Fluorometric detection of fluoride ion by ligand exchange reaction with 3-hydroxyflavone coordinated to a zirconium(IV)–EDTA complex

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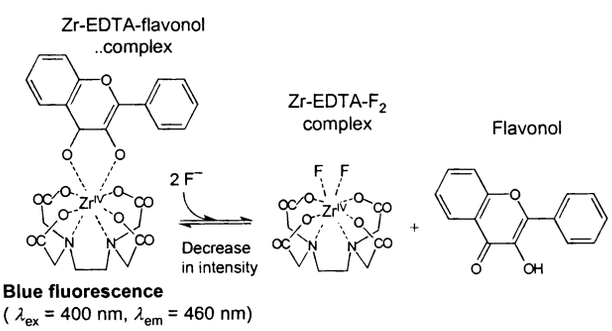
An aqueous solution composed of $[Zr(H_2O)_2edta]\cdot 2H_2O$ and 3-hydroxyflavone (flavonol) exhibits an intense blue fluorescence ($\lambda_{max} = 460$ nm) upon excitation at 400 nm and the signal intensity decreases with the addition of fluoride ion. This observation has been interpreted by the ligand exchange of flavonol coordinated to Zr(IV) with fluoride ion. Based on this phenomenon, we have fabricated a simple fluorescent detection system of fluoride ion available in aqueous media. The present signaling system provides a simple, rapid and selective detection method of fluoride ion, which covers the concentration range from 1×10^{-3} to 3×10^{-6} M without any significant interference from common anions.

Introduction

Rapid, sensitive and convenient determination of fluoride ion in an aqueous solution is essentially important for monitoring of the ion in industrial and environmental wastewaters.[1] While there are widely available methods of fluoride analysis such as ion selective electrodes and ^{19}F NMR, optical sensing systems provide a simple method for trace analysis of fluoride ion due to the possibility of naked eye detection.[2] Owing to the high electronegativity,[3] the fluoride ion can form stable fluoro complexes with tervalent and tetravalent metal ions and their complexes. Metal complexes of La(III), Ce(III) and Zr(IV) with dye compounds have been conventionally used for the colorimetric determination of fluoride.[4] However, these systems lack chemical stability and take some time for color development. Porphyrin related macroazacycles and heteroaromatic compounds have been examined as fluoride ion receptors *via* strong hydrogen bond formation.[5] Organometallic compounds having a Lewis acid center including B(III), Sn(IV) and Si(IV) have revealed a unique property with respect to a selective receptor of fluoride ion.[2,6] However this property occurs only in organic solvents.

Anion ligation to Zn(II) and Cu(II) complexes and their behavior in the presence of various anions has been studied in aqueous media.[7] An attractive approach has been reported using Eu(III) and Tb(III) complexes as emission switching devices associated with the exchange of coordinated water with anions.[8] It has been demonstrated that $[Zr(H_2O)_2edta]\cdot 2H_2O$ can bind fluoride ion as well as oxo anions of arsenic and selenium by ligand exchange with coordinated water.[9] Thus, combined use of $[Zr(H_2O)_2edta]\cdot 2H_2O$ as an anion receptor and appropriate probe molecules provides a feasible detection system of fluoride ion.

In the present study we have found that flavonol exhibits an intense fluorescence in the visible region in the presence of $[Zr(H_2O)_2edta]\cdot 2H_2O$. Furthermore, the signal intensity readily decreases by the addition of fluoride ion. These observations enabled us to construct a fluorometric detection system of fluoride ion in aqueous solution by monitoring the change in fluorescence intensity induced by the ligand exchange reaction (Scheme 1).



Scheme 1 Ligand exchange reaction of Zr–EDTA–flavonol with fluoride ion.

