

論文内容の要旨

論文題目 Construction of Ion-Pair Sensing Systems Utilizing a Tricoordinate Borane Moiety and Heteroaromatic Units

(3 配位ホウ素部位および複素芳香環を活用したイオン対センシングシステムの構築)

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Introduction

Detection of ions is attracting great interest not only in the field of chemistry, but also in biology, pharmacology, and environmentology. Among many methods for detection of ions, the application of fluorescent chemosensors has advantages in terms of sensitivity, cost, response time, and local observation. Although a lot of studies about cation- or anion-sensing have been reported, there are few examples of ditopic ion-pair sensing, which can recognize cations and anions at the same time, probably due to difficulty in synthesizing complicated receptors and overcoming energetic disadvantage by charge separation. Colorimetric ion-pair receptors can also be applied to molecular logic gates, elucidation of the biological functions, or salt extraction.

Since fluoride ion is closely relating to environmental problems and diseases such as caries or osteoporosis, fluoride ion sensing has been intensely studied using triarylboranes, which have strong affinity for F^- . On the other hand, cation sensors especially for transition metal ions often contain hetero aromatics, e.g., pyridine, azoles, and thiophene, which recognize metal ions by forming complexes.

Considering these properties, boranes bearing hetero aromatics can be used as chemosensors for ion-pairs. During my Ph.D. work, I have achieved the synthesis of boranes shown in Figure 1, which have the recognition abilities toward F^- and metal ions.

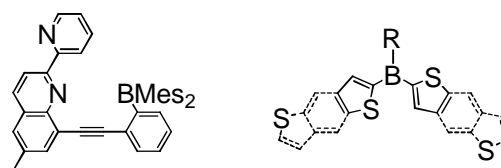


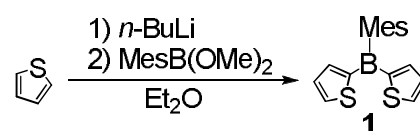
Figure 1. Molecular designs of ion-pair sensors.

Synthesis, Structures, and Optical Properties of Boranes Bearing Two Thiophenes or Thiophene Derivatives

To avoid oxidation and hydrolysis, ordinary triarylboranes require steric protection groups. However, these

groups seem to decrease the binding constant with F^- (e. g. Mes_3B : $K_F = 3.3 \times 10^5 M^{-1}$ in THF). Introduction of smaller aryl groups, such as thienyl groups instead of bulky ones reduces steric repulsion in the generated fluoroborates, and thus enhancement of the binding constant is expected. Furthermore, high affinity of sulfur atom for soft metal ions such as Hg^{2+} or Cd^{2+} seems to realize the selective recognition of soft metal ions by triarylboranes bearing thienyl groups. Moreover, a lot of boranes with extended π -conjugation systems often show intense fluorescence. Taking advantages of these merits, dithienylboranes were synthesized aiming at selective fluorescent chemosensors for soft metal-fluoride ion-pair.

Dithienylborane **1** was synthesized by the reaction of 2-lithiothiophene with $MesB(OMe)_2$ in Et_2O (Scheme 1). Benzothiophene derivative **2** (Figure 1) was also synthesized by a similar method. They were stable against air and moisture both in the solid state and in solution, but benzodithiophene derivative **3'** bearing a Mes group on the boron atom was slightly unstable and hydrolyzed during purification. Therefore, introduction of a bulkier Tip group, instead of the Mes group, was necessary in order to isolate stable compound **3**. X-ray crystallographic analyses of **1** and **2** revealed that the central boron plane and two thiophene rings are almost coplanar, which means that π -conjugation is extended to the whole molecular



Scheme 1. Synthetic scheme of dithienylborane **1**.

framework. All compounds **1**, **2**, and **3** exhibited longest absorption bands at 328, 362, and 423 nm in CH_2Cl_2 . In addition, **3** showed fluorescence at 472 nm ($\Phi = 0.097$) in CH_2Cl_2 , indicating the potential ability for a fluorescent chemosensor.

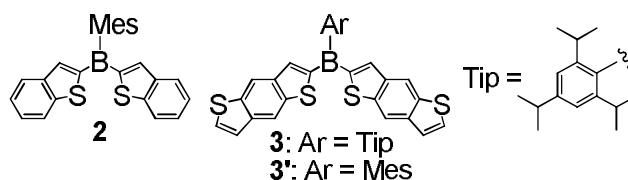


Figure 2. Structures of benzothiophene and benzodithiophene derivatives.

Ion Sensing Abilities of Boranes Bearing Two Thiophenes or Thiophene Derivatives

To clarify the sensing ability for fluoride ion, absorbance changes of **1**, **2**, and **3** upon addition of $n-Bu_4NF$ (TBAF) were observed. The longest absorption bands of each compound disappeared by addition of TBAF, and

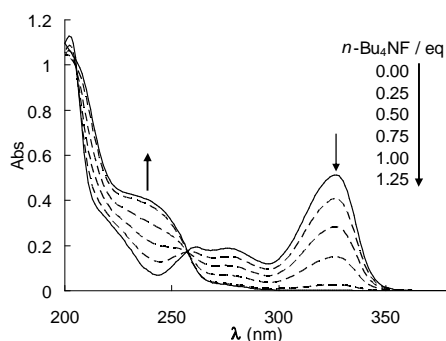


Figure 3. Changes in UV-vis absorption of **1** (20 μM) in CH_3CN upon addition of TBAF.

