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Both Visual and Fluorescent Sensor for Zn^{2+} Based on Quinoline Platform

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A fluorescent Zn^{2+} sensor 2-(hydroxymethyl)-4-methyl-6-((quinolinyl-8-imino)methyl)phenol (HMQP) based on the 8-aminoquinoline platform has been synthesized. This sensor displays high selectivity, sensitive fluorescence enhancement, strong binding ability, and ratiometric response to Zn^{2+} in Tris−HCl (50 mM, pH 7.54), THF−H_2O (9:1, v/v). And an obvious color change between HMQP and Zn^{2+}−MQP^- can be visually observed by the naked eye. The composition of the complex Zn^{2+}−MQP^- has been found to be 1:2 based on the fluorescence/absorption titration and further confirmed by X-ray crystallography.

Introduction

Zinc is the second most abundant transition metal in the human body behind iron, and it plays diverse roles in biological processes such as regulation of enzymes,[1] DNA binding or recognition, structural cofactors, neural signal transmission, associated diseases, catalytic center, and others.[2] However, many effective roles of Zn^{2+} in the human body are still poorly understood.[3] The demand for sensing Zn^{2+} is spectroscopically or magnetically silent because of its $3d^{10}4s^0$ electronic configuration.[4] In addition, it is still a challenge to develop chemosensors that can discriminate Zn^{2+} from Cd^{2+},[5] because cadmium and zinc are in the same group of the periodic table and have similar properties, which usually cause similar spectral changes after interacting with chemosensors. In this sense, the design and synthesis of fluorescent selective Zn^{2+} chemosensors are of great interest. Although there are many commercially available Zn^{2+} sensors,[6] to satisfy various needs, chemists still need to design novel ones that are simpler, easier to synthesize, and have better sensitivity, selectivity, and reliability.[7]

Currently, most of the available Zn^{2+} sensors detect the analyte concentration by an increase in the emission intensity. However, the emission intensity is also dependent on many other factors, such as emission collection efficiency, environment around the sensor, sensor concentration, bleaching, optical path length, and illumination intensity.[8] Therefore, it is desirable to eliminate the effects of these factors by using a ratiometric sensor. This kind of sensor exhibits a spectral shift upon reaction or binding to the analyte of interests, and the ratio of emission intensities between the ligand and its complex can be used to evaluate the analyte concentration.[9] The potential advantage of this approach is easy of

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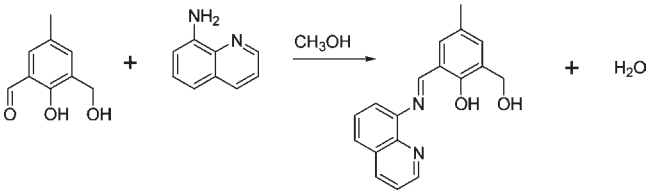
visualization by color.[10] Until now, there have been few commercially available Zn^{2+} ratiometric sensors, and thus the design of ratiometric probes for Zn^{2+} is highly desired.[11]

The commonly used Zn^{2+} fluorescent sensors are quinoline derivatives, namely, 6-methoxy-(8-*p*-toluenesulfonamido)quinolin (TSQ) and Zinquin.[12] Both of them are the requirement of ultraviolet excitation, which lead to an additional increase in autofluorescence and irreversible damages in cellular work.[13] Although there are many highly effective sensors, most of them often require laborious multistep organic synthesis, which slows the discovery process and causes the prohibitively high cost. To develop a simple, facile, and ratiometric Zn^{2+} sensor with long excitation wavelength (in the visible range), we herein introduced a Schiff base fluorescent sensor HMQP for Zn^{2+}, which is derived from 8-aminoquinoline. The absorption and fluorescence properties of HMQP in THF−H_2O, 9:1 (v/v) at pH 7.54 were investigated. When Zn^{2+} was introduced to HMQP, the intramolecular hydrogen bond of HMQP is broken, which prohibits intramolecular electron-transfer process,[14] and then enhances fluorescence emission. Simultaneously, the deprotonated MQP^- strengthens the electron-donating ability of the nitrogen atom of the 8-amino group to the quinoline ring. And the electron transfer from the nitrogen atom of the heterocycle to the metal ion further enhances the internal charge transfer (ICT) process. As a result, a red-shift in emission wavelength can be observed. In contrast, other transition metal ions were introduced, the fluorescence intensities are either unchanged or weakened. The unique enhancement of fluorescence is attributed to the strong binding of Zn^{2+}, which is evident from a large binding constant value ($\log K = 8.45$). Besides, HMQP can detect Zn^{2+} in visual, and the visible color change can be easily observed by the introduction of Zn^{2+}. Reaction of zinc(II) perchlorate with HMQP afforded the mononuclear neutral complex Zn-$(MQP)_2 \cdot H_2O$, which was characterized by elemental analysis and single-crystal X-ray structural determination.

