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REGULAR ARTICLE

A Novel Fluorescent Fluoride Chemosensor Based on Unmodified Poly(amidoamine) Dendrimer

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The methanol solution of G4.5 COONa-terminated PAMAM dendrimer displayed strong blue luminescence ($\lambda_{max} = 445$ nm) under UV irradiation at 370 nm and fluorescence intensity increased with fluoride ions. On the other hand, the remarkable changes of fluorescence spectra of the dendrimer solutions were not observed in the presence of other halogen anions (Cl^-, Br^-, and I^-). This result suggested that the PAMAM dendrimer is useful as fluoride ion selective sensor in methanol.
KEY WORDS: Dendrimer / Poly(amidoamine) / Chemosensor / Fluoride Ion / Fluorescence /

The sensing of anionic species is gaining considerable interest because of biological and environmental importance of anions.[1] In particular, the sensing of fluoride ions has attracted growing attention because of its great potential for biological applications, such as dental care and the treatment of osteoporosis.[2] The conventional approaches for the sensing of fluoride ion have used the specific Lewis acid-base interaction or the designed hydrogen bonding with the fluoride ion, and several types of chemosensors have been reported.[3,4] Broomsgrove *et al.* utilized ferrocene-derivatized Lewis acids as a chemosensor for fluoride ions.[5] Yamaguchi *et al.* have developed fluoride sensors based on boron-containing π-electron systems.[6] In both studies, the binding events of fluoride ions have been converted into a colorimetric change detectable by naked eye. On the other hand, fluorescence is another important detection method because of its simplicity and high sensitivity. Even though a number of compounds that are able to bind fluoride ion have been reported, there is a paucity of reports regarding a selective fluorescent sensor for fluoride ions in protic solvents.[7–10]

Meanwhile, poly(amidoamine) (PAMAM) dendrimers have attracted wide interest as a motif of chemosensor because of high solubility and biocompatibility.[11] Introducing chromophores of various natures into the periphery of the dendrimers allows altering the desired properties of new materials. Recent investigations have demonstrated the potential of PAMAM dendrimers to coordinate metal cations.[12] Grabchev *et al.* have reported sensors for metal cations based on green fluorescent from 1,8-naphthalimides at the periphery of PAMAM dendrimers.[13,14] However, there is no report on the fluorescent fluoride chemosensor based on the PAMAM dendrimers. Recently, Imae and co-workers have reported a strong fluorescence emission from aqueous solution of unmodified PAMAM dendrimers under acidic conditions.[15] They described it is crucial for the fluorescence of PAMAM dendrimers that the protonation of tertiary amine groups fills the whole dendritic interior with cations, and the strong charge-charge repulsion makes the structure of PAMAM dendrimer more rigid. This result prompts us to utilize unmodified PAMAM dendrimer as a chemosensor for fluoride ions because it is plausible that fluoride ions make the structure of PAMAM dendrimer rigid *via* the formation of hydrogen bonds between fluoride ions and amide groups of the dendrimer. Even though considerable effort has been devoted to developing fluorescent sensors using PAMAM dendrimer derivatives for cations guest, there is no reports regarding a fluorescent sensor for anions based on inherent fluorescence from PAMAM dendrimer. Here we report a commercially-available unmodified G4.5 COONa-terminated PAMAM dendrimer behaves as a fluorescent chemosensor for F^- detection, enabling selective F^- sensing among the halide ions in methanol.

EXPERIMENTAL

Materials

Methanol solutions of G4.5 COONa-terminated PAMAM dendrimer (10 wt %) and G5 NH_2-terminated PAMAM dendrimer (10 wt %) were purchased from Aldrich Chemical Co. Tetrabutylammonium fluoride (TBAF), tetrabutylammonium chloride (TBAC), tetrabutylammonium bromide (TBAB), and tetrabutylammonium iodide (TBAI) purchased from Tokyo Kasei Kogyo. KF, and CsF were obtained from Nacalai Tesque. 18-crown-6 ether was purchased from Acros Organics. These chemicals were used without special treatment.

