# Mechanism for Different Fluorescence Response of a Coumarin– Amide–Dipicolylamine Linkage to Zn(II) and Cd(II) in Water

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## **Supporting Information**

**ABSTRACT:** A coumarin-amide-dipicolylamine linkage (L) was synthesized and used as a fluorescent receptor for metal cations in water. The receptor dissolved in water with neutral pH shows almost no fluorescence due to the photoinduced electron transfer (PET) from the amide and amine nitrogens to the excited state coumarin moiety. Coordination of  $Zn^{2+}$  or  $Cd^{2+}$  with L creates strong fluorescence at 437 or 386 nm, respectively, due to the suppression of PET. In contrast, other metal cations scarcely show fluorescence enhancement. IR, NMR, and potentiometric analysis revealed that both  $Zn^{2+}$  and  $Cd^{2+}$  are coordinated with two pyridine N, amine N, and amide O; however, the  $Zn^{2+}$  center is also coordinated with a



hydroxide anion (OH<sup>-</sup>). The structure difference for Zn and Cd complexes results in longer- and shorter-wavelength fluorescence. Ab initio calculations revealed that  $\pi$  electrons on the excited state Cd complex are delocalized over the molecules and the Cd complex shows shorter-wavelength emission. In contrast,  $\pi$  electrons of OH<sup>-</sup>-coordinated Zn complex are localized on the coumarin moiety. This increases the electron density of coumarin moiety and shows longer-wavelength fluorescence.

## INTRODUCTION

Zn<sup>2+</sup> is an essential nutrient for the human body and plays important roles in many physiological and pathological processes.<sup>1</sup> Its deficiency leads to an acrodermatitis enteropathica,<sup>2</sup> but an excess dose causes several health problems such as superficial skin diseases, prostate cancer, diabetes, and brain diseases.<sup>3</sup> In contrast, Cd<sup>2+</sup> is highly toxic to the human body. Its intake causes several diseases such as renal dysfunction, calcium metabolism disorders, and prostate cancer.<sup>4</sup> The design of fluorescent signaling receptors for  $Zn^{2+}$  or  $Cd^{2+}$  has therefore attracted a great deal of attention, because they facilitate rapid monitoring of metal cations by simple fluorescence measurements. A variety of receptors showing a turn-on fluorescence response upon binding with  $Zn^{2+}$  or  $Cd^{2+}$  has been proposed. Most of these receptors, however, show similar fluorescence enhancement upon binding with these cations at the same wavelength, because Zn<sup>2+</sup> and  $Cd^{2+}$  are in the same group of the Periodic Table and have similar electronic and binding properties.<sup>5–16</sup> The design of receptors that show fluorescence enhancement at different wavelengths for  $Zn^{2+}$  and  $Cd^{2+}$  is currently the focus of attention.<sup>17–21</sup>

The most efficient and simple ligand system that shows fluorescence enhancement at different wavelengths upon binding with  $Zn^{2+}$  and  $Cd^{2+}$  is the amide-dipicolylamine (DPA) linkage proposed by Xu et al.<sup>22</sup> They synthesized a naphthalimide-amide-DPA linkage (Scheme 1). This molecule, when dissolved in water at a neutral pH, shows almost no fluorescence. Addition of  $Zn^{2+}$  and  $Cd^{2+}$ , however, leads to

Scheme 1. Proposed Coordination Structures of a Naphthalimide–Amide–DPA Linkage at Neutral pH<sup>22</sup>



fluorescence enhancement at 514 and 446 nm, respectively. The different fluorescence emissions were explained by the different coordination structures of the Zn and Cd complexes (Scheme 1). Both Zn and Cd complexes have tetracoordinated structures involving two pyridine N and amine N. The Zn complex involves amide N, whereas the Cd complex involves amide O. These different coordination structures are considered to affect the different fluorescence emissions. These coordination structures were, however, identified on the basis of <sup>1</sup>H NMR, 2D NOISY, and IR analysis in pure MeCN and DMSO solvents. Accurate coordination structures

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in water are unclear, and the mechanisms for different fluorescence wavelengths remain to be clarified.

The purpose of the present work is to clarify the mechanism for different fluorescence wavelengths for the amide-DPA receptor. Coumarin is one of the most popular dyes and has been studied extensively for application to fluorescent receptors due to high emission quantum yield and high photostability.<sup>23,24</sup> We synthesized a coumarin-amide-DPA linkage (L) that shows  $Zn^{2+}$  and  $Cd^{2+}$ -selective fluorescence enhancement at different wavelengths. This molecule dissolved in water at a neutral pH shows almost no fluorescence ( $\phi_{\rm F} = 0.05$ ). Addition of  $Cd^{2+}$  creates a purple emission at 386 nm ( $\phi_{\rm F}$  = 0.36), whereas addition of  $Zn^{2+}$  shows a blue emission at 437 nm ( $\phi_{\rm F}$  = 0.63). On the basis of the IR, NMR, and potentiometric titration analysis in aqueous solvents, the different fluorescence response to  $Zn^{2+}$  and  $Cd^{2+}$  was successfully explained by the coordination structures, as summarized in Scheme 2, which are different from those

