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A diketopyrrolopyrrole-based regular terpolymer bearing two different π-extended donor units and its application in solar cells

Sang Beom Kim, Hyun Ah Um, Hyung Jong Kim, Min Ju Cho**, Dong Hoon Choi*

Department of Chemistry, Research Institute for Natural Sciences, Korea University, 5 Anam-dong, Sungbuk-gu, Seoul 136-701, Republic of Korea

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ABSTRACT

In this study, to adjust the desired molecular energy levels and bandgap energies of polymers for photovoltaic applications, a regular terpolymer structure was designed. A new regular terpolymer, poly(DPP4T-*alt*-TBP), containing diketopyrrolopyrrole (DPP), BT, and BP units in the repeating group was successfully synthesized. The DPP-BT monomeric unit in polymer backbone enhanced chain packing and induced a high-lying highest occupied molecular orbital (HOMO) level and the DPP-BP segment induced a deeper HOMO level. The lowest unoccupied molecular orbital (LUMO) level of the terpolymer was also controlled in a similar manner. The HOMO level of the terpolymer was similar to that of poly(DPP-*alt*-BP), and the energies of the LUMOs were governed by the DPP-BT unit. The polymer chain arrangement of the terpolymer on the substrate was observed to be a mix of face-on and edge-on orientations, which is a different chain arrangement mode to those shown in both poly(DPP-*alt*-BP) and poly(DPP-*alt*-BT). A TFT fabricated with poly(DPP4T-*alt*-TBP) had a charge carrier mobility of 0.59 $cm^2 V^{-1} s^{-1}$ and a moderately high current on/off ratio. Furthermore, a polymer solar cell containing the terpolymer and $PC_{71}BM$ had a power conversion efficiency of 4.54%, which is significantly higher than those of the PCEs of poly(DPP-*alt*-BP) and poly(DPP-*alt*-BT)-based solar cells with identical device configurations.

1. Introduction

The semiconducting properties and synthesis of donor-acceptor type conjugated polymers have been extensively studied to investigate their potential for use in practical electronic and optoelectronic devices. In particular, polymer solar cells have attracted attention because of their low manufacturing costs, easy fabrication, and flexibility [1,2]. A number of studies have been conducted to improve the power conversion efficiency (PCE) of polymer solar cells (PSCs) [1,2].

Most conjugated polymers with high PCEs contain an electron deficient moiety and an electron rich moiety, the so called donor-acceptor (D-A) structure [3–9]. D-A structured polymers bearing properly selected donors and acceptors in the polymer backbone have small bandgap energies, which results in broad absorbance in the visible and near IR regions. Intrinsic molecular energy levels of the conjugated polymers depend on those of the donor and acceptor moieties of the repeating unit. Moreover, the open circuit voltage (V_{oc}) of the photovoltaic cell is mainly related to the HOMO level of the host conjugated polymer that is blended with a fullerene derivative. By controlling the energy levels of the polymer using suitable donor and acceptor moieties, a desirable high open-circuit voltage can be obtained.

When conjugated polymers are blended with fullerene derivatives in the photoactive layer, bulk heterojunctions (BHJ) are formed under appropriate photodiode device configurations [10]. In this configuration, excitons are separated more efficiently, yielding holes and electrons at the enlarged interface between these oppositely charged electronic components, leading to improvement in the photovoltaic properties of the device [11]. In the BHJ system, device performance depends on the morphology of the blended film, and conjugated polymers require moderate miscibility with phenyl C_{71}-butyric acid methylester ($PC_{71}BM$) or phenyl C_{61}-butyric acid methylester ($PC_{61}BM$)) [12–15]. However, precise control over the molecular packing of D-A polymers with the fullerene derivatives is limited because the polymer chains self-associate, resulting in segregation from the fullerene derivatives. To overcome this limitation, a new concept in the design of conjugated polymers is required.

* Corresponding author.
** Corresponding author.
E-mail addresses: chominju@korea.ac.kr (M.J. Cho), dhchoi8803@korea.ac.kr (D.H. Choi).

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Conjugated terpolymers composed of three different monomers in a repeating unit have been proposed to give versatility to polymer design [16]. In a binary D-A conjugated polymer, the molecular energy levels (i.e., HOMO and LUMO) and bandgap cannot be controlled by changing only the acceptor or donor. Unfortunately, there are few studies indicating how the design of polymer structure using single acceptor and donor monomers can simultaneously decrease the LUMO level and increase HOMO level.

