Anion Sensing with Luminescent Tris(β-diketonato)europium(III) Complexes and Naked-Eye Detection of Fluoride Anion

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Four kinds of tris(β-diketonato)europium(III) complexes were demonstrated to form highly coordinated complexes with inorganic anions and to exhibit anion-dependent luminescence. Their luminescence profiles were significantly dependent on the natures of β-diketonato ligands and external coordinative anions: Tris[3-(heptafluorobutyryl)-2-bornanonato]europium(III) complex gave F^- anion-enhanced luminescence, and tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octadionato)europium(III) complex responded to HSO_4^- and $CH_3CO_2^-$ anions. Although the employed europium complexes included similar β-diketonato ligands, UV and IR characterizations and luminescence lifetime measurements revealed that the structure of the β-diketonato ligand had significant influences on anion coordination and sensing behaviors of the europium complex. Since the observed anion-enhanced luminescence was high enough to be detected by the naked eye, visual detection of the F^- anion in an aqueous sample was realized with the tris[3-(heptafluorobutyryl)-2-bornanonato]europium(III) complex.

Tris(β-diketonato)lanthanide complexes are one representative of lanthanide complexes and are widely employed as functionalized materials.[1] Although they are electrically neutralized by three β-diketonato ligands, one or more solvent molecules are usually bound to the lanthanide centers. Since some external guests similarly form the highly coordinated complexes,[2] tris(β-diketonato)lanthanide complexes work well as shift reagents in NMR spectroscopy, catalysts in organic synthesis, and luminescence devices.[3] They are further used in luminescence labeling of biopolymers[4] and CD chirality sensing of biomolecules.[5] Typically, some tris(β-diketonato)europium(III) complexes were attached to the proteins, while the related tris(β-diketonato)praseodymium(III) complexes responded to the chirality of naturally occurring 1,2-diol substrates. We previously demonstrated that lanthanide complexes containing fluorinated β-diketonato ligands extracted zwitterionic amino acids from neutral aqueous solutions into organic solutions.[6] More recently, tris(β-diketonato)europium(III) complexes were successfully applied as Cl^- anion-selective electrode devices.[7] Since such lanthanide complexes have variable and versatile coordination modes as well as intense luminescence, a specific anion sensing system can be constructed via lanthanide coordination chemistry.

We report the anion sensing properties of luminescent tris(β-diketonato)europium(III) complexes **1a**, **1b**, **2a**, and **2b** (Fig. 1). Among a variety of biologically important anions, the F^- anion is of particular interest owing to its established roles in preventing dental carriers.[8] Although several fluorescent organic receptors have been developed for this purpose,[9] most of them have had severe limitations for use in aqueous media. The employed tris(β-diketonato)europium(III) complexes have several important features as luminescent anion sensory materials effective for aqueous samples: (1) intense and steady luminescence with long lifetimes; (2) highly coordinated complexation with particular anions; (3) chemical stability toward hydrolysis and ligand exchange; and (4) wide structural variations of β-diketonato ligands. Several types of lanthanide complexes have already been characterized as effective receptors and luminescence materials,[10] and some of them worked as anion sensing devices.[11,12] For example, armed cyclen (cyclen = 1,4,7,10-tetraazacyclododecane) complexes offered selective detection of the hydrogencarbonate anion, and cationic complexes with neutral oligopyridine ligands exhibited characteristic anion-response behaviors. We compare here the highly coordinated complexation behaviors and anion-dependent luminescence properties of four europium complexes, **1a**, **1b**, **2a**, and **2b**. Although all of them include β-diketonato ligands, their luminescence sensing profiles were significantly dependent on the ligand characteristics. The europium complexes **2a** and **2b** exhibited high selectivity for the F^- anion, though the europium complexes **1a** and **1b** responded to both HSO_4^- and $CH_3CO_2^-$ anions. Since the present type of tris(β-diketonato)lanthanide complexes acted as effective receptors in aqueous CH_3CN solutions, they have wide

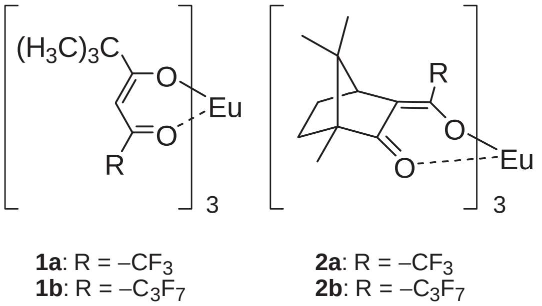

Fig. 1. Tris(β-diketonato)europium(III) complexes as anion receptors.

Published on the web May 12, 2006; DOI: 10.1246/bcsj.79.725

applications in practical sensing and determination of specific anions.

