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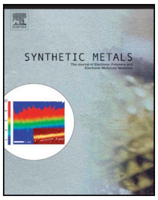

Synthesis and characterization of low band gap thiadiazolobenzo-imidazole chromophores

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ABSTRACT

Thiadiazolobenzoimidazole (**TBI**) acceptor was designed in order to increase the electron-withdrawing ability of 2,1,3-benzothiadiazole (**BT**). The key feature of **TBI** is the three electron deficient imine groups, rendering it a stronger acceptor than **BT**. Three **TBI**-containing compounds **TBI-a** to **TBI-c** were synthesized by reaction between 5,6-diamino-2,1,3-benzothiadiazole analogue and the corresponding anhydride and exhibit maximum absorption at 600 nm. The band gaps of **TBI-a** to **TBI-c** are in between that of **BT**-containing compounds and benzo(1,2-c:4,5-c′)bis[1,2,5]thiadiazole-containing compounds, ranging from 1.60 to 1.88 eV, which make them potentially useful for organic solar cell application. Moreover, all the compounds are electrochromic and become absorbing at the telecommunication wavelengths upon electrochemical switching.

1. Introduction

Organic compounds with π-conjugated structures have attracted significant attention due to their potential as semiconducting materials in optoelectronic devices, such as organic field-effect transistors (OFETs) [1–4], organic solar cells (OSCs) [5–7] and organic light-emitting diodes (OLED) [8]. However, compared to inorganic semiconductors, the band gaps of common conjugated organic materials are relatively large and this limits the performance of the devices in some applications, such as OSCs. One of the most widely used strategies to narrow the band gap is coupling an electron-rich (donor) with an electron-deficient (acceptor) unit in the conjugated backbone [9,10].

2,1,3-Benzothiadiazole (**BT**) is one of the most commonly used acceptors to construct semiconducting materials due to its electron-withdrawing ability and high electron mobility (Fig. 1) [11–15]. However, in some cases, the electron-withdrawing ability of **BT** is not strong enough to provide a desirable band gap, especially when it couples to weak donors. For example, the suitable band gap in application of OSCs is around 1.6 eV based on the theoretical calculation. While, simply coupling **BT** with a common electron donor fluorenylthienyl (**FT**) can only achieve the band gap of 2.0 eV for **BT-FT** (Fig. 2) [16]. In order to reach 1.6 eV, stronger donors and longer conjugation length are required, however, these special requirements limit the selection of donors.

Structural modifications of **BT** unit have been done mainly by introducing additional groups onto the benzene ring. A common strategy would be converting 5,6-diamino-2,1,3-benzothiadiazole analogue (**DABT**) to a number of heterocyclic compounds by ring closing reaction. Acceptor benzo(1,2-c:4,5-c′)bis[1,2,5]thiadiazole (**BBT**) and dibenzo[a,c][1,2,5]thiadiazolo[3,4-i]phenazine (**DBTP**) have been extensively studied for OLED and are very strong acceptors [17–19]. By coupling with donors, the band gaps of D–A compounds can be brought down to 1.3 eV or even lower (Fig. 2). The maximum absorptions of these compounds range from 700 to 950 nm. Their emissions are even more red-shifted into the NIR region. However, lack of high absorbance in the visible region and extremely low band gap make them not suitable in other applications such as OSCs.

Herein, we proposed and synthesized donor–acceptor compounds with thiadiazolobenzoimidazole (**TBI**) as an acceptor unit (Fig. 2). The unique feature of the **TBI** is that it has three electron deficient imine groups to contribute to the electron-withdrawing ability of the acceptor with the other nitrogen forming an amide. Therefore, **TBI** is expected to have the electron withdrawing ability in between **BT** and **BBT**. After coupling with the same donor **FT**, the band gap should be in between those of **BT-FT** and **BBT-FT** and will be suitable for OSC application (Fig. 2).

