Synthesis of Azole-fused Benzothiadiazoles as Key Units for Functional π -Conjugated Compounds

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2,1,3-Benzothiadiazole (BT) is a widely used electron-accepting unit in organic electronics including organic solar cells (OSCs). As modifications of BT skeleton, two types of azole-fused BT units were designed and synthesized; thiazole-fused BT with an electron-withdrawing C=N bond and imidazole-fused BT with an electron-donating nitrogen atom as well as an electron-withdrawing C=N bond. Electrochemical measurements and theoretical calculations suggest that thiazole-fusion enhances the electron-accepting ability, whereas imidazole-fusion endows the BT skeleton with electron-donating ability while maintaining its electron-accepting ability. Moreover, in thiazole-fused BT units, the electronic structure could be further modulated by varying the oxidation state of the sulfur atom in methylthio group at the fused thiazole ring.

Keywords: Benzothiadiazole, Acceptor unit, Ring-fusion, Thiazole, Imidazole

1. Introduction

2,1,3-Benzothiadiazole (BT) is a widely used electron-accepting unit in organic electronics [1–5]. Modified BT derivatives, such as 5,6-difluoro-BT, thiadiazoloquinoline, benzobisthiadiazole, naphthobisthiadiazole have been synthesized [6,7]. By the combination of these BT derivatives with electron-donating units, various donor–acceptor (D–A) polymers have been developed and utilized as photoelectric conversion materials in organic solar cells (OSCs). The outstanding characteristics of BT unit are the effective extension of π -conjugation as well as high electron-accepting ability, which could be explained by the considerable contribution of butadiene character and the presence of two electron-withdrawing C=N bonds (Fig. 1a). Similarly, another representative electron-accepting unit, diketopyrrolopyrrole (DPP) [8–10], can be regarded as butadiene moiety connected by electron-donating nitrogen atoms as well as electron-withdrawing C=O bonds (Fig. 1b).

In this paper, we describe two types of azole-fusion as further modifications of BT skeleton; thiazole-fusion and imidazole-fusion (Fig. 1c, d). We anticipated that thiazole-fusion enables the

Fig. 1. Diene character in (a) benzothiadiazole (BT) and (b) diketopyrrolopyrrole (DPP), and the molecular design of (c) thiazole-fused BT and (d) imidazole-fused BT.

further lowering of LUMO energy level by the existence of the electron-withdrawing imine moiety [11,12] (Fig. 2). Moreover, the LUMO energy level can be further controlled by changing the oxidation state of the substituted methylthio group. Imidazole-fusion is expected to induce the increase of HOMO energy level by the existence of an electron-

donating amine moiety while maintaining the LUMO level by the imine moiety (Fig. 2). Here we report the synthesis of thiazole-fused and imidazole-fused BT skeletons as key building units for functional π -conjugated compounds, and discuss the effect of azole-fusion on the electronic structure.

Fig. 2. Effect of azole-fusion on the electronic structure of BT skeleton. Calculated at B3LYP/6-31G(d) level of theory [13].

2. Experimental

2.1. General information

Melting points (mp) were measured on a Yanaco Micro Melting Point Apparatus. ^1H and ^{13}C NMR spectra were recorded with a JEOL JNM ECA500 (500 MHz for ^1H and 126 MHz for ^{13}C). Chemical shifts were reported in δ ppm using residual protons in the deuterated solvents for ^1H NMR and using solvent peaks for ^{13}C NMR as internal standards. IR spectra were taken with a Shimadzu FTIR-8400S spectrometer. Mass spectra were measured on a Bruker micrOTOF-Q II (APCI) and JEOL JMS-MS700V (FAB). Cyclic voltammetry (CV) was performed on an ALS/chi-620C electrochemical analyzer. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and an Ag/AgNO₃ reference electrode. The measurement was carried out under an argon atmosphere using CH₂Cl₂ solutions of samples (1 mM) with 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄N⁺PF₆⁻) as a supporting electrolyte. The redox potentials were calibrated with ferrocene as an internal standard. Thin layer chromatography (TLC) was performed on plates coated with 0.25 mm thick silica gel 60F-254 (Merck). Column chromatography was performed using silica gel PSQ 60B (Fuji Silysia) or PSQ 100B (Fuji Silysia). All reactions were carried out under an argon atmosphere except as otherwise noted.

