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A Highly Selective Fluorescent Sensor for Distinguishing Cadmium from Zinc Ions Based on a Quinoline Platform

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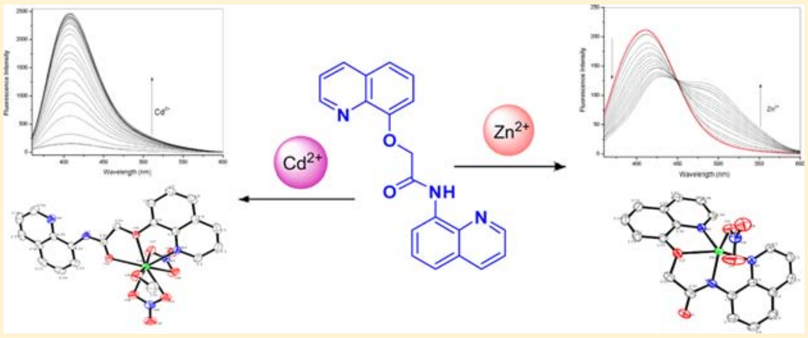
Supporting Information



ABSTRACT: A fluorescent sensor, *N*-(quinolin-8-yl)-2-(quinolin-8-yloxy)acetamide (**HL**), based on 8-aminoquinoline and 8-hydroxyquinoline platforms has been synthesized. This sensor displays high selectivity and sensitive fluorescence enhancement to Cd^{2+} in ethanol. Moreover, sensor **HL** can distinguish Cd^{2+} from Zn^{2+} via two different sensing mechanisms (photoinduced electron transfer for Cd^{2+}; internal charge transfer for Zn^{2+}). The composition of the complex Cd^{2+}/**HL** or Zn^{2+}/**L**$^-$ has been found to be 1:1, based on the fluorescence/absorption titration and further confirmed by X-ray crystallography.

■ INTRODUCTION

Cadmium, an important natural element, is widely used in many processes such as electroplating, metallurgy, agriculture, war industry, etc.[1] However, it is listed by the U.S. Environmental Protection Agency as one of 126 priority pollutants, and its half-life in humans is estimated to be between 15 and 20 years.[2] Humans are exposed to Cd^{2+} through the ingestion of contaminated food or water and the inhalation of cigarette smoke.[3] There have been many reports on the toxicity of Cd^{2+} to procreation, kidneys, nervous system, and tissues, consequently resulting in renal dysfunction, calcium metabolism disorders, and an increased incidence of certain forms of cancers.[4] Because cadmium can accumulate in the food chain, it is desirable to develop some analytical methods for detecting and monitoring cadmium in the environment or living cells.

In fact, a great number of fluorescent sensors have been designed to detect different kinds of heavy toxic metal ions because of their simplicity, high sensitivity, and real-time detection.[5] However, there are only a few cadmium-ion fluorescent sensors that have been reported.[6,7] More importantly, the greatest challenge for detecting Cd^{2+} comes from the interference of other transition-metal ions, in particular Zn^{2+}. They are in the same group of the periodic table and have similar properties. Therefore, similar fluorescence changes including the change of intensity and the shift of wavelengths are usually observed when Zn^{2+} and Cd^{2+} are coordinated with fluorescent sensors.[8] Thus, there is a great need for developing Cd^{2+}-selective sensors that can distinguish Cd^{2+} from Zn^{2+} with high sensitivity and selectivity.

8-Aminoquinoline (8-AQ) or 8-hydroxyquinoline (8-HQ) have been used traditionally for the quantitative chemical assay of Zn^{2+}, Cd^{2+}, or other transition-metal ions,[9,10] which are based on either a photoinduced electron-transfer (PET) or an internal charge-transfer (ICT) mechanism.[11,12] For a sensor based on the quinoline platform, fluorescence is quenched via PET from the amine group to the excited singlet state of quinoline. Upon complexation with a suitable metal ion, a large chelation-enhanced-fluorescence (CHEF) effect is observed because chelation abrogates the PET process. Meanwhile, the ICT mechanism[13] is widely exploited for ion sensing[14] because of the advantages of spectral shifts and quantitative detection. When a fluorophore contains an electron-donating group (often an amino group) conjugating to a fluorophore, it undergoes ICT from the donor to the fluorophore upon light excitation. If a cation promotes the electron-donating character of the electron-donating group, the absorption and fluorescence spectra should be red-shifted. Conversely, if the electron-donating character of the electron-donating group is reduced, blue shifts of both the absorption and fluorescence spectra are expected. Thus, the strategy to design one sensor that can simultaneously respond

