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Boron-Containing Monopyrrolo-Annelated Tetrathiafulvalene Compounds: Synthesis and Absorption Spectral/Electrochemical Responsiveness toward Fluoride Ion

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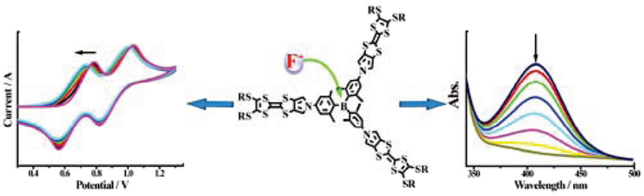

Two new boron-based conjugated compounds **1** and **2** containing one and three monopyrrolo-annelated tetrathiafulvalene (TTF) unit(s) were synthesized and characterized. They exhibit typical ICT absorptions which can be modulated after addition of fluoride ion. In addition, the oxidation potentials of **1** and **2** are shifted to low potential region in the presence of fluoride ion. Such absorption spectral and electrochemical responsiveness of **1** and **2** toward fluoride ion is due to the binding of the boron units with fluoride ion.

Boron-containing π-conjugated molecules have attracted attention because of their intriguing electronic and photophysical properties, which are due to the conjugation of the vacant p-orbital on boron with the π orbitals of the attached carbon π-conjugated moieties.[1] Accordingly, these boron-containing conjugated molecules are promising nonlinear optical and charge-transport materials as well as light-emitting materials for organic light-emitting devices (OLEDs).[2] It has also been reported that π-conjugated systems with boron show strong affinity toward fluoride ion.[3] The binding of fluoride ion to the boron center disrupts or perturbs the $p-\pi$ conjugation between the boron center and the aromatic chromophore, leading to absorption and fluorescent spectral changes. By taking advantage of boron-containing π-conjugated molecules, new selective and sensitive sensors for fluoride are developed.[4−6]

In typical boron-containing π-conjugated molecules, electron-donor units such as anthracene[2c] and substituted amine[4d,e] were linked to boron either directly or through conjugated spacers. These conjugated molecules exhibit intramolecular charge-transfer (ICT) absorption and ICT fluorescence in some cases. It is expected that the ICT interaction within the boron-containing π-conjugated molecules would be modulated if a stronger electron donor such as tetrathiafulvalene (TTF) is incorporated. It should be noted that TTF and its derivatives have been intensively investigated as strong electron donors for conducting materials, molecular machines, redox-fluorescence switches, and chemical sensors.[7−9] A number of TTF-based electron donor (D)−acceptor (A) dyads or triads have been studied for intramolecular CT interactions and photoinduced electron

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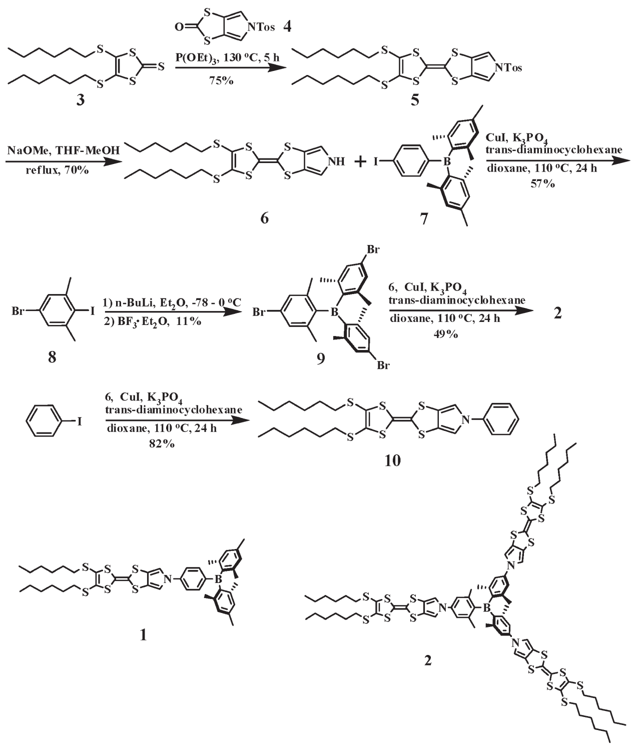
SCHEME 1. **Synthetic Approach to Compounds 1 and 2**



transfer processes.[8h,10−12] A TTF-based D−A compound with a boronic acid unit was synthesized as saccharide sensor.[13] However, to the best of our knowledge, no boron-containing conjugated molecules with TTF units have been reported. In this paper, we describe two new boron-based conjugated compounds **1** and **2** (Scheme 1) containing one and three monopyrrolo-annelated tetrathiafulvalene (TTF) unit(s), respectively. As will be discussed below, compounds **1** and **2** exhibit ICT absorptions which can be modulated upon binding with fluoride ion.

