J Fluoresc (2014) 24:1245–1251
DOI 10.1007/s10895-014-1407-y

ORIGINAL PAPER

Sensing of Zn^{2+}ion by *N*-Furfurylsalicylaldimine Based on CHEF Process†

**Swapan Kumar Jana · Madhusudan Bera ·
Horst Puschmann · Sudipta Dalai**

Received: 11 March 2014 / Accepted: 19 May 2014 / Published online: 8 June 2014
© Springer Science+Business Media New York 2014

Abstract The recognition ability of *N*-Furfurylsalicylaldimine (HL) toward various cations (Pb^{2+}, Hg^{2+}, Ba^{2+}, Cd^{2+}, Ag^{+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, K^{+}, Sr^{2+}, and Na^{+}) has been studied by UV–Vis and fluorescence spectroscopy. The compound showed highly selective fluorescence signaling behaviour for Zn^{2+} ions in methanol-water medium based on CHEF process and is capable of distinguishing Zn^{2+} from Cd^{2+} ion. From single crystal X-ray analysis it is revealed that a Zn^{2+} ion binds two ligand molecules through imine nitrogen and phenolate oxygen atom.

Keywords *N*-Furfurylsalicylaldimine · Zn(II) ion sensor · Fluorescence

Introduction

Much attention has been focused in recent years on the development of new chemical sensors for the recognition of heavy metal ions as well as anionic species [1]. Metal ions play a vital role in a wide range of chemical and biological processes [2], yet some of them are potentially toxic. It is indeed important to detect metal ions for applications in waste management and environmental toxicology [2]. Although zinc is only moderately abundant in nature, ranking twenty third of the elements in the Earth's crust, it is, however, a omnipresent and indispensable element in the human body and the second most abundant transition metal after iron [3]. In total, the adult human body contains 2–3 g of zinc [4]. For a long period of time, zinc has been known as an essential trace element, acting as a structural component of many protein scaffolds (e.g., carbonic anhydrase and zinc finger protein) [3, 5]. A considerable amount of zinc at a concentration of several milli-molar is accumulated in the presynaptic neurons of the brain and subsequently released when the neurons are active [6]. Thus, the detection and separation of zinc in a wide range of concentrations from nano-to the milli-molar scale is of immense interest and significance [7]. Furthermore, the greatest and most important challenge for the detection of zinc appears from the interference of other transition metal ions, in particular cadmium ion. Even though a number of techniques like atomic absorption spectroscopy, inductively-coupled plasma mass spectrometry and inductively coupled plasma atomic emission spectroscopy are available for the detection of these metal ions in food samples, they require tedious procedures and are also very expensive [8]. Optical signals based on changes in absorbance or fluorescence is the most frequently applied technique because of the simplicity of the experimental methods. A great number of fluorescent sensors have been designed to detect different kinds of metal ions. For the fluorescent detection of ions; fluorescence enhancement *"turn-on"* is preferable to fluorescence quenching *"turn-off",* because the former reduces the chance of false positive data by other fluorescent quenchers existing in samples. [9] Design of a fluorescent probe is generally based on intramolecular charge transfer (ICT) [10], photoinduced electron transfer (PET) [11], chelation-enhanced fluorescence (CHEF) [12], metal − ligand charge transfer (MLCT) [13],

---

Electronic supplementary material The online version of this article (doi:10.1007/s10895-014-1407-y) contains supplementary material, which is available to authorized users.

S. K. Jana · M. Bera · S. Dalai (✉)
Department of Chemistry and Chemical Technology,
Vidyasagar University, Midnapore 721 102, West Bengal, India
e-mail: sudipta@mail.vidyasagar.ac.in

S. Dalai
e-mail: icsdalai@gmail.com

H. Puschmann
Department of Chemistry, Durham University,
Durham DH13LE, UK

excimer/exciplex formation [14], imine isomerisation [15], intermolecular hydrogen bonding [16], excited-state intramolecular proton transfer [17], displacement approach [18], and fluorescence resonance energy transfer (FRET) [19]. In CHEF process, the electron pair is shared by coordination to a cation. As a result, the redox potential of the receptor is raised so that the highest occupied molecular orbital (HOMO) of the receptor becomes lower in energy than that of the fluorophore [20].