Results and Discussion

Characterization of Tris(β-diketonato)europium(III) Complexes. Four tris(β-diketonato)europium(III) complexes were characterized by several spectroscopic methods (Table 1) that have chromophoric β-diketonato ligands in acyclic and bicyclic frameworks. In IR spectra (KBr disc), the europium complexes **1a** and **1b** with acyclic β-diketonato ligands exhibited C=O characteristic bands at smaller wavenumbers than those with bicyclic ones, **2a** and **2b**. UV characterizations also revealed significant differences between the two ligand groups (**1a** and **1b** vs **2a** and **2b**). When complexes **1a** and **2a** were compared, their absorption band maxima were observed at 291 and 311 nm in CH_3CN solutions. Since complex **1b** also exhibited a UV signal at a smaller wavelength than complex **2b**, bicyclic β-diketonato ligands provided different coordination circumstances from acyclic ones.

Table 1. Spectroscopic Characteristics of Tris(β-diketonato)europium(III) Complexes

	IR (KBr) $\nu_{C=O}/cm^{-1}$	UV (CH_3CN) λ_{max}/nm	Luminescence Lifetime τ/ms
1a	1639	291	0.68
1b	1631	293	0.62
2a	1661	311	0.14
2b	1656	313	0.29

The employed four europium complexes exhibited intense luminescence signals at 595, 613, 651, and 699 nm upon excitation of β-diketonato chromophores (ca. 290 nm for **1a** and **1b**; and ca. 310 nm for **2a** and **2b**). Their luminescence lifetime values were determined in CH_3CN solutions. The europium complexes **2a** and **2b** with bicyclic β-diketonato ligands had smaller lifetime values than complexes **1a** and **1b** with acyclic β-diketonato ligands: 0.68 msec for **1a**; 0.62 msec for **1b**; 0.14 msec for **2a**; and 0.29 msec for **2b**. Furthermore, the europium complexes **2a** and **2b** have chiral β-diketonato ligands, but showed only weak circular dichroism (CD) signals at their absorption regions. These spectral observations suggest that the bulky bicyclic β-diketonato ligands form more variable and versatile coordination complexes than acyclic ones.

Anion-Dependent Luminescence with Tris(β-diketonato)europium(III) Complexes. Previous NMR titration and ESI-MS experiments demonstrated that tris(β-diketonato)lanthanide complexes formed highly coordinated 1:1 complexes

