



## RESEARCH PAPER

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## Schiff base fluorescent-on ligand synthesis and its application for selective determination of manganese in water samples

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Article published on August 14, 2018

**Key words:** Novel Schiff base, Fluorescence turn-on, Ligand, Manganese, Fluorescence intensity

### Abstract

Manganese contamination of water is becoming a serious health concern in recent years as even at lower levels of exposure it is toxic for living organisms. Manganese can bind to functionally important domains of biomolecules and thereby inactivates them. Therefore, a simple, sensitive and convenient method based on Schiff base fluorescent turn-on ligand for determination of trace amount of manganese was developed in real water samples. The novel Schiff base fluorescent turn-on ligand of 2-hydroxy-1-naphthaldehyde and 2-methoxybenzhydrazide was synthesized and characterized using X-Ray Diffraction (XRD), Proton nuclear magnetic resonance (<sup>1</sup>HNMR) and Fourier Transform Infrared Spectroscopic (FTIR) techniques. The ligand shows high selectivity and sensitivity for manganese over other metals studied with  $3.8 \times 10^{-6}$  M limit of detection. Chelation with manganese resulted in maximum enhancement in fluorescence intensity at pH 10 with 2:1 binding ratio of ligand to manganese from Job's plot analysis and with  $4 \times 10^6$  M<sup>-1</sup> association constant from Benesi-Hildebrand plot.

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## Introduction

Schiff base ligands have been extensively studied in coordination chemistry mainly due to their facile syntheses, easily tuneable steric, electronic properties and good solubility in common solvents. Schiff bases derived from a large number of carbonyl compounds and amines have been used however, the studies on their optical properties, such as fluorescence, are rare (Arpi *et al.*, 2006).

Schiff bases (imines) are known to be good ligands for heavy metals. In addition, Schiff base derivatives incorporating a fluorescent moiety are appealing tools for optical sensing of toxic heavy metals (Lina *et al.*, 2010). Schiff bases with N and O as donor atoms are well known to form strong complexes with heavy metals (Morteza *et al.*, 2010).

They have the potential to be used in different areas such as electrochemistry, bioinorganic, catalysis, metallic deactivators, separation processes, and environmental chemistry. Moreover they are becoming increasingly important in the pharmacological, dye, and plastic industries as well as in the field of liquid crystal technology (Ziyad *et al.*, 2011). Schiff bases derived from 2-hydroxy-1-naphthaldehyde have been extensively studied due to their wide range of applications in medicinal field and they form stable complexes with heavy metals due to the presence of a phenolic hydroxyl group at their o-position, which coordinates to the metal via deprotonation (Nagesh *et al.*, 2014).

Heavy metals are very toxic for living organisms even at very low concentrations (Ghaedi *et al.*, 2009). With the increasing use of a wide variety of metals in industry and in our daily life, heavy metals are intrinsic components of the environment.

Their presence is considered unique in the sense that it is difficult to remove them completely from the environment once they enter in it. Problems arising from toxic heavy metal pollution of water have gained serious dimensions (Santamaria, 2008).

Among the various heavy metals manganese is an extremely toxic element naturally present in the environment and also as a result of human activities (Subhra *et al.*, 2008). Manganese is more frequently of toxicological concern because it causes neurodegenerative disorders (Janelle and Wei, 2008) and is a severe poison for all living organisms (Castro and Méndez, 2008). It causes diarrhoea, and is carcinogenic and mutagenic (Duruibe *et al.*, 2007) in nature.

Though several analytical methods including UV-Vis spectroscopy, potentiometry, (Hosseini *et al.*, 2011) flame atomic absorption spectrometric analysis, (Rajesh and Madhoolika 2005) neutron activation analysis (Aschner *et al.* 2006) and inductively coupled plasma mass spectrometry (Dayu *et al.* 2008) are generally used for determination of manganese in waste water but these have limited use due to their high limit of detection, difficulty in sample preparation and costly instrumentation (Ya *et al.* 2014). In this paper, we describe the synthesis of Schiff base fluorescent-on ligand N-((2-hydroxynaphthalene-1-yl) methylene)-2-methoxy benzohydrazide and its fluorimetric application in the determination of manganese in industrial waste water samples.

## Experimental

### Chemicals and reagents

All chemicals and reagents used were of analytical reagent grade purity and were purchased from commercial sources. Analytical grade acetonitrile solution and distilled water was used throughout the experiments.  $1 \times 10^{-2}$  M stock solution of all required mineral salts,  $5 \times 10^{-3}$  M ligand solution and working solutions of low concentration were prepared by appropriate dilution with distilled water.

### Instrumentation

For FTIR spectra, the samples were prepared as KBr pellets and the spectrum was obtained on FTIR spectrophotometer Pretige 21 Shimadzu Japan in the region  $400-4000 \text{ cm}^{-1}$ .  $^1\text{H}$  NMR spectra of the

samples were obtained on Bruker Advance 400 MHz spectrometer. X-ray structural analysis of the sample was conducted using Bruker kappa APEXIICCD diffractometer. For the measurement of melting points a Bicote Stuart-SMP 10 Japan was used. UV-vis absorption spectroscopic measurements were conducted on UV-visible 1800 spectrophotometer. The emission spectra were monitored using fluorescence spectrophotometer RF 5301 PC Shimadzu Japan equipped with fluorescence free quartz cuvettes of 1cm path length. Slit width were 5nm both for excitation and emission and a steady state 150 W Xenon lamp was used as an excitation source. The pH of the test solution was monitored by a BANTE instrument pH meter. All measurements were conducted at room temperature.

*Synthesis of N-((2-hydroxynaphthalene-1-yl)methylene)-2 methoxy benzohydrazide*

The ligand was synthesized by modification of literature method (Mengyu *et al.*, 2014) by dissolving

10 mmol (1.72 g) of 2-hydroxy-1-naphthaldehyde in methanol, 2-3 drops of glacial acetic acid was added into this solution and the solution was stirred for 10 minutes at room temperature. An equimolar amount of 2-methoxybenzhydrazide 10 mmol (1.6618 g) was added into this solution, the colour changed to bright yellow and the reaction mixture was refluxed for 13 hours. Reaction progress was monitored by establishing thin layer chromatography in ethyl acetate and n-hexane (3:2) mixture. Afterward the solvent was evaporated under reduced pressure and the product was recrystallized in ethanol and pure crystals of ligand were obtained. The whole scheme of synthesis is shown in fig 1.

**Results and discussions**

*Characterization by Fourier transform infrared spectroscopy (FTIR)*

In order to determine the functional group in the *m* synthesized ligand FTIR spectroscopy was conducted the data is given in table 1.