Experimental Section

Materials and Methods. Fresh anhydrous THF was used in the spectroscopic studies. All other reagents and solvents employed for synthesis were commercially available and used as received without further purification. Tris−HCl solution (50 mM, pH 7.54) were prepared in THF−H_2O (9:1, v/v). A starting solution (THF−H_2O) of 100 mM NaOH and 10 mM NaCl (pH ∼13) was used for pH titrations. The pH values were lowered to ∼1.3 by the addition of aqueous HCl (THF−H_2O). All pH measurements were made with a pH-10C digital pH meter. Melting point was determined on a Kofler apparatus. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured on a Bruker DRX 400 spectrometer in *d*-DMSO solution with TMS as internal standard. ESI-TOF mass spectrum was measured on Mariner MS spectrometer. Absorption spectra were recorded using a Varian Cary 100 spectrophotometer and fluorescence measurements were made on a Hitachi F-4500 spectrofluorimeter equipped with quartz cuvettes of 1 cm path length with a xenon lamp as the excitation source. An excitation and emission slit of 5.0 nm were used for the measurements of fluorescence. Elemental analyses were conducted using an Elemental Vario EL. FT-IR spectra were recorded on Nicolet FT-170SX instrument using KBr discs in the 400−4000 cm^{-1} region. Fluorescent quantum yields were determined by an absolute method using an integrating sphere on FLS920 of Edinburgh Instrument. All the measurements have been done at room temperature unless otherwise stated.

Scheme 1. Synthesis of HMQP



Caution: *Although no problems were encountered during the preparation of perchlorate salts, suitable care should be taken when handling such potentially hazardous compounds.*

Synthesis of HMQP. The preparation of the target compound started with (2-hydroxy-3-hydroxymethyl)-5-methylbenzaldehyde which followed a published procedure (see Scheme 1).[15] In the last step, 8-aminoquinoline (0.512 g, 4 mmol) dissolved in 10 mL of methanol was added to 25 mL of a methanol solution of 2-hydroxy-3-(hydroxymethyl)-5-methylbenzaldehyde (0.664 g, 4 mmol) (see Scheme 1). The reaction mixture was stirred for 4 h at room temperature. A red solid was isolated after removing solvent under reduced pressure, and then recrystallization from ethyl acetate. The resulting Schiff base, 2-hydroxymethyl-4-methyl-6-((quinolinyl-8-imino)methyl)phenol, HMQP was obtained (yield = 1.02 g, 88%). M.p.: 136.3−136.8 °C. Anal. Calcd for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. Found: C, 74.02; H, 5.43; N, 9.64. ^{1}H NMR (*d*-DMSO, 400 MHz): δ 2.31 (s, 3H, Ar−CH_3), 4.83 (s, 2H, CH_2), 5.14 (m, 1H, CH_2−OH), 7.32, 7.40 (m, 2H, Ar−H), 7.62−7.94, 9.0, 9.07 (6H, Q-H), 8.40 (1H, HC=N), 14.3 (1H, Ar−OH). ^{13}C NMR (*d*-DMSO, 100 MHz): δ 20.21, 117.96, 118.03, 122.13, 126.53, 126.56, 126.82, 128.73, 130.10, 130.64, 132.03, 136.21, 141.78, 144.34, 150.58, 156.73, 164.26. FT−IR (KBr pellet) (cm^{-1}): 3420.05 (br), 1617.23 (s), 1610.64 (vs), 1534.58 (s), 1417.16 (m), 1369.70 (w), 1246.85 (w), 1203.00 (m) (br, broad; w, weak; m, medium; s, strong; vs, very strong). Ms: m/z 293.0 $(M+1)^+$.

