Int. J. Electrochem. Sci., 11 **(2016)** 1640 - 1650

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Optical and Electrochemical Selective Sensor for Zn^{2+} ions based on 4-(furan-2-ylmethyleneamino)-2,3-dimethyl-1-phenyl-1,2-dihydropyrazol-5-one

Vinod Kumar Gupta[1,2]

[1]Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee-247 667, India
[2]Department of Applied Chemistry, University of Johannesburg, Johannesburg, South Africa
E-mail: vinodfcy@iitr.ac.in, vinodfcy@gmail.com

Received: 5 December 2015 / *Accepted:* 28 December 2015 / *Published:* 1 January 2016

A simple 4-(furan-2-ylmethyleneamino)-2,3-dimethyl-1-phenyl-1,2-dihydropyrazol-5-one (M1) chemosensor was designed and positively applied for the selective recognition of Zn^{2+} ions in methanol. Sensing potential of chemosensor M1 with various metal ions was studied by the emission and absorption spectra. The favorable coordination of chemosensor with Zn^{2+} metal ion was initiated by Job's method. The binding constant and limit of detection (LOD) were calculated through titration methods. In DPV studies, chemosensor M1 also exhibits potential changes in the presence of Zn^{2+} ions that recognized complex behavior with Zn^{2+} ions. Reported chemosensor could be applied for bare eye metal sensing and real time sample analysis.

Keywords: Chemosensor M1, Zn^{2+}, fluorescent sensing, colorimetric, electrochemical sensing.

1. INTRODUCTION

In last two decades, growing interest on metal sensing provide a new research theme for the scientific community due to the crucial role of metal ions in the field of medicine and different industries. There are different significant techniques which assist the quantification of metal ions like: atomic absorption spectroscopy, voltammetry, inductively coupled plasma mass-spectrometry, and x-ray analysis [1–10]. All of above techniques have less effective owing to high cost, maintenance and instrumental expert. Colorimetric and fluorescence sensors are the most indispensable tool to detect real-time analysis of metal ions without any utilization of the special instrumentation that can be applied in medical diagnostics, industrial waste product treatment and environmental control [11–16]. Transition metal ions have impactful role in biological and environmental systems, Zinc metal ion exhibit vital roles in human body like as control the activity of enzymes, DNA synthesis, microtubule polymerization, apoptosis, gene expression, matrix metalloproteinase immune system function [17–20]. Zinc has negligible hazardous effect as compare d^{10} Transition metal Cd^{2+} and Hg^{2+} ions in trace level but in excess, it also triggered neurological and haematological disorders, Alzheimer's diseases and reproductive problems [21–23]. Consequently, it is highly desirable to investigate Zn^{2+} concentration in environmental and biological sample. Although previous research, optical sensors based on various families of fluorescent probes like as crown ether, rhodamine, fluorescein, quinoline and coumarin [24–48]. Most of reported colorimetric probes for Zn^{2+} showed poor selectivity for Zn^{2+} over Cd^{2+} and Cu^{2+} ions and provided effective sensing behavior only for higher concentration of Zn^{2+}.

On the basis of our research interest on small and simple optical sensor [49–53], 4-(furan-2-ylmethyleneamino)-2,3-dimethyl-1-phenyl-1,2-dihydropyrazol-5-one (M1) was synthesized through simple condensation reaction and serve as a significant fluorescent and colorimetric chemosensor for Zn^{2+} in the existence of different transition, alkali and alkaline earth metal ions. The favorable stoichiometry of chemosensor was initiated by Job's method and HRMS analysis. The high binding constant and low detection limit (LOD) were calculated through titration methods. Reported probe M1 could be applied as naked eye optical sensor for real time sample analysis.

2. EXPERIMENTAL PROCESS

2.1. Materials and instruments

Chemical reagents, different metal salts and solvents of analytical grade were purchased from Merck and Aldrich. Nitrate and chloride salts were potentially used for metal sensing studies. Chemosensor M1 was synthesized with the help of published procedure [54].

Proton NMR experiment were performed on a JEOL-400 MHz spectrometer and chemical shifts were recorded in ppm using $CDCl_3$ solvent. All colorimetric studies of chemosensor M1 were performed at 25 °C using a Shimadzu UV-2450 spectrophotometer (Japan). Electrospray ionization high resolution mass spectra (ESI-HRMS) analysis were collected on a Bruker-micrOTOF II (USA). DPV experiments were examined by using a CHI760E electrochemical workstation (USA). The pH response on sensing behavior of chemosensor were measured with an Eutech pH 510 (Singapore).

2.2. Preparation of Chemosensor (M1)

4-(furan-2-ylmethyleneamino)-2,3-dimethyl-1-phenyl-1,2-dihydropyrazol-5-one (M1) was designed and synthesized by previously reported method [55]. 10 mmol 4-aminoantipyrine (2.03 g) was dissolved in 15 mL methanol and added 10 mmol 4-Hydroxy-3-methoxybenzaldehyde (1.52 g) drop wise on stirring methanolic solution. The mixture was heated about for 4-5 h. The solid product was filtered off and recrystallized. Yield: 79 %, 1H NMR ($CDCl_3$, 400 MHz): δ, ppm; 9.61 (−N=C−, s, 1H), 7.55 (s, 1H), 7.47 (t, 2H), 7.39 (d, 2H), 7.32 (t, 1H), 6.78 (d, 1H), 6.49 (t, 1H), 3.14, (s, 3H) 2.47 ($–CH_2–$, t, 2H). HRMS m/z (M+): calcd, 281.1179; found, 281.1164 (Fig. 1,2).