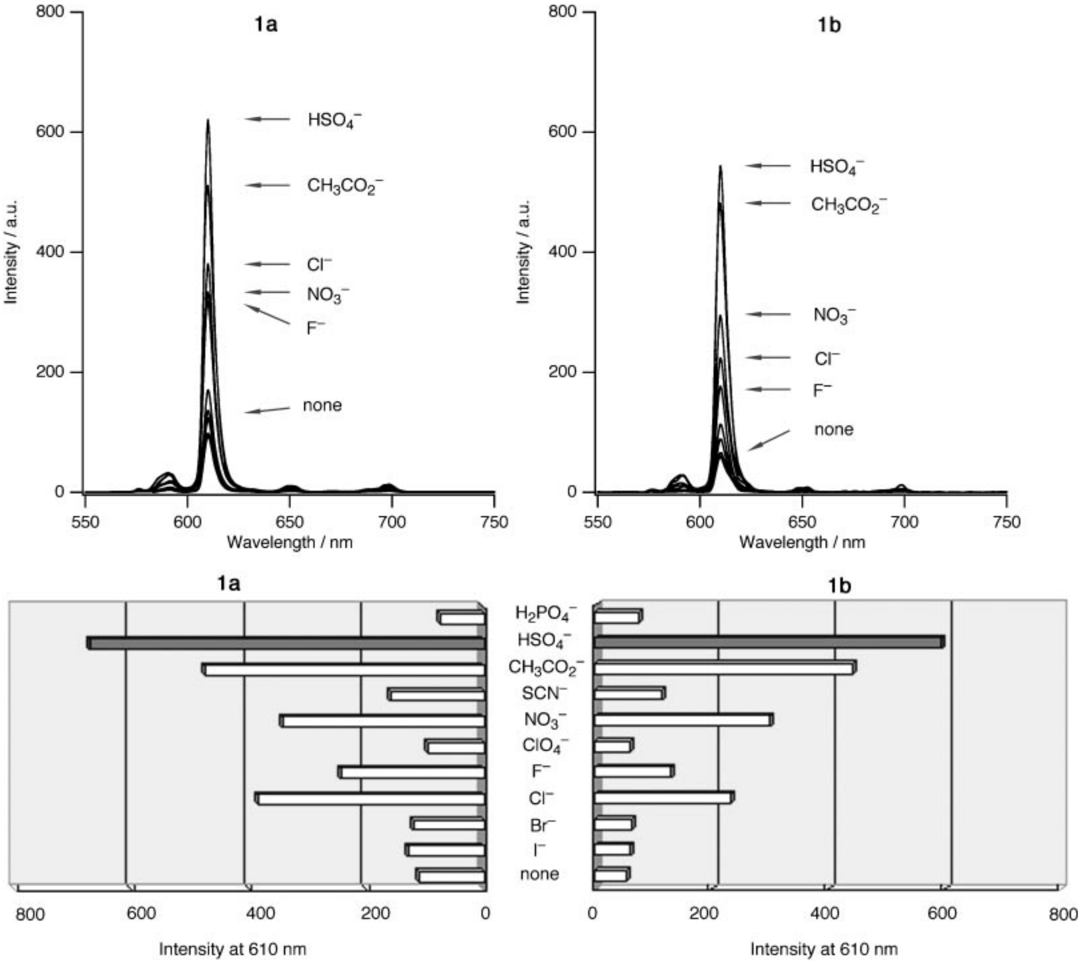

Fig. 2. Effects of external anions on luminescence properties of europium complexes **1a** and **1b**. $\lambda_{ex} = 291$ nm (**1a**) or 293 nm (**1b**). Complex, 3.5×10^{-5} mol L^{-1}; $n\mathrm{Bu_4N^+(Anion)^-}$, 1.0×10^{-4} mol L^{-1} in CH_3CN.

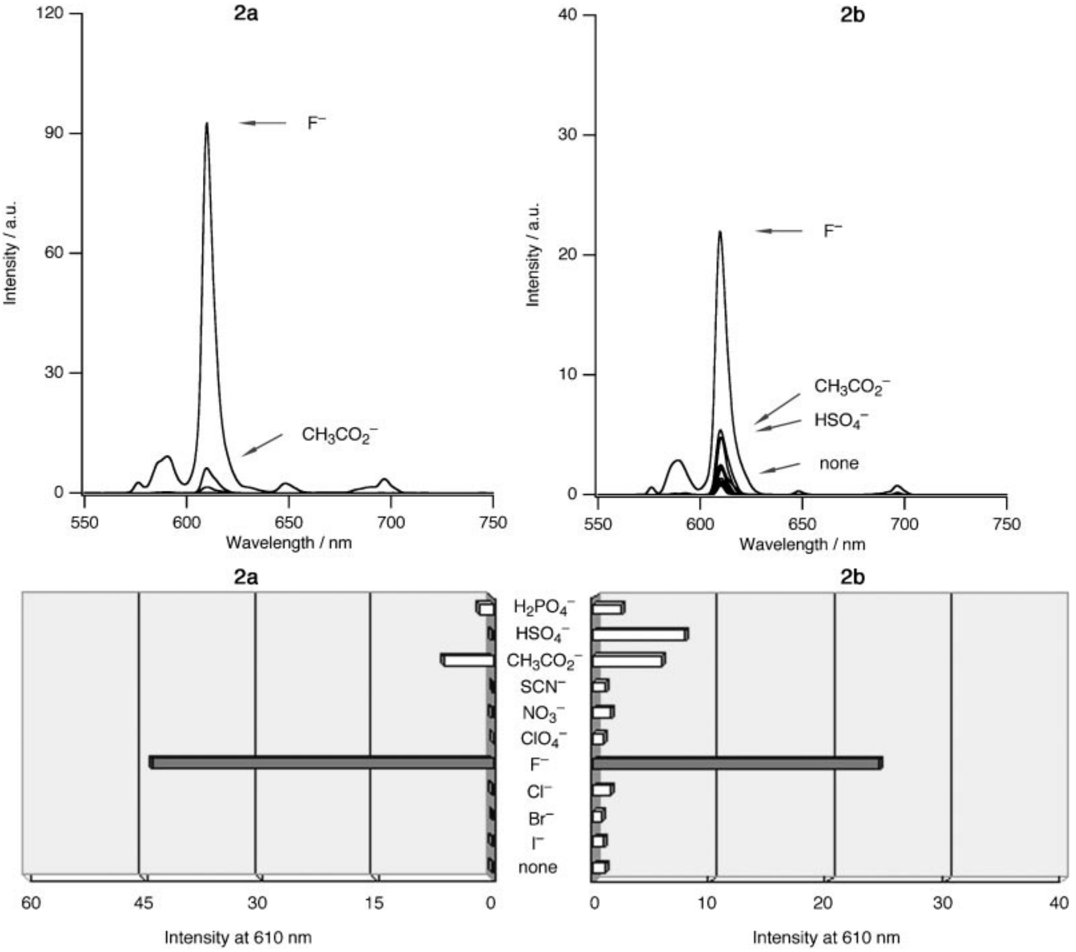

Fig. 3. Effects of external anions on luminescence properties of europium complexes **2a** and **2b**. $\lambda_{\mathrm{ex}} = 311$ nm (**2a**) and 313 nm (**2b**). Complex, 3.5×10^{-5} mol L^{-1}; $n\mathrm{Bu_4N^+(Anion)^-}$, 1.0×10^{-4} mol L^{-1} in CH_3CN.

with several inorganic anions in $CDCl_3$.[7a] Their stability constants largely depended on the natures of the guest anions, and the smaller Cl^- anion formed more stable complexes than larger Br^-, I^-, and ClO_4^- anions.[7] Such anion coordination properties of the tris(β-diketonato)lanthanide complexes were further applicable in the development of anion-selective electrodes. The europium complex **1b** typically exhibited high Cl^- anion selectivity in the electrochemical analysis of the aqueous samples.[7b]