**Table 1.** FTIR spectral frequencies for ligand.

IR-band (C=N) cm <sup>-1</sup>	IR-band (C-OH) cm <sup>-1</sup>	IR-band aliphatic (-C-O) cm <sup>-1</sup>	IR-band aromatic (-C-H) cm <sup>-1</sup>	IR-band aromatic (C=C) cm <sup>-1</sup>
1606	1260, 1217	1107, 1016	3035	1539,1505

**Table 2.** Crystal data and structure refinement for ligand.

Crystal parameters	Values
Empirical formula, Formula weight	C <sub>19</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> , 320.34
Crystal system, Space group	Monoclinic, P2 <sub>1</sub> /n
Temperature (K)	296
a, b, c, (Å)	7.1780 (18), 31.115 (8), 7.4635 (18)
β (°)	109.765 (8)
V (Å <sup>3</sup> )	1365.2 (4)
Z	4
Radiation type	Mo Kα
μ (mm <sup>-1</sup> )	0.09
Crystal colour	Yellow
crystal size (mm)	(0.42 × 0.30 × 0.26)
Data collection	
Diffractometer, scan mode	Bruker kappa APEXIICCD, Multi-scan and ωscan
No of measured, independent and observed [I > 2σ(I)] reflections	13509,3560,1502
R <sub>int</sub>	0.082
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.650
Refinements	
R[F <sup>2</sup> > 2σ(F <sup>2</sup> )], wR(F <sup>2</sup> ), S	0.056, 0.161, 0.93
No. of reflections	3560
No. of restraints	2
H-atom treatment	H-atom parameter constrained
Δ ρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.24, -0.26

In the region 400-4000  $\text{cm}^{-1}$  several absorption bands were observed in the FTIR spectrum of the ligand. Assignments of characteristics bands correspond to various functional groups present in the ligand were made by comparison method. The FTIR spectrum confirms the formation of imine bond

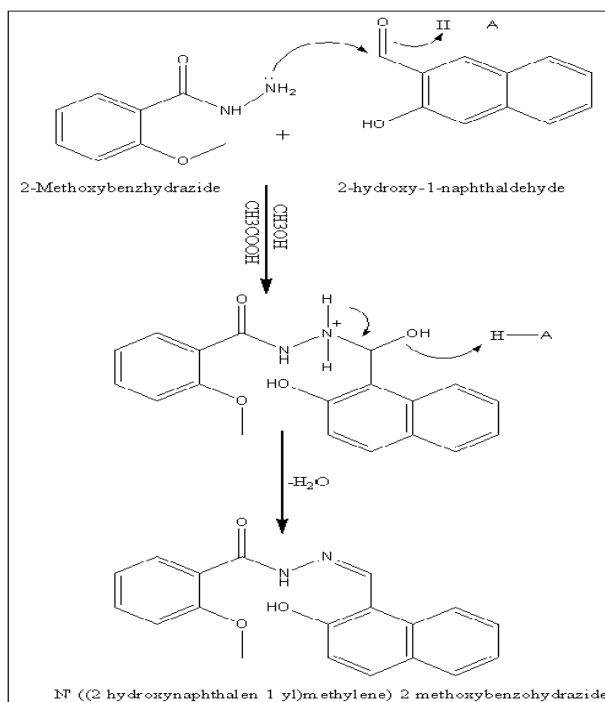
(-C=N) and no band assigned to (C=O) was detected. Thus, the disappearance of carbonyl (-C=O) peak in the region of 1700  $\text{cm}^{-1}$  and appearance of the (-C=N) peak in the region of 1606  $\text{cm}^{-1}$  confirms the formation of ligand.

**Table 3.** Comparison of ligand with already reported ligands.

Fluorophore	Analyte	Detection mode/ remarks	Optimal pH range	Detection limit (M)	Application	Ref
1,10-phenanthroline derivatives	Mn	Enhancement	3.2-6.7	$6.6 \times 10^{-3}$	Water samples	Wenling 2012
Rhodamine-based	Mn, Cu	Quenching	6.8-11	$7.4 \times 10^{-4}$	NA	Jurriaan 2013
Arsenazo	Mn	Enhancement	2.4-6.4	$3.9 \times 10^{-5}$	NA	Raju 2010
Asparagine derivatives	Mn, Zn	Quenching	5.7-8.9	$4.2 \times 10^{-4}$	NA	Juyoung 2006
Deferoxamine	Mn, Mg	Enhancement	4.1-6.4	$5.7 \times 10^{-3}$	NA	Claudia 2015
Hydrazide derivative	Mn	Enhancement	2-12	$3.8 \times 10^{-6}$	NA	This work

The band at 3035  $\text{cm}^{-1}$  corresponds to the stretching vibration of aromatic-C-H. The spectrum exhibit absorption band at 1539, 1505 and at 1260, 1217  $\text{cm}^{-1}$  typically of aromatic-C=C and phenolic-O-H

stretching vibration. The bands at 1107 and 1016  $\text{cm}^{-1}$  correspond to aliphatic-C-O (Tianzhi *et al.*, 2008). FTIR spectrum analysis of the ligand is shown in figure [2].



**Fig. 1.** The proposed reaction scheme for the synthesis of N-((2-hydroxynaphthalene-1-yl)methylene)-2-methoxybenzhydrazide, (ligand).

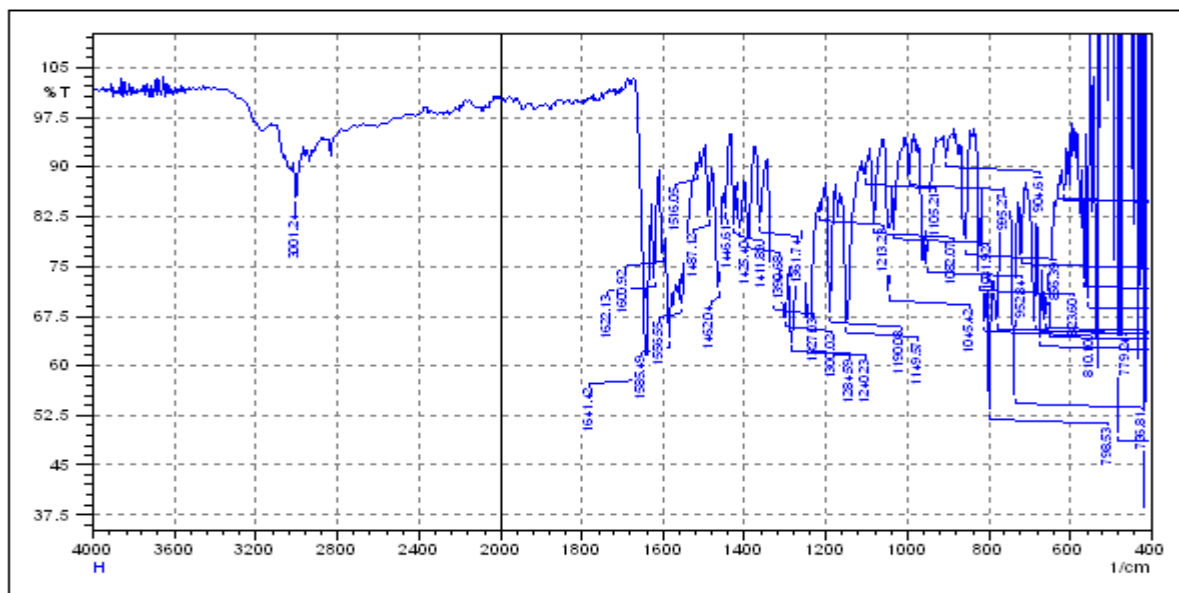
#### Characterization by single crystal X-ray diffraction