Introduction of three different monomeric units into the polymer backbone broadened the absorption range of the synthesized polymer, which increased the light harvesting efficiency of the solar cell. Appropriate combination of the monomer components with different electron affinities provided an opportunity to control the molecular energy levels of the final conjugated terpolymers. These properties of the terpolymers affect the performance of optoelectronic devices such as solar cells.

Kim et al. synthesized a series of random conjugated terpolymers bearing electron-deficient diketopyrrolopyrrole (DPP)-based units connected to two electron-rich selenophene and thiophene units. By employing a terpolymer composed of two electron donating groups under an optimized molar feeding ratio, the corresponding photovoltaic cells showed improved performance [17]. Zhang et al. combined two electron deficient DPP moieties and an isoindigo (IIG) moiety with electron-rich alkylthienyl substituted benzodithiophene (BDTT) moieties to prepare random terpolymers. Among the terpolymers reported in the literature, a solar cell fabricated with the terpolymer P5 (DPP:IIG = 1:1 M ratio) had the highest PCE of several other PV cells composed of D-A copolymers [18]. Although the properties of random terpolymers can be controlled by varying the stoichiometry of the mixing monomeric units [17–25], random terpolymers lack uniformity in composition and reproducibility.

In contrast, other than random terpolymers, the same monomer sequence can be observed throughout the chain of a regular terpolymer. Janssen et al. proposed an unusual synthetic route for regular terpolymers comprising DPP-based units and electron donating terthiophene and thiophene-phenylene-thiophene (TPT) moieties in a regular, alternating fashion [27]. Wang et al. investigated the advantages of the regular terpolymer (PTQTI), comparing it with random terpolymer (PTQTI-R) and copolymers (e.g., TQ-1 and PTI-1). The PCE of the regular terpolymer-based solar cell was found to be higher than that of a PSC made of a D-A binary copolymer [23]. Although the previously mentioned investigations have proposed several terpolymers to improve the performance of PSCs, only a few studies have been carried out investigating their physical, electronic, and optoelectronic properties [26–32].

In this work, a new, regular terpolymer, poly(DPP4T-*alt*-TBP)-containing BT and BP in the polymer backbone was designed and synthesized. Because the DPP-BT segment affects molecular packing and induces a high-energy HOMO, a DPP-BP segment with a low-lying HOMO level was used to tune the molecular energy levels. For precise comparison of the properties and for investigating the effect of terpolymer structure, poly(DPP-*alt*-BT) and poly(DPP-*alt*-BP) copolymers were also prepared and used as controls. The photophysical and electrochemical properties of these polymers were measured. We found that poly(DPP4T-*alt*-TBP) had finely tuned electrochemical parameters, and the polymer chains were oriented on the substrate in a mix of face-on and edge-on orientations on the substrate. A TFT fabricated with poly(DPP4T-*alt*-TBP) had a charge carrier mobility of 0.59 $cm^2\ V^{-1}\ s^{-1}$ with a moderately high current on/off ratio ($>10^5$), and the PSC composed of poly(DPP4T-*alt*-TBP) and $PC_{71}BM$ displayed a higher PCE (4.54%) than either the poly(DPP-*alt*-BP) or poly(DPP-*alt*-BT)-based solar cells with identical device configurations.

2. Experimental

2.1. Materials

All commercially available reagents and solvents were purchased from either Sigma Aldrich Chemical Co., Alfa Aesar Co., or Tokyo Chemical Industry Co. etc. and were used without additional purification. $PC_{71}BM$ was purchased from Nano-C (Westwood, MA, USA). Compounds **1**, **2**, and **6** were synthesized using literature methods [34]. Copolymers poly(DPP-*alt*-BP) and poly(DPP-*alt*-BT) were also prepared according to literature methods [34,35].