The europium complexes **1a**, **1b**, **2a**, and **2b** exhibited characteristic luminescence phenomena, based on highly coordinated complexation with external anions. When 3 equivalents of the HSO_4^- anion were typically added to a CH_3CN solution of complex **1b**, its europium luminescence observed at 610 nm was enhanced 10-fold (Fig. 2). The addition of $CH_3CO_2^-$, NO_3^-, F^-, and Cl^- anions also increased the luminescence intensity, but $H_2PO_4^-$, SCN^-, ClO_4^-, Br^-, and I^- anions caused only slight changes. The europium complex **1a** exhibited similar anion-responsive luminescence, but gave modest anion-selective enhancements. Competitive luminescence experiments were carried out, in which 3 equivalents of a second guest anion were further added to the mixture of complex **1b** and 3 equivalents of the HSO_4^- anion. F^- and $H_2PO_4^-$ anions decreased the luminescence intensity, while $CH_3CO_2^-$ and NO_3^- anions gave small changes. Relative luminescence of intensity, $I_{\mathrm{HSO_4^-+second\ anion}}/I_{\mathrm{HSO_4^-\ alone}}$, was recorded as 0.22 for $H_2PO_4^-$, 0.23 for F^- anion, 0.64 for $CH_3CO_2^-$, and 0.95 for NO_3^- anions. Since this trend was different from that of luminescence enhancements, the anion-responsive luminescence behaviors of complex **1b** corresponded with both the stability and luminescence ability of the highly coordinated complex with the guest anion. Figure 3 also illustrates the anion-enhanced luminescence signals of the europium complexes **2a** and **2b** upon addition of 3 equivalents of guest anions. These complexes gave more selective anion-response luminescence behaviors than complexes **1a** and **1b**. Competitive luminescence experiments with complex **2b** revealed that its anion-responsive luminescence behaviors were controlled by selective ternary complexation. When 3 equivalents of a second guest anion were added, the relative luminescence intensity, $I_{\mathrm{F^-+second\ anion}}/I_{\mathrm{F^-\ alone}}$, was recorded as 0.64 for $CH_3CO_2^-$, 0.76 for HSO_4^-, 0.91 for NO_3^-, and 0.93 for Cl^- anions. Complexes **2a** and **2b** were confirmed to bind the F^- anion strongly and exhibit highly luminescent signals, suggesting that the bulky β-diketonato ligands enhanced anion selectivity in the ternary complexation process. As indicated in Table 1, these complexes, **2a** and **2b**, gave weak luminescence, but steady luminescence signals were observed in the presence of 3 equivalents of the F^- anion. The lanthanide luminescence efficiency is generally governed by ligand nature, complex

