

# A New Highly Sensitive and Selective Fluorescent Cadmium Sensor

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**Abstract** Condensation product (**L**) of salicylaldehyde and semicarbazide behaves as a fluorescent sensor for  $\text{Cd}^{2+}$  ion, in 1:1 DMSO:H<sub>2</sub>O, over  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  ions. The emission peak of **L** at  $\lambda_{\text{max}}=520$  nm, on excitation with 420 nm wavelength photons, showed an enhancement in intensity of *ca* 60-fold when interacted with  $\text{Cd}^{2+}$  ion. The intensity was however found to remain unaltered when interacted with metal ions— $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$ . The intensity increases by approximately 20 fold on interaction with  $\text{Zn}^{2+}$  ion. The increase in the fluorescent peak can be explained on the basis of photo induced electron transfer (PET) mechanism. A 1:1 complexation between  $\text{Cd}^{2+}$  and **L** with  $\log \beta=4.25$  has been proved.

**Keywords** Cadmium · Salicylaldehyde · Semicarbazide · Fluorescence · Sensor · Photo induced electron transfer (PET)

## Introduction

In recent years there has been a significant interest in the design and development of fluorescent sensors for detecting transition and heavy metal ions [1–3]. Cadmium is an important natural element, and is present in air, water, or in plants, resulting from anthropogenic pollution. Anthropogenic sources of cadmium in the environment include mining and smelting metal ores, fossil fuel combustion and metal industries [4]. Cadmium frequently finds use in a variety of fields such as industry, agriculture, alloys,

electroplating, coloring matters, fertilisers as well as in the production of dry-cell batteries. Despite its many uses and applications, cadmium is unfortunately highly toxic to human beings and poses a severe threat to the human health and environment [5]. It accumulates in cells, liver and kidneys, thyroid glands and spleen resulting in physiological disorders or carcinogenic effects [6, 7]. The detection, development and sensing of cadmium in the environment and in vivo settings is thus a vital area of research [8].

So far, a good number of fluorescent sensors have been actualized which can detect and analyse different kinds of heavy toxic metal ions, due to their simplicity, high sensitivity and real-time detection [9]. However, only a few cadmium ion fluorescent sensors have been reported till date [10–13] and not many cadmium sensors are commercially available. The greatest challenge for detecting  $\text{Cd}^{2+}$  is the interference of other transition metal ions, particularly  $\text{Zn}^{2+}$  which belongs to the same group and exhibits many similar properties [14]. Therefore, both  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  cause similar spectral changes when coordinated with fluorescent sensors [15–17]. Thus it is necessary to develop  $\text{Cd}^{2+}$  selective fluorescent sensors that can distinguish  $\text{Cd}^{2+}$  from  $\text{Zn}^{2+}$  and other metal ions.

Recently, the trend of developing Cadmium fluorescent sensors has been increasing. An acetoimidoquinoline and dipicolamine based fluorescent sensor [14] has been synthesized for distinguishing  $\text{Cd}^{2+}$  from  $\text{Zn}^{2+}$  via PET and ICT mechanisms. A water soluble fluorescent sensor using anthracene and iminodiacetate receptor [18] was synthesized which was found to be highly selective for detecting  $\text{Cd}^{2+}$ . Fluorophore derivatives from 1, 8-naphthrydine have been reported which can signal  $\text{Cd}^{2+}$  selectively with fluorescent enhancement and red shift [19]. The fluorescent enhancement of commercially available

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Rhod-5 N on complexation with  $\text{Cd}^{2+}$  in buffer has been reported [20]. Costero et al. [21] has reported the design of 4,4'-substituted biphenyl moiety attached to 1-aza-18-crown-6 for selective detection of  $\text{Cd}^{2+}$  over  $\text{Zn}^{2+}$ . A coumarin-based fluorescent sensor [22] is also known for the detection of  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ . We have previously reported 2,7-dichlorofluorescein, as a fluorescent sensor for detecting  $\text{Cd}^{2+}$  over  $\text{Zn}^{2+}$ ,  $\text{Na}^{+}$ ,  $\text{K}^{+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  [23].

Here in this paper, we report a compound (**L**) derived from the condensation of semicarbazide and salicylaldehyde which exhibits a fluorescent peak at 520 nm on excitation by 420 nm wavelength photons, the solvent being 1:1 DMSO:  $\text{H}_2\text{O}$ . It has been found that the fluorescent intensity peak at 520 nm increases significantly to *ca* 60 times on interaction with  $\text{Cd}^{2+}$ , but little or no change at all in the intensity was observed on interaction with the other metal ions such as  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ . Although, an enhancement of about 20 times in the intensity of the fluorescent peak was observed on addition of  $\text{Zn}^{2+}$  to **L**, it was found to fluctuate with time.