2.2. Computation method

All calculations were conducted using the Gaussian 09 program [13]. The geometries were optimized at the B3LYP/6-31G(d) level of theory. The fact that these geometries are at the energy minimum was confirmed by frequency calculations at the same level of theory.

2.3. Synthesis

2.3.1. 2-(Methylthio)-1,3-benzothiazole-5,6-diamine (**6**)

To a 1 L two-necked flask were added 2-chloro-5-nitrobenzene-1,4-diamine (**3**) (10.0 g, 53.3 mmol), sodium ethylxanthate (16.9 g, 117 mmol), and dry DMF (350 mL). The mixture was stirred at 100 °C for 2.5 h and then cooled in a water bath. Methyl iodide (8.29 mL, 133 mmol) was added dropwise, and the mixture was stirred for 17.5 h. The reaction mixture was poured into water. The formed orange precipitates were collected by filtration, washed with water, and dried under vacuum at 50 °C to give benzothiazole **5**, which was used in the next reaction without further purification.

To a 1 L two-necked flask were added **5** (11.8 g, 48.9 mmol), SnCl₂·2H₂O (55.0 g, 244 mmol), MeOH (480 mL), distilled water (68 mL), and HCl aq. (12 M, 1.8 mL, 22 mmol). The mixture was stirred at 70 °C for 22 h. The reaction mixture was concentrated under reduced pressure and then neutralized with saturated Na₂CO₃ aq. (500 mL). The formed precipitates were collected by filtration, washed with water, and dried under vacuum at 50 °C. The crude product was purified by silica gel column chromatography (methanol/CH₂Cl₂ = 1:10 as eluent, R_f = 0.25) to give **6** (11.3 g, 65% from **3**) as yellow solids.

mp: 141.5–142.3 °C; ^1H NMR (500 MHz, DMSO-*d*₆): δ 6.98 (s, 1H), 6.92 (s, 1H), 4.76 (s, 2H), 4.71 (s, 2H), 2.67 (s, 3H); ^{13}C NMR (126 MHz, DMSO-*d*₆): δ 159.39, 146.14, 135.58, 134.84, 123.38, 105.32, 103.97, 15.65; HRMS (FAB) (*m/z*): [*M*]⁺ calcd. for C₈H₉N₃S₂, 211.0238; found, 211.0239.

2.3.2. 6-(Methylthio)thiazolo[5,4-*f*]-2,1,3-benzothiadiazole (**7**)

To a 500 mL two-necked flask were added **6** (3.00 g, 14.2 mmol), distilled triethylamine (15.8 mL, 114 mmol), and CH₂Cl₂ (200 mL), and the mixture was cooled in an ice bath. SOCl₂ (4.20 mL, 57.9 mmol) was added dropwise over 25 min. The mixture was allowed to warm to room temperature and was stirred for 17 h. The resulting mixture was neutralized with saturated Na₂CO₃ aq. (150 mL),

and the aqueous phase was extracted with CH₂Cl₂ (150 mL × 4). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (CH₂Cl₂ as eluent, *R*_f = 0.57) to give **7** (3.21 g, 94%) as yellow solids. mp: 171.5–172.4 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.37 (s, 1H), 8.32 (s, 1H), 2.87 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 172.94, 155.69, 153.93, 152.00, 140.61, 111.68, 110.53, 15.76; HRMS (FAB) (*m/z*): [M]⁺ calcd. for C₈H₅N₃S₃, 238.9646; found, 238.9646.

