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A highly selective fluorescent chemosensor based on quinoline derivative for zinc ion in pure water

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Abstract

A new simple receptor **1** based on quinoline was synthesized as a water-soluble fluorescent 'turn-on' chemosensor for zinc ions. In 100 % aqueous buffer solution, the sensor **1** displayed a selective fluorescence enhancement (317-folds) at 536 nm with Zn^{2+}. The detection limit (4.48 μM) of **1** for Zn^{2+} was far below than the WHO guideline (76 μM) in drinking water. Importantly, the sensor **1** could be used to detect and quantify Zn^{2+} in water samples. Moreover, the sensing ability of **1** for Zn^{2+} was supported by theoretical calculations. Thus, this sensor **1** has the ability to be a practical system for monitoring Zn^{2+} concentrations in aqueous samples.

Keywords: zinc ion, quinoline group, fluorescent, chemosensor, PET process

Introduction

As the second most abundant transition metal in the human body after iron, zinc ion has attracted a great deal of attention,[1] because it plays a crucial role in various fundamental biological processes including gene transition, regulation of metalloenzymes, neural signal transmission and apoptosis.[2] It is also associated with physical growth retardation and neurological disorders such as cerebral ischemia and Alzheimer's disease.[3] Although most Zn^{2+} is tightly bound to enzymes and proteins, free zinc pools exist in some tissues such as the brain, intestine, pancreas and retina.[4] Therefore, it is desirable to develop a method for monitoring and detecting Zn^{2+}, which would offer a promising approach to study its actions in biological, medical and environmental circumstances.

Detection of metal ions, such as Zn^{2+}, is still a challenge since those metals do not display spectroscopic and magnetic responses due to its d^{10} electron configuration.[5] In this regard, chemosensors based on ion-induced fluorescence changes provide the optimal choice to detect Zn^{2+} in biological samples due to their high sensitivity, selectivity, response time, simplicity and low detection limit.[6] Detection methods using fluorescence have, therefore, attracted a considerable attention in the detection of zinc ions.

Quinoline and its derivatives, particularly 8-aminoquinoline, are well known fluorogenic chelators for transition metal ions.[7] So far, various chemosensors based on quinoline derivatives which can detect zinc ion have been reported.[8] However, many of them have suffered from use of harmful organic solvents due to poor water solubility.[9] To improve the water solubility, therefore, we previously designed to combine 8-aminoquinoline with a ethanolamine having a hydrophilic character.[10] The resulting fluorescent chemosensor based on the combination of the quinoline moiety and 2-((pyridin-2-yl)methylamino)ethanol could detect zinc ions in water solution containing 0.3 % of methanol, although Cd^{2+} also induced a small fluorescence enhancement compared with Zn^{2+}. These results led us to synthesize a

new chemosensor, which contains a 8-aminoquinoline group as a fluorophore and two ethanolamine groups as a hydrophilic character[11] (Scheme 1). We expected that the new chemosensor **1** would be more soluble in water. Indeed, the **1** showed a good water-solubility and selectivity to zinc ion in 100 % of water solution.

Herein, we report a quinoline-based fluorescent chemosensor **1**, which was synthesized by condensation reaction of 3-chloro-N-(quinolin-8-yl)propanamide and diethanolamine. The sensor **1** could detect Zn^{2+} by fluorescence enhancement with high selectivity and discriminate Zn^{2+} particularly from Cd^{2+} in a fully aqueous solution. Moreover, **1** could detect and quantify Zn^{2+} in the water sample.

Experimental

General information

All the solvents and reagents (analytical grade and spectroscopic grade) were obtained from Sigma-Aldrich and used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian 400 MHz and 100 MHz spectrometer. Chemical shifts (δ) were reported in ppm, relative to tetramethylsilane $Si(CH_3)_4$. Absorption spectra were recorded at room temperature using a Perkin Elmer model Lambda 2S UV/Vis spectrometer. Electrospray ionization mass spectra (ESI-mass) were collected on a Thermo Finnigan (San Jose, CA, USA) LCQTM Advantage MAX quadrupole ion trap instrument. Fluorescence measurements were performed on a Perkin Elmer model LS45 fluorescence spectrometer. The precursor 3-chloro-N-(quinolin-8-yl)propanamide (CQP) was obtained by substitution reaction of quinolone-8-amine and 3-chloropropanoyl chloride according to the literature method.[12]

Synthesis of receptor 1

A solution of 3-chloro-N-(quinolin-8-yl)propanamide (0.24 g, 1 mmol) was added to

diethanolamine (0.19 g, 2 mmol) in 10 mL of acetonitrile. The reaction solution was stirred for 1 d at room temperature. The solvent was removed under the reduced pressure to obtain pale brown oil, which was purified by silica gel column chromatography (CH_2Cl_2:CH_3OH, 15:1, v/v). Yield: 0.22 g (72%); ^{1}H NMR (DMSO-d_6, 400 MHz, ppm) δ: 11.29 (s, 1H), 8.90 (d, J = 4.0 Hz, 1H), 8.68 (d, J = 4.0 Hz, 1H), 8.42 (d, J = 8.0 Hz, 1H), 7.65 (t, J = 8.0 Hz, 2H), 7.59 (t, J =8.0 Hz, 1H), 4.44 (t, J = 5.5 Hz, 2H), 3.59 (m, J = 6.0 Hz, 4H), 2.92 (t, J = 6.4 Hz, 2H), 2.71 (t, J = 6.0 Hz, 4H), 2.63 (t, J = 6.4 Hz, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 171.64, 149.16, 138.50, 137.16, 135.51, 128.37, 127.51, 122.45, 121.98, 117.13, 59.40, 56.42, 51.44, 35.05 ppm. ESI-MS m/z ($M+H^+$): calcd, 304.17; found, 304.20; Anal. Calc. for $C_{16}H_{21}N_3O_3$: C, 63.35; H, 6.98; N, 13.85; Found: C, 63.74; H, 7.09; N, 13.36.

