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Colorimetric Fluoride Ion Sensing by Boron-Containing π-Electron Systems

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Abstract: The boron-containing π-conjugated systems, including tri(9-anthryl)borane (**1**) and tris[(10-dimesitylboryl)-9-anthryl]borane (**2**), have been investigated as a new type of fluoride chemosensor. Upon complexation of **1** with a fluoride ion, a significant color change from orange to colorless was observed and, in the UV−visible absorption spectra, the characteristic band of **1** at 470 nm disappeared and new bands around 360−400 nm assignable to $\pi-\pi^*$ transitions of the anthryl moieties were observed. This change can be rationalized as a result of the interruption of the π-conjugation extended through the vacant p-orbital of the boron atom by the formation of the corresponding fluoroborate. The binding constant of compound **1** with the fluoride ion was quite high [$(2.8 \pm 0.3) \times 10^5$ M^{-1}], whereas **1** only showed small binding constants with AcO^- and OH^- of around 10^3 M^{-1} and no sensitivity to other halide ions such as Cl^-, Br^-, and I^-, thus demonstrating its selective sensing ability to the fluoride ion. In contrast to the monoboron system **1**, compound **2** having four boron atoms showed multistage changes in the absorption spectra by the stepwise complexation with fluoride ions.

Introduction

The recognition and sensing of anions is the current focus of supramolecular chemistry.[1] In particular, the sensing of a fluoride ion has attracted growing attention[2−11] because of its great potential for industrial and biological applications,[4,8] and several types of synthetic chemosensors have been developed to date. For the molecular designs of the chemosensors, how to achieve the specific recognition of a certain anion and how to convert the recognition event into a signal are the key points. The conventional approaches for the binding of the fluoride ion have used the specific Lewis acid−base interaction,[3−6] such as the strong affinity of a boron atom toward the fluoride ion,[12−14] or the designed hydrogen-bonding with the fluoride ion.[7−11] These binding events have been converted into an electrochemical[3] or fluorescent change,[4−7] or more directly, a colorimetric change detectable by the naked eye.[3,8−11] Especially, the last type of sensing is very worthy in view of its application, and therefore, conceptually new methodologies to realize it are still being intensively investigated.

We now disclose new colorimetric fluoride sensors based on boron-containing π-electron systems. Boron compounds bearing three identical π-conjugated groups on a boron atom have a unique LUMO in which the π-conjugation is divergently extended through the vacant p-orbital of the boron atom.[15,16] We have recently developed a series of trianthrylborane derivatives and showed their characteristic absorption properties due to the π-conjugation in the LUMO.[15a] Our present concept to realize the efficient sensing is based on the switching of this π-conjugation by recognition of the fluoride ion (Figure 1). Thus, the complexation of the boron π-electron systems with fluoride ion would interrupt the π-conjugation extended through the boron atom, causing a dramatic color change. Reported herein are the complexation and sensing ability of our trianthrylborane systems with the fluoride ion.

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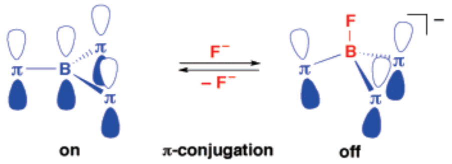
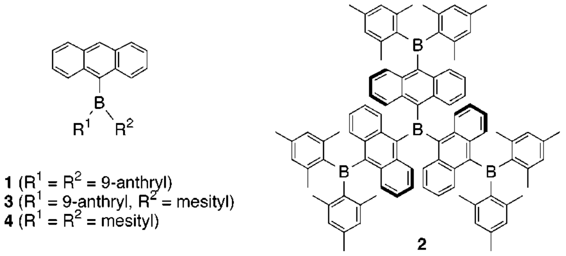
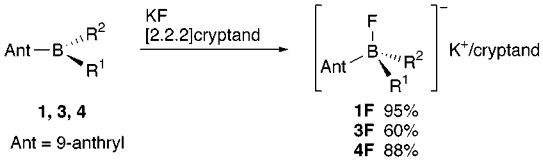


Figure 1. Schematic representation of the switching of π-conjugation in the LUMO of boron-based π-electron systems: π stands for π-conjugated moieties.

