A facile method for enhancing photovoltaic performance of low-band-gap D–A conjugated polymer for OPVs by controlling the chemical structure

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ABSTRACT

Stille coupling polymerization has been used to synthesize a series of new crystalline conjugated polymers with low-lying HOMO level: PABToBT, PPDToBT, PQTDPT. All of these polymers exhibited sufficient energy offsets with respect to those of fullerenes to allow efficient charge transfer and low-lying highest occupied molecular orbital (HOMO), from -5.04 to -5.27 eV. As a result, the photovoltaic device comprising a PPDToBT/$PC_{71}BM$ (1:4) blend system exhibited excellent performance, under AM1.5 G irradiation, with a V_{OC} of 0.878 V, a J_{SC} of 8.7 mA cm^{-2}, a FF of 0.51, and a promising PCE of 3.9%.

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Introduction

For the past several decades, aromatic ring-based conjugated polymers have been applied in the fabrication of various electronic devices, such as organic light-emitting diodes (OLEDs) [1–4], organic thin-film transistors (OTFTs) [5–7], and organic photovoltaic cells (OPVs) [8–12]. In particular, polymer solar cells (PSCs) with a bulk heterojunction (BHJ) structure in which a π-conjugated polymer donor and soluble fullerene derivative acceptors are combined have recently attracted a much attention due to advantages such as low cost, light weight, and flexibility [13–15].

Regio-regular poly(3-hexylthiophene) (P3HT) is a leading polymer donor for use in PSCs, whereas [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) is the most widely used acceptor. P3HT/PCBM-based devices with a power conversion efficiency (PCE) of up to 4–5% have been reported [16,17]. The PCE of the P3HT/PCBM system does not increase any further for the following reasons. First, the relatively large band gap (1.9 eV) of P3HT disturbs the effective light harvesting of photovoltaics [18,19]. Second, the low energy difference of the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) levels

causes P3HT/PCBM-based PSCs to have a low open-circuit voltage (V_{OC}, ~0.6 V) [20]. Recently, there has been demand for a polymer photovoltaic donor material with a low band gap and low HOMO energy level to facilitate the improvement of PSC efficiency [21–26]. Because the V_{OC} is determined by the difference between the HOMO (donor) and LUMO (acceptor) levels, it is a key factor in reducing the HOMO level of a donor polymer. A donor polymer with a low HOMO energy level not only allows for a higher V_{OC} but also results in high oxidative stability. Moreover, because durability is of great concern for industrial applications, the stability of materials in the field of organic electronics is regarded as an important property of organic semiconductors [27].

The synthesis of conjugated polymers intended to fabricate a polymer solar cell device with a high light-harvesting ability (low band gap) and open-circuit voltage is still dependent on the concept of donor–acceptor (D–A) alternate copolymers [28] because an electron donor unit can provide a low HOMO level and an electron acceptor unit can regulate the electronic band gap of a polymer. Several studies have reported using this approach on benzothiadiazole and various alkyl thiophene unit-based copolymers [29,30]. Among the derivatives with a low HOMO energy level, fused thiophene rings have a higher resonance stabilization energy than single thiophene molecules, which in turn reduces the HOMO energy level of the resulting copolymer [31,32]. In the polythiophene derivatives in which fused thiophene is introduced into the backbone, high molecular ordering characteristics and

high charge-carrier mobility have also been observed due to the planarity and rotational invariance of the thienothiophene unit [33]. As a way to obtain a larger absorption region by decreasing the band gap, the acceptor unit responsible for the electron-withdrawing properties of a copolymer could be introduced to the main chain of the polymer to yield a D–A-type polymer. 2,1,3-Benzothiadiazole (BT) and di-2-thienyl-2,1,3-benzothiadiazole (DTBT) are known as common strong electron acceptors. Recently, many studies have been published on how to improve the characteristics of OPVs by introducing DTBT. However, DTBT has a strong stacking ability due to its constituent thiophene units. As a result, synthesized polymers have low solubility and low molecular weight.

Heiser et al. reported the synthesis of a PTBzT-series polymer using thienothiophene and DTBT. Even though an attempt was made to increase the solubility and the degree of polymerization of the polymer via the introduction of a dodecyl chain to the thiophene spacer, the molecular weight (M_n, the number average molecular weight) and V_{OC} were as low as 12,000–16,000 and 0.55–0.67 V, respectively [34]. Since this time, the HOMO level has been reduced to as low as −5.43 eV by increasing the number of dodecyl thiophene units in the molecular structure. In contrast, the V_{OC} has remained at 0.79 V. With a decrease in FF after a morphology decline, PCE remained at 1.8% [28]. Therefore, studies have been reported in which the molecular weight increased when using DTBT derivatives with a side chain introduced; such polymers have been observed to exhibit good solubility [35–42]. A previous study reported results on the use of thienothiophene derivatives as a donor and quinoxaline derivatives with high solubility instead of DTBT as an acceptor. When pentadecyl thienothiophene instead of thienothiophene was introduced, a very low HOMO level was observed (−5.6 eV). Due to the steric hindrance and tilt caused by a long and bulky pentadecyl chain, however, low polymerization and a large band gap were found. PQTPDTT, to which a thiophene spacer was introduced, showed a relatively high V_{OC} (0.71 V) and low band gap (1.7 eV), and the best PCE obtained was 2.27% [31].