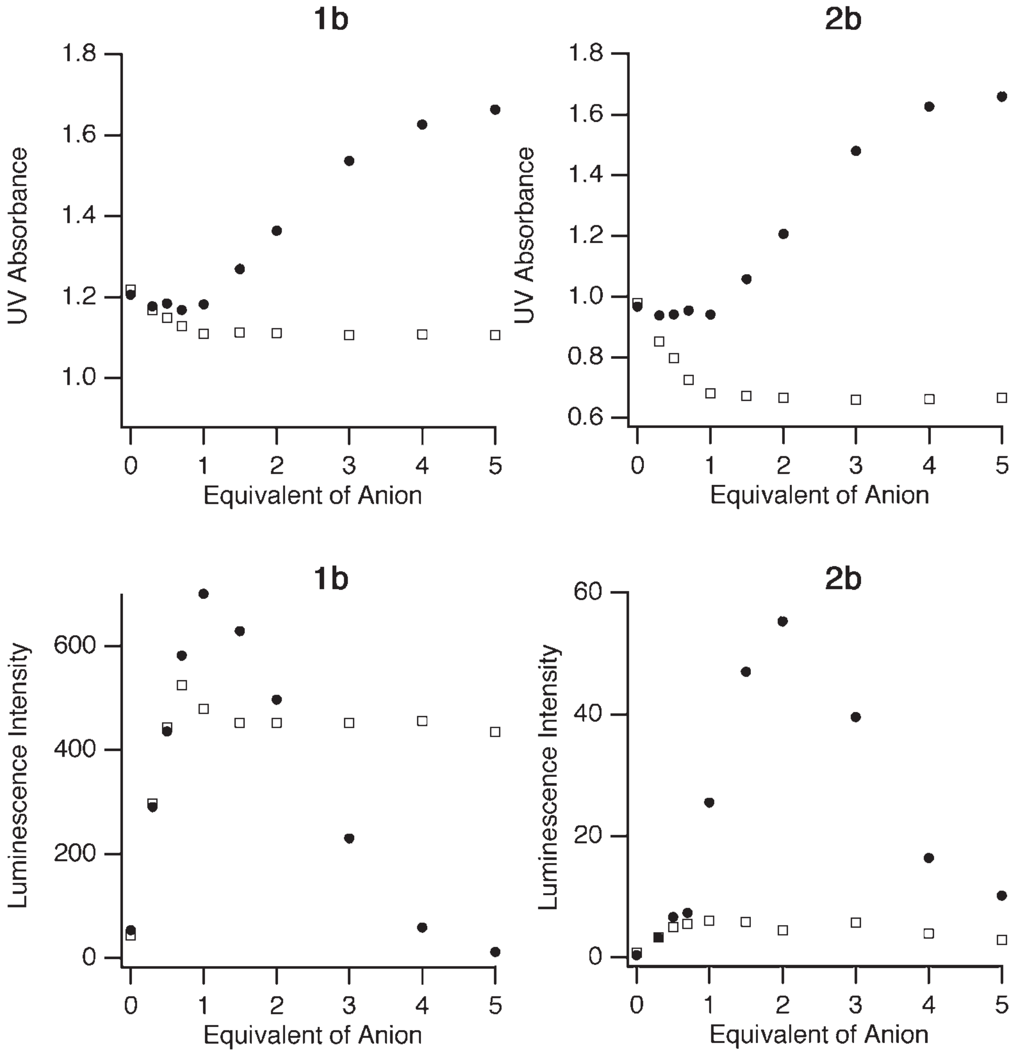

Fig. 4. Effects of HSO_4^- and F^- anions on UV and luminescence properties of europium complexes **1b** and **2b**. Solid circle: F^-, square: HSO_4^-. Absorbances at λ_{max} of **1b** (293 nm) and **2b** (313 nm) were plotted. $\lambda_{ex} = 330$ nm (for **1b**) and 313 nm (for **2b**). Complex, 3.5×10^{-5} mol L^{-1}; nBu$_4$NHSO$_4$ or nBu$_4$NF, 0–1.75×10^{-4} mol L^{-1} in CH_3CN.

geometry, and other coordination circumstances around the lanthanide center.[10,13] We found that substitution of the β-diketonato ligand largely modified the luminescence profile of the europium complex. In particular, the europium complexes **2a** and **2b** with bicyclic skeletons exhibited the F^- anion-enhanced luminescence.

Figure 4 compares the effects of HSO_4^- and F^- anions on UV absorption and the luminescence spectra of complexes **1b** and **2b**, though complex concentration, delay time, and other luminescence experimental conditions gave large influences on luminescence spectral details (see Experimental Section). When the HSO_4^- anion was gradually added to complex **1b**, the observed UV and luminescence signals had constant intensity at $[HSO_4^-]/[\mathbf{1b}] > 1$, suggesting that 1:2 and 1:1 complexes (HSO_4^-:**1b**) formed and they were stable in the presence of excess HSO_4^- anions. The F^- anion induced remarkably different spectral changes. Since both UV absorbance and luminescence intensity of complex **1b** changed greatly at $[F^-]/[\mathbf{1b}] > 1$, addition of excess F^- anions was thought to destroy the highly coordinated complexes. The largest luminescence enhancement for the $CH_3CO_2^-$ anion was recorded at [guest anion]/$[\mathbf{1b}] = 0.5$–1.0, while addition of the NO_3^- anion gradually increased the luminescence intensity at [guest anion]/$[\mathbf{1b}] \leq 3.0$. Complex **2b** also exhibited significant spectral changes upon addition of HSO_4^- and F^- anions. The intense luminescence signals were observed at $[F^-]/[\mathbf{2b}] = 1$–3, while the UV signal due to the free β-diketonato chromophore appeared in the presence of excess of F^- anions. Since the F^- anion gave larger luminescence enhancement than the HSO_4^- anion, the europium complex **2b** can offer selective detection of the F^- anion. The luminescence lifetime values of the europium complexes were measured in the presence of 1 equivalent of F^- and HSO_4^- anions, which showed comparable trends to those of luminescence intensities: 0.14 msec (no additive), 0.15 msec (+HSO_4^- anion), and 0.44 msec (+F^- anion) for **2a**; 0.29 msec (no additive), 0.36 msec (+HSO_4^- anion), and 0.41 msec (+F^- anion) for **2b**. The negative ESI-MS experiments were done with CH_3CN solutions containing tris(β-diketonato)europium(III) complexes and 3 equivalent of guest anions. Several peak signals supporting 1:1 complexation with F^- and HSO_4^- anions were detected with those assigned to [Eu(β-diketonato)$_4$]$^-$: $[\mathbf{1a} + \mathrm{F}]^- =$