In recent time several chemosenors for zinc ions are reported in the literature [21–23]. Hsieh *et al.* reported A simple Schiff base type fluorescent receptor which exhibits an 'off–on-type' mode with high selectivity in the presence of Zn^{2+} ion through the formation of a rigid structure [24]. Another Schiff's base chemosensor is reported by Li *et al.* which displays specific recognition to Zn^{2+}, and especially avoids the interference of Cd^{2+} when tested against a range of physiological and environmentally relevant metal ions [25]. Recently Kim *et al.* reported a simple receptor which could simultaneously detect three biologically important metal ions (Zn^{2+} Fe^{2+} and Cu^{2+}) in aqueous solution. The sensor could function as a "turn-on" fluorescence receptor only to Zn^{2+} ions and could be successfully applied to the detection of intracellular Zn^{2+} ion [26].

In this paper, we present *N*-Furfurylsalicylaldimine (HL) as a highly selective fluorescent sensor for Zn^{2+} ion in CH_3OH-H_2O mixture by chelation-enhanced fluorescence (CHEF). The fluorescence properties and high selectivity of the ligand for Zn^{2+} ion over other possible competitive cations were investigated in detail. The X-ray single crystal structure of the Zn(II) complex with the ligand is reported.

Experimental

Materials and Physical Measurements

The ligand *N*-Furfurylsalicylaldimine is prepared as per the literature method [27]. Furfurylamine (Sigma Aldrich), salisaldehyde (Merck, India) and zinc acetate dihydrate (Merck, India) have been used as received. Solution of HL is prepared in methanol medium. Metal salts such as nitrate of Na^+, Ag^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+} and chloride salt of Hg^{2+} were purchased from Merck, India and have been used as received. Metal salt solutions were prepared in a phosphate buffer (0.1 M) with KH_2PO_4 (0.1 M) and Na_2HPO_4 (0.1 M) solution (pH 7; MeOH:H_2O = 9:1, v/v). Buffer capsules were purchased from Merck India. Absorption and fluorescence spectra are recorded in Shimadzu 1601 spectrophotometer and Hitachi F-7000 spectrofluorimeter respectively.

Determination of the Binding Constant

The binding constant was calculated based on the titration curve of the HL with metal ions. Binding constant was determined by a nonlinear least squares fit of the data with the following equation as referenced elsewhere [30].

$$y = x/2 * a * b * (1-x)^2 + x * b/2$$

Where 'x' is $(I-I_o)/(I_{max}-I_o)$, 'y' is the concentration of metal ion, 'a' is the binding constant, and 'b' is the concentration of sample. Here $(I-I_0)/(I_{max}-I_0)$ is the fluorescence intensity ratio.

Determination of Fluorescence Quantum Yield

Here, the quantum yield φ was measured by using the following equation,

$$\varphi_x = \varphi_s(F_x/F_s)(A_s/A_x)\left(n_x^2/n_s^2\right)$$

Where, 'x' and 's' indicate the unknown and standard solution respectively, φ = quantum yield,

F = area under the emission curve, A = absorbance at the excitation wave length, n = index of refraction of the solvent. Here φ measurements were performed using anthracene in ethanol as standard [φ=0.27] (error ~ 10 %) [31].

