Inorganic Chemistry Communications 14 (2011) 1297–1301

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Synthesis, characterization and crystal structure of a new fluorescent probe based on Schiff Base for the detection of Zinc (II)

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ARTICLE INFO

Article history:
Received 9 April 2011
Accepted 16 May 2011
Available online 23 May 2011

Keywords:
Fluorescent probe
Zn (II)
Schiff base
4, 4′-diaminodiphenylmethane

ABSTRACT

A Schiff base compound (**L**) was synthesized using o-vanillin and 4, 4′-diaminodiphenylmethane and characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR, IR, electronic absorption spectra and X-ray diffraction single crystal analysis. The title compound(**L**) has no fluorescence intensity in a range of 450–650 nm, but its fluorescence spectrum shows enhancement in the intensity of the signal at 372 nm on binding with the Zn(II) cation from pH = 6 to 14. No such significant change was observed for other metal ions. Fluorescence intensity was linear with concentration of Zn (II) cation in a range from 1×10^{-7} mol·L^{-1} to 1.2×10^{-5} mol·L^{-1}. This Schiff base compound is a promising system for the development of new fluorescent probes for the detection of Zn (II) cation.

Zinc is the second most abundant transition metal in the human body, which plays an important role in biological functions, such as gene expression, apoptosis, enzyme regulation, and neurotransmission [1].The estimation of the extent of zinc deficiency which prevails upon the young children in many parts of Africa and Asia is a challenging problem because of the lack of suitable biochemical probes, which are specific for Zn (II) [2]. The design and synthesis of fluorescent sensors with high selectivity and sensitivity to zinc ions is a vibrant field [3]. In despite of having many commercial Zn(II) sensors such as variety of probes based on quinoline, dansyl, anthracene, and fluorescein for the sensing of Zn(II) [4] and most of them are excellent Zn(II) sensors, some of the reported synthesis methods are always too complicated or inadequate selectivity, insufficient sensitivity, depending on fluorescence upon the dye concentration. So it is important to design new ones to improve their sensitivity, selectivity, reliability and easily synthesized.

Schiff bases (imines) are known as the good ligands for metal ions [5]. Schiff bases and their transition metal complexes are well known in the antibacterial, antifungal, anticancer [6], clinical, analytical and pharmacological area [7] and as magnetic materials [8], etc.

In this paper, we synthesized fluorescent probe (Scheme 1) based on Schiff Base (**L**) [9] for the detection of Zn (II), which has high selective response to Zn (II). The IR, electronic spectra, selectivity, and the effect of Zn (II) ion concentration, pH and solution of the fluorescent probe (**L**) were studied. It shows that this Schiff base is a promising system for the development of new fluorescent probe for the detection of Zn (II) cation.

The structure of title compound (**L**) consists of $C_{29}H_{26}N_2O_4$ (Fig. 1). The bond lengths of N (1) – C (8) is 1.287 , shorter than other bond lengths of C – N (1.47), near C═N double bond (1.30). So we consider that N (1) and C (8) as C═N double bond. The distance between N (1) and H (1) is 1.878 , which is shorter than 2.63 Å, illuminating a generating hydrogen bond. The torsion of C (10) – C (9) – C (8) – N (1) is 2.5° and the torsion of O(1) – H(1) – N(1) – C(8) is 1.5°, showing that ring C(9)C(10)C(11)C(12)C(13)C(14) and C(8), N(1), O(1), H(1) generate a conjugated effect by hydrogen bond O(1) – H(1).The angle of C(4) – C(7) – C(4A) is 110.36°, which makes the whole molecule seem as “V” shaped. Selected bond distances and bond angles for **L** were summarized in Table 1.

