

# N-benzoate-N' salicylaldehyde ethylenediamine: A new fluorescent sensor for Zn<sup>2+</sup> ion by “off-on” mode

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**Abstract** Imbalance of zinc ion (Zn<sup>2+</sup>) in human body causes diseases like Alzheimer's and Parkinson's and therefore Zn<sup>2+</sup> estimation in biological fluids has diagnostic values. Fluorescence “off-on” sensors have advantages of high sensitivity and in situ application over other sensors. A new fluorescent “off-on” Zn<sup>2+</sup> sensor, N-benzoate-N' salicylaldehyde ethylenediamine (**L**), has been synthesised. In 1:1(v/v) CH<sub>3</sub>OH:PBS (PBS=phosphate buffer solution), **L** shows *ca.* 20 times enhancement in fluorescence intensity on interaction with Zn<sup>2+</sup>, due to snapping of photoinduced electron transfer (PET) process, which is selective over metal ions - Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup> and Pb<sup>2+</sup>. These metal ions either individually or all together does not interfere the sensing ability of **L** towards Zn<sup>2+</sup>. A 1:1 interaction between **L** and Zn<sup>2+</sup> ion with binding constant 10<sup>4.25</sup> has been established from spectroscopic data.

**Keywords** Benzoic acid · Ethylenediamine · Salicylaldehyde · Fluorescence · Sensors · Photoinduced electron transfer (PET) · “off-on” fluorescence sensor

## Introduction

In recent years, the recognition and sensing of biologically and environmentally important metal ions by fluorescence technique has emerged as a significant goal in the field of chemical sensors [1, 2]. Among the various analytical methods that are available for the detection of cations, the

techniques based on fluorescence sensors demonstrate substantial advantages in terms of sensitivity, selectivity, low cost, facile operation, response time, local observation and the widespread availability of equipment for analysis [3–5].

Zinc ion (Zn<sup>2+</sup>) is an important metal ion in biology and its imbalance in human body has been related to a number of diseases like Alzheimer's and Parkinson's [6–13]. For diagnosis of such diseases it is required to estimate Zn<sup>2+</sup> in biological fluids. Fluorescent sensors have advantages of being cheap and applicable for in situ estimation over other methods. “off-on” type fluorescent sensors have extra advantage of high sensitivity. Photoinduced electron transfer (PET) is one of the prime principle behind fluorescent “off-on” sensors for Zn<sup>2+</sup> [14–16]. In recent years, a number of fluorescent sensors for Zn<sup>2+</sup> have been developed [14]. A photo switchable Zn<sup>2+</sup> selective spiropyran-based sensor was developed by S. Giordani et al. [17]. Chen and co-workers reported a quinoline carboxaldehyde and phenylenediamine based ratiometric fluorescent sensor for Zn<sup>2+</sup> [18]. P. Banerjee et al. also reported the selective fluorescent zinc sensing property by certain Schiff base compounds [19]. A dual fluorescent sensor based on calyx-4-arene for Zn<sup>2+</sup> and Ni<sup>2+</sup> was reported by C.P. Rao *et al* [20]. We have previously reported fluorescent Zn<sup>2+</sup> sensors based on N, N, N, N-tetradentate macrocycle [21] and ferrocene derivative [22].

In this paper, we report a new compound (**L**) Scheme 1, synthesized by a two-step condensation reaction of benzoic acid, ethylenediamine and salicylaldehyde. In 1:1 (v/v) CH<sub>3</sub>OH:H<sub>2</sub>O, **L** was found to exhibit a fluorescent peak at λ<sub>max</sub> value 450 nm on excitation by 350 nm wavelength photons. **L** can detect Zn<sup>2+</sup> by fluorescence “on” mode with an enhancement in fluorescence intensity of *ca.* 20 times while metal ions Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup> and Pb<sup>2+</sup> do not interfere.