The **TBI**-containing compounds **TBI-a** to **TBI-c** can be simply synthesized by reaction between **DABT** and selected anhydrides (Scheme 1). The energy levels and band gaps can be tuned by changing the structure of the **TBI** core. Electronegative fluorine atoms are known to be very effective in lowering the HOMO and LUMO levels and thus were introduced in compound **TBI-b**. 1,8-Naphthalic anhydride which was introduced in compound **TBI-c** possesses

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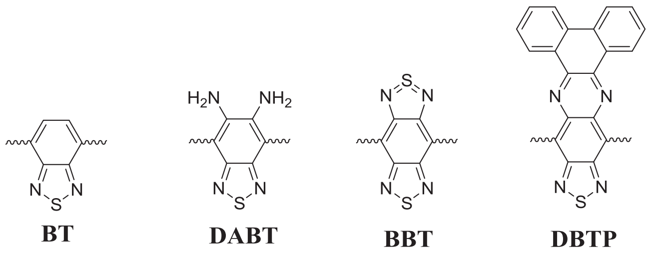

Fig. 1. Structures of **BT**, **DABT**, **BBT** and **DBTP**.

relatively longer conjugation length and was expected to provide a smaller band gap. In order to facilitate the systematic study of the relationship between the band gap and the structure, all the compounds have been designed to have the same donor **FT**.

Because the thienyl group of the donor is redox active [20], the designed three **TBI**-based compounds are also electrochromic and can be switched electrochemically to become NIR absorbing at the telecommunication wavelengths.

2. Experimental

2.1. Materials

Chemicals and reagents purchased from Aldrich and TCI were used directly without further purification. Compounds **3** and **4** were prepared according to the literature [18,21].

2.2. Characterization

^{1}H NMR spectra and ^{13}C NMR spectra were measured on Bruker Advance 300 instrument at 300 MHz and 75 MHz respectively. IR spectra were recorded on Varian 1000 FT-IR Scimitar Series. UV–vis spectra were measured on Perkin ELMER Lambda 900. PL spectra were measured on ManDEL Scientific RF-1501 spectrofluorophotometer. High Resolution ESI spectra were recorded on the 7.0 T Actively Shielded Fourier Transform Ion Cyclotron Resonance Mass Spectrometers. Cyclic voltammograms (CV) and other electrochemical experiments were performed on a BAS 100 electrochemical workstation. Glass carbon working electrode, platinum counter electrode and silver pseudoreference electrode were used together, all the potentials were corrected using ferrocenium/ferrocene (Fc$^+$/Fc^0) and reported relative to NHE.

2.3. Synthesis

2.3.1. ***TBI-a***

4,7-Bis(5-(9,9-dioctyl-9H-fluoren-2-yl)thiophen-2-yl)benzo[c][1,2,5]thia-diazole-5,6-diamine (1.10 g, 1.00 mmol) and phthalic anhydride (0.22 g, 1.50 mmol) were combined in 1,2-dichlorobenzene (15 mL). The mixture was heated to reflux under argon protection overnight. Then the solvent was removed by reduced pressure evaporation and the residue was purified by column chromatography (silica gel) with CH$_2$Cl$_2$ and hexane to afford blue solid (0.97 g, 80% yield). ^{1}H NMR (300 MHz, DMSO-d$_6$) δ (ppm): 8.81–8.42 (m, 1H), 8.42–8.39 (d, J = 5.4 Hz, 1H), 8.09–8.07 (d, J = 6.9 Hz, 1H), 7.87–7.50 (m, 13H), 7.43–7.40 (m, 2H), 7.35–7.30 (m, 8H), 2.01 (s, 8H), 1.11–0.96 (m, 40H), 0.73–0.69 (m, 12H), 0.52 (s, 8H). ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 151.6, 150.9, 150.0, 147.8, 140.6, 132.9, 132.1, 131.2, 130.9, 130.8, 130.5, 128.6, 126.8, 126.6, 124.9, 124.7, 123.7, 123.0, 120.7, 120.1, 119.8, 55.2, 40.4, 31.8, 30.1, 29.3, 23.8, 22.6, 14.0. ESI-MS (*m*/*z*): 1218.6 (M$^+$).

