Development of an Electron-Transporting $\pi$-Conjugated Polymer Containing Fluorine-substituted Naphthobisthiadiazole

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The development of new organic semiconductors for organic solar cell applications continues to be an important subject. We recently developed fluorinated naphthobisthiadiazole (FNTz) for use as a new electron-accepting unit for nonfullerene acceptors. In this letter we report on the design and synthesis of a new electron-transporting $\pi$-conjugated polymer containing FNTz and an investigation of the influence of the FNTz unit on the properties and photovoltaic characteristics of the molecule. The introduction of the FNTz unit led to red-shifted absorption and low-lying frontier orbital energy levels, compared to those of NTz. Organic solar cells based on the FNTz-containing polymer, when combined with poly(3-hexylthiophene) as a donor showed an improved power conversion efficiency of 1.13%. These results indicate that FNTz could be an effective electron-accepting unit for electron-transporting polymer.

Keywords: Organic solar cell, Acceptor, Organic semiconductors, Structure-property relationship, Fluorinated naphthobisthiadiazole

1. Introduction

$\pi$-Conjugated polymers have been extensively investigated as organic semiconductors in organic electronics such as organic light-emitting diodes, organic field-effect transistors, and organic solar cells (OSCs) [1-6]. To fabricate these devices, both hole-transporting and electron-transporting organic semiconductors are essential. It is known that tuning the relative energies between the frontier orbital of organic semiconductors and the Fermi level of metal electrodes is an effective approach for selectively injecting holes or electrons. Thus, the incorporation of electron-accepting units into $\pi$-conjugated systems is an important methodology for tuning the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels [1-5]. However, effective electron-accepting units for organic semiconductors are still limited [7-10].

Naphtho[1,2-c:5,6-c']bis[1,2,5]thiadiazole (NTz) [11] has been widely utilized as an electron-accepting unit of donor–acceptor type donor copolymers [12-15] and acceptor–acceptor type acceptors for bulk-heterojunction OSCs (Fig. 1) [16-19]. In an attempt to increase the electron-accepting character of NTz, we recently reported on the synthesis of fluorinated naphthobisthiadiazole (FNTz) and FNTz-containing small molecules for nonfullerene acceptor applications [20]. We also revealed that the overall performance of OSCs was enhanced compared to the corresponding NTz-based molecule. However, the potential of the FNTz unit for preparing electron-transporting polymers is still unclear. In this paper, we report on the synthesis, properties, and photovoltaic performance of a new acceptor–acceptor type copolymer FNTz-T-BTz and a comparison of its physical properties and photovoltaic characteristics with NTz-T-BTz (Fig. 1).
Fig. 1. Chemical structures of NTz, FNTz, FNTz-T-BTz, and NTz-T-BTz.

2. Experimental

Column chromatography was performed on silica gel, KANTO Chemical silica gel 60N (40–50 μm). Preparative GPC was performed on Japan Analytical Industry LC-918 equipped with JAIGEL 1H/2H. TGA was performed under nitrogen with Shimadzu TGA-50. UV–vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer. The surface morphology of organic films was observed by atomic force microscopy (Shimadzu, SPM9600). Photoelectron spectroscopy in air (PESA) was carried out using a Riken Keiki Co. Ltd. AC-3. Organic photovoltaic devices were prepared with a structure of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/active layer/Ca/Al. ITO-coated glass substrates were first cleaned by ultrasonication in toluene, acetone, H2O, and 2-propanol for 15 min, respectively, followed by an O2 plasma treatment for 20 min. The ITO-coated glass substrates were then activated by treatment with ozone for 1.5 h. PEDOT:PSS was spin-coated on the ITO surface at 3000 rpm for 1 min and dried at 135 °C for 10 min. Under these conditions, the thickness of the PEDOT:PSS is ca. 30 nm. The active layers were then prepared by spin-coating on the ITO/PEDOT:PSS electrode at 800 rpm for 2 min in a glove box. The active layer was then annealed at 130 °C for 15 min. Ca and Al electrodes were evaporated on the top of the 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 thicknesses of 30 and 70 nm, respectively, as determined by a quartz crystal monitor. After sealing the device from air, the photovoltaic devices were measured by a KEITHLEY 2400 source meter. External quantum efficiency (EQE) spectra were obtained by means of a Soma Optics Ltd. S-9240. The surface structures of the deposited organic film were observed by atomic force microscopy (AFM) (Shimadzu, SPM9600), and the crystallinity of the film was evaluated by an X-ray diffractometer (XRD) (Rigaku, SmartLab). Hole-only and electron-only devices were prepared with a structure of ITO/PEDOT:PSS/active layer/Au and ITO/TiOx/active layer/Ca/Au, respectively.