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## Experimental

### Materials and methods

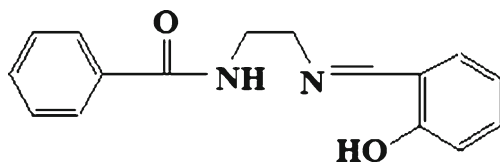
All the chemicals were from Merck except salicylaldehyde and ethylene diamine (Loba Chemie). The metal salts were recrystallized from water (Millipore) before use. Metal salt solutions ( $10^{-2}$  M) were prepared in phosphate buffer solutions (PBS) at pH 7.0. Fluorescent spectra were recorded in a Hitachi 2500 spectrophotometer using quartz cuvette (1 cm path length). A  $9.0 \times 10^{-4}$  M solution of **L** in 1:1 (v/v)  $\text{CH}_3\text{OH}$ :PBS, pH 7.0 was used in the experiments. The excitation wavelength was 350 nm, emission range was 400–600 nm ( $\lambda_{\text{max}}$  at 450 nm) and excitation/emission slit was 5 nm.

UV/Visible spectra of **L** ( $10^{-4}$  M in 1:1 (v/v)  $\text{CH}_3\text{OH}$ :PBS) 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.

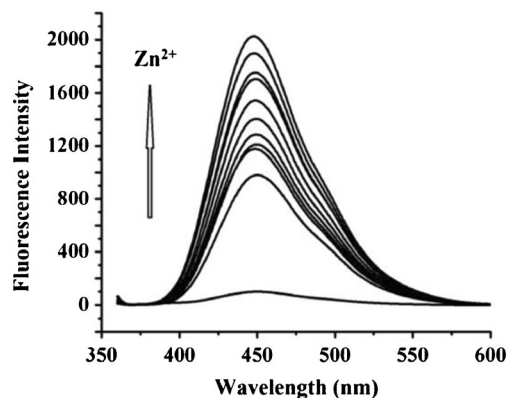
Electrochemical measurements were carried out in a CHI 600B electrochemical analyser, consisting of a three-electrode assembly with a glassy carbon disc as the working electrode,  $\text{Ag}/\text{AgCl}$  (3 M  $\text{NaCl}$ ) as the reference electrode and tetrabutylammonium perchlorate (TBAP, 0.01 M) as the supporting electrolyte. The working electrode was cleaned as reported [23] by polishing with 0.1  $\mu\text{M}$  alumina slurry using a polishing kit (CHI), followed by sonication in distilled water for 5 min.

### Synthesis of **L**

0.122 g (0.01 mol) of benzoic acid was dissolved in 10 mL of methanol and 0.067 g (0.01 M) of ethylenediamine was added to it. The mixture was refluxed for 1 h and the solvent was evaporated in rota-evaporator. The product, N-benzoateethylenediamine, thus obtained was dried and recrystallized from methanol. 0.164 g (0.01 M) of N-benzoateethylenediamine was taken in 10 mL methanol in a round bottom flask, 0.124 g (0.01 M) of salicylaldehyde was added and refluxed for 20 min. The solid compound (N-benzoate-N' salicylaldehyde ethylenediamine, **L**) obtained was separated by filtration and dried in a dessicator.



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



**Fig. 1** The fluorescent spectra of **L** ( $9 \times 10^{-4}$  M) in 1:1 (v/v)  $\text{CH}_3\text{OH}$ :PBS at  $\text{Zn}^{2+}$  concentration 0, 3.8, 4.6, 4.9, 5.8, 6.3, 6.9, 7.8, 8.2, 9.1, 9.9, 11.0 and  $11.9 \times 10^{-4}$  M. ( $\lambda_{\text{ex}}=350$  nm,  $\lambda_{\text{emi}}=400$ –600 nm)

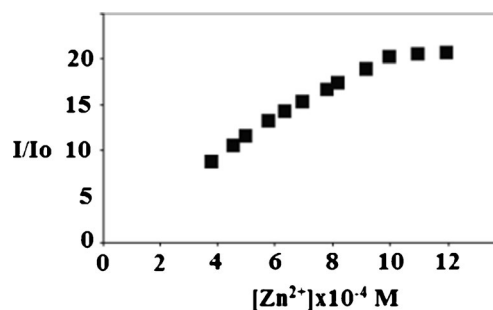
**FTIR** (KBr): 3448  $\text{cm}^{-1}$  ( $\nu_{\text{N-H}}$ ), 1638  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ), 2339  $\text{cm}^{-1}$  ( $\nu_{\text{C=N}}$ ) and 3427  $\text{cm}^{-1}$  ( $\nu_{\text{N-H}}$ ).