Chart 1



Scheme 1



Results and Discussion

The boron π-electron systems studied herein are trianthrylborane **1** and dimesitylboryl-substituted trianthrylborane **2** (Chart 1), both of which were recently synthesized by us.[15a] Dianthrylmesitylborane **3**[15a] and anthryldimesitylborane **4**[17] have also been examined for comparison with **1**. All these compounds are substantially air- and water-stable due to the steric protection around the boron atoms. While compounds **3** and **4** are fluorescent yellow in solution, the trianthrylborane derivatives **1** and **2** are intense orange and red in solution, respectively, due to the divergently extended π-conjugation through the boron atom(s).[15]

In the presence of a fluoride ion, all the triarylboranes are readily converted to the corresponding borates. Thus, the reactions of **1**, **3**, and **4** with a 1 mole amount of KF/[2.2.2]-cryptand as the fluoride source[18] afforded borates **1F**, **3F**, and **4F**, respectively, which were isolated in 60−95% yields as stable, nonhygroscopic colorless to pale yellow crystals (Scheme 1). Their structures were verified by ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectroscopies. Among the prepared borates, the crystal structure of **1F** was determined by X-ray crystallography, as shown in Figure 2. The borate **1F** has a tetrahedral structure with a rather flat geometry around the central boron atom ($\sum\angle C_{ipso}-B-C_{ipso} = 344.9°$, average of two independent molecules). Compared with the structure of **1**,[15a] **1F** has about 0.07−0.09 Å longer $C_{ipso}-B$ bond lengths.

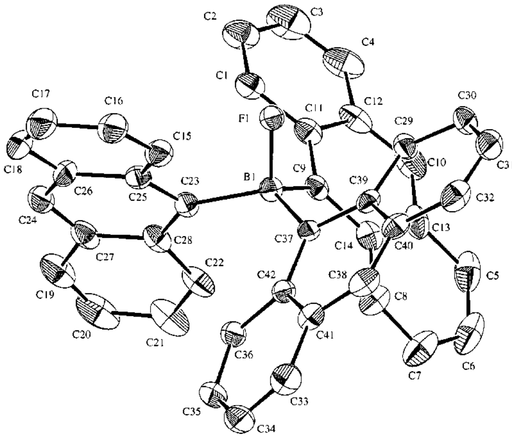


Figure 2. ORTEP drawing of **1F** (50% probability for thermal ellipsoids). One of the two independent molecules is shown here and K^+/[2.2.2]cryptand as a countercation is omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: B1−F1 1.466(5), B1−C9 1.669(7), B1−C23 1.677(7), B1−C37 1.675(6), C9−B1−C23 114.4(3), C9−B1−C37 115.0(4), C23−B1−C37 115.8(4).

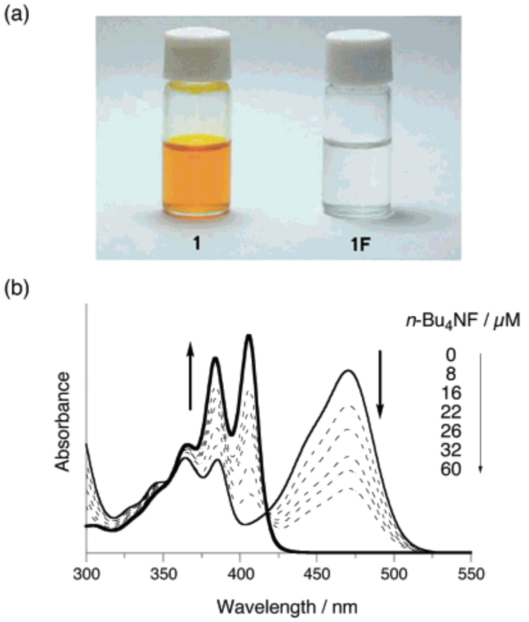


Figure 3. Colorimetric change of **1** upon addition of TBAF: (a) visual color change and (b) UV−vis absorption spectral change of **1** (4.0×10^{-5} M) in THF.

