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Colorimetric And Fluorimertic Sensing of Pb^{2+} Ion by A New N, N-Bis((Furan-2-Yl) Methylene) Benzene-1,2-Diamine Based Schiff Base Chemosensor

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Abstract

A new Schiff base N, N-bis (furan-2-yl) methylene) butane-1, 4-diamine (L) synthesized by the condensation of Furan-2-carboxaldehyde with benzene-1,2-diamine. The optical response of the compound L towards different metal ions is remarkable both colorimetric and fluorimertic response for Pb^{2+} ion only. The UV-Vis and fluorescence spectral studies of L with various metal ions were consistent of visual naked eye observation and stoichiometry high binding ability for new fluorescent probes for the detection of Pb (II) metal ions.

Keywords

Schiff base, Furan-2-carboxaldehyde, Benzene-1,2-diamine, colorimetric sensor, fluorimertic sensor

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1. INTRODUCTION

Lead is considered as one of the most hazards and cumulative environmental pollutants that affect all biological systems through exposure to air, water, and food sources. The exposure lead induces clinic pathological changes through toxicity occurring in kidney and endocrine system[1]. A high level of lead in animals resulted in reproductive failure. Lead is one of the global environmental pollutants, mainly found widely in industrial regions, as such that animals can easily be exposed to lead. Lead poisoning particularly in animals can be found from numerous sources in the general environment, and this can be traced back from contamination of feed, and soil from industrial pollution and agricultural practices. Furthermore, consuming high amount of lead has resulted in poor performance, poisoning, and death in animals. Accumulated lead is toxic in most of its chemical forms, whether it is ingested in water or feed[2]. The extent to which orally administered lead absorbed into the host is small. However due to its slow rate of elimination, harmful levels of lead can accumulate in tissues after prolonged exposure to low quantities, it is necessary to develop an efficient instrument for Pb^{2+} detection which possesses good selectivity, high sensitivity and simple operation[3].

In recent years the fluorescent chemosensor has been a highly sensitive and selective approach for

detection of metal ions with speed, precise accurateness and low-cost. Up to now, a variety of fluorescent Pb^{2+} chemosensor based on small organic molecules, nanoparticles and biomolecules were reported. Probes of Pb^{2+} sensing with high selectivity and sensitivity are still necessary. Schiff base molecules, which contain carbon-nitrogen double bond, can be easily synthesized by condensation reaction of aldehyde and amine. Several Schiff base molecules have been developed as specific chemosensors for ion due to their synthetic easiness and high complexation tendency[4]. In this paper, a novel Schiff base composed of furan-2-carboxaldehyde and benzene-1,2-diamine has been developed to behave as a highly selective and sensitive Fluorescent chemsensor for Pb^{2+} in ethanol solution. Moreover, this Schiff base presented the application potential as fluorescent for the detection of metal ions.

2. EXPERIMENTAL SECTION

2.1 Materials

All compounds were analytical grade and directly used as received. Furan-2-carboxaldehyde, Benzene-1,2-diamine, ethanol and the other chemical reagents were purchased from sigma Aldrich chemicals Ltd and used without further purification selectivity study of probe compounds towards different metal ions carried out by chloride or nitrate salts of Ba^{2+}, Sr^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{2+}, Hg^{2+}, Mg^{2+}, Ni^{2+} and Pb^{2+} ions were used to evaluate the metal ion binding properties with **L**.

2.2 Characterization

The NMR spectra data were recorded with chemical shifts as ppm with TMS as internal standard measured on a Bruker Advanced 400MHZ Ultra shield spectrometer. UV-vis absorption spectra data were obtained by JASCO-670 spectrophotometer. The infrared spectra of the Schiff base and highly selective metal complex were recorded by Perkin Elmer spectrum in the range of 400 to 4000cm^{-1}. A Perkin Elmer LS45 Fluorescence spectrometer was engaged to record the fluorescence spectra at room temperature.