**$^1\text{H}$ NMR** ( $\text{CDCl}_3$ , TMS,  $\delta$  ppm): 3.95 ( $-\text{CH}_2-$ , ethylenediamine), 6.86–7.29 ( $\text{C}_6\text{H}_5-$ ), 8.36 ( $-\text{NH}$ ).

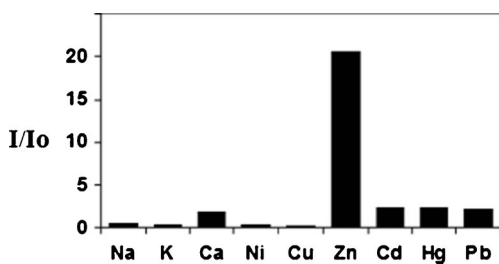
**$^{13}\text{C}$ NMR** ( $\text{CDCl}_3$ , TMS,  $\delta$  ppm): 166 ( $-\text{C=O}$ ), 160 ( $-\text{N=C-}$ ), 132–116 ( $\text{C}_6\text{H}_5-$ ), 59 & 31 ( $-\text{NHCH}_2\text{CH}_2\text{N=}$ ).

## Results and discussion

The fluorescence spectral changes of **L** on interaction with metal ions— $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$  was investigated in 1:1 (v/v)  $\text{CH}_3\text{OH}$ :PBS. It was observed that on excitation of **L** by 350 nm wavelength radiation, the emission band was obtained in the range 400–600 nm with the  $\lambda_{\text{max}}$  value at 450 nm. However, on addition of different concentration of  $\text{Zn}^{2+}$  ion ( $0.99 \times 10^{-4}$  M to  $9.0 \times 10^{-4}$  M), it was revealed that the intensity of the fluorescent peak at 450 nm increased remarkably with the increasing concentration of  $\text{Zn}^{2+}$  ion. The increase in the fluorescence intensity on addition of  $\text{Zn}^{2+}$  ions at the final added



**Fig. 2** Plot of  $I/I_0$  for **L** ( $9.0 \times 10^{-4}$  M, in 1:1 (v/v)  $\text{CH}_3\text{OH}$ :PBS) versus concentration of  $\text{Zn}^{2+}$ , where  $I_0$  is the fluorescent intensity of **L** at 0 M concentration of  $\text{Zn}^{2+}$  and  $I$  is the fluorescent intensity of **L** at a particular added concentration of  $\text{Zn}^{2+}$  ( $\lambda_{\text{ex}}=350$  nm)

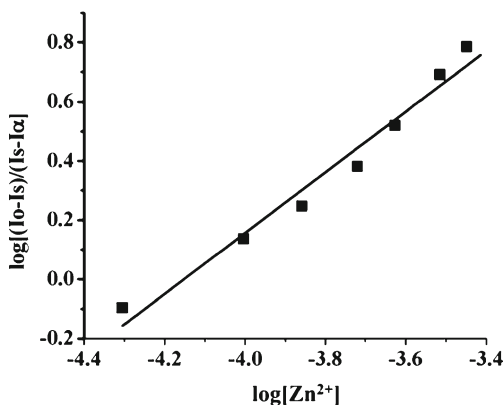


**Fig. 3** Bar diagram to compare the effect of different metal ions on the I/I<sub>0</sub> value of L (9.0 × 10<sup>-4</sup> M, λ<sub>ex</sub> = 350 nm) in 1:1 (v/v) CH<sub>3</sub>OH:PBS

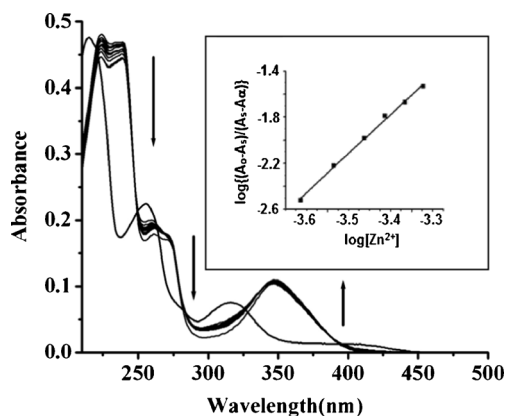
concentration was calculated to be approximately 20 times to the original one. Figure 1 depicts the fluorescence spectral changes of L upon addition of different concentration of Zn<sup>2+</sup> (from 0.99 × 10<sup>-4</sup> M to 9.0 × 10<sup>-4</sup> M). Figure 2 depicts the plot of I/I<sub>0</sub> as a function of Zn<sup>2+</sup> concentration, where I is the intensity at a given concentration of Zn<sup>2+</sup> and I<sub>0</sub> is the intensity at zero concentration of Zn<sup>2+</sup>. The I/I<sub>0</sub> value increased linearly (R<sup>2</sup> = 0.9561) to 20 till the concentration of Zn<sup>2+</sup> became 9.0 × 10<sup>-4</sup> M and remained constant thereafter.