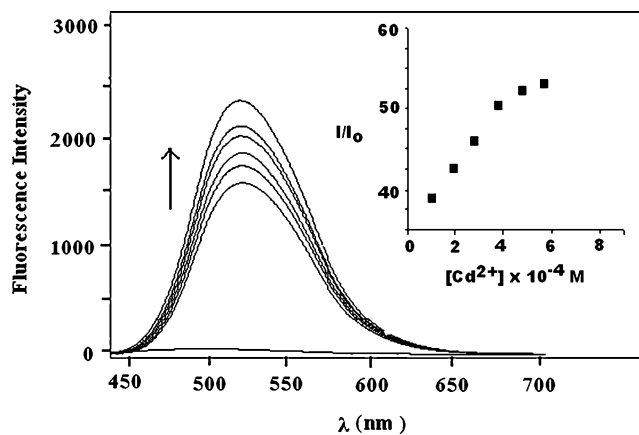
## Experimental

### Chemicals and Spectroscopic Measurements

All the chemicals and metal salts (sulphate) were purchased from Merck. The metal salts were recrystallized from water (Millipore). Metal salt solutions ( $10^{-5}$  M) were prepared in PBS, pH 7.0. Fluorescent spectra were recorded in a Hitachi 2500 spectrophotometer using quartz cuvette. A  $10^{-5}$  M solution of **L** in 1:1 (v/v) DMSO:  $\text{H}_2\text{O}$  (phosphate buffer solution, pH 7.0) was used in the experiments.

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, peaks were observed at 2742 & 2849  $\text{cm}^{-1}$  ( $\nu_{\text{C-H}}$ ), 3032  $\text{cm}^{-1}$  ( $\nu_{\text{O-H}}$ ), 1699  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ), 1619  $\text{cm}^{-1}$  ( $\nu_{\text{N-H}}$ ), 1487  $\text{cm}^{-1}$  ( $\nu_{\text{C=C}}$ ), 1275 & 1213  $\text{cm}^{-1}$  ( $\nu_{\text{C-N}}$ ), 905  $\text{cm}^{-1}$  ( $\nu_{\text{C-H}}$  bending). LC/MS was recorded in MS Waters Q-T of Premier and Equity UPLC instrument by sonication of **L** in a methanol and water mixture. The molecular peak was observed at *M/e* value 284.0 (calculated value of *M/e* is 283.0).

CHI 600B Electrochemical Analyser (USA), with a three-electrode environment was utilised for carrying out the electrochemical measurements. The cell assembly consisted of a platinum disc as the working electrode, Ag-AgCl (3 M NaCl) as the reference electrode and



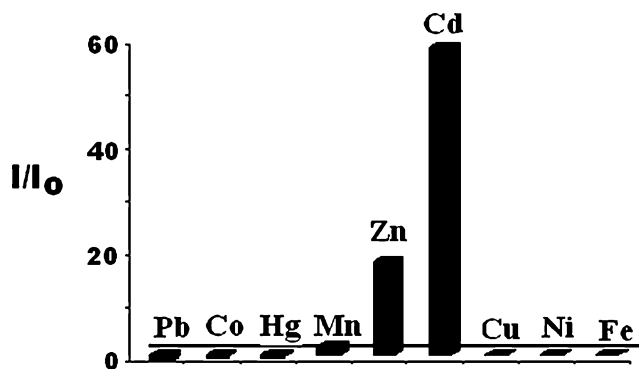
**Fig 1** Fluorescence emission spectra of **L** when 0, 0.99, 1.9, 2.9, 3.8, 4.7, 6.5, 7.4, 8.2 and  $9.0 \times 10^{-4}$  M  $\text{Cd}^{2+}$  ion was present in 1:1 DMSO:  $\text{H}_2\text{O}$ . ( $\lambda_{\text{ex}}=420$  nm;  $\lambda_{\text{emi}}=450\text{--}650$  nm; Inset: plot of  $I/I_0$  as a function of  $\text{Cd}^{2+}$  ion concentration)

tetrabutylammonium perchlorate (0.1 M) as the supporting electrolyte. The working electrode was cleaned by polishing with 0.1  $\mu\text{m}$  alumina slurry using a polishing kit (CHI), followed by sonication in distilled water for 5 min.

