

International Journal of Scientific Research and Reviews

Novel chalcone-based fluorescent sensor for selective sensing of Zn²⁺ complex

V.Aruldeepa¹, P.Tharmaraj^{2*} C.D. Sheela³ and J.JoneCelestina⁴

¹Department of Chemistry, Fatima College, Madurai, Tamil Nadu, India.

^{2*}Department of Chemistry, Thiagarajar College, Madurai, Tamil Nadu, India.

³Department of Chemistry, The American College, Madurai, Tamil Nadu, India.

⁴Department of Chemistry, Thiagarajar College, Madurai, Tamil Nadu, India.

ABSTRACT

Aminoantipyrine schiff bases were found to have a remarkable selectivity for zinc ions and simultaneous enhancement of fluorescence. The chalcone based Schiff base was synthesized from Aminoantipyrine and chalcone under reflux condition for three hours using ethanol as the solvent. Among the various metals employed it selectively sensed Zn²⁺ ions both calorimetrically and fluorimetrically. The stoichiometry of the complex was determined to be 1:1. The complex exhibited reversibility with EDTA. It is found that the ligand under study is able to sense Zn²⁺ in the concentration of 10⁻⁶ μm. The limit of detection was found out from the absorbance values. The synthesized zinc complex has its application in various fields.

KEYWORDS: Aminoantipyrine, Zinc, Fluorescence, Selective sensing.

***Corresponding Author**

P. Tharmaraj

Department of Chemistry

Thiagarajar College

Theppakulam-625 009, (Madurai), India.

E-mail: aruldeepa2k@gmail.com, rajtc1962@gmail.com

Mobile No: 9442555836

INTRODUCTION

Zinc is the second most abundant transition metal ion after iron in the human body, and essential with concentration ranging from 0.1mM to 0.3mM^{1,2}. It is a very important ion species in many biological activities such as cellular metabolism, gene expression, neural signal transmission, DNA binding or recognition, pathology, cell apoptosis and mammalian reproduction³⁻⁶. The disorder of zinc metabolism in biological systems is associated with diabetes, epilepsy and Alzheimer's diseases⁷. Therefore, there is a large demand for exploring novel development of Zn²⁺ chemosensors over other techniques⁸. The development of chemosensors for metal ions with high selectivity and sensitivity is an active field in analytical chemistry. Fluorescent chemosensors for metal ions have attracted particular attention due to their advantages such as low cost, good sensitivity, simplicity, capability of real-time detection and non-destructive emission signals⁹. Till date, numerous fluorescent chemosensors for zinc have been developed using indole, Coumarin^{10,11} which exhibited excellent selectivity and sensitivity towards zinc and some of them could be used for biological imaging in a physiological environment. Here, We planned to propose the novel ligand and its complex to sense the Zn²⁺ in low concentration. The ligand HPDP and its complex are characterized by UV, IR, ¹H-NMR and mass spectral studies.

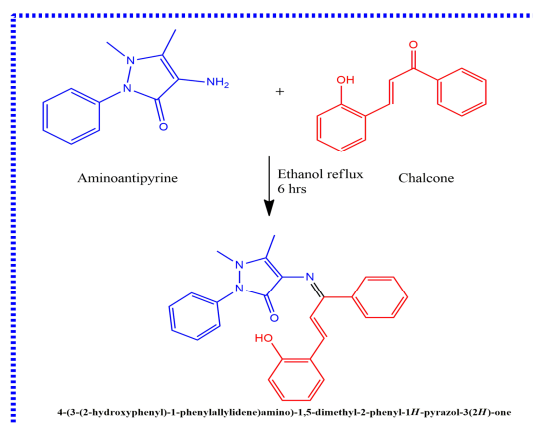
EXPERIMENTAL

Materials:

All the needed chemicals were purchased from Merck chemicals in AR grade. Ethanol is used as the solvent.