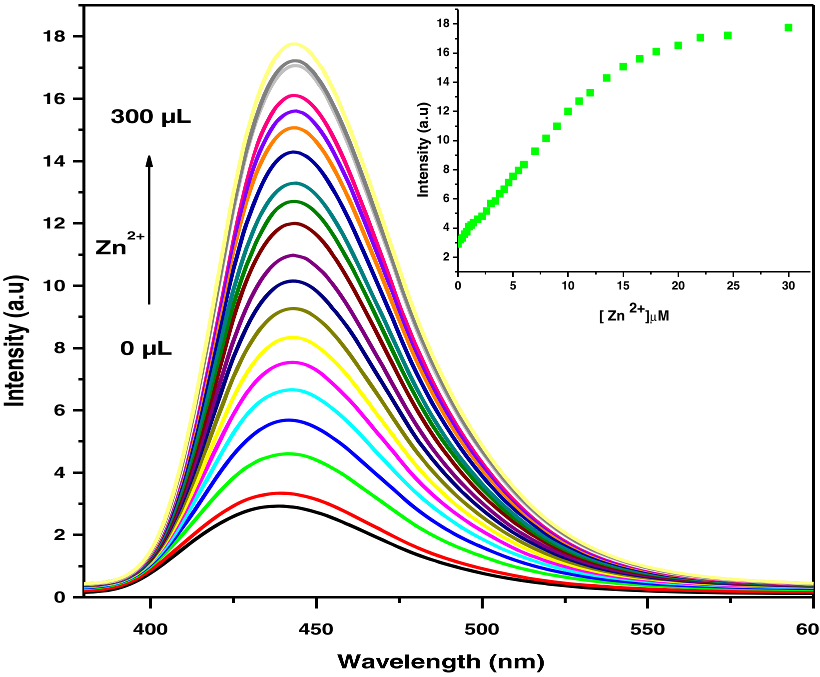
Synthesis of $[Zn(L)_2]$

Zinc(II) acetate.dihydrate (0.2915 g, 1 mmol) was dissolved in 10 ml methanol in a round-bottom flask. Methanolic solution (10 ml) of HL (0.2010 g, 1 mmol) was added drop-wise with constant stirring for about 20 min at room temperature. After that the whole reaction mixture was refluxed for 1 h to get a greenish-yellow solution. The solution was cooled to room temperature and filtered. The greenish-yellow filtrate was kept in air at room temperature for crystallization. After 2 weeks, pale yellow block shaped single crystals of diffraction quality were obtained on slow evaporation of the filtrate. Yield 70 %.

X-Ray Crystallography

Data collections of 1 was carried out at 120(2) K on an Oxford Diffraction Gemini Ultra diffractometer. Cell refinement, indexing and scaling of the data sets were done with CrysAlisPro package, Version 1.171.35.10 [32]. The structures were solved by using the olex2.solve solution program [33] using the charge flipping algorithm and refined by the full matrix least-squares method based on F^2 with all observed reflections [34]. The crystallographic details are listed in table 1.

Fig. 1 Fluorescence spectra of HL in the buffer solution (MeOH:H_2O = 9 : 1, pH=7) in the presence of increasing concentration of $Zn(NO_3)_2$. [HL]=2.0×10^{-5} M and [Zn^{2+}]= 2.0×10^{-4} M, Excitation at λ= 330 nm. Inset: The fluorescence intensity at 443 nm vs [Zn^{2+}] μM



Results and Discussion

Emission Studies

At first we have investigated the fluorescence properties of the ligand HL and its fluorescence response to various metal cations in methanol-water solvent. The ligand itself shows negligible fluorescence at 443 nm upon excitation at 330 nm, however, fluorescence enhancement is observed when Zn^{2+} ion is added to the methanolic solution of the ligand. The native fluorescence of the ligand is minimal, but when Zn^{2+} is added incrementally, fluorescence increases and reaches a maximum on addition of 300 micro litres Zn^{2+} solution (concentration, 30μM) at 443 nm (Fig. 1). The interaction of the ligand with Zn^{2+} ion resulted in fluorescence enhancement, which is attributed to a chelation-enhanced fluorescence (CHEF) effect. We believe that the zinc ion is effectively acting as an electrophile which attacks the electron-rich hydroxyl oxygen atom of the HL to form a rigid metal complex. The quantum yield of ligand HL remarkably changed from 0.003 to 0.321 on the formation of the complex

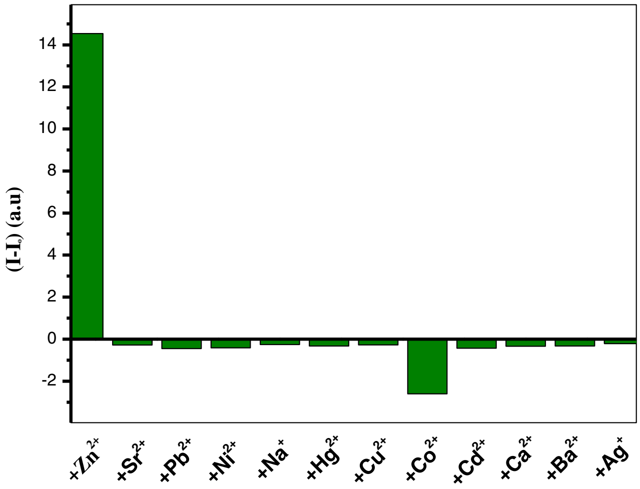


Fig. 2 Fluorescence intensity changes (I − I_0) of free HL (2×10^{-5} M) at 443 nm in the buffer solution (MeOH:H_2 = 9 : 1, pH=7) upon addition of various metal ions (2×10^{-4} M). I and I_0 denote fluorescence intensity of HL in the presence and absence of metal ions. Excitation wavelength: 330 nm