Results and discussion

Ternary complex formation

Ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (EDTA) forms a remarkably stable 1 : 1 complex with Zr(IV), whose formation constant has been determined as $\log K_{ML} = 29$.[10] Therefore the complex can be present in an aqueous solution over a wide pH range without hydrolysis of the zirconium ion. On the basis of X-ray structural analysis,[11] the $[Zr(H_2O)_2edta]$ complex is composed of a mononuclear eight-coordinate structure in which Zr(IV) is surrounded by hexadentate EDTA and two water molecules. Ternary complex formation has been demonstrated by replacement of the water molecules bound to Zr(IV) with various bidentate ligands.[12] Flavonol is known as a typical fluorescent compound that can be used for the detection of Zr(IV) since a particularly intense fluorescence is induced by metal complex formation.[13] The pK_a value of flavonol was determined to be 9.23 by spectrometric titration in an ethanol–water (20 v/v%) solution. We have attempted to use flavonol as the signal probe molecule by ternary complex formation

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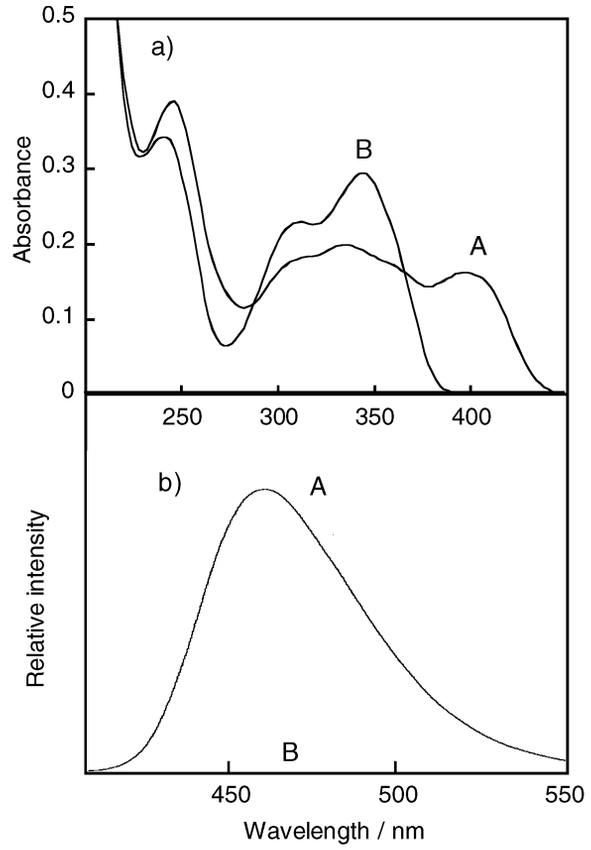

Fig. 1 Absorption and fluorescence spectra of (A) equimolar mixture of $[Zr(H_2O)_2edta]$–flavonol and (B) flavonol in ethanol–water (20 v/v%): a) UV–VIS absorption spectrum, b) fluorescence spectrum. $[Zr(H_2O)_2$-edta] = 1×10^{-5} M; [flavonol] = 1×10^{-5} M; pH 5.0 (acetate buffer); λ_{ex} = 400 nm.