Table 1. UV−Visible Absorption Spectral Data (λ_{max}) and Binding Constants (K_a) toward a Fluoride Ion[a]

borane	λ_{max}/nm (log ϵ)[b]	borate	λ_{max}/nm (log ϵ)[b]	K_a/M^{-1} [c]
1	470 (4.35)[d]	**1F**[e]	406 (4.45)	$(2.8 \pm 0.3) \times 10^5$
3	448 (4.14)[d]	**3F**[e]	406 (4.23)	$(2.6 \pm 0.2) \times 10^5$
4	420 (4.03)[d]	**4F**[e]	403 (3.90)	$(2.9 \pm 0.3) \times 10^5$

[a] The titration experiments were carried out by the addition of a THF solution of n-Bu$_4$NF to a THF solution of each borane. The spectral data for borates are those at the fluoride-saturated points. [b] Only the longest λ_{max} are given. [c] Binding constants, determined from the absorbance titration measurements monitoring the spectral change at the λ_{max} of the boranes at 20 °C in THF. [d] Reference 15a. [e] Countercation: n-Bu$_4$N$^+$.

The complexation abilities of boranes **1**, **3**, and **4** with a fluoride ion were investigated by using the UV−visible absorption technique. When n-Bu$_4$NF (TBAF) as a fluoride source was added to a THF solution of each borane, a dramatic color change was observed from orange to colorless for **1** as shown in Figure 3a, or from yellow to colorless for **3** and **4**. Their spectral data are summarized in Table 1 and the spectral change for **1** is shown in Figure 3b. Notably, upon complexation with a fluoride ion, the characteristic strong absorption band of **1** at 470 nm completely disappeared, and new bands due to the anthracene moieties appeared around 360−410 nm. Thus, a

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more than 60 nm λ_{max} shift occurred with this anion binding event. The λ_{max} shift becomes larger as the number of anthryl groups increases, as seen from the data for **1**, **3**, and **4**, and apparently depends on the extent of the π-conjugation in the boranes.

The binding constant of **1** was determined from the Benesi–Hildebrand plot and the data are included in Table 1 together with those for compounds **3** and **4**.[19] Compound **1** has a significantly large binding constant for the fluoride ion of $(2.8 \pm 0.3) \times 10^5$ M^{-1} at 20 °C in THF, which is comparable to those of compounds **3** and **4**. However, the resulting borate **1F** can revert to the starting borane **1** by the addition of water, like other fluoride chemosensors,[6,8] probably due to the preferential hydration of the fluoride ion. It should be noted here that compound **1** has a selective sensing ability for the fluoride ion. Thus, compound **1** showed smaller binding constants for AcO^- and OH^- [$(1.7 \pm 0.1) \times 10^3$ and $(1.1 \pm 0.1) \times 10^3$ M^{-1}, respectively] by titration with a THF solution of their Bu_4N^+ salts. Furthermore, no sign of complexation with other anions such as Cl^-, Br^-, I^-, ClO_4^-, and BF_4^- was observed in the UV–visible spectra upon the addition of an excess amount of such anionic species as their n-Bu_4N^+ salts. The sterically congested surroundings around the central boron atom might be partly responsible for the highly selective sensing of the small fluoride ion.

