

# *N,N,N,N*-tetradentate Macrocyclic Ligand Based Selective Fluorescent Sensor for Zinc (II)

Priyanka Goswami · Diganta Kumar Das

Received: 21 November 2011 / Accepted: 8 March 2012 / Published online: 28 March 2012  
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**Abstract** *N,N,N,N*-tetradentate macrocyclic ligand (**L**) has been synthesized by the condensation of benzil and semicarbazide and characterized. On excitation by light of wavelength 350 nm, **L** exhibited a fluorescent peak at  $\lambda_{\text{max}} = 454$  nm, which showed *ca* 6 times enhancement in intensity with a blue shift on interaction with  $\text{Zn}^{2+}$ . **L** has been found to act as a selective fluorescent sensor for  $\text{Zn}^{2+}$  ion over a host of other metal ions such as-  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Na}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ , in 1:1  $\text{CH}_3\text{OH}:\text{H}_2\text{O}$ . A 1:1 complex formation between **L** and  $\text{Zn}^{2+}$  was proved. The enhancement in the fluorescence could be explained on the basis of Photo induced electron transfer (PET) mechanism with  $\log \beta = 1.86$ .

**Keywords** Benzil · Salicyldehyde · Fluorescence · Sensor · Binding constant · Photo induced electron transfer (PET)

## Introduction

Fluorescent sensors are widely used for real-time monitoring and detection of metal ions at a molecular level without any special instrumentation, and are applicable in many fields such as medical, environmental monitoring, living cells and electronics [1]. Recently, there has been a significant interest in the design and synthesis of fluorescent sensors for detection of physiologically important ions and molecules [2] and for monitoring harmful pollutants in the environment [3]. Zinc ion is the second most abundant metal ion and is well known to play a number of roles in the

human body such as –influencing DNA synthesis, gene expression, enzyme catalysis [4], apoptosis [5], immune system function, and neuronal signal transmission [6]. However, in spite of its physiological importance, zinc ion is a metal pollutant and presence of a large amount of zinc in the environment may reduce the soil microbial activity causing phytotoxic effects [7] and also it is a common contaminant in agricultural and food wastes [8]. Moreover, zinc ion is also a contributory factor in neurological disorders such as Parkinson's disease, epilepsy and Alzheimer's disease [9].

So far, several analytical methods have been reported for the determination of zinc, such as UV/visible spectrometry [10–12], electrochemical [13, 14], fluorescent [15, 16] etc. However, owing to its simplicity and sensitivity, fluorescent detection of zinc ions has been widely preferred. Moreover,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  have similar chemical properties, due to which they cause similar spectral changes, when coordinated with fluorescent sensors [17–19]. Therefore, there is a need for developing such sensors which can distinguish  $\text{Zn}^{2+}$  from  $\text{Cd}^{2+}$  and other transition metal ions.

Recent years have seen increasing interest in the development of zinc sensors. A quinoline carboxaldehyde and phenylenediamine based ratiometric fluorescent sensor for zinc was developed by Chen and coworkers [20]. A novel fluorescent zinc sensor based on bis (pyrrol-2-yl-methylene-amine) ligand has been reported by J.S Ma et al. [21]. Further, a novel water soluble compound, 8-pyridyl methoxy-2-methyl-quinoline, was found to act as a highly sensitive fluorescent sensor for zinc [22]. P. Banerjee et al. also reported the selective fluorescent zinc sensing property by certain Schiff base compounds [23]. A coumarin based fluorescent sensor is also known for the detection of  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  [24]. We have also previously reported 2,7-dichlorofluorescein as a selective fluorescent sensor [25] for distinguishing  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and certain other metal ions. We

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have recently reported that the condensation product of salicylaldehyde and semicarbazide can detect  $\text{Cd}^{2+}$  [26].

In this paper, we report the fluorescence zinc (II) sensing property of a compound (**L**), synthesized by the condensation of benzil and ethylene diamine. In 1:1  $\text{CH}_3\text{OH}:\text{H}_2\text{O}$ , **L** was found to exhibit a fluorescent peak at  $\lambda_{\text{max}}$  value 454 nm on excitation by 350 nm wavelength photons. It has been observed that the fluorescent intensity peak at 454 nm increases significantly to *ca* 6 times on interaction with  $\text{Zn}^{2+}$ . However no such remarkable enhancement in intensity has been observed for the metal ions -  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Na}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ .

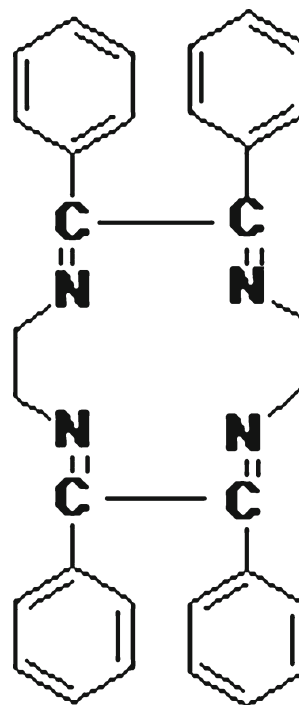
## Experimental

Benzil was purchased from Loba Chemie and ethylenediamine was obtained from Merck. All the metal salts (sulphate) and methanol were purchased from Merck. All chemicals were of analytical grade and used without further purification. The metal salts were recrystallized from water (Millipore). Fluorescence spectra were recorded in a Hitachi 2500 spectrophotometer using quartz cuvette. A  $10^{-5}$  M solution of **L** in 1:1 (v/v)  $\text{CH}_3\text{OH}:\text{H}_2\text{O}$  (phosphate buffer solution, pH 7.0) was used in the experiments. Metal salt solutions ( $10^{-5}$  M) were prepared in PBS, pH 7.0. Time resolved fluorescence spectra was recorded in Life Spec II (Edinbergh Instrument) using light source EPL – 375, picosecond pulsed diod laser.

Electrochemical measurements were carried out in a CHI 600B Electrochemical Analyser (USA), consisting of a three-electrode assembly with a platinum disc as the working electrode, Ag-AgCl (3 M NaCl) as the reference electrode and tetrabutylammonium perchlorate (TBAP, 0.1 M) as the supporting electrolyte. The working electrode was cleaned as reported [27] by polishing with 0.1  $\mu\text{m}$  alumina slurry using a polishing kit (CHI), followed by sonication in distilled water for 5 min.

UV/Visible spectra were recorded in a Shimadzu UV 1800 spectrophotometer.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded in a Bruker Ultrashield 300 spectrometer. All NMR spectra were obtained in  $\text{CDCl}_3$  at room temperature and the chemical shifts are reported in  $\delta$  values (ppm) relative to TMS. FTIR spectra were recorded for **L** in KBr pellet which shows peaks at 2835 and 2943  $\text{cm}^{-1}$  ( $\nu_{\text{C-H}}$ ), 1593 and 1508  $\text{cm}^{-1}$  ( $\nu_{\text{C-N}}$ ), 991  $\text{cm}^{-1}$  ( $\nu_{\text{C-H}}$  bending), 1438  $\text{cm}^{-1}$  ( $\nu_{\text{C-C}}$ ).

Synthesis of **L** was carried out as per reported procedure [27]. 0.210 mg (1 mol) of benzil was dissolved in 10 mL ethanol and an equimolar proportion of 0.05 mL ethylenediamine was added. 6 mL of conc. HCl was added dropwise to the resulting mixture and refluxed for 4 h till a yellow

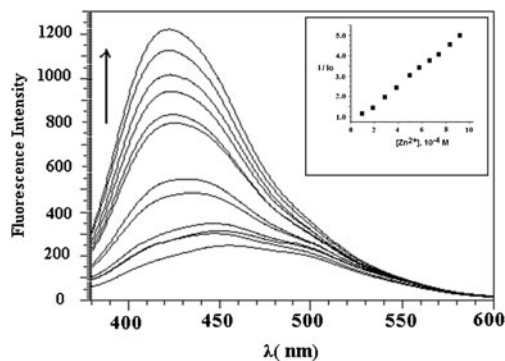


**Scheme 1** Structure of **L**

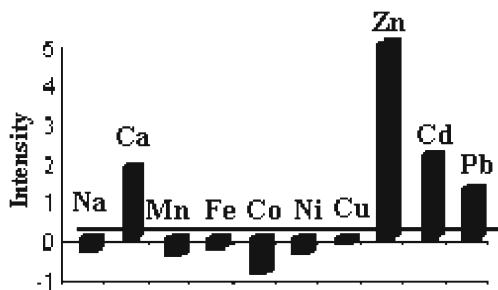
crystalline solid was obtained. This was washed with ethanol and dried Scheme 1.