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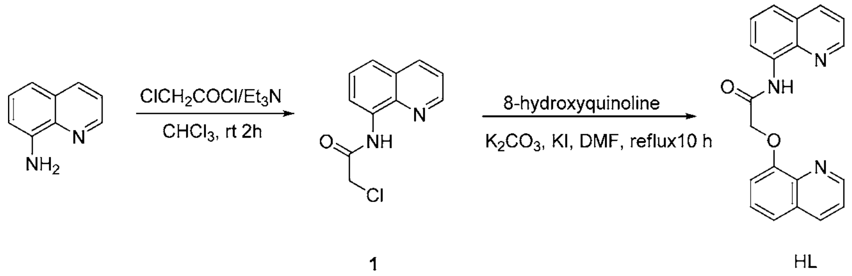
Scheme 1. Synthesis of HL



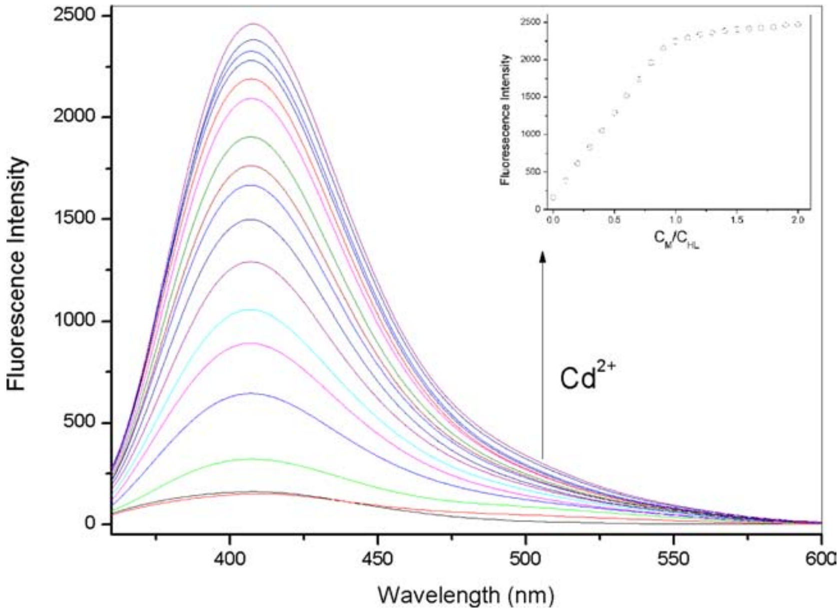


Figure 1. Fluorescence emission spectra of **HL** upon the addition of $Cd(NO_3)_2(H_2O)_6$ in ethanol. λ_{ex} = 329 nm at room temperature ([**HL**] = 0.10 mM; [Cd^{2+}] = 0, 0.010, 0.020, 0.030, 0.040, 0.050, 0.060, 0.070, 0.080, 0.090, 0.10, 0.20, 0.30, 0.40, 0.50, and 0.60 mM). (Inset) Corresponding $Cd(NO_3)_2(H_2O)_6$ titration profile according to the fluorescence intensity, indicating 1:1 stoichiometry for Cd^{2+}/**HL**.

to different metal ions via different mechanisms should be attractive and powerful for ion sensing.

We recently reported some fluorescent sensors based on 8-HQ or 8-AQ.[15,6f] These results encouraged us to improve the sensing properties by combining these two motifs. We expected that the combination of these two quinoline platforms would generate a novel sensor with high selectivity and sensitivity for cadmium or other metal ions. Herein, we present our design and synthesis of sensor **HL**, based on 8-AQ bearing the 8-HQ moiety, which is able to distinguish cadmium ions from zinc ions in ethanol. When binding Cd^{2+}, **HL** shows a bright “switch-on” state based on the PET mechanism. In contrast, upon binding Zn^{2+}, **HL** shows a distinct emission red shift based on the ICT mechanism with slight emission enhancements. These provide explicit information by absorption and fluorescence emission changes upon metal complexation.