In contrast to the monoboron compound **1**, the more extended π-electron system **2** was supposed to be capable of multistage sensing of the fluoride ion, since **2** has four boron atoms in two different environments, i.e., an internal trianthrylborane moiety and three external dimesitylanthrylborane moieties. The spectral change of a THF solution of **2** (4.0×10^{-5} M) upon the addition of TBAF has been investigated, as shown in Figure 4. As the concentration of TBAF increased, the absorption at 524 nm of **2** decreased and a new band appeared at 474 nm together with a broad shoulder band around 570 nm (Figure 4a) and the color of the solution changed from red to orange. This change became saturated when TBAF was added to about 10.0×10^{-5} M. The molar ratio analysis showed that the spectral change in this concentration range was ascribed to the 1:1 complexation of **2** with the fluoride ion. The binding constant was determined to be $(6.9 \pm 0.2) \times 10^4$ at 20 °C in THF. Significantly, the further addition of a large excess of TBAF caused subsequent spectral changes in two different concentration ranges, 15.0–40.0 $\times 10^{-5}$ and 0.9–6.0 $\times 10^{-3}$ M, with respective isosbestic points and the longest λ_{max} eventually shifted to 502 nm, as shown in Figures 4b and 4c. These changes can be interpreted as complexation with the second and third fluoride ions. The binding constants of **2** with the second and third fluoride ions were determined to be $(9.0 \pm 0.6) \times 10^2$ and $(2.1 \pm 0.4) \times 10^2$ at 20 °C in THF, respectively. It should be noted that the final spectrum (Figure 4c) is similar to and about 25 nm red-shifted from that of the trianthrylborane **1** (see Figure 3b), suggesting that the complexation of fluoride ions may have occurred not with the internal boron atom but with the external dimesitylanthrylborane moieties.

Finally, it is interesting to compare the present boron systems with the group 14 analogue, trianthrylfluorosilane **5**, which we have recently reported as a fluorescent fluoride chemosensor (Figure 5).[6] In the group 14 silicon case, the perturbation in the through-space interaction among anthracene moieties caused by the structural change from tetracoordinate fluorosilane **5** to pentacoordinate difluorosilicate **5F** is responsible for the fluorescence change. In contrast to this, in the present group 13 boron case, the colorimetric sensing is realized based on the turning-off of the π-conjugation extended through the vacant p-orbital on the boron atom by the formation of the fluoroborates. These results demonstrate clear-cut examples of the specific sensing dependence on the main-group elements to be employed. Further studies extending this idea to other main group elements are now in progress.

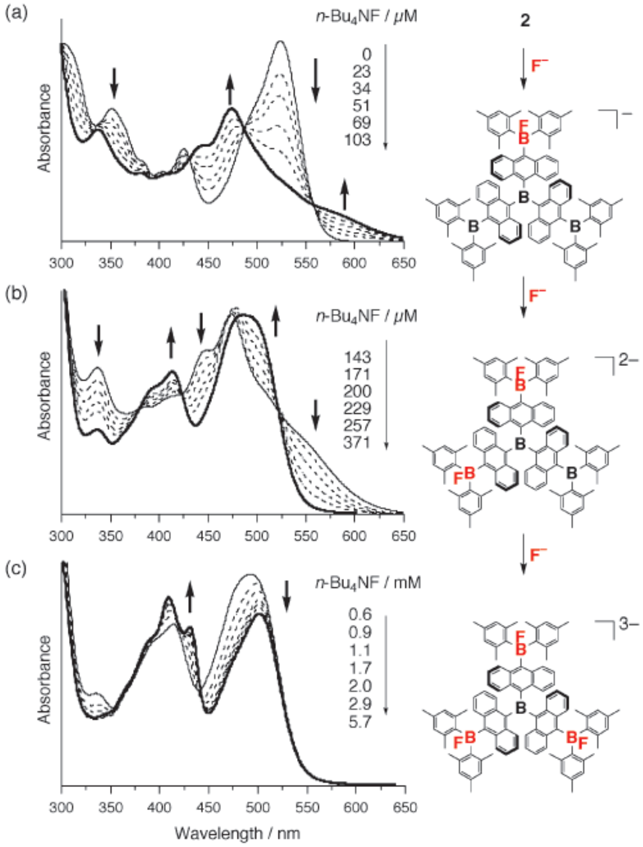
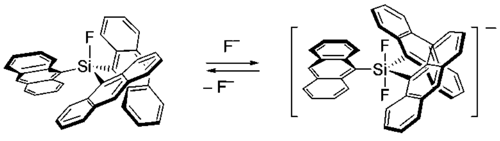


Figure 4. Spectral change of a THF solution of **2** (4.0×10^{-5} M) upon addition of TBAF.



5
weak fluorescence

5F
strong fluorescence

Figure 5. Fluorescent sensing of fluoride ion with trianthrylfluorosilane.