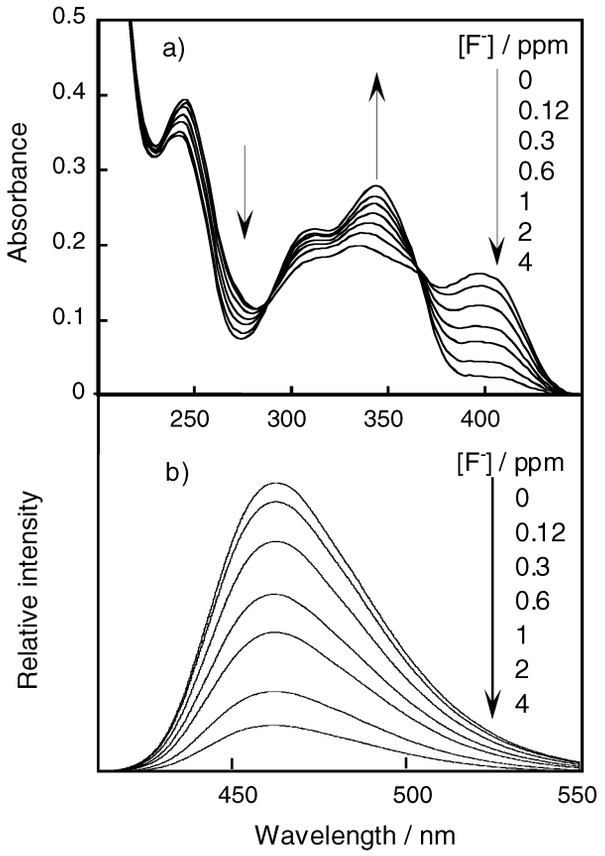

Fig. 2 Absorption and fluorescence spectral change of $[Zr(H_2O)_2$-edta]–flavonol solution upon addition of fluoride ion. $[Zr(H_2O)_2edta]$ = 1×10^{-5} M; [flavonol] = 1×10^{-5} M; pH 5.0 (acetate buffer); λ_{ex} = 400 nm.

with Zr–EDTA, thereby the signal can be switched by ligand exchange.

The absorption spectrum of flavonol changed upon addition of $[Zr(H_2O)_2edta]\cdot 2H_2O$ solution as shown in Fig. 1. Thus, an equimolar mixture (1×10^{-5} M, M = mol dm^{-3}) of $[Zr(H_2O)_2edta]\cdot 2H_2O$ and flavonol in an ethanol–water (20 v/v %) solution gave a characteristic absorption band with a peak at 400 nm; the flavonol λ_{max} was shifted by more than 60 nm in the presence of $[Zr(H_2O)_2edta]\cdot 2H_2O$. The appearance of a new absorption band at 400 nm coincides with the decrease in the absorption band due to the free flavonol at around 350 nm. In accord with the absorption spectral change, the aqueous solution gave an intense blue fluorescence with a peak at 460 nm upon excitation at 400 nm. The observed spectral changes can be interpreted as being due to the complexation of flavonol to Zr(IV)–EDTA, since fluorescence of free flavonol at around 460 nm is significantly small under the same conditions.

Molar ratio plots of fluorescence intensity against the concentration of $[Zr(H_2O)_2edta]\cdot 2H_2O$ at a fixed concentration of flavonol (Flav) indicated the 1 : 1 complex formation as given in eqn. (1), where flavonol acts as a bidentate ligand and $[Zr(H_2O)_2edta]\cdot 2H_2O$ as the ligand receptor. The conditional equilibrium constant of this reaction was determined to be 2.7×10^5 M^{-1} (pH = 5.0) at 293 K by curve analysis of the molar ratio plots.

$$[Zr(H_2O)_2edta] + Flav^- \rightleftharpoons [Zr(Flav)edta]^- + H_3O^+ \quad (1)$$

Fluorometric detection system of fluoride ion

Notably, the absorption peak that newly appeared at 400 nm was quenched upon addition of fluoride ion (NaF), whereas the peak intensity around 350 nm due to the flavonol moiety increased (Fig. 2(a)). The series of spectra observed gave distinct isosbestic points. In conjunction with the change in absorption spectra, the signal intensity of the blue fluorescence decreased by the addition of fluoride ion (Fig. 2(b)). These changes in absorption and fluorescence spectra apparently depend on the concentration of fluoride ion added. The observed quenching of fluorescence by the addition of fluoride ion can be attributed to the replacement of flavonol by the strongly competing fluoride ion as expressed in eqn.(2).

$$[Zr(Flav)edta]^- + 2F^- \rightleftharpoons [Zr\ F_2edta]^{2-} + Flav^- \quad (2)$$

Although a two-step reaction is involved in eqn. (2), the presence of isosbestic points in the absorption spectra suggest that release of flavonol would take place by the initial attack of a fluoride ion. Direct binding of the fluoride ion to Zr(IV)–EDTA giving mono and bis fluoride complexes has been demonstrated by the significant shift of ^{19}F-NMR peaks (122.38 ppm, 131.57 ppm) relative to the location of free fluoride upon addition of fluoride ion to aqueous $[Zr(H_2O)_2$-edta]$\cdot 2H_2O$ solution.[14] The formation constants between $[Zr(H_2O)_2edta]$ and fluoride ion have been determined as 4.6 and 2.8 for log K_1 and log K_2, respectively.[15]