Fluorescence studies of 1 with various metal ions

Receptor **1** (1.5 mg, 0.005 mmol) was dissolved in buffer (10 mM bis-tris, pH 7.0, 1 mL) to make the final concentration of 20 μM. Stock solutions (20 mM) of the nitrate or perchlorate salts of Al^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, K^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+} and Zn^{2+} ions were prepared in buffer (10 mM bis-tris, pH 7.0). 60 μL of the stock solutions (20 mM) of the metal nitrate or perchlorate salts was transferred to 3 mL of receptor **1** solution prepared above. After mixing them for a few seconds, the fluorescence spectra of **1** were taken at room temperature.

Fluorescence titration of 1

Receptor **1** (1.5 mg, 0.005 mmol) was dissolved in buffer (10 mM bis-tris, pH 7.0, 1 mL) and 12 μL of the receptor **1** (5 mM) was diluted to 2.988 mL buffer (10 mM bis-tris, pH 7.0) to make the concentraiton of 20 μM. $Zn(NO_3)_2{\cdot}6H_2O$ (6.1 mg, 0.02 mmol) was dissolved in buffer (10 mM bis-tris, pH 7.0, 1 mL). 3-105 μL of the zinc solution (20 mM)

were transferred to each receptor solution (20 μM) prepared above. After mixing them for a few seconds, fluorescence spectra were taken at room temperature.

UV-vis titration of 1

Receptor **1** (1.5 mg, 0.005 mmol) was dissolved in buffer (10 mM bis-tris, pH 7.0, 1 mL) and 12 μL of the receptor **1** (5 mM) was diluted to 2.988 mL buffer (10 mM bis-tris, pH 7.0) to make the concentraiton of 20 μM. $Zn(NO_3)_2 \cdot 6H_2O$ (6.1 mg, 0.02 mmol) was dissolved in buffer (10 mM bis-tris, pH 7.0, 1 mL). 3-105 μL of the zinc solution (20 mM) were transfered to each receptor solution (20 μM) prepared above. After mixing them for a few seconds, UV-vis absorption spectra were taken at room temperature.

Job plot measurement

Receptor **1** (1.5 mg, 0.005 mmol) was dissolved in buffer (10 mM bis-tris, pH 7.0, 1 mL). 30, 27, 24, 21, 18, 15, 12, 9, 6 and 3 μL of the receptor **1** solution were taken and transferred to vials. Each vial was diluted with buffer (10 mM bis-tris, pH 7.0) to make a total volume of 2.970 mL. $Zn(NO_3)_2 \cdot 6H_2O$ (1.5 mg, 0.005 mmol) was dissolved in buffer (10 mM bis-tris, pH 7.0, 1 mL). 0, 3, 6, 9, 12, 15, 18, 21, 24, 27, and 30 μL of the $Zn(NO_3)_2$ solution were added to each diluted receptor **1** solution. Each vial had a total volume of 3 mL. After shaking the vials for a few seconds, fluorescence spectra were taken at room temperature.

Competition with other metal ions

Receptor **1** (1.5 mg, 0.005 mmol) was dissolved in buffer (10 mM bis-tris, pH 7.0, 1 mL) and 12 μL of the receptor **1** (5 mM) was diluted to 2.868 mL buffer (10 mM bis-tris, pH 7.0) to make the final concentration of 20 μM. $M(NO_3)_3$ (M = Al, Cr, Fe 0.02 mmol),

$M(NO_3)_2$ (M = Zn, Cd, Cu, Mg, Co, Ni, Ca, Mn, Pb), MNO_3 (M = Na, K) and $M(ClO_4)_2$ (M = Fe) were separately dissolved in buffer (10 mM bis-tris, pH 7.0, 1 mL). 60 μL of each metal ion solution (20 mM) was taken and added into 2.868 mL of each receptor **1** solution (20 μM) prepared above to make 20 equiv. Then, 60 μL of zinc solution (20 mM) was added into the mixed solution of each metal ion and receptor **1** to make 20 equiv. After mixing them for a few seconds, fluorescence spectra were taken at room temperature.

NMR titration

For ^{1}H NMR titrations of **1** with Zn^{2+}, four NMR tubes of **1** dissolved in DMSO-d_6 (700 μL) were prepared and then four different concentrations (0, 0.0025, 0.005, 0.01 mmol) of $Zn(NO_3)_2 \cdot 6H_2O$ dissolved in DMSO-d_6 were added to each solution of **1**. After shaking them for a minute, ^{1}H NMR spectra were obtained at room temperature. In order to check the influence of water on the binding property, the same ^{1}H NMR titrations of **1** with Zn^{2+} were carried out in a mixture of D_2O-DMSO-d_6 (9:1, v/v). Nearly identical results were observed, indicating that water did not affect the binding interaction of **1** with Zn^{2+}. In addition, we tried to conduct ^{1}H NMR titration in D_2O, but it was not successful at 1 equiv of Zn ion, because some Zn complexes precipitated out. These results suggested that a high concentration of **1**-Zn^{2+} complex was not very soluble in buffer solution.

pH effect test

A series of buffers with pH values ranging from 2 to 12 were prepared by mixing sodium hydroxide solution and hydrochloric acid in buffer (10 mM bis-tris). After the solution with a desired pH was achieved, receptor **1** (1.5 mg, 0.005 mmol) was dissolved in buffer (10 mM bis-tris, pH 7.0, 1 mL), and then 12 μL of the receptor **1** solution (5 mM) was diluted with 2.928 mL buffers to make the final concentration of 20 μM. $Zn(NO_3)_2 \cdot 6H_2O$ (6.1

mg, 0.02 mmol) was dissolved in buffer (10mM bis-tris, pH 7.0, 1 mL). 60 μL of the Zn^{2+} solution (20 mM) was transferred to each receptor solution (20 μM) prepared above. After mixing them for a few seconds, fluorescence spectra were obtained at room temperature.