■ EXPERIMENTAL SECTION

Materials and Methods. Absolute anhydrous ethanol was used in spectroscopic studies. All other reagents and solvents employed for synthesis were commercially available and were used as received without further purification. Melting points were determined on a Kofler apparatus. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured on a Bruker DRX 400 spectrometer in a $CDCl_3$ solution with tetramethylsilane [$Si(CH_3)_4$] as the internal standard. Electrospray ionization time-of-flight mass spectrometry (MS) spectra were measured on a Mariner mass spectrometer. Absorption spectra were recorded using a Varian Cary 100 spectrophotometer, and fluorescence measurements were made on a Hitachi F-4500 spectrofluorometer equipped with a quartz cuvette of 1.0 cm path length with a xenon lamp as the excitation source. Excitation and emission slits of 5.0 nm were used for the measurements of fluorescence. Elemental analyses were conducted using an Elemental Vario EL. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet FT-170SX instrument using KBr disks in the 400−4000 cm^{-1} region. Fluorescent quantum yields were determined by an absolute method using an integrating sphere on an Edinburgh Instrument FLS920.[16] All of the measurements were performed at room temperature unless otherwise stated. The apparent stability constants (K_s) of **HL** with Cd^{2+} and Zn^{2+} were determined using the nonlinear least-squares analysis based on a 1:1 complex expression:[17]

$$\frac{F}{F_0} = 1 + \left(\frac{F_{max}}{2F_0} - \frac{1}{2}\right)\left[1 + \frac{C_M}{C_L} + \frac{1}{K_sC_L} - \sqrt{\left(1 + \frac{C_M}{C_L} + \frac{1}{K_sC_L}\right)^2 - 4\frac{C_M}{C_L}}\right]$$

where F and F_0 are the fluorescence intensities of ligand **HL** in the presence and absence of Cd^{2+} or Zn^{2+}, C_M and C_L are the concentrations of Cd^{2+} or Zn^{2+} and ligand **HL**, and K_s is the stability constant.

Synthesis of HL. *Preparation of 2-Chloro-N-(quinol-8-yl)-acetamide (1).* 2-Chloroacetyl chloride (5.31 mL) was dissolved in chloroform (5 mL) and then added dropwise to a cooled stirred solution of 8-aminoquinoline (2.88 g, 20 mmol) and Et_3N (3.0 mL) in chloroform (10 mL) within 1 h. After being stirred for 2 h at room temperature, the mixture was removed under reduced pressure to obtain a white solid, which was purified by silica gel column chromatography using dichloromethane as the eluent to afford **1**. Yield: 2.532 g (79.9%). Mp: 132.8−134.2 °C. Anal. Calcd for $C_{11}H_9N_2OCl$: C, 59.88; H, 4.11; N, 12.70. Found: C, 59.84; H, 3.92; N, 12.64. ^{1}HNMR ($CDCl_3$, 400 MHz, $Si(CH_3)_4$): δ 10.82 (NHCO, s, 1H), 8.78 (d, 1H), 8.70 (d, 1H), 8.10 (d, 1H), 7.47 (m, 2H), 7.39 (m, 1H), 4.32 ($COCH_2$, s, 2H). ^{13} C NMR ($CDCl_3$, 100 MHz): δ 43.22, 116.51, 121.57, 122.38, 126.92, 127.69, 133.25, 136.10, 138.78, 148.41, 164.29. FT-IR (KBr pellet, cm^{-1}): 3434 (br), 3323 (m), 1676 (s), 1539 (vs), 1485 (m), 1424 (m), 1390 (w), 1326 (m), 1272 (w) (br, broad; w, weak; m, medium; s, strong; vs, very strong); MS: m/z 221.75 $[(M + 1)^+]$.

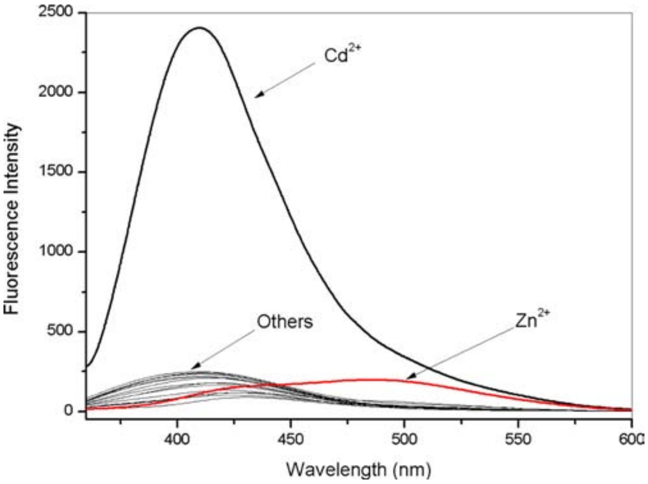


Figure 2. Fluorescence emission spectra of **HL** in the presence of different ions such as Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cu^{2+}, Co^{2+}, Al^{3+}, Cr^{3+}, Ni^{2+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, Cd^{2+}, Mn^{2+}, Hg^{2+}, and Pb^{2+} (metal ions as their NO^{3-} salts) in ethanol. λ_{ex} = 329 nm, [**HL**] = 0.1 mM, and $[M^{n+}]$ = 0.1 mM.