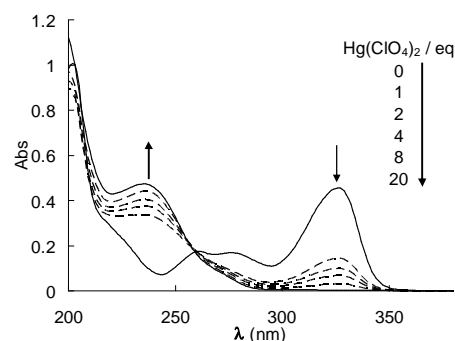


Figure 4. Changes in UV-vis absorption of **1** (21 μM) in CH_3CN upon addition of $Hg(ClO_4)_2$.

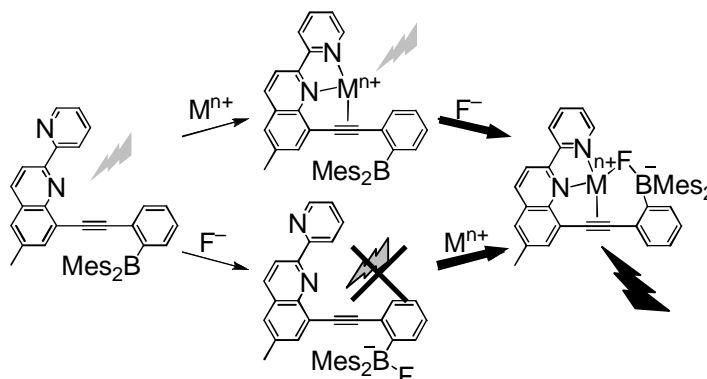
new bands arose with the isosbestic points, respectively (Figure 3). The titration experiment revealed their association constants are much larger than that of Mes_3B ($2.3 \times 10^6 M^{-1}$ for **1**, $6.2 \times 10^7 M^{-1}$ for **2**, and $1.3 \times 10^7 M^{-1}$ for **3** in CH_2Cl_2). In addition, the color change of **3**, from yellow to colorless, was observed, and it can be useful for colorimetric sensing of F^- by the naked eye. Furthermore, the blue fluorescence of **3** was quenched upon addition of TBAF, which realizes the use as a fluorescent chemosensor.

On the other hand, metal ion sensing abilities of **1**, **2**, and **3** were also investigated by the similar method.

Among all the investigated metal ions (Ag^+ , Au^+ , Cd^{2+} , Cu^+ , Hg^{2+} , Zn^{2+}), only Hg^{2+} caused spectral changes of **1**, **2**, and **3**. Upon addition of Hg^{2+} , blue shift of the absorption band and quenching the fluorescent emission were observed (Figure 4). The spectral changes of ^{11}B NMR of **1** indicated the decomposition of **1** giving boronic acid(s) by addition of Hg^{2+}

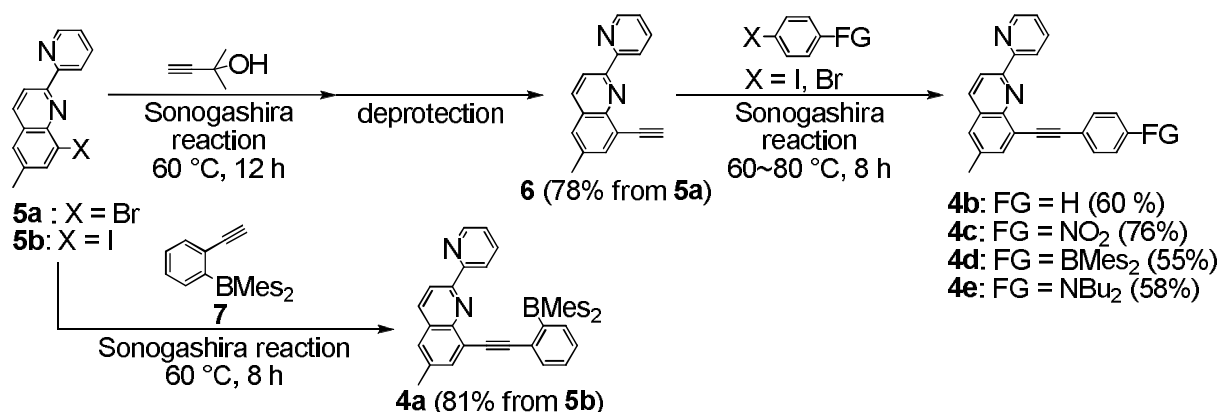
Synthesis, Structures, and Optical Properties of Pyridylquinolines Bearing an Arylethynyl Group

Although bipyridyl derivatives have high complexation ability for various metal ions, cation sensors with bipyridyl-based receptors have been reported much less than those with crown ether- or calixarene-based receptors. It is probably due to the lack of metal ion selectivity of bipyridyls, which can form complexes with a variety of d- and f-block elements. However, sensors with bipyridyl units have advantages



Scheme 2. The mechanism of ion-pair recognition.

such as high sensitivity, unnecessary of chromophore, and facility of the synthesis. In order to employ these advantages of bipyridyls, a borane bearing a pyridylquinoline moiety, which is a derivative of bipyridyl, was designed as an ion-pair sensor. Since an ethynyl group works as an effective ligand for soft metal ions, it is expected that selectivity for the soft metal ion should increase. Furthermore, proximity of both ion receptors will enable the ion-pair recognition due to the stabilization of zwitter ionic complex by intramolecular electrostatic interaction (Scheme 2).