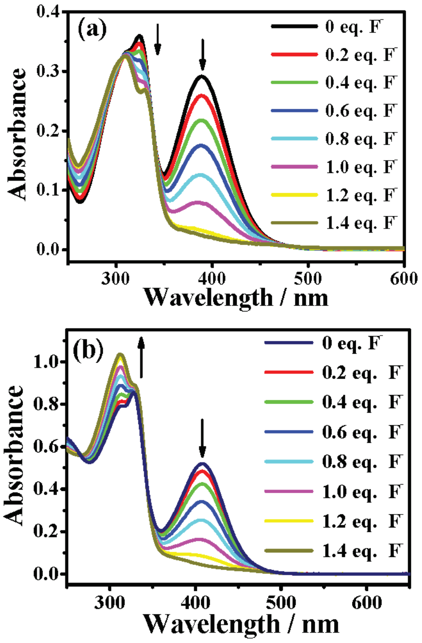


FIGURE 1. Absorption spectra of **1** (1.0×10^{-5} M in THF) (a) and **2** (1.0×10^{-5} M in THF) (b) upon addition of different amounts of *n*-Bu$_4$NF.

The synthetic approach to compounds **1** and **2** was outlined in Scheme 1. Compound **6**, the monopyrrolo-annelated tetrathiafulvalene, was synthesized by the cross-coupling of compounds **3**[12d] and **4**,[14] followed by removal of the tosylate group in compound **5** with NaOCH$_3$ (see the Supporting Information). Compounds **1** and **2** were obtained by *N*-arylation reaction of the pyrrole unit in **6** with (4-iodophenyl)-dimesitylborane (**7**) and tris(4-bromo-2,6-dimethylphenyl)-borane (**9**) (see the Supporting Information), respectively, in acceptable yields.[15] Compounds **7**[3] and **8**[16] were synthesized by following the procedures reported previously. For comparison, compound **10** was prepared via the coupling reaction between **6** and iodobenzene (see the Supporting Information).

Figure 1 shows the absorption spectra of compounds **1** and **2** in THF. Compared to those of compound **10** and compound **7** (or **9**), which exhibit no strong absorptions above 350 nm (see Figure S1, Supporting Information), compounds **1** and **2** show new absorptions around 400 nm. This should be due to the ICT absorptions from th TTF units to the boron centers in **1** and **2**. Moreover, the ICT absorption maximum of compound **2** is red-shifted by 20 nm compared to that of compound **1**. As discussed below, this is in agreement with the corresponding HOMO−LUMO energy gaps of **1** and **2** which are estimated theoretically. It is interesting to note that the absorption spectra of compounds **1** and **2** can be modulated by addition of fluoride ion. The ICT absorptions of **1** and **2** around 400 nm became progressively weaker as

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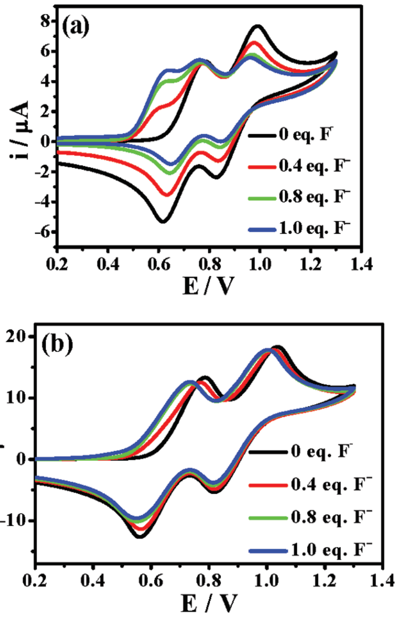

FIGURE 2. Cyclic voltammograms of compounds **1** (1.0×10^{-3} M) (a) and **2** (1.0×10^{-3} M) (b) in THF at 25 °C with n-Bu_4NPF_6 (0.1 M) as the supporting electrolyte and Ag/AgCl as reference electrode in the presence of increasing amounts of n-Bu_4NF.

demonstrated in Figure 1. The color of solutions of **1** and **2** changed from yellow to colorless after introduction of the fluoride ion. Such absorption spectral variation of **1** and **2** after addition of fluoride ion can be understood by considering the fact that the electron-withdrawing capacities of the boron units in **1** and **2** would be largely weakened upon binding with fluoride ion. Such absorption spectral change in the presence of fluoride is relevant to a LUMO-centered process.