2.3.2. ***TBI-b***

The procedure is similar to that described for **TBI-a**. Tetrafluorophthalic anhydride (0.33 g, 1.50 mmol) was used instead of phthalic anhydride. Blue solid was obtained (0.92 g, 71% yield). ^{1}H NMR (300 MHz, DMSO-d$_6$) δ (ppm): 8.58 (s, 2H), 7.85–7.78 (m, 10H), 7.40–7.30 (m, 6H), 1.99 (s, 8H), 1.04–1.84 (m, 40H), 0.72–0.67 (m, 12H), 0.51 (s, 8H). ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 151.6, 150.9, 141.1, 140.7, 140.5, 140.3, 132.6, 130.9, 127.1, 127.0, 126.8, 123.3, 123.1, 122.9, 120.3, 120.2, 120.1, 119.8, 119.7, 55.2, 40.4, 31.8, 30.1, 29.7, 29.3, 23.8, 22.6, 14.0. ESI-MS (*m*/*z*): 1308.5 (M+NH$_4^+$).

2.3.3. ***TBI-c***

The procedure is similar to that described for **TBI-a**. 1,8-Naphthalic anhydride (0.30 g, 1.50 mmol) was used instead of phthalic anhydride and the solvent was changed into *m*-cresol. Purple solid was obtained (0.53 g, 42% yield). ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 9.11–9.02 (m, 2H), 8.62–8.59 (d, J = 7.2 Hz, 1H), 8.29–8.19 (m, 2H), 7.87–7.69 (m, 10H), 7.63–7.53 (m, 2H), 7.42–7.27 (m, 7H), 2.10–2.00 (m, 8H), 1.42–1.27 (m, 40H), 0.78–0.60 (m, 20H). ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 158.3, 154.3, 153.8, 151.5, 151.4, 151.0, 150.9, 150.4, 148.4, 146.3, 143.6, 141.0, 140.8, 140.7, 136.3, 135.3, 134.3, 133.3, 133.1, 132.2, 131.7, 131.4, 130.7, 128.0, 127.6, 127.2, 127.0, 126.9, 126.8, 125.1, 124.8, 123.9, 123.4, 122.9, 122.8, 122.3,

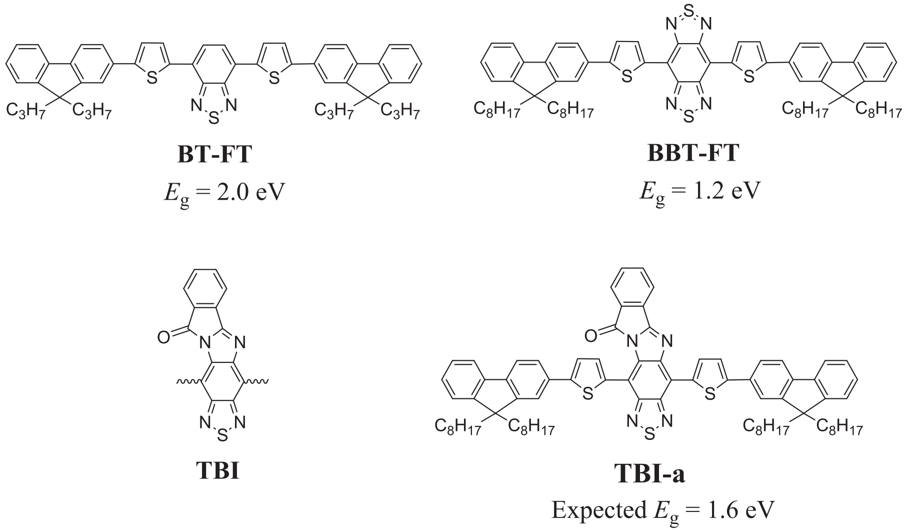

Fig. 2. Chemical structures of **BT-FT**, **BBT-FT**, **TBI** and **TBI-a**.