*Preparation of N-(Quinolin-8-yl)-2-(quinolin-8-yloxy)acetamide (**HL**).* **1** (1.11 g, 5 mmol), 8-hydroxyquinoline (8-HQ; 726 mg, 5 mmol), K_2CO_3 (891 mg, 6.5 mmol), and potassium iodide (10 mg) were added to *N,N*-dimethylformamide (30 mL). After stirring at reflux for 10 h, the mixture was cooled to room temperature and removed under reduced pressure to obtain a yellow oil, which was purified by a silica gel column chromatography using chloroform/methanol (10:1, v/v) as the eluent to afford the ligand **HL** (Scheme 1). Yield: 1.43 g (86.7%). Mp: 161.7−162.4 °C. Anal. Calcd for $C_{20}H_{15}N_3O_2$: C, 72.94; H, 4.49; N, 12.76. Found: C, 72.74; H, 4.38; N, 12.52. ^{1}H NMR ($CDCl_3$, 400 MHz, $Si(CH_3)_4$): δ 11.25 (NHCO, s, 1H), 9.07 (m, 1H), 8.82 (m, 1H), 8.69 (m, 1H), 8.18 (d, 1H), 8.11 (d, 1H), 7.57−7.23 (m, 7H), 5.08 ($COCH_2$, s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 69.58, 110.99, 116.67, 121.36, 121.44, 121.67, 121.98, 126.35, 126.89, 127.67, 129.40, 133.75, 135.71, 135.77, 138.63, 140.42, 148.23, 149.44, 153.45, 166.97. FT-IR (KBr pellet, cm^{-1}): 3341 (br), 1679 (s), 1569 (w), 1534 (vs), 1471 (s), 1418 (m), 1378 (s), 1320 (s), 1273 (m), 1246 (m), 1175 (m), 1106 (s). MS: m/z 330.2 $[(M + 1)^+]$.

*Synthesis of Zn(**L**)(NO_3).* A 10 mL acetonitrile solution of $Zn(NO_3)_2 \cdot 6H_2O$ (0.0297 g, 0.1 mmol) was added slowly to a magnetically stirred 10 mL methanol solution of the ligand **HL** (0.0329 g, 0.1 mmol). The mixture was stirred in air for 4 h, whereby a straw-yellow solution was formed. It was filtered and kept in air. Colorless block single crystals of Zn(**L**)(NO_3) suitable for X-ray crystallography were obtained on slow evaporation of the filtrate within 2 days. Anal. Calcd for $C_{20}H_{14}N_4O_5Zn$: C, 52.71; H, 3.10; N, 12.29. Found: C, 52.42; H, 3.24; N, 12.06. FT-IR (KBr pellet, cm^{-1}): 3418 (br), 3244 (w), 1659 (m), 1544 (vs), 1508 (w), 1449 (w), 1377 (vs), 1320 (s), 1262 (w), 1176 (w), 1127 (m), 1032 (w). MS: m/z 392.2 $([\mathbf{L}^- + Zn^{2+}]^+)$.

*Synthesis of Cd(**HL**)$(NO_3)_2(CH_3OH)$.* A 10 mL acetonitrile solution of $Cd(NO_3)_2 \cdot 6H_2O$ (0.0346 g, 0.1 mmol) was added slowly to a magnetically stirred 10 mL methanol solution of the ligand **HL** (0.0329 g, 0.1 mmol). The mixture was stirred in air for 4 h, whereby a colorless solution was formed. It was filtered and kept in air. Colorless block single crystals of Cd(**HL**)$(NO_3)_2(CH_3OH)$ suitable for X-ray crystallography were obtained on slow evaporation of the filtrate within 3 days. Anal. Calcd for $C_{21}H_{19}N_5O_9Cd$: C, 42.19; H, 3.20; N, 11.71. Found: C, 42.34; H, 3.08; N, 11.48. FT-IR