Similarly, the fluorescence spectral change of L was investigated by carrying out similar titrations with metal ions—Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup> and Pb<sup>2+</sup>. The results showed that although a slight increase in the fluorescence intensity up to ca. 2.5 times was observed on addition of Ca<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup> and Pb<sup>2+</sup> to L, the other metal ions Na<sup>+</sup>, K<sup>+</sup>, Cu<sup>2+</sup> and Ni<sup>2+</sup> quenched the fluorescence signal of L to a remarkable extent. Figure 3 is the bar diagram profile to show the effect of various metal ions, at 9.0 × 10<sup>-4</sup> M concentration, on the fluorescent intensity of L. The diagram clearly portrays the sensitivity and selectivity of the sensor compound towards Zn<sup>2+</sup>.

In order to determine the number of Zn<sup>2+</sup> bound to L and to determine the binding constant, log[(I<sub>0</sub> - I<sub>s</sub>)/(I<sub>s</sub> - I<sub>α</sub>)] was plotted against log[Zn<sup>2+</sup>] (Fig. 4) [24, 25]. Here I<sub>0</sub>, I and I<sub>α</sub> are the fluorescence intensity of L in absence of Zn<sup>2+</sup>, in presence of an intermediate concentration of Zn<sup>2+</sup> and at saturated



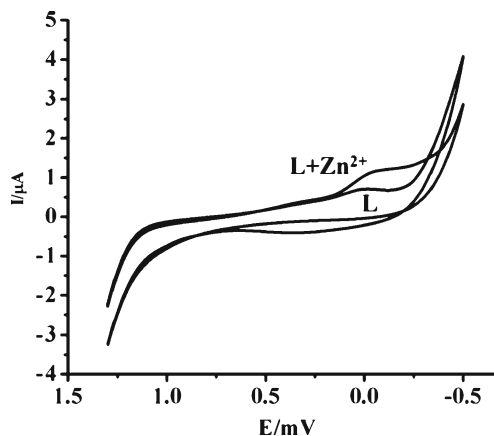
**Fig. 4** Plot of log[(I<sub>0</sub> - I<sub>s</sub>)/(I<sub>s</sub> - I<sub>α</sub>)] versus log[Zn<sup>2+</sup>] for L in 1:1 (v/v) CH<sub>3</sub>OH:PBS. The slope 1.03 indicates 1:1 binding between L and Zn<sup>2+</sup>. (R<sup>2</sup> = 0.971)



**Fig. 5** UV/Visible spectra of L in 1:1 (v/v) CH<sub>3</sub>OH:PBS at different added concentration of Zn<sup>2+</sup>. Inset: plot of log[(A<sub>0</sub> - A<sub>s</sub>)/(A<sub>s</sub> - A<sub>α</sub>)] versus log[Zn<sup>2+</sup>] for L in 1:1 (v/v) CH<sub>3</sub>OH:PBS. The slope 1.12 indicates 1:1 binding between L and Zn<sup>2+</sup> (R<sup>2</sup> = 0.996)

concentration of Zn<sup>2+</sup>, respectively. The plot obtained was linear, with the slope and the X-axis intercept representing the number of Zn<sup>2+</sup> bound and the log of binding constant (β) respectively. A least squares fitting of data (R<sup>2</sup> = 0.971) yielded the slope to be 1.03, indicating the binding of one Zn<sup>2+</sup> to L. The binding constant (β) was obtained to be 10<sup>4.25</sup>.

