Synthesis, Properties, and Photovoltaic Characteristics of Arch- and S-shaped Naphthobisthiadiazole-based Acceptors

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Fine-tuning physical properties by structural modification is important for developing organic semiconducting materials. In this work, we designed and synthesized new electron-accepting compounds containing naphtho[1,2-c:7,8-c']bis[(1,2,5]thiadiazole (vNTz) or naphtho[1,2-c:5,6-c']bis[1,2,5]thiadiazole (NTz) groups as electron-accepting units; these units are structural isomers. The vNTz-based compounds have an arch-shaped molecular backbone with $C_{2v}$ symmetry, whereas the NTz-based compound forms an S-shaped molecular backbone with $C_{2h}$ symmetry. Property measurements showed unique behavior originating from the vNTz core. An organic solar cell comprising the vNTz-based compound and poly(3-hexylthiophene) showed a power conversion efficiency of 2.06%. This result demonstrates the potential of vNTz as an electron-accepting unit in organic semiconducting materials.

Keywords: Organic solar cells, Nonfullerene acceptors, Organic semiconducting materials, $\pi$-Conjugated molecules, Naphthobisthiadiazole, Surface free energies

1. Introduction

$\pi$-Conjugated compounds have been intensively developed as semiconducting materials for organic solar cells (OSCs).[1,2] The active layer of OSCs consists of donor and acceptor materials, which form a bulk-heterojunction structure.[3] Low band-gap polymers have been extensively utilized as donor materials to acquire broad absorption.[4] However, poly(3-hexylthiophene) (P3HT) is still considered one of the most promising practical donors.[5] Among the various acceptor materials, nonfullerene acceptors (NFAs), which comprise planar $\pi$-conjugated backbones and electron-accepting units, have attracted significant attention due to their tunable electronic properties, synthetic accessibilities, and structural diversities.[6,7] Several $C_{2v}$-symmetric (arch-shaped) NFAs, such as ZY-4Cl[8] and Y6[9], have reportedly shown photovoltaic characteristics due to their high carrier mobilities and crystallinities, as well as the optimal phase separations of their blend films.[10-12] However, investigations into the influence of structural symmetry on acceptor performance are limited.

Recently, we have developed electron-accepting $\pi$-conjugated materials including a $C_{2h}$ symmetric naphtho[1,2-c:5,6-c']bis[1,2,5]thiadiazole (NTz) unit,[13] and found that NTz derivatives are promising constituents for NFAs.[14-16] The corresponding structural $C_{2v}$ isomer of NTz, naphtho[1,2-c:7,8-c']bis[1,2,5]thiadiazole (vNTz), was first synthesized by Mataka et al. in 1991.[17] However, acceptor materials comprising extend $\pi$-conjugated systems bearing vNTz units have not yet been investigated in detail.[18] In this contribution, we combined a vNTz unit with 3-ethylrhodanine[19] as a representative terminal

![Fig. 1. Chemical structures of target molecules.](image-url)
unit to investigate the properties and OSC characteristics of the resultant electron-accepting materials. Specifically, we synthesized the \( \pi \)-conjugated compounds \( \text{vNTz-TboR} \) and \( \text{vNTz-TaR} \) that feature \( C_{2v} \) symmetry (Fig. 1). For comparison, \( \text{NTz-TaR} \), bearing \( C_{2h} \) symmetry, was also synthesized.

2. Experimental

Cyclic voltammetry (CV) was carried out on a BAS CV-620C. UV-vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Fluorescence spectra were recorded using a Fluoromax-4 spectrometer in the photo-counting mode equipped with a Hamamatsu R928P photomultiplier. Photoelectron yield spectroscopy (PYS) was performed by Bunkoukeiki BIP-KV202GD. The surface structures of the active layers were observed by atomic force microscopy (AFM) using Shimadzu, SPM9600.

OSCs were prepared with a structure of ITO/ZnO/active layer/MoO\(_3/Ag\).[20] ITO-coated glass substrates were first cleaned by ultrasonication in acetone, water, and 2-propanol, respectively. The substrates were then activated by ozone treatment for 1 h. ZnO layer was spin-coated using the solution of zinc acetate dihydrate at 3000 rpm. and baked at 200 °C for 30 min in air. Subsequently, the active layer was then formed by spin-coating on the ITO/ZnO electrode using 10 mg mL\(^{-1}\) solutions including P3HT and acceptor at a weight ratio of 1:1 in chloroform, followed by thermal annealing at 130 °C for 10 min in a glove box. MoO\(_3\) 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 cm\(^2\)) under a vacuum of 10\(^{-5}\) Pa to a thickness of 10, 100 nm. After sealing the device from the air, the photovoltaic characteristics were measured in air under simulated AM 1.5G solar irradiation (100 mW cm\(^{-2}\)) (SAN-EI ELECTRIC, XES-301S) by using a KEITHLEY 2400 source meter. The external quantum efficiency (EQE) spectra were measured by using a Soma Optics Ltd. S-9240.