In the IR spectrum of the title compound (**L**), the presence of a broad band at 3386 cm^{-1} was assigned to v (O – H) of the hydroxyl group. The absorption band at 1617.9 cm^{-1} was attributed to v(C═N) of the Schiff base ligand [10]. The peak at 1201.8 cm^{-1} indicated the v(C – OH) of the hydroxyl group. Fig. 2 showed the electronic spectra of the title compound with (b) and without (a) Zn (II) ion solution in DMF. There is one absorption peak at 323 nm in a range of 300–550 nm in the spectrum of **L**. The peak is assigned to the *n*–π* transition of conjugation between a lone pair electron of the N atom in the C═N group and Π bond of the benzene ring. Two peaks appeared at 320 nm and 411 nm when the Zn (II) ion was added. The first peak is assigned to the *n*–π* transition of conjugation between a lone pair electron of the N atom in the C═N group and Π bond of the benzene ring. The peak at 411 nm is attributed to **L** to metal charge transfer (LMCT), which indicates that the **L** and Zn (II) have formed a complex.

Visual and fluorescence responses of **L** with and without Zn (II) ions (1.0 equiv) in DMF solution were shown in Fig. 3. The two photos were obtained in sunlight and upon excitation at 365 nm using a UV

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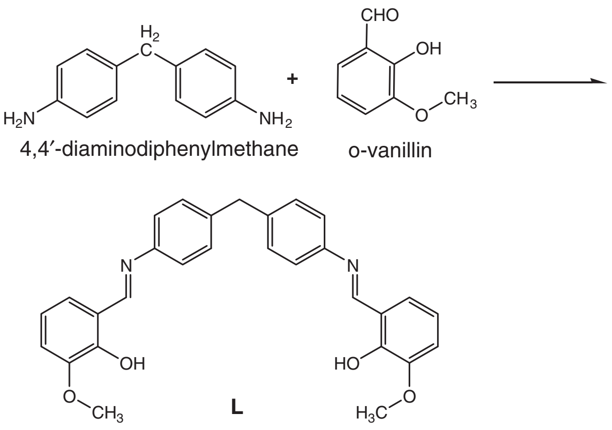
doi:10.1016/j.inoche.2011.05.015



Scheme 1. Synthesis of Schiff base compound **L**.

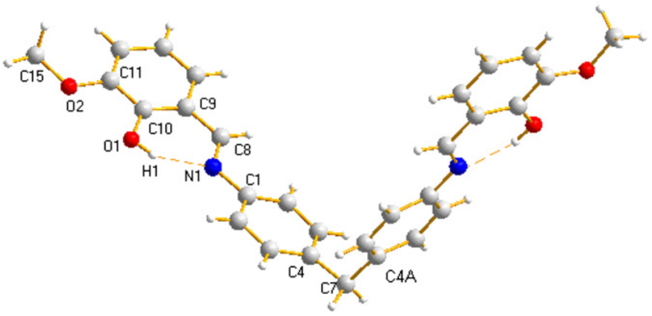


Fig. 1. A molecular structure of **L**.

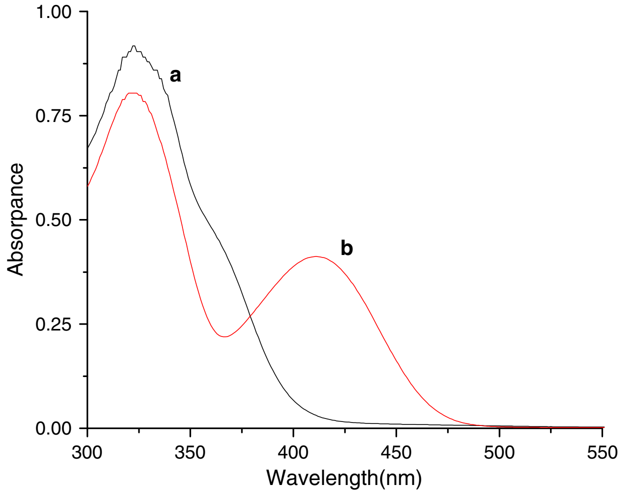


Fig. 2. Electronic spectra of **L** (a) and **L** added with Zn (II) (b) (solution in DMF).