A single crystal of the ligand was grown from slow evaporation of ethanol.

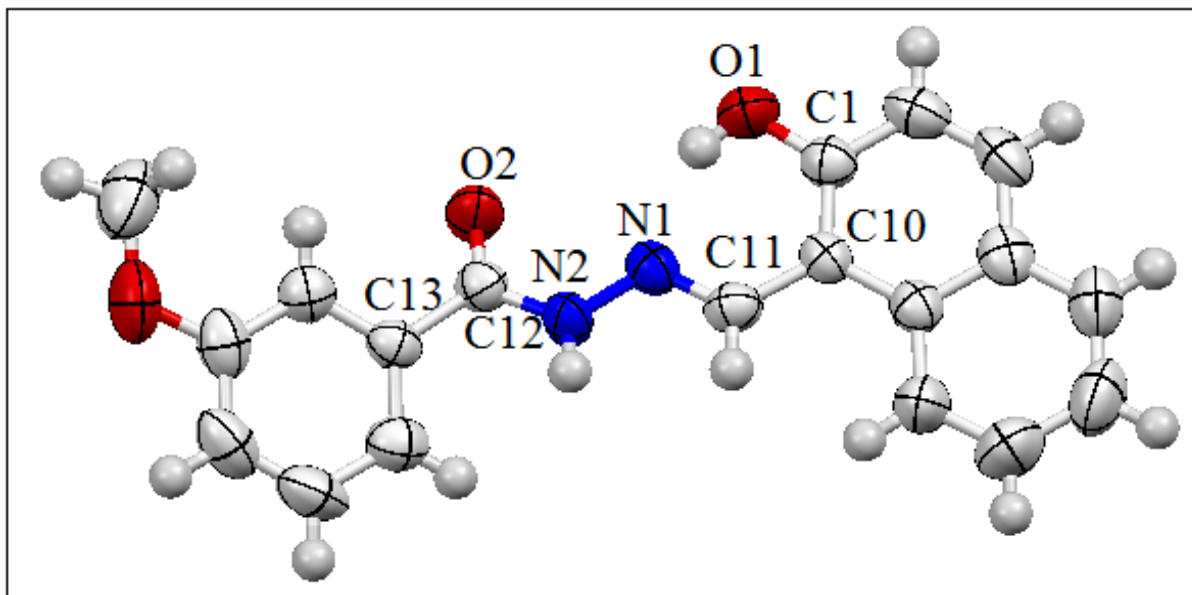
The solid state structure of ligand was confirmed by single crystal X-ray diffraction. Ligand crystallized in monoclinic unit cell of crystal system in which amine

moiety is twisted through  $84.74^\circ$  with respect to naphthalene moiety. The geometry around  $N_1$  is trigonal planar, showing that the lone pair of nitrogen is involved in conjugation without disturbing  $sp^2$  hybridization.

The bond distance between  $N_1-C_{11}$  is  $1.295 \text{ \AA}$ ,  $N_1-C_{12}$  is  $1.464 \text{ \AA}$  and  $C_1-O$  is  $1.267 \text{ \AA}$  (Mau *et al.*, 2003). Details of the X-ray structure determinations and refinements are provided in table 2. Based on these results the proposed structure of ligand is given in Figure 3.



**Fig. 2.** FTIR spectrum of ligand.



**Fig. 3.** Molecular structure of ligand with partial numbering scheme.

#### Characterization by $^1H$ NMR

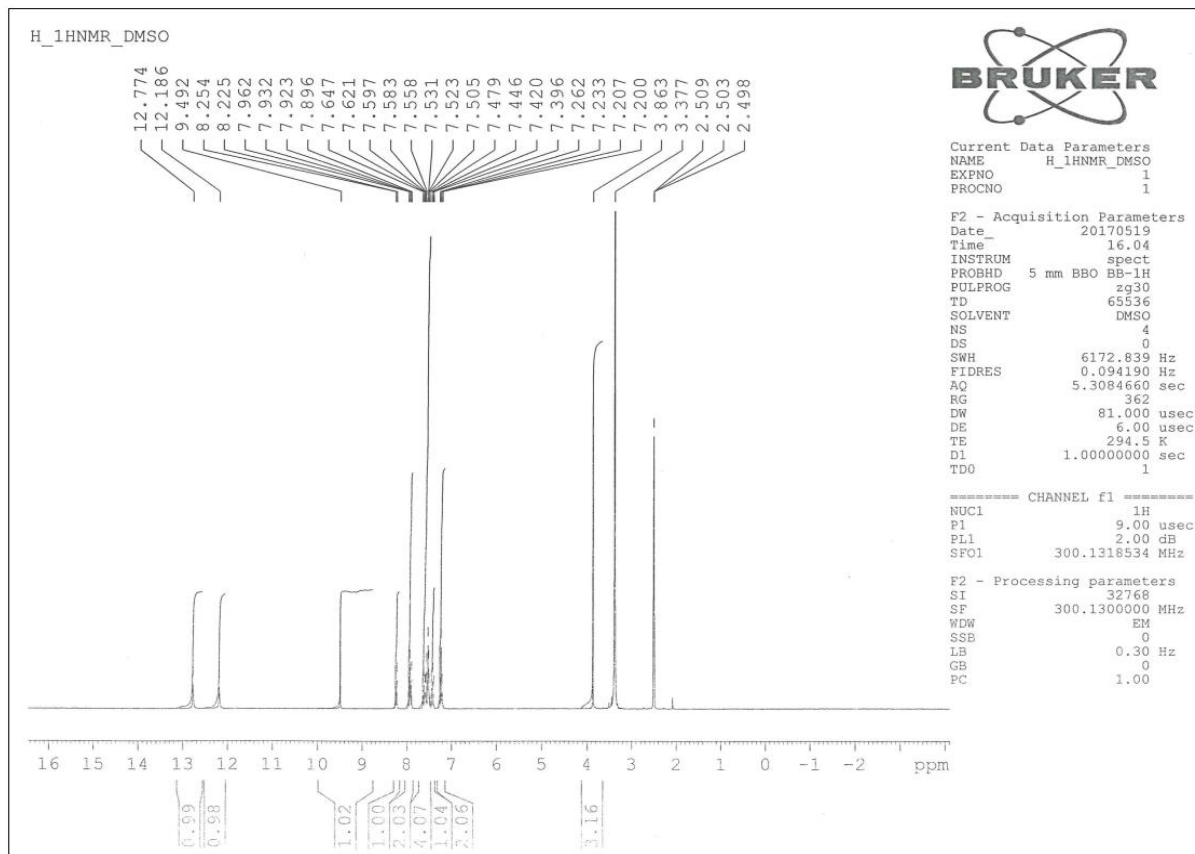
$^1H$  NMR spectra was recorded in  $d_6$ -DMSO solution using TMS as an internal standard.  $^1H$  NMR spectrum of Ligand; reveals the presence of aromatic protons at 8.34 (1H,d), 8.48 (1H,d), 8.37 (1H,d), 8.16 (1H,d), 7.24 (1H,d), 6.27 (1H,d), 6.29 (1H,s) ppm,

