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NOTES

π-Conjugated Organoboron Polymer as an Anion Sensor†

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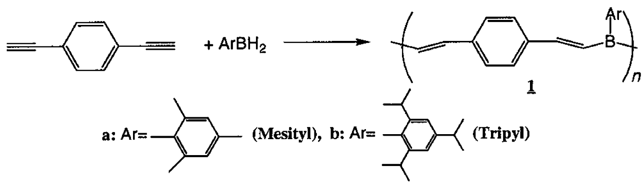
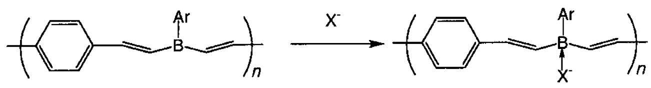
In recent years, the sensing of atomic and molecular species has received considerable attention by many research groups. In particular, π-conjugated polymers have been used as "molecular wire" amplifying signals mainly to detect cations.[2,3] However, responsive systems for anionic guest species are only now being realized.[4,5] For example, boron compounds were used to make complexes with anions. "Hydride sponge (1,8-naphthalenediylbis(dimethylborane))" was reported to make a complex with hydride, fluoride, or hydroxide anion.[6,7] 1,8-Naphthalenediylbis(dichloroborane) formed a complex with chloride.[8] Recently, ferroceneboronic acid was reported as a selective fluoride ion sensing material,[9,10] and boronic acid derivatives were also found to be fluoride anion sensing materials.[11,12] In most of these reports, fluoride ion was detected by electrochemical responses in cyclic voltammetry, and few examples were reported to recognize the anion visually.[10,11,13]

On the other hand, we have reported the synthesis of π-conjugated oragnoboron polymers by hydroboration polymerization of aromatic diyne compounds (Scheme 1).[14] In these polymers, π-conjugation length is extended *via* vacant *p*-orbital of boron atom, and they show intense blue emission in fluorescence emission spectra. If anion species are added to the organoboron polymer, some kinds of anion would coordinate the boron atom and the orbital of the boron atom should change from sp^2 to sp^3 (Scheme 2). The change would interrupt the extension of π-conjugation length and quench the fluorescence emission. Therefore, the π-conjugated organoboron polymer is expected as a colorimetric anion sensor which can detect anion by UV-vis absorption spectra or fluorescence emission spectra. In this paper, we describe the application of organoboron polymer as an anion sensor. As far as we concerned, this is the first example of boron containing polymer sensor that can detect anion with "naked eye" and the changes of spectra are amplified by the interruption of π-conjugation length.



Scheme 1.



Scheme 2.

RESULTS AND DISCUSSION

The organoboron polymers were prepared in a reported way[14] as shown in Scheme 1 (**1a**: M_n = 1500, M_w/M_n = 1.3, **1b**: M_n = 2000, M_w/M_n = 1.5). Figure 1 shows the UV-vis absorption spectra of the polymer **1b** in chloroform before and after the addition of the anions (10 equiv. to boron atom). **1b** showed an absorption maximum at 377 nm before the addition. Only in the case of fluoride ion, blue shift of the absorption maximum was observed and the color of the solution changed from yellow to colorless. The other anions used here (Cl^-, Br^-, I^-) did not bring about the dramatic change even after a few days stirring of the solutions. The polymer prepared from mesitylborane (**1a**) also showed similar results.

Next, the change of the fluorescence emission spectra was studied. The chloroform solution of the organoboron polymer showed an intense blue emission (λ_{em} = 438 nm) before the addition of the anions. Fig-