Synthesis of Zn(MQP)$_2 \cdot$H$_2$O. A 10 mL acetonitrile solution of $Zn(ClO_4)_2 \cdot 6H_2O$ (0.0185 g, 0.05 mmol) was added slowly to a magnetically stirred 10 mL acetonitrile solution of the ligand (HMQP) (0.0292 g, 0.1 mmol). The mixture was stirred in air for 4 h whereby a yellow solution was formed. It was filtered and kept in air. Pale yellow prismatic single crystals of $Zn(MQP)_2 \cdot H_2O$ suitable for X-ray crystallography were obtained on slow evaporation of the filtrate within 7 days. Anal. Calcd for $C_{36}H_{32}N_4O_5Zn$: C, 64.92; H, 4.84; N, 8.41. Found: C, 64.54; H, 4.95; N, 8.58. FT−IR

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Table 1. Crystal Data and Details of the Structure Determination for Zn-$(MQP)_2 \cdot H_2O$

formula	$C_{36}H_{32}N_4O_5Zn$
M_r	665.01
cryst syst	monoclinic
space group	$P2_1/c$
T (K)	296
a (Å)	16.752(6)
b (Å)	12.843(5)
c (Å)	16.098(6)
α (deg)	90
β /deg	115.507(5)
γ (deg)	90
V (Å^3)	3126(2)
Z	4
F(000)	1376
D_c (kg m^{-3})	1.410
μ (mm^{-1})	0.836
radiation (Å)	0.71073
unique data	5815
R(int)	0.038
observed data [$I > 2.0\sigma(I)$]	4179
R_1	0.0420
wR_2	0.1031
GOF	1.01

(KBr pellet) (cm^{-1}): 3424.89 (br), 1621.01 (s), 1602.20 (vs), 1543.62 (m), 1416.34 (m), 1324.56 (w), 1238 (w), 1219.58 (m).

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 $K\alpha$ radiation ($\lambda = 0.71073$ Å). The crystal was mounted inside a Lindemann glass capillary for data collection using the SMART and SAINT software.[16] An empirical absorption correction was applied using the SADABS program.[17] The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL-97 program package.[18]

Crystal data and details of the structure determination for Zn-$(MQP)_2 \cdot H_2O$ are summarized in Table 1. CCDC 737684 contains 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 absorption spectrum of HMQP exhibits a broad band at 338 nm at room temperature in Tris−HCl (50 mM, pH 7.54), THF−H_2O (9:1, v/v). To investigate the binding property of HMQP toward Zn^{2+}, we measured the UV−vis spectra of HMQP (0.1 mM) in the presence of various concentrations of Zn^{2+} (0−75 μM), as shown in Figure 1. The absorbance of HMQP at 338 nm gradually decreases with an increasing concentration of Zn^{2+}. Moreover, a new absorption band appears at 455 nm, and its absorbance gradually increases with the addition of Zn^{2+}. This absorption peak is likely due to the coordination of HMQP with Zn^{2+}.[19] The changes that occurred in the UV−vis spectra arise from the coordination of Zn^{2+} to the N_4O_2 binding sites, which broke the intramolecular hydrogen bond of HMQP, increased its coplanarity of the conjugated system and could be confirmed by X-ray crystallography.