3. Results and discussion

Synthetic route to target polymer is shown in Scheme 1. FNTz-Br was synthesized following our recently reported procedure [20]. 2-Dodecyloctyl-substituted thiophene units were introduced by a Stille coupling reaction to give 1, which was then treated with NBS to afford the dibromo monomer unit 2. Finally, FNTz-T-BTz was synthesized using 2 and bis(pinacol)ester BTz-B via a Suzuki polymerization. The crude polymer was purified by Soxhlet extraction with MeOH, hexane in order to remove the low molecular weight fractions, and high molecular weight fraction was collected by dissolving in chloroform (CHCl3). A similar method was used for the synthesis of NTz-T-BTz. The number average molecular weight of FNTz-T-BTz and NTz-T-BTz are 27.6 and 30.8 kg mol−1 with a molecular-weight dispersity of 2.32 and 1.94, respectively, measured by gel permeation chromatography, at a column temperature of 40 °C with CHCl3 as an eluent.

The UV-vis absorption spectra of the polymers were measured in CHCl3 solutions and in thin films on glass quartz plates. The summarized photophysical data are listed in Table 1. As shown
in Fig. 2, these polymers exhibit a similar absorption band in both solutions and films resulting from their similar \( \pi \)-conjugated components. However, these absorption bands for \( \text{FNTz-T-BTz} \) were somewhat red-shifted relative to those of \( \text{NTz-T-BTz} \). This phenomenon indicates that the stronger electron-accepting nature of the \( \text{FNTz} \) unit contributes to increasing the intramolecular charge transfer character of the molecule. Based on the calculated results for model compounds (Chart 1), a possible other explanation can be found in the different torsion angles between the naphthobisthiadiazole and thiophene units: the introduction of a fluorine atom in \( \text{FNTz} \) allows for enhanced planarization due to the presence of S-F interactions. Compared to the solution state, the absorption spectra of the films are red-shifted. This shift can be attributed to the interchain packing in the solid state. The optical HOMO–LUMO energy gaps (\( \Delta E_{\text{opt}} \)) of \( \text{FNTz-T-BTz} \) and \( \text{NTz-T-BTz} \), extracted from the absorption onset in the films, are estimated to be 1.74 and 1.83 eV, respectively.

Table 1. Properties of the polymers.

| Compounds   | \( \lambda_{\text{onset}}^a \) (nm) | \( \Delta E_{\text{opt}}^b \) (eV) | \( E_{\text{HOMO}}^c \) (eV) | \( E_{\text{LUMO}}^c \) (eV) |
|-------------|-----------------------------------|---------------------------------|-----------------|-----------------|
| \( \text{FNTz-T-BTz} \) | 569 (713) | 1.74 | –5.71 | –3.40 |
| \( \text{NTz-T-BTz} \) | 549 (678) | 1.83 | –5.58 | –3.22 |

\(^a\) In CHCl\(_3\); \(^b\) In film; \(^c\) \( \Delta E_{\text{opt}} = 1240/\lambda_{\text{onset}} \); \(^d\) Determined by PESA measurements; \(^e\) Determined by \( E_{\text{HOMO}} \) and \( \Delta E_{\text{opt}} \).

Fig. 2. UV-vis absorption spectra of \( \text{FNTz-T-BTz} \) (red) and \( \text{NTz-T-BTz} \) (black) in (a) CHCl\(_3\) solution and (b) thin films.

Cyclic voltammetry measurements were performed in \( \nu\)-DCB/CH\(_3\)CN (10:1) solutions containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF\(_6\)) to determine the reduction potentials of the polymers. Cyclic voltammograms (CVs) in Fig. 3(a) refer to the ferrocene/ferrocinium (Fc/Fc\(^+\)) redox couple, and the electrochemical data are summarized in Table 1. Both \( \text{FNTz-T-BTz} \) and \( \text{NTz-T-BTz} \) showed multiple reduction waves with onset first reduction potentials of –1.40 and –1.58 V, respectively. On the other hand, no oxidation wave was detected within the potential window of the solvent. Based on these reduction potentials and the assumption that the energy level of Fc/Fc\(^+\) is –4.8 eV below the vacuum level, the LUMO energy level (\( E_{\text{LUMO}} \)) of \( \text{FNTz-T-BTz} \) and \( \text{NTz-T-BTz} \) were calculated to be –3.40 and –3.22 eV, respectively.

Based on PESA measurements in the film state, the HOMO energy levels (\( E_{\text{HOMO}} \)) of \( \text{FNTz-T-BTz} \) and \( \text{NTz-T-BTz} \) were determined to be –5.71 and –5.58 eV, respectively (Fig. 3(b)). These results clearly indicate that the introduction of fluorine atoms in the naphthobisthiadiazole unit contribute to decreasing both HOMO and LUMO energy.
levels of the polymer.

To investigate the photovoltaic properties of these polymers, bulk heterojunction solar cells were fabricated. For the active layer, we used poly(3-hexylthiophene) (P3HT) as a donor and our synthesized polymer as an acceptor. The optimized active layer was formed by spin-coating a solution of P3HT with respective polymer (1:1 weight ratio) in o-dichlorobenzene under a concentration of 15 mg mL⁻¹, followed by thermal annealing at 130 °C for 15 min. The photovoltaic properties of the devices fabricated under optimized conditions are listed in Table 2 and the corresponding current-density versus voltage (J–V) curves of these devices are shown in Fig. 4(a).

