Solvent Effect on the Fluorescence Response of Hydroxycoumarin Bearing a Dipicolylamine Binding Site to Metal Ions

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The fluorescence behavior of a probe **dpa-HC**, which has a coumarin derivative that acts as a fluorophore and a dipicolylamine (DPA) unit that functions as a metal ion-recognition site, was investigated with various metal ions in aqueous and several non-aqueous solvents. In aqueous solution, the fluorescence of **dpa-HC** was enhanced by Zn^{2+} and Cd^{2+} , but was quenched by other metal ions. On the other hand, in an acetonitrile solution, only Mg^{2+} enhanced the fluorescence, and the addition of a small amount of water quenched this fluorescence. This dramatic selectivity change is explained by stabilization of a **metal-dpa-HC** complex due to acetonitrile coordination and ON-OFF switching of the intramolecular photoinduced electron transfer (PET) from the nitrogen lone pair of DPA to the coumarin derivative.

Keywords Ion recognition, dipicolylamine, solvent effect, fluorescence response, chemosensor

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Introduction

Metal ions, such as Ca^{2+} and Mg^{2+} , exist in the living body where they play vital roles. For example, Mg^{2+} regulates hormone release, muscle contraction, and cell proliferation. Studies have indicated that Mg^{2+} is a crucial modulator of cell function, and the knockdown of genes coding for magnesium transporters leads to cell death.^{1,2}

Fluorescent probes with high sensitivity and selectivity have become a powerful non-destructive tool for real-time monitoring.^{3,4} Fluorescent probes can sensitively detect toxic metal ions in the environment. Moreover, the emergence of metal ion imaging to examine changes in the intracellular distribution and the mobilization upon physiological or pathological stimuli is expected within the decade.¹

In recent years, new fluorescence-based applications have been developed, and some probes have a dipicolylamine (DPA) unit as the ion-recognition site. Dipicolylamine has a tridentate ligand with three nitrogen donors to afford good selectivity for Zn^{2+} and Cd^{2+} , and leaves the coordination sites free for anion binding.⁵ Many groups have reported that receptors having $\text{Zn}(\text{II})$ -DPA binding sites show high selectivity for phosphate oxoanions in aqueous solution, and because of this much attention has been given to $\text{Zn}(\text{II})$ -DPA anion receptors because such molecules are potentially useful tools for sensing biologically important anions.^{5,6} Fluorescent receptors for Mg^{2+} , which have diaza-18-crown-6, β -diketone, and calixarene moieties for ion recognition, have been reported.⁷⁻⁹ However, those receptors could not discriminate Mg^{2+} from Ca^{2+} due to the similar chemical properties of those two cations.¹⁰ Thus, the development of fluorescent probes with higher specificity and

selectivity is being pursued in earnest.

In this study, a fluorescent probe, **dpa-HC** (8-(2,2'-dipicolylaminomethyl)-7-hydroxycoumarin), for metal ion recognition was synthesized according to a reported procedure.¹¹ The fluorescence of **dpa-HC** may be affected by a solvent change because **dpa-HC** is sensitive to the solvent polarity,^{12,13} although details of the solvent effect have not yet been clarified. Herein, we examined the role of solvents in the fluorescence change of **dpa-HC** and discovered a dramatic selectivity change of **dpa-HC** from Zn^{2+} and Cd^{2+} in water to Mg^{2+} in acetonitrile.

Experimental

Reagents and chemicals

2,2'-Dipicolylamine and 7-hydroxycoumarin were purchased from Tokyo Chemical Industry Co., Ltd. Other chemicals were obtained as special-grade reagents from Wako Pure Chemical Industries, Ltd., and were used as received. Water was doubly distilled and deionized by a Milli-Q water system (Millipore) before use.

The probe **dpa-HC** was synthesized by the following procedure (Scheme 1).¹¹ 2,2'-Dipicolylamine (0.625 g, 3.14 mmol)

Scheme 1 Synthesis of 8-(2,2'-dipicolylaminomethyl)-7-hydroxycoumarin (**dpa-HC**).

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Fig. 1 Fluorescence spectra ($\lambda_{\text{ex}} = 340$ nm) of **dpa-HC** (50 μM) in the absence or presence of various metal ions (2 equiv. of Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Cd^{2+} , and Pb^{2+}) in a HEPES buffer solution (5 mM, pH 7.4, acetonitrile/water = 1/99, v/v) at 25°C.