2.3.3. 4,8-Dibromo-6-(methylthio)thiazolo[5,4-*f*]-2,1,3-benzothiadiazole (**1a**)

To a 100 mL two-necked flask were added **7** (3.16 g, 13.2 mmol) and FeCl₃·6H₂O (2.16 g, 7.99 mmol). Br₂ (22.0 mL, 427 mmol) was added, and the mixture was stirred at 50 °C for 5 h. Saturated NaHSO₃ aq. (200 mL) was added to consume the excess bromine. The formed precipitates were collected by filtration, washed with water, and dried under vacuum at 50 °C. The crude product was purified by silica gel column chromatography (CHCl₃ as eluent, *R*_f = 0.78) to give **1a** (4.85 g, 92%) as yellow solids.

mp: 241.0–241.8 °C; ¹H NMR (500 MHz, CDCl₃): δ 2.92 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 173.60, 152.53, 152.15, 149.82, 142.84, 102.96, 102.37, 16.15; HRMS (APCI) (*m/z*): [M+H]⁺ calcd. for C₈H₄Br₂N₃S₃, 395.7929; found, 395.7913.

2.3.4. 4,8-Dibromo-6-(methylsulfinyl)thiazolo[5,4-*f*]-2,1,3-benzothiadiazole (**1b**)

To a 100 mL two-necked flask were added **1a** (199 mg, 0.50 mmol) and CHCl₃ (40 mL). After cooled to 0 °C, *m*CPBA (124 mg, 0.50 mmol) was added, and the mixture was stirred at 0 °C for 4 h. Saturated NaHSO₃ aq. (40 mL) was added, and the aqueous phase was extracted with CHCl₃ (30 mL × 2). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (CHCl₃ as eluent, *R*_f = 0.43) to give **1b** (154 mg, 75%) as yellow solids. mp (decomp.): 271.2 °C; IR (KBr) ν = 1070 cm⁻¹ (S=O, sulfoxide); ¹H NMR (500 MHz, CDCl₃): δ 3.20 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 185.79, 152.65, 152.02, 150.45, 141.83, 107.85, 104.83, 43.07; HRMS (APCI) (*m/z*): [M+H]⁺ calcd. for C₈H₄Br₂N₃OS₃, 411.7878; found, 411.7867.

2.3.5. 4,8-Dibromo-6-(methylsulfonyl)-

thiazolo[5,4-*f*]-2,1,3-benzothiadiazole (**1c**)

To a 100 mL two-necked flask were added **1a** (199 mg, 0.50 mmol) and CHCl₃ (40 mL). *m*CPBA (493 mg, 2.00 mmol) was added and the mixture was stirred at room temperature for 30 h. Saturated NaHSO₃ aq. (20 mL) was added, and the aqueous phase was extracted with CHCl₃ (20 mL × 2). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (CHCl₃ as eluent, *R*_f = 0.57) to give **1c** (157 mg, 73%) as yellow solids.

mp (decomp.): 275.4 °C; IR (KBr) ν = 1324, 1148 cm⁻¹ (S=O, sulfone); ¹H NMR (500 MHz, CDCl₃): δ 3.54 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 171.12, 152.29, 151.09, 150.88, 141.59, 110.45, 104.85, 41.70; HRMS (APCI) (*m/z*): [M+H]⁺ calcd. for C₈H₄Br₂N₃O₂S₃, 427.7827; found, 427.7807.