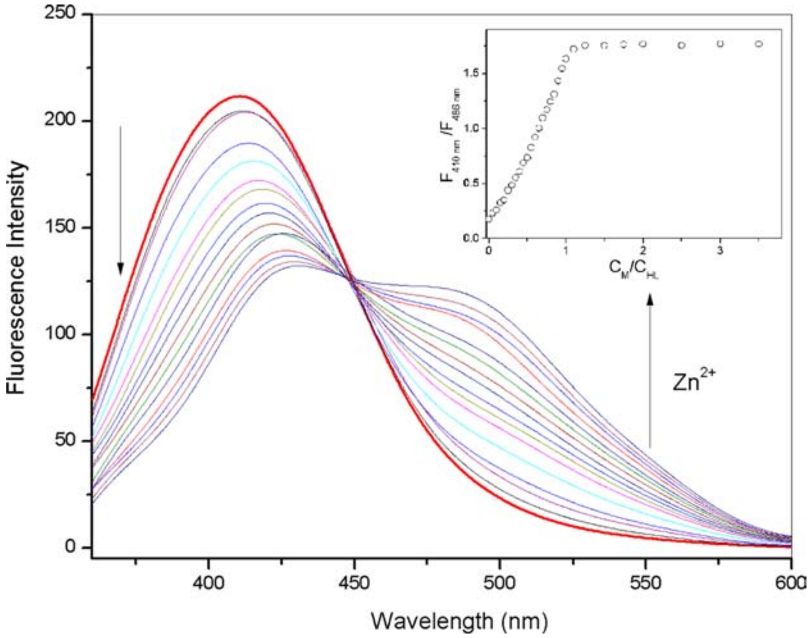


Figure 3. Fluorescence emission spectra of **HL** upon the addition of $Zn(NO_3)_2(H_2O)_6$ in ethanol. λ_{ex} = 329 nm at room temperature ([**HL**] = 0.10 mM; $[Zn^{2+}]$ = 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 95, and 100 μM). (Inset) Corresponding Zn^{2+} titration profile according to the ratiometric calibration curve $F_{486\ nm}/F_{410\ nm}$, indicating 1:1 stoichiometry for $Zn^{2+}/\mathbf{L}^-$.

(KBr pellet, cm^{-1}): 3424 (br), 1617 (s), 1502 (m), 1465 (vs), 1307 (s), 1262 (w), 1176 (w), 1111 (m), 1018 (w).

X-ray Diffraction Studies. Single-crystal X-ray diffraction measurements were carried out on a Bruker SMART 1000 CCD diffractometer operating at 50 kV and 30 mA using Mo Kα radiation (λ = 0.71073 Å). The crystal was mounted inside a Lindemann glass capillary for data collection using *SMART* and *SAINT* software.[18] An empirical absorption correction was applied using the *SADABS* program.[19] The structure was solved by direct methods and refined by full-matrix least squares on F^2 using the *SHELXTL-97* program package.[20]

Crystal data and details of the structure determination for Zn(**L**)(NO$_3$) and Cd(**HL**)(NO$_3$)$_2$(CH$_3$OH) are summarized in Table S1 in the Supporting Information (SI). CCDC 853385 and 853386 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi.

■ RESULTS AND DISCUSSION

Absorption Study. The UV−vis absorption spectrum of **HL** was recorded in an ethanol solution. The absorption spectrum of **HL** exhibits a maximum centered at 305 nm at room temperature, which is assigned to the $\pi-\pi^*$ transitions of the quinoline groups.[21] To obtain insight into the binding properties of **HL** toward Cd^{2+} and Zn^{2+}, the UV−vis spectral changes upon the addition of metal nitrates (Cd^{2+} and Zn^{2+}) to the ethanol solution of **HL** were investigated. Upon the addition of 1.0 equiv of Cd^{2+} to **HL**, the absorbance at 305 nm slightly decreased while the absorption at 358 nm gradually increased (Figure S1 in the SI). When **HL** was continuously titrated with Cd^{2+}, the absorbance remained constant up to a mole ratio (**HL**/Cd^{2+}) of 1:1 (Figure S1 in the SI, inset). On the other hand, upon the addition of 1 equiv of Zn^{2+}, the absorbance of **HL** at 305 nm gradually decreased with an increasing concentration of Zn^{2+} (Figure S2 in the SI). Moreover, a new absorption band appeared at 358 nm with an isosbestic point at 330 nm, illustrating that Zn^{2+} coordination led to an increase of the electron-donating ability of the nitrogen atoms of the quinoline moieties. Its absorbance at 358 and 305 nm changed linearly with the concentration of Zn^{2+} up to a molar ratio (**HL**/Zn^{2+}) of 1:1, and there was saturation (Figure S2 in the SI, inset). These indicate the 1:1 binding model between Zn^{2+}, Cd^{2+}, and **HL**, which was further confirmed by Job's plot and crystal structures.