Determination of Zn^{2+} in water samples

Fluorescence spectral measurements of water samples containing Zn^{2+} were carried by adding 12 μL of 5 mM stock solution of **1** and 0.30 mL of 100 mmol/L bis-tris buffer stock solution to 2.688 mL sample solutions. After thoroughly mixed, the solutions were allowed to stand at 25 ˚C for 2 min before the test.

Theoretical calculation methods

All DFT/TDDFT calculations based on the hybrid exchange-correlation functional B3LYP[13] were carried out using Gaussian 03 program[14]. The 6-31G** basis set[15] was used for the main group elements. In vibrational frequency calculations, there was no imaginary frequency for the optimized geometries of **1** and **1**-Zn^{2+}, suggesting that these geometries represented local minima. For all calculations, the solvent effect of water was considered by using the Cossi and Barone's CPCM (conductor-like polarizable continuum model)[16]. To investigate the electronic properties of singlet excited states, time-dependent DFT (TDDFT) was performed in the ground state geometries of **1** and **1**-Zn^{2+}. The 30 singlet-singlet excitations were calculated and analyzed. The GaussSum 2.1[17] was used to calculate the contributions of molecular orbitals in electronic transitions.

Results and discussion

Synthesis of 1

The receptor **1** was synthesized by substitution reaction of 3-chloro-N-(quinolin-8-yl)propanamide and diethanolamine with a 72% yield in acetonitrile (Scheme 1), and characterized by ^{1}H NMR, ^{13}C NMR, ESI-mass spectrometry and elemental analysis.

Fluorescence and absorption spectroscopic studies of 1 toward Zn^{2+} ion

To gain an insight into the fluorescent properties of receptor **1** toward metal ions, the emission changes were measured with various metal ions in buffer solution (10 mM bis-tris, pH 7.0). **1** exhibited weak fluorescence with a low quantum yield (Φ = 0.00084), which was much lower than that (Φ = 0.00810) in the presence of Zn^{2+} with excitation at 350 nm. In contrast, upon addition of other relevant metal ions such as Al^{3+}, Ca^{2+} , Cd^{2+}, Co^{2+}, Cr^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, K^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+} and Pb^{2+} either no or slight increase in intensity was observed (Fig. 1). For example, Fe^{2+} displayed a slight increase of the intensity in comparison with **1**. Notably, **1** can distinguish Zn^{2+} from Cd^{2+}, whereas the discrimination of Zn^{2+} from Cd^{2+} is well known to be a major obstacle.[18] A good distinction between Zn^{2+} and Cd^{2+} might be due to the high affinity of a hard Zn^{2+} to two hard oxygen atoms (Scheme 2).[19] This result suggests that **1** could act as "turn-on" sensor for Zn^{2+} and discriminate Zn^{2+} particularly from Cd^{2+}. The significant fluorescence enhancement might be due to the inhibition of a photo-induced electron transfer (PET) process (Scheme 2). Receptor **1** is poorly fluorescent (Φ = 10 %) in part due to PET process involving the non-bonding electron pair of tertiary nitrogen, which can transfer an electron to the excited fluorophore and quench the fluorescence. Metal coordination to the amino group renders it a less efficient electron donor. This makes PET-type fluorescence quenching less probable or inhibits it all together. Thus, the original fluorescence of the fluorophore is restored.

To investigate the chemosensing properties of **1**, fluorescence titration of receptor **1** with Zn^{2+} in bis-tris buffer was carried out (Fig. 2). The emission intensity of **1** at 536 nm gradually increased until the amount of Zn^{2+} reached 20 equiv. The binding properties of **1** with Zn^{2+} were further studied by UV-vis titration experiments (Fig. 3). On treatment with Zn^{2+} ion to the solution of **1**, the absorption band at 325 nm (ε = 5.5 x 10^3) gradually decreased, while the peaks at 275 nm (ε = 2.0 x 10^4) and 375 nm (ε = 2.0 x 10^3) increased with two isosbestic points at 302 and 343 nm. These observations indicate that only one product was generated from **1** upon binding to Zn^{2+}.

The Job plot analysis revealed a 1:1 stoichiometric ratio between **1** and the Zn^{2+} (Fig. S1), which was further confirmed by ESI-mass spectrometry analysis (Fig. 4). The positive ion mass spectrum indicated that a peak at m/z = 366.13 was assignable to [**1**($-H^+$) + Zn^{2+}] [calcd, m/z = 366.08].

The Zn^{2+} binding behavior of **1** was studied by ^1H NMR titrations in DMSO-d_6, in order to observe the change of the chemical shifts of the NH proton of amide moiety and the OH protons of ethanol moieties (Fig. 5). Upon the addition of Zn^{2+} to the **1**, the proton signal of -NH (H_7) at 11.3 ppm disappeared completely. Two protons of the -OH (H_{12} and $H_{12'}$) were gradually shifted downfield from 4.4 to 5.3 ppm. Meanwhile, the protons H_8, H_9, H_{10} and H_{11} displayed an apparent downfield shift. The protons $H_{1\text{-}6}$ of the quinoline group moved little until the addition of 1 equiv Zn^{2+} ion. These results suggested that three N atoms and two ethanolic O atoms of compound **1** participated in Zn^{2+} coordination, as shown in Scheme 2. The further addition of Zn^{2+} did not lead to any further evident change in the spectrum, which confirmed the 1:1 stoichiometry.

