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# Enhanced photocurrent generation by high molecular weight random copolymer consisting of benzothiadiazole and quinoxaline as donor materials

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We synthesized organic photovoltaic materials that have high molecular weight and good solubility. A new random copolymer named poly[carbazole-co-dithienylbenzothiadiazole-co-dithienylquinoxaline] (PC-TBT-TQ) was polymerized through the Suzuki coupling reaction. PC-TBT-TQ was dissolved in a common organic solvent, and its $M_n$ indicates a high molecular weight of 216.2 kg/mol. According to the result of thermal analysis, very high thermal stability was observed, with an approximately 5 wt% weight loss at 440 °C. The optical band gap of PC-TBT-TQ (1.89 eV) is slightly higher than that of PCDTBT (1.87 eV). The HOMO and LUMO levels of PC-TBT-TQ (HOMO level: 5.45 eV, LUMO level: 3.56 eV) are similar to those of PCDTBT (HOMO level: 5.45 eV, LUMO level: 3.58 eV). The OPV properties of the polymer were assessed by fabricating bulk-heterojunction polymer solar cells in the ITO/PEDOT:PSS/active-layer/$BaF_2$/Ba/Al structure. When PC-TBT-TQ and $PC_{71}BM$ were fabricated in a 1:4 ratio, the open-circuit voltage ($V_{OC}$), short-circuit current ($J_{SC}$), fill factor (FF) and power conversion efficiency (PCE) were 0.83 V, 9.5 mA/cm$^2$, 43.3% and 3.5%, respectively.

## 1. Introduction

For decades, semiconducting polymers have been studied in various fields, including organic light-emitting diodes (OLEDs) [1–3], organic photovoltaic cells (OPVs) [4–10] and organic thin-film transistors (OTFTs) [11,12]. In these applications, OPVs have been in the spotlight as a trending global technology due to their economic efficiency and ability to facilitate sustainable development without environmental destruction. Nevertheless, low power conversion efficiency (PCE) has been the greatest barrier to OPV applications [5].

To improve the PCE, the following ideal conditions should be met in a conjugated polymer: (1) low band gap with a broad light-absorption range, (2) crystal structure for good charge transport, (3) low HOMO energy level to obtain a high open-circuit voltage ($V_{OC}$) and (4) high molecular weight to improve the photocurrent.

Studies on the improvement of the photocurrent by creating polymers with high molecular weight have recently been reported [13,14]. The higher the molecular weight of a polymer is, the longer its conjugation length becomes. Therefore, more photons can be absorbed and thus higher photocurrent can be generated. In other words, it is necessary to introduce derivatives with good solubility when the molecular structure of a polymer is designed to have a high molecular weight.

Over the past few years, donor–acceptor (D–A)-type low-band-gap polymers have drawn great attention because their electronic properties can be easily modified through their unique bonding properties and their absorption range can be increased to capture long wavelengths of light. D–A polymers exhibit a wide range of molecular weights depending on the solubility of the acceptor.

The quinoxaline derivative, which contains electron-withdrawing nitrogen atoms, is highly electron-deficient and thus serves as an efficient electron acceptor; therefore, it easily forms intramolecular charge transfer (ICT) complexes with other donor components [15,16]. In addition, the quinoxaline derivative can have high solubility and be easily transformed structurally. Its electronic properties can also be modified by adding various substituents [17,18].

In this study, a polymer with a high molecular weight named poly[carbazole-co-dithienylbenzothiadiazole-co-dithienylquinoxaline] (PC-TBT-TQ) was polymerized by introducing quinoxaline (an acceptor unit with high solubility) and benzothiadiazole (an acceptor unit with high absorbance). To increase the solubility of the *n*-type polymer and stabilize excitons created by resonance effects in molecules, hexyloxybenzene was introduced into the quinoxaline unit [16]. In addition, the optical and electrochemical properties as a function of molecular weight were analyzed comparatively by polymerizing the well-known poly[carbazole-benzothiadiazole] (PCDTBT). The photovoltaic conversion efficiencies

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of PCDTBT and PC-TBT-TQ were compared by fabricating a bulk-heterojunction device using $PC_{71}BM$ (3′H-cyclopropa[8,25][5,6]fullerene-C70-D5h(6)-3′-butanoic acid, 3′-phenyl-, methyl ester).

## 2. Experimental section

### 2.1. Instruments and characterization

Unless otherwise specified, all reactions were carried out under a nitrogen atmosphere. Solvents were dried using standard procedures. All column chromatography was performed using silica gel (230–400 mesh, Merck) as the stationary phase. $^1$H–NMR spectra were measured on a Bruker ARX 400 spectrometer using solutions in $CDCl_3$, and chemical signatures were recorded in units of ppm with TMS as the internal standard. The elemental analyses were measured with an EA1112 using a CE Instrument. Electronic absorption spectra were measured in chloroform using an HP Agilent 8453 UV–vis spectrophotometer. Cyclic voltammetric curves were produced using a Zahner IM6eX electrochemical workstation with a 0.1 M acetonitrile (substituted with nitrogen for 20 min) solution containing tetrabutyl ammonium hexafluorophosphate ($Bu_4NPF_6$) as the electrolyte at a constant scan rate of 50 mV/s. ITO, a Pt wire and silver/silver chloride [Ag in 0.1 M KCl] were used as the working, counter and reference electrodes, respectively. The electrochemical potential was calibrated against $Fc/Fc^+$. The HOMO levels of the polymers were determined using the oxidation onset value. Onset potentials are the potential values obtained from the intersection of the two tangents drawn at the rising current and the baseline changing current of CV curves. TGA measurements were performed on a NETZSCH TG 209 F3 thermogravimetric analyzer. All GPC analyses were conducted using THF as the eluant and polystyrene standard as the reference. X-ray diffraction (XRD) patterns were obtained using a SmartLab diffractometer operated at 3 kW (40 kV 30 mA, Cu target, wavelength: 1.541871 ang), Rigaku, Japan. Topographic images of the active layers were obtained through atomic force microscopy (AFM) in tapping mode under ambient conditions using an XE-100 instrument.