Scheme 2. Proposed Coordination Structures of a Coumarin–Amide–DPA Linkage at Neutral pH<sup>a</sup>



<sup>*a*</sup>These photographs were taken under photoirradiation of water (HEPES 100 mM, pH 7.3) containing L (10  $\mu$ M) and 1 equiv of Zn<sup>2+</sup> or Cd<sup>2+</sup> with a hand-held UV lamp (365 nm) at 298 K.

reported for the naphthalimide–amide–DPA system.<sup>22</sup> Both  $Zn^{2+}$  and  $Cd^{2+}$  are coordinated with two pyridine N, amine N, and amide O. A hydroxide anion (OH<sup>-</sup>) is coordinated to the Zn center, whereas Cd complex does not involve OH<sup>-</sup>. The OH<sup>-</sup> coordination to the Zn center leads to a localization of  $\pi$  electrons on the coumarin moiety and results in red-shifted emission.

## RESULTS AND DISCUSSION

**Synthesis and Properties of Receptor.** The receptor L was synthesized via two step reactions (Scheme 3). Reaction of 7-amino-4-methylcoumarin (2) with chloroacetyl chloride

Scheme 3. Synthesis of the Receptor



afforded 1 with 73% yield. Condensation of di-2-picolylamine  $(DPA)^{25}$  and 1 with *N*,*N*-diisopropylethylamine (DIPEA) and KI gave L as a yellow oil with 65% yield (total yield: 47%). The purity of 1 and L was confirmed by <sup>1</sup>H, <sup>13</sup>C NMR and FAB-MS analysis (Figures S1–S6, Supporting Information).

Fluorescence properties of L in water were studied. Figure 1a (top) shows the fluorescence spectra ( $\lambda_{ex}$  = 327 nm) of L (10  $\mu$ M) measured without cations at different pHs (2–11) at 298 K. L exhibits very weak fluorescence at ca. 394 nm ( $\phi_{\rm F}$  <0.17) in the entire pH range. This is because the photoinduced electron transfer (PET) from the amine and/or amide nitrogens to the photoexcited coumarin moiety quenches the fluorescence. This is confirmed by the species of L formed at the respective pHs, which were calculated from the protonation constants determined potentiometrically (Table 1). The dotted lines in Figure 1a (bottom) plot the mole fraction distribution of the species versus pH. The triangle symbols in this figure plot the fluorescence intensity monitored at 386 nm. The protonation/deprotonation states of L are summarized in Scheme 4. At pH >6, L and  $LH_{-1}$  species with deprotonated amine and amide N exist predominantly. These species promote PET from both amine and amide N to the photoexcited coumarin moiety<sup>26</sup> and result in fluorescence quenching. At pH <6,  $H_2L$  and HL species exist mainly, and the fluorescence intensity becomes relatively strong although at the very weak level. The amine N of H<sub>2</sub>L and HL are protonated, but the amide N are still deprotonated. This thus promotes PET from the amide N to the photoexcited coumarin moiety. These data suggest that, in the entire pH range (2-11), PET from the amine and/or amide N to the coumarin moiety results in very weak fluorescence.

**Effect of Metal Cations.** Figure 2 shows the fluorescence spectra ( $\lambda_{ex} = 327$  nm) of L (10  $\mu$ M) measured in water (pH 7.3) with each respective metal cation (1 equiv). L itself shows very weak fluorescence ( $\phi_F = 0.05$ ). Addition of Zn<sup>2+</sup> and Cd<sup>2+</sup> (1 equiv), however, creates strong fluorescence at 437 nm ( $\phi_F = 0.63$ ) and 386 nm ( $\phi_F = 0.36$ ), respectively. This suggests that L shows different fluorescence spectra upon interaction with Zn<sup>2+</sup> and Cd<sup>2+</sup>, as does the naphthalimide–amide–DPA linkage.<sup>22</sup> In contrast, addition of other cations (Hg<sup>2+</sup>, Cu<sup>2+</sup>, Pb<sup>2+</sup>, Cr<sup>3+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Mg<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Ag<sup>+</sup>) to the solution shows almost no fluorescence enhancement. This indicates that L shows selective emission enhancement toward Zn<sup>2+</sup> and Cd<sup>2+</sup>.