Fluorescence Spectra and Titration. The optical properties of **HL** are mainly dominated by the quinoline group. In ethanol, **HL** shows excellent selectivity for Cd^{2+}. The emission spectrum of **HL**, which is excited at 329 nm, exhibits an emission maximum at 410 nm with a low quantum yield (Φ = 0.008), at room temperature in ethanol. Upon the addition of 1.0 equiv of Cd^{2+}, the fluorescence intensity of **HL** increased by about 14-fold; the quantum yield (Φ = 0.16) results in a more than 20-fold increase without a change in the wavelength. The coordination mode of **HL** to Cd^{2+} was investigated by fluorescence titration in ethanol (Figure 1). The observed fluorescence intensity was nearly proportional to the Cd^{2+} concentration. The saturation behavior of the fluorescence intensity after 1 equiv of Cd^{2+} reveals that the Cd^{2+} chemosensor has a 1:1 stoichiometry (Figure 1, inset). Titration of **HL** with Cd^{2+} was followed by fluorescence to determine the Cd^{2+}/**L**$^-$ binding ratio and binding constant (K_s = [Cd**L**]/[Cd][**HL**]). K_s of Cd^{2+}/**HL** is observed to be 9.8 × 10^5 by fluorescence titration (Figure S3 in the SI).[22] These results suggest that **HL** in solution should form a 1:1 complex with Cd^{2+}, which is confirmed by Job's plot (Figure S4 in the SI) and crystal structures (vide infra).

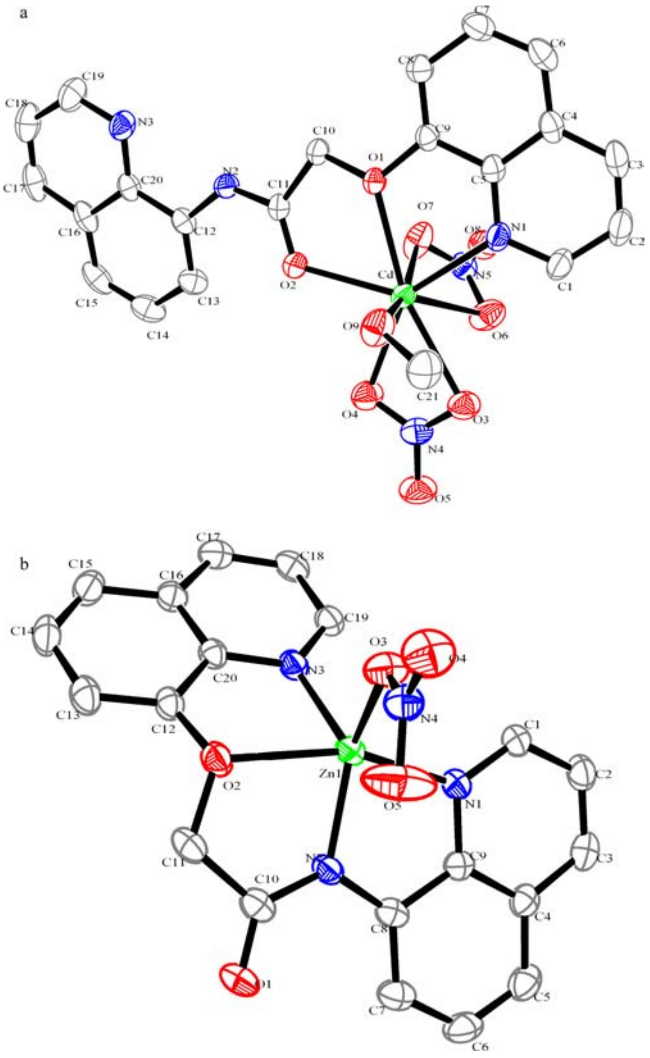


Figure 4. (a) Thermal ellipsoid (30% probability level) plot of Cd(**HL**)(NO$_3$)$_2$(CH$_3$OH). All hydrogen atoms were deleted for clarity. (b) Thermal ellipsoid (30% probability level) plot of Zn(**L**)(NO$_3$). All hydrogen atoms were deleted for clarity.