Fig. 2 Metal ion selectivity of **dpa-HC** (50 μM) in a HEPES buffer solution (5 mM, pH 7.4, acetonitrile/water = 1/99, v/v) at 25°C. Bars represented the fluorescence intensity at 448 nm of **dpa-HC** ($\lambda_{\text{ex}} = 340$ nm) in the absence or presence of 2 equiv. of Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Cd^{2+} , and Pb^{2+} .

and formaldehyde (37% aqueous solution, 0.32 mL, 3.2 mmol) were dissolved in 30 mL of acetonitrile and the mixture was stirred at 60°C for 30 min. To this was added 7-hydroxycoumarin (0.501 g, 3.14 mmol), and the entire reaction mixture was heated at 65°C for 3 h. The solvent was evaporated and chloroform was added. The organic layer was washed with deionized water to induce precipitate formation. The precipitate was filtered and washed well with deionized water. Purification by SEC (size exclusion chromatography) using chloroform afforded **dpa-HC** in 65% yield as a yellow solid (0.76 g, 2.04 mmol); ^1H NMR (500 MHz, CDCl_3) δ (ppm) 8.51 (d, $J_{\text{kJ}} = 4.5$ Hz, 2H), 7.72 (d, $J_{\text{ha}} = 9.0$ Hz, 1H), 7.68 (td, J_{ih} , $J_{\text{ij}} = 7.75$, 1.5 Hz, 2H), 7.36 (d, $J_{\text{cd}} = 4.25$ Hz, 1H), 7.33 (d, $J_{\text{hi}} = 8.0$ Hz, 2H), 7.22 (td, J_{jk} , $J_{\text{ji}} = 6.13$, 1.0 Hz, 2H), 6.78 (d, $J_{\text{dc}} = 8.5$ Hz, 1H), 6.11 (d, $J_{\text{ab}} = 9.25$ Hz, 1H), 4.04 (s, 2H), 3.89 (s, 4H); EI-HRMS (m/z) calcd. for $\text{C}_{22}\text{H}_{19}\text{N}_3\text{O}_3$ [$\text{M}]^+$ 373.1426, found 373.1435; Anal. Calcd. for $\text{C}_{22}\text{H}_{19}\text{N}_3\text{O}_3$: C, 70.76; H, 5.13; N, 11.25. Found: C, 70.13; H, 5.08; N, 11.26.

Apparatus

^1H NMR spectra were measured with a JNM-EXC300 spectrometer (JEOL, Ltd.) or a JNM-ECA 500 spectrometer (JEOL, Ltd.). EI-MS spectra were recorded on a JMS-700 instrument (JEOL, Ltd.). Elemental analysis was performed with a Perkin Elmer PE2400 II apparatus. Fluorescence spectra were measured with a HITACHI F-7000 fluorescence spectrometer (Hitachi, Ltd.) equipped with a 1.0-cm quartz cell. The scan speed was 60 nm min^{-1} . All fluorescence spectra were recorded under an aerated condition. UV-Vis spectra were measured with a HITACHI U-3900H UV-Vis spectrophotometer (Hitachi, Ltd.) equipped with a 1.0-cm quartz cell. The scan speed was 120 nm min^{-1} . X-ray diffraction data for the two compounds were analyzed on a Mercury CCD (Rigaku, Ltd.) equipped with a monochromator in the $\text{Mo } K_{\alpha}$ ($\lambda = 0.71069$ Å) incident beam. Each crystal was mounted on a glass fiber. The diffraction data were integrated and the structure was solved and refined using Crystal Structure Ver. 4.0.1. (Rigaku, Ltd.). All hydrogen atoms were placed in the calculated positions.

Results and Discussion

Metal ion selectivity of **dpa-HC** in an aqueous solvent

To examine the metal ion selectivity of **dpa-HC** in an aqueous solution, we measured the fluorescence in the presence or absence of metal ions, including Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Cd^{2+} , and Pb^{2+} . The fluorescence spectra were monitored in an aqueous solution containing 5.0×10^{-5} M ($\text{M} = \text{mol dm}^{-3}$) **dpa-HC**, in the presence or absence of 1.0×10^{-4} M metal ions at 25°C.