2.2. Synthesis

Synthesis of 6,6′-(5,5′-(bithiophene-2,2-diyl)bis(thiophene-5,2-diyl))bis(2,5-bis(2-decyltetradecyl)-3-(thiophen-2-yl)pyrrolo[3,4-c]-pyrrole-1,4(2H,5H)-dione) (T2(TDPP)$_2$, 3). 3-(5-Bromothiophen-2-yl)-2,5-bis(2-decyltetradecyl)-6-(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (1.10 g, 1.05 mmol) was dissolved in toluene (30 mL). To this solution, 5,5′-bis(trimethylstannyl)-2,2′-bithophene (228 mg, 523 μmol) was added, and the solution was stirred under an N_2 atmosphere. 5 mol% of tetrakis(triphenylphosphine) palladium (0) (34 mg, 29.2 μmol) was added to the reaction mixture, and the solution was heated to 100 °C under an N_2 atmosphere for 12 h. After cooling the reaction mixture, methanol was added to precipitate the product. Then, the crude product was purified by silica-gel column chromatography (eluent: dichloromethane and hexane (3:2 v/v)). Yield: 69% (763 mg) ^{1}H NMR ($CDCl_3$, 300 MHz): *δ(ppm)* 8.90 (d, J = 3.0 Hz, 4H), 7.61 (s, 2H), 7.32 (t, J = 3.0 Hz, 4H), 7.18 (d, J = 3.0 Hz, 2H), 7.13 (d, J = 3.0 Hz, 2H), 3.99–4.05 (m, 8H), 1.92 (m, 4H), 0.85–1.56 (m, 184H). Elemental Anal. Calcd for ($C_{132}H_{210}N_4O_4S_6$): C, 75.16; H, 10.03; N, 2.66; S, 9.12; Found: C, 75.2; H, 10.0; N, 2.67; S, 9.13.

Synthesis of 6,6′-(5,5′-(bithiophene-2,2-diyl)bis(thiophene-5,2-diyl))bis(2,5-bis(2-decyltetradecyl)-3-(thiophen-2-yl)pyrrolo[3,4-c]-pyrrole-1,4(2H,5H)-dione) (QT(BrTDPP)$_2$, 4). **3** (760 mg, 360 μmol) was dissolved in chloroform (40 mL) and, then, *N*-bromosuccinimide (141 mg, 793 μmol) was added to the mixture. The solution was stirred under an N_2 atmosphere for 6 h. Then, methanol was poured into the reaction mixture to cause precipitation. The crude product was purified by silica-gel column chromatography (eluent: dichlromethane/hexane, 3:2 v/v) and subsequently precipitated with methanol. Yield: 60% (487 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): *δ(ppm)* 8.90 (d, J = 4.0 Hz, 2H), 8.60 (d, J = 4.0 Hz, 2H), 7.21 (d, J = 4.0 Hz, 4H), 7.18 (d, J = 4.0 Hz, 2H), 7.14 (d, J = 4.0 Hz, 2H), 3.93–4.01 (m, 8H), 0.87–1.61 (m, 188H). Elemental Anal. Calcd for ($C_{132}H_{208}Br_2N_4O_4S_6$): C, 69.93; H, 9.25; Br, 7.05; N, 2.47; S, 8.49; Found: C, 70.03; H, 9.26; Br, 7.07; N, 2.51; S, 8.51.

Synthesis of poly(DPP4T-alt-TBP). Monomer **4** (230 mg, 0.1 mmol) and 1,3,2-dioxaborolane, 2,2′-[1,1′-biphenyl]-4,4′-diylbis[4,4,5,5-tetramethyl] (40 mg, 0.1 mmol) were dissolved in distilled toluene (15 mL) and 2 M K_2CO_3 (5 ml). The solution was degassed with nitrogen for 10 min and then $Pd_2(dba)_3$ (9.15 mg, 10 μmol), poly(*o*-tolyl)$_3$ (6.08 mg, 20 μmol), and a few drops of Aliquat 336 were added to the reaction mixture. The reaction was then stirred at 100 °C for 2 h under a nitrogen atmosphere. Subsequently, the solution was poured into methanol to precipitate the product polymer. Then, Soxhlet extraction was performed on the precipitate, using acetone, hexane, and chloroform, successively. The concentrated chloroform fraction was precipitated in methanol and filtered to yield poly(DDP4T-*alt*-TBP) as a dark purple solid. Yield: 75.18% (200 mg). (M_n = 150.3 kDa, PDI = 2.03). Elemental Anal. Calcd for ($C_{142}H_{214}N_4O_4S_6$) C, 76.36; H, 9.66; N, 2.51; S, 8.61; Found: C, 76.53; H, 9.74; N, 2.52; S, 8.58.