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# A novel fluorescent chemosensor for Zn(II) based on 1,2-(2'-oxoquinoline-3'-yl-methylideneimino)ethane

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## A R T I C L E I N F O

## ABSTRACT

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Keywords: Bis Schiff-base Fluorescence sensor Crystal structure Zn(II) complex A new bis Schiff-base ligand (1,2-(2'-oxoquinoline-3'-yl-methylideneimino)ethane, QSB) derived from 2-oxo-quinoline-3-carbaldehyde and ethylene diamine was synthesized and characterized by <sup>1</sup>H-NMR. Spectroscopic investigation revealed that the compound exhibited a high selectivity toward Zn(II) ion over other metal ions in acetonitrile solution. In addition, the crystal structure showed that the coordination form of QSB and Zn(II) was 1:1.

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In recent years, there has been an increasing focus on the design and synthesis of highly selective fluorescent chemosensors for zinc ion [1–7]. Zinc ion which is the second most abundant transition metal ion in the human body plays an important role in biological system such as neuronal signal transmission, regulator of enzymes and DNA-binding [8–10], in addition, too much zinc is also a harmful metal pollution to the environment [11]. However, the discrimination between Zn(II) and many other metal ions is difficult due to the similar chemical properties [12]. Therefore, the detection of fluorescent chemosensors for Zn(II) is very significant for diagnosing disease and controlling environment pollution [13].

Up to now, many fluorescent chemosensors based on quinoline derivatives have been reported and some show high fluorescence selectivity for Zn(II) [14–17], but only a few chemosensors can distinguish Zn(II) from Cd(II) [18]. Hence, the fluorescence chemosensors for Zn(II) rather than Cd(II) based on quinoline derivates need to be developed. Owing to simplicity and sensitivity of Schiff-base type fluorescence sensors, many fluorescent chemosensors based on Schiff-base have been designed and investigated [19–21]. Herein, we report a novel bis Schiff-base fluorescent sensor (QSB) derived from 2-oxo-quinoline-3-carbaldehyde and ethylene diamine. As a new fluorescent sensor for Zn(II), the QSB exhibits a high sensitivity and selectivity. Simultaneously, the 1:1 coordinative formation between QSB and Zn(II) is demonstrated by X-ray crystal diffraction.

As shown in Scheme 1, 2-oxo-quinoline-3-carbaldehyde was prepared according to the literature [22,23]. An ethanol solution containing ethylene diamine was added to another ethanol solution

containing 2-oxo-quinoline-3-carbaldehyde under reflux to obtain the QSB [24].

The single crystal of Zn–QSB complex was obtained by slow evaporation in CH<sub>3</sub>CN to understand the coordinative geometry between ligand and Zn(II) clearly. A yellow crystal of Zn(II) complex was measured on a Bruker APEX-II CCD diffractometer with graphite monochromatic Mok $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 296(2) K [25]. As shown in Fig. 1, the binding mode of ligand and Zn(II) was 1:1 coordination and the Zn(II) complex exhibited good symmetrical structure. There were two six atom rings and a five atom ring around the zinc atom and the coordinative structure was described as a standard octahedral geometry due to two coordinative H<sub>2</sub>O molecules (Zn<sub>1</sub>O<sub>1</sub>O<sub>2</sub>O<sub>3</sub>O<sub>4</sub>N<sub>2</sub>N<sub>3</sub>). In addition, the unit cell contained two non-coordinative nitrate radicals and the asymmetric unit cell of the complex consists of eight crystallographically independent molecules of the complex.

The influence of different solvent on the fluorescence intensities was investigated in detail. QSB was dissolved in DMSO to get a 1.0 mM concentration, then diluted with other solvents. As shown in Fig. 2, the fluorescence intensity and peak shape in aqueous solution was very different from that in other anhydrous solution (ethanol, acetone, acetonitrile, and chloroform), we deduced that this can be a quenching effect of water molecule and that the fluorescence intensity in acetonitrile solution was the largest. So all metal ions were from nitrate salts and were dissolved in acetonitrile at a concentration of 1.0 mM and the spectroscopic measurements (UV-Vis and fluorescence) were tested in acetonitrile solution.

The UV-Vis absorbance titration spectrum of QSB against Zn(II) showed that the absorbance at 225 nm had a pronounced redshift to 250 nm, simultaneously, the absorption peaks at 300 nm and 350 nm increased with the addition of Zn(II) and also exhibited appropriate

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Scheme 1. Synthesis of ligand (QSB).

redshift (Fig. 3). The changes of UV-Vis absorption spectrum of QSB with addition of Zn(II) illustrated that a new complex was generated between QSB and Zn(II).

