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Salicylaldehyde Phenylhydrazone: A New Highly Selective Fluorescent Lead (II) Probe

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Abstract The fluorescence intensity of salicylaldehyde phenylhydrazone (**L**), in 1:1 (v/v) CH_3OH:H_2O was enhanced by *ca.* 100 times with a blue shift in emission maximum, on interaction with Pb^{2+} ion. No enhancement in fluorescent intensity of **L** was observed on interaction with metal ions - Na^+, K^+, Ca^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+}. This signal transduction was found to occur via photoinduced electron transfer (PET) mechanism. A 1:1 complexation between Pb^{2+} and **L** with log $\beta = 7.86$ has been proved from fluorescent and UV/Visible spectroscopic data. The detection limit of Pb^{2+} was calculated to be 6.3×10^{-7}M.

Keywords Lead · Fluorescence · Probe · Salicylaldehyde phenylhydrazone · Photoinduced electron transfer

Introduction

The design and synthesis of fluorescent probes for transition and heavy metal ions is currently of prime importance for both environmental and biological applications [1, 2]. While transition metal ions play an important role in many fundamental physiological processes in organisms, heavy metal ions can often have a profoundly detrimental effect upon them. Among heavy metal ions, lead is the most abundant and occupies the second position among the list of toxic metals and is often encountered for contaminating the environment due to its wider distribution in nature [3]. As one of the major pollutants of the environment, Pb^{2+} toxicity is an ongoing danger to the human health and environment particularly in children [4, 5]. Lead (II) ions affect almost every organ and system of the human body, mainly the nervous system. Lead toxicity causes various symptoms such as anaemia, muscle paralysis, loss of memory, disorder of blood and even mental retardation [6–8]. Lead also increases blood pressure level and causes weakness in fingers, wrists and ankles. Moreover high exposures to lead can result in severe damage of kidneys and brain [9, 10]. Lead toxicity is mainly triggered by various sources such as air, drinking water, soil etc. Thus, the development of effective fluorescent probes [11, 12] for distinguishing lead ions from alkali, alkaline earth metal and transition metal ions [13–15] is quite important for detecting the presence of lead (II) in contaminated sources [16] as well as in the human body.

The importance of fluorescent probes has increased considerably over the past decade due to their easy use in solutions and owing to their high sensitivity and selectivity for trace analytes [17] and real time detection [18]. Thus, in the past decade, considerable efforts have been made to develop Pb^{2+}-responsive fluorescent probes due to their sensitivity, simplicity and adaptability to different platforms that facilitate routine screening [19]. As most of the heavy metals are known fluorescence quenchers, the development of selective as well as sensitive probes based on fluorescent enhancement for Pb^{2+} presents a challenge.

While a good number of fluorescent probes have been developed for Zn^{2+} [20, 21] and other heavy metal ions such as Cd^{2+} [22, 23], Hg^{2+} [24–27] etc., very few have been reported for Pb^{2+}. A ratiometric and selective fluorescent probe for Pb^{2+} based on polypeptide scaffolds equipped with a microenvironment-sensitive fluorophore has been reported [28]. Lu et al. utilized catalytic DNAs as a unique class of biosensors for Pb^{2+} [29]. A turn-on ratiometric fluorescent probe for Pb^{2+} was described by Cao and coworkers [30]. Ma et al. also reported a fluorescent probe based on the Pb^{2+}-catalyzed hydrolysis of phosphodiester [31]. A new fluorescent probe for Pb^{2+} based on a triazolothiadiazin derivative immobilized in polyvinyl chloride membrane was also developed [32]. A pyrene-containing

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fluorescent probe with high selectivity for Pb^{2+} was also reported [33]. Yoon and coworkers reported a highly selective fluorescent probe for Pb^{2+} [34]. An imidazole-annelated ferrocene derivative was synthesized [35] which was found to be a highly sensitive multichannel chemical probe for Pb^{2+}.

Herein, we report a fluorescent probe derived from the condensation of salicylaldehyde and phenylhydrazine which showed fluorescent peak at λ_{max} value 529 nm on excitation by 410 nm photon. A fluorescent enhancement (accompanied by a blue shift) of *ca.* 100 times was registered by Pb^{2+} in 1:1 (v/v) CH_3OH:H_2O while other metal ions - Na^+, K^+, Ca^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+} had no effect on the fluorescent property of the probe. The binding ratio, binding constant and detection limits were also determined.

