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A Simple Fluorescent Chemosensor for Mg^{2+} Based on C=N Isomerization with Highly Selectivity and Sensitivity

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A simple fluorescent chemosensor based on naphthalene has been prepared. It was shown to be selective for Mg^{2+} in acetonitrile based on C=N isomerization. The free ligand showed quite weak fluorescence emission due to the isomerization of C=N double bond in the excited state, however, after addition of Mg^{2+}, fluorescence emission results in a prominent fluorescence enhancement.

Mg^{2+} ion is one of the most abundant divalent ions and plays crucial roles in living systems, such as cell proliferation, cell death, the modulation of signal transduction, various transporters, and ion channels.[1–6] Hence, monitoring the Mg^{2+} concentration is very important and highly demanding. As we all know, fluorescent signaling is one of the first choices due to its high detection sensitivity and intrinsic operation simplicity. Designing fluoroionophores for Mg^{2+} has drawn much recent attention, but only a few signaling systems have been reported, including β-diketone,[7–12] diaza-18-crown-6,[13] benzo-15-crown-5,[14] calix[4]arene,[15] a porphyrin-related macrocycle,[16] and Schiff bases (imines).[17,18] Among these systems, Schiff bases with an unbridged C=N structure are often nonfluorescent due to C=N isomerization, but this may be inhibited by complexation with special ions resulting in high-intensity emission.[17,19] Based on this point, we have designed a simple compound named [(2-hydroxynaphthalen-1-yl)methylideneamino]oxazolidin-2-one (L),[20] in a one-step synthesis: Naphthalene was chosen as a fluorophore due to its charateristic photophysical properties and competitive stability in the environment. 3-Amino-2-oxazolidinone acts as an additional chelating moiety, and both parts are linked by a C=N bond to form a potential three coordination site for metal ions and may recognize specific metal ion for optical sensing.

Synthesis of L was readily achieved in 90% yield by 2-hydroxy-1-naphthaldehyde with 3-amino-2-oxazolidinone in ethanol under reflux for 3 h. The product was filtered and washed with ethanol (see Supporting Information).[23] IR(KBr pellet, cm^{-1}): 3456 (νO–H), 1759 (νC=N), 1622, 1414, 1250, 1225, 1109, 1026, 818, 748. The structure of L was characterized by X-ray crystallographic analysis.[21] X-ray crystallographic study reveals that the asymmetric unit consists of two independent molecules (Figure 1). The potential binding sites (O1, N1, and O2) and (O4, N3, and O5) lie on one side in the molecule, which can give three coordinated sites or form an appropriate cavity for some metal cations.

Fluorescence spectra were measured on a Cary Eclipse Fluorescence spectrophotometer at 25 °C. The concentration of the fluorescent reagent was 2×10^{-5} mol dm^{-3} in purified acetonitrile. Chloride salts and silver nitrate were used as metal ions.

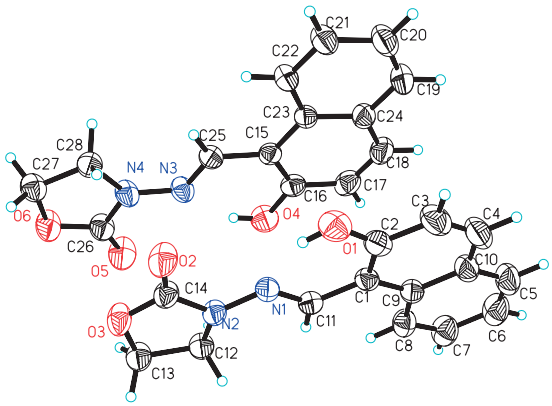


Figure 1. Crystal structure of L.

The optical properties of L were investigated in acetonitrile at 25 °C, and compound L showed two main absorption bands at 318 ($\varepsilon = 17923\ M^{-1}\,cm^{-1}$) and 349 nm ($\varepsilon = 13508\ M^{-1}\,cm^{-1}$) (Figure S1).[23] Compound L alone had a weak fluorescence emission at 445 nm when it was excited at 395 nm. The cation recognition behavior of L was comfirmed by screening alkali (Na^+ and K^+), alkaline earth (Ca^{2+}, Mg^{2+}, and Sr^{2+}), and transition-metal ions (Mn^{2+}, Ni^{2+}, Fe^{3+}, Co^{2+}, Cu^{2+}, Cd^{2+}, Ag^+, Pb^{2+}, and Hg^{2+}) (Figure 2). It can be clearly observed that upon addition of a 20 μM solution of Mg^{2+} to a solution of L resulted in a great enhancement of fluorescence emission (ca. 110-fold), Fluorescence quantum yield (Φ_f) of free L in acetonitrile is 0.001, wherea it reaches 0.114 when L binds with Mg^{2+} (quinine sulfate in 0.5 M H_2SO_4 as a standard, $\Phi_f = 0.55$), while Zn^{2+} and Ba^{2+} have a slight increase and other metal ions have no such significant change in the fluorescence spectrum upon addition of a 100 μM solution.

