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Excellent mercury(II) ion selective fluoroionophore based on a 3,6,12,15-tetrathia-9-azaheptadecane derivative bearing a nitrobenzoxadiazolyl moiety

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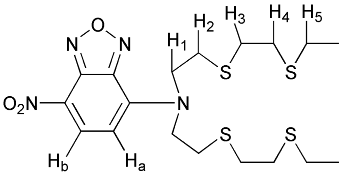
Selective and drastic fluorescence enhancement for mercury ion was observed in 1,4-dioxane–water (60/40) using a fluoroionophore bearing a nitrobenzoxadiazolyl group linked to a 3,6,12,15-tetrathia-9-azaheptadecane moiety.

It is very important to develop a easy mercury determination system for monitoring its concentration in polluted areas. Chromo- and/or fluoro-ionophores are very effective for determination for metal ion concentration in terms of handling and equipment. Although several analytical reagents have been made for the determination of Hg^{2+}, most lack selectivity and sensitivity.[1,2] It is well known that Hg^{2+} might quench the fluorescence of fluorescent reagents because of its open-shell, paramagnetic properties.[3,4] A fluoroinophore, constitituted of a thiaaza crown unit and a boron dipyrromethene dye moiety, for Hg^{2+} was reported recently.[5] The emission spectra of the fluoroinophore, however, changed with polarity of the solvent, and so the complexation experiments were mainly carried out in acetonitrile. To the best of our knowledge, we now report the first fluoroionophore which increases the fluorescence intensity according to the concentration of Hg^{2+} selectively in a polar solution containing water.

The novel fluoroionophores **1** and **2**,† prepared by the reaction of 4-chloro-7-nitrobenzoxadiazole with 3,6,12,15-tetrathia-9-azaheptadecane and 3,9-dithia-6-azaundecane, respectively, are constructed of ionophore and fluorophore moieties. The ionophore moiety contains sulfur atoms which have an affinity for soft metal ions such as Ag^+, Tl^+ and Hg^{2+}, because of its soft donor properties.[6,7] A nitrobenzoxadiazolyl moiety might function both as a fluorophore and as a chromophore.[8] It is expected that the electron density of the fluorophore moiety is reduced by the electron-withdrawing effect of coordinated metal ions and that remarkable changes in the fluorescence intensity and the absorption spectra should be caused when the ionophore moiety is complexed to a metal ion.[9]



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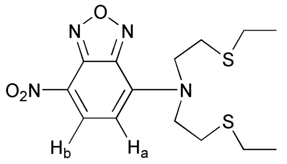

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On addition of various metal ions, changes in spectral properties of fluoroionophores **1** and **2** were measured by spectrophotometry and spectrofluorometry. 1,4-Dioxane–water (60/40 v/v) solution was used as solvent since the fluoroionophores are insoluble in pure water. The maximum wavelength of absorption (λ_{max}) for **1** is 492 nm, and that (λ_{em}) of the emission spectrum at an excitation wavelength of 492 nm is 536 nm. The spectral properties for **1** are independent of pH between pH 1 (0.1 mol dm^{-3} HNO_3) and neutrality. Fig. 1 shows the absorption and the emission spectra of 1,4-dioxane–water (40/60 v/v) solutions containing 1 × 10^{-5} mol dm^{-3} **1**, an equimolar quantity of a metal ion, *i.e.*, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Tl^+, Ag^+ or Hg^{2+}, and 0.1 mol dm^{-3} HNO_3. On addition of Hg^{2+} and Ag^+ to a solution of **1**, blue shifts were observed for the absorption spectra and the absorbances were decreased similarly. On the other hand, the emission spectrum of **1** in the presence of Hg^{2+} ion was enhanced much more than that for Ag^+ ion, while the fluorescence intensity of **1** for Ag^+ was slightly higher than that for free **1**. A hypsochromic shift of *ca.* 18 nm of λ_{max} was observed on addition of Hg^{2+} ion, caused by the interaction between the metal ion and the nitrogen atom, associated with the chromophore moiety on the ionophore unit. Similar hypsochromic shifts have been reported for donor–acceptor type chromoionophores.[10,11] In the presence of other metal ions, *i.e.*, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} or Tl^+, no spectral change for **1** was observed. Compound **2** exhibited no spectral change even in the presence of Hg^{2+} and Ag^+ ions under the same conditions as **1**. Such a difference in the spectral changes between **1** and **2** for Hg^{2+} and Ag^+ ions is attributable to a difference of stabilities of their complexes.[12,13]

Fig. 2 shows fluorescence intensity changes for **1** as a function of the concentration of the added metal ions. It is obvious that the fluorescence intensity increases with the concentration of Hg^{2+} and Ag^+. Compound **1** forms a 1:1 complex with Ag^+ quantitatively leading to small change in the

