Synthesis, Properties, and Photovoltaic Performance of a Donor–Acceptor Copolymer Having Pyradinobisthiazole as the Acceptor Unit

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1. Introduction

The development of donor–acceptor (D–A) copolymers, which consist of alternating electron-rich and electron-deficient units, has become subjects of intense interest, since it offers the straightforward approaches as hole-transporting (p-type) semiconducting materials in organic photovoltaics (OPVs) in terms of fulfilling a reduced band gap to broaden light absorption to the long-wavelength region and a low-lying highest occupied molecular orbital (HOMO) energy level to increase the open-circuit voltage [1,2]. Although a variety of π -conjugated compounds including benzo[1,2-*b*:4,5-*b'*]dithiophene (**BDT**) have been developed as donor units in D–A copolymers, the effective acceptor units are still limited due to the difficulty of molecular design that fulfills lowering the lowest unoccupied molecular orbital (LUMO). Thiazole-fused aromatic compounds such as thiazolothiazole and benzobisthiazole (**BBTz**) have been utilized as typical acceptor units in semiconducting materials [3–8]. On the other hand, we have recently reported that pyradinobisthiazole (**PBTz**), which replaced the benzene ring in **BBTz** with an electron-deficient pyrazine ring, can function as an acceptor unit in both p-type D–A and n-type A–A copolymers [9]. However, the potential of the **PBTz** unit under the combination with a typical donor unit is still unclear. In this paper, we report the synthesis, properties, and photovoltaic performance of a new D–A copolymer **P-PBTz-T¹²-BDT** based on **BDT** and **PBTz** as donor and acceptor units, respectively (Fig. 1).

Fig. 1. Chemical structures of **BBTz**, **PBTz**, **P-PBTz-T¹²-BDT**.

2. Experimental

Microwave irradiation was performed by a Biotage Initiator Ver. 2.5. The microwave power output was set at 400 W. The reaction temperature was kept at 180 °C, and internal temperature during the reaction was monitored by IR sensor. Analytical gel-permeation chromatography (GPC) was performed on a Hitachi High-Technologies Corporation L-2420/L-2130 equipped with a Shodex K-803L at 40 °C using chloroform as eluent. UV-vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Photoelectron spectroscopy in air (PESA) was carried out using a Riken Keiki Co. Ltd. AC-3 with a light intensity of 10 mW.

Indium tin oxide (ITO)-coated glass substrates were first cleaned by ultrasonication in toluene, acetone, H₂O, and 2-propanol for 10 min,

respectively, followed by O₂ plasma treatment for 10 min. ZnO layer was fabricated by spin-coating of a solution consists of Zn(OAc)₂·2H₂O (500 mg), 2-aminoethanol (144 mg) and 2-methoxyethanol (5 mL) on the ITO surface at 3000 rpm for 30 sec, followed by a thermal treatment at 200 °C for 30 min in ambient conditions. The active layers were then prepared by spin-coating on the ITO/ZnO electrode at 1000 rpm for 1 min in a glove box. The typical thickness of the active layer was 70–90 nm. Finally, MoO₃ and Ag electrodes were evaporated on the top of active layer through a shadow mask to define the active area of the devices (0.09 cm²) under a vacuum of 10^{−5} Pa to a thickness of 10 and 100 nm determined by a quartz crystal monitor. After sealing the device from the air, the photovoltaic characteristics were measured in air under simulated air mass 1.5 global (AM 1.5 G) with an irradiation intensity of 100 mW cm^{−2} (SAN-EI ELECTRIC, XES-301S). The current density–voltage characteristics of photovoltaic devices were measured by using a KEITHLEY 2400 source meter. The EQE spectra were measured by using a Soma Optics Ltd. S-9240.

3. Results and discussion

The monomer unit **1** was prepared by our established synthetic route [9]. Then, **1** was copolymerized with 1,1'-[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl]bis(1,1,1-trimethylstannane) (**2**) by the microwave-assisted Stille coupling reaction in the presence of Pd₂(dba)₃·CHCl₃ and P(*o*-tolyl)₃ in toluene/DMF (5/1) to give **P-PBTz-T¹²-BDT** in 86% yield (Scheme 1). The synthesized copolymer was purified using a Soxhlet apparatus by successive washing with methanol and hexane to remove low-molecular-weight fractions, and finally by extracting with chloroform. Analytical GPC using a polystyrene standard determined the number-average molecular weight of **P-PBTz-T¹²-BDT** to be 15.9 kDa with molecular-weight dispersity of 3.2.

The thermal gravimetical analysis (TGA) indicated that this copolymer possesses high thermal stability with 5%-weight-loss temperature of 294 °C (Fig. 2).

The photophysical properties in a chloroform solution and thin films were measured by UV-vis absorption spectrometry (Fig. 3). In chloroform solution, **P-PBTz-T¹²-BDT** showed the absorption maximum at 552 nm. The absorption spectrum in a

thin film showed apparent broadening between 400 and 500 nm with a distinct shoulder at 630 nm. This phenomenon in the solid state is generally regarded as the formation of crystalline structure. However, X-ray diffraction (XRD) measurements of the copolymer pristine films did not show any diffraction pattern (Fig. 4), indicating the amorphous nature in the solid state. The optical HOMO–LUMO energy gap (ΔE_g^{opt}) extracted from the absorption onset of the film was 1.86 eV.