In addition, we carried out FT-IR measurements to gain more understanding on the structure of **1**-Zn^{2+} complex (Fig. S2). Upon binding of Zn^{2+} with **1**, the band at 3319.2 associated with the N-H of the amide moiety disappeared (Fig. S2a), indicating Zn^{2+}-induced

deprotonation of the N-H of the amide one. At the same time, the significant shift was observed in the carbonyl absorption band from 1648.9 to 1582.1 cm^{-1} (Fig. S2b). Based on Job plot, ESI-mass spectrometry analysis, ^{1}H NMR titrations and FT-IR measurements, we proposed the structure of **1**-Zn^{2+} complex as shown in Scheme 2.

From the fluorescence titration, the association constant was calculated to be K = 1.4 x 10^{4} M^{-1} by Benesi-Hildebrand equation (Fig. S3).[20] This K value was in the range of those (1.0 - 1.0 x 10^{12}) previously reported for Zn^{2+}-binding chemosensors.[1f,3f,21] The detection limit determined based on the S/B criteria[22] was 4.48 μM (Fig. S4), which is far below the World Health Organization guideline (76 μM).[6f,23] This result indicates that **1** could be an influential chemosensor for the detection of zinc in the drinking water.

To utilize **1** as an ion-selective fluorescence chemosensor for Zn^{2+}, the effect of competing metal ions was studied (Fig. S5). For this purpose, **1** was treated with 20 equiv of Zn^{2+} in the presence of the same concentration of other metal ions. The fluorescence intensity caused by Zn^{2+} was retained with Cd^{2+}, Mg^{2+}, Ni^{2+}, Na^{+}, K^{+}, Ca^{2+}, Mn^{2+} and Pb^{2+}. Instead, Al^{3+}, Fe^{2+}, and Fe^{3+} showed about 50 - 80 % reduction of the intensity of **1**-Zn^{2+} complex. The addition of Cu^{2+}, Cr^{3+} and Co^{2+} caused a complete decrease in the intensity, which may be attributed to the fact that these transition metal ions have an intrinsic quenching nature.[24]

We investigated the effect of pH on the emission response of receptor **1** to Zn^{2+} ion in a series of buffers with pH values ranging from 2 to 12 (Fig. 6). The **1**-Zn^{2+} complex showed a significant fluorescence response between 7 and 12, which includes the environmentally relevant range of pH 7.0 - 8.4.[25] This result indicates that Zn^{2+} could be clearly detected by the fluorescence spectral measurement using **1** within the environment pH range.

In order to study the applicability of the chemosensor **1** in environmental samples, we constructed a calibration curve for the determination of Zn^{2+} by **1** (Fig. S6), which

exhibited a good linear relationship between the fluorescence intensity of **1** and Zn^{2+} concentration (0.0 - 20.0 μM) with a correlation coefficient of $R^2 = 0.9968$ (n = 3). Then, the chemosensor was applied for the determination of Zn^{2+} in water samples. We prepared artificial polluted water samples by adding various metal ions known as being in industrial processes into deionized water. The results were summarized in Table 1, which exhibited a satisfactory recovery and R.S.D. values for the water samples.

In parallel to the experimental study, to further understand the electronic structures of **1** and **1**-Zn^{2+} complex, we optimized energy-minimized structures of chemosensor **1** and **1**-Zn^{2+} complex at DFT/B3LYP/6-31G** level. The major bond lengths and angels of **1** and **1**-Zn^{2+} were shown in Fig. 7. The five-coordinated structure of **1**-Zn^{2+} complex was optimized based on the experimental studies. The bond lengths of Zn-O and Zn-N were similar to the reported Zn complex.[12,26,27]

To gain an insight into fluorescent sensing mechanism for **1**-Zn^{2+}, time-dependent density functional theory (TD-DFT) calculations were performed with the optimized geometries (S_0). In the case of **1**, the main molecular orbital (MO) contributions of the first and second lowest excited states were determined for HOMO → LUMO (337.51 nm) and HOMO -1 → LUMO (319.24 nm) transitions (Fig. S6). The HOMO and HOMO -1 were mainly localized in electron-donor parts, i.e., secondary amine in diethanolamine moiety, whereas the LUMO was composed of the fluorophore of the quinoline moiety (Fig. S7). These results indicate photo-induced electron transfer (PET) process from amine to fluorophore, resulting in low fluorescence of **1**. For **1**-Zn^{2+}, the main molecular orbital (MO) contribution of the second lowest excited state was determined for HOMO - 1 → LUMO transition (397.83 nm, Fig. S8). The HOMO - 1 was mainly localized in π orbitals of the quinoline group, whereas the LUMO was mainly localized in π* orbitals of the quinoline group (Fig. S8c). These results indicate that the chelation of Zn^{2+} changed the first excited

state from PET to $\pi \rightarrow \pi^*$ transition of the quinoline group. Therefore, the fluorescence sensing mechanism could be explained by blocking of the PET process of **1**, which displayed 'turned on' fluorescence in the fluorophore of $\pi \rightarrow \pi^*$ transition.

Conclusion

We have successfully designed and synthesized a fluorescent water-soluble chemosensor **1**, capable of recognizing zinc ions in a fully aqueous solution. The sensor **1** exhibited an excellent selectivity and sensitivity toward Zn^{2+} by fluorescent intensity enhancement. The detection limit of **1** for Zn^{2+} (4.48 μM) was much lower than that recommended in guideline of the WHO (76 μM), and recovery studies of the water samples added with Zn^{2+} showed a satisfactory recovery and R.S.D. values. Moreover, the sensing mechanism of Zn^{2+} by **1** was proposed to be the inhibition of photo-induced electron transfer (PET) process and supported by theoretical calculations.

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Appendix A. Supplementary data

Supplementary material associated with this article can be found, in the online version.