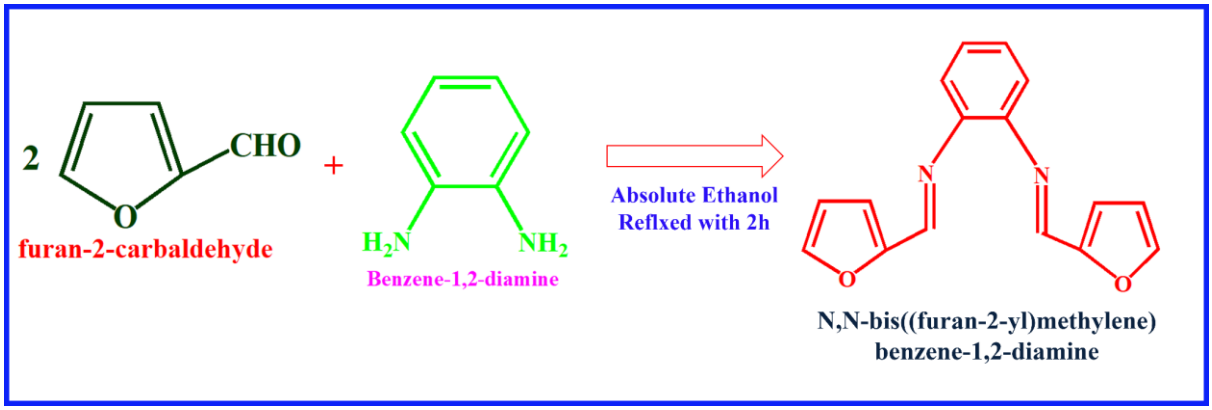
2:3 Synthesis of Schiff base L [L=N, N-bisbis(furan-2-yl) methylene) benzene-1,2-diamine

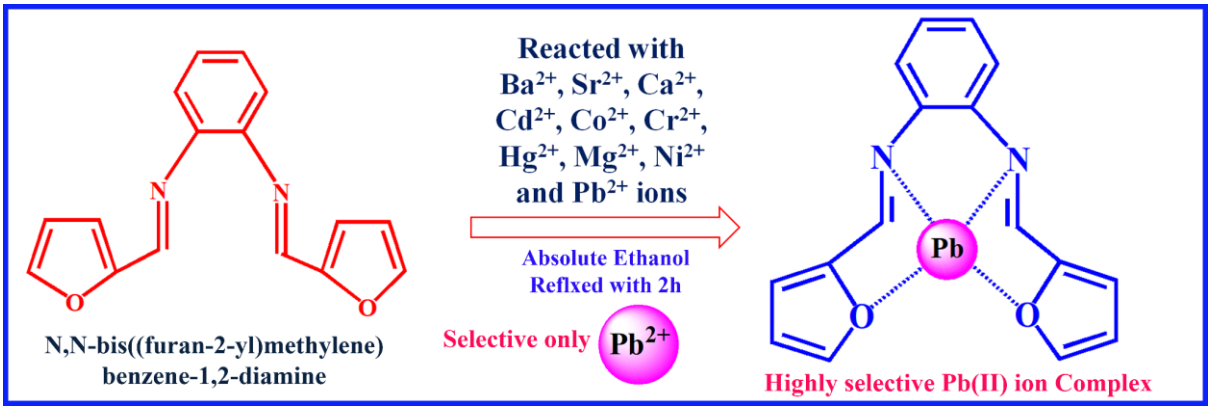
Benzene-1,2-diamine (4.52 ml, 50mmol) was added to a solution of Furan-2-carboxaldehyde (5.32ml, 50mmol) in absolute ethanol 50ml in 1:2 ratio. The reaction mixture was refluxing the solution for 2h and then filtered. The resulting reddish yellow colour solid product was extracted with purified by recrystallization from ethanol and then dried **Scheme 1.**

2:3 Synthesis of highly selective Pb^{2+}complex

The Pb (II) complex was prepared by adding a ethanol solution of $PbCl_2$ (0.549g, 2mmol) in small quantities with stirring to hot ethanolic solution of the Schiff base L (0.588g,2mmol) in ethanol (50ml) was added drop wise. The mixture was stirred and heated to reflux for 2h. The volume of the reaction mixture was reduced to 20-30 ml. The strong reddish brown colour solid complex which separated out was suction filtered washed first with aqeous ethanol and finally with ether and dried **Scheme 2.**

Scheme 1. Synthesis of Schiff base **L**.