Measurement

Fluorescence spectra were taken on a Jasco FP-6600 spectrofluorometer equipped with a lamp power supply (UXL-159, USHIO INC.), working at 25 °C. The excitation wavelength for emission spectra measurements was 370 nm. For fluorescence spectra measurements, a slit width was 2 nm, and a scan rate was 200 nm/min. The solutions used for emission measurement were placed in quartz cell of 10 mm path length. The pH values of the methanol solutions of the PAMAM dendrimer were obtained using HORIBA pH meter B-212.

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Fluorescence spectra of methanol solutions of the dendrimers were recorded as follows; methanol solutions of G4.5 COONa-terminated PAMAM dendrimer (10 wt %, 184 mg) and G5 NH_2-terminated PAMAM dendrimer (10 wt %, 201 mg) were dried under reduced pressure and dissolved in 2 mL of dried methanol to prepare the dendrimer solution (0.35 mM). TBAF, TBAC, TBAB, TBAI, KF, and CsF were used as sources for halide ions. For solubilization of KF in methanol, 18-crown-6-ether (92 mg, 0.35 mmol) was added to the solution. Before addition of halide ions, pH value of the dendrimer solution was adjusted using 12 N hydrochloric acid or sodium hydroxide solution. Prior to fluorescence measurement, resultant mixtures were kept at 25 °C for 24 h.

Fluorescence spectra of aqueous solutions of G4.5 COONa-terminated PAMAM dendrimer were recorded as follows; aqueous solution of G4.5 COONa-terminated PAMAM dendrimer (10 wt %, 184 mg) was dried under reduced pressure and dissolved in 2 mL of ion exchanged water to prepare the dendrimer solution (0.35 mM). Before addition of halide ions, pH value of the dendrimer solution was adjusted using 12 N hydrochloric acid. Prior to fluorescence measurement, resultant mixtures were kept at 25 °C for 24 h.

RESULT AND DISCUSSION

In order to ascertain that the G4.5 COONa-terminated PAMAM dendrimer can act as a fluorescent chemosensor for fluoride ion, we investigated the influence of different halide ions (F^-, Cl^-, Br^-, I^-) upon the fluorescent intensity of the dendrimer in methanol. The pH value of the solution was adjusted at 8.3 because Imae and co-workers reported that pH value of the dendrimer solution strongly affected the fluorescence intensity.[15,16] In the absence of halide ions, the solution exhibited week fluorescence, of which maximum emission band at 445 nm. Surprisingly, increasing concentration of tetrabutylammonium fluoride (TBAF) to 87 mM, the colorless solution of the PAMAM dendrimer began to display strong blue luminescence and the fluorescence intensity drastically increased as shown in Figure 1; the emission band position scarcely changed.

To compare fluorescence enhancement effect caused by other halide ions with that of fluoride ions, tetrabutylammonium chloride (TBAC), tetrabutylammonium bromide (TBAB), and tetrabutylammonium iodide (TBAI) were added to the dendrimer solutions. The remarkable changes were not observed in fluorescence spectra of G4.5 COONa-terminated PAMAM dendrimer with 87 mM of TBAC, TBAB and TBAI (Figure 1). More precisely it can be said that the florescence enhancement effect of fluoride ions is almost 4-fold as compared to that of the other halide ions at 445 nm when adding 87 mM of TBAF, TBAC, TBAB, and TBAI. Although the dendrimers did not exhibit any obvious spectral changes when concentrations of TBAB and TBAI were increased to 174 mM, the fluorescence intensity of the dendrimer solution was modestly enhanced by increasing the concentration of TBAC to 174 mM (Figure 2).

