>H<sub>75</sub>N<sub>1</sub>S<sub>4</sub>O<sub>2</sub>: C, 72.91; H, 8.19; N, 1.52; S, 13.91; O, 3.47. Found: C, 72.84; H, 8.22; N, 1.53; S, 13.99; O, 3.42.

### 2.2. Instruments and characterization

All of the reagents and chemicals were purchased from Aldrich and used as received unless otherwise specified. The <sup>1</sup>H NMR (400 MHz) spectra were recorded using a Brüker AMX400 spectrometer in CDCl<sub>3</sub>, and the chemical shifts were recorded in units of ppm with TMS as the internal standard. The elemental analyses were measured with EA1112 using a CE Instrument. The absorption spectra were recorded using an Agilent 8453 UV–vis spectroscopy

Download English Version:

<https://daneshyari.com/en/article/1398329>

Download Persian Version:

<https://daneshyari.com/article/1398329>

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