In this study, alkyl bithiophene and alkyl thienothiopehene were used as electron-donating units and DTBT moieties were used as the building blocks of an alternate copolymer to apply the band-gap-narrowing concept and thereby stabilize the HOMO level and obtain strong intermolecular π–π interaction. To compensate for the low solubility of DTBT, an alkoxy side chain was introduced into the benzothiadiazole core. The structure–property relationships caused by the difference between the bithiophene and fused thiophene donor molecules were investigated. To examine changes in the molecular energy level for different types of acceptor units, the acceptor units were compared using PQTPDTT, a polymer in which quinoxaline was used as an acceptor, by referring to previous studies. The synthesized DA-type polymers exhibited good crystallinity and low HOMO energy levels. In the synthesized polymer, PCE and V_{OC} were observed to increase to up to 3.9% and 0.878 V, respectively.

Experimental

Measurement and characterization

All reagents and chemicals were purchased from Aldrich and used as received unless otherwise specified. 4,7-Bis(5-bromothio-phen-2-yl)-5,6-bis(octyloxy)-2,1,3-benzothiadiazole (A1) [43], 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(4-(hexyloxy)phenyl)-6,7-bis(octyloxy)quinoxaline (A2), 4,4′-didodecyl-5-trimethylstannyl-2,2′-bithiophene (D1) [44], and 2,5-bis(trimethylstannyl)-3,6-dipentadecylthieno[3,2-b]thiophene (D2) [31] were prepared according to methods reported in the literature.

^{1}H NMR (400 MHz) spectra were recorded with a Bruker AMX400 spectrometer, using the resonances of the solvent as an internal reference. Chemical shifts (δ) are reported in ppm downfield from TMS. Absorption spectra were recorded on an Agilent 8453 UV–vis spectroscopy system. Photoluminescence (PL) spectra were measured using a Hitachi F-4500 spectrophotometer. The molecular weights of the polymers were measured using the GPC method with polystyrene standards. TGA measurements were performed on a TA Instruments 2050 analyzer. Electrochemical cyclic voltammetry was performed using a Zahner IM 6e electrochemical workstation with 0.1 M Bu_4NPF_6 in acetonitrile as the electrolyte. ITO glass coated with a thin polymer film was used as the working electrode, and a Pt wire and an Ag/Ag$^+$ electrode were used as the counter and reference electrodes, respectively. The electrochemical potential was calibrated against Fc/Fc$^+$. Current–voltage (I–V) curves of the PSC devices were measured using a computer-controlled Keithley 2400 source measurement unit (SMU) equipped with a Peccell solar simulator under AM1.5G illumination (100 mW cm^{-2}). The illumination intensity was calibrated using a standard Si photodiode detector equipped with a KG-5 filter. The output photocurrent was adjusted to match the photocurrent of the Si reference cell to obtain a power density of 100 mW cm^{-2}. The rated efficiency of 3.5% was measured with a P3HT/PC$_{61}$BM reference cell under illumination and verified to be 3.4% under AM1.5G illumination (100 mW cm^{-2}) at Konkuk University (Korea). After encapsulation, all devices were operated under ambient atmospheric conditions at 25 °C.

Photovoltaic cell fabrication and treatment

All bulk heterojunction PV cells were prepared using the following device fabrication procedure. Glass/indium tin oxide (ITO) substrates [Sanyo, Japan (10 Ω/γ)] were sequentially patterned lithographically, cleaned with detergent, ultrasonicated in deionized water, acetone, and isopropyl alcohol, dried on a hot plate at 120 °C for 10 min, and treated with oxygen plasma for 10 min to improve the contact angle just before film coating. Poly(3,4-ethylene-dioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS, Baytron P 4083 Bayer AG) was passed through a 0.45-mm filter before being deposited on ITO at a thickness of approximately 32 nm by spin-coating at 4000 rpm in air and then dried at 120 °C for 20 min inside a glove box. A blend of 1-(3-methoxycarbonyl)-propyl-1-phenyl-[6,6]-C71 (PC$_{71}$BM) and the polymer [1:2 (w/w), 1:3 (w/w), 1:4 (w/w)] at a concentration of 7.5 mg mL^{-1} in chlorobenzene was stirred overnight, filtered through a 0.2-mm poly(tetrafluoroethylene) (PTFE) filter, and then spin-coated (500–3000 rpm, 30 s) on top of the PEDOT:PSS layer. The device was completed by depositing thin layers of BaF$_2$ (1 nm) and Ba (2 nm) as an electron injection cathode, followed by the deposition of a 200-nm-thick aluminum layer at pressures below 10^{-6} torr. The active area of the device was 4 mm^2. Lastly, the cell was encapsulated using UV-curing glue (Nagase, Japan).

Hole-only devices were fabricated with a diode configuration of ITO(170 nm)/PEDOT:PSS (40 nm)/PQCQT:PC$_{71}$BM(50 nm)/MoO$_3$(30 nm)/Al(100 nm). The hole mobility of the active layers was calculated from the SCLC using the J–V curves of the hole-only devices measured in the dark as follows:

$$J = \frac{9}{8}\epsilon\epsilon_0\mu_{h(e)}\frac{V^2}{L^3}\exp\left(0.89\gamma\sqrt{\frac{V}{L}}\right)$$

where ε_0 is the permittivity of free space (8.85×10^{-14} F cm^{-1}); ε is the dielectric constant (assumed to be 3, which is a typical value for conjugated polymers) of the polymer; μ is the zero-field mobility of holes (electrons); L is the film thickness; and