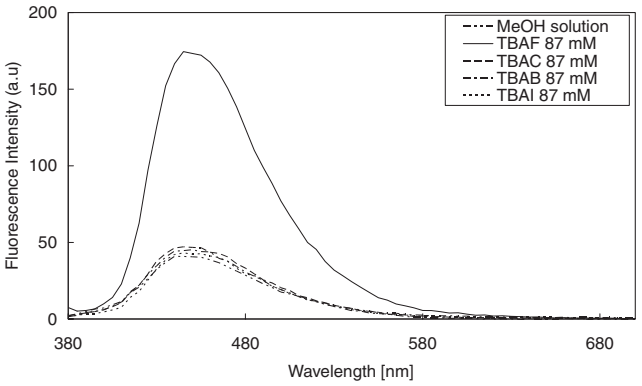

Figure 1. Fluorescent emission changes of G4.5 COONa-terminated dendrimers upon addition of TBAF (87 mM), TBAC (87 mM), TBAB (87 mM), and TBAI (87 mM) in MeOH.

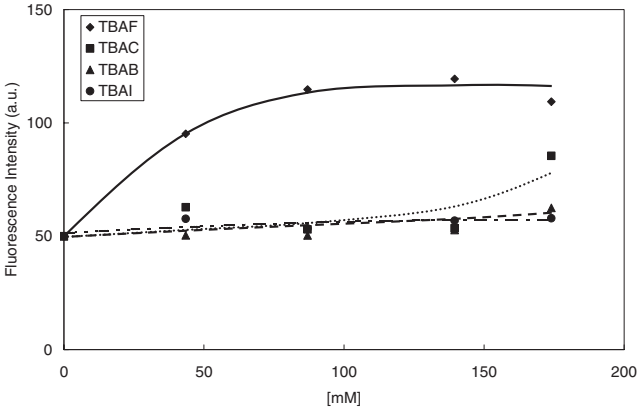

Figure 2. Dependence of fluorescence intensity of G4.5 COONa-terminated PAMAM dendrimers at 445 nm on the concentration of tetrabutylammonium fluoride, chloride, bromide and iodide in MeOH.

This result might be explained by structural change of the dendrimer after the addition of halide ions.[17] It is well known that fluoride ion has better hydrogen bond acceptor properties compared to the other halide ions.[18] Hence, strong hydrogen bonds between fluoride anion and amide proton fills the whole dendritic interior, and makes the structure of the PAMAM dendrimer more rigid.[16,19] Consequently, the fluorescence intensity of the dendrimers was enhanced as in the case of Imae's observation.[13] It is notable that the absence of a significant fluorescence enhancement effect caused by chloride, bromide, and iodide ions renders PAMAM dendrimers highly useful as fluoride ions selective sensors.

In marked contrast to G4.5 COONa-terminated PAMAM dendrimer, the methanol solution of G5 NH_2-terminated PAMAM dendrimer showed very weak fluorescence band and remarkable changes were not observed in fluorescence spectra of the PAMAM dendrimer on adding 87 mM of TBAF. This result indicates that G4.5 COONa-terminated PAMAM dendrimer is more suitable for detection of fluoride ions than G5 NH_2-terminated PAMAM dendrimer.

Aqueous solution of G4.5 COONa-terminated PAMAM dendrimer have also examined for comparison with methanol

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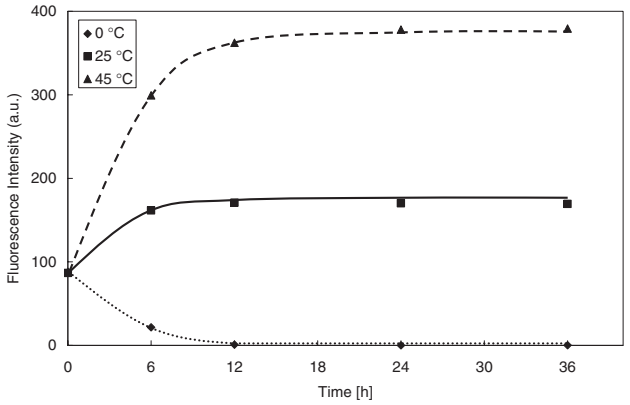

Figure 3. The fluorescent intensity of G4.5 COONa-terminated PAMAM dendrimers as a function of aging time at different temperatures. All solutions were added 43.5 mM of TBAF before aging.