The absorption spectra of **1** and **2** in the presence of different amounts of fluoride ion (n-Bu_4N^+ as the countercation) were measured. The corresponding Job plots (see Figure S2, Supporting Information) indicated that the binding of fluoride ion with compounds **1** and **2** exhibited a 1:1 stoichiometry. By fitting the absorbance variation at 390 and 408 nm for compounds **1** and **2**, respectively (see the Supporting Information), the binding constants of **1** and **2** with fluoride ion were estimated to be $(3.65 \pm 0.13) \times 10^4$ M^{-1} and $(1.65 \pm 0.06) \times 10^4$ M^{-1}, respectively. Therefore, compound **1** binds fluoride ion more strongly than compound **2**. The presence of three TTF units in **2** would weaken the electron-withdrawing capacity of the boron unit in **2**, thus reducing the binding with fluoride. Additionally, the boron center in **2** is surrounded by three bulky groups, which would make the binding of fluoride ion less favorable.

The absorption spectra of compounds **1** and **2** were also examined in the presence of other anions including AcO^-, Cl^-, Br^-, I^-, NO_3^-, HSO_4^-, PF_6^-, and ClO_4^-. The absorption spectra of **1** and **2** were almost unaltered in the presence of these anions (see Figures S3 and S4, Supporting Information). Therefore, it may be concluded that compounds **1** and **2** show selective binding with fluoride ion.

The electrochemical studies also confirmed the responsiveness of compounds **1** and **2** toward fluoride ion. Figure 2 shows the cyclic voltammograms of compounds **1** and **2** and those after additions of fluoride ion. Two quasireversible oxidation waves with $E^{1/2}(ox_1) = 0.70$ V and $E^{1/2}(ox_2) = 0.91$ V were observed for compound **1**, corresponding to the formation of the radical cation ($TTF^{\bullet+}$) and dication (TTF^{2+}) of the TTF unit, respectively, according to previous studies.[14] Similarly, the oxidation potentials of compound **2** were measured to be $E^{1/2}(ox_1) = 0.67$ V and $E^{1/2}(ox_2) = 0.93$ V. For comparison, the cyclic voltammogram of compound **10** was recorded, and the corresponding oxidation potentials were determined to be $E^{1/2}(ox_1) = 0.65$ V and $E^{1/2}(ox_2) = 0.87$ V (see Figure S7, Supporting Information). It is obvious that the oxidation potentials of compounds **1** and **2** are slightly more positive compared to those of compound **10**. This is probably due to the electron-withdrawing effects of boron units in **1** and **2**.

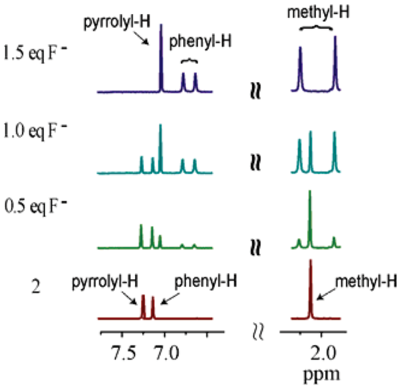

FIGURE 3. Partial ^1H NMR spectra of **2** (5.0×10^{-3} M in THF-d_8) after addition of different amounts of n-Bu_4NF.