Scheme 2. Synthesis of highly selective Pb (II) complex.

2:4 Fluorescence and UV-Vis spectra measurements

The double distilled water prepare solution for spectroscopic measurements fresh metal stock solutions (1mM) were prepared for the following metal ions Ba^{2+}, Sr^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{2+}, Hg^{2+}, Mg^{2+}, Ni^{2+} and Pb^{2+}. Stock solutions of metal ions were added to the sample with a micropipette and the fluorescence emission spectra and UV-Vis spectra recorded. The stoichiometry of complexes can be obtained using Job's plot method via the measurement of fluorescence spectra. Job's plot was drawn based on the measurement of a series of solutions in which the molar concentrations of L and metal ion. The maximum or the inflection point on the Job's plot appears at the mole ration corresponding to the combining ratio of the complex and the association constants of L with highly selective metal Pb^{2+} were calculated by Benesi-Hildebrand method using equation.

$1/ (I-I_o) = 1/K_a (I_{max}-I_o) [Q] +1/ (I_{max}-I_o)$. (1)

Where I and I_o represent the emission intensity of L in the presence and absence of Pb^{2+}, respectively; I_{max} is the saturation emission of L in the presence of an excess amount of Pb^{2+}; K_a is the binding constant [M^{-1}] for Pb^{2+} and [Q] is the concentration of Pb^{2+}. If the plot of $1/(I-I_o)$ Vs $1/[Pb^{2+}]$ gave a linear fitting, it indicates a 1:2 binding mode between the L and Pb^{2+}.

3. RESULTS AND DISCUSSION

3:1 FT-IR-spectral Analysis

The characteristic IR frequencies of the coordinating groups are influenced by the force constant of the metal L bond resulting in the shifting of the group frequencies. These shifts are useful in identifying the coordination sites. The important vibrating group in a free Schiff base L in naturally the imino group. The strong absorption due to this found to lie in region C=N 1638 cm^{-1}. However, on complexation the group frequency of the free azomethine is altered. The strong adsorption band shows that 3420 cm^{-1} in N-H stretching vibration. The band shows 2849 cm^{-1} in the presence of alkane C-H stretching frequency[5]. The bond 1591 cm^{-1} shows the presence of aromatic C=C stretching vibration and other bands show in shift base L in adsorption bands at stretching vibrations are C-N band in 1367 cm^{-1} and the band 752 cm^{-1} shows that phenyl ring vibration[6]. Fig 1 (a)