Experimental

Materials and Methods

Phenylhydrazine was purchased from Loba Chemie while salicylaldehyde 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 recrystallised from water (Millipore). Metal salt solutions (10^{-6}M) were prepared in 0.1 M phosphate buffer solution (PBS), pH7.0. Fluorescence spectra measurements were performed in a HITACHI FL-2500 florescence spectrophotometer using a quartz cuvette and both the excitation and emission band passes were set at 10.0 nm. A 4.0 μM solution of **L** in 1:1 (v/v) CH_3OH: H_2O (PBS, pH7.0) was used in all the experiments.

UV/Visible spectra were recorded in a Shimadzu UV 1800 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded in a Bruker Ultrashield 300 spectrometer. All NMR spectra were recorded in $CDCl_3$ at room temperature and the chemical shift values are reported in δ values (ppm) relative to TMS.

Electrochemical measurements were carried out in a CHI 600B Electrochemical Analyzer (USA), which consisted of a three-electrode cell arrangement. The electrode environment consisted of a platinum disc as the working electrode, Ag-AgCl (3 M NaCl) as the reference electrode and $NaNO_3$ (0.1 M) as the supporting electrolyte. The working electrode was cleaned by polishing with 0.1 μm alumina slurry using a polishing kit (CHI), followed by sonication in distilled water for 5 min.

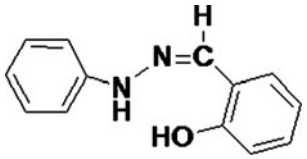
Synthesis of the ligand **L** was carried out according to the reported procedure [36] as follows; 0.105 mL (*ca.* 0.1 mol) salicylaldehyde was dissolved in 10 mL ethanol and an ethanolic solution of 0.100 mL (*ca.* 0.1 mol) phenylhydrazine was added. The resulting mixture was stirred in a magnetic stirrer for 30 min. The brownish yellow solid thus obtained was filtered, washed with distilled water and allowed to dry for carrying out the further experiments.

FTIR (KBr): 3290.56 cm^{-1} ($\nu_{C=N}$), 3051.39 cm^{-1} (ν_{C-H}), 1269.16 cm^{-1}, 3421.72 cm^{-1}(ν_{O-H}), 1,570 and 1600.42 cm^{-1} (ν_{C-N}) and 1482.75 cm^{-1} ($\nu_{C=C}$). **^{1}HNMR** ($CDCl_3$, δ ppm, TMS): 10.88(s,1H), 7.87 (s,1H), 7.5 (s,1H), 7.31–7.24 (m,3H), 7.14–6.91 (m,6H), 4.8 (s,1H) (Scheme 1).

Results and Discussion

The metal ion sensing property of **L** (10^{-6}M) towards Na^+, K^+, Ca^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} and Hg^{2+} has been investigated by fluorescence spectroscopy. Fluorescence of L in 1:1 (v:v) CH_3OH:H_2O was examined employing different excitation wavelengths from 250 nm to 410 nm at an interval of 10 nm in absence of any metal ions or in presence of any one of the above metal ions. The concentration ratio between L and the metal ion was kept at 1:1. No significant change in fluorescent property of L was observed when no metal ion was present. Fluorescence of L was found to enhance sharply by *ca.* 100 times when Pb^{2+} ion was present in the solution and the excitation wavelength was 410 nm.

Figure 1 shows the fluorescence response of **L** at zero and different added concentration of Pb^{2+} ion (from 0.49 μM to 4.3 μM). The fluorescence titration studies of **L** with Pb^{2+} revealed that the intensity of the fluorescent peak at 529 nm increased gradually with the increasing concentration of Pb^{2+} ion. The increase in the fluorescence intensity on addition of Pb^{2+} ion at the final added concentration was calculated to be *ca.* 100 times to the original one. Moreover, a blue shift in the λ_{max} value was also observed from 529 nm to 504 nm. Inset of Fig. 1 depicts the plot of I/I_o as a function of Pb^{2+} ion concentration, where I is the intensity at a given concentration of Pb^{2+} ion (at λ_{max} value 504 nm) and Io is the intensity at zero concentration of Pb^{2+} ion (at λ_{max} value 529 nm). The I/I_o value was found to increase linearly (R^2=0.9942) up to the value of *ca* 100 till the final concentration of Pb^{2+} became 4.3 μM and remained constant thereafter. The concentration ratio of L and Pb^{2+} ion at saturated fluorescent intensity being *ca*. 1:1.