Fig. 3 shows the plots of fluorescence signal intensity against pH in the absence and in the presence of fluoride ion along with the intensity difference between them. The concentration of $[Zr(H_2O)_2edta]\cdot 2H_2O$ as well as flavonol was fixed at 1.0×10^{-5} M throughout these experiments. Ternary complex formation with flavonol seems favorable at a pH ranging from 5.0 to 9.0. Obviously the signal intensity changes most sensitively between pH 4.5–6.0, where ligand exchange between flavonol and fluoride ion takes place most effectively. Time course experiments showed that the change of fluorescence signal intensity was appreciably rapid and terminated within 1 min upon addition of 1 ppm fluoride ion (pH = 5.0) at 298 K.

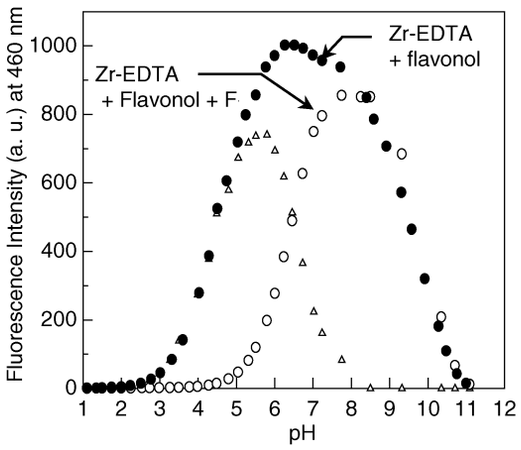

Fig. 3 Change in fluorescence signal intensity as a function of pH: ● equimolar mixture (1×10^{-5} M) of [$Zr(H_2O)_2$edta]–flavonol; ○ in the presence of fluoride ion (5.5×10^{-5} M); △ difference in the intensity; $\lambda_{ex} = 400$ nm; $\lambda_{em} = 460$ nm.

Potential utility of the present system

Fluoride concentration dependency of the signal intensity was examined at pH 5 to elucidate the applicability of this system and the result is given in Fig. 4. It is of note that the profile of

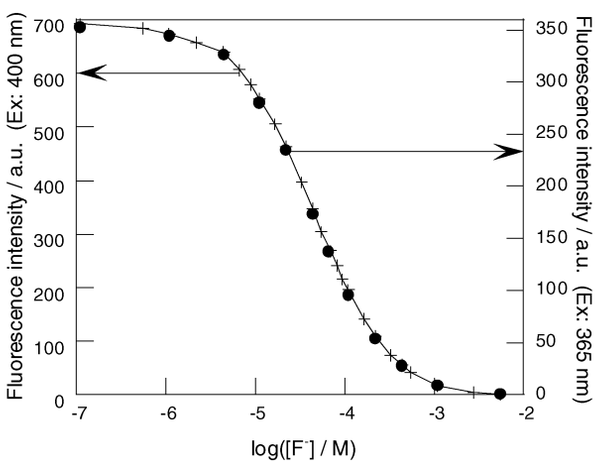

Fig. 4 Change in fluorescence signal intensity at 460 nm as a function of fluoride ion concentration: + excitation wavelength, 400 nm; ● excitation wavelength, 365 nm (wavelength at isosbestic point in the absorption spectra of Fig. 2(a). [$Zr(H_2O)_2$edta] = 1×10^{-5} M; [flavonol] = 1×10^{-5} M; pH 5 (acetate buffer).

the intensity change excited at 400 nm (absorption peak of the ternary complex) coincides with that excited at the isosbestic point (365 nm, see Fig. 2(a)); however the fluorescence intensity of the former is apparently much higher than that excited at 365 nm. This means that the observed fluorescence is mainly due to the contribution of the ternary complex and not of free flavonol. The detection range of fluoride ion is from 3×10^{-6} to 1×10^{-3} M; the lower limit of detection reaches 3×10^{-6} M (60 ppb). Five repeated analyses of the 0.2 ppm fluoride sample gave reproducible results with a variation coefficient of 0.6%. The fluorescence spectrum of each solution did not change for more than one week at room temperature. This can be attributed to the remarkable chemical stability of the Zr–EDTA complex[10] as well as the flavonol molecule.