Synthesis of HPDP:

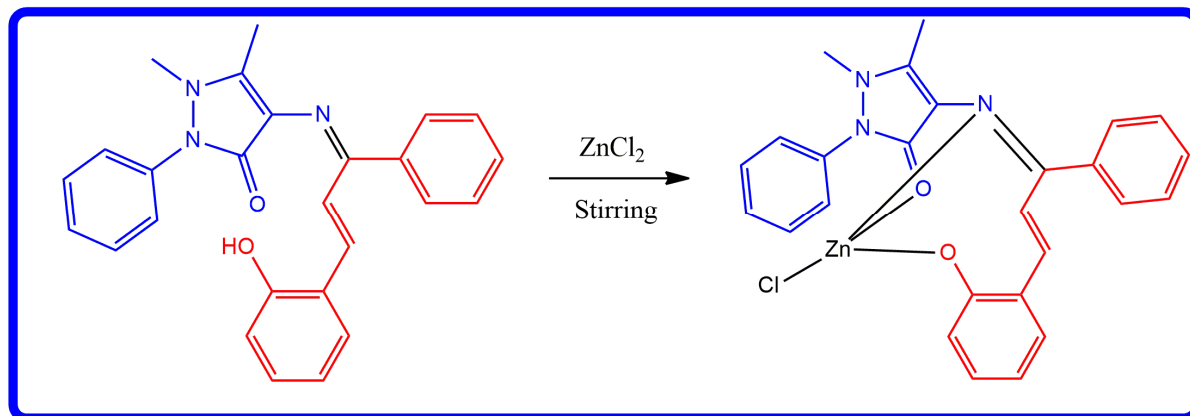
Aminoantipyrine(1mmol) was mixed with chalcone(2mmol) in ethanol and refluxed for 6hrs. The progress of the reaction was monitored by TLC. A dark yellow colour precipitate starts separating out, it was filtered and dried. This is given in **Scheme 1**.



Scheme 1: Synthesis of HPDP

Synthesis of Zn(II) complex:

The metal(II) complex was synthesized by addition of solution of Zinc(II) chloride (1mmol) to the solution of ligand (1mmol). The resulting mixture was stirred for 2 h and the complex was precipitated by filtration and washed with ethanol. Yield 67-75%. This is given in **Scheme 2**.



Scheme 2: Zinc (II) complex of the ligand (HPDP)

RESULTS AND DISCUSSION

The metal(II) complex of [ML.Cl] type were obtained in good yield through the reaction of (HPDP) with the corresponding metal salt. The ligand and metal(II) complexes were characterized through IR, elemental analyses, electronic absorption, NMR spectral data and arrived their structure. The analytical data and physical properties of the ligand and metal (II) complex are listed in the **Table 1**. Elemental analysis and Spectral data suggest that the molecular formula [ML.Cl] for zinc complex. From the NMR spectral analysis tetrahedral geometry of the complex was confirmed.

Table.1. Physical characterizations, analytical data of the ligand (HPDP) and [Zn(II) HPDP]Cl

Compounds	F.W. (g/mol)	Color	Calculated found (%)				
			C	H	N	O	M
HPDP	396	Dark Yellow	76.26	5.66	10.26	7.81	-
			76.10	5.58	10.21	7.74	
[Zn(II) HPDP]Cl	543	Pale yellow	61.31	4.35	8.25	6.28	12.84
			61.28	4.33	8.23	6.04	12.98

CHARACTERIZATION OF LIGAND (HPDP):**¹H-NMR of HPDP and its Zinc Complex:**

The ligand (HPDP) was characterized using ¹H-NMR data. ¹H-NMR was recorded using DMSO as the solvent. (N-CH) has a characteristic peak at 7.27 (δ). The aromatic protons has resonated in the range of (7.0-7.8)(δ)¹².