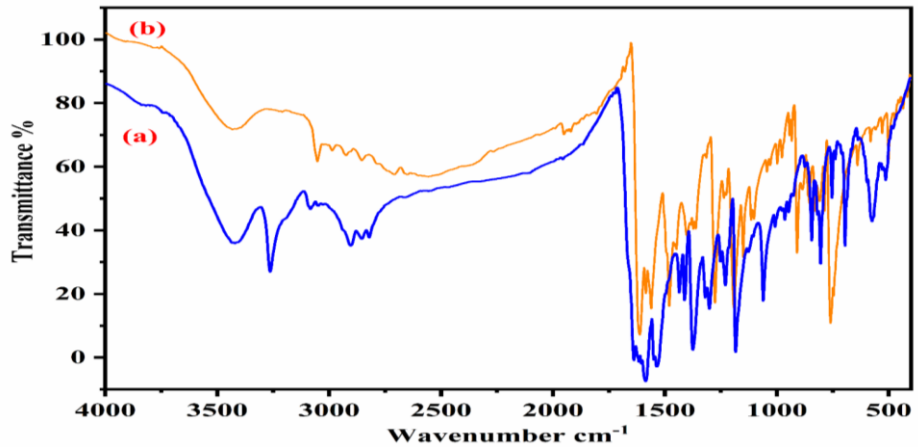


Fig.1. FT-IR spectrum of (a) L and (b) Highly selective Pb (II) ion complex

The highly selective metal Pb^{2+} complex for IR spectra of this complex show broad band centered around 3412 cm^{-1}. This is assigned to the coordination water molecule N-H stretching vibration. The infrared spectrum of the Schiff base L shows a strong band at 1624 cm^{-1}, which is assigned to the C=N stretching vibration. On complexation this band shifted to 1615 cm^{-1}. This indicates that the azomethine nitrogen is coordinated to the metal ion. The band in 1367 cm^{-1} in C-N aromatic stretching frequency shifted to 1324 cm^{-1} in metal complexation[7-8]. The band shows 752 cm^{-1} in phenyl ring vibration shows higher frequency in metal complex 734 cm^{-1} and the new bond shows that 573 and 424 cm^{-1} range indicating the formation of a linkage between the nitrogen and metal ion to chlorine Fig 1(b).

3:2 ^{1}H NMR Spectral Analysis: The ^{1}H NMR spectra of L were recorded in DMSO –D6 ^{1}H NMR spectrum L shows signal due to N-H at δ 12.41 in the free L (S 1H, N-H) and a singlet signal at δ7.52 ppm observed in the spectrum for the free L shows azomethine nitrogen (S, C=N). The down field δ7.45 and δ7.14 exhibits doublet in one aromatic hydrogen (d, 1H, Ar H) and the deshielding aromatic hydrogen show triplet in δ 5.15 (t,1H). The low field δ 6.84 present in the free L singlet one hydrogen (S, 1H). The upfield low frequency shielding protons are present δ1.23 and δ 3.06 multiplet shows that free L[9] Fig 2 (a).

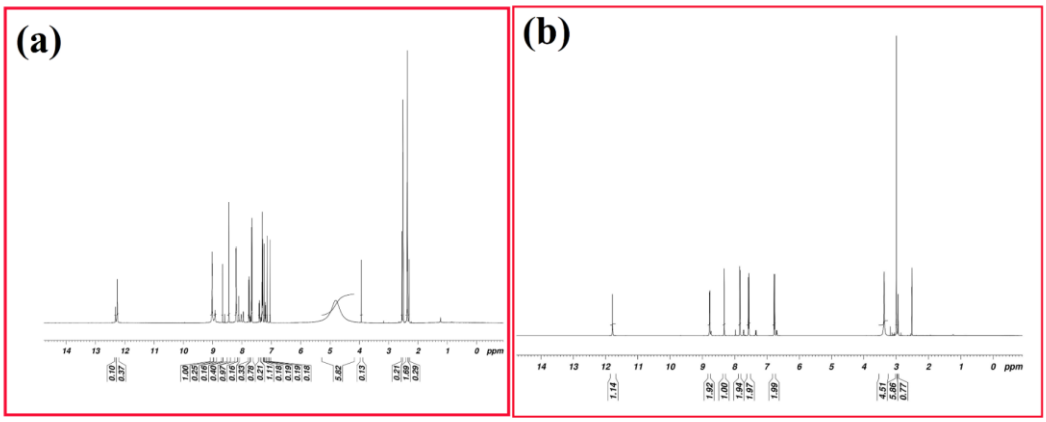


Fig.2. ^{1}H-NMR spectrum (a) Schiff base **L** (b) Highly selective Pb (II) ion complex.