As shown in Figs. 1 and 2, the addition of 2 equiv. of alkali metal elements and group-2 element ions (Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}) exhibited no obvious effects on the fluorescence emission, whereas the addition of Ni^{2+} or Cu^{2+} decreased the fluorescence intensity. In contrast, the addition of Zn^{2+} and Cd^{2+} strongly enhanced the fluorescence intensity. The observed metal-ion selectivity of **dpa-HC** was almost the same as that previously reported by Yoon *et al.*¹¹ and Kikuchi *et al.*¹⁴

The significant increase in fluorescence intensity could be explained as follows. The fluorescence response of **dpa-HC** is based on the photo-induced electron transfer (PET) mechanism. The inherent fluorescence of **dpa-HC** is quenched by the intramolecular PET from DPA to the coumarin derivative. However, upon addition of metal ions, the receptor chelates the metal ions to form stable complexes, thereby deactivating the quenching by PET due to stabilization of the receptor's HOMO so that it lies below the energy level of the fluorophore's HOMO, and increasing the fluorescence intensity of the coumarin moiety.^{15,16}

Such transition metals as Fe^{2+} , Ni^{2+} , Cr^{2+} , Cu^{2+} , and Co^{2+} are paramagnetic ions with an unfilled d shell, and are known to induce fluorescence quenching. Though Fe^{2+} and Ni^{2+} can take both high-spin and low-spin states, it is known that the fluorescence was quenched by the paramagnetic metal ions with a high-spin state.

The mechanisms for electron transfer (eT) and energy transfer (ET) are well defined, although various factors are known to cause fluorescence quenching.¹⁷ On the addition of Cu^{2+} , the **Cu-dpa-HC** complex induced not chelation-enhanced fluorescence (CHEF), but fluorescence quenching by eT and ET

Fig. 3 Fluorescence spectra ($\lambda_{\text{ex}} = 356$ nm) of **dp**a-**HC** (50 μM) in the absence or presence of various metal ions (2 equiv. of Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Cd^{2+} , and Pb^{2+}) in a acetonitrile solution (acetonitrile/water = 99/1, v/v) at 25°C.

to the metal ion. In the case of alkali and alkaline earth metal ions, the hydrated ions are much more stable than the **metal-dpa-HC** (**M-dpa-HC**) complex; therefore, the formation of the **M-dpa-HC** complex does not proceed and the fluorescence of **dp**a-**HC** is quenched by intramolecular PET.

Metal ion selectivity of **dp**a-**HC** in organic solvent

To clarify the metal ion selectivity of **dp**a-**HC** in an organic solvent, we observed the fluorescence responses in the presence or absence of metal ions. The fluorescence spectra in 99% acetonitrile-1% water (v/v) containing 5.0×10^{-5} M **dp**a-**HC** were measured in the presence or absence of 1.0×10^{-4} M metal ions at 25°C.

To our surprise, the addition of 2 equiv. of Mg^{2+} resulted in a significant enhancement of the fluorescence intensity in acetonitrile (Figs. 3 and 4), although Mg^{2+} exhibited no obvious effect on the fluorescence response of **dp**a-**HC** in water. The fluorescence intensities in the presence of Zn^{2+} and Cd^{2+} were markedly diminished when measurements were conducted in acetonitrile in comparison with those when measurements were done in water.

To examine the structures and binding conditions of **M-dpa-HC** by changing the solvent, we measured the UV-Vis spectra of **dp**a-**HC** in the presence or absence of metal ions (Figs. S1 and S2, Supporting Information). In water, the UV-Vis spectra exhibited significant changes in the presence of Zn^{2+} , whereas Mg^{2+} did not cause any spectral changes (Fig. S3, Supporting Information). In acetonitrile, on the other hand, dramatic changes were noted for Mg^{2+} (Fig. S4, Supporting Information). To obtain further evidence from the spectral changes, titrations experiments by the addition of 1–5 equiv. of Mg^{2+} and Zn^{2+} in acetonitrile were performed, and significant 1:1 responses in the UV-Vis spectra were observed for both Zn^{2+} and Mg^{2+} (Figs. S8 and S9, Supporting Information). No spectral changes were induced by the presence or absence of Mg^{2+} , indicating that Mg^{2+} did not form the complex with **dp**a-**HC** in an aqueous solution. In general, Mg^{2+} is strongly hydrated, and it is difficult to form stable complex in water. However, **dp**a-**HC** can form Mg^{2+} complex in acetonitrile because acetonitrile promotes the coordination between Mg^{2+} and **dp**a-**HC** by replacing the water