azomethine proton at 7.29 (1H,s) ppm, methyl protons at 1.12(3H,t) ppm. Similarly two doublet protons exhibited at  $\delta$  7.8-8.4 are assigned for the naphthalene. The spectra is shown in fig. 4 (Charity *et al.*, 2017).

### Fluorescence studies

The fluorescence intensity of the ligand and its Metal complexes were studied in acetonitrile.

The sensing ability of ligand was studied by mixing it with alkali, alkaline and transition metals to investigate the effect of tested metal on the fluorescence intensity of the ligand.



**Fig. 4.** <sup>1</sup>H NMR spectra of the ligand.

The ligand did not show any remarkable fluorescence separately. Upon excitation at 270 nm, the free ligand, shows very weak fluorescence intensity in the range 685-727 nm with  $\lambda_{em}$  at 365 nm. Upon addition of an equivalent of metal to the solution of ligand, caused enhancement in fluorescence intensity of ligand.

Upon formation of complex with manganese resulted highest enhancement in fluorescence intensity at 365 nm as compared to other heavy metal as shown in figure 5. The enhancement in fluorescence intensity is due to metal chelation enhancement effect and the proposed binding mode can be explained on the basis of photoinduced electron-transfer (PET) inhibition phenomenon.

The free ligand was almost non fluorescent due to transfer of electron from hydroxyl oxygen atom to phenyl ring. Complexation of manganese with ligand blocked PET phenomenon, resulting in highly efficient chelation-enhanced fluorescence effect, therefore fluorescence intensity of ligand enhanced remarkably at 365 nm upon formation of manganese complex (Zhaochao *et al.*, 2010).

### UV- vis spectroscopic analysis

As the ligand was not soluble in 100% aqueous media therefore acetonitrile was used as a co-solvent when UV-vis spectra of ligand was taken in a mixed aqueous media in the absence and presence of different concentration of manganese in distilled water.

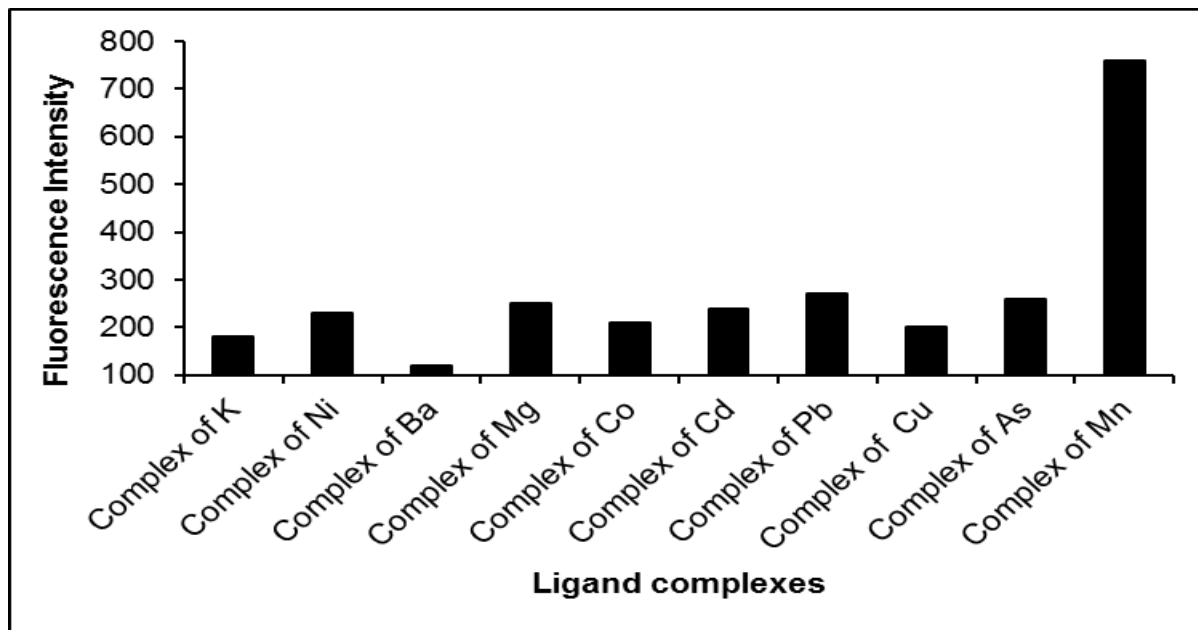


Fig. 5. Fluorescence spectra of the ligand ( $15 \times 10^{-6}$  M) upon addition of metal ( $200 \times 10^{-6}$  M) with an excitation at 270 nm.