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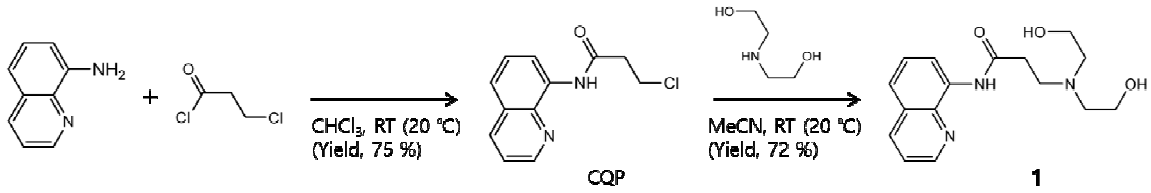
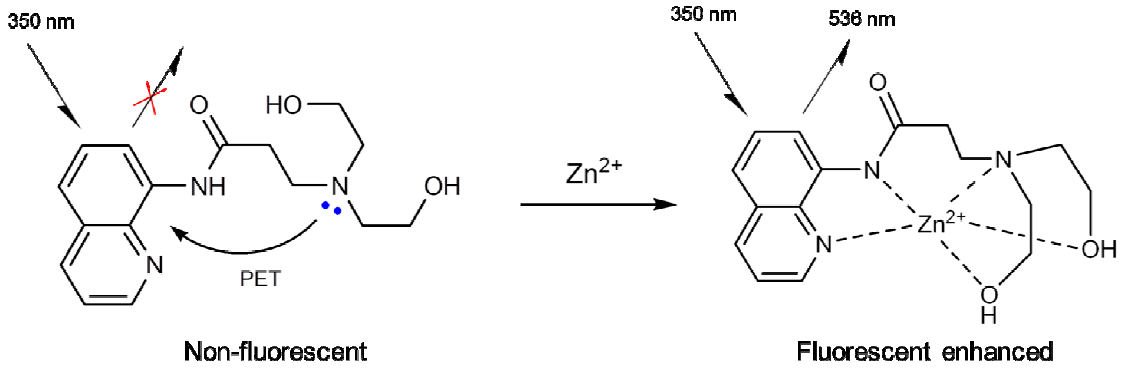


Scheme 1. Synthesis of **1**.



Scheme 2. Proposed sensing mechanism of **1** for Zn^{2+}.

Table 1. Determination of Zn(II) in water samples

Sample	Zn(II) added (μmol/L)	Zn(II) found (μmol/L)	Recovery (%)	R.S.D (n=3) (%)
Water Sample [a]	0.00	6.30	105.0	6.1
	4.00	10.43	104.3	8.7

[a] Synthesized by deionized water, 6.0 μmol/L Zn(II), 6.0 μmol/L Cd(II), Pb(II), Na(I), K(I), Ca(II), Mg(II). Conditions: [**1**] = 20 μmol/L in 10mM bis-tris buffer (pH 7.0).

Figure Captions

Fig. 1. (a) Fluorescence spectral changes of **1** (20 μM) in the presence of different metal ions (20 equiv) such as Al^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, K^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, Pb^{2+} and Zn^{2+} with an excitation of 350 nm in buffer solution (10 mM bis-tris, pH 7.0). (b) Bar graph shows the relative emission intensity of **1** at 536 nm upon treatment with various metal ions.

Fig. 2. Fluorescence spectral changes of **1** (20 μM) in the presence of different concentrations of Zn^{2+} ions in buffer solution (10 mM bis-tris, pH 7.0). Inset: fluorescence intensity at 536 nm *versus* the number of equiv of Zn^{2+} added.

Fig. 3. UV-vis spectral changes of **1** (20 μM) in the presence of different concentrations of Zn^{2+} ion in buffer solution (10 mM bis-tris, pH 7.0). Inset: Absorbance at 325 nm *versus* the number of equiv of Zn^{2+} added.

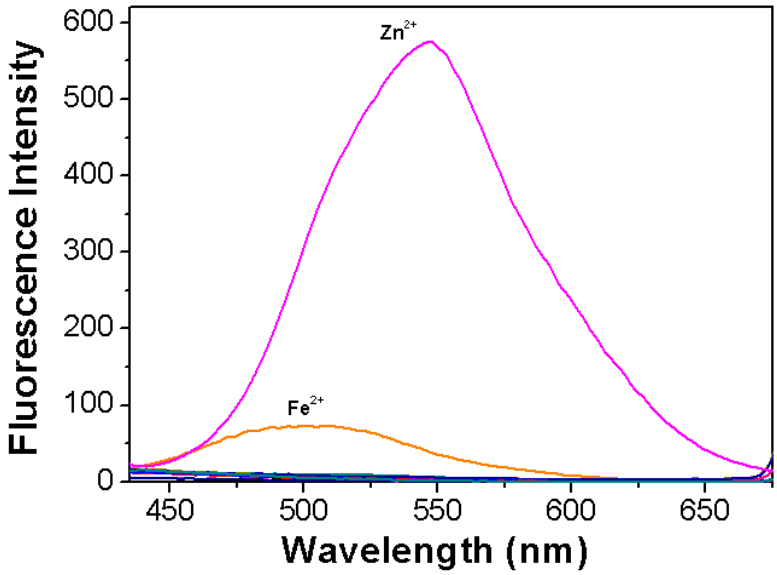
Fig. 4. Positive-ion electrospray ionization mass spectrum of **1** (100 μM) upon addition of 1 equiv of Zn^{2+}.

Fig. 5. ^{1}H NMR titration of **1** (0.01 mmol) with various concentrations of $Zn(NO_3)_2$ in DMSO-d_6 . The broad peaks at the range of 4.2-5.6 ppm were enlarged.

Fig. 6. Fluorescence intensity of **1**-Zn^{2+} (20 μM) after addition of 20 equiv of Zn^{2+} at various ranges of pH in buffer solution (10 mM bis-tris) at room temperature.