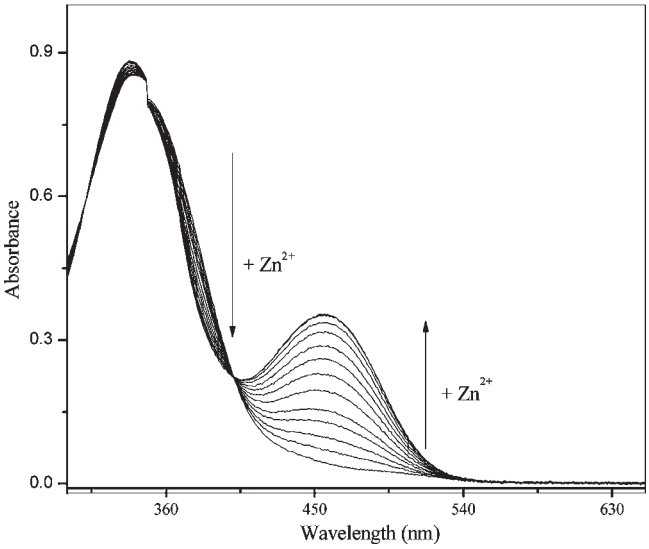

Figure 1. UV−vis spectral changes of HMQP upon addition of Zn^{2+} in Tris−HCl (50 mM, pH 7.54), THF−H_2O (9:1, v/v) at room temperature ([HMQP] = 0.1 mM, [Zn^{2+}] = 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, and 75 μM).

Fluorescence Spectra and Titration. The optical properties of HMQP are mainly dominated by the quinoline group. The fluorescent response of HMQP for Zn^{2+} is sensitive in some aqueous solvent systems, such as THF, MeOH, DMF, and DMSO−H_2O (9:1, v/v) (Figure 2, S1, S2, and S3), among which THF−H_2O (9:1, v/v) shows excellent selectivity. The emission spectrum of HMQP, which is excited at 455 nm, exhibits the emission maximum at 515 nm with a low quantum yield ($\Phi = 0.006$), at room temperature in Tris−HCl (50 mM, pH 7.54), THF−H_2O (9:1, v/v) (Figure 2). Upon the addition of 0.5 equivalents of Zn^{2+}, the fluorescence intensity of HMQP increases by 14-fold, the emission maximum shifts from 515 to 565 nm and the quantum yield ($\Phi = 0.045$) results in a more than 7-fold increase. While the introduction of other metal ions, no obvious red-shift can be observed in the fluorescence spectra, revealing that this change is specific for Zn^{2+}. The fluorescence intensity of HMQP is slightly quenched with some cations such as Cu^+, Cu^{2+}, Co^{2+}, and Fe^{3+}. Other cations such as Na^+, K^+, Li^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Hg^{2+}, Fe^{2+}, Cd^{2+}, Pb^{2+}, Ag^+, Cr^{3+}, and Ni^{2+} have little effect on the fluorescence spectra of HMQP, showing selective chelation-enhanced fluorescence in the presence of Zn^{2+}.[20]

In the case of Zn^{2+}, the emission maximum of HMQP was shifted to 565 nm with significant visual color change from colorless to yellow (Figure 2, inset). However, other metal ions did not show any visual changes. The new emission band (565 nm) of Zn^{2+}−MQP^- may arise from two effects. First, the binding of MQP^- to Zn^{2+} can form a five-membered chelate ring with the aminoquinoline moiety through two nitrogen atoms and a six-membered chelate ring with the Schiff base −C=N and Ar−OH, which enlarges the conjugated system, and thus reduces the energy difference between n and π^* orbital.[21] Moreover, the dipole moment of the complex is also increased

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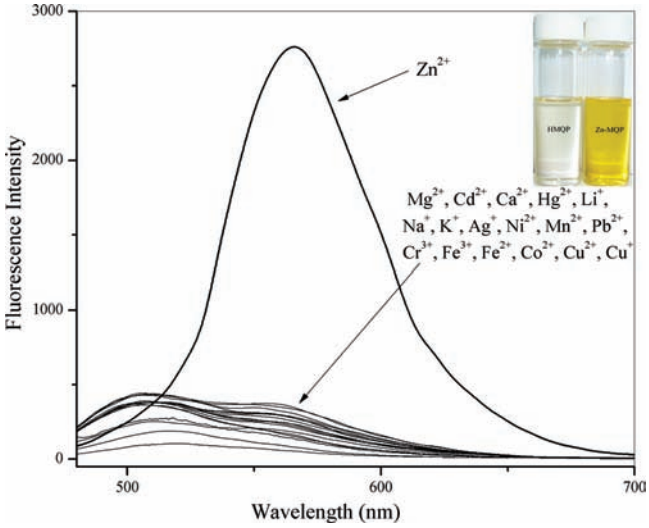