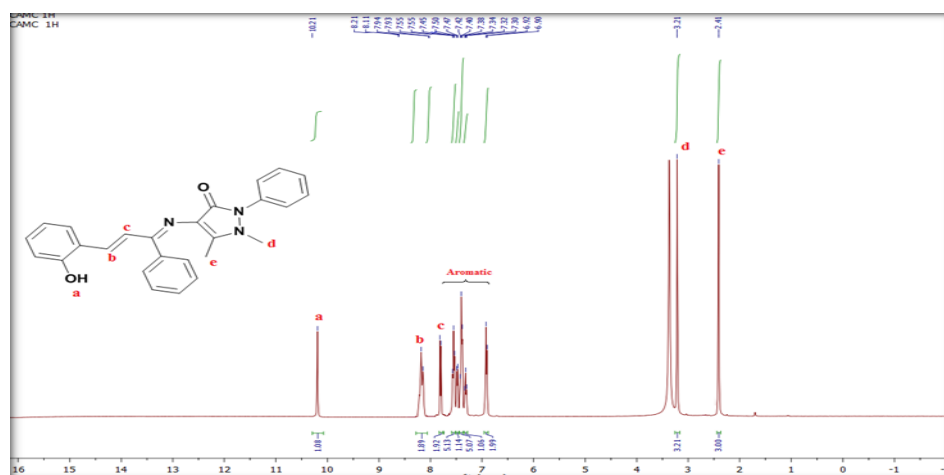


Fig.1:NMR Spectrum of ligand (HPDP)

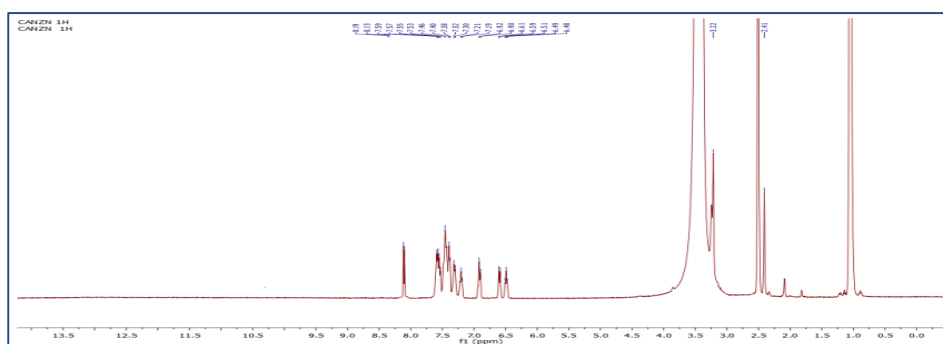


Fig.2: NMR Spectrum of [Zn(HPDP)]Cl complex

INFRARED SPECTRAL STUDIES:

The IR spectral studies of the ligand and metal(II) complex were carried out in the range 4000-400 cm^{-1} . **Table.2.** showed the spectral data of the ligand and its complex. A broad band centred at 3108 cm^{-1} is due to (OH). The IR spectrum of the ligand shows a broad band at 3138 cm^{-1} which is a characteristic of ν (N-H) stretching vibration shifted itself to 3109 in Zinc HPDP complex. The band at 1628 cm^{-1} is assigned to ν (C =N) which is downshifted to 1598 cm^{-1} . ν (M-O) peak is at 712 ν (M-N) peak is at 568 cm^{-1} . The FT-IR spectra are depicted in **Fig.3.** IR spectrum of the Metal(II) complex show considerable variations compared with the ligand (HPDP)¹³⁻¹⁵.

Table.2. IR spectral data of ligand (HPDP) and its metal(II) complexes (cm^{-1}).

Compounds	ν (C-N)	ν (C=N)	ν (N-H)	ν (-M-O)	ν (-M-N)
HPDP	1332	1628	3138	-	-
[Zn(II) HPDP]Cl	1313	1590	3109	712	568