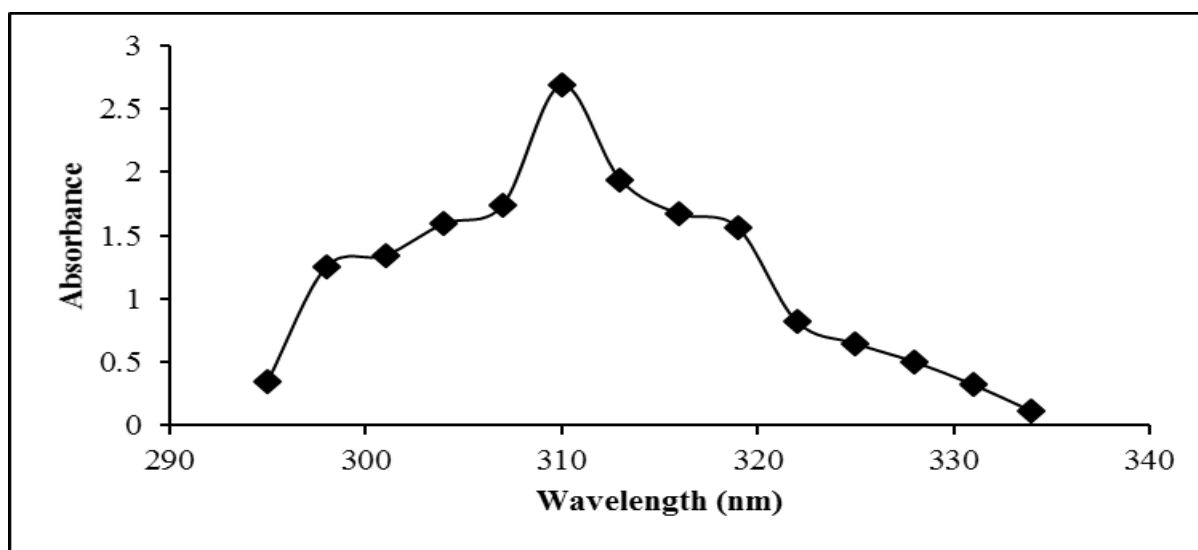


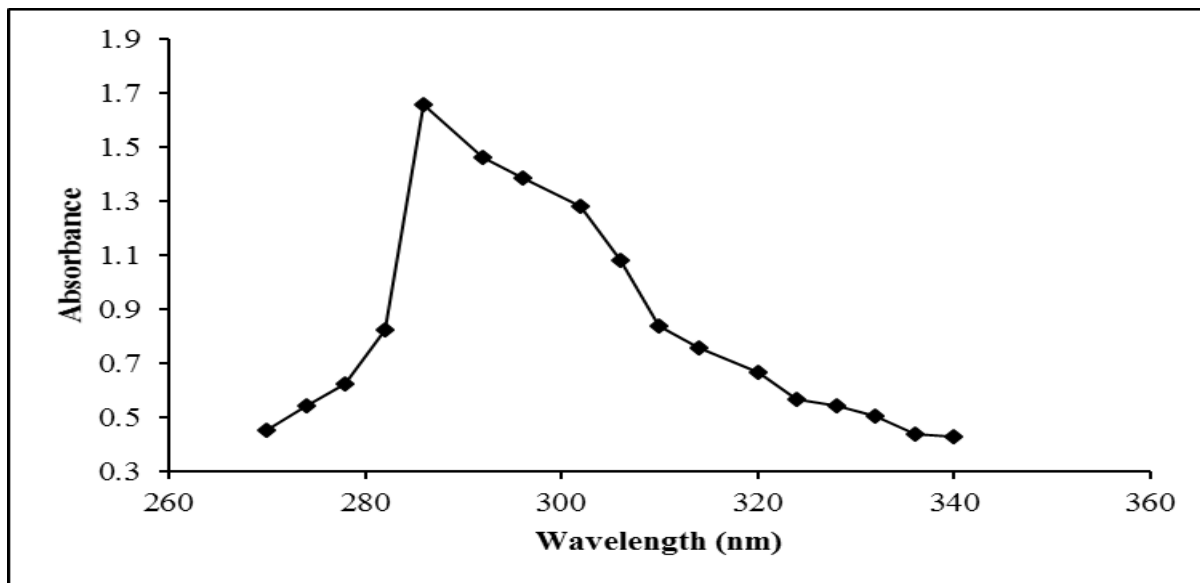
Fig. 6. UV absorption spectrum of the ligand ( $10 \times 10^{-6}$  M) in acetonitrile.

The UV-vis spectrum of ligand exhibited characteristic main absorption band in the range 290-340 nm with  $\lambda_{max}$  of 297 nm as shown in Fig.6. Upon addition of manganese to ligand  $\lambda_{max}$  shifts to 286 nm. The shift in the  $\lambda_{max}$  of ligand is indicative of the coordination involving the hydroxyl and imine as a receptor and manganese as an analyte as shown in the Fig. 7. When various concentration of manganese were added to the solution of ligand the absorbance at 286 nm was enhanced as shown in the Fig. 7.

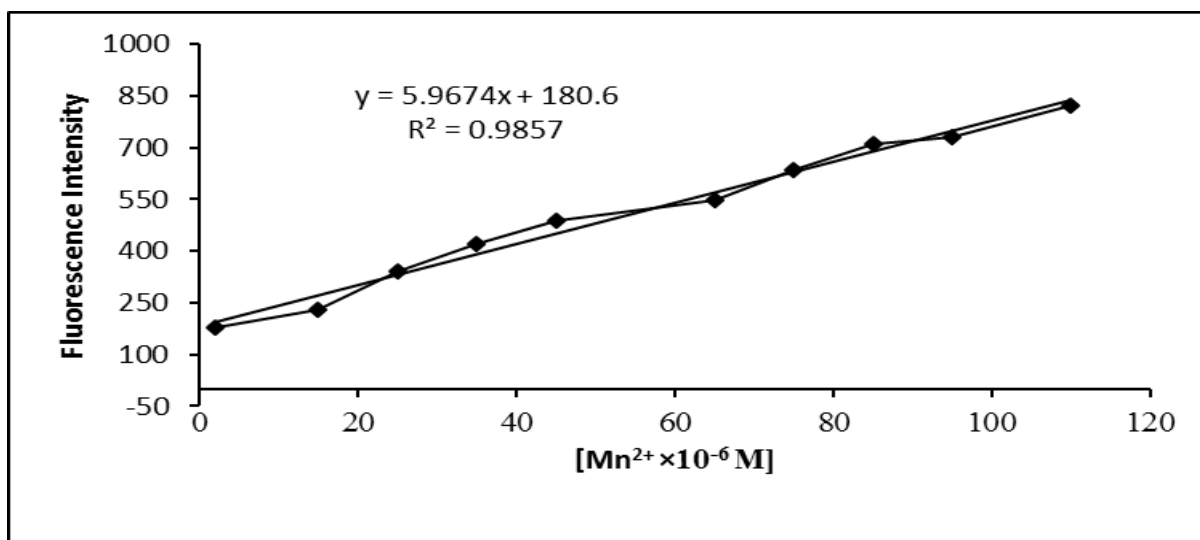
Test samples were prepared by using  $10 \times 10^{-6}$  M solution of ligand and various concentrations of manganese.

