



Conjugated polymer consisting of benzothiadiazole and phenazine as donor materials for organic photovoltaics



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ABSTRACT

Two new polymers, poly(thiophene-benzothiadiazole) (PThBT) and poly(thiophene-dibenzophenazine) (PThFQ), were successfully polymerized through a Stille coupling reaction. PThBT exhibited the formation of an ordered lamellar structure with conventional edge-on π -stacking. In contrast, the PThFQ backbones were oriented face-on relative to the substrate. For solar cells using a 1:6 ratio of PThFQ to PC₇₁BM, the resulting Voc, Jsc, FF and PCE were 0.73 V, 3.4 mA/cm², 30.5% and 0.76%, respectively. The value of the FF for PThFQ increased by 22% compared to PThBT due to the effects of the backbone planarity of the polymers and the face-on orientation.

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Introduction

For several decades, semiconducting polymers have been used in diverse applications, such as organic light emitting diodes (OLEDs) [1–3], organic photovoltaic cells (OPVs) [4–10] and organic thin film transistors (OTFTs) [11–13]. Of these applications, OPVs have garnered a great deal of attention due to the global technology trend toward economic feasibility and continuous development while preserving the environment. Low power conversion efficiency (PCE) has been the largest obstacle to the development of OPVs [6]. Over the past few years, donor–acceptor (D–A) type low-band gap polymers have attracted a lot of attention, as their electronic properties can easily be changed based on the unique combination of the D–A unit. These polymers can also exhibit broader absorption spectra to longer wavelengths compared to more traditional polymers.

Among the D–A polymer acceptor units, quinoxaline derivatives have been widely used due to the electron-withdrawing properties of their two imine nitrogens. Quinoxaline derivatives can easily be structurally deformed and exhibit high solubility. In addition, the quinoxaline derivatives exhibit electronic properties that can be changed with various substituents [14,15]. Recently, the Jen group reported that with the two phenyl rings connected to the single bond between the *ortho*-positions, the PCE of OPVs improved by 0.55% to achieve an efficiency of 6.24% [16]. These phenazine derivatives with fused-phenyl rings can enhance the efficiency through a reduction in the energetic disorder of the polymer after facilitating polymer coplanarity and interchain π – π interactions. In these phenazine derivatives, however, it is difficult to introduce the alkyl-chains necessary for the polymers to become highly soluble. Recently, we reported D–A polymers of quinoxaline and dibenzo-phenazine derivatives that introduced alkoxy-chains at the 6th and 7th or the 11th and 12th positions [17]. These dibenzo-phenazine derivatives exhibit high solubility and maintain the absorption spectrum and electronic properties of quinoxaline. In particular, the polymer of the alkoxy-dibenzo-phenazine derivative exhibited effective intra-molecular charge transfer (ICT) and coplanar properties.

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In this study, two new polymers, poly(thiophene-benzothiadiazole) (PThBT) and poly(thiophene-dibenzophenazine) (PThFQ), were successfully polymerized. Compared with PThBT, a more effective π - π interaction is expected for PThFQ because of the superior coplanarity properties of the fused-phenyl rings, which enables high FF in OPVs.

Experiment

Instruments and characterization

Unless otherwise specified, all reactions were performed under a nitrogen atmosphere. The solvents were dried using standard procedures. All of the column chromatography measurements were performed with silica gel (230–400 mesh, Merck) as the stationary phase. $^1\text{H-NMR}$ spectra were collected with a Bruker ARX 400 spectrometer using CDCl_3 solutions with chemical concentrations recorded in ppm units and with TMS as the internal standard. The elemental analyses were performed with an EA1112 apparatus using a CE Instrument. The electronic absorption spectra were measured in chloroform using an HP Agilent 8453 UV-vis spectrophotometer. The cyclic voltammetric waves were obtained using a Zahner IM6eX electrochemical workstation with a 0.1 M acetonitrile (purged 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. The onset potentials are the values obtained from the intersection of the two tangents drawn at the rising current and the baseline changing current of the CV curves. TGA measurements were performed on a NETZSCH TG 209 F3 thermogravimetric analyzer. All of the GPC analyses were performed using THF as an eluent and a polystyrene standard as a reference. X-ray diffraction (XRD) patterns were obtained using a SmartLab 3 kW (40 kV 30 mA, Cu target, wavelength: 1.541871 Å) instrument from 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. Theoretical analyses were performed using density functional theory (DFT), as approximated by the B3 LYP functional and employing the 6-31G* basis set in Gaussian09.