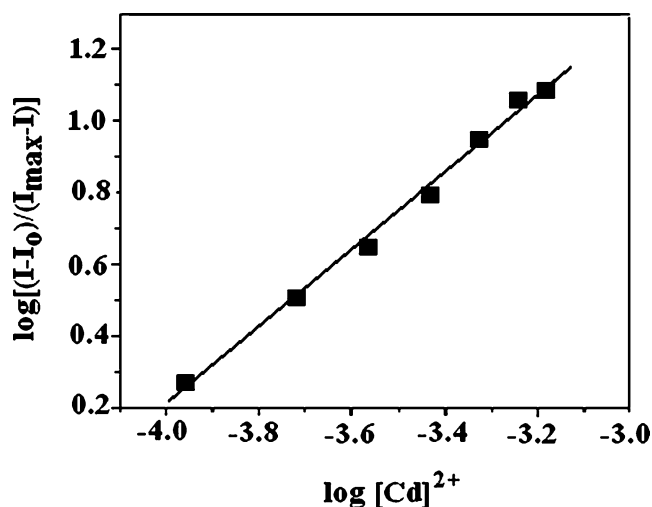
**Synthesis of L** 0.230 mg (0.1 mol) of semicarbazide was dissolved in 20 mL ethanol and an ethanolic solution of 4.2 mL (0.2 mol) salicylaldehyde was added to this solution. The resulting mixture was refluxed for 4 h and a brownish precipitate was obtained. This was further treated to solvent evaporation in a rotary evaporator. The brownish solid so obtained was washed with ethanol and dried.

## Results and Discussion

The fluorescence spectrum of **L** was recorded in 1:1 DMSO:  $\text{H}_2\text{O}$  at room temperature. It was revealed that, on excitation by 420 nm wavelength radiation, **L** exhibited an emission band at 450 nm to 650 nm with a  $\lambda_{\text{max}}$  at 498 nm.



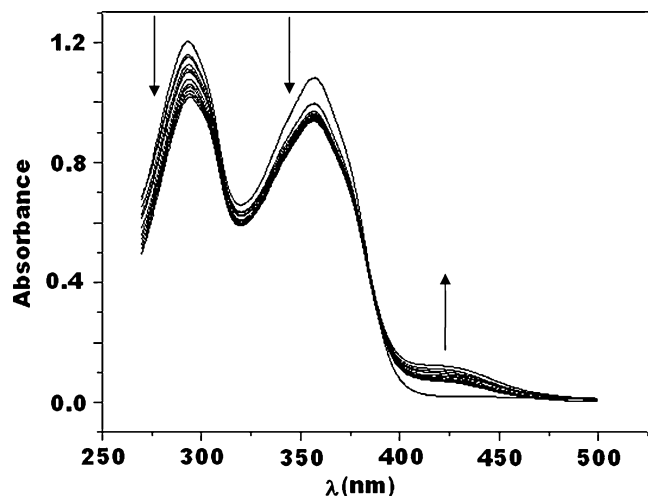
**Fig 2** Bar diagram showing effect of 1 equivalent of different metal ions ( $9.0 \times 10^{-4}$  M) on the fluorescent intensity of **L**, in 1:1 DMSO:  $\text{H}_2\text{O}$



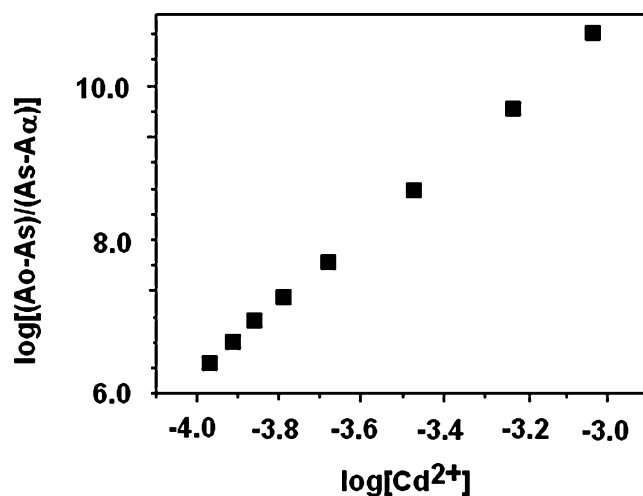
**Fig 3** Plot of  $\log [(I-I_0)/(I_{\max}-I)]$  as a function of  $\log [Cd^{2+}]$  for titration of **L** against  $Cd^{2+}$  in 1:1 DMSO:H<sub>2</sub>O