Fig. 4 Metal ion selectivity of **dp**a-**HC** (50 μM) in acetonitrile solution (acetonitrile/water = 99/1, v/v) at 25°C. Bars represented the fluorescence intensity at 425 nm of **dp**a-**HC** ($\lambda_{\text{ex}} = 356$ nm) in the absence or presence of 2 equiv. of Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Cd^{2+} , and Pb^{2+} .

hydration with acetonitrile solvation. In contrast, the **Zn-dpa-HC** complex was formed as confirmed by the marked red-shift of UV-Vis spectra, indicating that the hydroxyl group in the coumarin moiety was involved in the coordination of Zn^{2+} with **dp**a-**HC**. In an organic solvent, the absorption changes at 360 nm suggested that **dp**a-**HC** formed complexes with both Zn^{2+} and Mg^{2+} in a similar manner. For other metal ions, such as Ag^+ and Pb^{2+} , no significant fluorescence and UV-Vis spectral response were noted in acetonitrile (Fig. 3 and Fig. S2 (Supporting Information)).^{18,19}

The **dp**a-**HC** requires a suitable size for coordination with metal ions. This fact supports the similar complex formation ability of Mg^{2+} with Zn^{2+} , since the ionic radii of Zn^{2+} and Mg^{2+} are nearly identical (Zn^{2+} radius is 0.736 Å whereas Mg^{2+} is 0.728 Å²⁰). X-ray structure analysis indicated that **dp**a-**HC** had difficulty in coordinating with a large metal ion because of conformational space limitations caused by the three nitrogen donors of DPA and the hydroxy group of the coumarin derivative (the single crystal structure²¹ is shown in Fig. S10, Supporting Information). Regarding the cation size, even though alkaline earth metal ions such as Ca^{2+} and Ba^{2+} have similar chemical properties to Mg^{2+} , their radii are too large to allow for coordination with the recognition site. Those cations, therefore, exhibited no obvious effect on the fluorescence behavior affected by a solvent change. One reason why **dp**a-**HC** has high selectivity for Mg^{2+} may be the efficient interaction of the hydroxyl moiety (hard base) in **dp**a-**HC** with Mg^{2+} (hard acid), based on the Hard and Soft Acid and Bases (HSAB) theory.²²

To determine the binding constant of **dp**a-**HC**, we assumed that **dp**a-**HC** formed a 1:1 complex with metal ions, and that the resultant fluorescence intensity changes as a function of the metal ion concentration were well fitted with the theoretical curve for 1:1 complex formation. The obtained binding constants (K_{11}) are summarized in Table 1. The fitting analysis is described in Supporting Information, section 4 (Figs. S11–S13, Supporting Information).

The results indicated that the binding constant of **Mg-dpa-HC** was higher in acetonitrile ($K_{11} = (1.01 \pm 0.92) \times 10^7 \text{ M}^{-1}$) than in water, whereas the binding constant of **Zn-dpa-HC** decreased by changing the solvent from water ($K_{11} > 10^7 \text{ M}^{-1}$) to acetonitrile ($K_{11} = (1.62 \pm 0.89) \times 10^6 \text{ M}^{-1}$). Thus, the binding

affinity of the **Zn-dpa-HC** complex in acetonitrile was reduced, resulting in the low fluorescence intensity. This may be due to the coordination of acetonitrile to Zn^{2+} , as mentioned later.

Fluorescence behavior by changing the acetonitrile/water ratio

As described above, the metal ion selectivity of **dpa-HC** in aqueous and organic solvents showed different responses: **dpa-HC** displayed excellent selectivity for and sensitivity to Zn^{2+} and Cd^{2+} in an aqueous solvent, whereas it exhibited high selectivity for and sensitivity to Mg^{2+} in an organic solvent. To elucidate those interesting fluorescence responses, we examined the fluorescence behavior in both the absence or presence of metal ions by changing the water/acetonitrile composition.