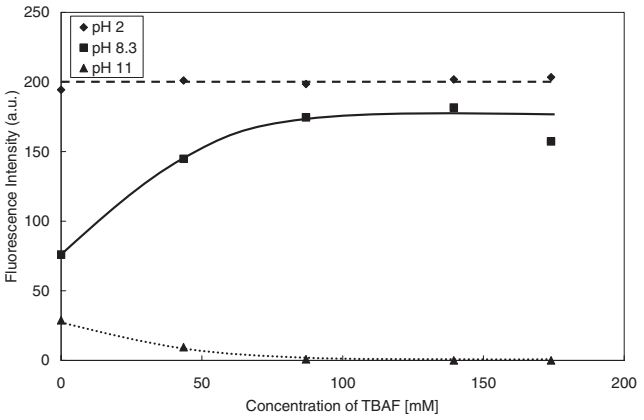

Figure 4. Dependence of fluorescence intensity of G4.5 COONa-terminated PAMAM dendrimers at 445 nm on the concentration of TBAF at different pH values in MeOH.

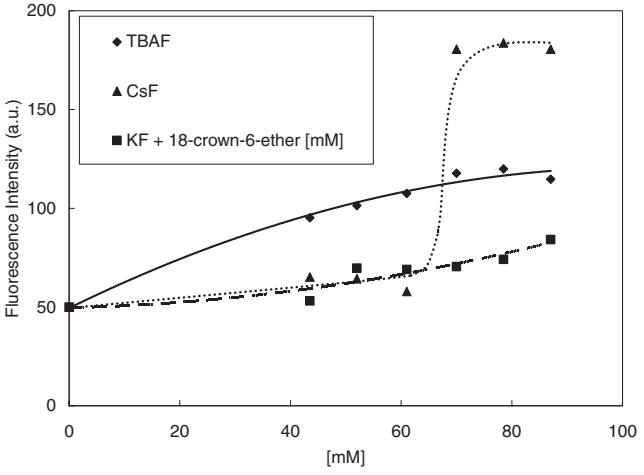

Figure 5. Dependence of fluorescence intensity of G4.5 COONa-terminated PAMAM dendrimers at 445 nm on the concentration of TBAF, CsF and KF with 18-crown-6-ether (174 mM) in MeOH.

solution of the dendrimer as a sensor for fluoride anions. In the case of aqueous solution, there was no significant change in emission intensity. This result indicates that methanol solution of G4.5 COONa-terminated PAMAM is more suitable for detection of fluoride ions than that of aqueous solution.

In respect that fluoride ions usually coexist with other halide ions, it is necessary to test the influence of other halide ions toward fluoride ions detection. The fluorescence spectra were recorded by adding TBAC into the G4.5 COONa-terminated PAMAM dendrimer methanol solution with 87 mM of TBAF. The remarkable changes of fluorescence spectra of the dendrimer solutions were not observed as chloride ions were added into the dendrimer solution. The result indicates that G4.5 COONa-terminated PAMAM dendrimer is able to detect fluoride ions with the coexistence of chloride ions.

We also investigated effect of temperature of G4.5 COONa-terminated PAMAM dendrimer. Three methanol solutions of the dendrimer include 43.5 mM TBAF, and they were kept at 0, and 25, and 45 °C, respectively. As shown in Figure 3, there was an obvious difference in time dependence of emission intensity at different temperatures. The fluorescent intensity reached maximum within 12 h for solutions at 25 and 45 °C, whereas the fluorescent intensity was decreased at low temperature. This result proves that fluorescence intensity of PAMAM dendrimers was obviously influenced by temperature because fluorescence-emitting moieties were formed at higher temperature more efficiently.[16]

To study pH-dependence of emission intensity, the pH values of methanol solutions of G4.5 COONa-terminated PAMAM dendrimer were adjusted at 2, 8.3, and 11. At pH 8.3, as plotted Figure 4, the fluorescent intensity was enhanced regularly with increase of the concentration of TBAF. At pH 11, fluorescence intensity was weak in the absence of TBAF. Furthermore, addition of 87 mM of TBAF led to a complete disappearance of the emission. On the other hand, at pH 2, fluorescence intensity reached maximum without TBAF. Furthermore, remarkable changes were not observed in fluorescence intensity with increase of the concentration of TBAF. This result suggested that strong basic or acidic conditions were not suitable to detect fluoride ions.