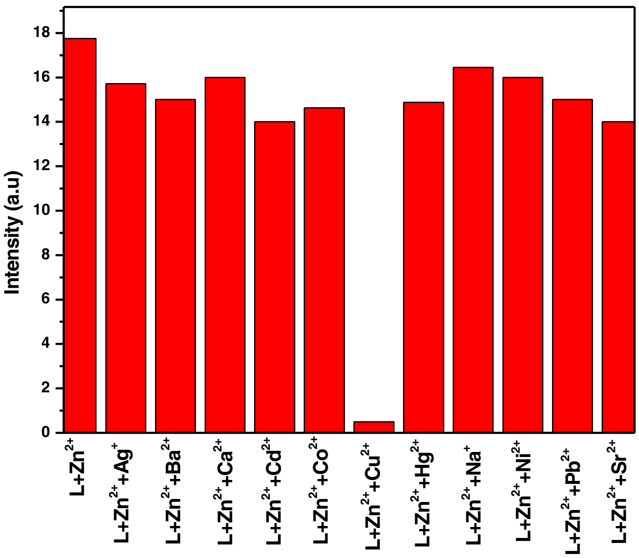


Fig. 3 Fluorescence intensity profile of **HL + Zn^{2+}** and in the presence of various cations (7 equiv. Zn^{2+} and 3 equiv. other metal cations) in buffer at pH 7 at room temperature (excitation wave length 330 nm)

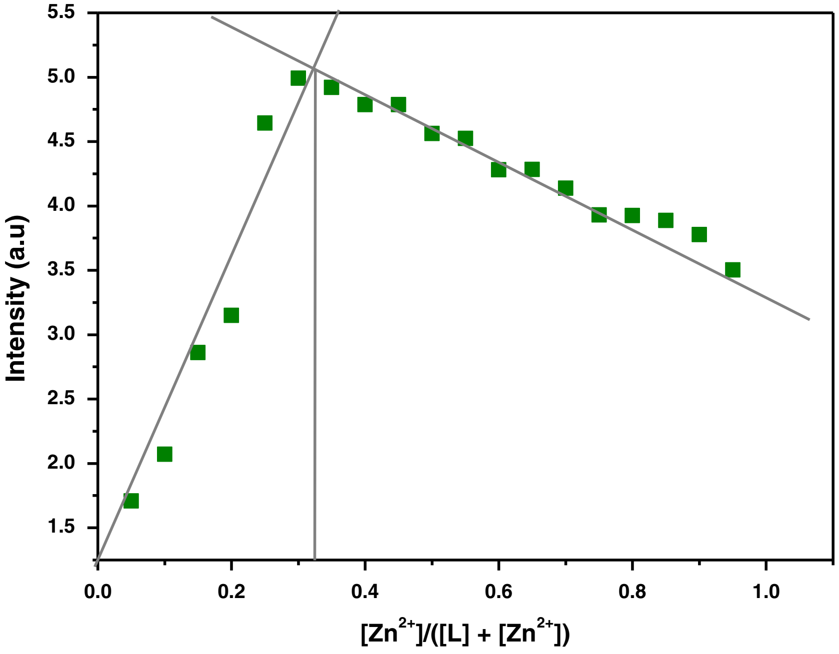


Fig. 4 Job's plot for determining the stoichiometry of HL and Zn^{2+}. The total concentration ([L] + [Zn^{2+}]) was 2.0×10^{-5} M. λ_{ex}= 330 nm

with Zn^{2+} metal ion, which indicates 107 folds enhancement in quantum yield.

Ion selectivity is an important property of the fluorescence probes. Thus, we evaluated the fluorescent response of HL with different metal ions, including Ag^+, Na^+, Ca^{2+}, Ba^{2+}, Sr^{2+}, Pb^{2+}, Hg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Cd^{2+} in buffer solution and found the perfect selectivity for Zn^{2+} with a considerable signal output (Fig. 2). It is worth noting, that the ligand distinguishes Zn^{2+} from Cd^{2+}, which might cause interference since both metal cations have very similar properties [28].

The existence of other transition metal ions may affect the detection ability of HL. The Zn^{2+} selectivity and the fluorescence behaviour of HL remain uninterrupted with the presence of many other metal ions. Compared with some available Zn^{2+} sensors, which exhibit some enhancement of the fluorescence for Cd^{2+} [28], the ligand HL has a selective response to Zn^{2+} without the interference of Cd^{2+} in the buffered