*Effect of manganese concentration*

The sensing mechanism of ligand was studied from the fluorescence intensity of ligand. A series of experiments were conducted upon sequentially adding different concentrations of manganese in the range  $2-110 \times 10^{-6}$  M.



**Fig. 7.** The UV absorption spectrum of ligand-manganese complex, manganese ( $300 \times 10^{-6}$  M) and ligand  $10 \times 10^{-6}$  M in acetonitrile,  $\lambda_{max}$  is 286 nm.



**Fig. 8.** Fluorescence intensity at 365 nm as a function of manganese concentration in  $10^{-6}$  M.

The free ligand exhibited a very weak fluorescence intensity at 365 nm, when excited at 270 nm. Upon addition of manganese resulted greatest enhancement in fluorescence intensity at 365 nm due to inhibition of PET phenomenon by giving linear fluorescence response in the range  $2-110 \times 10^{-6}$  M. The results are shown in figure 9 (Ji *et al.*, 2005).

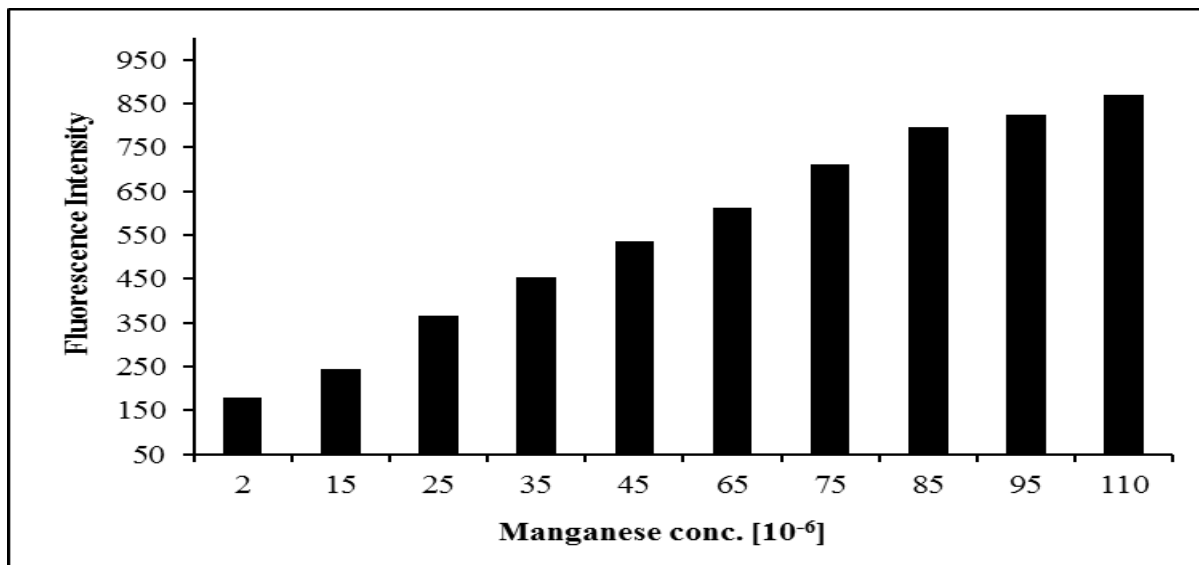
*Effect of pH*

The effect of pH on the fluorescence intensity of ligand was studied in a wide pH range from 2 to 12 of

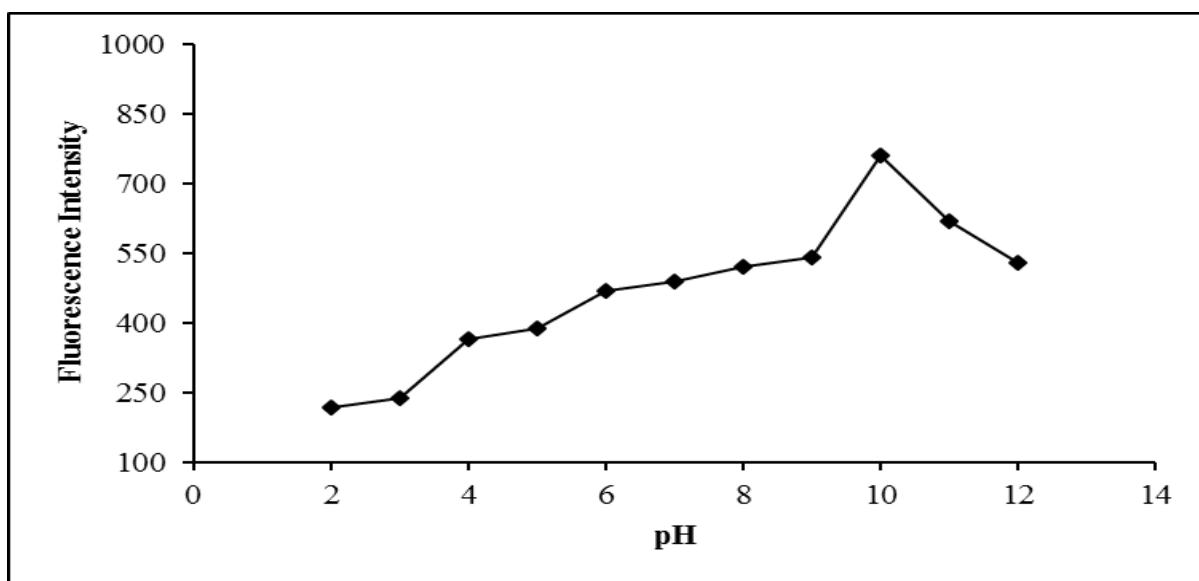
the solution. pH was adjusted by adding  $1 \times 10^{-2}$  M sodium hydroxide and  $25 \times 10^{-2}$  M hydrochloric acid and their fluorescence intensity at 365 nm was examined as shown in figure 10.

It is cleared from these results that in acidic pH, the fluorescence intensity was low, indicating poor stability of complex due to protonation of hydroxyl group. Fluorescence intensity was enhanced with increasing pH due to deprotonation of OH (Di *et al.*, 2013).





**Fig. 9.** Enhancement in fluorescence intensity of ligand ( $10 \times 10^{-6}$  M) in acetonitrile upon increasing concentration of manganese ( $2$ - $110 \times 10^{-6}$  M) with an excitation at  $270$ nm.



**Fig. 10.** Fluorescence intensity of ligand ( $10 \times 10^{-6}$  M) in the presence of manganese ( $20 \times 10^{-6}$  M) as a function of pH,  $\lambda_{ex}=270$  nm,  $\lambda_{em}=365$  nm.