Figure 2. Fluorescence emission spectra of HMQP in the presence of different ions such as Li^+, Na^+, K^+, Ag^+, Mg^{2+}, Ca^{2+}, Cu^{2+}, Cu^+, Co^{2+}, Cr^{3+}, Ni^{2+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+} (Fe^{2+} as $Fe(SO_4)_2$, Cu^+ as $Cu(NH_3)_2Cl$, any other metal ions as their ClO_4^- salts) in Tris−HCl (50 mM, pH 7.54), THF−H_2O (9:1, v/v). λ_{ex} = 455 nm, [MQP^-] = 0.1 mM, [M^{n+}] = 0.05 mM. (Inset) The color change of HMQP in Tris−HCl (50 mM, pH 7.54), THF−H_2O (9:1, v/v) without and with addition of $Zn(ClO_4)_2$.

by the binding of Zn^{2+} to HMQP, causing a higher electron mobility in the π orbital. Second, the deprotonated ligand upon complexation with Zn^{2+} leads to the increase in both the electronic density of the 2-hydroxy-3-(hydroxymethyl)-5-methylbenzaldehyde and the electron-donating ability from the nitrogen atom of the 8-amino group to the quinoline ring, enhancing the ICT process from the nitrogen atom of the heterocycle to the metal ion.

The coordination mode of HMQP to Zn^{2+} was investigated by fluorescence titration in Tris−HCl (50 mM, pH 7.54), THF−H_2O (9:1, v/v) (Figure 3). The intensity ratio between 565 and 515 nm ($F_{565\ nm}/F_{515\ nm}$) increases linearly with the concentration of Zn^{2+} (0−1.5 equiv.) up to a mole ratio (HMQP/Zn^{2+}) of 2:1 (Figure 3, inset). Titration of HMQP with Zn^{2+} was followed by fluorescence and absorption spectroscopy to determine the Zn^{2+}−MQP^- binding ratio and binding constant ($K = [Zn(MQP)_2]/[Zn^{2+}][MQP^-]^2$). The log K of Zn^{2+}−MQP^- is observed to be 8.45 by fluorescence titration (Supporting Information, Figure S4) and 8.48 by absorption titration (Figure S5), which unambiguously demonstrates the strong binding ability of HMQP with Zn^{2+}. The binding ratios are determined to be 2.0128 and 1.9678. These results suggest that MQP^- in solution should form 2:1 complex with Zn^{2+}, which is confirmed by Job's plot (Figure S6) and the crystal structure of $Zn(MQP)_2 \cdot H_2O$ (Figure 4). In addition, it is found that the fluorescence intensity of HMQP was enhanced by Mg^{2+} or Ca^{2+} in some mixed solvents except THF−H_2O (9:1, v/v) (Figures 2 and S1−S3). It may be due to the solvent effects, as we determined the binding constants of HMQP with these three metals (Ca^{2+}, Mg^{2+}, and Zn^{2+}) in these mixed solvents, and found that the log K of Zn^{2+}−MQP^- was quite higher than those of Ca^{2+}−MQP^- and Mg^{2+}−MQP^- (Table S1 in the Supporting Information).

The fluorescence properties of the sensor in aqueous solution are very important for application in living systems.

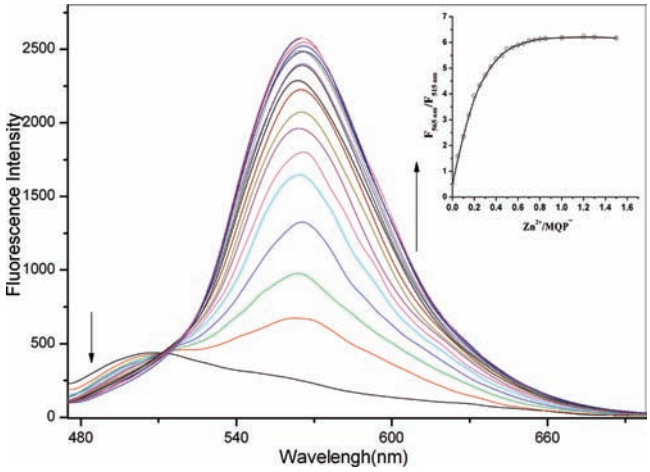

Figure 3. Fluorescence emission spectra of HMQP upon addition of Zn^{2+} in Tris−HCl (50 mM, pH 7.54), THF−H_2O (9:1, v/v), λ_{ex} = 455 nm at room temperature ([HMQP] = 0.10 mM, [Zn^{2+}] = 0, 0.005, 0.010, 0.015, 0.020, 0.025, 0.030, 0.035, 0.040, 0.045, 0.050, 0.060, 0.075, 0.10, and 0.15 mM). (Inset) The corresponding Zn^{2+} titration profile according the ratiometric calibration curve $F_{565\ nm}/F_{515\ nm}$, indicating the 1:2 stoichiometry for Zn^{2+}−MQP^-.