Fig. 7. Energy-minimized structures of (a) **1** and (b) **1**-Zn^{2+} complex.

(a)


Fluorescence Intensity
Wavelength (nm)
Zn2+
Fe2+
0
100
200
300
400
500
600
450
500
550
600
650

(b)

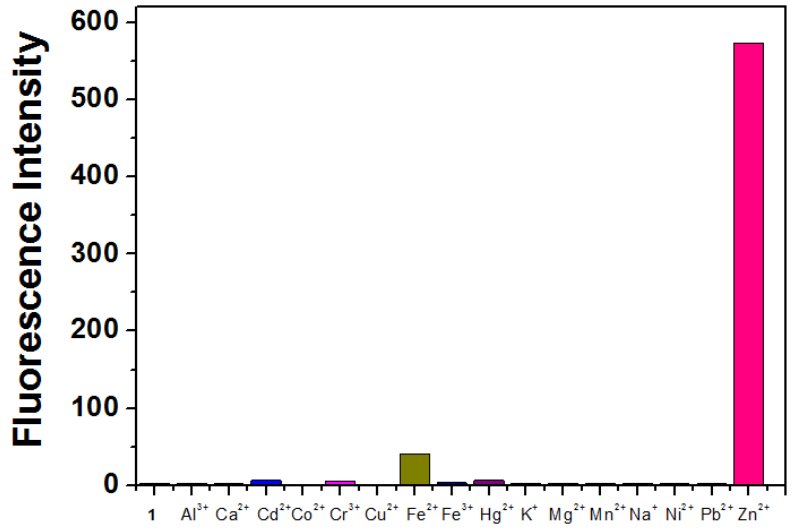

Fluorescence Intensity
0
100
200
300
400
500
600
1 Al3+ Ca2+ Cd2+ Co2+ Cr3+ Cu2+ Fe2+ Fe3+ Hg2+ K+ Mg2+ Mn2+ Na+ Ni2+ Pb2+ Zn2+

Fig. 1

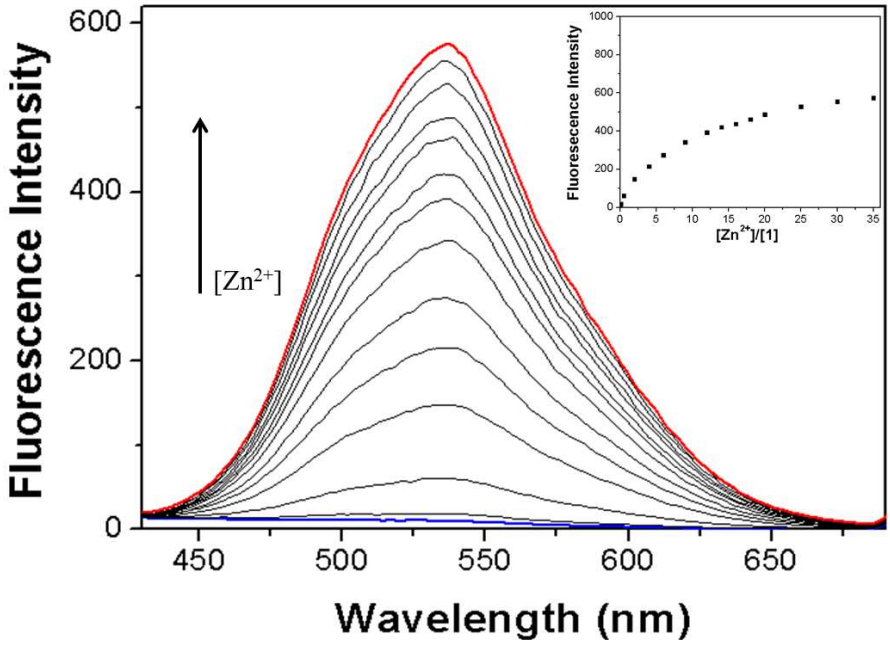

Fluorescence Intensity
600
400
200
0
450
500
550
600
650
Wavelength (nm)
[Zn2+]
Fluoresecence Intensity
1000
800
600
400
200
0
0
5
10
15
20
25
30
35
[Zn2+]/[1]