The ^{1}H NMR spectrum of highly selective Pb (II) complex in DMSO d6 solvent confirmed that structure and the complex shows a broad signal at δ 6.13 ppm due to imine protons a broad peak at δ 1.15 due to the hydrogen resonance whilst and another Hydrogen protons in metal complex appear at δ 2.67 ppm[10]. The multiplet resonances in the range δ 2.18-2.62 ppm are related to butane protons and the signals of aromatic protons of the L and metal complex appear in the region δ 7.05 – 7.31 ppm[11] Fig 2 (b).**3:3 UV:Vis Spectra analysis:** The absorption spectra of L (10µM) with Pb^{2+} (2.0 equiv) other metal ions (2.0 equiv) were measured in EtOH- H_2O. In the absence of Pb^{2+}, the solutions of L produced absorption band at 224 nm which could be attributed to n-π transition of C=N and π- π* transitions of Furan rings, respectiviely[12]. Upon addition of Pb^{2+} a new absorption band centered at 242 nm appeared with an increasing intensity complex between L and Pb^{2+}. The selectivity of L toward other metal ions includes heavy, transition and alkali earth ions such as Ba^{2+}, Sr^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{2+}, Hg^{2+}, Mg^{2+}, Ni^{2+} and Pb^{2+}. The addition of other metal ions resulted in negligible changes in the absorption spectrum of **L**[13-14]**.** and the colour of the solutions containing these ions remained relatively unchanged, only Pb^{2+} gave an obvious absorption showing that L has a good selectivity Fig.3.

3.4 Fluorescence Spectra Analysis

The fluorescence spectral response of L (10 µM) to Pb^{2+} was investigated in EtOH –H_2O aqueous media the free sensor L showed very strong fluorescence emission intensity at 434 nm with bright dark reddish brown colour fluorescence when excited at 390 nm[15]. The addition of Pb^{2+} (2.0 equiv) to the solution of **L** fluorescence intensity of the sensor L was almost completely quenched accompanied by an obvious colour change from red colour to slightly colorless. These may be that the size, charge and electron configuration of Pb^{2+} to **L** was very suitable for each other to form metal complex compared to other ions. Some of these potentially competitive metal ions also induced a new emission peak of 434 nm but the intensities were very weak, which may be due to their very weak interaction with sensor of **L**[16]. These

observations indicate that L has an excellent selectivity to Pb^{2+} ion Fig.4.

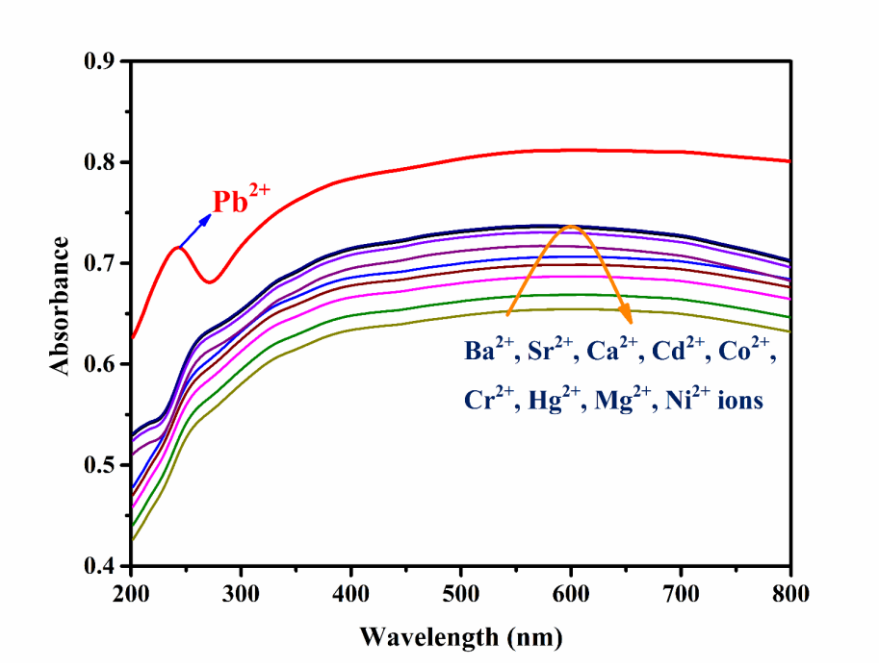


Fig.3. UV-Vis adsorption response of **L** and upon addition of various metal ions solution.