lamp, respectively. To evaluate the fluorescence selective ability of **L** binding metal ion, the changes in fluorescence intensity of **L** upon addition of different metal salts were recorded. The experiment was carried out by additions of the metal ion to equivalent concentration of the solution of **L**, recording the emission spectra at $\lambda_{ex}=372$ nm in the range 450–650 nm. The fluorescence spectra of **L** with Na(I), Mg(II), Ca(II), Al(III), Cu(II), Co(II), Ni(II), Cd(II), Mn(II), Sn(IV), Pb(II), Cr(III), Fe(III), La(III), Yb(III), Er(III), and Pr(III) compared to **L** with Zn(II) ion were shown in Fig. 4.

Fig. 4 clearly shows that in the absence of Zn(II), the fluorescence emission of **L** ($\lambda_{em}=538$ nm) is very weak, due to isomerization of the C=N double bond and effect of intramolecular charge transfer (ICT) consists in Schiff base **L**. Compounds with an unbridged C=N structure are often nonfluorescent due to the C=N isomerization. But it may be inhibited by complexation with special ion [11]. Upon addition of Zn (II) to the solution of **L**, there is a significant enhancement in fluorescence intensity at 538 nm (Fig. 4a). The large increase in fluorescence intensity with red shift is attributed to the reduction of intramolecular charge transfer (ICT) effect in **L** and the formation of a new extended π-electron conjugation system between **L** and Zn (II). Furthermore, with the coordination to metal ion, a selective chelation-enhanced fluorescence effect is observed, which is a significant enhancement of the fluorescence intensity of Schiff-base emerged quickly [12]. In order to investigate the effect of other metal ions on the fluorescence spectra of **L,** Na(I), Mg(II), Ca(II), Al(III), Cu(II), Co(II), Ni(II), Cd(II), Mn(II), Sn(IV), Pb(II), Cr(III), Fe(III), La(III), Yb(III), Er(III), and Pr(III) were used to evaluate the metal ion binding properties to **L**. As shown in Fig. 3 (b), no such significant changes in fluorescence spectra were observed when **L** is exposed to other ions under the same experimental conditions. This interesting feature reveals that **L** can serve as an excellent selective fluorescent probe for Zn (II).

In order to explore the practical utility of **L** as an ion-selective fluorescence probe for Zn (II), competitive experiments were carried out in the presence of other metal ions by titrating Zn (II) and other metal ions [100 equivalent of Zn (II)] to solution of **L.** The concentration of **L** was 1×10^{-3} mol·L^{-1}, and the concentration of Zn (II) was 1×10^{-5} mol·L^{-1}. The results of experiment, as shown in Fig. 5, indicated that at high concentration of **L,** there is no significant change in the fluorescence intensity even at 100 equivalent additions of other metal ions, suggesting that the system formed by Zn (II) and **L** is stable when other metal ion are existed. Thus it may be concluded that **L** is a Zn (II) selective receptor even in the presence of other interference metal ions.

To learn more about the properties of **L** as a receptor for zinc, fluorescence titration was carried out, recording the emission spectra

Table 1
Selected bond lengths (Å) and angles (°) for the **L.**

Bond names	Bond lengths	Bond angles	Angle
C(1) – N(1)	1.418	C4 – C7 – C4A	110.36
C(10) – O(1)	1.354	C1 – N1 – C8	121.49
C(8) – C(9)	1.454	N1 – C8 – C9	121.83
C(8) – N(1)	1.287	C(10) – O1 – H(1)	109.46
C(11) – O(2)	1.377	C(9) – C(10) – O1	122.94
C(15) – O(2)	1.424	C(11) – O(2) – C(15)	117.12
C(4) – C(7)	1.512		

Symmetry code: −x + 1, −*y*, *z*.