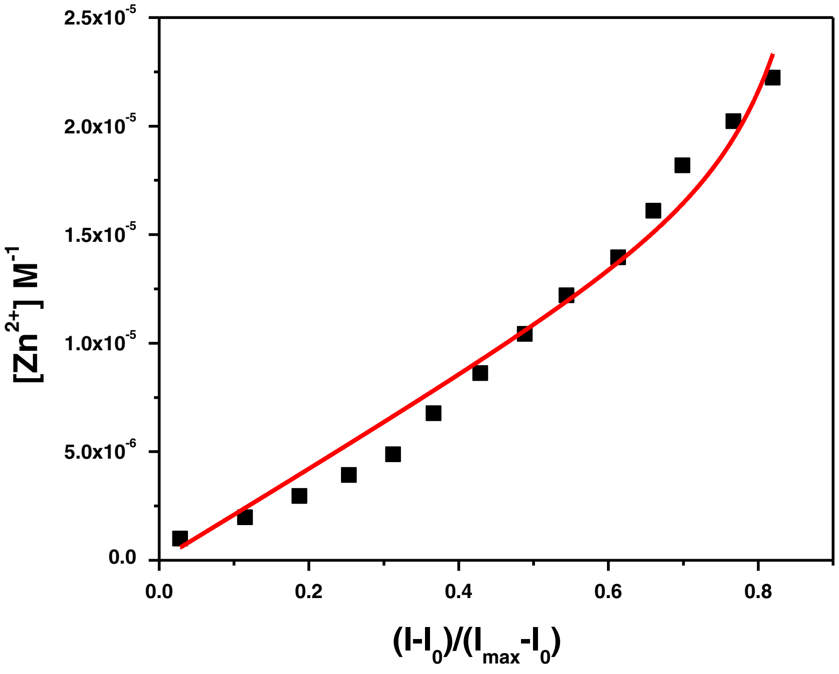
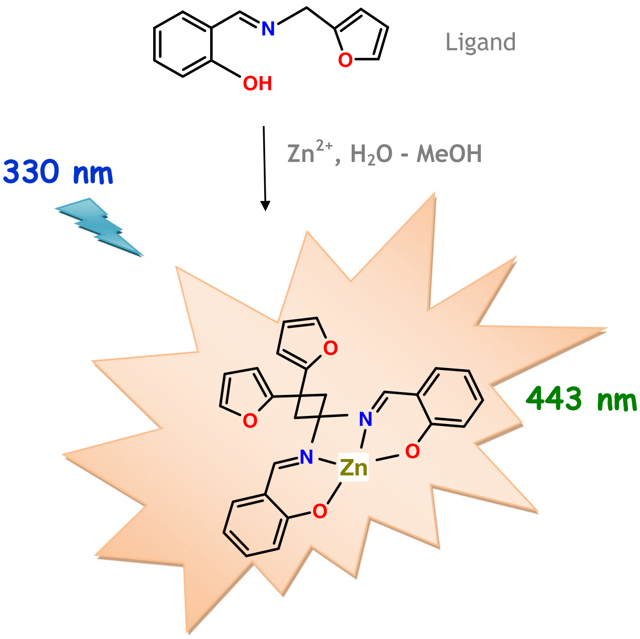


Fig. 5 Plot of [Zn^{2+}]M^{-1} vs (I-I_0)/(I_{max}-I_0) for determination of binding constant. The red line is the nonlinear fitting curve obtained assuming a 2:1 association between HL and Zn^{2+}. λ_{ex}=330 nm, [HL]=2.0×10^{-5} M



Scheme 1 Formation of the complex i.e. $[Zn(L)_2]$ (1)

solution, whereas, the existence of copper obviously quenched the fluorescence intensity [28, 29]. (Fig. 3)

We have studied the binding ability of HL towards Zn^{2+} by fluorescence titration. A Job's plot indicates the 1:2 coordination stoichiometry of Zn^{2+} with HL (Fig. 4), exhibiting a binding constant $a=4.7\times10^{10}\,M^{-2}$, ($R^2=0.9783$) (Fig. 5) from the theoretical nonlinear square fit of experimental data to a 1:2 binding model. The obtained data indicate a typical CHEF effect, originating from the coordination of the de-protonated ligand (L^-) through the imine nitrogen and de-protonated phenolate oxygen atom (Scheme 1). The detection limit of the HL towards Zn^{2+} was found to be about 3.2 μM based on fluorescence titration experiments.