## Results and Discussion

The fluorescence property of **L** was examined in 1:1  $\text{CH}_3\text{OH}:\text{H}_2\text{O}$  at room temperature. The emission spectrum of **L** was obtained in the range 370–600 nm, on excitation by light of wavelength 350 nm. The maximum intensity fluorescent peak was observed at 454 nm. The effect on the fluorescent intensity of **L** on interaction with a number of metal ions -  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Co}^{2+}$ ,



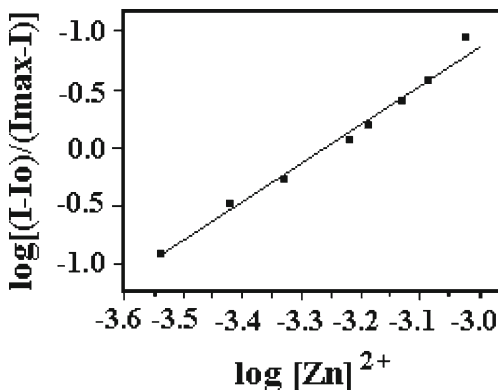
**Fig. 1** Fluorescence emission spectra of **L** on addition of  $\text{Zn}^{2+}$  in 1:1  $\text{CH}_3\text{OH}:\text{H}_2\text{O}$  {[0, 0.99, 1.9, 2.9, 3.8, 4.7, 6.5, 7.4, 8.2 and 9.0 ( $\times 10^{-5}$  M)] (in order of increasing intensity);  $\lambda_{\text{ex}}=350$  nm;  $\lambda_{\text{emi}}=370\text{--}600$  nm; Inset: plot of  $I/I_0$  as a function of  $\text{Zn}^{2+}$  ion concentration



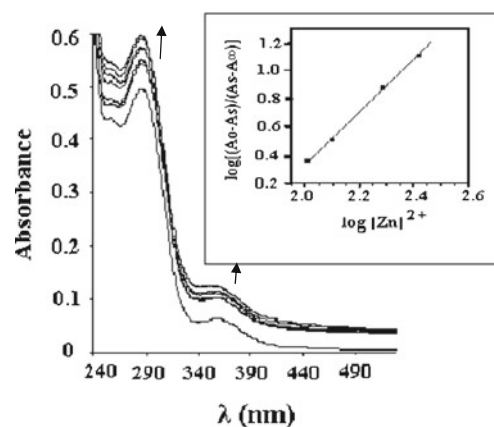
**Fig. 2** Bar diagram showing effect of 1 equivalent of different metal ions ( $9.0 \times 10^{-5} \text{M}$ ) on the fluorescent intensity of L, in 1:1  $\text{CH}_3\text{OH}:\text{H}_2\text{O}$

$\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  was investigated in 1:1  $\text{CH}_3\text{OH}:\text{H}_2\text{O}$ . It was found that the intensity of the fluorescent peak of L increases with gradual addition of  $\text{Zn}^{2+}$  ion into the solution and attains the maximum (5.5 times to the original intensity) at  $9.9 \times 10^{-5} \text{M}$  concentration of  $\text{Zn}^{2+}$ . The intensity enhancement was accompanied by a blue shift in the  $\lambda_{\text{max}}$  from 454 nm to 420 nm. Figure 1 portrays the fluorescence spectra of L at zero and at various added concentration of  $\text{Zn}^{2+}$  ( $0.99 \times 10^{-5}$  to  $10.71 \times 10^{-5} \text{M}$ ). Inset of Fig. 1 shows the plot of  $I/I_0$  as a function of  $\text{Zn}^{2+}$  ion concentration, where I refers to the intensity at a given concentration of  $\text{Zn}^{2+}$  ion and  $I_0$  is the intensity at zero concentration of  $\text{Zn}^{2+}$ . The  $I/I_0$  value increased linearly ( $R^2=0.9561$ ) to 5.5 till the concentration of  $\text{Zn}^{2+}$  became  $9.9 \times 10^{-5} \text{M}$  and remained constant thereafter. The detection limit of L for  $\text{Zn}^{2+}$  was calculated to be  $2.754 \times 10^{-5} \text{M}$ .