Fluorescence titration of **HL** with various metal ions was conducted to examine the selectivity (Figure 2). The fluorescence intensity of **HL** was slightly quenched with some cations such as Cu^{2+}, Co^{2+}, and Fe^{3+}. Other cations such as Na$^+$, K$^+$, Li$^+$, Mg^{2+}, Ca^{2+}, Mn^{2+}, Hg^{2+}, Fe^{2+}, Pb^{2+}, Al^{3+}, Cr^{3+}, and Ni^{2+} did not cause any significant changes, showing selective CHEF in the presence of Cd^{2+}.[22] However, upon binding Zn^{2+}, **HL** showed a large spectral red shift to 486 nm with a quantum yield of 0.019; a well-defined isoemissive point at 450 nm is also observed (Figure 3). The intensity ratio between 486 and 410 nm ($F_{486\ \mathrm{nm}}/F_{410\ \mathrm{nm}}$) increases linearly with the concentration of Zn^{2+} (0−3.5 equiv) up to a mole ratio (**HL**/Zn^{2+}) of 1:1 (Figure 3, inset), which allowed detection of Zn^{2+} by the ratiometric fluorescence method. Furthermore, the Zn^{2+}/**L**$^-$ binding ratio and binding constant (K_s = [Zn**L**]/[Zn][**HL**]) were determined by fluorescence titration; K_s of Zn^{2+}/**L**$^-$ is observed to be 1.8 × 10^4 (Figure S5 in the SI).[22] These results suggest that **HL** in solution should form a 1:1 complex with Zn^{2+}, which is confirmed by Job's plot (Figure S6 in the SI) and crystal structures (vide infra).

Crystal Structure of Cd(HL)(NO$_3$)$_2$(CH$_3$OH) and Zn(L)(NO$_3$). The structures of the Cd^{2+} and Zn^{2+} complexes with **HL**

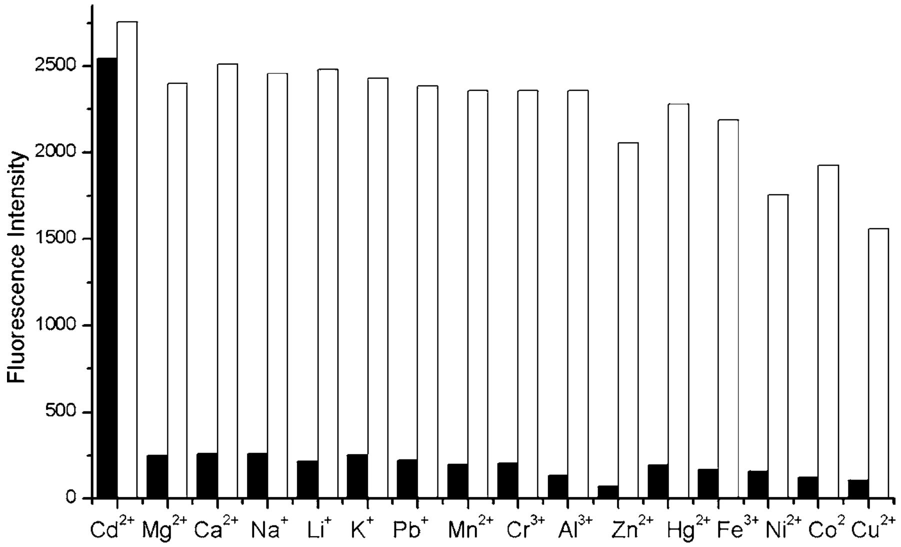


Figure 5. Selectivity of **HL** for Cd^{2+} in the presence of other metal ions in ethanol. $\lambda_{ex} = 329$ nm. The response is normalized with respect to the background fluorescence of the free ligand (F_0). Black bars represent the addition of an excess of the appropriate metal ion (5 mM for Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, and Cu^{2+} and 1 mM for all other metal ions) to a 0.1 mM solution of **HL**. White bars represent the subsequent addition of 0.1 mM $Cd(NO_3)_2(H_2O)_6$ to the solution.

are shown in Figure 4.Selected bond lengths and angles are given in Table S2 in the SI. They crystallize in the monoclinic system, with space group *P*2(1)/*n* from a methanol solvent. As shown in Figure 4a, Cd^{2+} is eight-coordinate and surrounded by one carbonyl oxygen atom, one quinoline oxygen atom, and one quinoline nitrogen atom coming from the ligand (O1, O2, and N1), four nitrate oxygen atoms (O3, O4, O6, and O7), and one oxygen atom (O9) from methanol. The bond length of Cd1−N is 2.304(2) Å, and the Cd1−O distnace ranges from 2.306(2) to 2.492(2) Å (Table S2 in the SI). In $Zn(L)(NO_3)$, as illustrated in Figure 4b, the Zn^{2+} center lies in a distorted square-pyramidal coordination environment, defined by three nitrogen donors from the quinoline groups of one ligand (N1, N2, and N3), one oxygen donor from 8-HQ (O2), and a unidentate coordinated nitrate group (O3). The bond length of Zn1−N varies from 1.995(3) to 2.072(3) Å, and the Zn1−O distances are 2.019(3) and 2.267(2) Å (Table S2 in the SI). As shown in Figure 4, we can see that **HL** adopts two coordination conformations in sensing Cd^{2+} and Zn^{2+}. For sensor **HL**, the 8-HQ group would grasp Cd^{2+} in a suitable conformation, and the increased emission intensity of **HL** is attributed to the coordination of the amide oxygen with metal ions, which results in the efficient inhibition for the PET process of the amide group. However, **L** could chelate Zn^{2+} through a deprotonation process of the NH moiety of the aminoquinoline, and the whole ligand almost forms a conjugated rigid plane structure, which is entirely different from the coordination conformation of **HL**/Cd^{2+}, and consequently a distinct emission red shift with slight enhancements at ~480 nm could be observed.[6a,23] A similar phenomenon was also observed in the sensor HMQP,[15a] in which the deprotonation of the phenol group enhanced the interaction between Zn^{2+} and oxygen and consequently weakened the interaction between Zn^{2+} and aminonquinoline.