As shown in Fig. 5, the fluorescence intensity of **dpa-HC** in the presence of Mg^{2+} was significantly enhanced in an acetonitrile/water mixed solvent containing >95% acetonitrile. Mixed solvents containing lower percentages of acetonitrile exhibited no obvious effects on the fluorescence response. The results demonstrated that the fluorescence behavior of **Mg-dpa-HC** changed noticeably in the presence of a small amount of water. Therefore, **Mg-dpa-HC** shows potential for use as a highly sensitive sensor for the quantitative measurement of a trace amount of water in organic solvents²³ and real time imaging sensor for Mg^{2+} in the cell membrane.

Table 1 Binding constants of **dpa-HC** to metal ion (K_{11})

Metal ion	$K_{11}/\text{dm}^3 \text{ mol}^{-1}$	
	1% acetonitrile - 99% water	99% acetonitrile - 1% water
Zn^{2+}	ND ($>10^7$)	$(1.62 \pm 0.89) \times 10^6$
Cu^{2+}	$(1.35 \pm 0.14) \times 10^6$	ND ($>10^7$)
Mg^{2+}	—	$(1.01 \pm 0.92) \times 10^7$

^1H NMR studies

To clarify the structure of the **Mg-dpa-HC** complex, ^1H NMR analyses were carried out in 100% acetonitrile- d_3 at 300 MHz. ^1H NMR signals appearing of around 7.0–8.5 ppm are attributed to the resonance corresponding to the DPA protons of **dpa-HC**. In contrast to the addition of Mg^{2+} , the addition of 1 equiv. of Ca^{2+} and Ba^{2+} hardly changed the signals. To clarify the molecular motion in detail, titration analysis by the addition of Mg^{2+} was carried out. Figure 6 illustrates the result of a ^1H NMR titration analysis by the addition of 0–1.5 equiv. of

Fig. 5 Selectivity of **dpa-HC** (50 μM) for metal ions (1 equiv. of Mg^{2+} , Zn^{2+}) in acetonitrile/water (volume ratio of acetonitrile: 1 to 99%) (v/v) at 25 $^{\circ}\text{C}$ (λ_{ex} = 367 nm).

Fig. 6 ^1H NMR titration of **dpa-HC** in the presence of 0–1.5 equiv. Mg^{2+} (300 MHz, CD_3CN).

Mg^{2+} . Proton peaks of DPA located around 7.0 – 8.5 ppm showed downfield shifts, and new peaks appeared due to the formation of the Mg^{2+} complex. The spectra suggested that the molecular motion of the **Mg-dpa-HC** complex was restricted by the formation of a metal complex, which resulted in signal broadening.

Fluorescence behavior induced by solvent changes

To understand the solvent effects more clearly, fluorescence responses in water, DMSO, methanol, ethanol, and acetonitrile were examined.

As revealed in Fig. 7, **dpa-HC** only showed high selectivity for Mg^{2+} in acetonitrile. The results of UV-Vis spectra in water, DMSO, methanol, ethanol, and acetonitrile (Figs. S3 – S7, Supporting Information) indicated that the evidence of Mg^{2+} coordination with DPA moiety based on the changes in the UV-Vis spectra were only noted for the solvents of methanol, ethanol, and acetonitrile. Considering the fluorescence intensity difference before and after the addition of Mg^{2+} , acetonitrile was superior to methanol and ethanol for obtaining the higher Mg^{2+} selectivity. The result also supported the finding that **dpa-HC** exhibited high selectivity for Zn^{2+} not in an organic solvent but in an aqueous solution.

From the decrease in the fluorescence intensity in non-coordinating solvents, it became clear that **dpa-HC** required coordinating solvents to exhibit high selectivity for Mg^{2+} . Among the relative fluorescence intensities of free **dpa-HC**, **dpa-HC** in protic solvent such as methanol, ethanol and water showed the stronger fluorescence intensity, verifying that the protic solvent could enhance the fluorescence intensity of **dpa-HC**.

Fluorescence behaviors based on coordination ability

To clarify the structural effect of coordinating solvents, such as acetonitrile, benzonitrile and pyridine, the fluorescent behavior of **M-dpa-HC** was examined.