†See ref 1.
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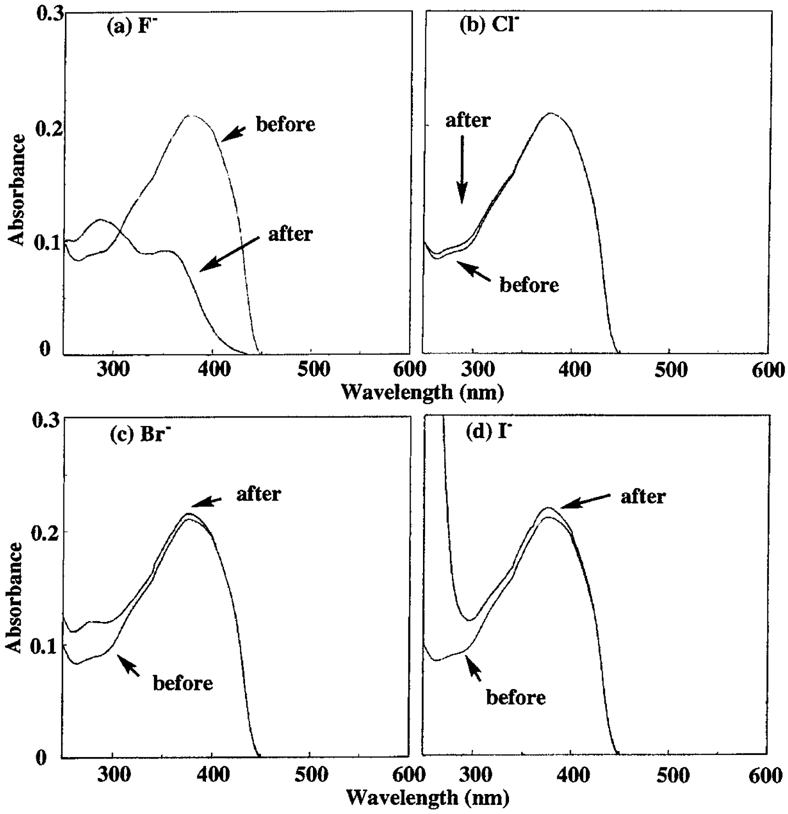

Figure 1. UV-vis absorption spectra of **1b** in $CHCl_3$ (10^{-5} M) before and after the addition of anion (10 equiv., as tetrabutylammonium salt).

ure 2 shows the fluorescence emission spectra of the polymer **1b** before and after the addition of the anions (excited at 380 nm, at r. t.). As shown in the figure, the blue emission disappeared after the addition of fluoride ion (Figure 2a). An excitation at another wavelength also gave no emission. In the cases of the other anions used here, a quench of the emission was not observed. Even after the addition of 1/2 equiv. of fluoride ion, similar change was observed. However, 1/10 equiv. of fluoride ion did not lead to the dramatic decrease of the intensity of the emission, though the detection limit would depend on the molecular weight of the polymer (Figure 3). These results show that the organoboron polymer can be used as a selective fluoride ion sensor and the amplifying ability as a molecular wire was also confirmed. The selectivity might be explained by strong Lewis acid-base interaction between boron atom and fluoride ion. The compact size of fluoride ion compared with other anions should also be one of the important factors for the selectivity.

The orbital change of boron atom was also supported by ^{11}B NMR spectra (in $CDCl_3$). The original polymer showed one peak around 30 ppm, which is assigned to dialkenylarylborane structure.[14] After the addition of fluoride ion, a peak was observed around 0 ppm. This peak is characteristic to tetravalent boron atom. When other halide ions were added to the polymer solution, no peak was observed around 0 ppm.

CONCLUSION

We discovered that π-conjugated organoboron polymer can be used as a selective fluoride ion sensor. The existence of fluoride ion is detected by the changes of UV-vis absorption spectra and fluorescence emission spectra, and these changes can be seen visually. Since the polymer showed drastic changes in the absorption and photoluminescence spectra after the addition of small amount of fluoride ion, the amplification of the signal as a molecular wire was confirmed. The behavior of the polymer film and the sensing abilities toward other anions would be reported in near future.

EXPERIMENTAL SECTION

The organoboron polymers used here were prepared by using 1,4-diethynylbenzene as a diyne monomer. The hydroboration polymerization was carried out in a reported way[14] using mesitylborane or tripylborane. ^{11}B NMR spectra were recorded in $CDCl_3$ on a JEOL EX-270 instrument. UV-vis absorption spectra were recorded on a JASCO V-530 spectrophotometer. Fluorescence emission spectra were recorded on a Perkin–Elmer LS50B luminescence spectrometer.