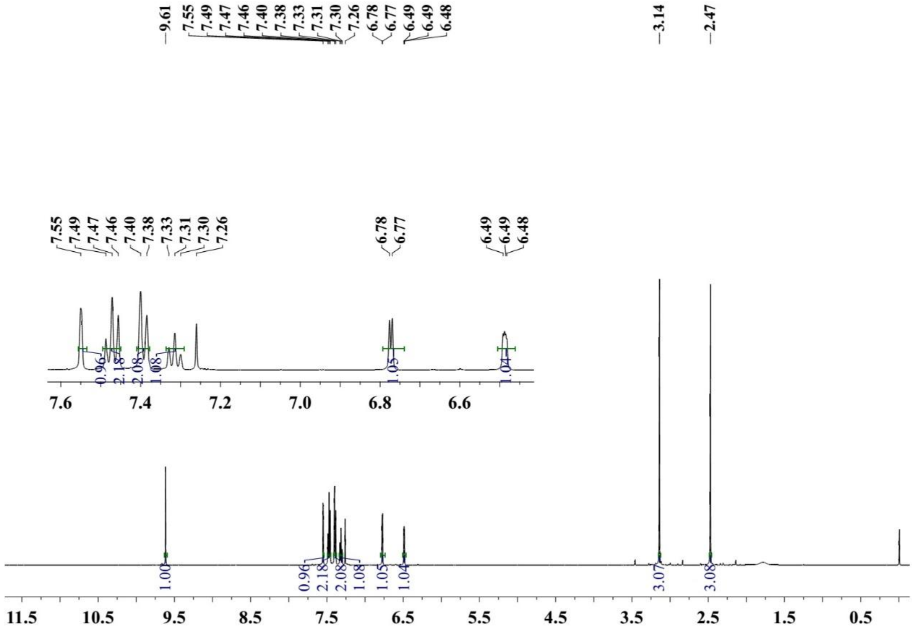

Figure 1. 1H NMR spectrum of chemosensor **M1**.

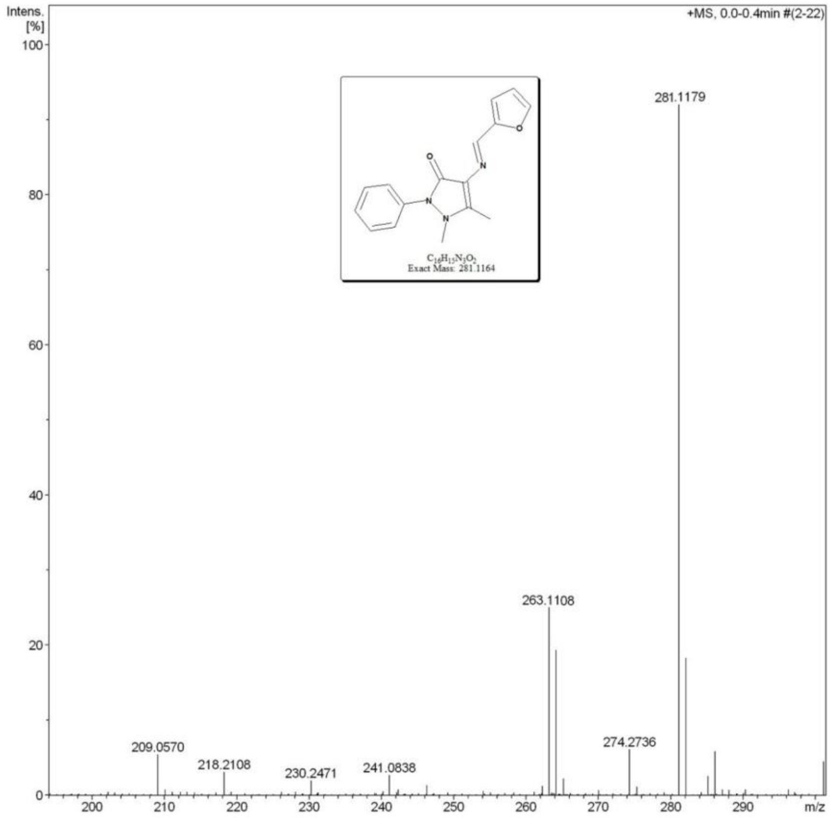

Figure 2. HRMS spectrum of chemosensor **M1**.