Scheme 3. Synthetic schemes of pyridylquinolines bearing an arylethynyl group.

Ortho-boryl substituted compound **4a** was prepared by Sonogashira reaction of **5b** with reported terminal alkyne **7** in good yield (Scheme 3). Pyridylquinolines **4b-e** were synthesized by a similar method in order to elucidate the effect of functional groups and their substituted position on the optical properties. **4b**, **4d**, and **4e** showed intense fluorescence in visible region, while **4a** and **4c** exhibited very weak fluorescence at room temperature. The optical properties of **4** were largely changed by the functional group (Table 1). The solvent effects on the emission wavelength and the fluorescence quantum yield of **4e** were observed, because of its polar

excited state.

Table 1. Optical properties of **4a-e**

	4a	4b	4c	4d	4e
λ_{abs} (nm) (in CH ₃ CN)	335	348	349	349	398
ε (10 ⁴ M ⁻¹ cm ⁻¹)	2.0	1.8	2.0	3.2	1.6
λ_{em} (nm) (in CH ₃ CN)	467 ^a	412 ^a	408 ^b	399, 412 ^b	565 ^c
Φ^{d} (in CH ₃ CN)	0.015	0.39	0.047	0.67	0.25

^a excited at 340 nm. ^b excited at 350 nm. ^c excited at 400 nm. ^d absolute photoluminescent yield.

Ion-Pair Sensing Abilities of Pyridylquinolines Bearing a Boryl Group

Ion and ion-pair recognition abilities of **4a** were investigated.

Although complexation of **4a** with Ag⁺, Cd²⁺, Cu²⁺, Fe²⁺, Hg²⁺, Ni²⁺, and Zn²⁺ proceeded, remarkable increase of photoluminescence intensity was not observed. Addition of halide ion also hardly affected the photoluminescent property of **4a**.

However, addition of both Cd²⁺ and F⁻ caused the observation of bright green phosphorescence at room temperature. Next, in order to reveal the selectivity, various metal ions and halide ions were added one-by-one, and luminescence spectra were measured. The bright green phosphorescence was observed only in the case of

Cd²⁺-F⁻ ion-pair, meaning achievement of highly selective ion-pair sensing. These results also mean the possibility to apply **4a** as an AND logic gate. Moreover, recognition ability for Cd²⁺ was enhanced in the presence of F⁻, which means the positive allosteric effect by F⁻. Then, the effect of an ethynyl group on complexation with soft metal ions was investigated. The improvement of recognition ability of **4b** for a soft metal ion such as Cd²⁺ and Ag⁺ compared to pyridylquinoline **8** was confirmed by UV-vis spectra titration. In addition, **4a** recognized CN⁻ and exhibited blue fluorescence, which was not observed in the case of halide ion. Summarizing these phenomena, compound **4a** can be used both as a cadmium-fluoride recognition sensor and as a cyanide ion selective anion sensor.

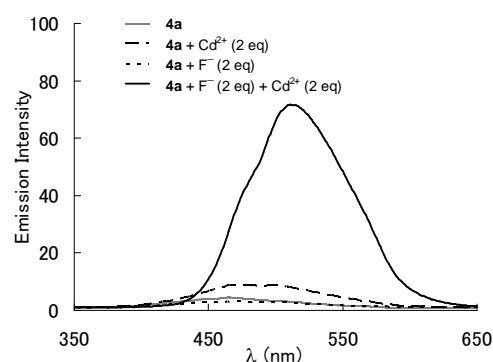
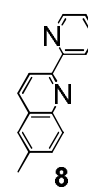


Figure 5. Changes of photoluminescence spectra of **4a** (20 μM) in CH₃CN upon addition of TBAF and/or Cd(ClO₄)₂.



Conclusion

Two classes of ion-pair recognition molecules bearing a tricoordinate borane site and hetero aromatics were synthesized and their abilities to recognize metal ions and fluoride ion were investigated. Dithienylboranes showed high recognition ability for fluoride ion, and selective sensing of mercury ion. Benzodithiophene derivative **3** showed absorption and fluorescence in visible region, and hence it has potential ability as a fluorescent chemosensor. It was also revealed that cadmium and fluoride ion pair can be detected selectively by appearance of photoluminescence of **4a**. This compound exhibited blue fluorescence only by addition of cyanide ion, meaning the availability of **4a** as a selective cyanide ion sensor.