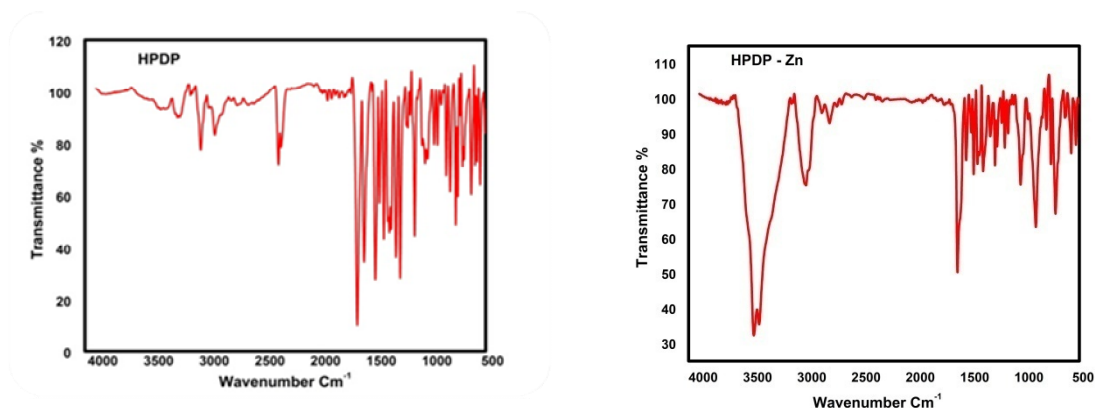
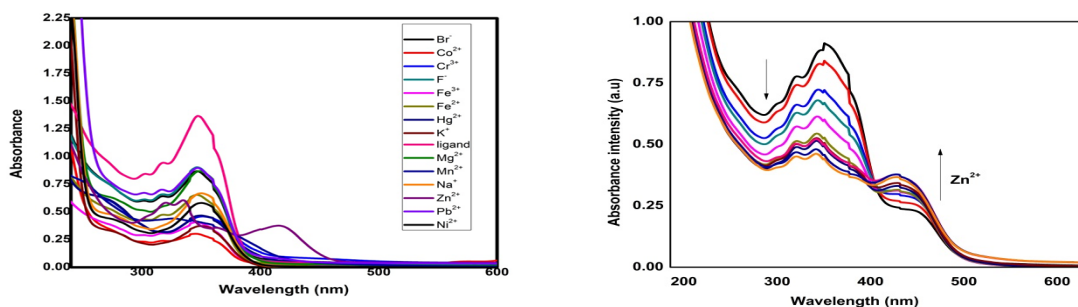


Fig.3: IR Spectrum of ligand and[Zn(HPDP)]Cl complex

ABSORBANCE STUDIES:

Absorption spectra of both HPDP have been recorded in presence of different concentrations of Zn^{2+} in ethanol solution. Free HPDP shows peak at 349 nm. When Zn^{2+} ions are added to HPDP, spectral behaviour changes markedly. A new peak emerges at 415nm with gradual increase intensity (bathochromic shift) with the addition of Zn^{2+} ion while the intensity of probe 349 nm decreases. Changes in the intensities almost saturate when one equivalent of Zn^{2+} is added. Isosbestic point is noticed at 399 nm. Upon gradual addition of the metal ion, intensity at 349 nm decreases sequentially and at the same time, a new peak at 417nm emerges with increasing intensity. The N, O donor atoms of both the Schiff-bases coordinate to the metal centre to form the chelate ring. As a consequence, conjugation in the structure is extended, showing the new absorption band at a longer wavelength. All of these facts suggests that Zn^{2+} is able to interact with both the probes to form the corresponding Zn-bound Schiff-base compound^{16,17}.

Fig.4: UV-Visible Spectrum of ligand with different metals and Zn^{2+} at different dilutions.



FLUORESCENCE STUDIES:

Fluorescence spectra of both HPDP have been recorded in the presence of different concentrations of Zn^{2+} in ethanol. HPDP displays emission peaks at 425 nm with moderate intensity when it is excited at 350 nm.

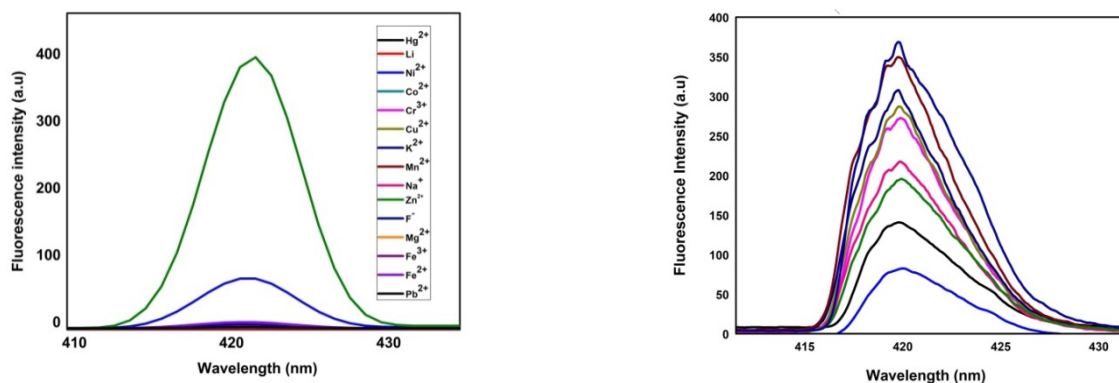


Fig.5: Fluorescence spectrum of ligand with different metals and Zn^{2+} at different dilutions