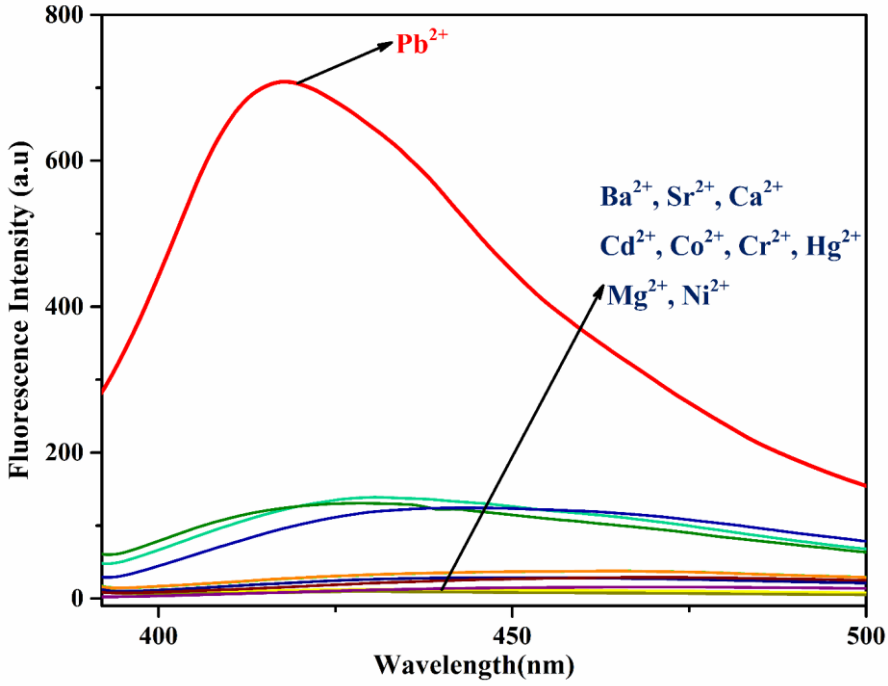


Fig.4. Fluorescence spectra of L with upon addition of various metal ions solution

3.5 Fluorescence Titration and Binding Stoichiometry Measurements:

To evaluate the sensing property of **L** toward Zn^{2+} for fluorescence titration experiment of **L** (10µM) with the increasing concentration ratio **L** metal ion as shown in Fig 5. We can observe that the emission peak appeared a maximum fluorescence at 436 nm[17]. To investigate the binding mechanism between L and

Pb^{2+}, the Job's plot for the fluorescence intensity was tested by sustaining the total concentration of 10 µM for L mixed Zn^{2+} 0 to 1.0. The maximum Fluorescence was observed when the mole fraction of Pb^{2+} reached 0.33 Fig 6.

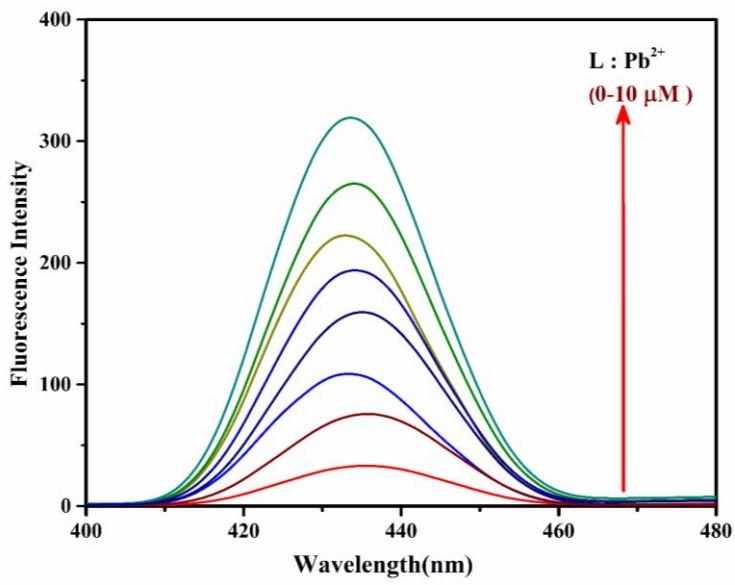


Fig.5. Stepwise changes of **L** with increasing concentrations of Pb^{2+} ions.