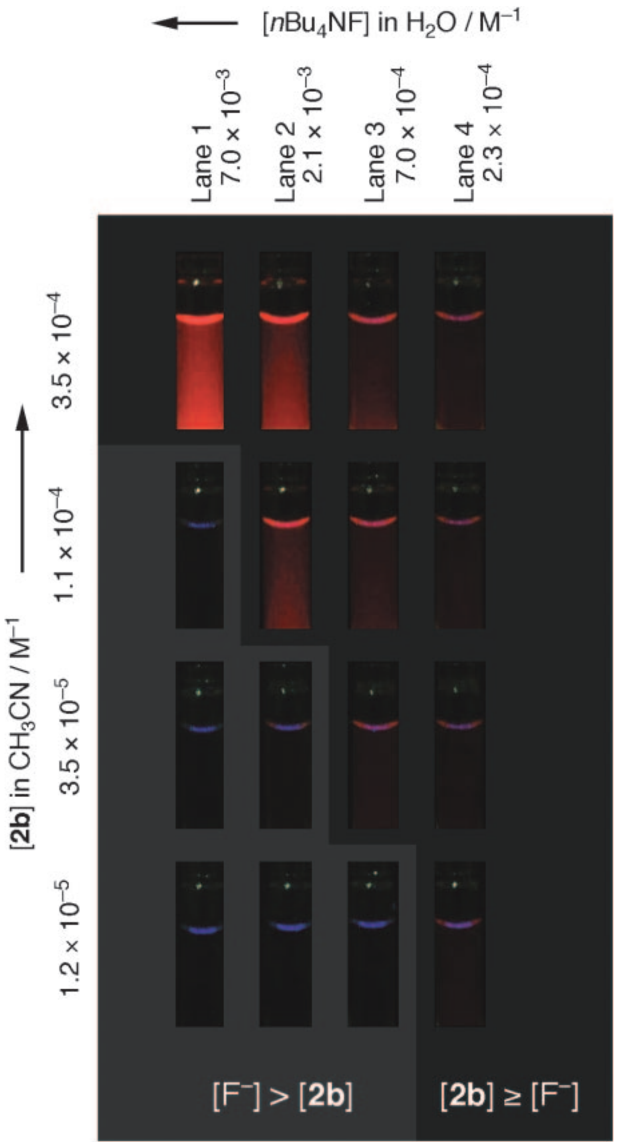

Fig. 5. Visual sensing of F$^-$ anion concentration with Europium complex **2b**: pictures of europium luminescence upon irradiation of TLC detection lamp (4 W). Conditions: see Experimental Section.

755; [**1b** + F]$^-$ = 1055; [**2a** + F]$^-$ = 911; [**2b** + F]$^-$ = 1211; [**1a** + HSO$_4$]$^-$ = 833; [**1b** + HSO$_4$]$^-$ = 1133; [**2a** + HSO$_4$]$^-$ = 989; and [**2b** + HSO$_4$]$^-$ = 1289 (See Supporting Information).

Naked-Eye Detection of Fluoride Anion with Europium Complex 2b. Figure 5 lists pictures of mixtures of the F$^-$ anion in H$_2$O samples and the europium complex **2b** in CH$_3$CN solutions. When an aqueous sample solution of the F$^-$ anion (7.0 × 10^{-4} mol L^{-1}, 0.5 mL) was typically added to a series of CH$_3$CN solutions containing complex **2b** (9.5 mL) (see Lane 3 in Fig. 5), intense luminescence was observed at [**2b**]/[F$^-$] $\geq$ 1. An excess of F$^-$ anions did not give intense luminescence at the same concentration of complex **2b** (see Lane 2 in Fig. 5). Since the use of complex **2b** allowed F$^-$ anion detection in the aqueous sample at ca. 4 ppm (2.3 × 10^{-4} mol L^{-1}), the naked-eye observations realized an approximate estimate of the F$^-$ anion concentrations in the aqueous sample. Such europium luminescence is often depressed in aqueous media, but the present type of tris(β-diketonato)europium(III) complexes are still active in 5% H$_2$O-containing CH$_3$CN solutions. The luminescence lifetime value of complex **2b** was measured in 5% H$_2$O- or D$_2$O-containing CH$_3$CN solution. When we added 1 equivalent of the F$^-$ anion, the same lifetime value of 0.21 msec was recorded in both solvent systems. Thus, no water molecule coordinated the luminescent europium center, and the highly coordinated complexation with the F$^-$ anion occurred even in the employed media. Although a hand-held UV lamp at weak power (4 W) was used here from a practical point of view, the use of luminescent lanthanide complexes provided an effective basis for in situ determination of a biologically important anion.

We demonstrated above that tris(β-diketonato)europium(III) complexes worked as anion-specific luminescent receptors upon the highly coordinated complexation with particular guest anions. They exhibited anion-responsive luminescence properties and were applicable in the naked-eye determination of the F$^-$ anion. Several organic receptors have been developed for F$^-$ anion sensing,[9] but visual sensing with the europium complex can have practical applications. Since several europium complexes are used to label biomolecules in the areas of clinical chemistry and molecular biology, a further combination of the luminescent lanthanide center and the designed ligand can offer new sensory systems effective for biologically interesting guests.