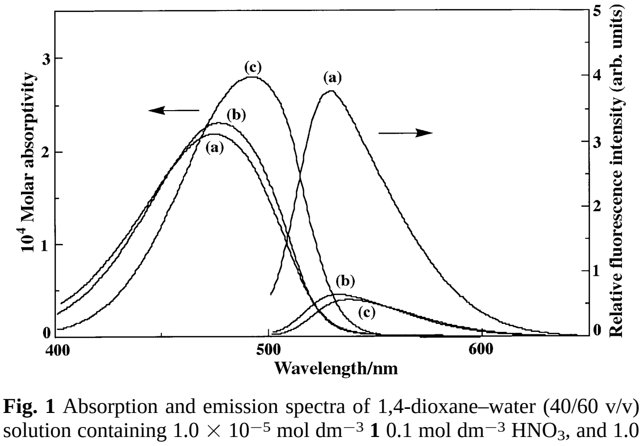

Fig. 1 Absorption and emission spectra of 1,4-dioxane–water (40/60 v/v) solution containing 1.0 × 10^{-5} mol dm^{-3} **1** 0.1 mol dm^{-3} HNO_3, and 1.0 × 10^{-5} mol dm^{-3} of metal ion. (a) Hg^{2+} added; (b) Ag^+ added; (c) Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Tl^+ added or absence of metal ion.

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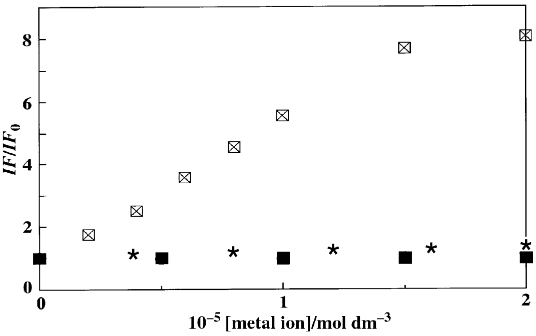

Fig. 2 Relative fluorescence intensity *vs.* metal ion concentration plots for 1×10^{-5} mol dm^{-3} **1** in 0.1 mol dm^{-3} HNO_3; (■) Mn^{2+}, (●) Co^{2+}, (▲) Ni^{2+} (◆) Cu^{2+}, (□) Zn^{2+}, (◇) Cd^{2+}, (○) Pb^{2+}, (⊙) Tl^{+} (all overlapped), Ag^{+} (*), Hg^{2+} (☒). Values of *IF/IF*$_0$ indicate the relative fluorescence intensity for **1** in the presence of metal ion and were calculated using the value corresponding to free **1** as unity.

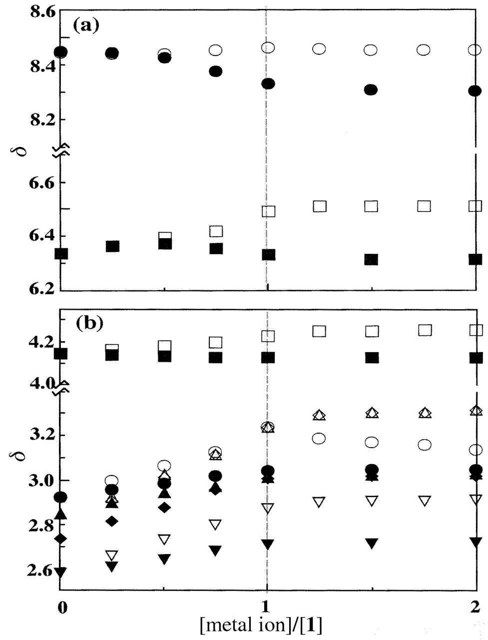

Fig. 3 Metal ion induced changes in chemical shifts for protons of **1** using acetonitrile-d_3 as a solvent. Open and filled symbols are for $(CF_3CO_2)_2Hg$ and CF_3SO_3Ag, respectively. (a) Plots of chemical shifts for protons of fluorophore moiety *vs.* [Metal ion]/[**1**]. (□, ■): H_a, (○, ●): H_b. (b) Plots of chemical shifts for protons of the ionophore moiety *vs.* [Metal ion]/[**1**]. (□, ■) H^1, (○, ●) H^2, (△, ▲) H^3, (◇, ◆) H^4, (▽, ▼) H^5.

fluorescence intensity. On the other hand, the complex of **1** with Hg^{2+} was gradually formed even above an $[Hg^{2+}]$/[**1**] ratio of 1 ($[Hg^{2+}] = 1.0 \times 10^{-5}$ mol dm^{-3}) and drastic enhancement in the fluorescence intensity compared with that for the complex with Ag^{+} was observed. These results demonstrate that the fluorescence intensity of the Hg(II) complex of **1** is much higher than that of the Ag(I) complex, although the former complex is less stable. The spectroscopic properties of the complex should preferentially depend on the strength of the interaction between a metal ion and the nitrogen atom connected to the nitrobenzoxadiazolyl moiety while the stability of the complex is governed by the degree of the affinity of the ionophore moiety to the metal ion.