Scheme 1. Copolymerization of **P-PBTz-T¹²-BDT**.

Fig. 2. TGA curve of **P-PBTz-T¹²-BDT** with a scanning rate of 10 °C min^{−1} under N₂.

This value is smaller than the corresponding copolymer consisting of **BDT** and **BBTz** (2.13 eV) [5]. On the basis of similar HOMO energy levels of these copolymers in the electrochemical estimation (−5.71 eV for **BBTz**-based copolymer [5] and −5.65 eV for **PBTz**-based copolymer), the smaller ΔE_g^{opt} value of **P-PBTz-T¹²-BDT** than that of the **BBTz**-based copolymer indicates the lower LUMO energy level of **P-PBTz-T¹²-BDT** and thus the more electron-deficient characteristics of the **PBTz** unit than that of **BBTz**.

Fig. 3. UV-vis absorption spectra of **P-PBTz-T¹²-BDT** in chloroform solution (dashed line) and as film (solid line).

Fig. 4. XRD measurements of the pristine **P-PBTz-T¹²-BDT** and **P-PBTz-T¹²-BDT/PC₆₁BM** blend films on ZnO-coated ITO glass.

Further accurately, the ionization potential of the thin film was measured using PESA, which determined that the HOMO energy level (E_{HOMO}) of **P-PBTz-T¹²-BDT** is -5.51 eV (Fig. 5). Based on E_{HOMO} and $\Delta E_{\text{g}}^{\text{opt}}$, E_{LUMO} was calculated to be -3.65 eV.

The charge-transporting characteristics of **P-PBTz-T¹²-BDT** was investigated by the space-charge-limited currents (SCLC) method. Hole-only device was prepared with the structure of ITO/PEDOT:PSS/**P-PBTz-T¹²-BDT**/Au. The active layer was prepared from 10 mg mL^{-1} chloroform solution of the copolymer. The hole mobility of this device was calculated by the following equation: $J = 9V^2 \varepsilon \varepsilon_0 \mu / 8d^3$, where ε , ε_0 , μ , and d are the dielectric constant of the active layer, the permittivity of free space, the carrier mobility, and the measured thickness of the active layer, respectively. Under this condition, **P-PBTz-T¹²-BDT** showed hole mobility of $4.3 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Fig. 6), whose value is almost

comparable to that of our developed **PBTz**-containing p-type copolymer [9]. The appearance of hole-transporting characteristics indicates that this copolymer has a potential for p-type OPV semiconducting material.

Fig. 5. PESA of **P-PBTz-T¹²-BDT** film.

Fig. 6. J - V characteristics of hole-only device for **P-PBTz-T¹²-BDT**.

In order to evaluate the OPV performance of **P-PBTz-T¹²-BDT**, bulk hetero-junction (BHJ) solar cell was fabricated with an inverted structure of glass/ITO/ZnO/active layer/MoOx/Ag. To investigate the p-type characteristics of **P-PBTz-T¹²-BDT**, the active layer was fabricated under the combination of **P-PBTz-T¹²-BDT** with [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) as an n-type semiconductor. The fabrication conditions of the active layer were optimized by varying the blending ratio, concentration, and processing solvent; the optimal weight ratio of **P-PBTz-T¹²-BDT/PC₆₁BM** combinations was 1:1, 10 mg mL^{-1} of *o*-dichlorobenzene/chloroform (4/1) solution. The active layer was prepared by spin-coating under a nitrogen atmosphere without thermal annealing. This device showed typical photovoltaic

characteristics with a power conversion efficiency (PCE) of 1.08%, with an open-circuit voltage of 0.79 V, a short-circuit current density of 3.45 mA cm^{-2} , and a fill factor of 0.40 (Fig. 7(a)). This PCE value is comparable to that for the reported OPV devices based on the corresponding **BBTz**-incorporated copolymers with PC₇₁BM under similar fabricating conditions [5]. The external quantum efficiency (EQE) spectrum of this device exhibited photoresponses between 300 and 700 nm with a maximum value of 20% at 550 nm (Fig. 7(b)).

Fig. 7. (a) J - V curves under illumination (solid line) and dark (dashed line) and (b) EQE spectrum of the **P-PBTz-T¹²-BDT/PC₆₁BM** OPV devices.

No characteristic crystallization peaks were detected by the XRD profile of the blend films (Fig. 4). Atomic force microscopy (AFM) images showed relatively smooth and featureless surface morphology (Fig. 8). These results indicate the amorphous nature of the blend film.

In summary, we developed **PBTz**-containing new D-A copolymer **P-PBTz-T¹²-BDT**. E_{HOMO} and E_{LUMO} were determined by the combination of PESA and UV-vis measurements in the solid state. SCLC measurements showed the hole-transporting

characteristics. BHJ solar cells based on **P-PBTz-T¹²-BDT** and PC₆₁BM showed a moderate PCE of 1.08%. To further improve the PCE, the fine-tuning of the film morphology by the alkyl side-chain engineering and/or the structural modification of π -conjugated backbones have become important, which will lead to increasing the crystallinity in the solid state. Nevertheless, the obtained results confirm that **PBTz** has been positioned as a good candidate for the acceptor unit for the development of high-performance organic semiconducting materials.

Fig. 8. AFM image of the **P-PBTz-T¹²-BDT/PC₆₁BM** blend films.

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