It must be noted that the fluorescence enhancement upon addition of  $Zn^{2+}$  or  $Cd^{2+}$  terminates within 2 min (Figure S7, Supporting Information), indicating that L enables rapid detection of  $Zn^{2+}$  and  $Cd^{2+}$ . As shown in Figure S8 (Supporting Information), the fluorescence emissions created upon addition of  $Zn^{2+}$  and  $Cd^{2+}$  are unaffected by the addition of other metal cations (Ag<sup>+</sup>, Co<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Hg<sup>2+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>). In contrast, a small quenching effect on the Zn<sup>2+</sup>-induced fluorescence is observed upon addition of Cr<sup>3+</sup>. In addition, Cu<sup>2+</sup> strongly quenches the fluorescence created by both Zn<sup>2+</sup> and  $Cd^{2+}$ , suggesting that the coordination of  $Cu^{2+}$  with L is much stronger than those of Zn<sup>2+</sup> and Cd<sup>2+</sup>. These findings indicate that L detects Zn<sup>2+</sup> or Cd<sup>2+</sup> selectively even in the presence of many other cations except for  $\mathrm{Cu}^{2_{+}}$  and  $\mathrm{Cr}^{3_{+}}.$  It must also be noted that addition of  $Zn^{2+}$  together with  $Cd^{2+}$  to the solution containing L leads to an increase in the longerwavelength emission at 437 nm (Figure S9, Supporting Information). This indicates that L coordinates with Zn<sup>2</sup>

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Figure 1. (Top) pH-dependent change in fluorescence spectra ( $\lambda_{ex} = 327 \text{ nm}$ ) of L (10  $\mu$ M) measured in water at 298 K (a) without cations, (b) with  $\text{Zn}(\text{ClO}_4)_2$  (1 equiv), and (c) with  $\text{Cd}(\text{ClO}_4)_2$  (1 equiv). Both excitation and emission slit widths are 3 nm. The numbers denote the pH of solution. (Bottom) change in fluorescence intensity. Triangle and circle symbols show the intensity monitored at 386 and 437 nm, respectively. The dotted lines denote the mole fraction distribution of the species. All measurements were performed after stirring the solution for 2 min at the adjusted pH.

Table 1. Protonation Constants (log K) for L and Stability Constants for Coordination with  $Cd^{2+}$  or  $Zn^{2+a}$ 

reaction	log K
$3\mathbf{H}^{+} + \mathbf{L}\mathbf{H}_{-1} = \mathbf{H}_{2}\mathbf{L}$	17.50
$2\mathbf{H}^{+} + \mathbf{L}\mathbf{H}_{-1} = \mathbf{H}\mathbf{L}$	15.32
$\mathbf{H}^{+} + \mathbf{L}\mathbf{H}_{-1} = \mathbf{L}$	9.35
$Cd^{2+} + H^+ + LH_{-1} = CdL$	15.12
$Cd^{2+} + LH_{-1} = CdLH_{-1}$	8.65
$Cd^{2+} + OH^{-} + LH_{-1} = Cd(OH)LH_{-1}$	-1.23
$Zn^{2+} + H^+ + LH_{-1} = ZnL$	13.98
$\operatorname{Zn}^{2+} + \mathbf{L}\mathbf{H}_{-1} = \operatorname{Zn}\mathbf{L}\mathbf{H}_{-1}$	6.19
$Zn^{2+} + OH^{-} + LH_{-1} = Zn(OH)LH_{-1}$	-0.87

 $^a\mathrm{The}$  measurements were carried out in an aqueous NaCl (0.15 M) solution at 298 K.

more strongly than  $Cd^{2+}$ , as is observed for naphthalimide–amide–DPA linkage.<sup>22</sup>

**Stoichiometry for Coordination.** Figure 3 shows the change in fluorescence spectra of L with the amount of  $Zn^{2+}$  or  $Cd^{2+}$  added. Stepwise addition of respective cation leads to an increase in the fluorescence intensity. The spectral change almost terminates upon addition of 1 equiv of  $Zn^{2+}$  or  $Cd^{2+}$ , implying that L interacts with  $Zn^{2+}$  or  $Cd^{2+}$  in a 1:1



**Figure 2.** Fluorescence spectra ( $\lambda_{ex} = 327 \text{ nm}$ ) of L (10  $\mu$ M) measured in water (HEPES 100 mM, pH 7.3) with each respective metal cation (1 equiv) at 298 K. Both excitation and emission slit widths are 3 nm. Measurements were performed after stirring the solution for 2 min.

stoichiometry. This is confirmed by the Job's plot analysis (Figure S10, Supporting Information). The fluorescence intensity shows a maximum at the mole fraction 0.5, indicative of the 1:1 association. The 1:1 coordination is also confirmed by ESI-MS. An MeCN solution containing L with 1 equiv of  $Zn^{2+}$  or  $Cd^{2+}$  shows a peak at m/z 577.1 or m/z 627.1, assigned







**Figure 3.** Fluorescence titration ( $\lambda_{ex} = 327 \text{ nm}$ ) of L (10  $\mu$ M) in water (HEPES 100 mM, pH 7.3) with (a) Zn<sup>2+</sup> and (b) Cd<sup>2+</sup> at 298 K. Both excitation and emission slit widths are 3 nm.

to  $[\mathbf{L} + \mathbf{Zn}^{2+} + \mathbf{ClO}_4^{-}]^+$  or  $[\mathbf{L} + \mathbf{Cd}^{2+} + \mathbf{ClO}_4^{-}]^+$  ion (Figures S11 and S12, Supporting Information).