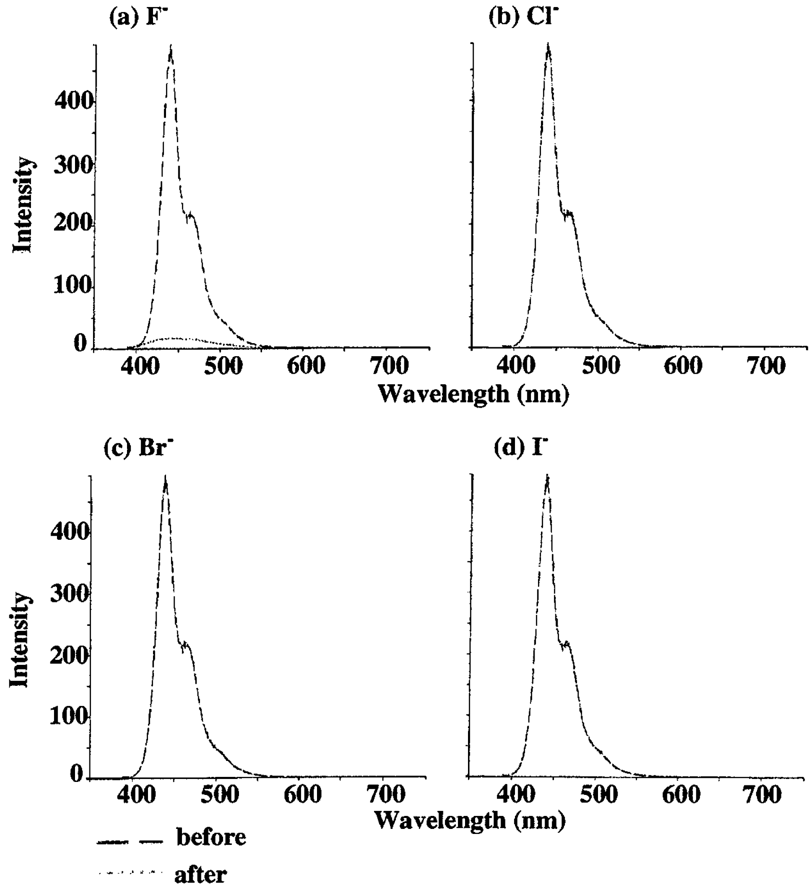

Figure 2. Fluorescence emission spectra of **1b** in $CHCl_3$ (10^{-6} M) before and after the addition of anion (10 equiv., as tetrabutylammonium salt).

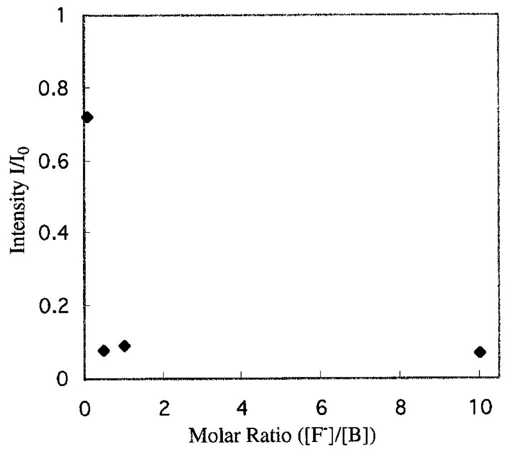

Figure 3. Plots of fluorescence intensity ratio of after (I) and before (I_0) the addition of fluoride ion *vs.* molar ratio ($[F^-]/[B]$) (polymer **1b**).

Anion sensing experiments were carried out by adding anions (F^-, Cl^-, Br^-, I^-) to chloroform solutions of the polymers. These anions were added as their tetrabutylammonium salts. UV-vis absorption spectra were measured in 10^{-5} *M* solutions (in $CHCl_3$) and fluorescence emission spectra were measured in 10^{-6} *M* solutions (in $CHCl_3$).

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