

Fluorescence-responsive H_2PO_4^- Receptor Based on Macrocyclic Boron Complex

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Macrocyclic boron complex showed selective fluorescence response toward H_2PO_4^- via hydrogen-bond network, Lewis acid–base interaction, and inhibition of PET.

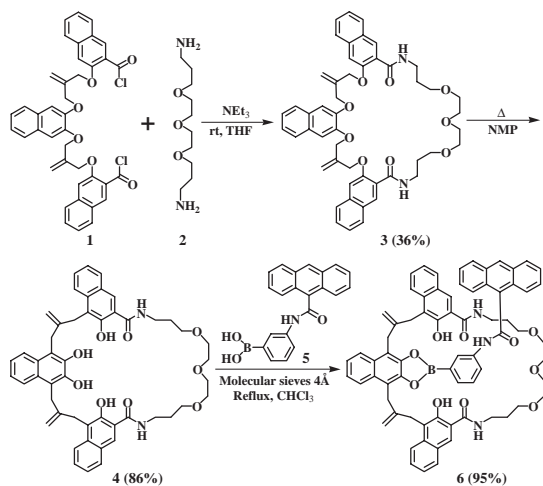
Various anion sensors having recognition and response sites have been developed so far.¹ Supramolecular metal complexes are interested in the field of anion binding^{1,2} and sensing^{1,3} because of the unique three-dimensional recognition-site toward specific anion and the Lewis acidic metal center in the complex which is possible to interact with anion. Boron compounds such as boric acid and its ester derivatives have been known to act as hard acid and strongly interact with anions changing the orbital from sp^2 to sp^3 .⁴ Therefore, many boron complexes bearing fluorophore and chromophore as sensing agents for anions and sugars have been synthesized.^{5–7} Fluorescence response of those sensing agents utilizes the changing of the photoinduced electron transfer (PET) between fluorophore and boron moiety, the efficiency of the energy transfer from donor to acceptor. Recently, we succeeded in the construction of a chromogenic anion receptor based on a noncyclic boron-complex whose central boron consisted of a four-coordinated structure which was negatively charged and was not able to interact with anion.⁸

In this work, we designed and synthesized macrocyclic boron complex having plural hydrogen-bonding sites such as hydroxy, amide, oxyethylene, and a fluorophoric anthracene linked to phenyl borate. We investigated the complexation and the fluorescence response abilities of the boron complex toward various anions by using fluorescence and ¹H NMR spectroscopy.

Scheme 1 shows a synthetic process of novel macrocyclic boron complex. Macrocyclic compound **3** was obtained by cycli-

zation reaction between dicarboxylic acid dichloride **1** and diamine **2** under high dilution conditions. Then, tandem Claisen rearrangement (160 °C, 1 h, in *N*-methylpyrrolidinone (NMP)) was carried out to introduce plural hydroxy groups into **3**.⁹ Complexation between **4** and boric acid derivative **5** in the presence of molecular sieves gave only macrocyclic boron complex **6** in excellent yield.¹⁰

Fluorescence response of the boron complex toward various anions having tetrabutylammonium ion as a counter cation was investigated. Figure 1a shows fluorescence spectra of the anthracene moiety in the boron complex in the presence and the absence of H_2PO_4^- in $\text{CH}_3\text{CN}/\text{CHCl}_3$ (9/1). The fluorescence intensity increased with increase in the concentration of H_2PO_4^- . The molar ratio plot in Figure 1b indicated an intersection at the molar ratio of 1.0, which corresponds to a 1:1 (=Boron complex: H_2PO_4^-) stoichiometry. On the other hand, the variations of the fluorescence intensity of the boron complex in the presence of HSO_4^- and CH_3COO^- were remarkably smaller than that of H_2PO_4^- as shown in Figure 1b. For Cl^- , Br^- , and I^- , the spectral change was not observed at all. The variation of the fluorescence intensity by the addition of F^- was strange, although the shape of spectra did not change. The binding constant (β_1) between the boron complex and anions was determined by using the general equation¹⁰ related to the variation of the fluorescence intensity in Figure 1b. The β_1 values were in the order of H_2PO_4^- ($10^{4.89}$) \gg HSO_4^- ($10^{1.90}$) $>$ CH_3COO^- ($10^{1.75}$) \gg Cl^- , Br^- , I^- (no response) which were not corresponding to the order of the basicity of anions. The β_1 value of F^- was not able to be calculated because of the strange spectral change.



Scheme 1. Synthesis of novel macrocyclic boron complex.

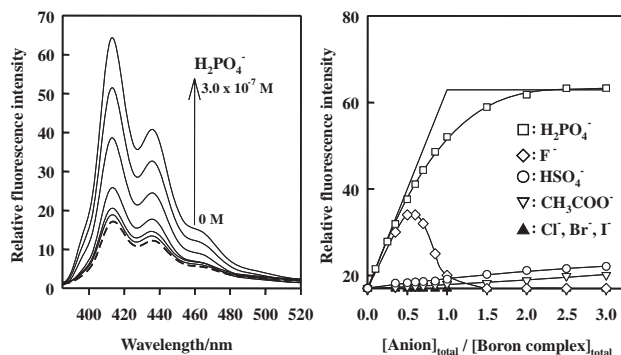


Figure 1. a) Fluorescence spectra of 1.0×10^{-7} M boron complex in the presence and the absence of 1.0×10^{-8} – 3.0×10^{-7} M H_2PO_4^- in $\text{CH}_3\text{CN}/\text{CHCl}_3$ (9/1). Excitation at 380 nm. b) Molar ratio plots between boron complex and various anions. Solid lines except for F^- were calculated by using the general equation and the obtained β_1 value.

To clear the above behavior of the boron complex toward various anions, the interaction and the complexation between the boron complex and anions were studied by ^1H NMR spectroscopy. Both hydroxy and amide (NH) peaks in the macrocyclic moiety of the boron complex shifted to lower magnetic field in the presence of H_2PO_4^- , while the amide (NH) between anthracene and phenyl borate was not changed.¹⁰ The peaks of the oxyethylene protons also shifted to lower magnetic region. These results strongly suggest that the hydroxy, the amide (NH) groups, the ether oxygens in the macrocyclic moiety of the boron complex take part in the hydrogen-bond formations with H_2PO_4^- . The spectrum change in the HSO_4^- case was similar to that of the H_2PO_4^- case, however, the degree was very small. For the interaction with CH_3COO^- , Cl^- , Br^- , or I^- , only the hydroxy and the amide (NH) in the macrocycle moiety of the boron complex slightly shifted to lower magnetic field. Both the strength of the interaction and the stability of the anion complex between the boron complex and those anions should be lower than those of the complex with H_2PO_4^- . In the presence of F^- , not only the hydroxy and the amide (NH) of the macrocycle but also the amide (NH) between anthracene and phenyl borate significantly shifted to lower magnetic field. This means that the amide (NH) between anthracene and phenyl borate also participates in the hydrogen-bond formation with F^- which is more basic than other halide ions and has the smallest ionic radius among halide ions.

Boron and phenyl group of the phenyl borate moiety in the boron complex can act as Lewis acid and electron acceptor, respectively, and will contribute to the binding and the fluorescence response for anion. Hayashita et al. have found that a phenyl boric acid linked to pyrene indicates the strong fluorescence in the aqueous alkaline solution.⁷ They concluded that the phenomenon would be ascribed to the inhibition of photoinduced electron transfer (PET) from pyrene to phenyl borate by the complexation of the boron with hydroxide ion. This PET process is applicable to the present system. Similar PET from anthracene to phenyl borate in the present boron complex must be inhibited by the complexation with H_2PO_4^- through plural hydrogen-bond formations and the Lewis acid–base interaction as illustrated in Figure 2. Although the enhancement of the fluorescence intensity might occur commonly in the case of F^- which strongly interacts with boron,^{4,11} the tendency was remarkably different from that of H_2PO_4^- . This should be due to the contribution of another PET¹² by the hydrogen-bond formation of the amide (NH) between anthracene and phenyl borate with F^- as described in the above ^1H NMR study. As results, we were able to develop a highly selective sensing agent for H_2PO_4^- which can be detected by the fluorescence response.

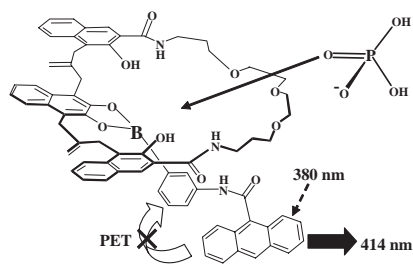


Figure 2. Optical response of the boron complex toward H_2PO_4^- .

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- Supporting Information available. Synthesis of **5**. ^1H NMR, IR, ESI-MS of **3**, **4**, **5**, and **6**; General equation for determination of binding constant; ^1H NMR spectra of boron complex in the presence and absence of H_2PO_4^- and F^- .
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