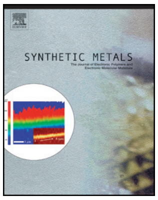
Synthetic Metals 220 (2016) 440–447

Contents lists available at ScienceDirect

Synthetic Metals

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



Synthesis and photovoltaic properties of donor-acceptor type narrow bandgap copolymers based on benzo[*def*]carbazole

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ARTICLE INFO

Article history:
Received 13 May 2016
Received in revised form 8 July 2016
Accepted 14 July 2016
Available online 22 July 2016

Keywords:
Benzo[*def*]carbazole
Donor-acceptor
Narrow band gap
Conjugated polymer
Organic photovoltaic cells

ABSTRACT

Three kinds of narrow bandgap copolymers were synthesized by combination of a donor unit of benzo[*def*]carbazole with each acceptor unit of benzothiadiazole, thienopyrrole-4,6-dione, and 1,4-diketopyrrolopyrrole. Basic properties of these polymers were investigated for applications in bulk heterojunction polymer solar cells. These copolymers had broad absorption bands in UV and visible regions from 350 to 800 nm that overlapped with the major region of the solar spectrum, and their optical band gaps were in the range of 1.68–2.11 eV. The highest occupied molecular orbitals of these copolymers were situated in the range of −5.22 eV to −5.34 eV, which could provide good air stability and high open circuit voltages in photovoltaic applications. Initial performances of these copolymers in bulk heterojunction photovoltaic devices revealed that the power conversion efficiencies exceeded 1.4% under irradiation of AM 1.5 solar-simulated light (100 mW cm^{-2}).

1. Introduction

Over the past decades, the bulk heterojunction (BHJ) polymer solar cells (PSCs) as renewable energy sources have attracted much attention because of their many unique features such as low cost, easy fabrication, lightweight and good flexibility [1–3]. BHJ PSCs have been the most widely adopted device architecture, in which blend layer of an electron-donating conjugated polymer and an electron-accepting fullerene derivative with phase separation in nanoscale is sandwiched between cathode and anode [4–6]. In order to obtain high-performance PSCs, it is necessary to design and synthesize conjugated polymers with desired properties, such as (1) sufficient solubility to make a good miscible thin-layer with an n-type material, (2) a narrow bandgap matched with the high photon flux region of the solar spectrum for enough light harvesting to increase short-circuit current (J_{sc}), and (3) high hole mobility for efficient charge transport [7–10]. It has been also well known that the use of a polymer whose highest occupied molecular orbital (HOMO) is situated close to −5.5 eV [3] could lead to a large open-circuit voltage (V_{oc}) in solar cell devices [11]. Because of these complicated factors in relation of trade-off, developments of new polymers with proper properties for photoabsorption, semiconducting, energy levels, and stability have been challenging researches up to date.

A simple strategy to synthesize narrow bandgap polymers is to construct donor-acceptor (D-A) type conjugated copolymers, which have a polymer backbone composed of alternating electron donating (D) and electron accepting (A) units. One of the most successful D-A type copolymers is poly(2,7-carbazole-alt-dithienylbenzothiadiazole) (**PCDTBT**) shown in Fig. 1. The power conversion efficiencies (PCEs) of **PCDTBT**-based PSCs achieved 4.6% [12]. However, compared to typical narrow-bandgap copolymers, **PCDTBT** has a large band gap [13]. A polycyclic aromatic compound, benzo[*def*]carbazole, is a unique building block, because it has a large π-conjugation system and electron-donating ability stronger than carbazole [14]. Moreover, the bridging nitrogen-atom in benzo[*def*]carbazole offers a center for solubilizing functionality and tuning of energy levels of molecular orbitals by introducing appropriate substituents as well as carbazoles [15].