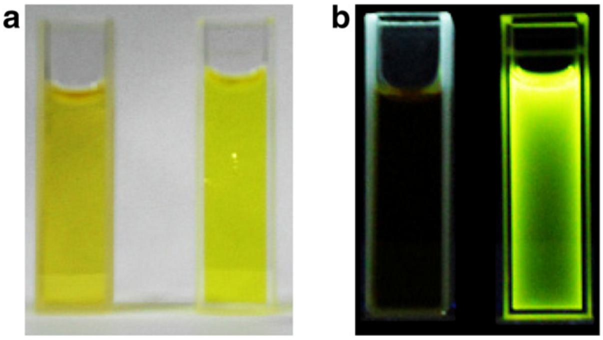


Fig. 3. Visual (a) and fluorescence responses (b) of **L** (1.0×10^{-4} mol·L^{-1}) with (right) and without (left) Zn (II) ions (1.0 equiv) in DMF solution, fluorescence response was excitation at 365 nm using a UV lamp.

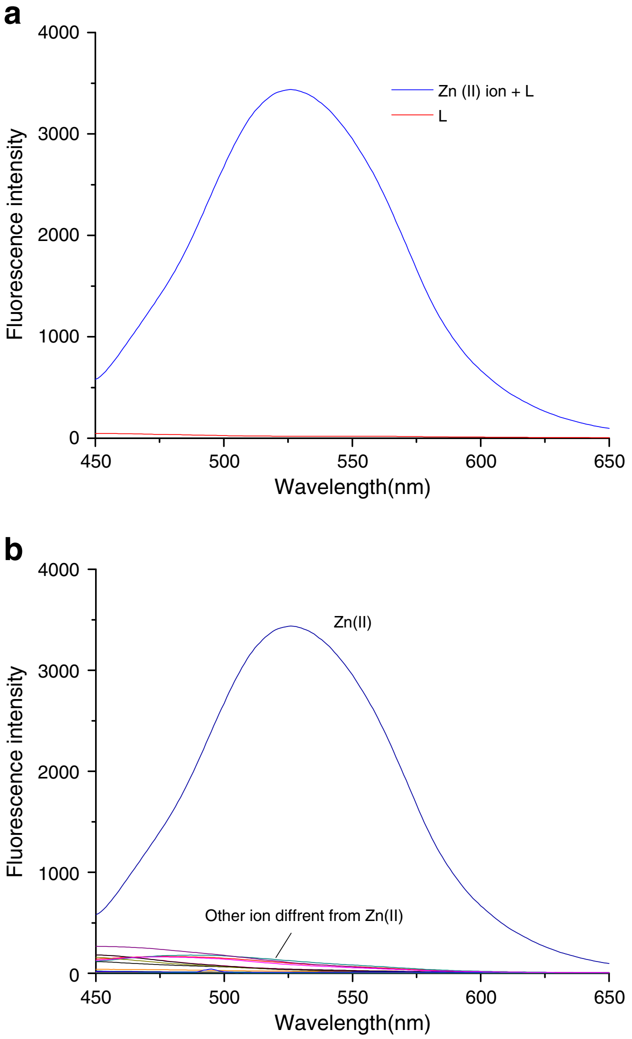


Fig. 4. (a) Fluorescence spectra of **L** (1.0×10^{-3} mol·L^{-1}) and **L**–Zn (II) (1.0×10^{-3} mol·L^{-1}) with an excitation at 372 nm. (b) Fluorescence spectra of L (1.0×10^{-3} mol·L^{-1}) with different ions (1.0×10^{-3} mol·L^{-1}) with an excitation at 372 nm. Other ion include Na(I), Mg(II), Ca(II), Al(III), Cu(II), Co(II), Ni(II), Cd(II), Mn(II), Sn(II), Pb(II), Cr(III), Fe(III), La(III), Yb(III), Er(III) and Pr(III) ion.