$\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions induced about two times enhancement in the fluorescent peak of L but unlike  $\text{Zn}^{2+}$  no shift in the  $\lambda_{\text{max}}$  value of the fluorescent emission peak was observed. On the other hand, the metal ions –  $\text{Na}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  were found to quench the intensity of the fluorescent peak of L to a remarkable extent. The maximum quenching effect was seen for  $\text{Co}^{2+}$  ion. The metal ion selectivity profile of L is shown by a bar diagram (Fig. 2), which depicts the effect of different metal ions on



**Fig. 3** Plot of  $\log [(\text{I}-\text{I}_0)/(\text{I}_{\text{max}}-\text{I})]$  as a function of  $\log [\text{Zn}^{2+}]$  for titration of L against  $\text{Zn}^{2+}$  in 1:1  $\text{CH}_3\text{OH}:\text{H}_2\text{O}$

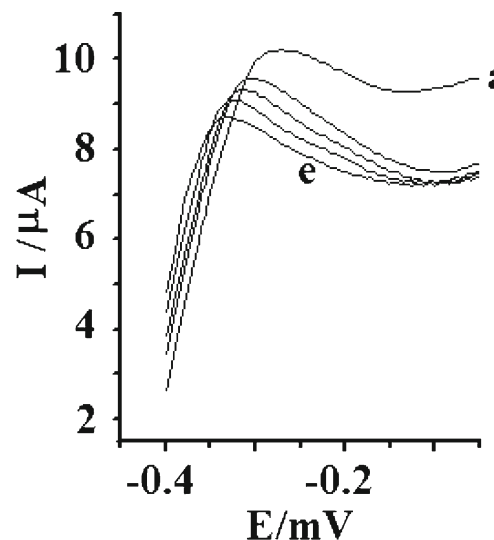


**Fig. 4** Change in U/V visible spectra of L when concentration of  $\text{Zn}^{2+}$  ion was changed from 0 to  $9.0 \times 10^{-5} \text{M}$ . Inset: Plot of  $\log[(\text{A}_0-\text{A}_5)/(\text{A}_s-\text{A}_\alpha)]$  versus  $\log[\text{Zn}^{2+}]$

the fluorescence spectra of L. The bar diagram clearly indicates that L acts as a selective fluorescent sensor for  $\text{Zn}^{2+}$  over all the other metal ions.

Determination of the number of  $\text{Zn}^{2+}$  ions bound to L and the binding constant was done by plotting  $\log [(I - I_0)/(I_{\text{max}} - I)]$  against  $\log[\text{Zn}^{2+}]$  (Fig. 3) [26]. The plot obtained was linear ( $R^2=0.984$ ) with the slope and the X-axis intercept representing the number of  $\text{Zn}^{2+}$  ions bound and the log of binding constant ( $\beta$ ) respectively. The slope was calculated to be 1.092, indicating the binding of one  $\text{Zn}^{2+}$  ion to L and the log  $\beta$  value was 1.86.

The UV/Visible spectra of L in 1:1 (v/v)  $\text{CH}_3\text{OH}:\text{H}_2\text{O}$  showed two absorption peaks with  $\lambda_{\text{max}}$  values at 284 nm and 354 nm. On increasing the concentration of  $\text{Zn}^{2+}$  ion ( $0.99 \times 10^{-5} \text{M}$  to  $9.0 \times 10^{-5} \text{M}$ ) in the solution, the absorbance of both the peaks were found to increase



**Fig. 5** Square Wave Voltammogram of L in 1:1  $\text{CH}_3\text{OH}:\text{H}_2\text{O}$  at  $\text{Zn}^{2+}$  ion concentration 0 (a),  $1.9 \times 10^{-5} \text{M}$  (b),  $2.9 \times 10^{-5} \text{M}$  (c),  $3.8 \times 10^{-5} \text{M}$  (d) and  $4.7 \times 10^{-5} \text{M}$  (e)

(Fig. 4). In order to confirm the number of  $\text{Zn}^{2+}$  ions bound to **L**,  $\log [(A_0-A_s)/(A_s-A_\infty)]$  value was plotted against  $\log [\text{Zn}^{2+}]$  (Fig. 4, inset) for the absorbance values of 354 nm peak. Here,  $A_0$ ,  $A_s$  and  $A_\infty$  are the absorbances of **L** at zero, at an intermediate and at infinite concentration of  $\text{Zn}^{2+}$  respectively. The plot was found to be linear ( $R^2=0.987$ ) with slope 1.12 indicating and thus further confirming the binding of one  $\text{Zn}^{2+}$  ion to **L**. The  $\log \beta=1.97$  value found to be in conformity to that obtained from fluorescent intensity calculation.