The UV/Visible spectra of L in 1:1 (v/v) CH<sub>3</sub>OH:H<sub>2</sub>O at different added concentration of Zn<sup>2+</sup> has been shown in Fig. 5. In absence of Zn<sup>2+</sup>, L showed peaks at λ<sub>max</sub> values 220 nm, 255 nm and 320 nm. Interaction with Zn<sup>2+</sup> shifted the 220 nm peak to 230 nm with a shoulder at 235 nm, the 255 nm peak was shifted to 260 nm with a shoulder at 272 nm, the 320 nm peak significantly shifted to 354 nm with an enhancement in absorbance. In order to confirm the number of Zn<sup>2+</sup> bound to L, obtained from fluorescence data, log[(A<sub>0</sub> - A<sub>s</sub>)/(A<sub>s</sub> - A<sub>max</sub>)] value was plotted against log[Zn<sup>2+</sup>] for the absorbance values of 354 nm peak (Fig. 4, inset). Here, A<sub>0</sub>, A<sub>s</sub> and A<sub>max</sub> are the absorbances of L at zero, at an



**Fig. 6** Cyclic voltammogram for L (10<sup>-4</sup> M) and L in presence of one equivalent of Zn<sup>2+</sup> in 1:1 (v/v) CH<sub>3</sub>OH:PBS. Working electrode GC, Reference electrode Ag/AgCl (3 M NaCl), Supporting electrolyte TBAP, 0.01 M

intermediate and at saturated concentration of  $\text{Zn}^{2+}$  respectively. The plot was found to be linear ( $R^2=0.996$ ) with slope 1.12 indicating that one  $\text{Zn}^{2+}$  binds to **L** and the binding constant ( $\beta$ ) value was found to be  $10^{4.54}$ . These values are in conformity to those obtained from fluorescent intensity calculations.

The significant change in the fluorescent intensity of **L** on interaction with  $\text{Zn}^{2+}$  may be explained on the basis of the disruption of the efficient thermodynamically favourable PET mechanism [26] initially prevailing in **L**. The  $\text{Zn}^{2+}$  likely binds to **L** via the two N-atoms of the ethylenediamine moiety. In **L** the PET process exists due to the transfer of electron density, originating at the lone pairs of electrons on N atoms of the receptor part (ethylenediamine) to the LUMO of the fluorophore part (salicylaldehyde). This results in the quenching of the fluorescence intensity of **L**. Both fluorescence and UV/Visible spectral titration indicate the binding of one  $\text{Zn}^{2+}$  to **L**. 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 regenerated. We have already reported a fluorescent sensor for  $\text{Pb}^{2+}$ , having structure similar to **L**, which is also based on PET [27] Fig. 6.

The Cyclic voltammogram of **L** ( $10^{-4}$  M) was recorded in 1:1 (v/v)  $\text{CH}_3\text{OH}$ :PBS solution using glassy carbon (GC) disc as the working electrode and  $\text{Ag}/\text{AgCl}$  (3 M NaCl) as the reference electrode. An irreversible voltammogram was observed with a reduction peak potential at  $-0.010$  V. Upon additions of different concentration of  $\text{Zn}^{2+}$  ( $0.99 \times 10^{-4}$  M to  $9.0 \times 10^{-4}$  M) to the electrolytic medium, the reduction peak potential of **L** was shifted to  $-0.035$  V (Fig. 6). Thus  $\text{Zn}^{2+}$  interaction results a 0.025 V shift in reduction potential of **L** towards the negative direction. No change in the cyclic voltammogram of **L** was observed when similar titrations were carried out with the other metal ions-  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$ . From this electrochemical data, the selective interaction between **L** and  $\text{Zn}^{2+}$  could be further confirmed.

To summarize, in this paper we have presented a simple and cost effective new fluorescent sensor for  $\text{Zn}^{2+}$  over  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$ . The fluorescence intensity enhancement is *ca.* 20 fold due to snapping of PET process. This fluorescent intensity enhancement is higher than that reported for many other sensors [28–32]. This sensor also shows electrochemical response towards  $\text{Zn}^{2+}$  and sensors showing both fluorescent and electrochemical response towards  $\text{Zn}^{2+}$  are not very common. A 1:1 complex formation between **L** and  $\text{Zn}^{2+}$  with binding constant value  $10^{4.25}$  is proved.

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