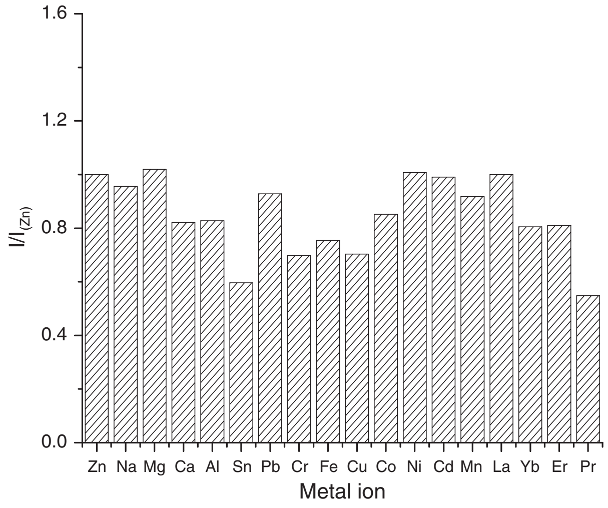


Fig. 5. Effect of competitive metal ion ([**L**] = 1×10^{-3} mol·L^{-1}, [Zn] = 1×10^{-5} mol·L^{-1}), other ions are 100 equivalents of [Zn].

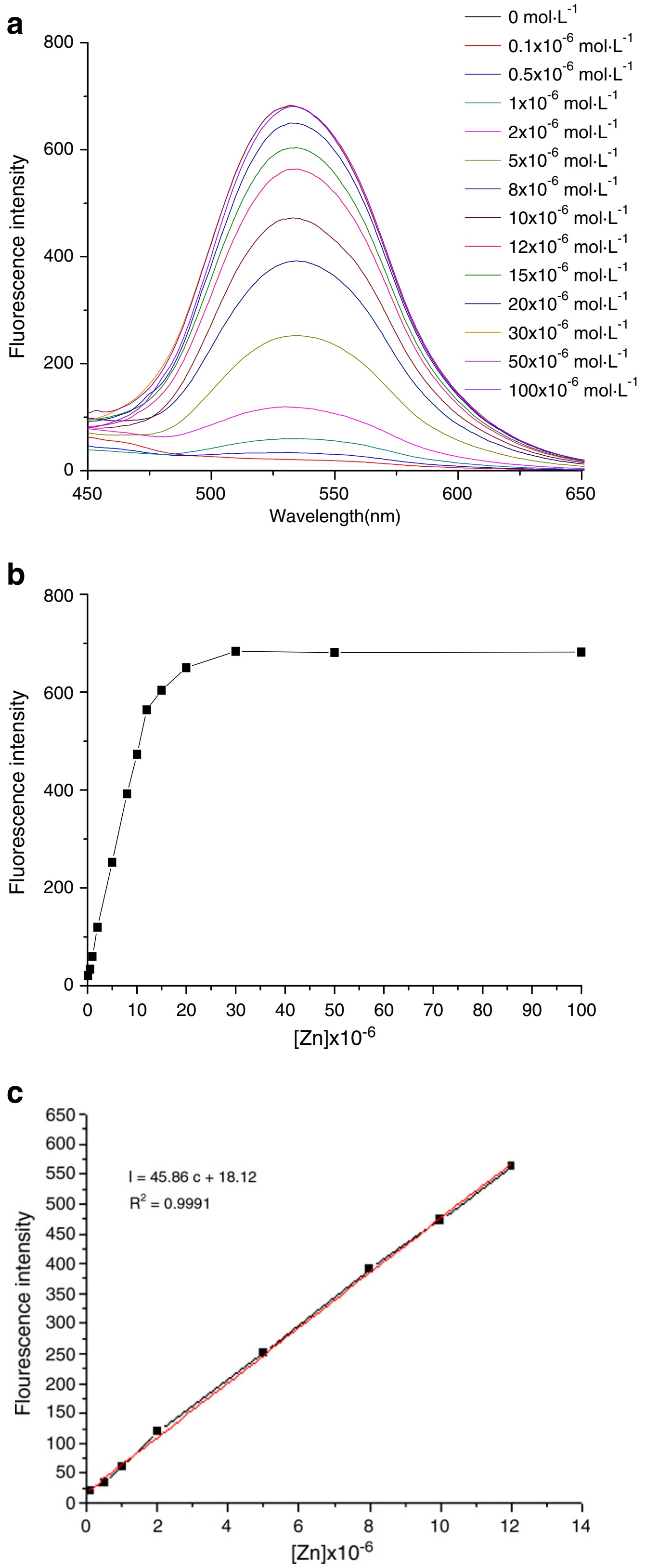


Fig. 6. (a) Fluorescence spectra change of **L** (1×10^{-5} mol·L^{-1}) upon addition of zinc salt (0 mol·L^{-1}–100×10^{-6}mol·L^{-1}) in mixture solution of DMF and ethanol (8:2, v/v). (b) Changes in the fluorescence intensity of **L** upon titration of Zn(II) in DMF and ethanol (8:2, v/v), plots denote the fluorescence intensity of L at 538 nm (excited at 273 nm) after the addition of various concentrations of Zn (II);(c) Linear regression equation of **L** (1×10^{-5}mol·L^{-1}) upon addition of zinc salt (0 mol·L^{-1}–1.2×10^{-5} mol·L^{-1}) in mixture solution of DMF and ethanol (8:2, v/v), data obtained from the emission spectra of displayed in Fig. 6(a).

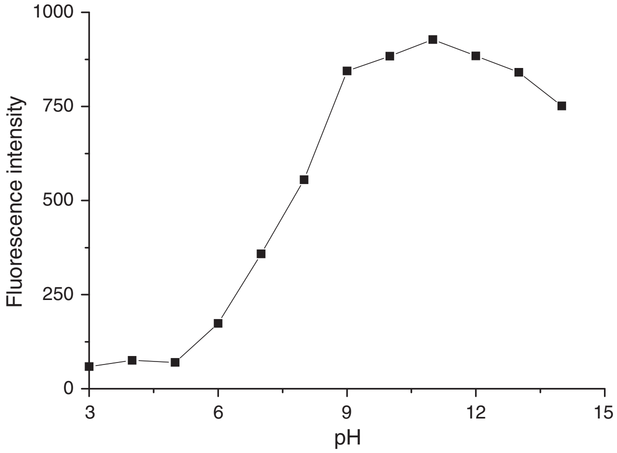


Fig. 7. Fluorescence intensity (at 538 nm) of L with Zn (II) (both in 1.0×10^{-4} mol·L^{-1}) under different pH values with an excitation at 273 nm.

in the range 450–650 nm ($\lambda_{ex} = 372$ nm), maintaining the concentration of **L** 1×10^{-5} mol·L^{-1} with the increase in concentration of Zn(II). With the increase of the concentration of Zn (II) ion, the fluorescence intensity has enhanced, while the shape of the emission band is not changed too much (Fig. 6). The title compound (**L**) exhibits a high sensitivity toward zinc. Fluorescence intensity is linear with concentration of Zn (II) cation in a range from 0.1×10^{-6} mol·L^{-1} to 1.2×10^{-5} mol·L^{-1}. Linear regression equation is $I = 45.86c + 18.12$, $R^2 = 0.9991$.

The effect of pH on the fluorescence intensity was studied in a range from 3 to 14. It can be seen (Fig. 7) that the fluorescence kept tiny intensity between pH 3 and 5, which was because the C=N double bond of Schiff base damaged in a low pH value. However, the fluorescence intensity increased sharply when pH value rose upon 6.0. The fluorescence intensity was at its highest point at pH 11, and then fluorescence intensity declined slowly. It indicates that the fluorescence intensity of **L**–Zn (II) system stay stable in alkaline, neutral and weakly acidic and can be damaged in strong acidic such as below pH 5.