Scheme 1 Structure of L

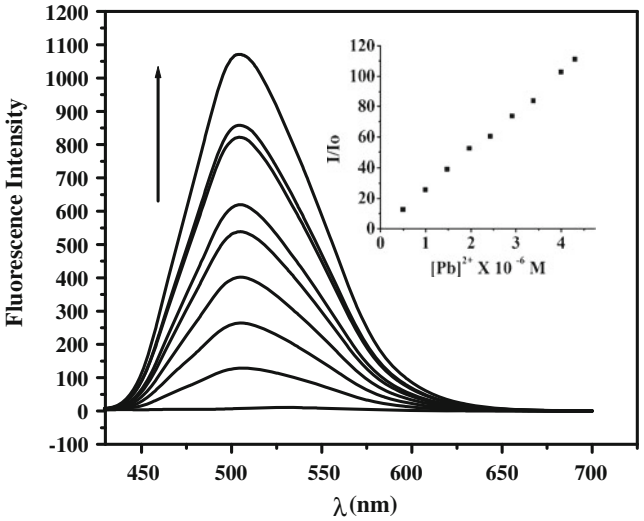


Fig. 1 Fluorescence emission spectra of **L** when 0, 0.49, 0.99, 1.47, 1.96, 2.43, 2.91, 3.38, 3.84 and 4.3×10^{-6}M Pb^{2+} ion was present in 1:1(v/v) CH_3OH:H_2O. (λ_{ex}=410 nm; λ_{emi}=450 – 600 nm; Inset: plot of I/Io as a function of Pb^{2+} ion concentration)

The detection limit of L for Pb^{2+} was calculated to be 6.3×10^{-7}M.

Similar fluorescence titrations were also performed with the other metal ions Na^+, K^+, Ca^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+} using 410 nm as the excitation wavelength. The results showed that titration with these metal ions did not induce any significant changes in the fluorescence emission spectra of **L.** Addition of Zn^{2+}, Ca^{2+} and Hg^{2+} ions caused a slight increase of about 3 times in the fluorescence spectra of **L**. However, addition of all the other metal ions triggered a very small quenching effect in the fluorescence intensity of **L**. The metal ion selectivity profile of **L** is depicted in Fig. 2 by a bar diagram to show the effect of diverse metal ions, at 4.3×10^{-6}M concentration, on the fluorescent intensity of **L**. The diagram clearly portrays the sensitivity and selectivity of the probe towards Pb^{2+} ions.

The number of Pb^{2+} ions bound to **L** and the binding constant was determined by plotting $\log[(I_o\text{-}I)/(I\text{-}I_{max})]$ against $\log[Pb^{2+}]$ (Fig. 3) [37], the slope and the X-axis intercept representing the number of Pb^{2+} ions bound and the log of binding constant (β) respectively. A least squares fitting of data (R^2=0.9864) yielded the slope to be 1.082, indicating the binding of one Pb^{2+} ion to **L** and the log β value was calculated as 7.86.

The UV/visible spectra of **L**, recorded in 1:1(v/v) CH_3OH: H_2O showed two absorption peaks with λ_{max} values at 300 nm and 346 nm. Figure 4 displays the changes in the absorption spectra of **L** on increasing the concentration of Pb^{2+} ions (0.49 μM to 4.3 μM) in the solution. While no changes in the absorption spectra were recorded on addition of the other metal ions to **L**, it was revealed that titration with Pb^{2+} ions resulted in a remarkable change. Addition of Pb^{2+} ions resulted in an increase in the absorbance of the peak at 300 nm and a decrease in the absorbance of the peak at 346 nm. Inception of a new absorption peak was observed at 650 nm with the addition of Pb^{2+} ion. This new absorption peak should be responsible for the high fluorescene of L: Pb^{2+} adduct excited by 410 nm photon. In order to further confirm the number of Pb^{2+} ions bound to **L** and the binding constant, log [(Ao-As)/(As-A_{max})] value was plotted against log[Pb^{2+}] from the absorption titration studies (Fig. 4). Here, Ao, As and A_{max} are the absorbances of **L** at zero, at an intermediate and at saturated concentration of Pb^{2+} ion respectively. A least square fitting of the data (R^2=0.9976) yielded the slope as 1.006 confirming 1:1 binding between **L** and Pb^{2+}. The binding constant log β was calculated to be 7.45 which is close to the value calculated from the fluorescence data.