The cyclic voltammograms of **1** and **2** were changed after the addition of fluoride ion as demonstrated in Figure 2. The first oxidation wave of compound **1** was progressively shifted to low-potential region. No further shifts were detected for the oxidation potentials of **1** after the addition of more than 1.0 equiv of fluoride ion (see Figure S6, Supporting Information).[17] The first oxidation peak potential of **1** was shifted from 0.78 to 0.64 V in the presence of 1.0 equiv of fluoride ion. The second oxidation wave was also slightly shifted to low-potential region. Similar variation was detected for compound **2**. The first oxidation peak potential of **2** was shifted from 0.79 to 0.73 V when 1.0 equiv of fluoride ion was added, but the oxidation waves were not changed further after addition of more than 1.0 equiv of fluoride ion (see Figure S6, Supporting Information). Such oxidation potential shifts can be interpreted by considering the fact that the binding of the boron centers in **1** and **2** with fluoride ion will weaken the electron-withdrawing effects of boron units in **1** and **2**. The oxidation potential shift upon addition of fluoride ion for compound **2** is smaller than that for compound **1**. This may be due to the fact the electron-withdrawing capacity of the boron unit in **2** is weaker because of the presence of three TTF units compared to that of the boron unit in **1**, and as a result, the binding of the boron unit in **2** with fluoride will not significantly modify the electronic structure of **2**.

The binding of compounds **1** and **2** with fluoride ion was also investigated with ^1H NMR spectroscopy. Figure 3 shows

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(17) The control cyclic voltammetric experiment with fluoride ion (see Figure S6, Supporting Information) indicates that the slight variation of the oxidation waves of **1** after the addition of more than 1.0 equiv of fluoride ion is due to the excess fluoride ion.

the partial ^{1}H NMR spectrum of **2** and those in the presence of different amounts of fluoride ion. The protons of the methyl groups linked to benzene rings and those of the benzene and pyrrole rings show signals at 2.1, 7.1, and 7.3 ppm, respectively, before the addition of fluoride ion. New signals at 1.8, 2.2, 6.6, 6.8, and 7.0 ppm gradually emerged, and the original signals became weak after introduction of fluoride ion to the solution. The signals due to protons of the benzene and pyrrole rings were shifted upfield after the addition of 1.5 equiv of fluoride ion. This is likely due to the binding of the boron center in **2** with fluoride ion, which will make the boron unit less electron-deficient. Two singlet signals at 1.8 and 2.2 ppm were observed for the protons of the methyl groups after addition of 1.5 equiv of fluoride ion. Such variations of ^{1}H NMR signals are induced by the binding of boron center in **2** with fluoride ion; as a result, the hybridization of boron center in **2** will be changed from sp^2 to sp^3, leading to a configuration change for the whole molecule. Consequently, the protons on the methyl groups become nonequivalent. Similar ^{1}H NMR spectral variation was detected for compound **1** after the addition of fluoride ion (see Figure S5, Supporting Information). This ^{1}H NMR spectral variation provides further evidence for the binding of compounds **1** and **2** with fluoride ion.

Finally, theoretical calculations were carried out for compounds **1** and **2** using B3LYP/6-31G* with Gaussian 03 (see the Supporting Information). The calculation results indicate that the boron centers in **1** and **2** exhibit three-coordinated propeller-like conformations (see Figure S8, Supporting Information). The HOMO and LUMO energies of **1** were calculated to be −4.76 and −1.82 eV, and those of **2** were −4.82 and −2.32 eV. The energy gaps were 2.94 and 2.50 eV for **1** and **2**, respectively. Compound **2** has a smaller energy gap than compound **1**. This is consistent with the fact the maximum ICT absorption of **2** appears at 408 nm, longer than that of compound **1** (390 nm). The HOMO orbitals mainly reside on the TTF units, and the LUMO orbitals are mainly localized on the boron units for both compound **1** and **2** as demonstrated in Figure S9, Supporting Information, but the atoms in the pyrrole ring(s) of the TTF unit(s) also contribute slightly to the LUMO orbitals of **1** and **2** (see Figure S9, Supporting Information). These results indicate that weak interactions between the TTF and boron units in **1** and **2** exist.

In summary, two new boron-based compounds **1** and **2** containing one and three monopyrrolo-annelated tetrathiafulvalene (TTF) unit(s) were synthesized and characterized. Compounds **1** and **2** exhibit typical ICT absorptions by virtue of the electron-donating and -withdrawing character of the TTF and boron units. Moreover, the maximum ICT absorption of **2** appears at longer wavelength than that of **1**, which is in agreement with the theoretical calculations. It is interesting to note that both ICT absorption and cyclic voltammograms of **1** and **2** can be modulated after the addition of fluoride ion. Thus, compounds **1** and **2** show absorption spectral and electrochemical responsiveness toward fluoride ion. Additionally, the binding of compounds **1** and **2** with fluoride ion were studied with ^{1}H NMR spectroscopy. These results indicate that such TTF-based conjugated D−A molecules are promising for selective chemical sensors and even interesting for electronic materials. Therefore, they deserve further investigations.