The addition of Zn^{2+} ions to the HPDP results in a gradual increase in emission intensity at 425 nm. The increase in emission intensity of HPDP. The addition of Zn^{2+} ion causes significant changes in the fluorescence spectrum of HPDP. The enhancement in emission intensity of HPDP could be explained based on the photo induced electron transfer (PET). Due to the formation of metal complex with Zn^{2+} PET is turned on^{18, 19}.

MASS SPECTRUM and BINDING STUDIES:

The binding stoichiometry of ligand and complex was determined using the Job's plot analysis²⁰. The fluorescence intensity was plotted against the molar fraction of the chemosensor under a constant total concentration. A maximum intensity was observed when the molar fraction was 0.5 M, which indicates a 1:1 ratio for the Zn^{2+} complex. Limit of detection was found out to be 0.1 μ m. In order to confirm the formation of metal complex in 1:1 stoichiometry HR-LCMS mass spectrum for the complex was analysed and the value was observed at m/z 543 which is accounted by the presence (M+Cl+H) from that of expected mass of m/z 507^{21,22}.

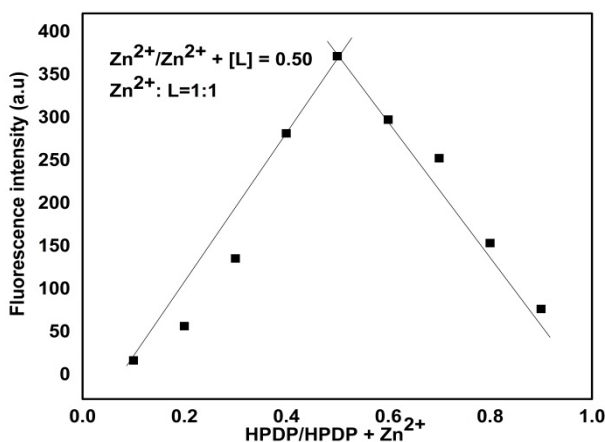


Fig.6 Job's plot of BNHNTA with Zn^{2+} showing 1:1 stoichiometric ratio of the synthesized metal complex