2.3.6. 4,8-Dibromo-6-(5-(2-ethylhexyl)thiophen-2-yl)-5H-imidazo[5,4-*f*]-2,1,3-benzothiadiazole (**11**)

To a Schlenk tube were added **10** (234 mg, 0.721 mmol), dry DMSO (5.0 mL), TFA (11 μL, 0.14 mmol) and 5-(2-ethylhexyl)thiophene-2-carbaldehyde (210 μL, 0.759 mmol). The mixture was stirred at 100 °C for 16.5 h and then cooled to room temperature. DDQ (418 mg, 1.84 mmol) was added, and the mixture was stirred at 40 °C for 0.5 h. The reaction mixture was poured into saturated NaHCO₃ aq. (80 mL). The formed yellow precipitates were collected by filtration and washed with water. The residue was then dissolved in CH₂Cl₂, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (CH₂Cl₂ as eluent, *R*_f = 0.27) to give **11** (333 mg, 87%) as yellow solids.

mp: 223.9–224.9 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.83 (d, *J*(H,H) = 4.0 Hz, 1H), 6.89 (d, *J*(H,H) = 4.0 Hz, 1H), 2.82 (d, *J*(H,H) = 6.5 Hz, 2H), 1.65 (m, 1H), 1.39–1.25 (m, 8H), 0.92–0.87 (m, 6H); ¹³C NMR (126 MHz, DMF-*d*₇): δ 156.36, 153.11, 151.11 (2C), 149.01, 141.62, 132.70, 130.79, 128.69, 98.95, 89.70, 42.51, 34.97, 33.36, 29.72, 26.49, 23.86, 14.73, 11.45; HRMS (APCI) (*m/z*): [M+H]⁺ calcd. for C₁₉H₂₁Br₂N₄S₂, 526.9569; found, 526.9569.

2.3.7. 4,8-Dibromo-6-(5-(2-ethylhexyl)thiophen-2-yl)-5-methyl-imidazo[5,4-*f*]-2,1,3-benzothiadiazole (**2**)

In a Schlenk tube were added **11** (603 mg, 1.14 mmol), dry DMF (3.0 mL), K₂CO₃ (320 mg, 2.32

mmol), and methyl iodide (141 μ L, 2.26 mmol). The mixture was stirred at 100 $^{\circ}$ C for 16.5 h and then poured into saturated NH_4Cl aq. (150 mL). The formed yellow precipitates were collected by filtration and washed with water. The residue was then dissolved in CH_2Cl_2 , dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (CH_2Cl_2 as eluent, $R_f = 0.47$) to give **2** (365 mg, 50%) as yellow solids.

mp: 136.8–137.3 $^{\circ}$ C; ^1H NMR (500 MHz, CDCl_3): δ 7.60 (d, $J(\text{H,H}) = 3.5$ Hz, 1H), 6.91 (d, $J(\text{H,H}) = 4.0$ Hz, 1H), 4.38 (s, 3H), 2.84 (d, $J(\text{H,H}) = 7.0$ Hz, 2H), 1.68 (m, 1H), 1.42–1.31 (m, 8H), 0.94–0.89 (m, 6H); ^{13}C NMR (126 MHz, CDCl_3): δ 157.15, 152.36, 150.65, 149.90, 147.44, 138.97, 131.52, 127.79, 126.69, 100.09, 89.53, 41.58, 35.30, 34.31, 32.39, 28.83, 25.52, 22.96, 14.11, 10.79; HRMS (APCI) (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{20}\text{H}_{23}\text{Br}_2\text{N}_4\text{S}_2$, 540.9725; found, 540.9700.

2.4. X-Ray crystal structure analysis

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1540942 (**1a**) and CCDC-1540941 (**2**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.4.1. Compound **1a**

Single crystals suitable for X-ray analysis were obtained by diffusion of methanol into a solution of **1a** in CH_2Cl_2 . Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II) with Mo K α radiation ($\lambda = 0.71073$ $\text{\AA}$) and graphite monochromator. A total of 4923 reflections were measured with a maximum 2θ angle of 51.0° , of which 2050 were independent reflections ($R_{\text{int}} = 0.0230$). The structure was solved by direct methods (SHELXS-97[14]) and refined by the full-matrix least-squares on F^2 (SHELXL-97[14]). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $\text{C}_8\text{H}_3\text{Br}_2\text{N}_3\text{S}_3$; FW = 397.13, crystal size $0.55 \times 0.07 \times 0.03$ mm^3 , Monoclinic, $C2/c$, $a = 16.513(4)$ $\text{\AA}$, $b = 3.9266(10)$ $\text{\AA}$, $c = 34.128(9)$ $\text{\AA}$, $\beta = 94.065(3)^{\circ}$, $V = 2207.2(10)$ $\text{\AA}^3$, $Z = 8$, $D_c = 2.390$ g cm^{-3} . The refinement converged to $R_1 = 0.0368$, $wR_2 = 0.0802$ ($I > 2\sigma(I)$), GOF = 1.336.