Fig. 2

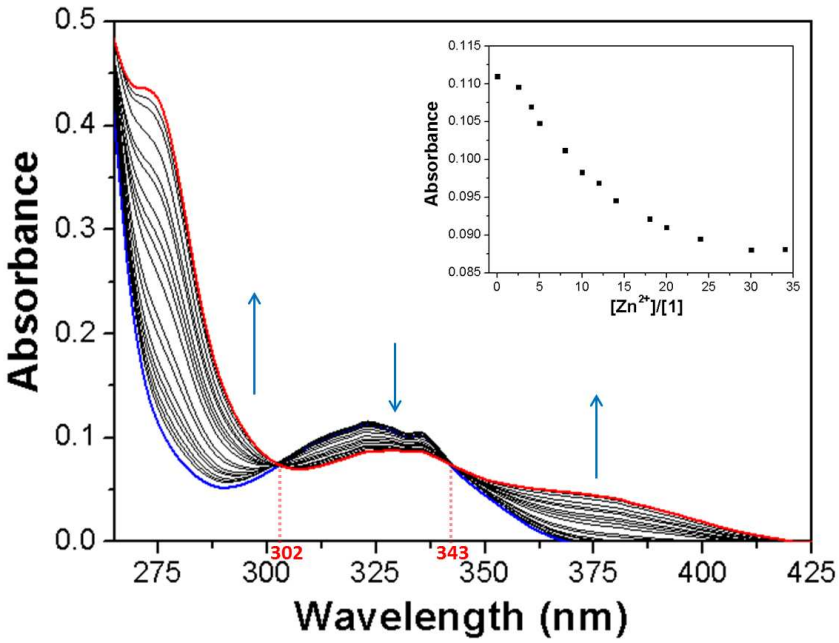


Fig. 3

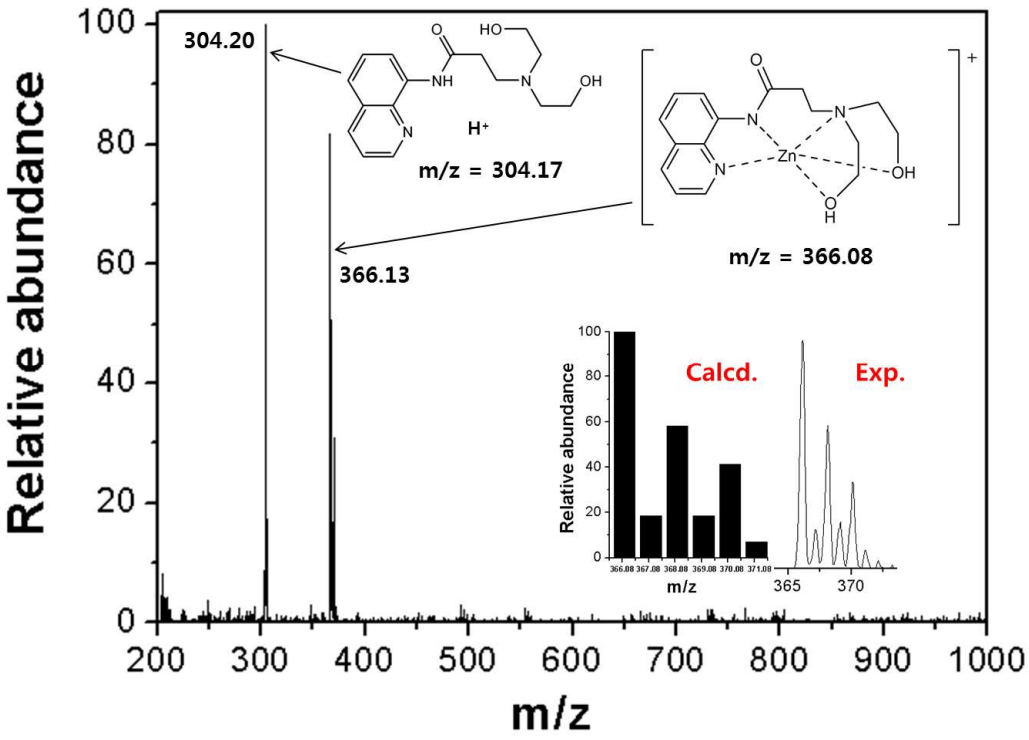

Relative abundance
m/z
304.20
366.13
m/z = 304.17
m/z = 366.08
H+
Calcd.
Exp.