First, we compared acetonitrile with benzonitrile. The emission intensity of **Mg-dpa-HC** in acetonitrile was higher than that in benzonitrile (Fig. S14, Supporting Information).

Fig. 7 Metal ion selectivity of **dpa-HC** (50 μM) in different solvents (Water: 99% water-1% acetonitrile (v/v), DMSO: 1% water-99% DMSO (v/v), Methanol: 1% water-99% methanol (v/v), Ethanol: 1% water-99% ethanol (v/v), and Acetonitrile: 1% water-99% acetonitrile (v/v)) at 25°C. Bars represented fluorescence intensity of **dpa-HC** in the absence or presence of 2 equiv. of Mg^{2+} , Zn^{2+} .

Scheme 2 Plausible mechanism of emission enhancement and quenching.

This result indicated that benzonitrile had a low coordination ability to the metal ion in **M-dpa-HC** due to the electron withdrawing effect of benzene ring. Therefore, **M-dpa-HC** could be used as a sensor to recognize the structural differences of donor ligand derivatives in solution.

We then compared acetonitrile with pyridine based on their coordination ability. **M-dpa-HC** in acetonitrile showed an enhancement of the emission intensity upon the addition of pyridine, while the fluorescence response of **dpa-HC** exhibited no obvious effect for pyridine (Fig. S15, Supporting Information), indicating that the ligand exchange from acetonitrile to pyridine took place because the coordination ability of pyridine was higher than that of acetonitrile. This result supported that the solvent coordination affected the fluorescence behaviors of **M-dpa-HC**.

Fluorescence emission mechanism

Scheme 2 shows a plausible fluorescence emission mechanism. The inherent fluorescence of **dpa-HC** is quenched by the intramolecular PET from the nitrogen lone pair of DPA to the coumarin moiety. In the case of Mg^{2+} , the coordinating solvents, such as acetonitrile, are required for complex formation with **dpa-HC**. The formation of a **Mg-dpa-HC** complex would deactivate the quenching by PET and increase the fluorescence intensity of the coumarin derivative.

Conversely, the type of solvent (water or acetonitrile) is irrelevant to the formation of the **Zn-dpa-HC** complex. It should be noted that the metal-DPA binding is markedly affected by the solvation network in acetonitrile. As a result, **dpa-HC** in acetonitrile does not form a stable complex with Zn^{2+} compared with **dpa-HC** in water. Thus, PET is not efficiently inhibited, even though the **Zn-dpa-HC** complex is formed, resulting in the low fluorescence intensity in acetonitrile.

Conclusions

We have synthesized a fluorescent probe (**dpa-HC**) for metal ion recognition, and evaluated its fluorescence response to various metal ions. The **dpa-HC** showed high selectivity for and sensitivity to Zn^{2+} and Cd^{2+} in water. On the other hand, the probe showed high selectivity for Mg^{2+} in acetonitrile. The inherent fluorescence of **dpa-HC** was quenched by the intramolecular PET from the nitrogen lone pair of DPA to the coumarin derivative. In the case of Mg^{2+} , coordinating solvents, such as acetonitrile, were required for the complex formation of **dpa-HC** with Mg^{2+} . The use of coordinating solvents could lead to the formation of a **Mg-dpa-HC** complex, thereby deactivating the quenching by PET and increasing the fluorescence intensity of the coumarin derivative. In the case of Zn^{2+} , **Zn-dpa-HC** complex was formed regardless of the solvent used (water or acetonitrile). However the metal-DPA binding was found to be strongly affected by the solvation network in acetonitrile. As a result, it was plausible that **dpa-HC** in acetonitrile did not form a stable complex with Zn^{2+} compared with **dpa-HC** in water. Thus, PET was not efficiently inhibited, resulting in a low fluorescence intensity, similar to the free **dpa-HC**. Consequently, we revealed a dramatic selectivity change of **dpa-HC** from Zn^{2+} and Cd^{2+} in water to Mg^{2+} in acetonitrile.

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Supporting Information

The ORTEP diagram of **dpa-HC**, UV-Vis spectra, theoretical formula, fluorescence spectra, and 1H NMR spectra are enclosed in Supporting Information. These material are available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

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