2.4.2. Compound **2**

Single crystals suitable for X-ray analysis were obtained by diffusion of hexane into a solution of **2** in CH_2Cl_2 . Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II) with Mo K α radiation ($\lambda = 0.71073$ $\text{\AA}$) and graphite monochromator. A total of 5223 reflections were measured with a maximum 2θ angle of 51.0° , of which 3838 were independent reflections ($R_{\text{int}} = 0.0201$). The structure was solved by direct methods (SHELXS-97[14]) and refined by the full-matrix least-squares on F^2 (SHELXL-97[14]). The 2-ethylhexyl moiety (C13–C23) was partially disordered, which was solved using appropriate models. Thus, two sets of disordered parts, i.e., (C14, C19, C20) and (C21, C22, C23) were placed with the occupancy of 0.68 and 0.32, respectively. All non-hydrogen atoms, except for the disordered carbons of C21, C22, C23, were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $\text{C}_{20}\text{H}_{18}\text{Br}_2\text{N}_4\text{S}_2$; FW = 538.32, crystal size $0.31 \times 0.29 \times 0.01$ mm^3 , Triclinic, $P-1$, $a = 8.1304(19)$ $\text{\AA}$, $b = 8.692(2)$ $\text{\AA}$, $c = 16.315(4)$ $\text{\AA}$, $\alpha = 74.878(3)^{\circ}$, $\beta = 79.871(3)^{\circ}$, $\gamma = 73.059(3)^{\circ}$, $V = 1058.6(4)$ $\text{\AA}^3$, $Z = 2$, $D_c = 1.689$ g cm^{-3} . The refinement converged to $R_1 = 0.0375$, $wR_2 = 0.0996$ ($I > 2\sigma(I)$), GOF = 1.084.

3. Results and discussion

3.1. Synthesis

We have previously reported the construction of thiazole-fused BT skeleton by thermal [11] or oxidative [12] cyclization of thioamide. In those cases, aryl groups have to be introduced at 4,7-position of BT before the cyclization. Here we developed a new synthetic methodology which enables the synthesis of 4,7-dibrominated derivatives (Scheme 1). The reaction of commercially available *o*-haloaniline **3** with sodium ethylxanthate gave the intermediate **4** [15], which was treated with methyl iodide to give methylthiobenzothiazole **5**. Reduction of the nitro group by tin (II) chloride gave diamine **6** in 65% yield from **3** [16]. Condensation with thionyl chloride gave thiazole-fused BT **7** in 94% yield. The dibromination was achieved by the reaction with bromine in the presence of iron (III) chloride [17], which yielded **1a** with a methylthio group in 92% yield. One advantage of introducing the methylthio group is that the electronic structure could be modulated by varying the oxidation state of the sulfur atom. **1b** with a methylsulfoxide group was

synthesized by the reaction with *m*CPBA at 0 °C in 75% yield, while **1c** with a methylsulfonyl group was synthesized by treating with excess amount of *m*CPBA at room temperature in 73% yield [18].