Fig. 4

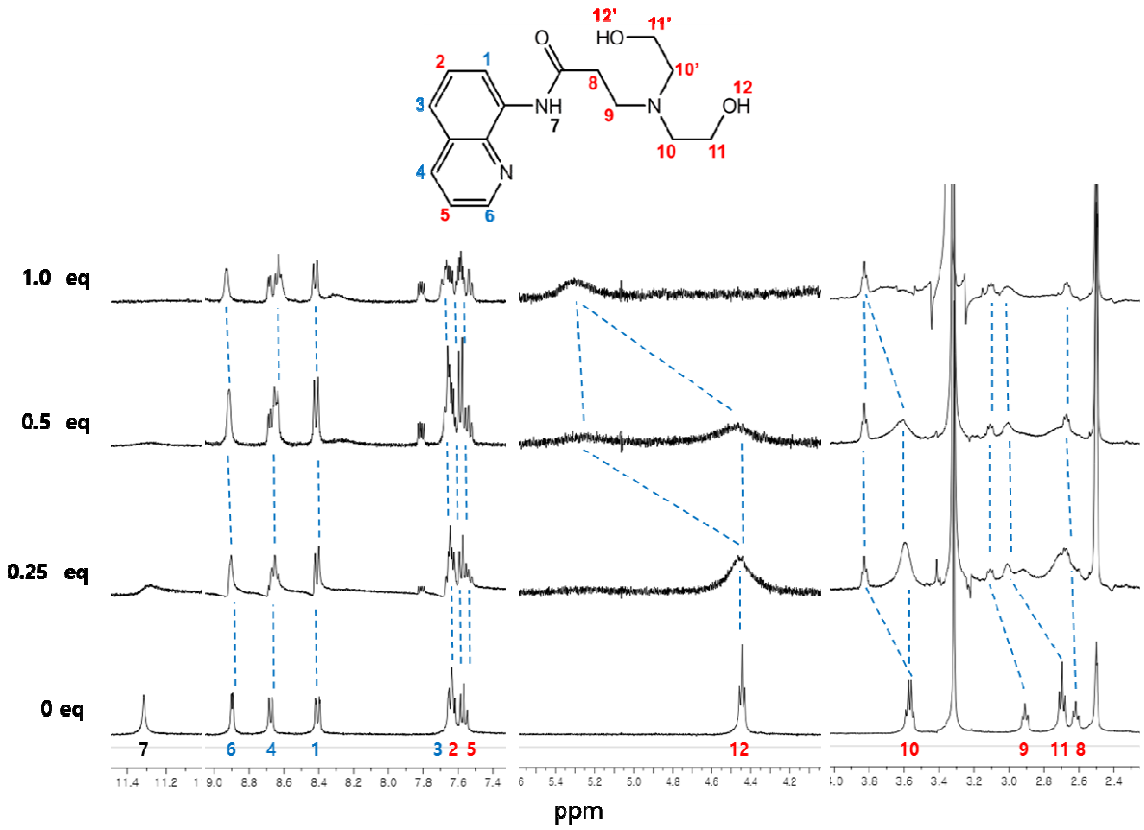


Fig. 5

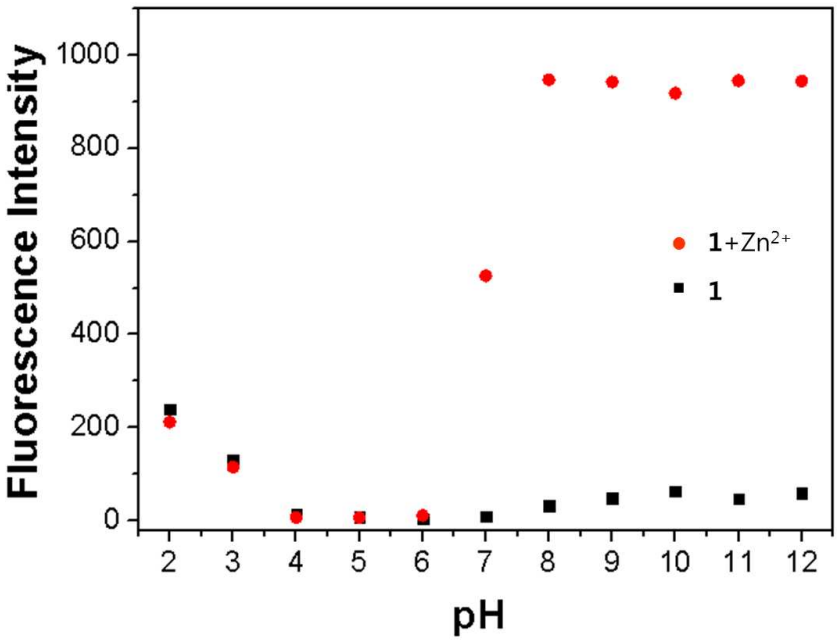
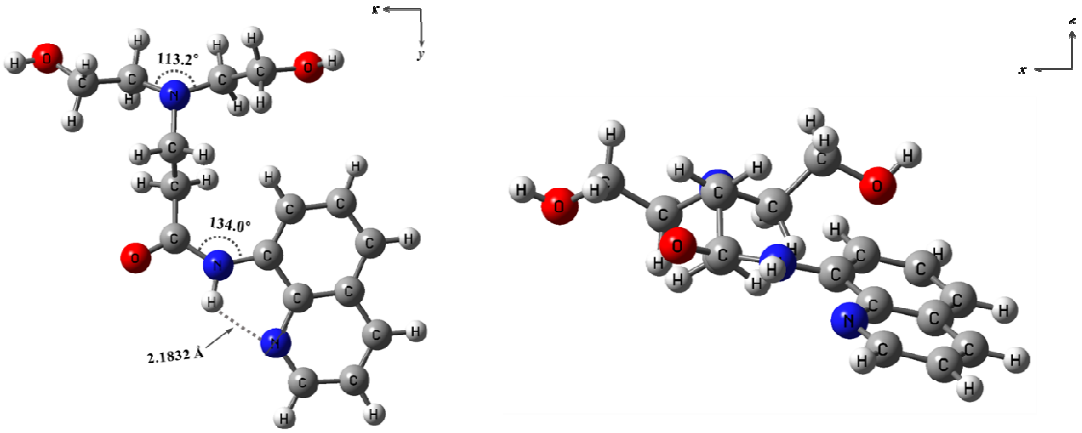

Fluorescence Intensity
1000
800
600
400
200
0
2
3
4
5
6
7
8
9
10
11
12
pH
1+Zn2+
1

Fig. 6

(a)



(b)

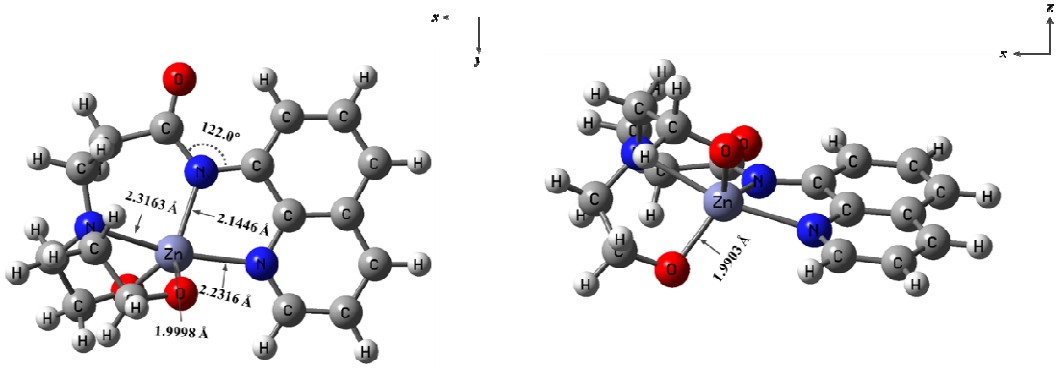
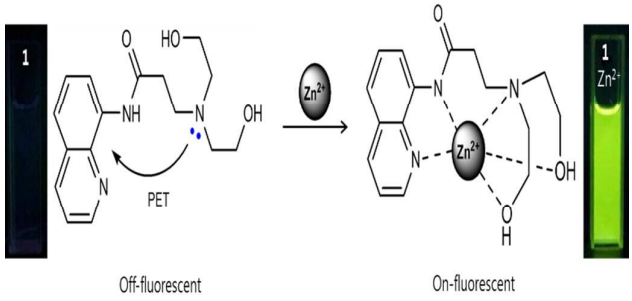


Fig. 7

Graphical abstract



A water-soluble fluorescent sensor with a low detection limit could be used to detect and quantify Zn^{2+} in water samples.