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Benzodithiophene based ternary copolymer containing covalently bonded pyrrolo[3,4-*c*]pyrrole-1,3-dione and benzothiadiazole for efficient polymer solar cells utilizing high energy sunlight

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ABSTRACT

A new electron deficient monomer (PDBT) unit incorporating a weak electron accepting unit, pyrrolo[3,4-*c*]pyrrole-1,3-dione (DPPD), and a strong electron accepting unit, 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (BT), with a configuration of DPPD-BT-DPPD was prepared, and copolymerized with a benzodithiophene (BDTT) derivative to afford a new alternating ternary copolymer P(BDTT-PDBT). The estimated optical band gap (E_g) and highest occupied/lowest unoccupied (HOMO/LUMO) molecular orbital energy levels of P(BDTT-PDBT) were 1.72 eV and −5.45 eV/−3.62 eV, respectively. A field effect transistor made from P(BDTT-PDBT) exhibited a hole mobility of 3.2×10^{-3} cm^2 V^{-1} s^{-1}. Conventional single layer polymer solar cells (PSCs) prepared using P(BDTT-PDBT) with an additive offered a maximum power conversion efficiency (*PCE*) of 5.73% with an open-circuit voltage (V_{oc}) of 0.90 V, a short-circuit current (J_{sc}) of 9.73 mA/cm^2, and a fill factor (*FF*) of 0.66. Interestingly, the PSC device prepared without an additive also showed a similar *PCE* of 4.84% (V_{oc} ~ 0.92 V, J_{sc} ~ 8.08 mA/cm^2, and FF ~ 0.65). This paper reports the preparation of an efficient ternary copolymer for polymer solar cells utilizing high energy sunlight, as well as the property modulation of an alternating binary copolymer, P(BDTT-DPPD), containing BDTT and DPPD derivatives via the insertion of a strong electron accepting BT unit on the P(BDTT-DPPD) backbone.

1. Introduction

The crucial advantages of polymer solar cells (PSCs), such as high solar to electrical energy conversion efficiency, light weight, low cost for large area device fabrication, and solution processability make PSCs an efficient solar to electrical energy conversion technique [1–10]. The continuous improvement in the power conversion efficiency (*PCE*) of polymer solar cells (PSCs) is essential for reducing the cost of electricity in terms of dollars per kilowatt-hour. Over the last decade, many novel structured π–conjugated polymers [11–14] and fullerene derivatives [15] were reported for polymer solar cells (PSCs) with the aim of improving the performances of PSCs. These efforts have rapidly enhanced the *PCE* of PSCs up to 11% [1–15]. Earlier reports confirmed that the π–conjugated polymers and fullerene derivatives used in the photovoltaic layer of PSCs are the most crucial factors for determining the photovoltaic performances of PSCs, and the small structural changes in polymers or fullerene derivatives induce a large difference in their photovoltaic performances [11–15]. In this regard, the authors have focused on the preparation of efficient polymeric donor materials for PSCs. Recently, pyrrole-based, imide-functionalized novel electron accepting pyrrolo [3,4-*c*]pyrrole-1,3-dione (DPPD) derivatives were developed for the preparation of high energy converting wide band gap polymeric donor materials for PSCs [16–22]. The DPPD-based wide band gap (E_g ~ 2.04 eV) donor-acceptor (D-A) alternating binary copolymer, P(BDTT-DPPD), containing a benzodithiophene (BDTT) derivative displayed an

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impressive photovoltaic performance (*PCE* ~ 6.57%) [17]. Nevertheless, the wide band gap of P(BDTT-DPPD) limits the light harvesting ability of PSCs, resulting in a relatively lower short-circuit current (J_{sc} ~ 10.12 mA/cm^2) [17].

In general, low band gap (E_g ~ 1.7–1.4 eV) polymers are superior candidates to wide band gap polymers for PSCs because the absorption ability of the polymers is directly proportional to the short-circuit current (J_{sc}) of their corresponding PSCs [1–10]. Many low band gap polymers reported previously exhibited higher short-circuit currents (~20 mA/cm^2) and impressive photovoltaic performances (PCE ~ 10–11%) [1–10]. To enhance the J_{sc} of DPPD-based wide band binary copolymers, relatively strong electron deficient units have been inserted randomly into the copolymer backbones [23–27]. As expected, DPPD-based ternary copolymers exhibited a broader absorption band and lower band gap than those of their corresponding alternating polymers [23–27], and offered a relatively higher J_{sc}. On the other hand, the random insertion of second electron acceptor units decreased the overall photovoltaic performances slightly due mainly to the lower V_{oc} and *FF* [23–27]. A recent study showed that the alternate arrangement of two different electron acceptor units is favourable for obtaining high photovoltaic performances compared to that of the random arrangement [28]. In this instance, the alternate incorporation of strong electron accepting units on the backbone of P(BDTT-DPPD) is expected to offer a high energy converting ternary copolymer for PSCs. Therefore, in this study, a new electron deficient monomer (PDBT) unit containing covalently bonded pyrrolo [3,4-*c*]pyrrole-1,3-dione (DPPD) and 4,7-di(thiophen-2-yl)benzo[c] [1,2,5]thiadiazole (BT) derivatives with a configuration of DPPD-BT-DPPD was prepared, and copolymerized with a BDTT derivative to afford a new alternating ternary copolymer, P(BDTT-PDBT). BT was chosen as a strong electron acceptor unit because it is the most promising electron acceptor unit for the preparation of high energy converting low band gap polymers for PSCs [1–3,8]. Note that the maximum *PCE* of BT-based alternating copolymer was 11.7%, which is the highest value reported for PSCs thus far [1–3,8]. The opto-electrical, charge transport, and photovoltaic properties of P(BDTT-PDBT) were studied and compared with those of P(BDTT-DPPD) to understand the property modulation originated from the insertion of a BT unit.