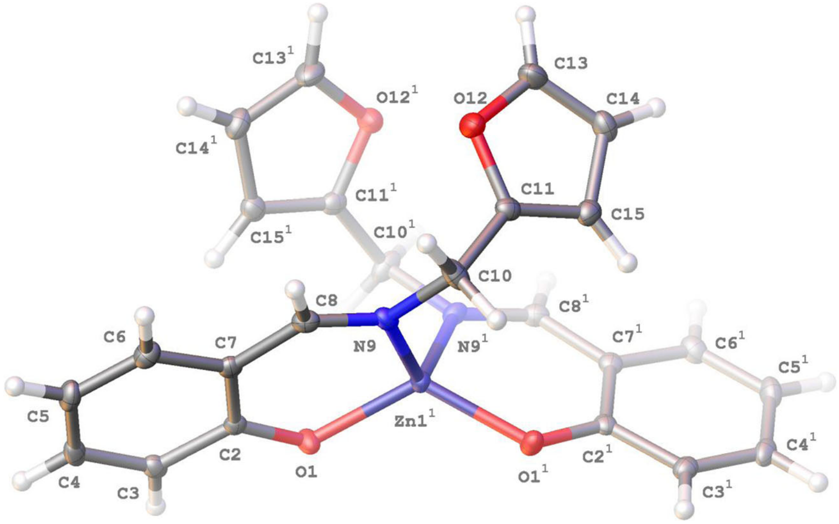
X-ray Crystallography

The crystal structure of the Zn^{2+} complex of the HL shows 1:2 binding and a distorted tetrahedral geometry around Zn^{2+} is identified. As seen in Fig. 6, an imine nitrogen atom (N9) from the receptor is at the apex of the tetrahedral zinc ($Zn1^1$) and the phenolate oxygen atom (O1) of the same receptor molecule is also coordinated to Zn(II). An imine nitrogen ($N9^1$) and a phenolate oxygen ($O1^1$) from another receptor moleculecompletes tetrahedral coordination. Thus the two receptor molecules are chelated with zinc atom. The N-Zn-N and O-Zn-O bond angles are 121.29° and 123.04° respectively. The bond lengths and the bond angles are listed in Table 2.

UV–Vis Spectroscopic Studies

We have also studied the change in absorption behaviour of the ligand upon binding with Zn^{2+} ion. As the concentration of Zn^{2+} was increased, the intensity of the absorption bands produced by the Zn^{2+}-free ligand at 317 and 256 nm gradually decreased, accompanied by new absorption bands at 238, 272 and 363 nm produced by the Zn^{2+}-bound ligand appearing at longer wavelength with gradual increase in the intensity (Fig. 7). The spectra obtained during the stepwise addition showed four isosbestic points indicates a clean conversion of HL into its corresponding Zn^{2+} complex. In addition Cu^{2+}, Co^{2+} and Ni^{2+} show increased absorption bands at 238, 272 and 363 nm but the intensity is less than Zn^{2+} indicates that the ligand is sensitive for Zn^{2+} which is shown in bar graph representation (Fig. 8).

Fig. 6 X-ray structure of $[Zn(L_2)]$ (**1**)



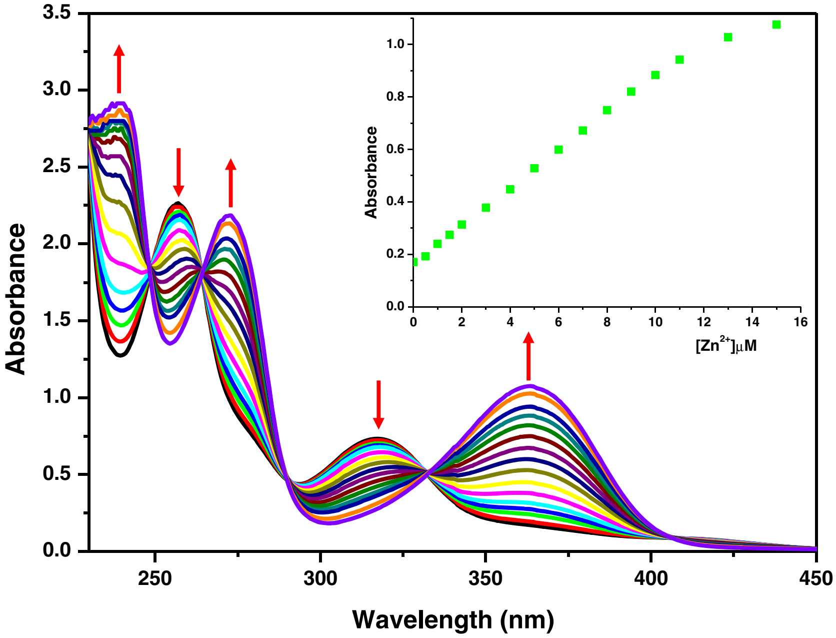


Fig. 7 Absorption spectra of receptor in methanol with the increase of $Zn(NO_3)_2$. Inset: The absorbance at 363 nm vs $[Zn^{2+}]$ μM

Conclusion

In this paper we have studied a sensor for Zn^{2+} ion. The thorough investigation of the fluorescence sensing and binding properties of the ligand HL displays high selectivity luminescent probe for Zn^{2+}. The increase in emission in the presence of Zn^{2+} ion is accounted for by the formation of a rigid metal-ligand complex. The X-ray crystal structure reveals that the Zn(II) complex is mononuclear with distorted tetrahedral geometry. An 107-fold increase in quantum yield is identified upon coordination of HL with Zn(II) ion is attributed as Zn^{2+}-selective chelation-enhanced fluorescence response.