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http://dx.doi.org/10.1016/j.synthmet.2016.07.019
0379-6779/

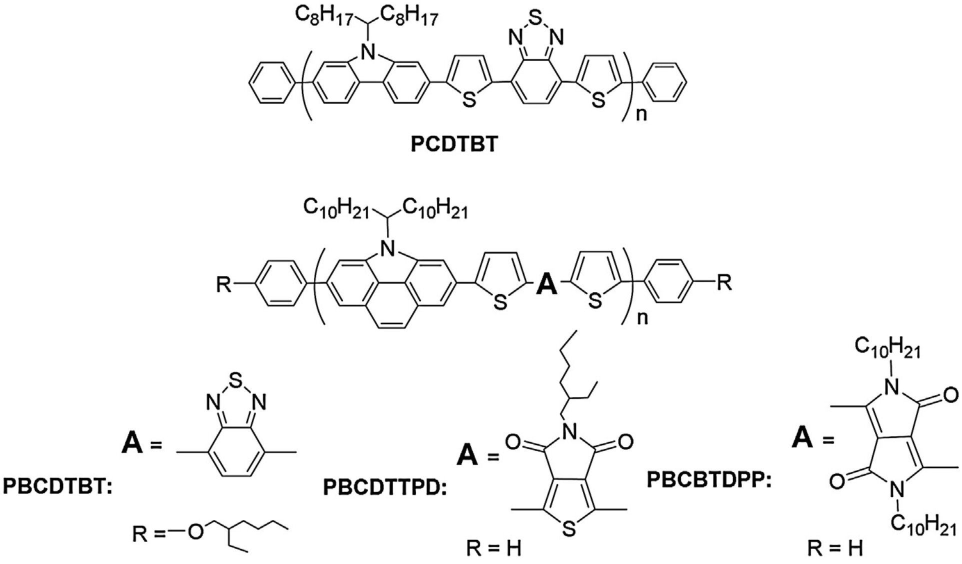

Fig. 1. Chemical structures of **PCDTBT**, **PBCDTBT**, **PBCDTTPD**, and **PBCBTDPP**.

Therefore, benzo[*def*]carbazole is chosen as the donor unit to construct new D-A type copolymers.

In this study, three D-A type benzo[*def*]carbazole-based copolymers, poly[4-(1-decylundecyl)- 4H-benzo[*def*]carbazole-2,6-diyl-thiophene-2,5-diyl-2,1,3-benzothiadiazole-4,7-diyl-thiophene-2,5-diyl] (**PBCDTBT**), poly[4-(1-decylundecyl)-4H-benzo[*def*]carbazole-2,6-diyl-thiophene-2,5-diyl-5-(2-ethylhexyl) thieno[3,4-*c*]pyrrole-4,6-dione-1,3-diyl-thiophene-2,5-diyl] (**PBCDTTPD**) and poly[4-(1-decylundecyl)-4H-benzo[*def*]carbazole-2,6-diyl- thiophene-2,5-diyl-2,5-didecylpyrrolo-[3,4-*c*]pyrrole-1,4-dione-3,6-diyl-thiophene-2,5-diyl] (**PBCBTDPP**), shown in Fig. 1 are synthesized and characterized. Benzothiadiazole (**BT**) having an electronegative heterocyclic system, thienopyrrole-4,6-dione (**TPD**) having an electron withdrawing imino-bridged system, and diketopyrrolopyrrole (**DPP**) having an electron withdrawing pyrazolone system were chosen as the typical A unit. The effects of the A segment on the absorption spectra, energy levels, and the photovoltaic performances of the copolymers were also investigated.

2. Experimental

2.1. Materials and methods

2,6-Dibromo-4-(1-decylundecyl)-4H-benzo[*def*]carbazole **1** was synthesized following our another report [16]. 5-(2-Ethylhexyl)-1,3-di-2-thienyl-4H-thieno[3,4-*c*]pyrrole-4,6-dione **3** [17] and 4,7-bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole **8** [18] were synthesized according to the procedures reported previously. Reagents and solvents were purchased from Kanto Chemical, Tokyo Chemical Industry, Aldrich, and Nacalai Tesque Inc. The other solvents and all commercially available reagents were used without further purification.