*Effect of reaction time on fluorescence intensity of ligand*

To investigate the effect of reaction time on the fluorescence intensity of ligand towards manganese, the fluorescence of ligand-manganese complex was monitored at different intervals of time. The fluorescence intensity at  $365$  nm increased remarkably in  $120$  s and further enhancement was not pronounced with increasing reaction time as shown in figure 11.

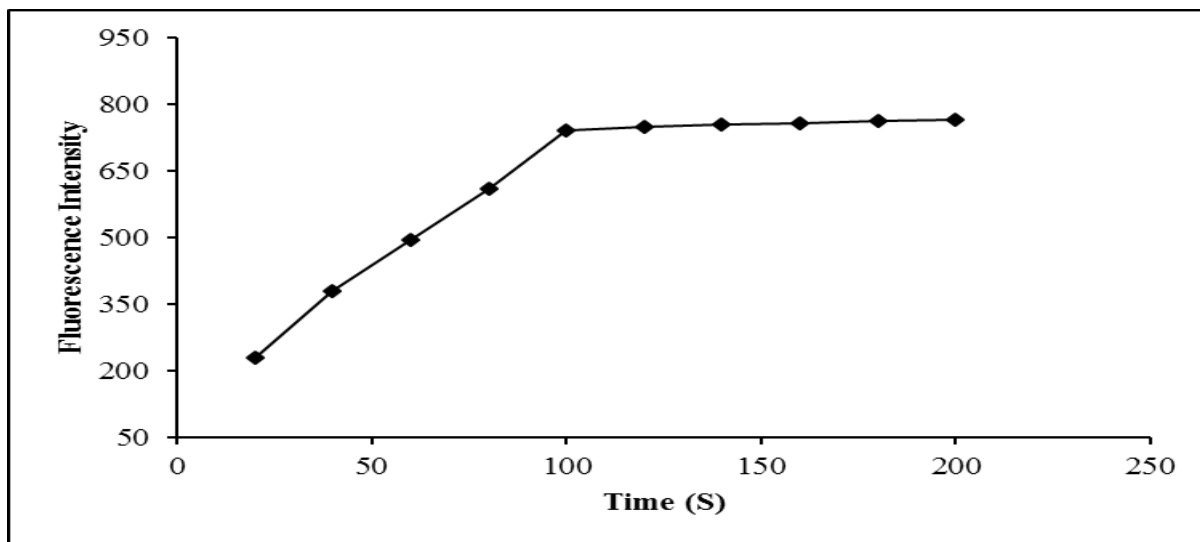
Therefore ligand can be used as selective fluorescent-on ligand for real-time determination of manganese (Jayaraman *et al.*, 2014).

*Job's plot analysis for determining binding stoichiometric ratio of ligand with manganese*

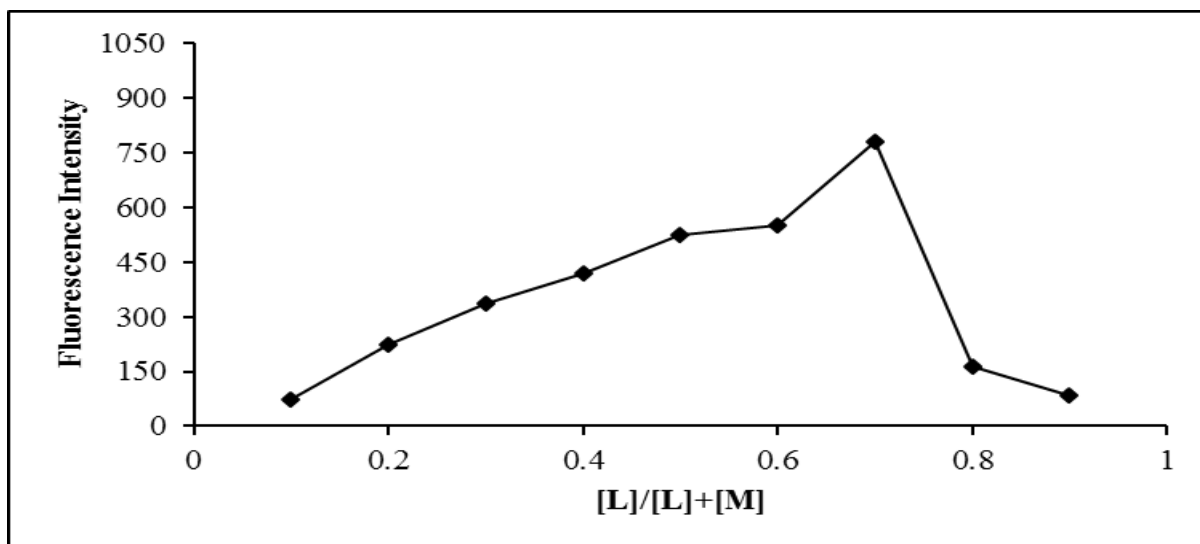
For determination of binding stoichiometry of ligand-manganese complexes, Job's plot analysis was carried out. For spectroscopic analysis equimolar solutions of ligand and manganese were prepared and mixed in

different ratios by continuous increase of one constituent with the similar decrease of second constituent keeping total concentration constant at  $300 \times 10^{-6}$  M. The molar fraction of ligand was varied from 0.1-0.9. Binding stoichiometry was determined by plotting the graph between the molar fraction of

ligand and respective fluorescence emission intensity at 365 nm. The results as shown in figure 12 show that fluorescence intensity reached maximum when molar fraction was 0.7 showing 2:1 binding stoichiometry meaning two parts of ligand bind with one part of manganese (Ahmed *et al.*, 2015).



**Fig. 11.** The time dependent fluorescence intensity of ligand  $10 \times 10^{-6}$  M and manganese  $20 \times 10^{-6}$  M, at room temperature at 365 nm with  $\lambda_{ex}$  at 270 nm.



**Fig. 12.** Job's plot of ligand and manganese, [manganese] + [ligand] concentration is  $300 \times 10^{-6}$  M,  $\lambda_{ex}$  is 270 nm and  $\lambda_{em}$  is 365 nm.

*Association constant determination*

On the basis of 2:1 binding stoichiometry determined by Job's plot, the association constant ( $K_a$ ) of ligand with manganese was calculated from experiment of

manganese concentration effect on fluorescence by Benesi-Hildebrand plot to be  $4 \times 10^6$   $M^{-1}$  as given in figure 13. the method and materials was deleted. No need of it here.