As the solubility of HMQP in water was poor, efforts are under way to design and synthesize water-soluble analogues, which can be used for detecting Zn^{2+} in the living system.

Metal Ion Competition Studies. The individual emission response of HMQP against different transition metal ions revealed a remarkable selectivity of Zn^{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 HMQP for Zn^{2+}, we measured the fluorescence intensity of HMQP in the presence of Zn^{2+} mixed with various metal ions in Tris−HCl (50 mM, pH 7.54), THF−H_2O (9:1, v/v) (Figure 5). The emission intensity of Zn^{2+}-bound HMQP are unperturbed in the presence of 5 mM Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Fe^{2+}, and Cu^+, indicating excellent selectivity for Zn^{2+} over these biologically competing cations. Similar unperturbed emission intensity of Zn^{2+}−MQP^- are also observed in the presence of 5 equiv. of Li^+, Mn^{2+}, Hg^{2+}, Cd^{2+}, Pb^{2+}, Ag^+, Cr^{3+} and Ni^{2+}, whereas 5 mM Cu^{2+} and 0.5 mM Co^{2+} quench the fluorescence. The quenching is not due to the heavy-atom effect because other heavy-atom did not quench the fluorescence, but due to the displacement of Zn^{2+} by Cu^{2+} or Co^{2+} from Zn^{2+}−MQP^-.[22]

To explain the quenched fluorescence of Zn^{2+}−MQP^- in the presence of Cu^{2+} or Co^{2+}, we investigated the absorption titration of HMQP with Cu^{2+} and Co^{2+}, similar absorbance changes of HMQP with Cu^{2+}, Co^{2+}, and Zn^{2+} were observed (Figure S7, S8 and 1). These results imply that HMQP has the similar coordination mode to Cu^{2+}, Co^{2+} and Zn^{2+}. The binding constants ($K = [M(MQP)_2]/[M^{2+}][MQP^-]^2$) of Cu^{2+}−MQP^- and Co^{2+}−MQP^- were determined according to the absorption

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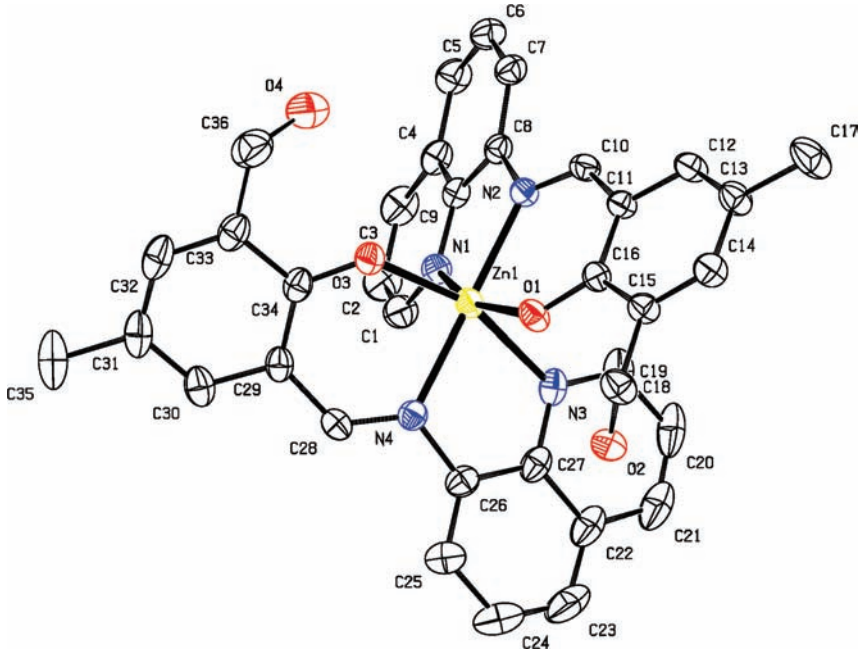

Figure 4. Thermal ellipsoid (30% probability level) plot of $Zn(MQP)_2 \cdot H_2O$. All hydrogen atoms, disordered hydroxyl, and solvent molecules were deleted for clarity.