### 2.2. Fabrication and characterization of polymer solar cells

All of the 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 and ultrasonicated in deionized water, acetone and isopropyl alcohol. The substrates were then dried on a hot plate at 120 °C for 10 min and treated with oxygen plasma for 10 min to improve the contact angle immediately before the film-coating process. Poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS, Baytron P 4083 Bayer AG) was passed through a 0.45-μm filter before being deposited onto ITO at a thickness of *ca.* 32 nm by spin-coating at 4000 rpm in air; it was then dried at 120 °C for 20 min inside a glove box. Composite solutions of the polymers and PCBM were prepared using 1,2-dichlorobenzene (DCB). The concentration was controlled adequately over a 0.5 wt% range, and the solutions were then filtered through a 0.45-μm PTFE filter and then spin-coated (500–2000 rpm, 30 s) on top of the PEDOT:PSS layer. Device fabrication was completed by depositing thin layers of $BaF_2$ (1 nm), Ba (2 nm) and Al (200 nm) at pressures below $10^{-6}$ Torr. The active area of the device was 4.0 mm$^2$. Finally, the cells were encapsulated using UV-curing glue (Nagase, Japan). In this study, all of the devices were fabricated with the following structure: ITO glass/PEDOT:PSS/polymer:PCBM/$BaF_2$/Ba/Al/encapsulation glass.

The illumination intensity was calibrated using a standard Si photodiode detector that was 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$^2$. After the encapsulation, all of the devices were operated under ambient atmosphere at 25 °C. The current–voltage (*I*–*V*) curves of the photovoltaic devices were measured using a computer-controlled Keithley 2400 source measurement unit (SMU) that was equipped with a Peccell solar simulator under AM 1.5 G (100 mW/cm$^2$) illumination. The thicknesses of the thin films were measured using a KLA Tencor Alpha-step 500 surface profilometer with an accuracy of 1 nm.

Hole-only devices were fabricated with a diode configuration of ITO (170 nm)/PEDOT:PSS (40 nm)/polymer:$PC_{71}BM$ (50 nm)/$MoO_3$ (30 nm)/Al (100 nm). The hole mobilities of the active layers were calculated from the SCLC using the *J*–*V* curves of the hole only devices in the dark as follows:

$$J=\frac{9}{8}\varepsilon_r\varepsilon_0\mu_{h(e)}\frac{V^2}{L^3}\exp\left(0.89\sqrt{\frac{V}{E_0L}}\right)$$

where $\varepsilon_0$ is the permittivity of free space ($8.85\times10^{-14}$ C/Vcm); $\varepsilon_r$ is the dielectric constant (assumed to be 3, which is a typical value for conjugated polymers) of the polymer; $\mu_{h(e)}$ is the zero-field mobility of holes (electrons); $L$ is the film thickness; and $V=V_{\text{appl}}-(V_r+V_{\text{bi}})$, where $V_{\text{appl}}$ is the voltage applied to the device, $V_r$ is the voltage drop due to series resistance across the electrodes and $V_{\text{bi}}$ is the built-in voltage.

### 2.3. Materials

All reagents were purchased from Aldrich, Acros or TCI. All chemicals were used without further purification. The following compounds were synthesized following modified literature procedures: 4,7-bis(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole (M2) [17], 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(4-(hexyloxy)phenyl)quinoxaline (M3) [16].

#### 2.3.1. Poly[carbazole-co-dithienylbenzothiadiazole-co-dithienylquinoxaline] (PC-TBT-TQ)

9-(Heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (M1) (0.36 g, 0.55 mmol), 4,7-bis(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole(M2)(0.115 g,0.25 mmol), 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(4-(hexyloxy)phenyl)quinoxaline(M3)(0.201 g,0.25 mmol)$Pd(PPh_3)_4$(0)(0.017 g, 0.015 mmol) and aliquat336 were placed in a Schlenk tube, purged by performing three nitrogen/vacuum cycles and, under a nitrogen atmosphere, added with 2 M degassed aqueous $K_2CO_3$ (10 mL) and dry toluene (20 mL). The mixture was heated to 90 °C and stirred in the dark for 48 h. Following polymerization, the polymer was end-capped with bromothiophene. After quenching the reaction, the entire mixture was poured into methanol. The precipitate was filtered off and purified by Soxhlet extraction in the following order: methanol, acetone and chloroform. The polymer was recovered from the chloroform fraction and precipitated in methanol. The final product was obtained after drying in vacuum. Dark purple solid. (0.42 g, 41%) Anal. Calcd for $C_{114}H_{134}N_6O_2S_5$:C, 76.89; H, 7.59; N, 4.72; S, 9.00; O, 1.8. Found: C, 75.26; H, 7.40; N, 4.59; S, 8.85; O, 2.8.

## 3. Results and discussion

### 3.1. Material synthesis

As shown in Scheme 1, the polymer was polymerized through the Suzuki coupling reaction with molar ratios of 50%, 25% and 25%