This might inform that the stoichiometric binding mode for L and Pb2+ was 1:2 in media18. The ^{1}HNMR experiments were performed for more in-depth study of the complex, for the L - Zn^{2+} formation of 1:2 complexes. The L exhibits a high selectivity and sensitivity of Zn^{2+}, Benesi-Hildebrand method was shown in Fig.7. The binding constant was calculated by Benesi-Hildebrand equation (Eq (1)). As seen in Benesi-Hildebrand plot, in the presence of different concentrations of Pb^{2+} (0-10µM), the measured emission intensity [1/(I-I$_o$)] varied as a function of 1/[Pb^{2+}] in a linear relationship to the calculated result K_a value was 1.85X10^5 M^{-1} based on slope and intercept[19-20].

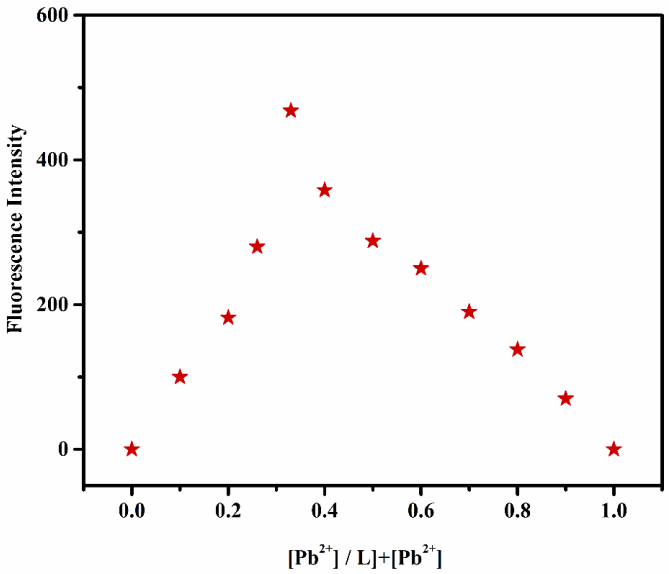


Fig.6. Job's plot for **L** and upon addition of Pb^{2+}ion

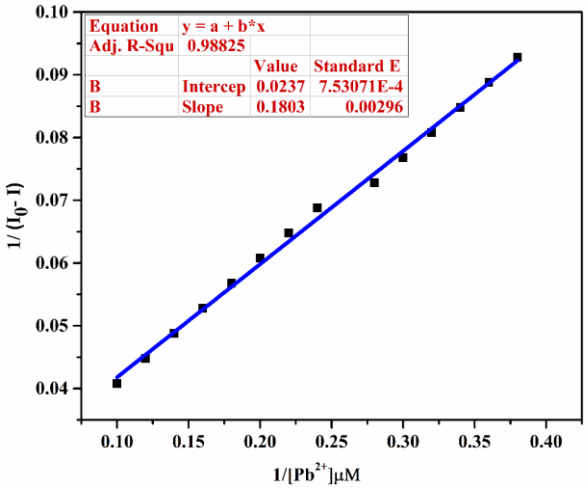


Fig.7. Benesi-Hildebrand plots to calculate the binding constant of **L** towards Pb^{2+}.