Experimental

General. Luminescence spectra were obtained on a Perkin-Elmer LS-50B equipped with a Hamamatsu R-928 photomultiplier, and IR spectra were recorded with a Perkin-Elmer Spectrum One FT-IR spectrometer. CD spectra were measured with a JASCO J-820, and ESI-MS data were collected with a JEOL JMS-700T.

Materials. The tris(β-diketonato)europium(III) complexes illustrated in Fig. 1 were obtained from Dojindo Laboratories (**1a**, **1b**, and **2a**) and Sigma-Aldrich, Japan (**2b**). These were used without further purification. The employed tetrabutylammonium salts were received from Sigma-Aldrich, Japan (CH$_3$CO$_2$$^-$, H$_2PO_4$$^-$, NO$_3$$^-$, HSO$_4$$^-$, I$^-$, and Br$^-$), Nacalai Tesque Inc. (ClO$_4$$^-$), Merck Ltd. Japan (F$^-$), Fluka Inc. (Cl$^-$), and Tokyo Chemical Ind. Co. (SCN$^-$). They were used after drying in vacuo, except for ClO$_4$$^-$ salt. CH$_3$CN was a special grade solvent of Nacalai Tesque Inc. and used as received.

Luminescence and UV Experiments. The luminescence experiments were mostly carried out in CH$_3$CN using the excitation of ligand chromophore. For all luminescence experiments, europium emission was collected for 3 ms after a 1 ms delay time after pulsed excitation by xenon lamp. The concentrations of the tris(β-diketonato)lanthanide complexes and external guests are shown in each figure. Because the anion complexation offered UV spectral changes, the ligand-excitation luminescence spectra were recorded with the complex solutions at constant concentration. The relative luminescence intensities summarized as the bar graphs in Figs. 2 and 3 were calculated after corrections of absorbance changes at the excitation wavelengths (293 or 313 nm). This gave only semi-quantitative corrections in the F$^-$ anion-complexation processes, because dissociation of the acetylacetonato ligands was observed in the presence of 3 equivalents of the F$^-$ anion. Furthermore, the collection times in the luminescence measurements apparently influenced the anion-response selectivity, suggesting that 1:2 complex and related species exhibiting different luminescence lifetime values existed. Independent 2–4 measurements were done for each anion system and the obtained values were averaged. We employed relatively high concentration conditions to observe steady luminescence signals with the europium complexes **2a** and **2b**. This caused too much high absorbance of the β-diketonato chromophore to characterize the europium luminescence profiles quantitatively in the presence of excess F^- anions.

The naked-eye detection experiments were carried out by mixing aqueous solutions of the F^- anion with CH_3CN solutions of complex **2b**. The pictures in Fig. 5 were taken under the following final concentration conditions: $[n\mathrm{Bu_4NF}] = 1.17 \times 10^{-5}$–$3.50 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$; $[\mathbf{2b}] = 1.17 \times 10^{-5}$–$3.50 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ in CH_3CN/H_2O (95/5, v/v). The excitation was done using a hand-held UV lamp for TLC detection (4 W).

The luminescence lifetime values (τ) were the averaged values of at least 3 separate measurements, each of which was made by monitoring the emission intensity at 613 nm after 20 different delay times spanning a range of at least two lifetime values. The decay curves were fitted by an equation of the form $I(t) = I(0)\exp(-t/\tau)$ using a curve-fitting program. A high correlation coefficient was observed in each case.

The authors are grateful to Professor Rakesh Kumar Mahajan of Guru Nanak Dev University, India, and Professor Hiroyuki Miyake of Osaka City University for their valuable comments. This work was supported by a Grant-in-Aid for Priority Research (No. 16080217) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information

Mass spectra (ESI, negative) of europium complexes **1a**, **1b**, **2a**, and **2b** in the presence of 3 equivalents of the F^- and HSO_4^- anions. This material is available free of charge on the web at: http://www.csj.jp/journals/bcsj/.

References

1 a) H. C. Aspinall, *Chem. Rev.* **2002**, *102*, 1807. b) K. Binnemans, C. Gorller-Walrand, *Chem. Rev.* **2002**, *102*, 2303. c) J. Kido, Y. Okamoto, *Chem. Rev.* **2002**, *102*, 2357. d) H. Tsukube, S. Shinoda, *Chem. Rev.* **2002**, *102*, 2389.

2 Several kinds of highly coordinated complexes with tris(β-diketonato)lanthanide complexes were isolated and their crystal structures were determined: a) I. Baxter, S. R. Drake, M. B. Hursthouse, K. M. A. Malik, J. McAleese, D. J. Otway, J. C. Plakatouras, *Inorg. Chem.* **1995**, *34*, 1384. b) H. J. Batista, A. V. M. de Andrade, R. L. Longo, A. M. Simas, G. F. de Sa, N. K. Ito, L. C. Thompson, *Inorg. Chem.* **1998**, *37*, 3542.