^1H NMR titration of **1** with metal ions was carried out using acetonitrile-d_3 as solvent. Fig. 3 shows Hg^{2+} and Ag^{+} induced changes in the ^1H NMR chemical shifts for the protons of **1**. Addition of Hg^{2+} and Ag^{+} caused downfield shifts for the methylene protons of the sulfur containing moiety, indicating the coordination of sulfur atoms to the metal ion in which metal ion is probably wrapped by the tetrathiazaalkane moiety. A drastic downfield shift of H_a was observed on the addition of Hg^{2+}. This phenomenon suggests a decrease in the π-electron density of the nitrobenzoxadiazolyl moiety. The much larger change in the chemical shifts for the protons of the nitrobenzoxadiazolyl moiety upon the addition of Hg^{2+} relative to that of Ag^{+} suggests that the interaction of the nitrogen atom of the tetrathiazaalkane moiety with Hg^{2+} is stronger than with Ag^{+}.

In conclusion, the present study demonstrates that 3,6,12,15-tetrathia-9-azaheptadecane **1** bearing a nitrobenzoxadiazolyl moiety is a viable candidate as a fluoroionophore for a new Hg^{2+} ion sensor. This fluoroionophore **1** can discriminate Hg^{2+} ion well among heavy metal ions by an enhancement of the fluorescence intensity. In this case, the calibration curve for the relative fluorescence intensity *vs.* concentration of added Hg^{2+} shows linearity up to $[Hg^{2+}]$ 1.5×10^{-5} mol dm^{-3} 1,4-dioxane–water (60/40 v/v) (Fig. 2). This fluoroionophore can thus determine trace amounts of Hg^{2+} selectively even in acidic polar media containing water.

Notes and references

† The fluoroionohores **1** and **2** were synthesized as follows: 7-chloro-4-nitrobenzoxadiazole (2.2 mmol), the corresponding thiazaalkane (2 mmol)[13] and potassium carbonate (2 mmol) were dissolved in EtOH (50 mL) and stirred over night. After the reaction was complete, the solvent was evaporated *in vacuo* and 100 mL of water was added to the residue. The aqueous solution was extracted with $CHCl_3$ (3 × 100 mL) and the extract dried over $MgSO_4$. After removal of the solvent, the product was purified by column chromatography.

Selected data: for **1**: deep red solid, yield 59.9%, mp 55.0–56.0 °C; $\delta_H(CDCl_3,TMS)$: 1.27 (t, 6H, CH_3), 2.48–3.23 (m, 16H, SCH_2), 4.16 (t, 4H, NCH_2), 6.18 (d, 1H, Ar), 8.40 (d, 1H, Ar); EI-MS: *m/z* 471 (M^+); Anal. Calc. for $C_{18}H_{28}N_4O_3S_4$: C, 45.38; H, 5.88; N, 11.74. Found: C, 45.33; H, 5.77; N, 11.62%.

For **2**: deep red solid, yield: 74.0%, mp 74.0–75.0 °C; $\delta_H(CDCl_3,TMS)$: 1.31 (t, 6H, CH_3), 2.56–2.99 (m, 8H, SCH_2), 4.16 (t, 4H, NCH_2), 6.18 (d, 1H, Ar), 8.42 (d, 1H, Ar): EI-MS: *m/z* 356 (M^+); Anal. Calc. for $C_{14}H_{20}N_4O_3S_2$: C, 47.19; H, 5.62; N, 15.73. Found: C, 47.11; H, 5.52; N, 15.45%.

1 E. B. Sandell, *Colorimetric Determination of Trace of Metals*, Interscience publishers, New York, 3rd edn., 1958, p. 621.
2 Z. Marczwnko, *Separation and Spectrophotometric Determination of Elements*, Ellis Horwood Limited, Chichester, 1986, p. 371.
3 D. Y. Sasaki and B. E. Padilla, *Chem. Commun.*, 1998, 1581.
4 G. G. Talanova, N. S. A. Elkarim, V. S. Talanov and B. A. Bartsch, *Anal. Chem.*, 1999, **71**, 3106.
5 K. Rurack, M. Kollmannsberger, U. Resch-Genger and J. Daub, *J. Am. Chem. Soc.*, 2000, **122**, 968.
6 K. Saito, Y. Masuda and E. Sekido, *Anal. Chim. Acta*, 1983, **151**, 447.
7 K. Chayama and E. Sekido, *Anal. Sci.*, 1987, **3**, 535.
8 K. W. Street Jr. and S. A. Krause, *Anal. Lett.*, 1986, **19**, 735.
9 J. Ishikawa, H. Sakamoto and H. Wada, *J. Chem. Soc., Perkin Trans. 2*, 1999, 1273.
10 M. Takagi, in *Cation Binding by Macrocycles*, ed. Y. Inoue and G. W. Gokel, Marcel Dekker, Inc., New York and Basel, 1990, pp. 465–495.
11 H.-G. Hôhr and F. Vôgtle, *Acc. Chem. Res.*, 1985, **18**, 65.
12 H. Sakamoto, J. Ishikawa and M. Otomo, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 2831.
13 J. Ishikawa, H. Sakamoto, T. Mizumo, K. Doi and M. Otomo, *Analyst*, 1998, **123**, 201.