To investigate the fluorescent selectivity of QSB for various transition metal ions in detail, the fluorescent titration spectrum was studied systemically (Fig. 4). The ligand ( $20 \mu$ L, 1 mM) was titrated with metal ions ( $40 \mu$ L, 1 mM). With addition of 2 equiv. of Zn (II), the emission intensity at 423 nm increased strongly, however, in presence of other metal ions such as K(I), Na(I), Mg(II), Cr(III), Cd(II), Cu(II), Ni(II), Co(II), the fluorescence changed weakly. This phenomenon demonstrated that the QSB exhibited a high selectivity for Zn(II)



**Fig. 1.** ORTEP view of Zn–QSB complex showing the atom numbering of scheme and 30% thermal ellipsoids probability for the non-hydrogen atoms.



Fig. 2. Fluorescence intensity change of QSB with addition of 2 equiv. of Zn(II) in different solvent (water, ethanol, acetone, acetonitrile, chloroform).

ion over the other ions. Fig. 5 showed the relative fluorescence intensity of QSB in the presence of metal ions and without metal ions. And that the histogram illuminated clearly that the QSB exhibited high selectivity for Zn(II) in acetonitrile.

Furthermore, the fluorescence titration experiment in acetonitrile solution was conducted to measure the fluorescence-on behavior in



Fig. 3. UV-Vis titration spectra of QSB (10.0  $\mu M)$  in the presence of different concentrations of Zn(II) ion (0, 2.5, 5.0, 7.5, 10.0, 12.5, 15.0, 17.5 and 20.0  $\mu M)$  in acetonitrile solution.



Fig. 4. Fluorescence intensity of QSB (10  $\mu$ M) in the presence of various metal ions (20  $\mu$ M) in acetonitrile solution (excitation 305 nm, emission 423 nm).







Fig. 6. Fluorescence intensity emission spectrum of QSB in presence of different concentration Zn(II) (0, 2.5, 5.0, 7.5, 10.0, 12.5, 15.0, 17.5, 20.0, 22.5, 25.0, 27.5 and 30.0 µM) in acetonitrile solution.

the presence of Zn(II). As shown in Fig. 6, the fluorescence intensity of 423 nm increased significantly and reached saturation with the addition of Zn(II). A plot of relative fluorescence intensity  $(I/I_0)$ versus [Zn]/[QSB] explicitly (Fig. 6 inset) illustrated that there was a more than 20 fold increase when compared to QSB. Simultaneously, the formation of 1:1 metal complex between Zn(II) and QSB was also illustrated by the inset [26]. This coordinative mode from fluorescence titration was corresponding to the structure from X-ray diffraction.

In conclusion, a novel fluorescent chemosensor (QSB) based on a bis Schiff-base ligand derived from 2-oxo-quinoline-3-carbaldehyde and ethylene diamine is developed. Compared with other metal ions, the chemosensor QSB exhibits high selectivity and sensitivity for Zn (II) in acetonitrile solution, moreover, the single crystal between the ligand and Zn(II) is also obtained, so the coordinative geometry is demonstrated clearly according to the single crystal analysis. The remarkable photophysical properties of the chemosensor will be helpful for the development of fluorescent sensor based on quinoline derivates.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2010.02.014.

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- [24] An ethanol solution (10 mL) containing ethylene diamine (0.12 g, 2.0 mmol) was added to another ethanol solution (10 mL) containing 2-oxo-quinoline-3-carbaldehyde (0.692 g, 4.0 mmol). The mixture was refluxed for 6 h with stirring and a white precipitate separated out. The precipitation was filtrated under decompression and washed with ethanol. Recrystallization from DMF/H2O (V:V=1:1) gave the ligand, which was dried under vacuum. Yield, 70%. m.p: 317-319 °C. <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>  $300 \text{ MHz}); \delta 11.992 (2H, s, -N^1-H), \delta 8.562 (2H, s, -CH=N), \delta 8.441 (2H, s, -C^{4,4'}-H), \\ \delta 7.9797-7.838 (2H, m, -C^{8,8'}-H), \delta 7.490-7.567 (2H, m, -C^{7,7'}-H), \delta 7.279-7.317 (2H, m, -C^{5,5'}-H), \delta 7.152-7.224 (2H, m, -C^{6,6'}-H), \delta 3.915 (4H, s, -C^{10,10'}-H).$
- [25] X-ray crystal data of Zn–QSB. Formula, C22 H22 N6 O10 Zn1; Crystal system, C2/c; Space group, Monoclinic; *a*(Å), 27.000(2), *b*(Å), 25.6160(17), *c*(Å), 7.0703(5);  $\alpha(°)$ , 90.00,  $\beta(°)$ , 91.009(2),  $\gamma(°)$ , 90.00; Reflections collected, 3851/5039; Abs coeff  $(mm^{-1})$ , 0.0998; Final *R* indices, R1 = 0.0343, wR2 = 0.0823.
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