One of the important characteristics of the signaling system is its selectivity in the presence of foreign ions since a practical sample can contain various competing ions. As shown in Table 1, the presence of common anions including Cl^-, SO_4^{2-}, NO_3^-, $H_2PO_4^-$ and acetate did not interfere significantly with the signal intensity up to 100 times that of the fluoride ion (0.2 ppm). While metal cations including Al(III), Fe(III), Cu(II) appreciably interfered due to the competing complexation of flavonol with these metal ions. However, addition of EDTA solution effectively masked these cations except for Al(III).[15] An improved tolerance for Al(III) was realized by the use of *N*,*N*,*N*′,*N*″,*N*″-diethylenetriaminepentaacetic acid (DTPA).

Table 1 Influence of foreign ions on the determination of F^- at 0.2 ppm (1.1×10^{-5} M)

Ions		Conc./M		Recovery[a] (%)
None				100.0
Cl^-		1×10^{-3}		103.9
SO_4^{2-}		1×10^{-3}		100.9
NO_3^-		1×10^{-3}		101.4
PO_4^{3-}		1×10^{-3}		102.2
Al(III)		1×10^{-5}		121.4
	+ EDTA		1×10^{-4}	108.9
	+ DTPA		1×10^{-4}	104.8
Fe(III)		1×10^{-5}		7.6
	+ EDTA		1×10^{-4}	100.6
Cu(II)		1×10^{-5}		98.3
	+ EDTA		1×10^{-4}	100.3

[a] Recovery denotes the percentage of fluorescence signal intensity before and after addition of foreign ions.

In conclusion, the ligand exchange reaction between fluoride ion and flavonol coordinated to Zr–EDTA leads to a rapid change in the fluorescence intensity, providing a simple and particularly selective detection system of fluoride ion in aqueous solutions.

Experimental

Reagents

A stock solution of fluoride ion was prepared by dissolving guaranteed reagent grade NaF into deionized water. [$Zr(H_2O)_2$edta]·$2H_2O$ was synthesized according to the reported procedure[16] and was dissolved in deionized water to give a 5×10^{-3} M stock solution. 3-Hydroxyflavone (flavonol) purchased from Tokyo Kasei Ltd. (Tokyo, Japan) was recrystallized three times from methanol and dissolved in ethanol to give a 5×10^{-5} M stock solution. Stock solutions of anions for the interference study were prepared by dissolving NaCl, Na_2SO_4, $NaNO_3$ and K_2HPO_4 in deionized water. All other reagents and solvents used were of guaranteed reagent grade.

Instruments

The fluorescence spectra were recorded on a Hitachi F-3000 fluorescence spectrophotometer at a band path of 3 nm for both excitation and emission. Absorption spectra were recorded on a Hitachi U-3310 spectrophotometer with 1 cm quartz cells.

Spectral measurements

Typically, 50 μl of 5×10^{-3} M [$Zr(H_2O)_2$edta]·$2H_2O$, 5 ml of 5×10^{-5} M flavonol solution and 250 μl of 1 M acetate buffer solution (pH 5) were added to solutions of various fluoride ion concentrations. The mixture was made up to 25 ml with deionized water and used for the absorption and fluorescence spectra.