3 S. Shinoda, H. Miyake, H. Tsukube, in *Handbook on the Physics and Chemistry of Rare Earths*, ed. by K. A. Gschneidner, Jr., J.-C. G. Bünzli, V. K. Pecharsky, Elsevier B. V., Amsterdam, **2005**, Vol. 35, Chap. 226, pp. 273–335.

4 a) G. E. Buono-Core, H. Li, *Coord. Chem. Rev.* **1990**, *99*, 55. b) M. H. V. Werts, M. A. Duin, J. W. Hofstraat, J. W. Verhoeven, *Chem. Commun.* **1999**, 799. c) M. Taki, H. Murakami, M. Sisido, *Chem. Commun.* **2000**, 1199. d) J. Yuan, G. Wang, K. Majima, K. Matsumoto, *Anal. Chem.* **2001**, *73*, 1869.

5 a) K. Nakanishi, J. Dillon, *J. Am. Chem. Soc.* **1971**, *93*, 4058. b) C. Lyons, D. R. Taylor, *J. Chem. Soc., Chem. Commun.* **1976**, 647. c) H. Tsukube, M. Hosokubo, M. Wada, S. Shinoda, H. Tamiaki, *Inorg. Chem.* **2001**, *40*, 740. d) H. Tsukube, M. Wada, S. Shinoda, H. Tamiaki, *Chem. Commun.* **1999**, 1007.

6 H. Tsukube, S. Shinoda, J. Uenishi, T. Kanatani, H. Itoh, M. Shiode, T. Iwachido, O. Yonemitsu, *Inorg. Chem.* **1998**, *37*, 1585.

7 Stability constant, *K*, for complex **1b** (M^{-1}, in $CDCl_3$): 600 for Cl^- anion, 89 for Br^- anion. a) R. K. Mahajan, I. Kaur, R. Kaur, Y. Uchida, A. Onimaru, S. Shinoda, H. Tsukube, *Chem. Commun.* **2003**, 2238. b) R. K. Mahajan, I. Kaur, R. Kaur, A. Onimaru, S. Shinoda, H. Tsukube, *Anal. Chem.* **2004**, *76*, 7354.

8 a) R. Martinez-Manez, F. Sancenon, *Chem. Rev.* **2003**, *103*, 4419. b) P. D. Beer, P. Gale, *Angew. Chem., Int. Ed.* **2001**, *40*, 486.

9 a) Y. Kubo, M. Yamamoto, M. Ikeda, M. Takeuchi, S. Shinkai, S. Yamaguchi, K. Tamao, *Angew. Chem., Int. Ed.* **2003**, *42*, 2036. b) S. Kondo, M. Nagamine, Y. Yano, *Tetrahedron Lett.* **2003**, *44*, 8801. c) M. Boiocchi, L. D. Boca, D. E. Gomez, L. Fabrizzi, M. Licchelli, E. Monzani, *J. Am. Chem. Soc.* **2004**, *126*, 16507. d) D. A. Jose, D. K. Kumar, B. Ganguly, A. Das, *Org. Lett.* **2004**, *6*, 3445. e) M. Melaime, F. P. Gabbai, *J. Am. Chem. Soc.* **2005**, *127*, 4680. f) E. J. Cho, B. J. Ryu, Y. J. Lee, K. C. Nam, *Org. Lett.* **2005**, *7*, 2607.

10 a) A. Inamoto, K. Ogasawara, K. Omata, K. Kabuto, Y. Sasaki, *Org. Lett.* **2000**, *2*, 3543. b) Y. Hasagewa, T. Ohkubo, K. Sogabe, Y. Kawamura, Y. Wada, N. Nakashima, S. Yanagida, *Angew. Chem., Int. Ed.* **2000**, *39*, 357. c) Y. Suzuki, D. A. P. Tanaka, H. Matsunaga, T. M. Suzuki, *Chem. Lett.* **2002**, 722. d) M. Watanabe, T. Nankawa, T. Yamada, T. Kimura, K. Namiki, M. Murata, H. Nishihara, S. Tachimori, *Inorg. Chem.* **2003**, *42*, 6977. e) M. A. Subham, T. Suzuki, A. Fuyuhiro, S. Kaizaki, *Dalton Trans.* **2003**, 3785.

11 a) Review: T. Gunnlaugsson, J. P. Leonard, *Chem. Commun.* **2005**, 3114. b) Y. Bretonniere, M. J. Cann, D. Parker, R. Slater, *Org. Biomol. Chem.* **2004**, *2*, 1624.

12 a) Review: H. Tsukube, T. Yamada, S. Shinoda, *J. Alloys Compd.* **2004**, *374*, 40. b) S. Mameri, L. T. Charbonniere, R. F. Ziessel, *Inorg. Chem.* **2004**, *43*, 1819. c) T. Yamada, S. Shinoda, H. Tsukube, *Chem. Commun.* **2002**, 1218.

13 T. Yamada, S. Shinoda, H. Sugimoto, J. Uenishi, H. Tsukube, *Inorg. Chem.* **2003**, *42*, 7932.