Experimental Section

General. Melting point (mp) determination was performed with a Yanaco MP-S3 instrument. ^1H, ^{13}C, ^{11}B, and ^{19}F NMR spectra were measured with a JEOL EX-270 (270 MHz for ^1H, 67.8 MHz for ^{13}C, 86.6 MHz for ^{11}B, and 254 MHz for ^{19}F) spectrometer in appropriate solvents. UV–visible absorption spectra were measured with a Shimadzu UV-3100PC spectrometer, using degassed spectral grade THF as a solvent. Spray-dried KF and [2.2.2]cryptand were purchased from Wako Co. and Aldrich Co., respectively, and used without further purification. Anthrylborane derivatives **1**–**3** were prepared according to the procedure reported in our previous report.[15a] Compound **4** was prepared according to the procedure reported in the literature.[17] n-$Bu_4NF{\cdot}xH_2O$ (TBAF) was purchased from Tokyo Chemical Industry Co. and the content of H_2O was determined by the elemental analysis. A THF stock solution of TBAF was used for titration experiments of the boranes.

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[19] The molar ratio analysis showed a 1:1 stoichiometry of the complexation of **1** with fluoride ion.

A Typical Procedure for the Preparation of Potassium/Cryptand Salts of Fluoroborates: Tri(9-anthryl)fluoroborate·K^+·[2.2.2]-cryptand (1F). A mixture of compound **1** (543 mg, 1.0 mmol), spray-dried KF (57.5 mg, 0.99 mmol), and [2.2.2]cryptand (377 mg, 1.0 mmol) in dry benzene (4 mL) was stirred at room temperature for 2 days to form pale yellow precipitates. After filtration, the precipitates were washed with dry benzene (2 mL × 2) to afford spectroscopically pure **1F** (923 mg, 0.94 mmol) in 95% yield based on KF: mp 156 °C dec. ^1H NMR (THF-d_8): δ 2.38 (t, $J = 4.6$ Hz, 12H), 3.36 (t, $J = 4.6$ Hz, 12H), 3.39 (s, 12H), 6.25−6.35 (m, 6H), 6.82−6.91 (m, 6H), 7.65 (d, $J = 8.4$ Hz, 6H), 8.02 (s, 3H), 8.30−8.40 (br d, 6H). ^{13}C NMR (DMSO-d_6): δ 53.16, 66.94, 69.76, 120.83, 123.31, 124.17, 127.94, 131.54, 132.35, 135.02, 162.93 (d, $^2J_{CF} = 19.5$ Hz). ^{11}B NMR (DMSO-d_6): δ 6.04. ^{19}F NMR (DMSO-d_6): δ −133.32. UV−vis (THF) λ_{max}/nm (log ϵ): 406 (4.45), 384 (4.39), 366 (4.13). Anal. Calcd for $C_{60}H_{63}BFKN_2O_6$: C, 73.76; H, 6.50; N, 2.87. Found: C, 73.90; H, 6.60; N, 2.75.

Di(9-anthryl)mesitylfluoroborate·K^+·[2.2.2]cryptand (3F). In essentially the same manner as described for **1F**, compound **3F** (496 mg) was obtained in 60% yield (based on KF) from **3** (484 mg, 1.0 mmol), spray-dried KF (55 mg, 0.9 mmol), and [2.2.2]cryptand (377 mg, 1.0 mmol) in dry benzene (6 mL): mp 215 °C dec. ^1H NMR (THF-d_8): δ 1.66 (s, 6H), 2.17 (s, 3H), 2.43 (t, $J = 4.6$ Hz, 12H), 3.40 (t, $J = 4.6$ Hz, 12H), 3.44 (s, 12H), 6.44 (s, 2H), 6.44−6.54 (br m, 4H), 6.91−7.01 (m, 4H), 7.69 (d, $J = 8.1$ Hz, 4H), 8.01 (s, 2H), 8.51−8.61 (br m, 4H). ^{13}C NMR (THF-d_8): δ 20.69, 25.14, 53.16, 66.96, 69.80, 120.56, 123.33, 123.58, 131.16, 131.47, 132.28 (br), 141.22, 156−157 (br), 163.2−164.2 (br). ^{11}B NMR (THF-d_8): δ 6.34. ^{19}F NMR (THF-d_8): δ −152.55. UV−vis (THF) λ_{max}/nm (log ϵ): 406 (4.23), 384 (4.21), 365 (3.99). Anal. Calcd for $C_{55}H_{65}BFKN_2O_6$: C, 71.88; H, 7.13; N, 3.05. Found: C, 71.84; H, 7.15; N, 3.16.