The enhancement of the fluorescence intensity of **L** on interaction with  $\text{Zn}^{2+}$  is due to the efficient Photoinduced electron Transfer Mechanism (PET) between **L** and  $\text{Zn}^{2+}$ . Initially, the fluorescence of **L** is quenched due the transfer of electron density from the N-atoms of the receptor part (ethylene diamine) to the LUMO of the fluorophore part (benzil). Both fluorescence and UV spectral titration indicate that one  $\text{Zn}^{2+}$  binds to **L**. The  $\text{Zn}^{2+}$  preferably coordinates to **L** via the four N-atoms of the two ethylene diamine groups. Due to the binding of  $\text{Zn}^{2+}$  to **L** the energy of the electrons originating at the N atoms are lowered and the PET process is hindered, as a result of which the fluorescence intensity is enhanced.

We have carried out fluorescence lifetime studies to confirm the involvement of PET process in the fluorescence signalling action. A multiexponential fluorescence behaviour was observed for **L** yielding decay parameters :  $\tau_1=0.204$  ns (57.39 %),  $\tau_2=1.236$  ns (32.33 %) and  $\tau_3=4.457$  ns (10.28 %). The complex nature of the fluorescence decay behaviour is a reflection of the flexibility of the molecule [28]. The components with life time  $\tau_1=0.204$  ns and  $\tau_2=1.236$  ns favours PET process in 89.42 % of the total molecules. Addition of  $\text{Zn}^{2+}$  ion results in the disappearance of the shorter lifetime component with the formation of a new component at  $\tau_1=4.75$  ns. Disappearance of the shorter life time components confirm the suppression of the PET process [29].

The Osteryoung Square Wave Voltammetric response of **L** in 1:1 (v/v)  $\text{CH}_3\text{OH}:\text{H}_2\text{O}$  was investigated. The experiments were carried out by using Glassy carbon disc as the working electrode and Ag-AgCl as the reference electrode. The redox peak potential value was obtained at - 0.272 V. On addition of  $\text{Zn}^{2+}$  ion the peak potential of **L** shifted gradually in negative direction till it became -0.328 V at  $\text{Zn}^{2+}$  ion concentration  $4.7 \times 10^{-5}$  M (Fig. 5). However, no significant change was observed when metal ions-  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Na}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  were added to the electrolytic medium alone or together. This electrochemical result further confirmed the selective interaction between **L** and  $\text{Zn}^{2+}$  ion.

In summary, we have shown that the sensor **L**, synthesized by condensation of benzil and semicarbazide, showed remarkable enhancement in the fluorescence intensity with

blue shift on interaction with  $\text{Zn}^{2+}$ . Interaction with the metal ions -  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Ca}^{2+}$  enhances the fluorescent intensity by a small amount without any blue shift. On the other hand metal ions  $\text{Fe}^{2+}$ ,  $\text{Na}^{+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  quenches the fluorescence intensity of **L**. A 1:1 complexation between **L** and  $\text{Zn}^{2+}$  ion is proved to be formed which snaps the PET process in **L** leading to fluorescent enhancement.

**Acknowledgement** UGC, New Delhi is thanked for financial support to the department under SAP and RFSMS to PG. DST, New Delhi is thanked for FIST to the department. SIF, IIT – Guwahati is thanked for time resolved fluorescence spectroscopy.