Fabrication and characterization of polymer solar cells

All of the bulk-heterojunction PV cells were prepared using the following device fabrication procedure. The glass/indium tin oxide (ITO) substrates [Sanyo, Japan ($10 \Omega/\gamma$)] were sequentially lithographically patterned, 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-ethylene-dioxythiophene): poly(styrene-sulfonate) (PEDOT:PSS, Baytron P 4083 Bayer AG) was passed through a 0.45 μm filter before being deposited onto the ITO substrates at a thickness of ca. 32 nm by spin-coating at 4000 rpm in air and then dried at 120 °C for 20 min inside a glove box. Composite solutions with polymers and PCBM were prepared using chlorobenzene (CB) with 1,8-diodooctane (DIO). The concentration was adequately controlled in the 0.3–0.5 wt% range. The solutions were then filtered through a 0.45 μm PTFE filter and spin-coated (500–2000 rpm, 30 s) on top of the PEDOT:PSS layer. The device fabrication was completed by

depositing thin layers of Al (200 nm) at pressures of less than 10^{-6} Torr. The active area of the devices was 4.0 mm^2 . Finally, the cell was encapsulated using a UV-curing glue (Nagase, Japan). In this study, all of the devices were fabricated with the following structure: ITO/glass/PEDOT:PSS/polymer:PCBM/Al/encapsulation glass.

The illumination intensity used to test the OPVs was calibrated using a standard a 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 an 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 an illumination of AM 1.5G (100 mW/cm^2). The thicknesses of the thin films were measured using a KLA Tencor Alpha-step 500 surface profilometer with an accuracy of 1 nm.

Materials and synthesis of the monomers

All reagents were purchased from Aldrich, Acros, or TCI. All of the chemicals were used without further purification. The following compounds were synthesized following modified literature procedures: 2,5-bis(trimethylstannyl)thiophene [7], 4,7-dibromo-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole (M1), 10,13-dibromo-11,12-bis(octyloxy)dibenzo[a,c]phenazine (M2) [17].

Polymerization

Poly[thiophene-alt-benzothiadiazole] (PThBT)

2,5-Bis(trimethylstannyl)thiophene (0.22 g, 0.54 mmol) and M1 (0.3 g, 0.54 mmol), $\text{Pd}(\text{PPh}_3)_4(0)$ (0.008 g, 0.007 mmol), were placed in a Schlenk tube, purged with three nitrogen/vacuum cycles, and under a nitrogen atmosphere, added to dry toluene (10 mL). The mixture was heated to 90 °C and stirred in the dark for 24 h. After the polymerization was completed, the polymer was end-capped with bromothiophene. After reaction quenching, the entire mixture was poured into methanol. The precipitate was filtered off and purified with a Soxhlet extraction in the following order: methanol, acetone and chloroform. The polymer was recovered from the chloroform fraction and precipitated into methanol. The final product was obtained after drying in vacuum. Dark red solid (0.19 g 74%). $^1\text{H NMR}$ (400 MHz; CDCl_3 ; Me_4Si): δ = 8.75–8.55 (m), 7.57–7.29 (m), 4.35–4.14 (m), 2.07–1.96 (m), 1.53–1.27 (m), 0.91–0.86 (m).

Poly[thiophene-alt-dibenzophenazine] (PThFQ)

2,5-Bis(trimethylstannyl)thiophene (0.17 g, 0.43 mmol) and M2 (0.3 g, 0.43 mmol), $\text{Pd}(\text{PPh}_3)_4(0)$ (0.008 g, 0.007 mmol), were placed in a Schlenk tube, purged with three nitrogen/vacuum cycles, and under a nitrogen atmosphere, added to dry toluene (10 mL). The mixture was heated to 90 °C and stirred in the dark for 24 h. After the polymerization was complete, the polymer was end-capped with bromothiophene. After reaction quenching, the entire mixture was poured into methanol. The precipitate was filtered off and purified with a Soxhlet extraction in the following order: methanol, acetone and chloroform. The polymer was recovered from the chloroform fraction and precipitated into methanol. The final product was obtained after drying under vacuum. Dark violet solid (0.13 g 48%). $^1\text{H NMR}$ (400 MHz; CDCl_3 ; Me_4Si): δ = 9.62–9.47 (m), 8.63–8.48 (m), 8.41–8.34 (m), 7.85–7.34 (m), 4.46–4.22 (m), 2.11–1.88 (m), 1.46–1.17 (m), 0.96–0.76 (m).

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