The fluorescence titration data obtained with  $Zn^{2+}$  or  $Cd^{2+}$  (437 and 386 nm) were plotted by  $log(I - I_0)/I_0$  vs  $log[M^{2+}]$  (Figure S13, Supporting Information). A linear increase in the fluorescence intensity is observed at the concentration range >50 nM ( $Zn^{2+}$ ) and >60 nM ( $Cd^{2+}$ ), respectively. The US Environmental Protection Agency (EPA) set the maximum contaminant levels of Zn and Cd in drinking water at 76 and 45 nM, respectively.<sup>27</sup> The detection limits of L to  $Zn^{2+}$  and  $Cd^{2+}$  are close to these regulation levels.

NMR and IR Analysis for Zn and Cd Complexes. <sup>1</sup>H NMR analysis was performed to clarify the coordination structures for Zn and Cd complexes. The solubility of L in water is only ca. 100  $\mu$ M, which is insufficient for <sup>1</sup>H NMR and IR analysis (10 mM). We therefore employed a  $D_2O/CD_3CN$ mixture (1/2 v/v) for these analysis. Figure 4 shows the <sup>1</sup>H NMR spectra of L measured in a D<sub>2</sub>O/CD<sub>3</sub>CN mixture (1/2 v/v, pH 7.3) with and without  $Zn^{2+}$  or  $Cd^{2+}$  (1 equiv). All chemical shifts were identified by <sup>1</sup>H-<sup>1</sup>H COSY analysis (Figures S14–16, Supporting Information). Addition of Zn<sup>2+</sup> or Cd<sup>2+</sup> leads to a large downfield shift of the pyridine protons (H<sup>f</sup>, H<sup>g</sup>, H<sup>h</sup>, H<sup>i</sup>) and methylene protons (H<sup>e</sup>) adjacent to the amine moiety. These shifts are due to the decrease in electron density of the pyridine and methylene moieties by the cation-N coordination.  $^{28,29}$  This indicates that both  $Zn^{2+}$  and  $Cd^{2+}$  are coordinated with two pyridine N and amine N, as shown in Figure 4, similar to the naphthalimide-amide-DPA linkage.<sup>22</sup>

The cation-amide O coordination in both Zn and Cd complexes is confirmed by IR analysis in aqueous media (Figure 5). IR spectrum of 2, a reference compound (Scheme 3), measured in a D<sub>2</sub>O/CD<sub>3</sub>CN mixture (1/2 v/v, pH 7.3) shows an absorption band at 1706 cm<sup>-1</sup> assigned to the C=O vibrational stretching for coumarin moiety.<sup>31,32</sup> L measured without metal cation shows a band at 1698 cm<sup>-1</sup>, similar to 2, indicating that amide C=O band overlaps the coumarin C=O



**Figure 4.** <sup>1</sup>H NMR chart (400 MHz) of L (10 mM) measured in a  $D_2O/CD_3CN$  mixture (1/2 v/v, pH 7.3) in the absence and presence of  $Zn^{2+}$  or  $Cd^{2+}$  (1 equiv) at 303 K. The pH of solutions was adjusted with DCl and NaOD (pH = pD - 0.5).<sup>30</sup>



Figure 5. IR spectra of 2 or L (10 mM) measured in a  $D_2O/CD_3CN$  mixture (1/2 v/v, pH 7.3) in the absence and presence of  $Zn^{2+}$  or  $Cd^{2+}$  (1 equiv).

band. Addition of  $Zn^{2+}$  or  $Cd^{2+}$  to the solution creates a new band at 1655 cm<sup>-1</sup>, which is assigned to the amide C=O band shifted by the decrease in electron density via the coordination of amide O with  $Zn^{2+}$  or  $Cd^{2+}$ .<sup>33,34</sup> This suggests that both  $Zn^{2+}$ and  $Cd^{2+}$  are coordinated with amide O. It must be noted that, as shown in Figure S17 (Supporting Information), these complexes show the C=O band at 1655 cm<sup>-1</sup> also in acidic or basic media. This indicates that both Zn and Cd complexes involve the metal cation–amide O coordination at the entire pH region.

**Coordination and Fluorescence Properties of Zn Complexes.** The above NMR and IR results indicate that both Zn and Cd complexes coordinate with two pyridine N, amine N, and amide O. However, as shown in Figure 2, different-wavelength-fluorescence appears upon addition of Zn<sup>2+</sup> (437 nm) and Cd<sup>2+</sup> (386 nm). To clarify this difference, the coordination structures of Zn and Cd complexes and their fluorescence behaviors were studied at the entire pH region. Figure 1b (top) shows the fluorescence spectra of L measured with 1 equiv of Zn<sup>2+</sup>. At lower pH, shorter-wavelength emission (350–500 nm) appears, but at pH >6, longer-wavelength

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emission (350-550 nm) appears along with a decrease in shorter-wavelength emission.