We also investigated whether **L** could be used for determining Zn (II) in other solutions such as N, N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), tetrahydrofuran (THF), toluene, chloroform. The concentration of **L** and Zn (II) was 10^{-7} mol·L^{-1}. The fluorescence intensity is obvious in addition of Zn (II) in these solutions of **L**. (Fig. 8). As is well known, THF, toluene and chloroform are hard to be coordinated for the lack of easy-coordinated atom [11]. When dissolved in THF, toluene and chloroform, the **L**–Zn (II) system displayed fluorescence property. So we can speculate that no solution molecule contributes to the coordination and **L** could be used for determining Zn (II) in other solutions such as N, N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), tetrahydrofuran (THF), toluene, chloroform.

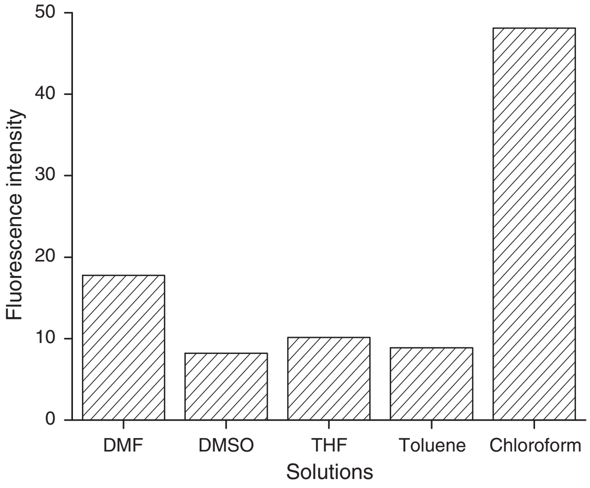


Fig. 8. Fluorescence intensity of **L**–Zn (II) (1.0×10^{-7} mol·L^{-1}) in different solutions.

In conclusion, we have synthesized a novel Schiff base fluorescent probe for Zn (II) derived from o-vanillin and 4, 4′-diaminodiphenylmethane. This fluorescent probe is based on a significant enhancement in fluorescence intensity after adding Zn (II) in DMF, DMSO, THF, toluene and chloroform. This fluorescent probe has high selectivity for binding Zn (II). This is reflected in competitive binding experiments with a range of metal cations. This **L**–Zn (II) system is stable at pH 6 to 14. A very good linear relationship of fluorescence intensity is observed in a Zn (II) concentration ranging from 1×10^{-7} mol·L^{-1} to 1.2×10^{-5} mol·L^{-1} in DMF solution.

Acknowledgements

This work was supported by the National Science Foundation of China (No. 21071134 and No. 20971115).

Appendix A. Supplementary material

Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.05.015.

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[9] O-vanillin (12 mmol, 1.824 g) was mixed with methanol (30 mL), stirring and a methanol solution (30 mL) of 4, 4′-diaminodiphenylmethane (5 mmol, 0.991 g) was slowly added. The reaction mixture was stirred at room temperature for 12 h; Orange solid then separated out, washed with methanol and dried. The orange solid was dissolved in ethanol; red crystals were obtained from the ethanol solution after 30 days by slow evaporation at room temperature. Mp: 191–193 °C. Anal.Calcd. (%) for C29H26N2O4: C, 74.59; H, 5.55; N, 6.00. Found (%): C, 74.56; H, 5.43; N, 5.96. ^{1}H NMR (600 MHz $CDCl_3$): δ 13.76 (s, 2H), 8.62 (s, 2H), 7.25 (m, 8H), 7.02 (d, 2H), 6.98 (d, 2H),6.88 (t, 2H), 4.04 (s, 2H), 3.94 (s, 6H); ^{13}C NMR (600 MHz $CDCl_3$): δ 162.28, 151.56, 148.62, 146.46 , 140.08, 130.07, 123.86, 121.54, 119.26, 118.69, 114.74, 77.25, 56.34, 41.19. IR (KBr, cm^{-1}): ν (O–H), 3386; ν(C=N), 1617.9 m; ν(C–OH), 1201.8.

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