Table 2. Key photovoltaic parameters of OPV devices.

| Active layers      | $V_{oc}$ /V | $J_{sc}$ /mA cm⁻² | FF  | PCE /% |
|--------------------|-------------|-------------------|-----|--------|
| P3HT/FNTz-T-BTz    | 0.96        | 2.63              | 0.46| 1.13   |
| P3HT/NTz-T-BTz     | 0.84        | 0.73              | 0.48| 0.29   |

Fig. 4. (a) J–V curves of based on P3HT/FNTz-T-BTz (red) and P3HT/NTz-T-BTz (black) under illumination (solid line) and dark (dashed line) and (b) EQE spectra of these devices.

To understand the origin of the different photovoltaic characteristics, we investigated the properties of blend films. The charge-transporting characteristics of blend films were investigated by the space-charge-limited currents (SCLC) method. The electron-only devices showed that the P3HT/FNTz-T-BTz films have one order of magnitude higher electron mobility ($9.8 \times 10^{-5}$ cm² V⁻¹ s⁻¹) compared to that of P3HT/NTz-T-BTz (8.5 $\times 10^{-6}$ cm² V⁻¹ s⁻¹). The hole-only devices showed that the hole mobility of the P3HT/FNTz-T-BTz films (9.5 $\times 10^{-5}$ cm² V⁻¹ s⁻¹) are higher than that of P3HT/NTz-T-BTz (1.5 $\times 10^{-5}$ cm² V⁻¹ s⁻¹). The improvement in $J_{sc}$ is explainable by the fact that the P3HT/FNTz-T-BTz films exhibited balanced carrier mobilities both higher hole and electron mobility than the P3HT/NTz-T-BTz films.

The morphologies of the P3HT/FNTz-T-BTz and the P3HT/NTz-T-BTz blend films were characterized by AFM measurements. As shown in Figs. 5(a)(b), AFM images of the P3HT/FNTz-T-BTz films showed a relatively smooth surface morphology with an average roughness ($R_a$) of 0.59 nm, as compared to that of P3HT/NTz-T-BTz (1.57 nm). The relatively large $R_a$ value of the P3HT/NTz-T-BTz films indicates the occurrence of poor intermixing between the donor and the acceptor interface. As shown in Fig. 5(c), XRD measurements of these blend films showed the appearance of XRD signals at $2\theta = 2.5^\circ$ and $5.4^\circ$. Based on the XRD signals of pristine films (Fig. 5(d), these signals were assigned to the ordered acceptor and P3HT, respectively. Since an increase in the intensity at $2\theta = 5.4^\circ$ was clearly observed, we concluded that the crystallinity of P3HT is enhanced for the P3HT/NTz-T-BTz films. The photoluminescence (PL) spectra of the P3HT/FNTz-T-BTz films showed more effective quenching of the fluorescence from P3HT than that of the P3HT/NTz-T-BTz films (Fig. 5(e)). These results suggest that photoinduced charge separation between P3HT and FNTz-T-BTz takes place effectively, leading to a higher $J_{sc}$.  

The FNTz-T-BTz–based device shows a much improved PCE of 1.13% with an open-circuit voltage ($V_{oc}$) of 0.96 V, a short-circuit current density ($J_{sc}$) of 2.63 mA cm², and a fill factor (FF) of 0.46, while the devices based on NTz-T-BTz exhibited lower PCE of 0.29%. The observed PCE improvement can be mainly attributed to the increased $J_{sc}$. As shown in Fig. 4(b), the EQE spectra of these devices exhibited photoresponse between 300 nm and 700 nm with a maximum of 28% and 7% for P3HT/FNTz-T-BTz and P3HT/NTz-T-BTz blend films, respectively.
4. Conclusion

In summary, to investigate the potential of FNTz as an electron-accepting unit of electron-transporting polymers for nonfullerene acceptor applications, we designed and synthesized FNTz-T-BTz and its reference compound NTz-T-BTz. Photophysical, electrochemical, and physicochemical measurements indicated that the introduction of fluorine atoms on the NTz unit contributed to a red-shifted absorption and low-lying frontier orbital energy levels, compared to those of NTz. Conventional organic solar cells based on FNTz-T-BTz as an acceptor with P3HT as a donor showed a superior photovoltaic performance of up to 1.13% compared to the corresponding P3HT/NTz-T-BTz-based device. Based on an investigation of a blend film, the P3HT/FNTz-T-BTz films showed superior charge-transporting characteristics and improved blend film morphologies. These results indicate that the utilization of the FNTz unit led to efficient charge generation and transport in the case of the P3HT/FNTz-T-BTz film. Further studies on the development of FNTz-based organic semiconductors for nonfullerene acceptors and donor–acceptor-type donor are currently underway.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (B) (16H04191) and "Dynamic Alliance for Open Innovation Bridging Human, Environmental and Materials" from The Ministry of Education, Culture, Sports, Science and Technology, Japan. This work was partially supported by Takahashi Industrial and Economic Research Foundation.

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