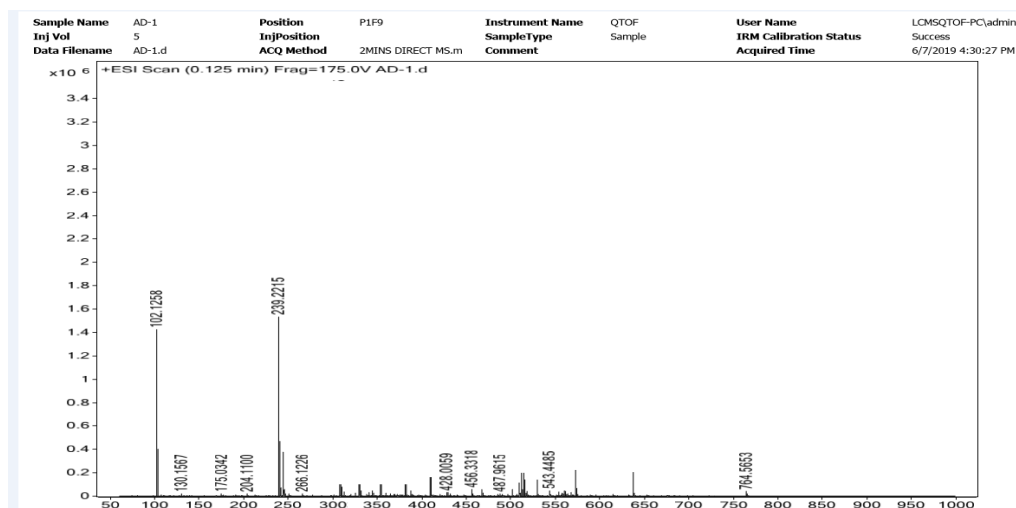


Fig.7 HR-LCMS Spectrum of Zn²⁺ (HPDP) Complex

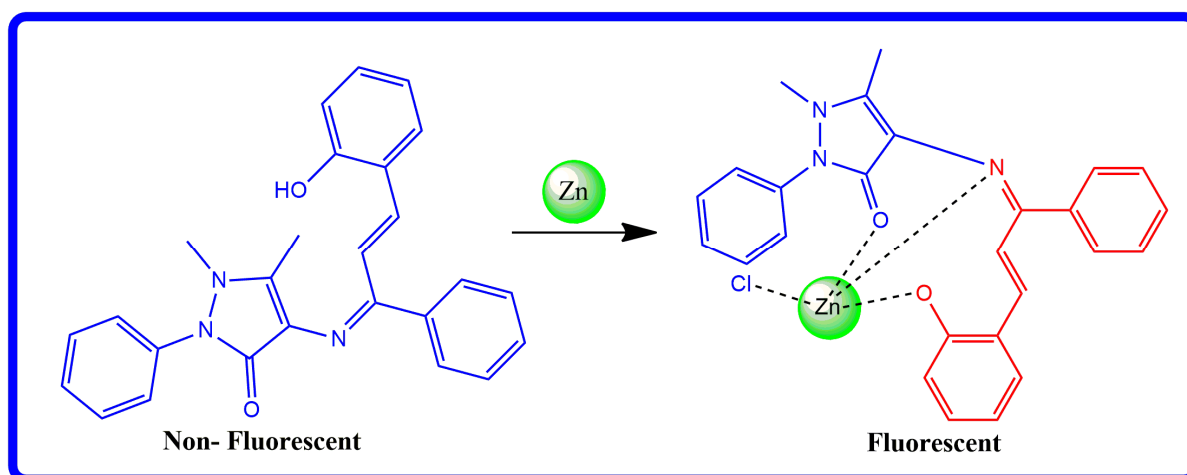


Fig.8 Sensing mechanism of Zn²⁺ (HPDP) Complex

CONCLUSION

A novel chalcone based Schiff base ligand was prepared by the condensation of chalcone and Aminoantipyrine and characterized by spectroscopic studies. It displays high selectivity and sensitivity for detection of zinc ions in ethanol. The stoichiometric ratio is found to be 1:1 with an obvious colour change from yellow orange to brown. It is found that the ligand (HPDP) sense Zn²⁺ in the concentration of 10⁻⁶ μm. The detection limits was very low compared to the recently reported sensors. It enhanced the fluorescence intensity of ligand up to 400 nm in presence of zinc. An obvious red shift is observed. Therefore this chemosensor can be applied in industrial and real life samples.

ACKNOWLEDGEMENT

The authors thank the Management and the Principal of Thiagarajar College and Fatima college, Madurai for providing laboratory. Our sincere thanks to Gandhigram Rural Institute, Dindigul, IIT, Bombay and ANJA College, Sivakasi for providing analytical facilities.