2. Experimental section

2.1. Materials and measurements

The reagents were obtained from Sigma-Aldrich. The compounds prepared in this study were purified by column chromatography (silica gel, Merck Kieselgel 60, 70–230 mesh ASTM). The nuclear magnetic resonance (NMR) spectra of the compounds and polymers were recorded on a Varian Mercury Plus spectrometer (300 MHz for ^{1}H and 75 MHz for ^{13}C). The high resolution fast atom bombardment (FAB) mass spectra of the compounds were analyzed using a JEOL JMS-700 mass spectrometer. An Agilent 1200 Infinity Series separation module was used to determine the molecular weights of the polymer using gel permeation chromatography (GPC) with chloroform as an eluent at ambient temperature. The GPC instrument was calibrated with the polystyrene standard prior to analysis. The UV-visible absorption spectra of the polymer in the solution and film states were recorded on a JASCO V-570 spectrophotometer, and a CH Instruments Electrochemical Analyzer was used for cyclic voltammetry (CV) of the polymer. The polymer cast film on the platinum working electrode was immersed in an acetonitrile solution containing 0.1 M tetrabutylammonium tetrafluoroborate (Bu_4NBF_4), Ag/AgCl as the reference electrode and platinum wire as the counter electrode, and the measurements were then performed. Before starting CV analysis, the instrument was calibrated with the most common ferrocene/ferrocenium ion (Fc/Fc^+) standard. Atomic force microscopy (AFM) was performed using a Seiko instruments SPI 3800N-SPA 400.

2.2. Device fabrication and characterization of OTFTs

The organic field effect transistors (OFETs) were fabricated on highly n-type-doped silicon (Si) substrates with a 200 nm layer of thermally grown silicon oxide (SiO_2). The Si substrates were subjected to an UV-ozone treatment for 30 min for activation and then treated with an octadecyltrichlorosilane (OTS) self-assembled monolayer. The n-type doped Si substrate functions as a gate electrode and the SiO_2 layer acts as a gate dielectric. The chlorobenzene (CB) solution of the polymer (8 mg/mL) was spin-cast on top of the Si substrate (2000 rpm) and dried at room temperature (RT) for 30 min. The source and drain electrodes (Au, 70 nm) were deposited on top of the polymer layer by thermal evaporation in a vacuum of approximately 2 × 10^{-6} Torr. The channel length (L) and channel width (W) of the device was 50 μm and 3.0 mm, respectively. The output and transfer characteristics of the OFETs were measured using a Keithley semiconductor parametric analyzer (Keithley 4200). All preparation processes and the characterization of the OFETs were performed inside a N_2-atmosphere glove box. The mobility (μ) was determined using the following equation in the saturation regime:

$$I_{DS,sat} = \mu(WC_i/2L)(V_{GS} - V_T)^2$$

where C_i is the capacitance per unit area of the SiO_2 dielectric ($C_i = 15$ nF cm^{-2}) and V_T is the threshold voltage.

2.3. Device fabrication and characterization of PSCs

The PSCs were fabricated with the simple device structure of ITO-coated glass substrate/PEDOT:PSS/polymer:$PC_{70}BM$/Al. The pre-cleaned ITO-coated glass substrate was dried overnight in an oven. A 40 nm thick layer of PEDOT:PSS (Baytron PH) was spin-cast from an aqueous solution onto an ITO-coated glass substrate. The substrate was dried for 10 min at 140 °C in air and then transferred to a glove box to spin-cast the photoactive layer. A solution containing a mixture of P(BDTT-PDBT):$PC_{70}BM$ (at various ratios) in dichlorobenzene (DCB) with various total concentrations were then spin-cast (at different speed) on top of the PEDOT/PSS layer. In the case of a photoactive layer prepared with the additive materials, 1,8-diiodooctane (DIO) was added as an additive to the solution of the P(BDTT-PDBT):$PC_{70}BM$ in DCB with a volume ratio of 97:3 (DCB: DIO). The film was then dried for 30 min at RT in a glove box. Subsequently, an aluminum (Al, 100 nm) electrode was deposited by thermal evaporation in a vacuum of approximately 3 × 10^{-6} Torr. The current density-voltage (*J–V*) characteristics of the PSC devices were measured using a Keithley 2400 Source Measure Unit. The solar cell performance was determined using an Air Mass 1.5 Global (AM 1.5 G) solar simulator with an irradiation intensity of 1000 W m^{-2}. The spectral mismatch factor was calculated by comparing the solar simulator spectrum with the AM 1.5 spectrum at RT.

2.4. Synthesis of polymers

2.4.1. Synthesis of diethyl 2-(5-bromothiophen-2-yl)-1-octyl-5-(thiophen-2-yl)-1H-pyrrole-3,4-dicarboxylate (2)

To a stirred solution of diethyl 1-octyl-2,5-di(thiophen-2-yl)-1*H*-pyrrole-3,4-dicarboxylate (4.30 g, 8.80 mmol), which was prepared using the reported procedures, [17,20] in 40 mL of