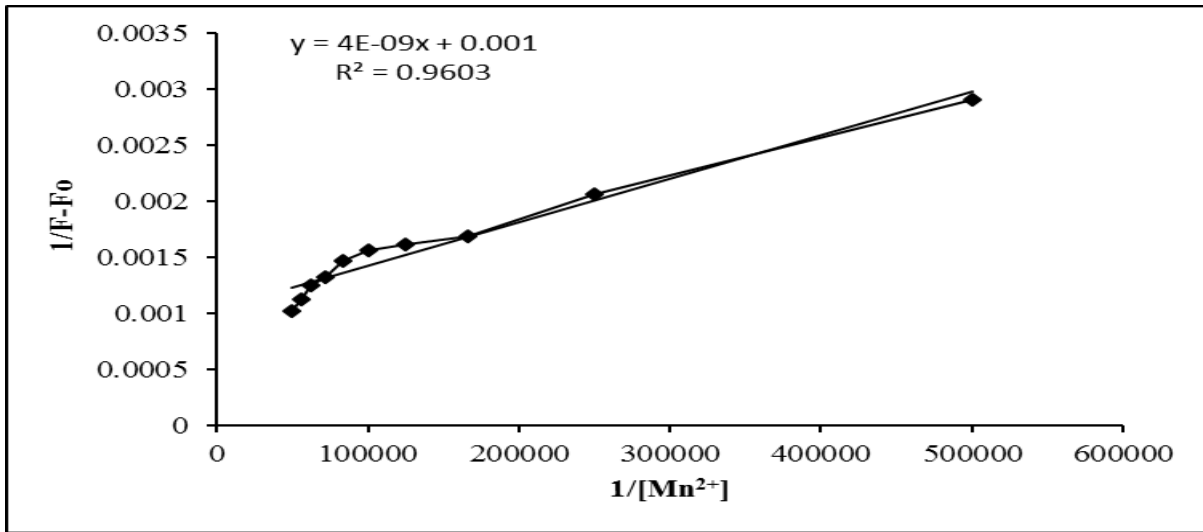
*Comparison of the synthesized ligand with previously reported ligands*

A number of analytical properties of ligand were compared with those of other previously reported ligands for manganese determination. The comparison results are summarized in Table 3.

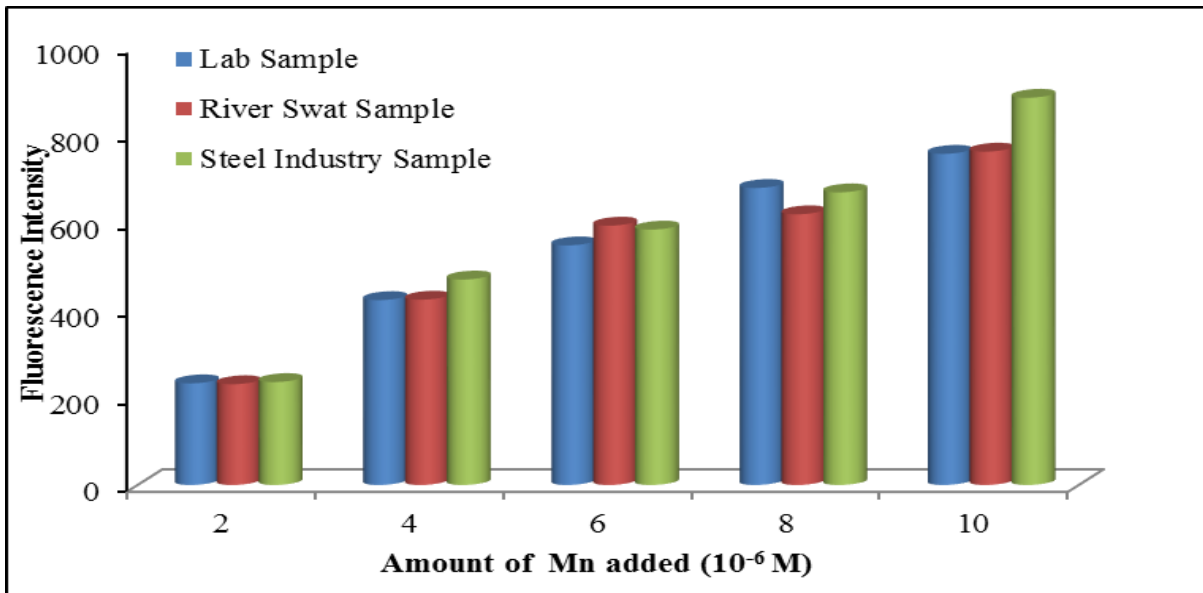
It is evident that the present ligand exhibits better linear range and lower limit of detection, compared to other reported ligands in literature.

*Manganese determination in water samples*

The synthesized ligand was used for determination of manganese in different water samples. High degree selectivity possessed by the ligand for manganese, makes it potentially useful for determination of trace amount of manganese.



**Fig. 13.** Benesi-Hildebrand plot from fluorescence data of ligand ( $5 \times 10^{-6}$  M) with manganese ( $2-20 \times 10^{-6}$ ).



**Fig. 14.** Linear change in fluorescence intensities of ligand ( $12 \times 10^{-6}$  M) at 365 nm upon addition of manganese ( $2-10 \times 10^{-6}$  M) in spiked water samples.

The water samples analysed include laboratory, natural water sample taken from river Swat located in

the northern region of Khyber-Pakhtunkwa and industrial waste water of steel industry.

The water samples were collected by routine methods, preserved and stored in pre-washed polyethylene bottles and were spiked and assayed. For spectrofluorometric analysis, different concentrations of manganese were added into water samples. The results are shown in figure 14. Fluorescence intensities were proportional to manganese concentration with correlation value of  $R^2 = 0.96$  (Tolpygin *et al.*, 2012).

### Recommendations

Manganese is more frequently of toxicological concern because overexposure to the metal can lead to progressive, permanent, neurodegenerative damage, resulting in syndromes similar to idiopathic Parkinson's disease, Cardiovascular toxicity, and hepatotoxicity, therefore during experiments it should be handled with care and all safety precautions should be followed. As far as environment is concerned, it is strongly recommended that the government and industrialists should launch various research projects in order to eliminate trace level of manganese from the environment and the common people should be made aware of manganese toxicity.

### Conclusion

In conclusion, a novel Schiff base fluorescent turn-on ligand was synthesized and was used for determination of manganese in water samples with high selectivity, sensitivity and lower limit of detection.

The ligand coordinated to the manganese through azomethine nitrogen and phenolic oxygen atoms. Due to PET inhibition phenomenon the ligand shows coordination with manganese. Relative standard deviation (RSD) was found to be 0.31 % for 8 replicate analyses with  $3.8 \times 10^{-6}$  M limit of detection.

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