The contact angles of film surface were measured by a NiCK LSE-ME1 using distilled water and glycerol. SFEs were estimated based on the theory established by Kaelble and Uy.[21]

3. Results and discussion

3.1. Synthesis

We began our study with the syntheses of \( \text{vNTz-TboR} \) and \( \text{NTz-TaR} \) (Scheme 1), which have 2-butyloctyl moieties as solubilizing groups. The dibromo compound \( \text{vNTz-Br} \) [17] was cross-coupled via Migita–Kosugi–Stille reactions to obtain 1. Compound 1 was then formylated by the Vilsmeier–Haack reaction in dichloroethane (DCE)[22] followed by condensation reactions with 3-ethylrhodanine to give the target compound \( \text{vNTz-TboR} \). The \( \text{NTz-TaR} \) compound was synthesized in the same manner. Since \( \text{vNTz-TboR} \) is relatively soluble, we also synthesized \( \text{vNTz-TaR} \) bearing a 2-ethylhexyl group.

The solubilities of the synthesized compounds against chloroform, chlorobenzene, and \( o \)-dichlorobenzene (as representative solvents) in OSCs are summarized in Table 1. Compared to \( \text{NTz-TaR} \), \( \text{vNTz-TaR} \) showed higher solubilities. This result is consistent with the reported phenomenon that acceptors with \( C_{2v} \) symmetry provide improved solubilities.[12]
rpm. and baked at 200 °C for 30 min in air.

[...]

Thus, the LUMO energy levels for vNTz- and NTz-based compounds were estimated to be –3.41 and –3.49 eV, respectively, which indicate that these compounds can be employed as acceptors in OSCs when combined with P3HT as a donor.[23]

3.3. Properties

To investigate the electrochemical properties of the synthesized compounds, CV measurements were performed. Fig. 3 shows the voltammograms of vNTz-TboR and NTz-TboR, and the electrochemical data extracted from them are listed in Table 2. NTz-TboR showed one reversible reduction wave, but no additional reduction wave was observed when differential pulse voltammetry was employed in further negative sweep (data not shown). In contrast, three reversible reduction waves were observed for vNTz-TboR. The first half-wave reduction potentials (E_{red}^{1/2}) of vNTz-TboR and NTz-TboR were −1.22 and −1.21 V, respectively. Thus, the LUMO energy levels for vNTz-TboR (−3.58 eV) and NTz-TboR (−3.59 eV) showed similar values. This result indicates that the structural geometry of the NTz skeleton has little influence on the LUMO energy levels.

Chloroform solutions and thin films on quartz plates of the synthesized compounds were...
evaluated by UV-vis absorption spectroscopy (Fig. 4(a)). The corresponding spectroscopic data are summarized in Table 2. The UV-vis absorption spectra of \( \text{vNTz-TboR} \) and \( \text{vNTz-TehR} \), i.e., the compounds with the same \( \pi \)-conjugated structure, showed negligible differences when superimposed. This was true for both their solution and film states, indicating that the different alkyl groups do not significantly alter the photophysical properties of these \( \text{vNTz} \)-based compounds. The absorption maxima (\( \lambda_{\text{abs}} \)) of the \( \text{vNTz} \)-based compounds were blue-shifted by 56 nm relative to that of \( \text{NTz-TboR} \).

Additionally, the molar absorption coefficient of the \( \text{vNTz} \)-based compounds \( (7.4 \times 10^4 \ \text{L mol}^{-1} \ \text{cm}^{-1}) \) was higher than that of \( \text{NTz-TboR} \). Fluorescence measurements showed that the emission maximum (\( \lambda_{\text{em}} \)) of \( \text{NTz-TboR} \) was bathochromically shifted by 36 nm with respect to that of the \( \text{vNTz} \)-based compounds. Based on the \( \lambda_{\text{abs}} \) and \( \lambda_{\text{em}} \) values (Fig. 4(b)), the Stokes shifts were calculated as 3000 cm\(^{-1} \) for \( \text{vNTz-TboR} \) and 2000 cm\(^{-1} \) for \( \text{NTz-TboR} \). The higher Stokes shift of \( \text{vNTz-TboR} \) is ascribed to its slightly twisted structure (Fig. 2).

Apparent red shifts were observed in the bands of the absorption and emission spectra of both compounds (\( \text{vNTz-TboR} \): 47 nm, \( \text{NTz-TboR} \): 78 nm) when they converted to the film state from the solution state. The relatively large red shift noted for \( \text{NTz-TboR} \) implies that the \( \pi-\pi \) stacking interactions of its film state are stronger than those of its solution state. The relatively large red shift noted for \( \text{NTz-TboR} \) implies that the \( \pi-\pi \) stacking interactions of its film state are stronger than those of its solution state.