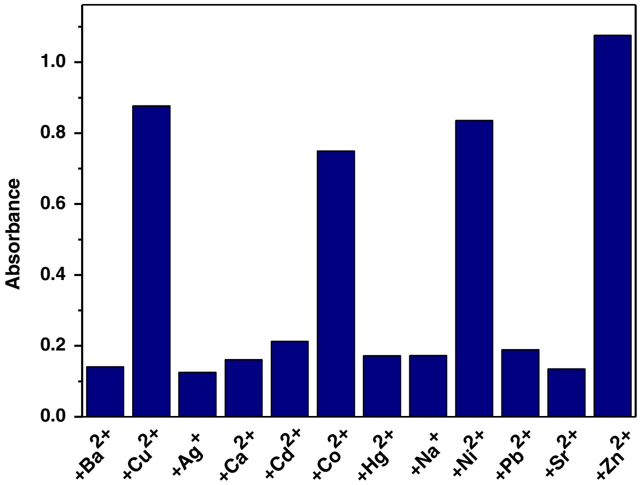


Fig. 8 Bar diagram represents the absorbance value of compound ($[HL]=2\times10^{-5}(M)$) in presence of different metal ions ($[M^{2+}]=2\times10^{-4}(M)$) in H_2O:MeOH (1:9; v/v, pH=7) solution at 363 nm

Acknowledgments This project was financially supported by CSIR, New Delhi, India [No. 01(2536)/11/EMR-II]. S.K.J. is thankful to UGC for providing research fellowship.

References

1. ThomasIII SW, Joly GD, Swager TM (2007) Chemical sensors based on amplifying fluorescent conjugated polymers. Chem Rev 107:1339–1386
2. Szacilowski K, Macyk W, Matuszek AD, Brindell M, Stochel G (2005) Bioinorganic photochemistry: frontiers and mechanisms. Chem Rev 105:2647–2694
3. Vallee BL, Falchuk KH (1993) The biochemical basis of zinc physiology. Physiol Rev 73:79–118
4. Frederickson CJ, Koh J-H, Bush AI (2005) The neurobiology of zinc in health and disease. Nat Neurosci 6:449–462
5. Berg JM, Shi YG (1996) The galvanization of biology: a growing appreciation for the roles of zinc. Science 271:1081–1085
6. Assaf SY, Chung SH (1984) Release of endogenous Zn^{2+} from brain tissue during activity. Nature 308:734–736
7. Outten CE, O'Halloran TV (2001) Femtomolar sensitivity of metalloregulatory proteins controlling zinc homeostasis. Science 292:2488–2492
8. Spichiger-Keller US (1998) Chemical sensors and biosensors for medical and biological applications. Wiley-VCH, Weinheim
9. Nolan EM, Lippard SJ (2008) Tools and tactics for the optical detection of mercuric ion. Chem Rev 108:3443–3480
10. Xu Z, Xiao Y, Qian X, Cui J, Cui D (2005) Ratiometric and selective fluorescent sensor for Cu^{II} based on internal charge transfer (ICT). Org Lett 7:889–892
11. Gunnlaugsson T, Davis AP, O'Brien JE, Glynn (2002) M fluorescent sensing of pyrophosphate and Bis-carboxylates with charge neutral PET chemosensors. Org Lett 4:2449–2452
12. Lim NC, Schuster JV, Porto MC, Tanudra MA, Yao L, Freake HC, Bruckner C (2005) Coumarin-based chemosensors for Zinc(II): toward the determination of the design algorithm for CHEF-type and ratiometric probes. Inorg Chem 44:2018–2030