Figure 1b (bottom) shows the change in emission intensity monitored at 386 nm (triangle) and 437 nm (circle), where the dotted lines denote the mole fraction distribution of the species, which were calculated from the protonation and stability constants determined potentiometrically (Table 1). Coordination structures of the species at different pH can be summarized in Scheme 5a. Coordination of L with  $Zn^{2+}$  occurs

Scheme 5. Proposed Coordination Structure for (a) Zn and (b) Cd Complexes at Different pHs



at pH >3 and produces ZnL species, which is coordinated with two pyridine N and amide O, where the amine N is protonated. The formation of ZnL species is consistent with the appearance of shorter-wavelength emission. In contrast, at pH >6, two species form, such as ZnLH<sub>-1</sub> species coordinated with two pyridine N, amine N, and amide O as a minor species, and Zn(OH)LH<sub>-1</sub> species coordinated with two pyridine N, amine N, and amide O, and a hydroxide anion (OH<sup>-</sup>) as a major species. The distribution of Zn(OH)LH<sub>-1</sub> species is consistent with the intensity of longer-wavelength emission. This suggests that Zn(OH)LH<sub>-1</sub> is the emitting species for the longerwavelength emission observed at neutral pH upon Zn<sup>2+</sup> addition (Figure 2).

**Coordination and Fluorescence Properties of Cd Complexes.** Figure 1c shows the data obtained with 1 equiv of  $Cd^{2+}$ . As also for the Zn complex (Figure 1b), shorter- and longer-wavelength emissions appear at lower and higher pH, wavelength emission. In contrast, for the Zn complex (Figure 1b), the OH<sup>-</sup>-coordinated Zn(OH)LH<sub>-1</sub> species exists at this pH range and shows a longer-wavelength emission. This suggests that, at neutral pH, the structure difference for CdLH<sub>-1</sub> and Zn(OH)LH<sub>-1</sub> results in different-wavelength fluorescence (Figure 2).

At pH >9 (Figure 1c),  $OH^-$  is coordinated to the Cd center, as is the case for Zn complex, and the  $Cd(OH)LH_{-1}$  species shows a longer-wavelength emission. This suggests that OHcoordination to the metal center creates a longer-wavelength emission for both Zn and Cd complexes, although mass spectrometric analysis of the solutions containing L with Zn<sup>2+</sup> or Cd<sup>2+</sup> does not show ions assigned to the OH<sup>-</sup>-coordinated species due to the instability of these complexes. At neutral pH, OH<sup>-</sup> coordination to the Zn center occurs, thus showing a longer-wavelength emission. In contrast, OH<sup>-</sup> coordination to the Cd center does not occur at neutral pH and shows a shorter-wavelength emission. It is well-known that the electrostatic interaction between the metal cation and the ligand molecules is strengthened by the decrease in ionic radius of metal cations.<sup>35</sup> The ionic radius of  $Zn^{2+}$  (0.74 Å) is smaller than that of Cd<sup>2+</sup> (0.92 Å).<sup>36</sup> The stronger coordination of OH<sup>-</sup> with Zn<sup>2+</sup> therefore probably results in OH<sup>-</sup> coordination to  $Zn^{2+}$  at lower pH.

The above findings indicate that, as shown in Scheme 5, both Zn and Cd complexes show similar coordination sequence, although OH<sup>-</sup> coordination occurs at different pH. The similar sequences are supported by nanosecond time-resolved fluorescence decay measurements at different pH (Figure S18, Supporting Information). As summarized in Table 2, the fluorescence decay time ( $\tau_F$ ) of ZnL species (0.9 ns) is similar to that of CdL (0.7 ns). In addition, the decay time of ZnLH<sub>-1</sub> (2.1 ns) is similar to that of CdLH<sub>-1</sub> (2.2 ns), and the decay time of Zn(OH)LH<sub>-1</sub> (2.7 ns) is also similar to that of Cd(OH)LH<sub>-1</sub> (2.8 ns). These data clearly support the similar coordination sequence for Zn and Cd complexes. These findings again suggest that the OH<sup>-</sup> coordination to the metal center is the crucial factor for different fluorescence spectra upon addition of Zn<sup>2+</sup> and Cd<sup>2+</sup> at neutral pH (Figure 2).