The ionization potentials (\( I_p \)) of the compounds as thin-films were determined by PYS measurements (Fig. 5). Based on the onset, the \( I_p \) values of

\[ \text{vNTz-TehR}, \text{vNTz-TboR}, \text{and NTz-TboR} \] were determined to be 5.04, 5.19, and 5.06 eV, respectively. The \( I_p \) of \( \text{vNTz-TboR} \) was deeper than that of \( \text{NTz-TboR} \), which is in good agreement with the DFT calculation (Fig. 2).
The spectra of vNTz-TboR that of the vNTz-based compounds. Based on the bathochromically shifted by 36 nm with respect to stronger than those of its solution state. Apparent red shifts were observed in the bands of 2000 cm$^{-1}$ for solution state. The relatively large red shift noted for these vNTz-based compounds. The absorption significantly alter the photophysical properties of indicating that the different alkyl groups do not This was true for both their solution and film states, showed negligible differences when superimposed. Compounds with the same summarized in Table 2. The UV-vis absorption evaluated by UV-vis absorption spectroscopy (Fig. 3). Cyclic voltammograms of vNTz-TboR, NTz-TboR, and vNTz-TehR were determined by PYS measurements (Fig. 7). The photovoltaic characteristics of our newly synthesized compounds when employed in OSCs were then investigated. In Fig. 6(a) and Table 3, the current-density–voltage ($J$–$V$) curves and the corresponding photovoltaic parameters of the devices are presented. Under the same fabrication conditions, vNTz-TehR and NTz-TboR showed comparable power conversion efficiencies (PCEs) of ~0.6%. However, a higher PCE of 2.06% was achieved by the vNTz-TehR-based OSC, which was mainly due to a significant increase in its short-circuit current density ($J_{SC}$). As indicated in Fig. 6(b), the external quantum efficiencies (EQEs) corresponded to the $J_{SC}$ values of OSCs, and a maximum EQE of 52% was observed for the vNTz-TehR-based OSC.

To investigate the film morphologies of the active layers, AFM was performed. As shown in Fig. 7, all active layers had smooth surfaces suitable for OSCs; however, the NTz-TboR-based films were found to have slightly rougher surfaces.

As long as the AFM measurements, no clear correlation was identified with respect to the morphological observations of these active layers. We previously reported a correlation between the dispersion component ($\gamma^d$) of the surface free energy (SFE) for benzothiadiazole-based NFA films and the $J_{SC}$ value of the OSCs they were employed in.[24] This correlation suggested that the donor–acceptor interfaces of the $\pi$-conjugated frameworks of acceptors with large $\gamma^d$ values are more exposed than those of acceptors with small $\gamma^d$ values, which is advantageous for charge separation. To obtain insight into the film properties of the acceptors synthesized in this work, their SFE, $\gamma^d$, and polar component ($\gamma^p$) values were determined from contact-angle measurements using water and glycerol as the probe liquids (Fig. 8 and Table 3). We then plotted the $\gamma^d$ values of the acceptors against the $J_{SC}$ values of the OSCs we employed them in (Fig. 6(c)). This plot showed a clear correlation between the two parameters, where the large $\gamma^d$ component of vNTz-TehR

| compounds      | $J_{SC}$ / mA cm$^{-2}$ | $V_{OC}$ / V | FF / % | PCE / % | $\gamma^d$ / mJ cm$^{-2}$ | $\gamma^p$ / mJ cm$^{-2}$ | SFE / mJ cm$^{-2}$ |
|----------------|------------------------|-------------|--------|---------|--------------------------|--------------------------|-----------------|
| vNTz-TehR      | 6.34                   | 0.68        | 48     | 2.06    | 17.9                     | 7.2                      | 25.0            |
| vNTz-TboR      | 2.36                   | 0.62        | 41     | 0.61    | 8.8                      | 10.0                     | 18.8            |
| NTz-TboR       | 2.13                   | 0.70        | 37     | 0.56    | 6.8                      | 12.1                     | 19.9            |

Table 3. OSC device data and surface free energies of acceptor films.

3.4 Photovoltaic Characteristics

Fig. 7 AFM height images on active layers.

Fig. 6 (a) $J$–$V$ characteristic and (b) external quantum efficiency spectra of OSC devices. (c) Plot of $\gamma^d$ vs $J_{SC}$ values for acceptor materials used in this study.

Fig. 8 Contact angles of thin films.
implies that the \( \pi \)-conjugated framework of this film is exposed. This trend is in good agreement with the photovoltaic results.

4. Conclusion

New, arch-shaped NFAs, \( \text{vNTz-TboR} \) and \( \text{vNTz-TehR} \), were developed by introducing a \( \text{vNTz} \) unit into the central part of a \( \pi \)-conjugated backbone. Upon comparing \( \text{vNTz-TboR} \) to \( \text{NTz-TboR} \), it was evident that the low-symmetry unit (\( \text{vNTz} \)) of the former material provided it with a higher solubility than that of the latter. Furthermore, electrochemical measurements indicated that \( \text{vNTz-TboR} \) and \( \text{NTz-TboR} \) showed almost identical LUMO energy levels. An OSC based on P3HT/\( \text{vNTz-TboR} \) showed a PCE of 2.06\%, and the contact angle measurements implied that the \( \text{vNTz-TboR} \) film has a favorable surface for photo-carrier generation. Thus, this study demonstrated the potential applicability of arch-shaped NTz derivatives in organic electronics.

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