Acknowledgements

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References

1 D. G. Gilles and R. C. Loher, *J. Environ. Eng.*, 1994, **120**, 72.
2 H. Miyaji and J. L. Sessler, *Angew. Chem., Int. Ed.*, 2001, **40**, 154; D. H. Lee, H. Y. Lee, K. H. Lee and J.-H. Hong, *Chem. Commun.*, 2001, 1188; S. Yamaguchi, S. Akiyama and K. Tamao, *J. Am. Chem. Soc.*, 2001, **123**, 11372.
3 D. F. Schriver, P. W. Atkins and C. H. Langford, *Inorganic Chemistry*, Oxford University Press, Oxford, 2nd edn., 1994, p. 44.
4 R. Belcher, M. A. Leonard and T. S. West, *J. Chem. Soc.*, 1959, 3577; S. S. Yamamura, M. A. Wade and J. H. Sikes, *Anal. Chem.*, 1962, **34**, 1308; T. Lay and T. S. West, *Anal. Chem.*, 1971, **43**, 136.
5 M. Shionoya, H. Furuta, V. Lynch, A. Harriman and J. L. Sessler, *J. Am. Chem. Soc.*, 1992, **114**, 5714; M. Tabata, K. Kaneko, Y. Murakami, Y. Hisada and H. Miura, *Microchem. J.*, 1994, **49**, 136; C. R. Cooper, N. Spencer and T. D. James, *Chem. Commun.*, 1998, 1365; H. Miyaji, P. Anzenbacher, Jr., J. L. Sessler, E. R. Bleasdale and P. A. Gale, *Chem. Commun.*, 1999, 1723; P. A. Gale, L. J. Twyman, C. I. Handlin and J. L. Sessler, *Chem. Commun.*, 1999, 1851; M. Nicolas, B. Fabre and J. Shimonet, *Chem. Commun.*, 1999, 1881; P. Anzenbacher, Jr., A. C. Try, H. Miyaji, K. Jursikova, V. M. Lynch, M. Marquez and J. L. Sessler, *J. Am. Chem. Soc.*, 2000, **122**, 10268.
6 H. E. Katz, *J. Am. Chem. Soc.*, 1986, **108**, 7640; K. Tamao, T. Hayashi and Y. Ito, *J. Am. Chem. Soc.*, 1990, **112**, 2424; M. Newcomb, J. H. Horner, M. T. Branda and P. J. Squattrito, *J. Am. Chem. Soc.*, 1989, **111**, 6294; F. P. Schmidychen and M. Berger, *Chem. Rev.*, 1997, **97**, 1609.
7 M. G. B. Drew, M. McCann and S. M. Nelson, *J. Chem. Soc., Chem. Commun.*, 1979, 481; R. J. Motekaitis and A. E. Martell, *Inorg. Chem.*, 1992, **31**, 5534; K. Konishi, K. Yahara, H. Toshishige, T. Aida and S. Inoue, *J. Am. Chem. Soc.*, 1994, **116**, 1337; G. De Santis, L. Fabbrizzi, M. Licchelli, A. Poggi and A. Taglietti, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 202; L. Fabbrizzi, G. Francese, M. Licchelli, A. Perotti and A. Taglietti, *Chem. Commun.*, 1997, 581.
8 L. Spaulding and H. G. Brittain, *Inorg. Chem.*, 1985, **24**, 3692; J. I. Bruce, R. S. Dickins, L. J. Govenlock, T. Gunnlaugsson, S. Lopinski, M. P. Lowe, D. Parker, R. D. Peacock, J. J. B. Perry, S. Aime and M. Botta, *J. Am. Chem. Soc.*, 2000, **122**, 9674.
9 A. Yuchi, T. Ban, H. Wada and G. Nakagawa, *Inorg. Chem.*, 1990, **29**, 136; T. M. Suzuki, D. A. P. Tanaka, M. L. Tanco, M. Kanesato and T. Yokoyama, *J. Environ. Monit.*, 2000, **2**, 550.
10 A. E. Martell and R. M. Smith, *Critical Stability Constants*, Plenum Press, New York and London, 1974, vol. 1, p. 207.
11 I. Pozhidaev, M. A. Porai-Koshits and T. N. Polynova, *Zh. Strukt. Khim.*, 1974, **15**, 644.
12 B. J. Intorre and A. E. Martell, *J. Am. Chem. Soc.*, 1964, **83**, 3618.
13 W. C. Alford, L. Shapiro and C. E. White, *Anal. Chem.*, 1951, **23**, 1149.
14 D. P. A. Tanaka, S. Kerketta, M. L. Tanco, T. Yokoyama and T. M. Suzuki, *Sep. Sci. Technol.*, in press.
15 A. Yuchi, N. Hokari, H. Terao and H. Wada, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 3173.
16 H. G. Langer, *J. Inorg. Nucl. Chem.*, 1964, **36**, 59.