We also tested whether interaction between L and Pb^{2+} was effected by other metal ions such as Na^+, K^+, Ca^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+} or not. For this purpose 1 μM solution of **L** already having 10 μM Pb^{2+} ion was prepared and fluorescene intensity recorded. A particular metal ion was added so that its concentration becomes

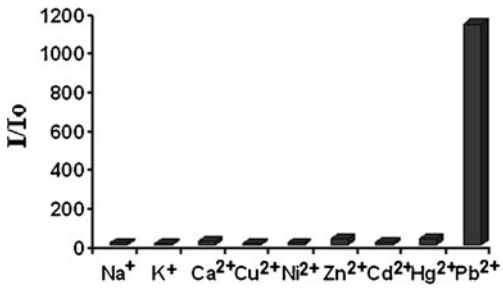


Fig. 2 Bar diagram showing effect of 1 equivalent of different metal ions (4.3×10^{-6}M) on the fluorescent intensity of **L**, in 1:1(v/v) CH_3OH: H_2O

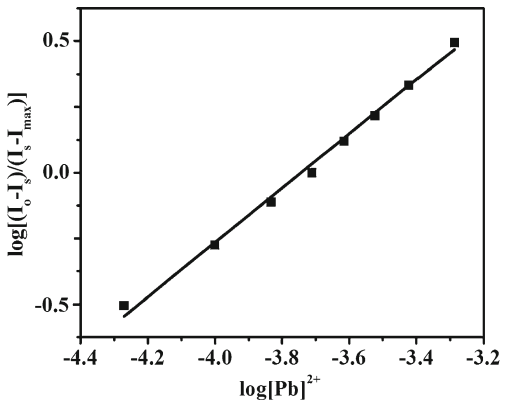


Fig. 3 Plot of $\log[(I_o–I_s)/(I_s–I_{max})]$ versus $\log[Pb^{2+}]$ for titration of **L** against Pb^{2+} in 1:1(v/v) CH_3OH: H_2O. The plot shows a slope of 1.082 (R^2=0.9864) indicating binding of one Pb^{2+} ion to **L** with log β=7.86

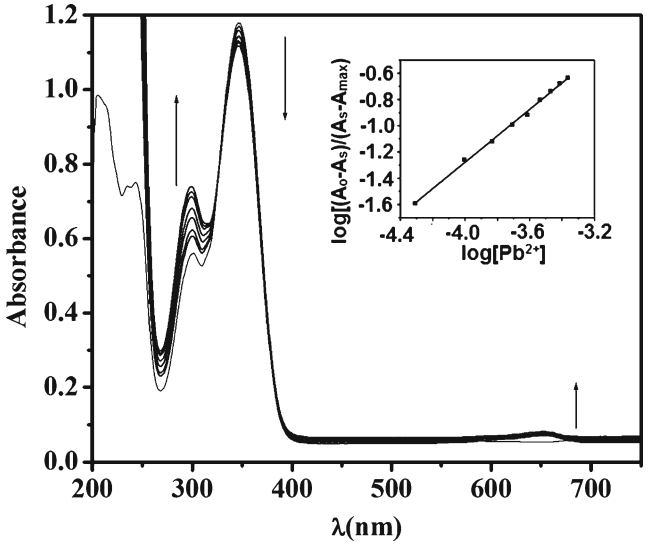


Fig. 4 Change in the UV/visible spectra of **L** when the concentration of Pb^{2+} ion was varied from 0 to 4.3×10^{-6}M. Inset: Plot of log [(Ao−As)/(As−A∞)] as a function of Pb^{2+} ion concentration. The plot shows a slope of 1.006 (R^2=0.9976) indicating binding of one Pb^{2+} ion to **L** with log β=7.45

10 μM and fluorescence intensity recorded. It was found that the fluorescence intensity of L+Pb^{2+} ion system was effected only to a very small extent by other metal ions. The result has been summarised by a bar diagram of fluorescence intensity ratio of L+Pb^{2+} ion to L+Pb^{2+} in presence of other metal ions (Fig. 5). This confirms that binding between L and Pb^{2+} ion is much stronger than the interaction between L and other metal ions.

The remarkable change in the fluorescent signal transduction of **L** on interaction with Pb^{2+} may be explained on the basis of the disruption of efficient photoinduced electron transfer (PET) mechanism prevailing in **L** [38]. In **L,** the PET process occurs due to the transfer of electron density, originating at the lone pairs of electrons on N atoms of the phenylhydrazine group to the LUMO of the fluorophore part (salicylaldehyde). This results in quenching of the fluorescence intensity of **L**. Both from the fluorescence and