2,6-Bis(4,4,5,5-tetramethyl-1-3-2-dioxaborolan-2-yl)-4-(1-decylundecyl)-4H-benzo[def]carbazole (**2**). Suspension of **1** (1.07 g, 1.71 mmol), bis(pinacolato)diboron (1.04 g, 4.12 mmol), potassium acetate (1.18 g, 12 mmol), and 1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) ($PdCl_2(dppf)$) (0.086 g, 0.24 mmol) in 30 mL dioxane was stirred at 80 °C for 24 h under argon atmosphere. After cooling to room temperature, the mixture was poured into water. After extraction with CH_2Cl_2, drying over $MgSO_4$ and the solvent evaporation, the crude product was purified by column chromatography (silica gel, hexane/CH_2Cl_2, 1:1, as an eluent) to give a pure white solid (1.1 g, 90%). ^1H NMR (400 MHz, $CDCl_3$) δ [ppm]: 8.26 (s, 2H), 8.02 (s, 2H), 7.97 (s, 2H), 4.80-4.68 (m, 1H), 2.42-2.38 (m, 2H), 2.06-2.01 (m, 2H), 1.47 (s, 24H), 1.26-1.11 (m, 32H), 0.88-0.82(m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ [ppm]: 138.6, 132.3, 127.5, 126.3, 123.7, 121.8, 114.2, 83.8, 57.7, 34.6, 31.8, 31.6, 29.5, 29.4, 29.3, 29.2, 26.8, 24.9, 22.6, 14.1.

1,3-Bis(5-bromothiophen-2-yl)-5-(2-ethylhexyl)-5H-thieno [3,4-c]pyrrole-4,6-dione (**4**). Excess N-bromosuccinimide (NBS) (0.45 g, 2.5 mmol) was added to the solution of **3** (0.43 g, 2.07 mmol) in 19 mL $CHCl_3$, followed by addition of acetic acid (1.2 mL). The mixture was stirred at room temperature overnight. After extraction with CH_2Cl_2 from water, drying over $MgSO_4$ and the solvent evaporation, the crude product was purified by column chromatography using CH_2Cl_2/hexane (1:4, v/v) to afford a yellow solid (0.55 g, 94%).^1H NMR (400 MHz, $CDCl_3$) δ [ppm]: 7.66 (d, J = 4.4 Hz 2H), 7.08 (d, J = 4.4 Hz 2H), 3.55 (d, J = 7.2 Hz 2H), 1.84–1.81 (m, 1H), 1.33–1.27 (m, 8H), 0.92–0.87 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ [ppm]: 162.7, 135.4, 133.7, 131.1, 129.8, 128.8, 116.7, 42.6, 38.3, 30.6, 28.5, 27.5, 23.9, 23.0, 14.1.

2,5-Didecyl-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4 (2*H*,5*H*)-dione (**6**). Suspension of **5** (0.12 g, 0.4 mmol), 1-bromodecane (0.29 g, 1.3 mmol), potassium carbonate (0.18 g, 1.32 mmol) and 18-crown-6 (0.001 g, 0.013 mmol) in 2 mL of DMF was stirred at 80 °C for 12 h, and then cooled to room temperature slowly. Precipitates were collected by filtration and were redissolved in 20 mL of $CHCl_3$. The mixture was poured into water. After extraction with CH_2Cl_2, drying over $MgSO_4$ and the solvent evaporation, the crude product was purified by column chromatography using an eluent of $CHCl_3$:hexane (1:1, v/v) to yield a dark reddish brown solid (0.15 g, 64%). ^1H NMR (400 MHz, $CDCl_3$) δ [ppm]: 8.92 (d, J = 5.2 Hz 2H), 7.64 (d, J = 5.2 Hz 2H), 7.28 (t, J = 5.2 Hz 2H), 4.07 (t, J = 8 Hz 4H), 1.75–1.73 (m, 4H), 1.41–1.25 (m, 28H), 0.89–0.85(m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ [ppm]: 161.3, 140.0, 135.2, 130.6, 129.8, 128.6, 107.6, 42.2, 31.8, 30.2, 29.5, 29.4, 29.3, 29.2, 26.8, 22.6, 14.1.

3,6-Bis-(5-bromo-thiophen-2-yl)-2,5-didecyl-pyrrolo[3,4-*c*] pyrrole-1,4-dione (**7**). N-Bromosuccinimide (0.11 g, 0.58 mmol) was added to the solution of **6** (0.15 g, 0.26 mmol) in 48 mL of $CHCl_3$, which was covered with aluminum foil. The reaction mixture was stirred for 48 h at room temperature. After extraction with CH_2Cl_2, drying over $MgSO_4$, and the solvent evaporation, the crude product was purified by column chromatography using an eluent of CH_2Cl_2:hexane (1:1, v/v) to yield a dark reddish brown