Figure 1 shows the fluorescence spectra of **L** at zero and different added concentration of  $Cd^{2+}$  (from  $0.99 \times 10^{-4}$  M to  $9.0 \times 10^{-4}$  M). The intensity of the emission spectra was found to increase with the concentration of  $Cd^{2+}$  ion. A red shift in  $\lambda_{\max}$  was also observed from 498 nm to 520 nm. The intensity of the emission spectra at the final concentration of  $Cd^{2+}$  was calculated to be approximately 60 times than that of the original one. Inset of Fig. 1 shows the plot of  $I/I_0$  as a function of  $Cd^{2+}$  ion concentration, where  $I$  is the intensity at a given concentration of  $Cd^{2+}$  ion and  $I_0$  is the intensity at zero concentration of  $Cd^{2+}$  ion. The  $I/I_0$  value increased linearly ( $R^2=0.991$ ) till the concentration of  $Cd^{2+}$  ion became  $5 \times 10^{-4}$  M and remained constant thereafter.

Fluorescent spectra of **L** was also recorded at different added concentration (from 0.1 mM to 0.9 mM) of metal



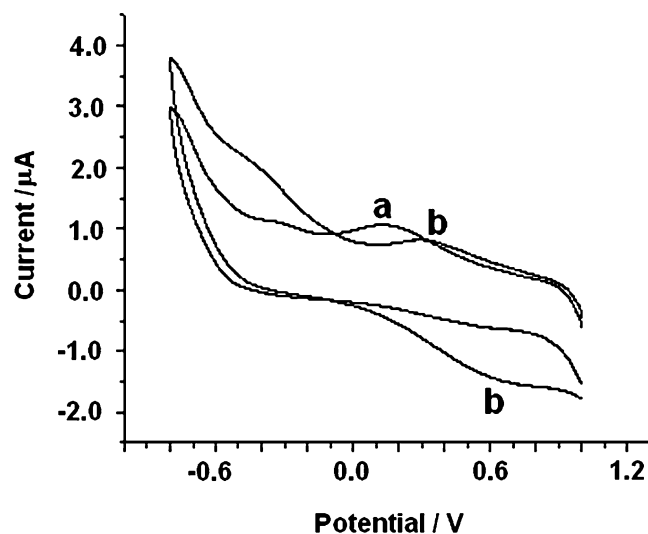
**Fig 4** UV/Visible spectral titration of **L** against  $Cd^{2+}$  ion. The concentration of  $Cd^{2+}$  ion was varied from 0.0 mM to 0.9 mM



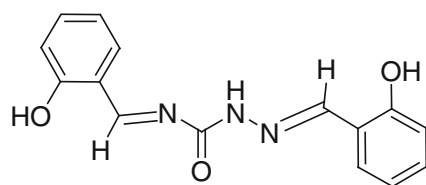
**Fig 5** Plot of  $\log [(A_0-A_s)/(A_s-A_\infty)]$  as a function of  $Cd^{2+}$  ion concentration. The plot shows a slope of 1.05 and Y axis intercept 4.25 ( $R^2=0.9978$ ) indicating binding of one  $Cd(II)$  ion to **L** with  $\log \beta=4.25$

ions— $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Cu^{2+}$ ,  $Pb^{2+}$  and  $Hg^{2+}$ . Figure 2 is the bar diagram profile to show the effect of various metal ions, at  $9.0 \times 10^{-4}$  M concentration, on the fluorescent intensity of **L**. Although the fluorescent intensity of **L** increased in presence of  $Zn^{2+}$  ion the intensity fluctuated with time in between  $I/I_0=18$  to 21. The average value of 20 has been considered for the diagram. This fluctuation in fluorescent intensity of **L** on interaction with  $Zn^{2+}$  infers a weak interaction between **L** and  $Zn^{2+}$ .

No noticeable change in fluorescent intensity was registered when **L** interacted with  $Pb^{2+}$ ,  $Hg^{2+}$  and  $Mn^{2+}$ . The metal ions— $Cu^{2+}$ ,  $Fe^{2+}$ ,  $Ni^{2+}$  and  $Co^{2+}$  quenched the fluorescence intensity of **L** to a small extent. The metal ion



**Fig 6** Cyclic voltammogram response of a 1 mM solution of **L** in 1:1 (v/v) DMSO:H<sub>2</sub>O; **b** 1 mM solution of **L** in presence of 1 mM  $Cd^{2+}$  in 1:1 (v/v) DMSO:H<sub>2</sub>O



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

selectivity profile of **L** is shown by a bar diagram (Fig. 3) which portrays the effect of various divalent ions on the fluorescence intensity of **L**. From the diagram, the predominance of  $\text{Cd}^{2+}$  over all the other metal ions is quite predictable.