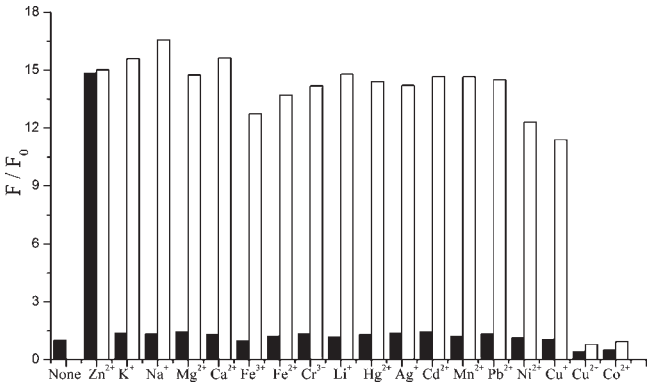

Figure 5. Selectivity of HMQP for Zn^{2+} in the presence of other metal ions in Tris−HCl (50 mM, pH 7.54), THF−H_2O (9:1, v/v), λ_{ex} = 455 nm. The response is normalized with respect to the background fluorescence of the free ligand (F_0). Black bars represent the addition of an excess of the appropriate metal ion (5 mM for Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Fe^{2+}, Cu^+ and Cu^{2+}, 0.5 mM for all other metal ions) to a 0.1 mM solution of HMQP. White bars represent the subsequent addition of 0.05 mM Zn^{2+} to the solution.

titration spectra, and the calculated values of log K are about 9.24 and 9.12, respectively (Figure S9, S10), both of which are higher than the log K of Zn^{2+}−MQP^- (8.48, Figure S5). Furthermore, the combine abilities of Cu^{2+} and Co^{2+} with HMQP were investigated by the fluorescence titration of Cu^{2+} and Co^{2+} on Zn^{2+}−MQP^-. It is found that the Zn^{2+}-induced fluorescence enhancement of HMQP was prevented more and more as the concentrations of Cu^{2+} and Co^{2+} gradually increased (Figures S11 and S12 in the Supporting Information). Therefore, Cu^{2+} and Co^{2+} could form complexes with HMQP and thus quenched the fluorescence. There are many other Zn^{2+} sensors, which have exhibited similarly depressed responses due to the competition from these ions (Cu^{2+}, Co^{2+}).[23] However, these free cations would have little influence in vivo because they exist at a very low concentration.[24] As a beneficial attempt, HMQP shows an outstanding selectivity for Zn^{2+} in the presence of 5 mM dextrose or some amino acid such as lysine, alanine, glutamic acid, etc. (see Figure S13 in the Supporting Information).

Effect of pH. In addition to metal ion selectivity, for many biological applications, it is very important that the sensor can be suitable for measuring specific cation in the physiological pH range. Therefore, we measured the fluorescence intensity of HMQP in the absence and presence of Zn^{2+} at various pH values. As can be seen from Figure 6, the emission intensity of HMQP slightly increases gradually at first and then decreases in acid conditions with maximal fluorescence occurring at pH ~5.0. And essentially no change can be observed under neutral and alkaline conditions (pH 7−13). However, the Zn^{2+}-induced fluorescence enhancement of HMQP continues increasing in the pH 1.3−7 range, which may be due to the competition of H^+.[3b,7] The emission of Zn^{2+}−MQP^- maintains fairly intense from pH ~7 to pH ~9.5 and is ~60% quenched at higher pH (~13). The observed decreasing response at pH > 9.5 may be due to the formation of $Zn(OH)^+$ or $Zn(OH)_2$ and thus reducing the concentration of Zn^{2+}−MQP^-. However, HMQP exhibits satisfactory Zn^{2+} sensing abilities when the pH is in the range of 7−9.5, indicating that HMQP possesses the highest sensing ability in an environment similar to serum (pH ca. 7.3).