Metal-Ion Competition Studies. The individual emission response of **HL** against different transition-metal ions revealed a remarkable selectivity of Cd^{2+} binding (Figure 2). However, the most important criterion for a selective cation probe is the ability to detect a specific cation in the vicinity of other competing ions. To further explore the selectivity of **HL** for Cd^{2+}, we measured the fluorescence intensity of **HL** in the presence of Cd^{2+} mixed with various metal ions in ethanol (Figure 5). The emission intensity of Cd^{2+}-bound **HL** is unperturbed in the presence of 5 equiv of Na^+, K^+, Ca^{2+}, Mg^{2+}, Li^+, Mn^{2+}, Hg^{2+}, Pb^{2+}, Al^{3+}, and Cr^{3+}, indicating excellent selectivity for Cd^{2+} over these competing cations. The response of **HL** for Cd^{2+} detection in the presence of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Fe^{3+} is relatively low but clearly detectable. The anion responses to the detection systems were further investigated. These results indicate that only AcO^- quenched the fluorescence intensity of **HL**/$Cd(NO_3)_2$; other anions such as Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, $H_2PO_4^-$, and HSO_4^- slightly quenched the intensity but can be clearly detectable (Figure S7 in the SI). For the **HL**/$Zn(NO_3)_2$ system, sensing for Zn^{2+} is hardly interfered with by these anions (Figure S8 in the SI).

These significant differences when binding Cd^{2+} versus Zn^{2+} make **HL** highly selective toward Cd^{2+}. Furthermore, the combine abilities of Cd^{2+} with **HL** were investigated by the fluorescence titration of Cd^{2+} on **HL**/Zn^{2+}. The **HL**/Zn^{2+} complex displays a broad band with a maximum at 486 nm. When Cd^{2+} was added to a solution of the **HL**/Zn^{2+} complex, Zn^{2+} was displaced by Cd^{2+}, resulting in a significant increase of the emission band centered at 414 nm (attributed to the formation of a **HL**/Cd^{2+} complex; Figure S9 in the SI). Therefore, the affinity of **HL** with Cd^{2+} is stronger than that with Zn^{2+}, which is confirmed by the values of K_s for these two complexes. Thus, **HL** can be used as a selective fluorescent sensor for Cd^{2+} detection in the presence of the competing metal ions.

■ CONCLUSIONS

We have successfully developed a new highly sensitive and selective fluorescent sensor for Cd^{2+} and investigated the Cd^{2+} fluorescence sensing and binding properties of **HL**. Although **HL** can bind to both Cd^{2+} and Zn^{2+}, these two metal ions can be differentiated by this sensor via two coordination conformations. It displays high selectivity for Cd^{2+} and can be used as a ratiometric Zn^{2+} fluorescent sensor. The design strategy of the sensor will help to improve the development of fluorescent sensors for discriminating other ion pairs, and the special structure selectivity relationships may give some insight into how to construct receptors with special properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic structure for [Zn(**L**)(NO_3)] and [Cd(**HL**)(NO_3)$_2$(CH_3OH)] in CIF format, absorption titration of Cd^{2+} and Zn^{2+}, fluorescence titration of Cd^{2+} with **HL**, Job's plots and fluorescence spectra of **HL**/Zn^{2+} in the presence of different concentrations of Cd^{2+}, anion response to **HL**-Cd(NO_3)$_2$ and **HL**-Zn(NO_3)$_2$ systems, details of the crystallographic parameters, data collection and refinements, and selected bond distances and angles for [Zn(**L**)(NO_3)] and [Cd(**HL**)(NO_3)$_2$(CH_3OH)]. This material 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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