We also investigated influences of counter ions on the fluorescence intensity. Figure 5 shows plots of the change in the fluorescence intensity of the PAMAM dendrimers in the presence of different concentration of TBAF, KF, and CsF. In the case of KF, the fluorescence intensity of the PAMAM dendrimers was modestly enhanced. For CsF, when the concentration increased to 70 mM, the emission intensity was drastically enhanced. This observation indicate that CsF enhance the fluorescence intensity efficiently than KF. In the case of TBAF, the fluorescent intensity was enhanced regularly with increase of the concentration of TBAF.

Figure 6 shows the dependence of counter ions on the fluorescent enhancement (FE).[20] The $FE = I/I_0$ has been determined from the ratio of maximum fluorescence intensity I at 445 nm (concentration of KF was 87 mM, TBAF was 70 mM, and CsF was 78.5 mM) and minimum fluorescence intensity I_0 at 445 nm (absence of TBAF, CsF, and KF). 18-

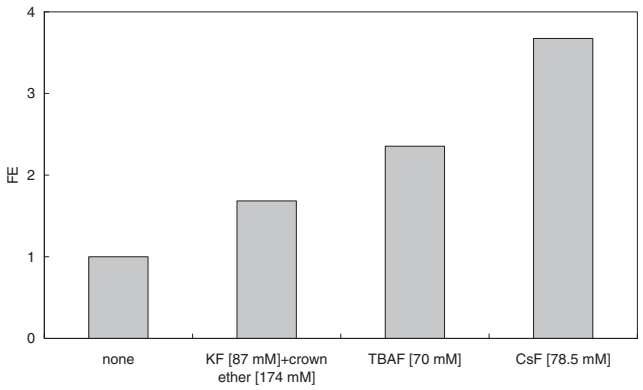

Figure 6. Fluorescence enhancement factor (FE) of G4.5 COONa-terminated PAMAM dendrimers in the presence of different sources for fluoride ion in MeOH. The FE = I/I_0 has been determined from the rate of maximum fluorescence intensity I and minimum fluorescence intensity I_0.

crown-6-ether (92 mg) was added to the PAMAM dendrimers to dissolve KF in methanol.[21] Fluorescence intensity of PAMAM dendrimers was obviously influenced by counter ions of fluoride anions. The fluorescence enhancement factors in the presence of CsF, TBAF, and KF were 3.6, 2.4, and 1.8, respectively.

Hence, the FE effect produced by the different counter cations can be ranked as follows: $Cs^+ > (Bu)_4N^+ > K^+$. This phenomenon might be explained on the basis of the following possible reason: (a) Fluorescence intensity of the PAMAM dendrimer is enhanced moderately by sole fluoride ions. This result indicated by KF and 18-crown-6 ether system. (b) Fluoride ions enhance the fluorescence intensity with the aid of counter cations. The interaction of tertiary amines with Cs^+ and $(Bu)_4N^+$ lead to rigid and dense shell conformation of the dendrimers. However, the exact nature of the effect of counter ions on the fluorescence intensity of the PAMAM dendrimers is not yet clear and remains to be experimentally determined.

CONCLUSION

The results described herein show the first example of the fluorescent chemosensor for fluoride ions detection in protic solvent using unmodified PAMAM dendrimer. In the presence of fluoride ions, fluorescence intensity of methanol solution of G4.5 COONa-terminated PAMAM dendrimer was increased almost 4-fold as compared to that of the other halide ions. Fluorescence intensity enhancement effect of fluoride ion might arise from hydrogen bond formation between fluoride and amide proton of the dendrimer. Further work is in progress to explore the applications and advantages of fluorescent chemosensor based on PAMAM dendrimers.

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