In order to find out the number of  $\text{Cd}^{2+}$  ions bound to **L** and to determine the binding constant,  $\log[(I_0 - I)/(I - I_{\text{max}})]$  was plotted against  $\log[\text{Cd}^{2+}]$  (Fig. 22). The plot was found to be linear ( $R^2 = 0.9942$ ) with the slope representing the number of  $\text{Cd}^{2+}$  ions bound which was 1.02 and the  $\log \beta$  was found to be 4.20.

To confirm the number of  $\text{Cd}^{2+}$  bound to **L** and the binding constant, the UV/Visible spectra of **L** in 1:1 (v/v) DMSO:H<sub>2</sub>O at different added concentration of the ion was recorded (Fig. 4). **L** showed two absorption maximum at  $\lambda_{\text{max}}$  value 294 nm and 357 nm. Upon addition of  $\text{Cd}^{2+}$  ions, the absorbance of all the peaks decreased and a new peak was observed at  $\lambda_{\text{max}}$  value 429 nm. The  $\log [(A_0 - A_s)/(A_s - A_\infty)]$  value, for  $\lambda_{\text{max}} = 294$  nm peak, was plotted against  $\log [\text{Cd}^{2+}]$  (Fig. 5). Here,  $A_0$ ,  $A_s$  and  $A_\infty$  are the absorbances of **L** at zero, at an intermediate and at infinite concentration of  $\text{Cd}^{2+}$  respectively. A least square fitting of the data yielded slope = 1.05 ( $R^2 = .9978$ ) confirming 1:1 binding between **L** and  $\text{Cd}^{2+}$  and  $\log \beta$  value was calculated as 4.25 which is similar with that calculated from fluorescence data 22.

The enhancement in fluorescence intensity of **L** on interaction with  $\text{Cd}^{2+}$  may be explained on the basis of the thermodynamically favourable photo induced electron transfer (PET) mechanism<sup>24</sup> between **L** and  $\text{Cd}^{2+}$ . The  $\text{Cd}^{2+}$  ion is likely to bind to **L** via the three N-atoms of the semicarbazide moiety. **L** consists of a receptor part (semicarbazide) and a fluorophore part (salicylaldehyde) (Scheme 1). The PET process occurs due to the transfer of electron density, originating at the lone pairs of electrons on N atoms of the receptor moiety, to the LUMO of the fluorophore. Binding of  $\text{Cd}^{2+}$  to **L** through the N atom lone pairs will obviously hinder the PET process leading to fluorescence intensity enhancement of **L** on interaction with  $\text{Cd}^{2+}$  ions.

The Cyclic voltammogram of **L** ( $10^{-4}$  M) was recorded in 1:1 (v/v) DMSO: H<sub>2</sub>O using Glassy carbon disc as the working electrode and Ag-AgCl as the reference. An irreversible cyclic voltammogram was obtained which showed only the reduction peak at potential +0.329 V. The effect of  $\text{Cd}^{2+}$  on the voltammogram of **L** was investigated

by adding different concentration (from  $0.99 \times 10^{-4}$  M to  $9.0 \times 10^{-4}$  M) of  $\text{Cd}^{2+}$  in the electrolytic medium. On interaction with  $\text{Cd}^{2+}$  the irreversible cyclic voltammogram observed for **L** became quasi reversible with reduction peak at +0.142 V and oxidation peak at +0.683 V (Fig. 6). No change in the cyclic voltammogram of **L** was observed when metal ions— $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  were added into the electrolytic medium alone or together. However, a slight shift of 0.02 V in the reduction peak position of **L** was observed on interaction with  $\text{Zn}^{2+}$  but no new oxidation peak was observed. Thus, electrochemically also **L** could distinguish  $\text{Cd}^{2+}$  from  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$ .

In summary, we have presented a salicylaldehyde and semicarbazide based sensor that showed preferential binding for  $\text{Cd}^{2+}$  over  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$ . The high selectivity for  $\text{Cd}^{2+}$  is marked by a significant fluorescent enhancement and a red shift in emission spectra. The enhancement in fluorescence of **L** on binding  $\text{Cd}^{2+}$  ion is due to the photo induced electron transfer (PET) process.

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