## References

- Silva AP, Gunaratne HQN, Gunnlaugsson T, Huxley AJM, Mc Coy CP, Rademacher JT, Rich TE (1997) Signalling recognition event with fluorescent sensors and switches. *Coord Chem Rev* 97:1515–1566
- Spichiger-Keller YE (1998) US-sensors and biosensors for medical and biological applications. Wiley-VCH, New York
- Mason CF (2002) Biology of freshwater pollution, 2nd edn. Longman, New York
- Lippard SJ, Berg JM (1994) Principles of bioinorganic chemistry. University Science, Mill Valley, Ca, USA
- Kimura E, Aoki S, Kikuta E, Koike T (2003) A macrocyclic zinc (II) fluorophore as a detector of apoptosis. *Proc Natl Acad Sci USA* 100:3731–3736
- Czarnik AW (1993) Fluorescent chemosensors for ion and molecule detection. American Chemical Society, Washington DC
- Voegelin A, Poster S, Scheinost AC, Marcus MA, Kretzschmar (2005) Changes in zinc speciation in field soil after contamination with zinc oxide. *Environ Sci Technol* 39:6616–6623
- Callender E (2000) The Urban environmental gradient: anthropogenic influences on the spatial and temporal distributions of lead and zinc in sediments. *Environ Sci Technol* 34:232–238
- Weiss JH, Sensi SL, Koh JY (2000)  $\text{Zn}^{2+}$ : a novel ionic mediator of neutral injury in brain disease. *Trends Pharmacol Sci* 21:395–401
- Whitlock BJ, Whitlock HW (1990) Concave functionality: design criteria for nonaqueous binding sites. *J Am Chem Soc* 112:3910–3915
- Benesi HA, Hildebrand JH (1949) A spectrophotometric investigation of the interaction of iodine with aromatic hydrocarbons. *J Am Chem Soc* 71:2703–2707
- Hanna MW, Ashbaugh AL (1964) Nuclear magnetic resonance study of molecular complexes of 7,7,8,8-tetracyanoquinodimethane and aromatic donors. *J Phys Chem* 68:811–816
- De Voogt P, van Hattum B, Feenstra JF, Peereboom JWC (1990) *Toxicol Environ Chem Rev* 3:89
- Burdette SC, Walkup GK, Spingler B, Tsien RY, Lippard SJ (2001) Fluorescent sensors for  $\text{Zn}^{2+}$  based on a fluorescein platform: synthesis, properties and intracellular distribution. *J Am Chem Soc* 123:7831–7841
- Swale DF, Sepaniak MJ (1991) Determination of metal ions by capillary zone electrophoresis acid. *Anal Chem* 63:179–185
- Fabbrizzi L, Licchelli G, Rabaioli A, Taglietti A (2000) The design of luminiscent sensors for anions and ionisable analytes. *Coord Chem Rev* 205:85
- Nolan EM, Ryu JW, Jaworski J, Feazell RP, Sheng M, Lippard SJ (2006) Zinspy sensors with enhanced dynamic range for imaging

- neuronal cell zinc uptake and mobilization. *J Am Chem Soc* 128:15517–15528
18. Komatsu K, Kikuchi K, Kojima H, Urano Y, Nagano T (2005) Selective zinc sensor molecules with various affinities for Zn<sup>2+</sup>, revealing dynamics and regional distribution of synaptically released Zn<sup>2+</sup> in hippocampal slices. *J Am Chem Soc* 127:10197–10204
  19. Henary MM, Wu YG, Fahrni CJ (2004) Zinc(II)-selective ratiometric fluorescent sensors based on inhibition of excited-state intramolecular proton transfer. *Chem Eur J* 10:3015–3025
  20. Chen H, Wu Y, Cheng Y, Yang H, Li F, Yang P, Huang C (2007) A ratiometric fluorescent sensor for zinc(II) with high selectivity. *Inorg Chem Commun* 10:1413–1415
  21. Wu Z, Chen Q, Yang G, Xiao C, Liu J, Yang S, Ma JS (2004) Novel fluorescent sensor for Zn(II) based on bis(pyroll-2-yl-methyleneamine) ligands. *Sensors and Actuators B* 99:511–515
  22. Weng Y, Chen Z, Wang F, Xue L, Jiang H (2009) High sensitive determination of zinc with novel water-soluble small molecular fluorescent sensor. *Anal Chim Acta* 647:215–218
  23. Roy P, Dhara K, Manassero M, Banerjee P (2009) Synthesis, characterization and selective fluorescent zinc(II) sensing property of three Schiff-base compounds. *Inorg Chim Acta* 362:2927–2932
  24. Kulatililke CP, Silva SA, Eliav Y (2006) A coumarin based fluorescent photoinduced electron transfer cation sensor. *Polyhedron* 25:2593–2596
  25. Goswami P, Das DK (2010) 2, 7-Dichlorofluorescein, a fluorescent sensor to detect Cd<sup>2+</sup> over Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup> Indian. *J Chem* 49A:1617–1620
  26. Dong X, Yang Y, Sun J, Liu Z, Liu Bi-F (2009) Two -photon excited fluorescent probes for calcium based on internal charge transfer. *Chem Commun* 3883–3885
  27. Chandra S, Raizada S, Rani S (2008) Structural and spectral studies of palladium(II) and platinum(II) complexes derived from N, N, N, N-tetradentate macrocyclic ligands. *Spectrochimica Acta A* 71:720–724
  28. Sarkar M, Banthia S, Samanta A (2006) A highly selective ‘off-on’ fluorescence chemosensor for Cr(III). *Tetrahedron Letters* 47:7575–7578
  29. Ashokkumar P, Ramakrishnan VT, Ramamurthy P (2011) Photoinduced Electron Transfer (PET) Based Zn<sup>2+</sup> Fluorescent Probe: transformation of turn-on sensors into ratiometric ones with dual emission in Acetonitrile. *J Phys Chem A* 2011:14292–14299