REFERENCES

1. Sil A, Maity A, Giri D, Patra SK A. phenylene–vinylene terpyridine conjugate fluorescent probe for distinguishing Cd^{2+} from Zn^{2+} with high sensitivity and selectivity. *Sensors Actuators B Chem*: 2016; 226:403–11.
2. Zhou L, Zhang X, Wang Q, Lv Y, Mao G, Luo A, Wu Y, Wu Y, Zhang J, Tan W. Molecular engineering of a TBET-based two photon fluorescent probe for ratiometric imaging of living cells and tissues. *J Am Chem Soc.*:2014;136:9838–41.
3. Goswami S, Aich DS, Das AK, Mannaa A, Halder S. A highly selective and sensitive probe for colorimetric and fluorogenic detection of Cd^{2+} in aqueous media. *Analyst*:2013; 138: 1903–07.
4. Weiss JH, Sensi SL, Koh JY. Zn^{2+} : a novel ionic mediator of neural injury in brain disease. *Trends Pharmacol Sci .*:2000;21:395–401.
5. Roy P, Dhara K, Manassero M, Banerjee P. Synthesis, characterization and selective fluorescent zinc(II) sensing property of three Schiff-base compounds. *Inorg Chim Acta*:2009;362:2927–32.
6. D. Noy, I. Solomonov, O. Sinkevich, T. Arad, K. Kjaer, I. Sagi, Zinc-amyloid β interactions on a millisecond time scale stabilize non-fibrillar alzheimer-related species, *J. Am. Chem. Soc.*:2008;130:1376–83.
7. Y. Cai, X. Meng, S. Wanga, M. Zhu, Z. Pan, Q.X. Guo. A quinoline based fluorescent probe that can distinguish zinc(II) from cadmium(II) in water. *Tetrahedron Lett.*:2013;54: 1125-28.
8. Ammann D, Bissig R, Gugli M, Pretsch E, Simon W, Borwitz IJ, Weiss L. Preparation of neutral ionophores for alkali and alkaline earth metal cations and their application in ion selective membrane electrodes. *Helv Chim Acta .*:1975;58(6):1535–48.
9. Chandra S, Raizada S, Rani S. Structural and spectral studies of palladium(II) and platinum(II) complexes derived from N, N, N, N-tetradentatamacrocyclicligands. *SpectrochimActa.*:2008;A71:720–24.
10. Das DK, Goswami P, Sarma S, Salicylaldehyde phenyl hydrazone: A new highly selective lead(II) probe. *J Fluoresc.*:2013;23:503–08.

11. Ji YF, Wang R, Ding S, Du CF, Liu ZL. Synthesis, crystal structures and fluorescence studies of three new Zn(II) complexes with multidentate Schiff base ligands. *Inorg. Chem. Commun.*:2012;16: 47–50.
12. Schweinfurth, D. Sommer, M. G. Atanasov, M. Demeshko, S. Hohloch, S.Meyer, F. Neese, F. Sarkar, B. The Ligand Field of the Azido Ligand: Insights into Bonding Parameters and Magnetic Anisotropy in a Co(II)–Azido Complex. *J. Am. Chem. Soc.*: 2015; 137: 1993–2005.
13. Zhu, H. Fan, J. Wang, B. Peng, X. Fluorescent, MRI, and colorimetric chemical sensors for the first-row d-block metal ions. *Chemical Society reviews*: 2015; 44 (13): 4337-66.
14. Wang, P. Liu, L. X. Zhou, P. P. Wu, W. Y. Wu, J. Liu, W. S. Tang, Y. A peptide-based fluorescent chemosensor for multianalyte detection. *Biosensors & bioelectronics*: 2015; 72: 80-86.
15. Gupta V.K., Singh A.K., Kumawat L.K., Thiazole Schiff base Turn-On Fluorescent Chemosensor for Al³⁺ Ion, *Sens. Actuator B*: 2014;195: 98–108.
16. Gupta V.K. Singh A.K., Mergu N., Antipyrine based Schiff bases as Turn-on Fluorescent sensors for Al(III) ion, *Electrochim. Acta*: 2014;117:405– 12.
17. Yang L, Zhu W, Fang M, Zhang Q, Li C, A new carbazolebased Schiff-base as fluorescent chemosensor for selective detection of Fe³⁺ and Cu²⁺. *SpectrochimActaA*:2013;109:186–92.
18. Rosatzin T, Bakker E, Suzuki K, Simom W, Lipophilic and immobilized anionic additives in solvent polymeric membranes of cation-selectivechemicalsensors. *AnalChimActa*:1993;280(2):197–208.
19. Ashokkumar P, Ramakrishnan VT, Ramamurthy P ,Photoinduced electron transfer (PET) Based Zn²⁺ fluorescent probe: Transformation of turn-on sensors into ratiometric ones with dual emission in acetonitrile. *J PhysChemA*:2011; 115:14292– 99.
20. Xue L, Liu C, Jiang H, Highly sensitive and selective fluorescent sensor for distinguishing cadmium from zinc ions in aqueous media. *Org Lett*:2009; 11(7):1655–58.
21. Li HY, Gao S, Xi Z. A colorimetric and “turn-on” fluorescent chemosensor for Zn(II) based on coumarin Schiff base derivative. *InorgChemCommun*:2009; 12(4):300–03.
22. Tong H , *J. Am. Soc. Mass Spec.*:1999;10:1174-87.