CONCLUSION

In summary, we have successfully synthesized L Pb^{2+} ion and their recognition capability for various metal ions was investigated. The L exhibited obvious fluorescence quenching behavior toward Pb^{2+} high selectivity over other metal ions and can be used as fluorescence sensor. Job's plot suggested 1:2 complex formations between L and Pb^{2+} ion. Furthermore, the higher binding stoichiometry constant provides a new approach for the recognition of Pb^{2+} ion.

REFERENCES

[1] K.H. Falchuk, Mol. Cell. Biochem, 188 (1998) 41-48.
[2] W. Maret, C. Jacob, B.L. Vallee, E.H. Fischer, Proc. Natl. Acad. Sci. U.S.A. 96 (1999) 1936-1940.
[3] M.P. Cuajungco, G.J. Lees, Nuerobiol. Dis, 4 (1997) 137-169.
[4] Ch.Bimola Devi, Th. Nandakishore, Sangeeta N, Gomi Basar, N.Omita Devi, Sungdirenla Jamir, M.Amuba Singh, J. Dental and Medi sci., 13 (7) (2014) 18-23.
[5] Dr. Vidyavati SD, Dr. Sneha A, Dr. Katti SM., International J of Healthcare and Biomedical Research., 04 (2016) 18-20.
[6] Wei-Dong Yu, Yan-Mei Nie, Hao Yuan, Jun Yan, Hai-Bo Yi, Inorg. Chem. Commun., 84 (2017) 134-137.
[7] Jie Du, Guanglong Zou, Inorg. Chem. Commun., 69 (2016) 20-23.
[8] Qingyu Liu, Xuehua Dong, Guohong Zou, Dingguo Xu, Zhien Lin, Inorg. Chem. Commun., 96 (2018) 97-100.
[9] Barbara Panunzi, Fabio Borbone, Amedeo Capobianco, Simona Concilio, Rosiata Diana, Andrea Peluso, Stefano Piotto, Angela Tuzi, amalia Velardo, Ugo Caruso, Inorg. Chem. Commun., 84 (2017) 103-108.
[10] Hong-Ge Le,Zheng-Yin Yang, Dong-Dong Qin, Inorg. Chem. Commun., 77(2009) 494-497.
[11] Yufei Wang,Kuan Gao, Jingjing Li, Liping Wang, Jie Wu, Inorg. Chem. Commun. 96 (2018) 189-193.
[12] Reza Azadbakht, Tayebe Almasi, Hassan Keypour, Majid Rezaeivala, Inorg. Chem. Commun., 33 (2013) 63-67.
[13] Qiu Yan Yue, Yi Ming Lu, Fan Xin Chuan, Dian Yu Chen, Gao Wen Yang, Qiao-Yun Li, Inorg. Chem. Commun., 68 (2016) 68-71.
[14] Li Gui, Quanquan Zhang, Yue Wang, Kelong Fang, Ao Wang, Xin You, Lin Zhou, Jiahong Zhou, Shaohua Wei, Inorg. Chem. Commun., 75 (2017) 1-4.
[15] R. Keerthiga, T.Kaliyappan, P.Kannan. Inorg. Chem. Commun., 99 (2019) 26-30.
[16] A.A. Ksenofontov, G.B. Guseva, E.V. Antina, E.N. Nuraneeva, J. Lumin., 192 (2017) 1203-1210.
[17] De-Yun Ma, Jiamin Xie, Zhiwei Zhu, Hailan Huang, Yutao chen, Rongxing Su, Huimin Zhu, Inorg. Chem. Commun., 86 (2017) 128-132.
[18] Kishor Arora, D.Kumar, Kiran Burman, Sonal Agniotri, Bhoop Singh, J. Saudi.Chemical society.,15 (2011) 161-165.
[19] Tanmony Basak, Michael G.B. Drew, shouvik Chattopadhyay. Inorg. Chem. Commun., 98 (2018) 92-98.
[20] Daying Liu, Xinxing Deng, Xin Yin, Yuting Wang, Jing Guo, Jiatong Chen, Guangming Yang, Huarui He, Inorg. Chem. Commun., 101 (2019) 117-120.