(9-Anthryl)dimesitylfluoroborate·K^+·[2.2.2]cryptand (4F). In essentially the same manner as described for **1F**, compound **4F** (686 mg, 0.80 mmol) was obtained in 88% yield (based on KF) from **4** (426 mg, 1.0 mmol), spray-dried KF (53 mg, 0.9 mmol), and [2.2.2]cryptand (377 mg, 1.0 mmol) in dry toluene (4 mL): mp 193 °C dec. ^1H NMR (THF-d_8): δ 1.81 (br s, 12H), 2.15 (s, 6H), 2.43 (t, $J = 4.6$ Hz, 12H), 3.42 (t, $J = 4.6$ Hz, 12H), 3.45 (s, 12H), 6.43 (s, 4H), 6.54−6.64 (br m, 1H), 6.80−6.90 (br m, 1H), 6.96−7.16 (br m, 2H), 7.64−7.72 (m, 2H), 7.95 (s, 1H), 8.45 (d, 1H), 8.89 (d, $J = 8.1$ Hz, 1H). ^{13}C NMR (THF-d_8): δ 15.70, 21.38, 54.57, 68.28, 71.18, 120.27, 120.70, 123.48, 123.56, 123.86, 127.90, 128.41, 128.89, 131.08, 132.70, 133.10, 136.01, 136.19, 136.78, 137.91, 143.09, 157.10−159.62 (br), 166.47−168.07 (br). ^{11}B NMR (THF-d_8): δ 5.15. ^{19}F NMR (THF-d_8): δ −157.57. UV−vis (THF) λ_{max}/nm (log ϵ): 403 (3.90), 382 (3.96), 364 (3.76). Anal. Calcd for $C_{50}H_{67}BFKN_2O_6$ as 4F·H_2O: C, 68.32; H, 7.91; N, 3.19. Found: C, 68.60; H, 7.99; N, 3.05.

X-ray Crystal Structure Analysis of 1F. Single crystals of **1F** suitable for X-ray crystal analysis were obtained by recrystallization from acetone. Intensity data were collected on a Rigaku RAXIS-IV imaging plate area detector with graphite-monochromated Mo Kα radiation. The data were corrected for Lorentz and polarization effects and secondary extinction. The crystal structures were solved by direct methods in SIR92[20] and full-matrix least-squares refinement was carried out for all non-hydrogen atoms. The crystal contained crystallographically independent two borate molecules and two acetones. One of acetones was disordered and solved using the disordered model. All hydrogen atoms were included except for those of the disordered acetone, but not refined. All the calculations were performed with the teXsan crystallographic package from Molecular Structure Corp. The crystal data and analytical conditions are as follows: MF for **1F**/acetone, $C_{63}H_{69}N_2O7_6BFK$; FW = 1035.15, crystal size 0.30 × 0.30 × 0.20 mm^3, monoclinic, $P2$(No.3), $a = 20.8599(9)$ Å, $b = 12.1728(5)$ Å, $c = 22.338(1)$ Å, $\beta = 102.134(2)°$, $V = 5545.5(4)$ Å^3, $Z = 4$, $D_c = 1.240$ g cm^{-3}, μ(Mo Kα) = 1.54 cm^{-1}, number of unique reflections = 9251, temperature = −100 °C, $R = 0.064$, $R_w = 0.084$, and GOF = 1.23.

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Supporting Information Available: Experimental details, crystal structures, and tables of experimental data for **1F** (PDF) and X-ray crystallographic data of **1F** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA015957W

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