3. RESULTS AND DISCUSSION

3.1. UV–vis absorption spectral studies

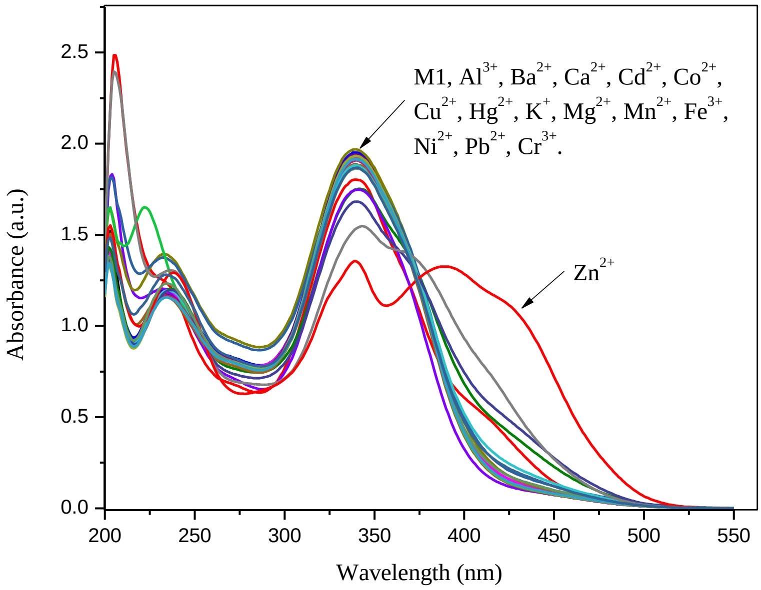

Figure 3. Absorbance spectra of chemosensor **M1** in the presence of differ metal ions.

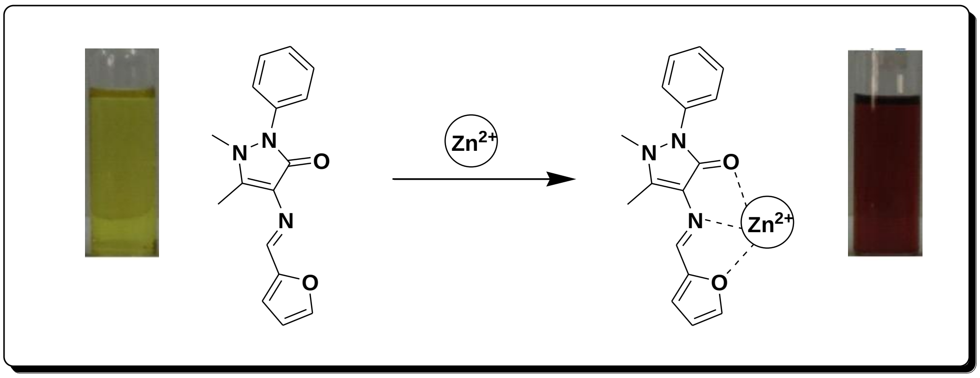

Figure 4. Colorimetric sensing response of probe **M1** toward Zn^{2+}.

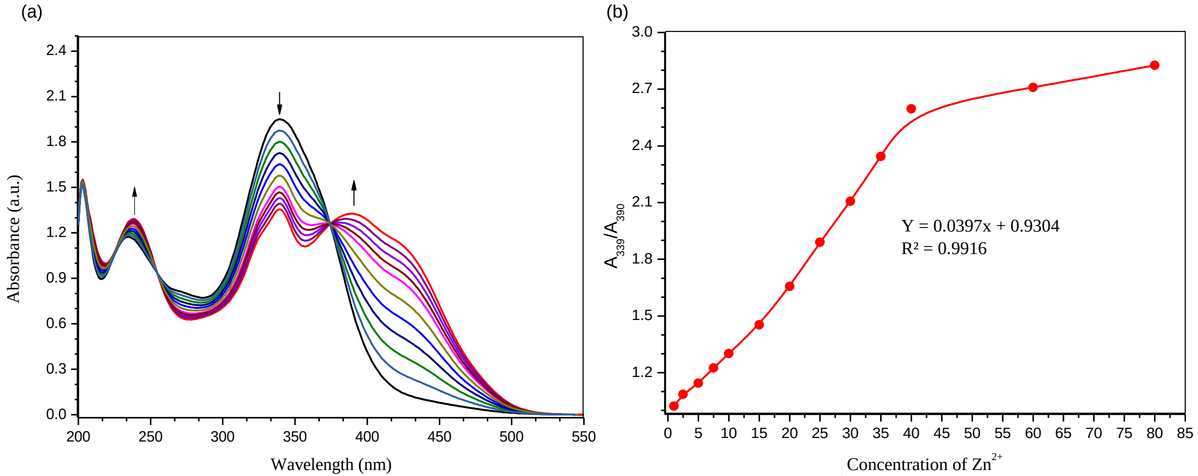

Figure 5. (a) Absorbance titration spectra of **M1** with 0-5 equiv. Zn^{2+} ions in methanol solution, (b) linear response of titration.

High gratitude sensing profiles of chemosensor M1 toward various transition and alkaline metal ions primarily investigated by absorbance spectra in methanol. As displayed in figure 3, chemosensor M1 exhibited strong absorption band at 203, 245 and 342 nm that was remain unchanged after the addition of K^+, Cd^{2+}, Cu^{2+}, Ni^{2+}, Ba^{2+}, Mn^{2+}, Ca^{2+}, Hg^{2+}, Co^{2+}, Mg^{2+}, Cr^{3+}, Pb^{2+}, Fe^{3+}, and Al^{3+} metal ions. Therefore, a new absorbance band at higher wavelength 391 nm was observed in the presence of Zn^{2+} ions and the color of sample solution ($M1+Zn^{2+}$) changed yellow to dark yellow that could be easily detected by the bare eye (Fig. 4). The quantitative absorbance titration spectra of M1 (40 μM) with 0–5 equivalent Zn^{2+} metal ions recorded in methanolic solution (Fig. 5a) that reveals significant changes in spectra at 342 and 392 nm. Further proceeding of Zn^{2+} ion solution, absorption band centred at 392 nm, gradually increased with 0–5 equivalent of zinc metal ions. The gradual changes in absorbance spectra were expressed by a linear plot in figure 5b.

3.2. Fluorescence studies

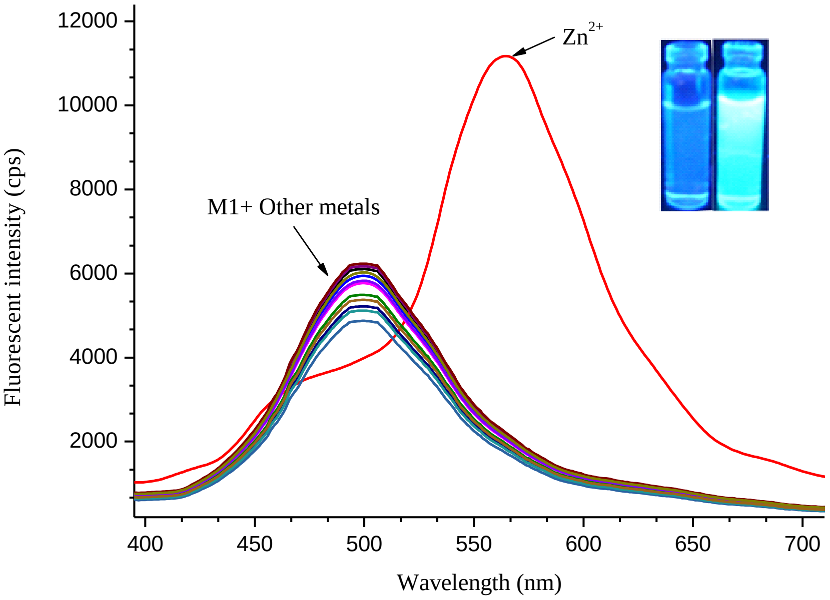

Figure 6. Fluorescence emission spectra of the probe **M1** (40 μM) in the appearance of differ metal ions, such as K^+, Ba^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, Ca^{2+}, Hg^{2+}, Co^{2+}, Mg^{2+}, Cr^{3+}, Pb^{2+}, Fe^{3+}, Al^{3+} and Zn^{2+} in MeOH.

Similarly, the photophysical properties of probe M1 (40 μM) with 5 equivalent various metal ions were examined in methanolic solution at excitation wavelength 380 nm. Fluorescence emission spectrum of probe M1 (40 μM) showed low emission intensity band centred at 494 nm (figure 6). After addition of K^+, Ba^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, Ca^{2+}, Hg^{2+}, Co^{2+}, Mg^{2+}, Cr^{3+}, Pb^{2+}, Fe^{3+}, and Al^{3+} metal ions in methanolic solution of chemosensor M1 did not show any significant changes in emission intensity whereas in addition of Zn^{2+} ion fluorescence intensity of emission band was shifted to higher wavelength 564 nm with a decrease in the fluorescence intensity at 494 nm assisted by red shift ($\Delta\lambda$ = 70 nm). These red shift in absorbance and fluorescence spectra can be explained by simple ICT (intramolecular charge transfer) mechanism [56]. Moreover, quantitative fluorescence sensing response of chemosensor M1 with growing concentration of Zn^{2+} ion was pictured in Fig. 7a. The fluorescence intensity of emission band at 564 nm, increased significantly and got saturation after adding 1 equiv. (40 μM) of Zn^{2+}. Here, an intense fluorescence change for receptor M1 was occurred at 564 nm from the titration studies (figure 7b).

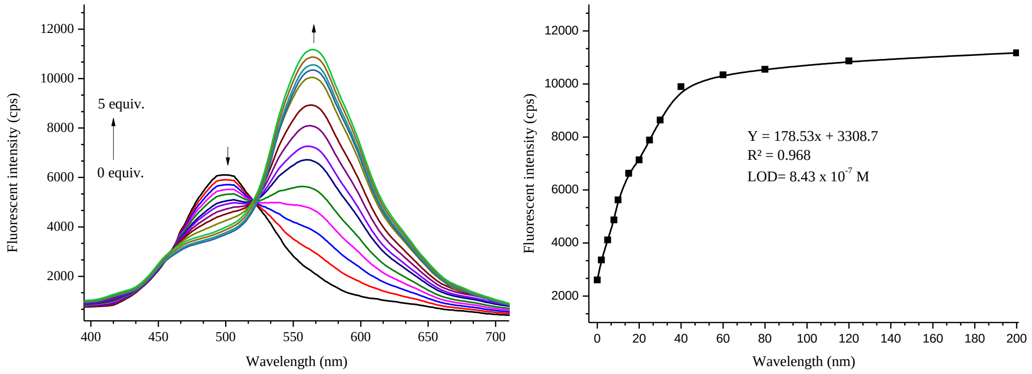

Figure 7. (a) Fluorescence emission titration spectra of **M1** with 0-5 equiv. Zn^{2+} ions in methanol solution, (b) linear response of probe in titration (Excitation wavelength 380 nm).

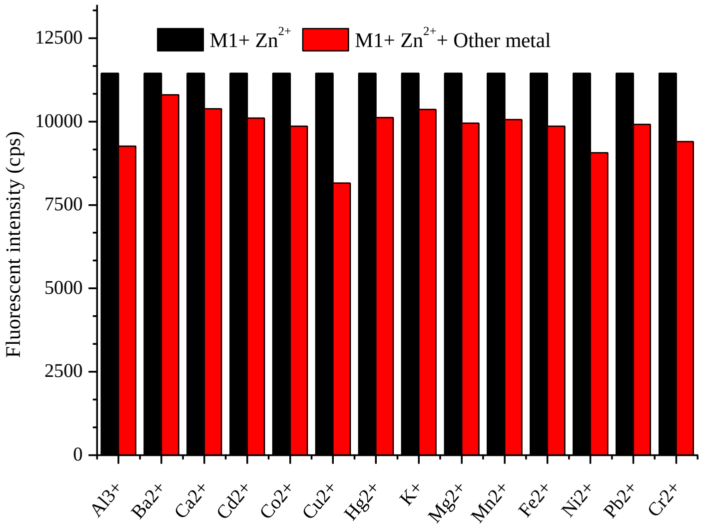

Figure 8. Competitive studies of sensing probe **M1**+Zn^{2+} in the presence of differ metal ions.

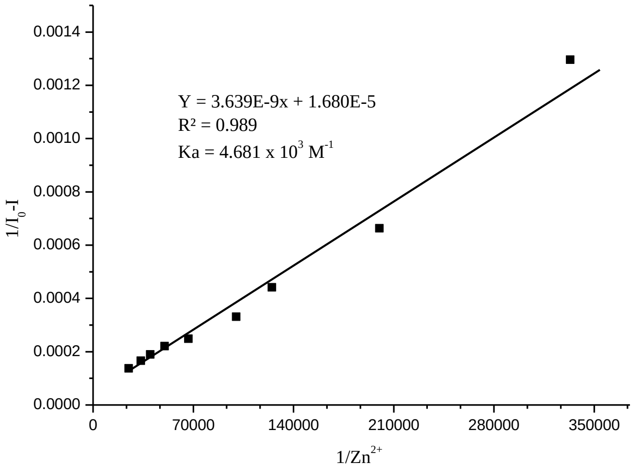

Figure 9. Binding constant measurement for probe **M1** via Benesi−Hildebrand plot.

Moreover, the detection limit of probe M1 for the Zn^{2+} ion was determined by blank standard method and calculated 0.843 μM. In the presence of competitive metal ions, the spectrofluorometric response of probe M1 towards Zn^{2+} ion was examined by competitive experiments (figure.8). For M1+Zn^{2+}, the fluorescence intensity of emission band at 564 nm was remain unchanged after addition of 1 equivalent competitive metal ion K^{+}, Ba^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, Ca^{2+}, Hg^{2+}, Co^{2+}, Mg^{2+}, Cr^{3+}, Pb^{2+}, Fe^{3+}, and Al^{3+} in sample solution. These results showed significant sensitivity and selectivity towards Zn^{2+} ion over different competitive metal ions.

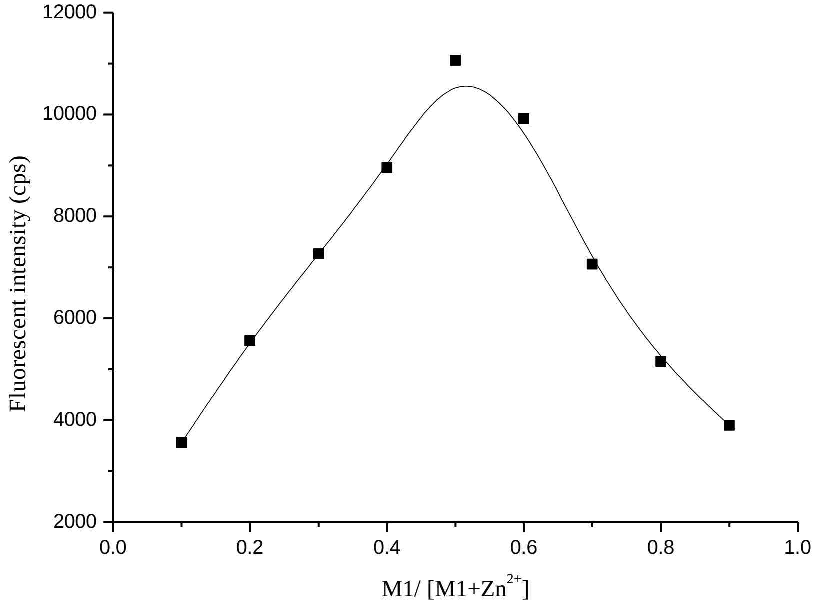

Figure 10. Job’s plot spectra for chemosensor **M1** and Zn^{2+} ions.

The binding stoichiometry of M1+Zn^{2+} was carried out through emission titration experiments. As showed in figure 9, the fluorescence intensity at 564 nm was enhanced maximum with 0.5 molar equivalent of Zn^{2+} that indicate 1:1 Stoichiometric complexation between chemosensor M1 and Zn^{2+} ions. Therefore, the binding constant (Ka) value of probe M1 was calculated *via* Benesi–Hildebrand method [57] and obtained 0.68×10^{4} M^{-1} that represented high metal-binding properties of probe M1 (Fig. 10).

3.3. Electrochemical response

Electrochemical sensing performance of chemosensor M1 toward Zn^{2+} ions was investigated on CHI760E electrochemical workstation (USA). Here, chemosensor M1 explored some remarkable changes with zinc metal ion in methanol. As showed in figure 11, probe M1 (80 ppm) alone exhibited the oxidation potential ($E_{ox.}$) at 0.382 V, however the addition of Zn^{2+}, oxidation potential for M1+Zn^{2+} was shifted to more positive value 0.439 V. This notable potential shift ($E_{ox.}$) was displayed bonding attraction between the chemosensor M1 and Zn^{2+} ions. The result also provided useful information about electrochemical sensing nature of probe M1.

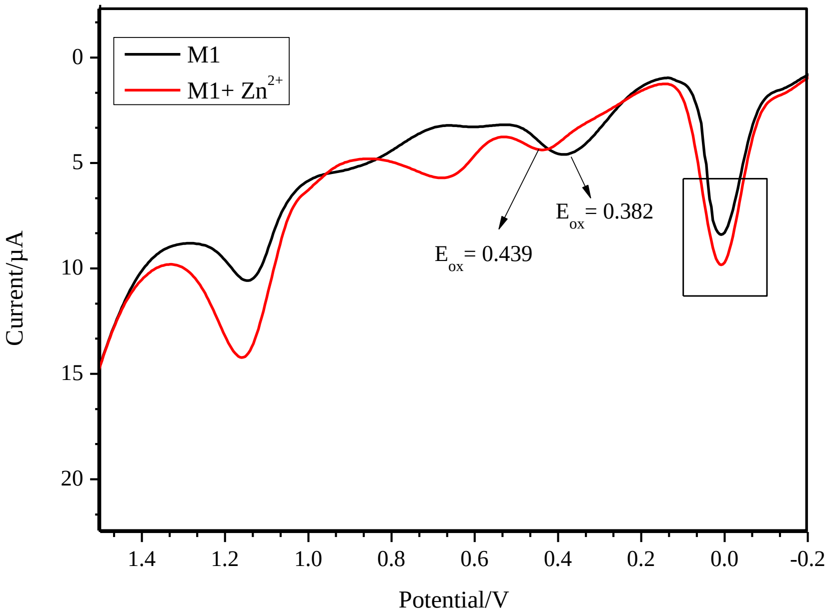

Figure 11. Electrochemical sensing studies of probe **M1** (80 µM) with equal concentration of Zn^{2+} ions.

3.4. Optimization of pH conditions

The fluorescence sensing response of probe M1 (40 µM) was regulated over a wide range of pH 2–12 in water : methanol (v/v, 2:8) solution. As showed in figure 12, at acidic pH probe M1 showed significant changes in the presence and absence of metal ions whereas in basic medium M1+Zn^{2+} did not show notable changes due to interference of –OH group. Here, chemosensor M1 exhibited optimum fluorescence sensing in acidic pH range.

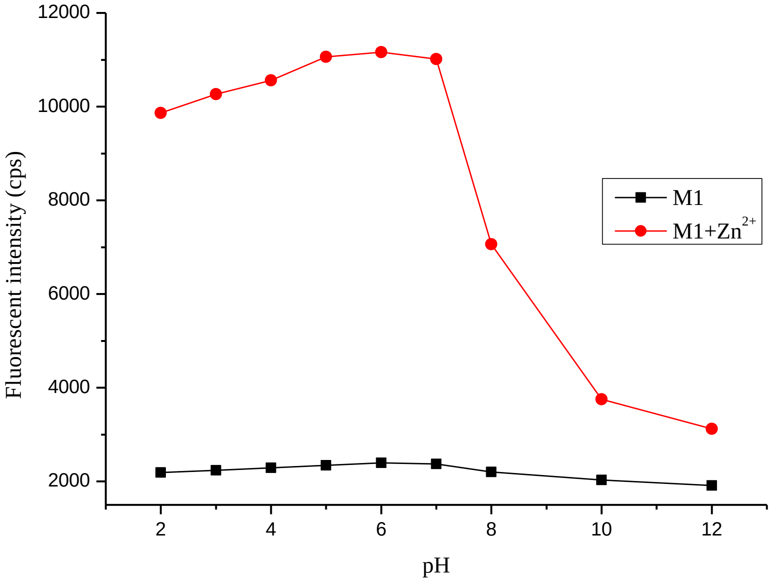

Figure 12. pH effect on fluorescence emission intensity of **M1** and **M1**+Zn^{2+} complex.

3.5. Application of sensor

3.5.1. Naked eye detection of metal ion

To investigate a naked eye response chemosensor M1 for Zn^{2+} metal ion in presence of different metal ions was carried out with in methanol/water (8/2: v/v solution). After addition of 5 equivalents of metal salt in probe M1, a rapid color change light yellow to yellowish orange was obtained only with the Zn^{2+} ion (after 10 minute of mixing).

3.5.2. Real sample analysis

Proposed optical sensor M1 could successfully recover Zn^{2+} ion from tap water containing different amount of zinc ions [58–73]. Different amounts of Zn^{2+} were spiked with methanol/water solution (v/v, 8:2) and measured. The obtained results were showed good selectivity in the Table 1.

Table 1. Determination of zinc ion in methanol/water (v/v, 8:2) samples solution.

Zn(II) (mg L^{-1})		
Added	Found	Recovery (%)
5	5.15±0.05	103.0
10	10.22±0.06	102.2
20	19.88±0.05	99.40

4. CONCLUSION

A new probe 4-(furan-2-ylmethyleneamino)-2,3-dimethyl-1-phenyl-1,2-dihydropyrazol-5-one (M1) was designed and applied as optical and electrochemical sensor in methanol. It exhibited a sensitive and selective ratiometric optical response towards Zn^{2+} ions over various metal ions. The favorable 1:1 stoichiometry coordination between chemosensor M1 with Zn^{2+} was obtained by Job's method and the high binding constant 0.68×10^4 M^{-1} and low limit of detection (LOD) 8.43×10^{-7} M were calculated through titration methods. Furthermore, the chemosensor M1 also exhibited notable potential changes with Zn^{2+} ions in DPV. Reported chemosensor could be applied for routine analysis as bare eye and real time sensor.

Reference

1. Z. Xu, J. Yoon and D. R. Chem, *Chem. Soc. Rev.*, 39 (2010) 1996.

2. A.P. de Silva, H.Q.N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, *Chem. Rev*., 97 (1997) 1515.
3. M. Suresh, A. Ghosh, A. Das, *Chem. Commun*., (2008) 3906.
4. M.R.B. Binet, R. Ma, C.W. McLeod, R.K. Poole, *Anal. Biochem*., 318 (2003) 30.
5. A. Matusch, C. Depboylu, C. palm, B. Wu, G.U. Hogliner, M.K.H. Schafer, J.S. Becker, *J. Am. Soc. Mass Spectrom*., 21 (2010) 161.
6. Q. Zhao, F. Li and C. Huanga, *Chem. Soc. Rev*., 39 (2010) 3007.
7. M. Taki, J.L. Wolford, T.V. O'Halloran, *J. Am. Chem. Soc*., 126 (2004) 712.
8. F. Qian, C.-L. Zhang, Y.-M. Zhang, W.-J. He, X. Gao, P. Hu, Z.-J. Guo, *J. Am. Chem. Soc*., 131 (2009) 1460.
9. Z. Guo, F. Feng, Y. Hou, N.J. Renault, *Talanta*, 65 (2005) 1052.
10. M. Shamsipur, M. Yousefi, M. Hosseini, M.R. Ganjali, H. Sharghi and H. Naeimi, *Anal. Chem*., 73 (2001) 2869.
11. J.M. Berg, Y. Shi, *Science*, 271 (1996) 1081.
12. W. Maret, *Biometals*, 14 (2001) 187.
13. B.L. Vallee, K.H. Falchuk, *Physiol. Rev*., 73 (1993) 79.
14. K. Tayade, J. Gallucci, H. Sharma, S. Attarde, R. Patil, N. Singh and A. Kuwar, *Dalton Trans*., 43 (2014) 3584.
15. G.J. Fosmire, *Am. J. Clin. Nutr*., 51 (1990) 225.
16. S. Homma, R. Jones, J. Qvist, W.M. Zapol, L. Reid, *Hum. Pathol*., 23 (1992) 45.
17. P. Roy, K. Dhara, M. Manassero, J. Ratha and P. Banerjee, *Inorg. Chem*., 46 (2007) 6405.
18. N.K. Wills, V.M.S. Ramanujam, N. Kalariya, J.R. Lewis and F.J.G.M. van Kuijk, *Eye Res*., (2008) 878.
19. L.C. Costello and R.B. Franklin, *Mol. Cancer*, 5 (2006) 17.
20. T.-B. Wei, P. Zhang, B.-B. Shi, P. Chen, Q. Lin, J. Liu, Y.-M. Zhang, *Dyes Pigments*, 97 (2013) 297.
21. J. Mertens, F. Degryse, D. Springael and E. Smolders, *Environ. Sci. Technol*., 41 (2007) 2992.
22. V. Amendola, L. Fabbrizzi, F. Forti, M. Licchelli, C. Mangano, P. Pallavicini, A. Poggi, D. Sacchi and A. Taglieti, *Coord. Chem. Rev*., 250 (2006) 273.
23. R.R. Crichton, Biological inorganic chemistry: an introduction, *Elsevier*, 2008.
24. M. Kumar, L.K. Kumawat, V.K. Gupta, A. Sharma, *ChemistryOpen*, 4 (2015) 626.
25. V.K. Gupta, A.K. Singh, L.K. Kumawat, *Sens. Actuators* B, 195 (2014) 98.
26. L.K. Kumawat, N. Mergu, A.K. Singh, V.K. Gupta, *Sens. Actuators* B, 212 (2015) 389.
27. V.K. Gupta, M.R. Ganjali, P. Norouzi, H. Khani, A. Nayak, S. Agarwal, *Crit. Rev. Anal. Chem*., 41 (2011) 282.
28. P. Jiang, Z. Guo, *Coord. Chem. Rev*., 248 (2004) 205.
29. M. Dutta, D. Das, *TrAC-Trend. Anal. Chem*., 32 (2012) 133.
30. Z. Dong, Y. Guo, X. Tian, J. Ma, *J. Lumin*., 134 (2013) 635.
31. V.K. Gupta, A.K. Singh, N. Mergu, *Electrochim. Acta*, 117 (2014) 405.
32. G. Sivaraman, T. Anand, D. Chellappa, *Analyst*, 137 (2012) 5881.
33. L. Xue, Z. Fang, G. Li, H. Wang, H. Jiang, *Sens. Actuators B* 156 (2011) 410.
34. N. Mergu, A.K. Singh, V.K. Gupta, *Sensors*, 15 (2015) 9097.
35. J.S. Kim, D.T. Quang, *Chem. Rev*. 107 (2007) 3780.
36. S.K. Shoora, A.K. Jain, V.K. Gupta, *Sens. Actuators* B, 216 (2015) 86.
37. Y.-J. Gong, X.-B. Zhang, C.-C. Zhang, A.-L. Luo, T. Fu, W. Tan, G.-L. Shen and R.-Q. Yu, *Anal. Chem*., 84 (2012) 10777.
38. X.L. Hu, I.C. Rodriguez, K. Meyer, *J. Am. Chem. Soc*., 126 (2004) 13464.
39. Y. Cai, X. Meng, S. Wanga, M. Zhu, Z. Pan, Q.X. Guo, *Tetrahedron Lett*., 54 (2013) 1125.
40. V.K. Gupta, A.K. Singh, L.K. Kumawat, N. Mergu, *Sens. Actuators* B, 222 (2016) 468.

41. P. Li, X. Zhou, R. Huang, L. Yang, X. Tang, W. Dou, Q. Zhao and W. Liu, *Dalton Trans*., 43 (2014) 706.
42. K. Kaur, M. Kaur, A. Kaur, J. Singh, N. Singh, S.K. Mittal and N. Kaur, *Inorg. Chem. Front*., 1 (2014) 99.
43. D.-Y. Wu, L.-X. Xie, C.-L. Zhang, C.-Y. Duan, Y.-G. Zhao and Z.-J. Guo, *Dalton Trans*., (2006) 3528.
44. Y. Weng, Z. Chen, F. Wang, L. Xue, H. Jiang, *Anal. Chim. Acta*, 647 (2009) 215.
45. S.C. Yin, J. Zhang, H.K. Feng, Z.J. Zhao, L.W. Xu, H.Y. Qiu, B.Z. Tang, *Dyes Pigment*, 95 (2012) 174.
46. H.G. Lee, J.H. Lee, S.P. Jang, In Hong Hwang, S.-J. Kim, Y. Kim, C. Kim, R.G. Harrison, *Inorg. Chim. Acta*, 394 (2013) 542.
47. Z. Wu, Q. Chen, G. Yang, C. Xiao, J. Liu, S. Yang, J.S. Ma, *Sens. Actuators B*, 99 (2004) 511.
48. X.Y. Liu, D.R. Bai and S. Wang, *Angew. Chem. Int. Ed*., 118 (2006) 5601.
49. V.K. Gupta, N. Mergu, L.K. Kumawat, A.K. Singh, *Sens. Actuators* B, 207 (2015) 216.
50. V.K. Gupta, N. Mergu, L.K. Kumawat, *Sens. Actuators* B, 223 (2016) 101.
51. V.K. Gupta, S.K. Shoora, L.K. Kumawat, A.K. Jain, *Sens. Actuators* B, 209 (2014) 15.
52. V.K. Gupta, N. Mergu, L.K. Kumawat, A.K. Singh, *Talanta*, 144 (2015) 80.
53. V.K. Gupta, N. Mergu, A.K. Singh, *Sens. Actuators* B, 220 (2015) 420.
54. M. Kumar, L.K. Kumawat, V.K. Gupta, A. Sharma, *RSC Adv.*, 5 (2015) 106030.
55. V.K. Gupta, A.K. Singh, L.K. Kumawat, *Sens. Actuators* B, 204 (2014) 507.
56. T. Wei, J. Wang, Y. Chena and Y. Han, *RSC Adv.*, 5 (2015) 57141.
57. H.A. Benesi, J.H. Hildebrand, *J. Am. Chem. Soc*., 71 (1949) 2703.
58. V.K. Gupta, R.N. Goyal, M.A. Khayat, P. Kumar and N. Bachheti, *Talanta*, 69 (2006) 1149.
59. V.K. Gupta, D.K. Chauhan, V.K. Saini, S. Agarwal, M. Antonijevic and H. Lang, *Sensors*, 3 (2003) 223.
60. V.K. Gupta, A.K. Jain, R. Mangla, P. Kumar, *Electroanalysis*, 13 (2001) 1036.
61. V.K. Gupta, A. Kumar, R. Mangla, *Sens. Actuators B*, 76 (2001) 617.
62. V. K. Gupta, A. K. Jain and G. Maheshwari, *Talanta*, 72(4) (2007) 1469-1473.
63. V. K. Gupta, M. R. Ganjali, P. Norouzi, H. Khani, A. Nayak, and Shilpi Agarwal, *Critical Reviews in Analytical Chemistry*, 41(2011)282–313.
64. V. K. Gupta, A. K. Jain, Shiva Agarwal and G. Maheshwari, Talanta, 71(2007)1964-1968 .
65. R. Jain, V. K. Gupta , N. