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Synthesis of supramolecular boron complex with anthryl groups exhibiting specific optical response for chloride ion

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Abstract—Supramolecular boron complex having plural hydrogen bonding sites and anthracene moieties was synthesized and showed an excimer emission selectively accompanied with capture of chloride ions.

Highly organized supramolecular metal complexes via self-assembly of polydentate ligands with metal ions often possess the binding sites and the cavity toward another cations,[1,2] anions,[1,3] and organic molecules.[1,4] In particular, the supramolecular metal complexes bearing binding site and optical-response site such as chromophore and fluorophore are applicable to sensing for specific ions, molecules and construction of switching systems.[5] Recently, we have reported that the complexation of the catechol ligand bearing functional groups with boric acid selectively gave a boron complex composed of ligand/boron = 2:1,[6,7] and the boron complex having plural hydrogen bonding site and quinolyl moieties could act as a high selective chromophore toward phosphoric acid.[7]

In the present work, we synthesized a novel boron complex appended not only plural hydroxy and amide (NH) groups as proton donor but also anthracene moieties as fluorophore. Both the binding and the optical-response abilities of the boron complex toward various anions in $CHCl_3$ were studied by fluorescence, UV/vis absorption, and ^1H NMR spectroscopies.

Scheme 1 shows the synthetic route of the ligand and the boron complex. The novel catechol ligand **2**[9] was obtained via tandem Claisen rearrangement of the corresponding polyether compound **1**[8] (160 °C, 1 h, in *N*-methylpyrrolidinone). Complexation between the ligand **2** and the excess amount of $B(OH)_3$ in the presence of triethylamine as base in methanol was carried out at room temperature. After 1 h, solid was precipitated, and then the precipitates were collected and washed with the small amount of cooled methanol. ESI-MS (anionic mode) measurement of an acetonitrile solution of the obtained residue showed only one peak at *m*/*z* 2043, $[2\text{Ligand} + B^{3+} - 4H^{+}]^{-}$corresponding to a mononuclear complex composed of Ligand/B = 2:1. ^1H NMR spectrum of the boron complex in $CDCl_3$ indicated the structural information, in which the hydroxy groups of catechol moiety took part in the complexation with boron since those hydroxy protons completely disappeared. Furthermore, each protons of two ligands in the boron complex were observed as the same chemical shifts, therefore, the complex has the symmetrical four coordinated structure.[10] Thus, the boron complex, having not only plural proton donating groups such as the hydroxy and the amide (NH) groups but also anthracene moieties, was easily synthesized in high yield.

The binding and the optical-response abilities of the boron complex toward various anions in $CHCl_3$ were studied by using fluorescence spectrophotometry. The fluorescence spectrum arising from the anthracene moiety in the boron complex was measured (excited at 350 nm). The fluorescence spectrum consisted of three sharp bands at 393, 412, and 434 nm, with a shoulder at 466 nm as shown in Figures 1 and 2, which are corresponding to the monomer fluorescence of anthracene. Figures 1 and 2 indicate the variation of the monomer fluorescence by the addition of various anions such as

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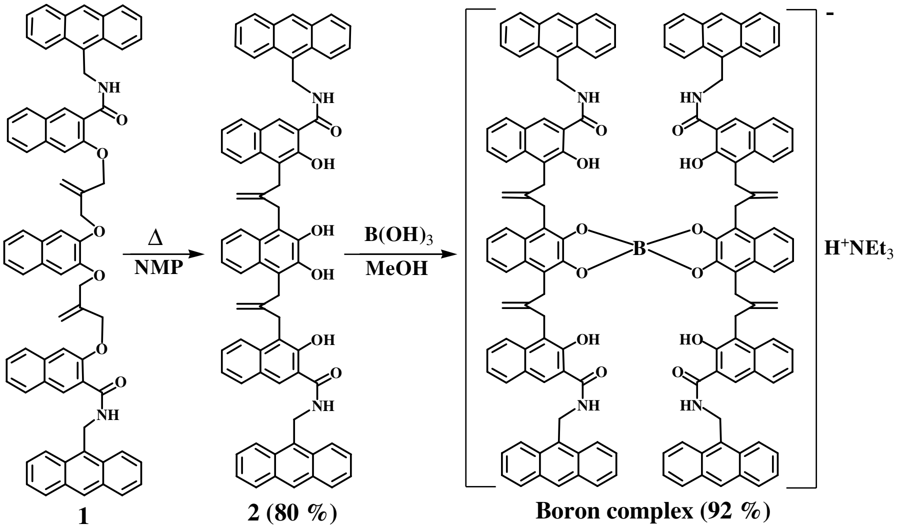

Scheme 1. Synthesis of novel boron complex.

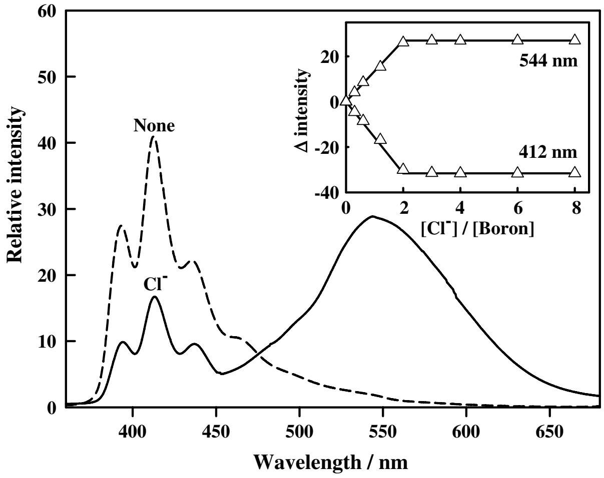

Figure 1. Fluorescence spectra of 2.0×10^{-6} M boron complex in the presence and absence of 4.0×10^{-6} M Cl^- in $CHCl_3$. Excitation at 350 nm. Inset shows the molar ratio plot against the apparent fluorescence intensity at 412 and 544 nm.

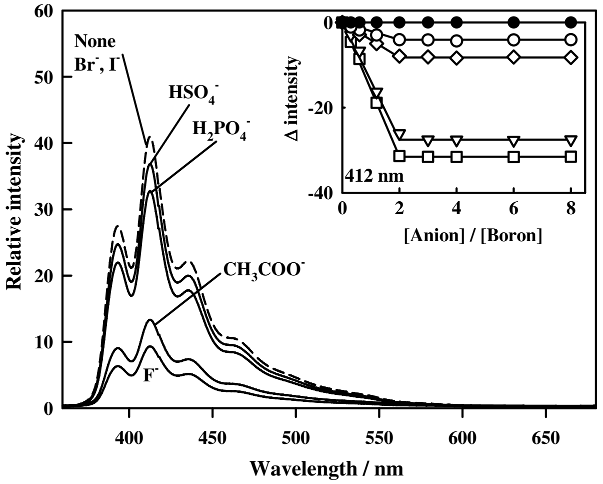

Figure 2. Fluorescence spectra of 2.0×10^{-6} M boron complex in the presence and absence of 4.0×10^{-6} M various anions in $CHCl_3$. Excitation at 350 nm. Inset shows the molar ratio plot against the apparent fluorescence intensity at 412 nm. □ F^-, ▽ CH_3COO^-, ◇ $H_2PO_4^-$, ○ HSO_4^-, ● Br^- and I^-.

F^-, Cl^-, Br^-, I^-, CH_3COO^-, $H_2PO_4^-$, and HSO_4^- having tetrabutyl ammonium as counter cation. The spectrum change by the addition of Cl^- was obviously different from those of other anions. The monomer fluorescence decreased in the presence of Cl^-, alternately a broad band appeared around at 544 nm, which will be corresponded to the excimer emission between anthracenes. On the other hand, for other anions except for Br^- and I^-, the decrease of the monomer fluorescence were observed as shown in Figure 2. Both insets in Figures 1 and 2 indicate the relationship between the variation of the fluorescence intensity at 412 nm (and 544 nm) and the molar ratio of anions to the boron complex. The molar ratio plots of F^-, CH_3COO^-, $H_2PO_4^-$, HSO_4^-, and Cl^- obviously indicated an intersection at the molar ratio of 2, which corresponds to a 1:2 (= Boron complex/anion) stoichiometry. These results suggest that the boron complex captured those two anions in $CHCl_3$.

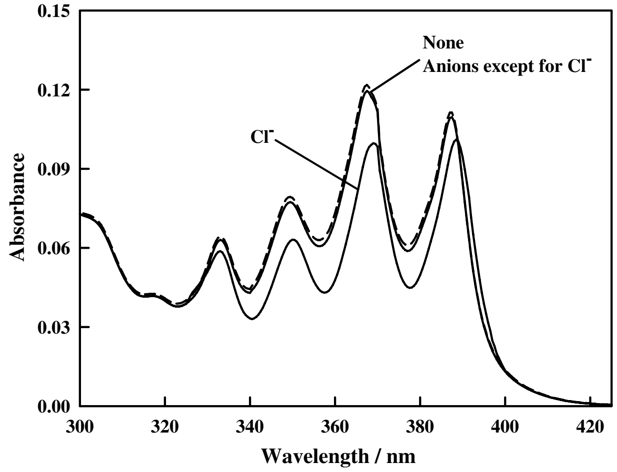

Figure 3. Absorption spectra of 2.0×10^{-6} M boron complex in the presence and absence of 4.0×10^{-6} M anions in $CHCl_3$.

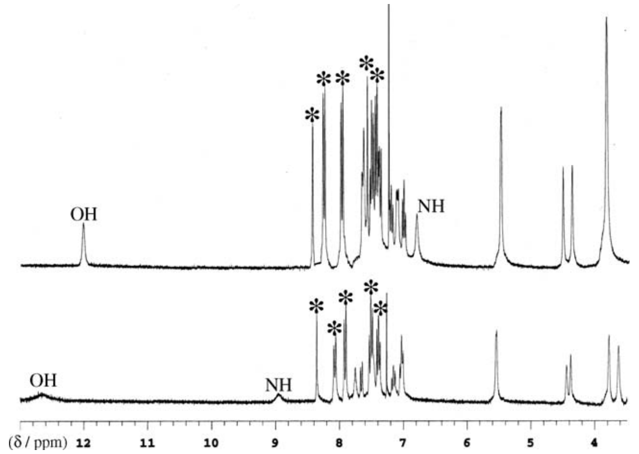

Figure 4. ^{1}H NMR spectra of 2.0×10^{-3} M boron complex in the absence (upper) and the presence (lower) of 4.0×10^{-3} M Cl^- in $CDCl_3$. Asterisks denote all protons of anthracene moieties.

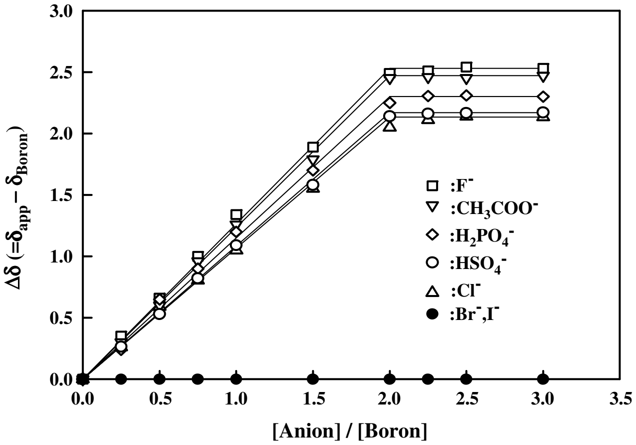

Figure 5. Variation of chemical shift of amide (NH) in boron complex in the presence of various anions $CDCl_3$. δ_{app}: apparent chemical shift of NH; δ_{Boron}: chemical shift of NH in the absence of anion.

Absorption spectra of the boron complex in the presence and absence of anions were also measured to support those variations of fluorescence spectra. Figure 3 indicates that the absorption band of the anthracene in the boron complex was hardly affected by F^-, Br^-, I^-, CH_3COO^-, $H_2PO_4{}^-$, and $HSO_4{}^-$. On the other hand, the absorption band showed the bathochromic shift in the presence of Cl^- in comparison with the spectrum of the boron complex. This result suggests an existence of the interaction and association between anthracenes at ground states.[5,11] The appearance of the new fluorescence band at longer wavelength region in Figure 1 must be ascribable to the excimer fluorescence between anthracenes.

^{1}H NMR study was performed to clarify the binding and the optical-response of the boron complex toward anions. Both peaks of the hydroxy protons and the amide (NH) protons in the boron complex were shifted to the lower magnetic field by the complexation with F^-, CH_3COO^-, $H_2PO_4{}^-$, $HSO_4{}^-$ and Cl^- (Figs. 4 and 5). These results exhibit the existence of hydrogen bonding between the hydroxy protons, the amide (NH) protons and those anions. In the presence of Br^- and I^-, the chemical shifts of the hydroxy and amide NH protons were not changed (Fig. 5), namely, the formation of the hydrogen bonding between the boron complex and Br^-, I^- was not occurred under given conditions. The variation of the chemical shifts of anthracene moiety denoting asterisk in the presence of Cl^- was remarkably different with those of other anions, in which all protons in the anthracene were slightly sifted to the higher magnetic field ($-\Delta\delta = 0.01$–0.22 ppm) as shown in Figure 4. The similar shift of anthracene moiety was not observed

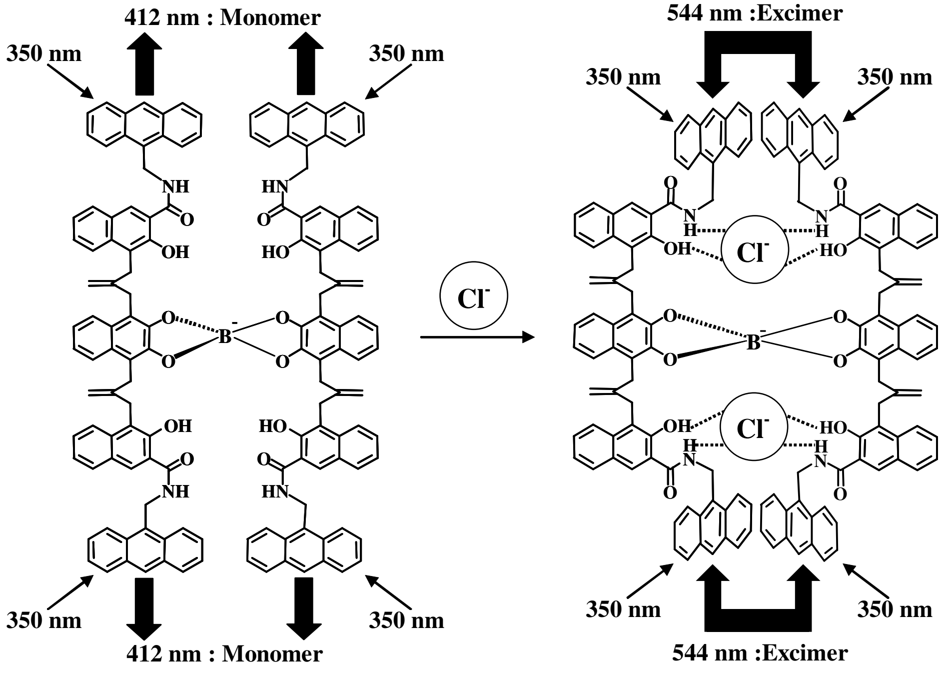

Figure 6. Optical response for Cl^- via supramolecular boron complex.

in other anions. Above results suggested that the binding of Cl^- via plural hydrogen bonding induced the reduction of distance between two anthracenes which were separately sited at two ligands of the boron complex, and the formation of the excimer (Fig. 6). Larger anions such as CH_3COO^-, $H_2PO_4{}^-$, and $HSO_4{}^-$ must be difficult to form the excimer complex, since the both anthracenes need to approach each other reasonably. Although the boron complex could capture F^- stably as expected from the largest shift of amide proton ($\Delta\delta_{NH} = 2.53$, see Fig. 5), hydroxy proton ($\Delta\delta_{OH} = 0.83$) which were larger than those of Cl^- case ($\Delta\delta_{NH} = 2.13$, $\Delta\delta_{OH} = 0.72$), the steric location and the direction of anthracene aromatic rings for the excimer formation may be deviated each other even if the anthracenes are possible to approach each other because of the smallest size of F^-.

It was elucidated that the boron complex having plural proton donors (OH, amide NH) is able to bind two anions in $CHCl_3$. However, the optical response of the anthracene moieties in the boron complex toward Cl^- was remarkably different with those of various anions. Namely, the boron complex expressed the appearance of the excimer fluorescence with the decrease of the monomer fluorescence as optical response toward Cl^-. On the other hand, the optical response toward F^-, CH_3COO^-, $H_2PO_4{}^-$, and $HSO_4{}^-$ corresponded to the quenching of the monomer fluorescence whose mechanism was still not cleared in this work. Thus, the novel boron complex is expected to be utilized as a selective sensor and receptor for Cl^-.

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8. Polyether 1: **1** was synthesized by the reaction between the diacid dichloride isobutenylarylether derivative[7] and 9-aminomethylanthracene in the presence of NEt_3 in THF at rt (93%). ^1H NMR (300 MHz, $CDCl_3$), 3.39 ppm (s, 4H, Ar–CH_2), 4.16 (s, 4H, Ar–CH_2), 4.56 (s, 2H, $CH_2{=}C$), 4.66 (s, 2H, $CH_2{=}C$), 5.56 (d, 4H, Anthryl–CH_2), 6.16 (s, 2H, Naphthyl), 6.85 (s, 2H, Naphthyl), 7.30–7.50 (dd, 8H, Anthryl, dd, 6H, d, 4H, Naphthyl), 7.81 (d, 4H, Anthryl), 7.84 (d, 2H, Naphthyl), 8.16 (s, 2H, Naphthyl), 8.22 (t, 2H, NH), 8.27 (d, 4H, Anthryl), 8.78 (s, 2H, Anthryl); IR (KBr), 3388 cm^{-1} (NH), 1653, 1524 (HNC=O); ESI-MS (cationic mode), 1041.3 ($M+Na^+$).
9. Ligand 2: ^1H NMR (300 MHz, $CDCl_3$), 3.95 ppm (s, 4H, Ar–CH_2), 3.98 (s, 4H, Ar–CH_2), 4.54 (s, 2H, $CH_2{=}C$), 4.62 (s, 2H, $CH_2{=}C$), 5.68 (d, 4H, Anthryl–CH_2), 6.24 (s, 2H, OH), 6.66 (t, 2H, NH), 7.17 (dd, 2H, Naphthalene), 7.26 (dd, 2H, Naphthyl), 7.36 (dd, 2H, Naphthyl), 7.53 (dd, 4H, Anthryl), 7.53 (d, 2H, Naphthyl), 7.63 (dd, 4H, Anthryl), 7.64 (s, 2H, Naphthyl), 7.69 (d, 2H, Naphthyl), 7.80 (dd, 2H, Naphthyl), 8.09 (d, 4H, Anthryl), 8.36 (d, 4H, Anthryl), 8.55 (s, 2H, Anthryl), 12.39 (s, 2H, OH); IR (KBr), 3441 cm^{-1} (br, OH), 1649, 1524 (HNC=O); ESI-MS (cationic mode), 1041.3 ($M+Na^+$).
10. Boron complex: ^1H NMR (300 MHz, $CDCl_3$), 3.87 ppm (s, 8H, Ar–CH_2), 3.91 (s, 8H, Ar–CH_2), 4.43 (s, 4H, $CH_2{=}C$), 4.52 (s, 4H, $CH_2{=}C$), 5.54 (d, 8H, Anthryl–CH_2), 6.83 (br, 4H, NH), 7.02 (t, 4H, Naphthyl), 7.13 (dd, 4H, Naphthyl), 7.22 (t, 4H, Naphthyl), 7.39 (d, 4H, Naphthyl), 7.44 (dd, 8H, Anthryl), 7.53 (dd, 8H, Anthryl), 7.59 (s, 4H, Naphthyl), 7.65 (dd, 4H, Naphthyl), 7.68 (d, 4H, Naphthyl), 7.99 (d, 8H, Anthryl), 8.27 (d, 8H, Anthryl), 8.44 (s, 4H, Anthryl), 12.20 (s, 4H, OH), 0.96 (t, 9H, NEt_3), 2.72 (q, 6H, NEt_3); IR (KBr), 3410 cm^{-1} (br, OH), 1648, 1524 (HNC=O); ESI-MS (anionic mode), 2042.8 ($M-1$); Elemental analysis, found (calcd for $(C_{70}H_{52}N_2O_6)_2B$), C, 81.09 (81.66); H, 5.73 (5.63); N, 3.20 (3.26).
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