Scheme 1. Synthesis of thiazole-fused BT unit. Reagents and conditions: i) Sodium ethylxanthate (2.2 equiv), DMF, 100 °C, 2.5 h; ii) MeI (2.5 equiv), DMF, rt, 17.5 h; iii) SnCl₂·2H₂O (5.0 equiv), MeOH/HCl aq., 70 °C, 22 h, 65% from **3**; iv) SOCl₂ (4.1 equiv), Et₃N (8.0 equiv), CH₂Cl₂, 0 °C to rt, 17 h, 94%; v) Br₂ (32 equiv), FeCl₃·6H₂O (0.6 equiv), 50 °C, 5 h, 92%; vi) *m*CPBA (1.0 equiv), CHCl₃, 0 °C, 4 h, 75%; vii) *m*CPBA (4.0 equiv), CHCl₃, rt, 30 h, 73%.

For the synthesis of imidazole-fused BT unit, diamine **10** was synthesized from commercially available dibromobenzothiadiazole **8** following the reported procedure [19]. Construction of the fused imidazole ring was achieved by the condensation of **10** with arylaldehyde [20,21] using TFA as a catalyst, which yielded **11** in 87% yield (Scheme 2). Finally, methylation of imidazole [22] afforded the imidazole-fused BT **2** in 50% yield.

3.2. Crystal structure

Single crystals of **1a** or **2** were obtained from slow diffusion of methanol or hexane into the solution in CH₂Cl₂, respectively. X-ray diffraction analyses of these crystals confirmed that thiazole-fused and imidazole-fused BT adopt highly planar structures, and the dihedral angle between the fused imidazole and the thiophene ring was 8.0° (Fig. 3). In thiazole-fused BT **1a**, the bond lengths for C2–C3 (1.370(8) Å) and C4–C5 (1.378(7) Å) are shorter than the other bond lengths in the benzene ring,

similar to the bond alternation in **8** (1.356(7) Å and 1.364(6) Å) [23]. The same trend was observed for imidazole-fused BT **2**, with the bond length of C2–C3 (1.371(5) Å) and C4–C5 (1.369(4) Å). These features suggest the considerable contribution of butadiene character in these azole-fused BT skeletons.

Scheme 2. Synthesis of imidazole-fused BT unit. Reagents and conditions: i) Fuming HNO₃, conc. H₂SO₄, 50 °C, 23 h, 34%; ii) Fe (12.0 equiv), AcOH, 50 °C, 8.5 h, 77%; iii) 5-(2-ethylhexyl)thiophene-2-carbaldehyde (1.1 equiv), TFA (20 mol%), DMSO, 100 °C, 16.5 h, then DDQ (2.6 equiv), 40 °C, 0.5 h, 87%; iv) MeI (2.0 equiv), K₂CO₃ (2.0 equiv), DMF, 100 °C, 16.5 h, 50%.

Fig. 3. Crystal structure of **1a** and **2**. All hydrogen atoms and 2-ethylhexyl group are omitted for clarity. Only selected atoms are labeled. (a) ORTEP drawing (thermal ellipsoids at 50% probability) of **1a**. Selected bond lengths (Å): C(1)–C(2), 1.411(7); C(2)–C(3), 1.370(8); C(3)–C(4), 1.440(7); C(4)–C(5), 1.378(7); C(5)–C(6), 1.416(8); C(1)–C(6), 1.439(7). (b) ORTEP drawing of **2**. Selected bond lengths (Å): C(1)–C(2), 1.423(5); C(2)–C(3), 1.371(5); C(3)–C(4), 1.449(5); C(4)–C(5), 1.369(4); C(5)–C(6), 1.415(6); C(1)–C(6), 1.443(6).

3.3. Electrochemical properties

To evaluate the effect of thiazole and imidazole fusion on the electrochemical properties of the BT skeleton, cyclic voltammograms of **1a–1c** and **2** were recorded, and the results were compared with those of reference compound **8** (Fig. 4, Table 1). Thiazole-fused BT **1a** with a methylthio group

shows a reversible reduction wave at $E_{1/2} = -1.56$ V (vs. Fc/Fc^+), which is shifted by ca. 0.12 V to less negative potential compared to that of non-fused derivative **8** ($E_{1/2} = -1.68$ V). This result indicates the enhanced electron-accepting ability by thiazole-fusion. **1b** and **1c** with methylsulfoxide and methylsulfonyl groups shift the reduction potential to less negative at $E_{\text{pc}} = -1.41$ V and $E_{\text{pc}} = -1.26$ V, respectively, suggesting that the electron-accepting ability can be systematically enhanced by increasing the oxidation state of sulfur atom in methylthio group at the fused thiazole ring. In the oxidation