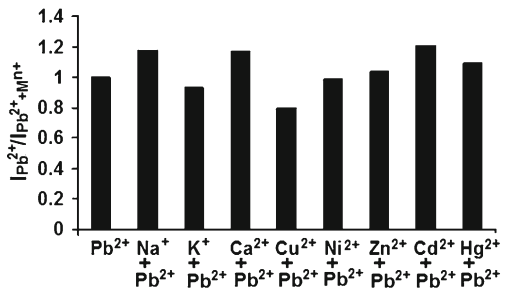


Fig. 5 Fluorescent response of **L** (1 μM) containing 10 μM Pb^{2+} to the selected 10 μM metal ions M^{n+} (Na^+, K^+, Ca^{2+}, Cu^{2+}, Ni^+, Zn^{2+}, Cd^{2+} and Hg^{2+}) in 1:1(v/v) CH_3OH: H_2O. The excitation wavelength, λ_{ex} was set at 410 nm

UV/Visible spectral titrations, it is evident that one Pb^{2+} ion binds to **L**, likely through the two N-atoms present in the phenylhydrazine moiety. Thus interaction of Pb^{2+} ion with **L** disrupts the PET process and results the enhancement in fluorescence intensity.

In PET process, the driving force (ΔG_{et}) from the receptor group to the excited fluorophore is expressed by the modified Weller [39] equation as follows, $\Delta G_{et} = -E_s - E_{red.fluor} + E_{ox.receptor}$, where E_s, $E_{red.fluor}$ and $E_{ox.receptor}$ denote the singlet energy, reduction potential of the fluorophore and the oxidation potential of the receptor respectively. The cyclic voltammetric response of **L** (10^{-5} M) in 1:1(v/v) CH_3OH: H_2O was investigated by utilizing a platinum disc as the working electrode and Ag/AgCl as the reference electrode. A reversible redox couple was obtained which displayed the reduction peak potential value at −0.020 V and the oxidation peak at +0.3365 V. However, in the presence of different concentration of Pb^{2+} ion (0.49 μM to 4.3 μM), it was observed that at the final added concentration, the reduction peak value shifted to −0.176 V and the oxidation peak shifted to +0.044 V towards the negative direction (Fig. 6). Thus, from the modified Weller equation, it is evident that the binding of Pb^{2+} ion to **L** increases the ΔG_{et} value, consequently leading to the cessation of the PET process. No change in the cyclic voltammogram of **L** was observed when metal ions - Na^+, K^+, Ca^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+} were added into the electrolytic medium alone or together. From this electrochemical data, the selective interaction between **L** and Pb^{2+} could be further confirmed.

The selectivity of **L** for Pb^{2+} over Na^+, K^+, Ca^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+} is particularly important because Pb^{2+} targets both Ca^{2+}- and Zn^{2+}-binding sites in vivo [40, 41] and Cd^{2+}, Hg^{2+} and Cu^{2+} are metal ions that frequently interfere with Pb^{2+} ion detection. To summarize, we have presented an efficient yet simple probe derived from the condensation of

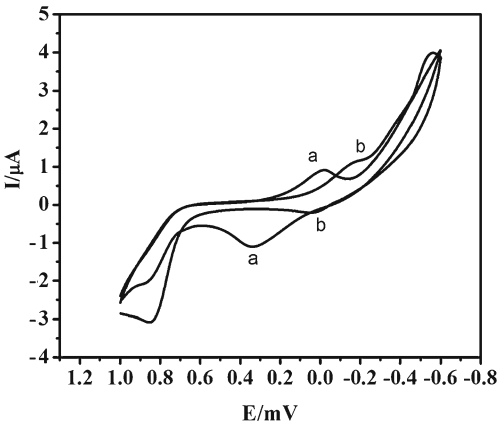


Fig. 6 Cyclic voltammetric response of (**a**) 1 μM solution of **L** in 1:1(v/v) CH_3OH: H_2O; and (**b**) 1 μM solution of L in presence of 4.3 μM Pb^{2+} in 1:1 (v/v) CH_3OH: H_2O

phenylhydrazine and salicylaldehyde, which displayed a high selectivity for Pb^{2+} ion in 1:1 (v:v) CH_3OH:H_2O at excitation wavelength 410 nm. This excitation wavelength is much higher than the UV/Visible absorption peaks of the probe. The interaction between the probe and Pb^{2+} ion results the high fluorescence intensity. The presence of the other metal ions in the solution does not offer any hindrance to the enhancement in the fluorescence intensity. The remarkable increase in the fluorescence intensity of *ca* 100 times on interaction with Pb^{2+} was accompanied by a blue shift in the emission spectra. A 1:1 complexation between **L** and Pb^{2+} ion is proved to be formed which snaps the PET process in **L** leading to fluorescent enhancement.

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