13. Beer PD (1998) Transition-metal receptor systems for the selective recognition and sensing of anionic guest species. Acc Chem Res 31: 71–80
14. Nishizawa S, Kato Y, Teramae N (1999) Fluorescence sensing of anions via intramolecular excimer formation in a pyrophosphate-induced self-assembly of a pyrene-functionalized guanidinium receptor. J Am Chem Soc 121:9463–9464
15. Wu J-S, Liu W-M, Zhuang X-Q, Wang F, Wang P-F, Tao S-L, Zhang X-H, Wu S-K, Lee S-T (2007) Fluorescence turn on of coumarinderivatives by metal cations: a new signaling mechanism based on C=N isomerization. Org Lett 9:33–36
16. Sahana A, Banerjee A, Guha S, Lohar S, Chattopadhyay A, Mukhopadhyay SK, Das D (2012) Highly selective organic fluorescent probe for azide ion: formation of a “molecular ring”. Analyst.137:1544-1546.
17. Peng X, Wu Y, Fan J, Tian M, Han KJ (2005) Colorimetric and ratiometric fluorescence sensing of fluoride: tuning selectivity in proton transfer. J Org Chem 70:10524–10531
18. Das S, Guha S, Banerjee A, Lohar S, Sahana A, Das D (2011) 2-(2-Pyridyl) benzimidazole based Co(II) complex as an efficientfluorescent probe for trace level determination of aspartic and glutamic acid in aqueous solution: A displacement approach. Org Biomol Chem 9:7097–7104
19. Serin JM, Brousmiche DW, Frechet JMJ (2002) A fret-based ultraviolet to near-infrared frequency converter. J Am Chem Soc 124: 11848–11849
20. Majzoub AE, Cadiou C, Olivier ID, Tinant B, Chuburu F (2011) Cyclam-methylbenzimidazole: a Selective OFF-ON Fluorescent Sensor for Zinc. Inorg Chem 50: 4029-4038 and references there in
21. Song EJ, You JKGR, Park GJ, Kim YKS-J, Kim C, Harrison RG (2013) A single molecule that acts as a fluorescence sensor for zinc and cadmium and a colorimetric sensor for cobalt. Dalton Trans 42: 15514–15520
22. Ganguly A, Paul BK, Ghosh S, Kar S, Guchhait N (2013) Selective fluorescence sensing of Cu(II) and Zn(II) using a new Schiff base-derived model compound: naked eye detection and spectral deciphering of the mechanism of sensory action. Analyst 138: 6532–6541
23. Xiao F, Shen J, Qu J, Jing S, Zhu D-R (2013) A fluorescent sensor with mixed N/O/Se donor atoms for probing Zn(II) ion. Inorg Chem Commun 35:69–71
24. Hsieh WH, Wanb C-F, Liao D-J, Wua A-T (2012) A turn-on Schiff base fluorescence sensor for zinc ion. Tetrahedron Lett 53:5848–5851
25. Li L, Dang Y-Q, Li H-W, Wang B, Wu Y (2010) Fluorescent chemosensor based on Schiff base for selective detection of zinc(II) in aqueous solution. Tetrahedron Lett 51:618–621
26. Kim KB, Kim H, Song EJ, Kim S, Noh I, Kim CA (2013) cap-type Schiff base acting as a fluorescence sensor for zinc(II) and a colorimetric sensor for iron(II), copper(II), and zinc(II) in aqueous media. Dalton Trans 42:16569–16577
27. Bhagwat UA, Mukhedkar VA, Mukhedkar AJ (1980) Study of ligand isomeric complexes of N-Furfurylsalicylaldimine. J Chem Soc Dalton Trans:2319
28. Hanaoka K, Kikuchi K, Kojima H, Urano Y, Nagano T (2004) Development of a Zinc ion-selective luminescent lanthanidechemosensor for biological applications. J Am Chem Soc 126:12470–12471
29. Baek NY, Heo CH, Lim CS, Masanta G, Cho BR, Kim HM (2012) A highly sensitive two-photon fluorescent probe for mitochondrial zinc ions in living tissue. Chem Commun 48:4546–4548
30. (a) Kubo Y, Kato M, Y Misawa, Tokita S (2004) A fluorescence-active 1,3-bis(isothiouronium)-derived naphthalene exhibiting versatile binding modes toward oxo anions in aqueous MeCN solution: new methodology for sensing oxoanions. Tetrahedron Lett 45:3769-3772. (b) Yang MH, Thirupathi P, Lee KH (2011) Selective and Sensitive Ratiometric Detection of Hg(II) Ions Using a Simple Amino Acid Based Sensor. Org Lett 13:5028-5031
31. Morris JV, Mahaney MA, Huber JR (1976) Fluorescence quantum yield determinations. 9, l0-diphenylanthracene as a reference standard in different solvents. J Phys Chem 80(9):969–974
32. Aligent (ed) (2010) CrysAlis PRO. Agilent Technologies Ltd, Yarnton
33. Dolomanov OV, Bourhis LJ, Gildea RJ, Howard JAK, Puschmann H (2009) OLEX2: a complete structure solution, refinement and analysis program. J Appl Crystallogr 42:339–341
34. Sheldrick GM (2008) A short history of SHELX. Acta Crystallogr A64:112–122