Fluorescence monitoring of the Mg^{2+} addition was also performed by using a 20 μM solution of L in acetonitrile at 25 °C (Figure 3). The results showed that L was a weak emission, upon addition of Mg^{2+} ions, the fluorescence intensity of L was increased and saturated at 25 μM. This is due to the C=N isomerization inhibited upon the coordination of L to Mg^{2+}.[17,19] Binding analysis was taken from the method of continuous variations (Job plot). This approach reveals that the relative L–Mg^{2+} complex concentration clearly approaches a maximum when the molar function of Mg^{2+} $\{[Mg^{2+}]/([L] + [Mg^{2+}])\} = 0.33$ (Figure 4), suggesting the formation of a 2:1 stoichiometric complex between L and Mg^{2+}. Using the equation: $[G]_{tot} = \alpha/2K_{21}(1-\alpha)^2[H]_{tot} + \alpha[H]_{tot}/2$, where $[G]_{tot}$ is total concentration of Mg^{2+}, $[H]_{tot}$ is the total concentration of L, $\alpha = (I - I_0)/(I_i - I_0)$ with I being the fluorescent intensity at a particular Mg^{2+} concentration while I_0 and I_i are the intensities at zero and

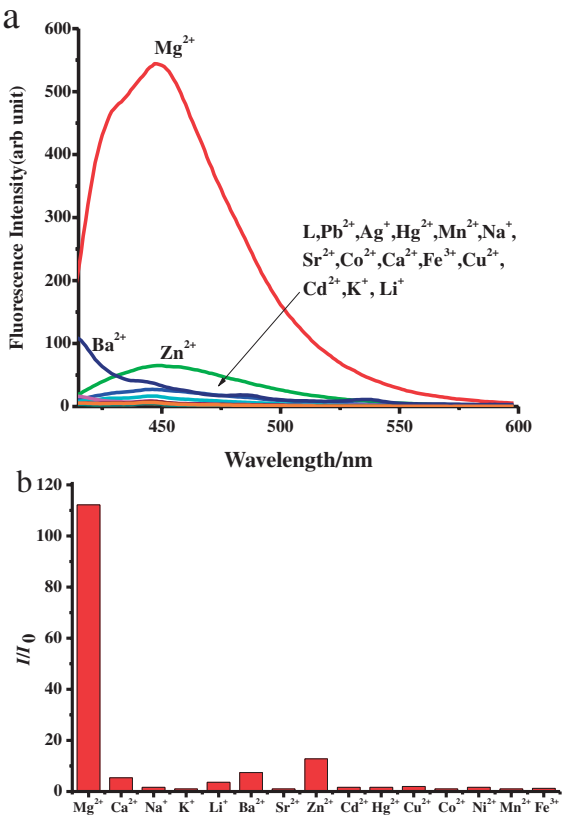


Figure 2. (a) Fluorescence-spectral changes of L and (b) fluorescence ratio I/I_0 of L upon the addition of various metal ions in acetonitrile at 25 °C. [L] = 20 μM, [Mg^{2+}] = 20 μM, [other metal ions] = 100 μM.

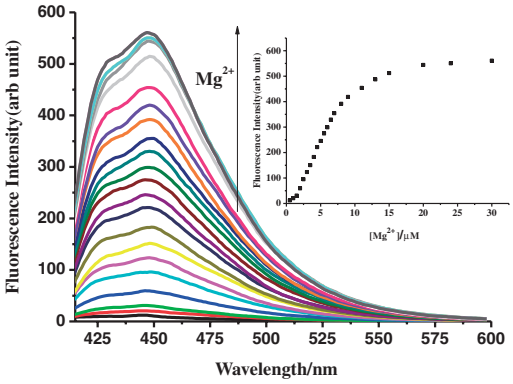


Figure 3. Fluorescence spectra of L (20 μM) upon the addition of increasing amounts of Mg(II) ions (0–30 μM) in acetonitrile at 25 °C. Inset: Changes in fluorescent intensity of L upon the addition of increasing [Mg^{2+}].