Experimental Section

Synthesis of Compound 1. A flamed-dried Schlenk reaction tube charged with a mixture of **6** (77 mg, 0.16 mmol), **7** (146 mg, 0.32 mmol), K_3PO_4 (103 mg, 0.48 mmol), and CuI (9.2 mg, 0.048 mmol) was degassed with N_2 for 10 min. After the addition of racemic *trans*-diaminocyclohexane (10 μL) and freshly distilled dioxane (2 mL) under N_2, the reaction mixture was stirred with heating at 110 °C for 24 h. After being cooled to room temperature, the mixture was filtered. The filtrate was collected and concentrated to obtain a dark green residue which was purified with silica chromatography using CH_2Cl_2/petroleum ether (60 °C−90 °C) (v/v, 1/20) as the eluant to give **1** as a yellow solid (74 mg, 57%): mp 134−136 °C; ^{1}H NMR (400 MHz, THF-d_8) δ 0.90 (t, J = 6.1 Hz, 6H), 1.29 −1.35 (m, 8H), 1.38−1.49 (m, 4H), 1.63−1.68 (m, 4H), 2.01 (s, 12H), 2.27 (s, 6H), 2.85 (t, J = 6.7 Hz, 4H), 6.81 (s, 4H), 7.32 (s, 2H),7.44 (d, J = 7.6 Hz, 2H), 7.54 (d, J = 7.4 Hz, 2H); ^{13}C NMR (150 MHz, THF-d_8) δ 13.4, 20.3, 22.5, 22.7, 28.1, 29.7, 31.3, 35.8, 110.2, 110.3, 117.5, 118.8, 123.0, 127.6, 128.0, 128.1, 138.3, 138.4, 140.3, 141.4, 142.5, 142.7; MALDI-TOF (*m*/*z*) calcd for $C_{44}H_{54}BNS_6$ 799.27, found 799.3. Anal. Calcd for $C_{44}H_{54}BNS_6$: C, 66.05; H, 6.80; N, 1.75; S, 24.05. Found: C, 66.02; H, 7.00; N, 1.85; S, 24.21.

Synthesis of Compound 2. A flamed-dried Schlenk reaction tube charged with a mixture of **6** (246 mg, 0.52 mmol), **9** (72 mg, 0.13 mmol), K_3PO_4 (329 mg, 1.56 mmol), and CuI (5 mg, 0.026 mmol) was degassed with N_2 for 10 min. After the addition of racemic *trans*-diaminocyclohexane (10 μL) and freshly distilled dioxane (2 mL), the system was evacuated three times and backfilled with N_2. The reaction mixture was heated to 110 °C and stirred for 24 h. After being cooled to room temperature, the mixture was filtered and the solid washed with CH_2Cl_2. The filtrate was collected and concentrated to obtain a dark green residue which was purified with silica chromatography using CH_2Cl_2/petroleum ether (60 °C−90 °C) (v/v, 1/15) as the eluant to give **2** as an orange solid (110 mg, 49%): mp >280 °C; ^{1}H NMR (400 MHz, THF-d_8) δ 0.91 (t, J = 6.5 Hz, 18H), 1.30−1.33 (m, 24H), 1.43−1.47 (m, 12H), 1.62−1.67 (m, 12H), 2.13 (s, 18H), 2.86 (t, J = 7.1 Hz, 12H), 7.14 (s, 6H), 7.27 (s, 6H); ^{13}C NMR (150 MHz, THF-d_8) δ 14.5, 23.5, 25.8, 29.1, 30.8, 32.3, 36.9, 111.0, 111.2, 118.6, 120.1, 123.2, 128.6, 142.0, 143.7, 144.8; MALDI-TOF (*m*/*z*) calcd for $C_{84}H_{108}BN_3S_{18}$ 1745.36, found 1745.4. Anal. Calcd for $C_{84}H_{108}BN_3S_{18}$: C, 57.73; H, 6.23; N, 2.40; S, 33.02. Found: C, 57.82; H, 6.46; N, 2.44; S, 32.62.

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Supporting Information Available: Synthesis and characterization of compounds **5**, **6**, **9**, and **10**; Job plots; absorption spectra of **1** and **2** in the presence of other anions; ^{1}H NMR spectra of **1** in the presence of F$^-$; theoretical computations; ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.