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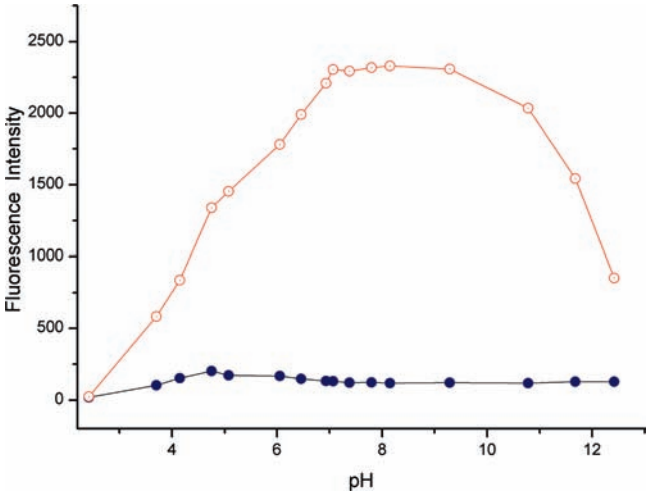

Figure 6. Fluorescence intensities of HMQP and Zn^{2+}−MQP^- at various pH values at room temperature, THF−H_2O (9:1, v/v), λ_{ex} = 455 nm. Red line, the fluorescence intensities at 565 nm of Zn^{2+}−MQP^- at various pH ([HMQP] = 0.10 mM, [Zn^{2+}] = 0.05 mM); blue line, the fluorescence intensities at 515 nm of HMQP at various pH ([HMQP] = 0.10 mM).

Crystal Structure of $Zn(MQP)_2 \cdot H_2O$. The structure of the Zn^{2+} complex with HMQP is shown in Figure 4. Selected bond lengths and bond angles are given in Table 2. It crystallizes in the monoclinic system, with space group $P2_1/c$ from acetonitrile solvent. The Zn^{2+} is six-coordinate with two oxygen atoms and four nitrogen atoms from two MQP^- ligands which forms a five−membered distorted chelate ring and a six-membered chelate ring with each one MQP^- ligand. The dihedral angle between the benzene and quinoline rings of the ligand is about 29.54°. And a free water molecule exists in this complex. The bond lengths of Zn1−N1 and Zn1−N2 are 2.212 and 2.091 Å, respectively, which are well within the range for normal Zn−N bonds with quinoline−like ligands, indicating that HMQP has a strong chelation-enhanced fluorescence with Zn^{2+}.[25]

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg)

Zn1−O1	2.026(2)	Zn1−O3	2.013(2)
Zn1−N1	2.212(3)	Zn1−N2	2.091(2)
Zn1−N3	2.217(3)	Zn1−N4	2.106(2)
O1−Zn1−O3	98.04(9)	O1−Zn1−N1	160.39(9)
O1−Zn1−N2	87.95(9)	O1−Zn1−N3	88.04(9)
O1−Zn1−N4	96.55(9)	O3−Zn1−N1	94.80(9)
O3−Zn−N2	95.31(9)	O3−Zn1−N3	161.01(9)
O3−Zn1−N4	86.33(9)	N1−Zn1−N2	76.12(9)
N1−Zn1−N3	84.54(10)	N1−Zn1−N4	99.02(9)
N2−Zn1−N3	102.91(10)	N2−Zn1−N4	174.96(9)
N3−Zn1−N4	75.07(10)		

Conclusions

We have successfully developed a simple, "naked-eye", and ratiometric fluorescent sensor, HMQP for Zn^{2+}, and investigated the Zn^{2+} fluorescence sensing and binding properties of HMQP. It displays high selectivity for Zn^{2+} and can be used as a ratiometric Zn^{2+} fluorescent sensor under visible light excitation. An approximately 14-fold Zn^{2+} selective chelation-enhanced fluorescence response in Tris−HCl (50 mM, pH 7.54), THF−H_2O (9:1, v/v) is attributed to the strong coordination ability of Zn^{2+} with HMQP. The poor water solubility of the sensor will be improved by the introduction of appropriate substituents into HMQP, which is expected to detect Zn^{2+} in the living system.

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Supporting Information Available: CIF file; Table S1 and Figures S1−S13 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.