Effect of OH<sup>-</sup> Coordination on Fluorescence. Mechanism for the formation of longer-wavelength emission upon coordination of OH<sup>-</sup> to the metal center must be clarified. Ab initio calculation was performed with the Gaussian 03 program<sup>37</sup> using the time-dependent density functional theory (TDDFT), where the polarizable continuum model (PCM) was employed with water as a solvent to capture the solvent

Table 2. Absorption and Emission Properties of Zn and Cd Complexes and Their Electronic Excitation Properties Determined by TDDFT Calculations

species	$\tau_{\rm F}/{ m ns}^a$	$\lambda_{ m abs,max}/ m nm^b$		main orbital transition	CIC <sup>c</sup>	E/eV	$\lambda/nm$	f
ZnL	0.9	324	$S_0 \rightarrow S_1$	$HOMO \rightarrow LUMO$	0.65217	3.6391	340.70	0.0730
$ZnLH_{-1}$	2.1	323	$S_0 \rightarrow S_1$	$HOMO \rightarrow LUMO$	0.65950	3.7404	331.47	0.6031
$Zn(OH)LH_{-1}$	2.7	323	$S_0 \rightarrow S_1$	$HOMO \rightarrow LUMO$	0.65195	3.6139	343.08	0.7400
CdL	0.7	325	$S_0 \rightarrow S_1$	$HOMO \rightarrow LUMO$	0.65236	3.5642	347.86	0.1163
$CdLH_{-1}$	2.2	325	$S_0 \rightarrow S_1$	$HOMO \rightarrow LUMO$	0.65699	3.6731	337.54	0.6767
$Cd(OH)LH_{-1}$	2.8	327	$S_0 \rightarrow S_1$	$HOMO \rightarrow LUMO$	0.64721	3.4983	354.41	0.6016

<sup>a</sup>Fluorescence decay time determined by nanosecond time-resolved analysis (Figure S18, Supporting Information). <sup>b</sup>Maximum wavelengths for the absorption band of respective species (Figure S19, Supporting Information). <sup>c</sup>CI expansion coefficients for the main orbital transitions.

stabilization effects on the molecules. Scheme 6 shows the optimized structures of  $Zn(OH)LH_{-1}$  and  $CdLH_{-1}$  complexes.

Scheme 6. Optimized Structures for the  $Zn(OH)LH_{-1}$  and  $CdLH_{-1}$  Complexes<sup>*a*</sup>



<sup>*a*</sup>Gray, blue, red, yellow, and orange atoms of the molecular framework indicate the C, N, O, Cd, and Zn atoms.

The H<sup>c</sup> protons of these complexes are located above the pyridine ring. The distances between H<sup>c</sup> proton and the pyridine N for the respective complexes are determined to be 5.62 and 5.97 Å, respectively. As reported,<sup>38</sup> protons located above aromatic ring is magnetically shielded by the ring current

effect, and the effective shielding distance for pyridine ring is ca. 8.8 Å. This suggests that the H<sup>c</sup> protons of  $Zn(OH)LH_{-1}$  and CdLH<sub>-1</sub> complexes lie within the shielding zone of pyridine ring. As shown in Figure 4, <sup>1</sup>H NMR analysis revealed that the H<sup>c</sup> protons of these complexes shift upfield as compared to the free ligand. The upfield shift of H<sup>c</sup> proton is therefore attributable to the ring current effect by the pyridine aromatic ring. Table 2 summarizes the main orbital transition of the respective Zn and Cd complexes. The lowest singlet electronic transitions of all Zn and Cd complexes are mainly contributed by HOMO  $\rightarrow$  LUMO transition. The calculated transition energies of all species are similar to  $\lambda_{max}$  of the absorption spectra (Figure S19, Supporting Information). The above findings clearly suggest that the calculated results precisely represent the coordination structures and electronic properties of Zn and Cd complexes.

The  $\pi$ -electrons of HOMO for all complexes are localized on the coumarin moiety. In contrast,  $\pi$ -electrons of LUMO for CdL, CdLH<sub>-1</sub>, ZnL, and ZnLH<sub>-1</sub> species, which do not coordinate with OH<sup>-</sup>, are distributed over the coumarin and pyridine moieties. This indicates that intramolecular charge transfer (ICT) from the coumarin to pyridine moieties occurs by the electronic excitation. In contrast,  $\pi$ -electrons of LUMO for OH<sup>-</sup>-coordinated Zn(OH)LH<sub>-1</sub> and Cd(OH)LH<sub>-1</sub> species are localized on the coumarin moiety. This indicates that ICT from the coumarin to pyridine moiety does not occur. As reported,<sup>39</sup> fluorescence wavelengths for coumarin derivatives





"Gray, blue, red, yellow and orange atoms of the molecular framework indicate the C, N, O, Cd, and Zn atoms. Green and deep red parts on molecular orbitals refer to the different phases of the molecular wave functions, where the isovalue is 0.02 au.

strongly depend on their electron densities; increased electron density creates a longer-wavelength fluorescence. The electron densities of coumarin moieties for the excited-state CdL, CdLH<sub>-1</sub>, ZnL, and ZnLH<sub>-1</sub> species are decreased by ICT to the pyridine moieties. This may result in shorter-wavelength emission. In contrast, the OH<sup>-</sup> coordination to the metal centers suppresses ICT and creates a longer-wavelength emission.

The  $\pi$ -electron distribution on the pyridine moieties of LUMO for CdL, CdLH<sub>-1</sub>, ZnL, and ZnLH<sub>-1</sub> species are due to the stabilization of  $\pi$ -electrons on the pyridine moieties by the cation—pyridine N coordination.<sup>40</sup> The OH<sup>-</sup> coordination to the metal center weakens the cation—pyridine N coordination and results in the decrease in electron density of the pyridine moieties. The average cation—pyridine N distances for the ZnL and ZnLH<sub>-1</sub> species, determined by DFT calculation, are 2.16 and 2.12 Å, respectively; however, Zn(OH)LH<sub>-1</sub> has a longer distance (2.21 Å). In addition, the distance for Cd(OH)LH<sub>-1</sub> (2.44 Å) is also longer than that for CdL and CdLH<sub>-1</sub> (2.40 and 2.34 Å). These data suggest that the OH<sup>-</sup> coordination to the metal centers indeed weakens the cation—pyridine N coordination. This destabilizes the  $\pi$ -electrons on the pyridine moieties and results in the decrease in electron density.

## CONCLUSION

We studied the fluorescence behaviors of a coumarin–amide– dipicolylamine linkage (L) for metal cations in water. The molecule dissolved in water at neutral pH shows selective fluorescence enhancement upon addition of Zn<sup>2+</sup> and Cd<sup>2+</sup> at 437 and 386 nm, respectively, whereas other cations show almost no enhancement. The different fluorescence wavelengths for the Zn and Cd complexes are due to their different coordination structures. Both Zn and Cd complexes involve the coordination with two pyridine N, amine N, and amide O, but the Zn center is coordinated also with OH<sup>-</sup>. The OH<sup>-</sup> coordination to the Zn center leads to a localization of  $\pi$ electrons on the coumarin moiety. This increases the electron density on the coumarin moiety and results in longerwavelength fluorescence.

## EXPERIMENTAL METHODS

**Materials.** All reagents were supplied from Wako, Sigma-Aldrich, and Tokyo Kasei and used without further purification. Perchlorate (Hg<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Cr<sup>3+</sup>, Mn<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>), nitrate (Ni<sup>2+</sup>, Co<sup>2+</sup>), and tetrafluoroborate (Ag<sup>+</sup>) salts were used as the metal cation source. Water was purified by the Milli-Q system. DPA was synthesized according to literature procedure.<sup>25</sup> 7-[(2-Chloroacetyl)amino]-4-methylcoumarin (1) and 7-[(2-(di-2-picolylamino)acetyl)amino]-4methylcoumarin (L) were synthesized as follows.

**Synthesis of 1.** 7-Amino-4-methylcoumarin (149 mg, 0.85 mmol) and chloroacetyl chloride (140 μL, 1.76 mmol) were refluxed in ethyl acetate (4 mL) for 2 h under N<sub>2</sub>. The resultant was recovered by filtration, affording 1 as a white solid (156 mg, 73%). Mp: 278.8–279.5 °C.  $\lambda_{max}$  (water, pH 7.3): 325 nm ( $\epsilon$  14011 M<sup>-1</sup> cm<sup>-1</sup>). <sup>1</sup>H NMR (400 MHz, DMSO, TMS):  $\delta$  (ppm) = 10.71 (s, 1H), 7.73–7.75 (m, 2H), 7.50 (dd, *J* = 1.83 Hz, 8.70 Hz, 1H), 6.28 (d, *J* = 0.92 Hz, 1H), 4.32 (s, 2H), 2.41 (d, *J* = 1.37 Hz, 3H). <sup>13</sup>C NMR (100 MHz, DMSO, TMS):  $\delta$  (ppm) = 165.24, 159.81, 153.51, 152.91, 141.62, 125.97, 115.42, 115.23, 112.51, 105.83, 43.48, 17.87. FAB-MS: *m*/*z* calcd for C<sub>12</sub>H<sub>10</sub>NO<sub>3</sub>Cl, 251.03; found, 252.15 [M + H]<sup>+</sup>.

Synthesis of L. 1 (74 mg, 0.29 mmol), DPA (70.1 mg, 0.35 mmol), DIPEA (0.5 mL), and KI (32.3 mg, 0.19 mmol) were added to MeCN (50 mL), and the mixture was refluxed for 12 h under N2. The resultant was concentrated by evaporation, and the obtained brown oil was purified by silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 20/1), affording L as a yellow solid (78.3 mg, 65.1%). Mp: 112.3-112.8 °C. λ<sub>max</sub> (water, pH 7.3): 326 nm ( $\varepsilon$  15391 M<sup>-1</sup> cm<sup>-1</sup>). <sup>1</sup>H NMR (400 MHz, DMSO, TMS):  $\delta$  (ppm) = 10.97 (s, 1H), 8.58–8.60 (m, 2H), 7.83 (d, J = 1.83 Hz, 1H), 7.74-7.79 (m, 3H), 7.58 (dd, J = 2.29 Hz, 8.70 Hz, 1H), 7.45 (d, J = 7.79 Hz, 2H), 7.27-7.30 (m, 2H), 6.27 (d, J = 1.37 Hz, 1H), 3.95 (s, 4H), 3.52 (s, 2H),2.41 (d, I = 0.92 Hz, 3H). <sup>13</sup>C NMR (100 MHz, DMSO, TMS):  $\delta$  (ppm) = 170.19, 159.91, 158.30, 153.64, 152.97, 148.90, 141.87, 136.64, 125.92, 123.05, 122.36, 115.11, 115.02, 112.20, 105.42, 59.34, 57.83, 17.89. FAB-MS: m/z calcd for  $C_{24}H_{22}N_4O_3$ ; 414.17; found, 415.17  $[M + H]^+$ .

**Spectroscopic Analysis.** Absorption spectra were measured on an UV–vis photodiode-array spectrophotometer (Shimadzu; Multispec-1500) equipped with a temperature controller (S-1700).<sup>41</sup> Steady-state fluorescence spectra were measured on a JASCO FP-6500 fluorescence spectrophotometer. The fluorescence lifetime was measured on a PTI-3000 apparatus (Photon Technology International) at 298  $\pm$  1 K using a Xe nanoflash lamp filled with N<sub>2</sub>.<sup>42,43</sup> <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained by a JEOL JNM-AL400 spectrometer using TMS as standard. FAB and ESI-MS analysis were performed on a JEOL-JMS 700 mass spectrometer. IR spectra were recorded at room temperature using a FTIR-610 spectrometer (JASCO Corp.) using a liquid sample cell with a CaF<sub>2</sub> window.

Potentiometric Titration. The titrations were performed on a COMTITE-550 potentiometric automatic titrator (Hiranuma Co, Ltd.) with a glass electrode GE-101.44,45 Aqueous solution containing L with or without metal cations was kept under  $N_2$  with an ionic strength of I = 0.15 M (NaCl) at 298 K. Titration was done at 298  $\pm$  1 K using an aqueous NaOH solution. The program HYPERQUAD was used for determination of protonation and stability constants.<sup>46</sup> The  $K_w$  $(=[H^+]\cdot[OH^-])$  value used was  $10^{-14}$  (298 K). The stability constants for Zn hydroxide (298 K) were  $\log K(Zn(OH)/$  $Zn \cdot OH$  = -9.25,  $\log K(Zn(OH)_2/Zn \cdot 2OH)$  = -17.19,  $\log$  $K(Zn(OH)_3/Zn\cdot 3OH) = -28.40, \log K(Zn(OH)_4/Zn\cdot 4OH) =$ -40.63, log K(Zn<sub>2</sub>(OH)/2Zn·OH) = -8.71, and log  $K(Zn_2(OH)_6/2Zn\cdot 6OH) = -57.51$ , respectively. The stability constants for Cd hydroxide (298 K) were  $\log K(Cd(OH)/$  $Cd \cdot OH$  = -10.37,  $\log K(Cd(OH)_2/Cd \cdot 2OH)$  = -20.64,  $\log$  $K(Cd(OH)_{3}/Cd\cdot 3OH) = -33.30, \log K(Cd(OH)_{4}/Cd\cdot 4OH)$ = -46.78,  $\log K(Cd_2(OH)/2Cd \cdot OH) = -9.10$ , and  $\log K(Cd_2(OH)/2Cd \cdot OH) = -9.10$ , and  $\log K(Cd_2(OH)/2Cd \cdot OH) = -9.10$ , and  $\log K(Cd_2(OH)/2Cd \cdot OH) = -9.10$ ,  $\log K(Cd_2(OH)/2Cd \cdot OH)$ ,  $\log K(Cd_2(OH)/2Cd \cdot OH) = -9.10$ ,  $\log K(Cd_2(OH)/2Cd \cdot OH)$ ,  $\log K(OH)/2Cd \cdot O$  $K(Cd_4(OH)_4/4Cd\cdot 4OH) = -32.28$ , respectively.<sup>47</sup>

**Computational Details.** Ab initio calculations were carried out with the Gaussian 03 program.<sup>37</sup> Geometry optimization was performed with DFT using the B3LYP function. The Zn and Cd complexes were calculated using the 6-31G\* basis set for all atoms except for Zn and Cd, for which the LANL2DZ basis set with effective core potential was used. The electronic excitation energies and oscillator strengths were calculated with TDDFT at the same level of optimization using PCM with water as a solvent. Cartesian coordinates for respective complexes are summarized in the end of Supporting Information.

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#### **S** Supporting Information

Compound characterization data (<sup>1</sup>H NMR, <sup>13</sup>C NMR, FAB-MS, Figures S1–S6), time dependence for fluorescence enhancement (Figure S7), effect of other metal cations (fluorescence spectra, Figures S8 and S9), Job's plot (Figure S10), ESI-MS charts (Figures S11 and 12), fluorescence titration data (Figure S13), gCOSY charts (Figures S14–S16), IR spectra (Figure S17), fluorescence decay data (Figure S18), absorption spectra (Figure S19), and Cartesian coordinates for complexes. This material (PDF) is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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