infinite Mg^{2+} concentrations,[18,22] respectively, the association constant K_{21} was determined as $2.4 \times 10^{10}\,M^{-2}$, which revealed that strong complexation was formed between L with Mg^{2+}, indicating the coordinate moiety of L matches perfectly with Mg(II) instead of other ions (Table S1).[23] It is probably due to several combined influences cooperating to achieve the unique selectivity for Mg^{2+}, such as suitable coordination geometry

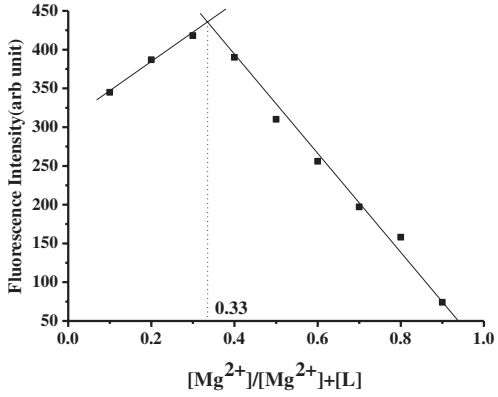
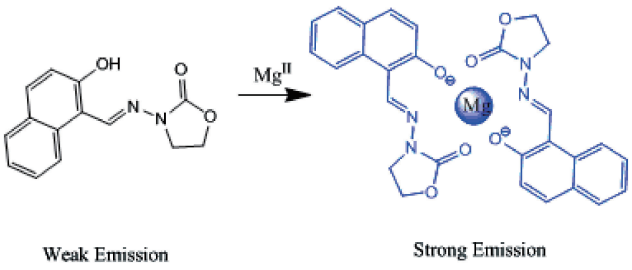


Figure 4. Job's plots according to the method for continuous variations. The total concentration of L and Mg^{2+} is 20 μM.



Scheme 1. Schematic representation of Mg^{2+}-induced fluorescence.

conformation of the receptor, appropriate ion radius, and sufficient binding energy of the Mg^{2+} ion. Combined with the crystal structure of L, a sixth coordinated complex maybe formed by Mg(II) binding at the NO_2 sites with two L moleculas in the excited states (Scheme 1).

In conclusion, we have synthesized a simple fluorescent indicator L, which displayed high selectivity to Mg^{2+} in an efficient way. It is an excellent example of a fluorescent sensor which can distinguish Mg^{2+} from Ca^{2+}. L and Mg^{2+} form a 2:1 stoichiometric complex with high association constant K_{21} ($2.4 \times 10^{10}\,M^{-2}$). When L bonded with Mg^{2+}, the C=N isomerization was eliminated, thus it induced an enhancement in the fluorescence intensity of L. We believe that it can be extended to other sensing systems for recognition of different species. The present work also provides a novel concept for design of fluorescent probes/chemosensors with remarkable changes in fluorescence. Investigations along these lines for the development of more sophisticated systems based on the same mechanism for recognition of cations, especially in aqueous solution, are in progress in our laboratory.

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20 Crystallographic date reported in this paper has been deposited with the Cambridge Crystallographic Date Center, CCDC No. 790129 for L. Copies of these information may be obtained free of charge from the Director, CCDC, 12, Union Road, Cambridge, CB2 1EZ, U.K. (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).
21 Crystal structure determination of the complex. A crystal ($0.5 \times 0.4 \times 0.4\,\mathrm{mm}^3$) was mounted on a SMART CCD equipped with graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. The $T_{max} = 0.961$ and $T_{min} = 0.954$. The relevant crystal data and structural parameters are: fw 256.26; space group $P2(1)/c$; $a = 14.3488(5)$, $b = 7.0816(3)$, $c = 24.3706(8)$ Å; $V = 2472.04(16)$ Å^3; $Z = 8$; $\rho = 1.377\,\mathrm{g\,cm^{-3}}$; μ (Mo Kα) $= 0.099\,\mathrm{cm^{-1}}$, the intensities were collected at 293(2) K. The final R_1 ($R_1 = \sum||F_o| - |F_c||/\sum|F_o|$) value was 0.0333, wR_2 ($[\sum(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$) value was 0.0856.
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23 Supporting Information is available online electronically on CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