Fig. 4. Cyclic voltammograms of **1a–1c**, **2**, and reference compound **8**; recorded in CH_2Cl_2 (1 mM) at a scan rate of 100 mV s^{-1} using $n\text{-Bu}_4\text{NPF}_6$ (0.1 M) as the supporting electrolyte.

Table 1. Electrochemical properties of **1a–1c**, **2**, and **8**.

	E_{ox} [V] ^a	E_{red} [V] ^a	E_{HOMO} [eV] ^b	E_{LUMO} [eV] ^b
1a	(+1.51)	−1.56	−6.47	−3.63
1b	(+1.75)	(−1.41)	−6.63	−3.80
1c	—	(−1.26)	< −6.9	−3.96
2	(+1.11)	(−1.74)	−6.08	−3.52
8	—	−1.68	< −6.9	−3.50

^aPotentials in parentheses refer to irreversible oxidation/reduction peaks. ^bEstimated by: $-(E_{\text{onset}} + 5.1 \text{ eV})$ [24].

process, **1a** and **1b** show oxidation waves at $E_{\text{pa}} = +1.51$ V and $E_{\text{pa}} = +1.75$ V, respectively, whereas no oxidation waves are observed for **1c** and **8** in the

potential window of CH_2Cl_2 ($\sim +1.8$ V). This suggests that electron-donating ability is slightly enhanced by thiazole-fusion, and can be controlled by the substituents at the fused thiazole ring. As for imidazole-fused BT **2**, an irreversible oxidation wave is observed at less positive potential of $E_{\text{pa}} = +1.11$ V even compared with **1a** (+1.51 V), indicating that the electron-donating ability can be further enhanced on account of imidazole-fusion. The irreversible reduction wave at $E_{\text{pc}} = -1.74$ V indicates a subtle change in the electron-accepting ability. The HOMO and LUMO levels were estimated from these potentials (Table 1), which suggests the decrease of LUMO energy level by thiazole-fusion as well as the increase of HOMO energy level by imidazole-fusion.

3.4. Theoretical calculations

To gain insights into the effects of the azole-fusion on the electronic structure, DFT calculations were conducted on model compounds **1a'–1c'**, **2'**, and **8'**, in which the bromine atoms were replaced by hydrogen atoms and the 2-ethylhexyl group was replaced by a methyl group (Fig. 5). The frontier orbitals of BT **8'** indicate the considerable contribution of butadiene character, which is maintained in azole-fused BTs. The LUMO energy level is lowered by thiazole-fusion as well as

Fig. 5. Calculated energy diagram and depictions of the frontier orbitals of **1a'–1c'**, **2'**, and **8'** (B3LYP/6-31G(d)) [13].

increasing the oxidation state of the attached sulfur atom of methylthio group, whereas the HOMO energy level is elevated by imidazole-fusion. These trends are qualitatively in good agreement with the experimental energy levels estimated from cyclic voltammetry.

4. Conclusion

In summary, two types of azole-fused benzothiadiazoles were designed and synthesized as new electron-accepting units. We exhibited that thiazole-fusion induces the lowering of the LUMO energy level, whereas imidazole-fusion increases the HOMO energy level while maintaining the LUMO energy level. Moreover, in thiazole-fused BT units, the electronic structure could be further modulated by varying the oxidation state of the sulfur atom in methylthio group at the fused thiazole ring. A variety of D–A molecules and polymers would be developed using these electron-accepting units by combining with various electron-donating and π -conjugated units [25–32], which is currently in progress in our laboratory.

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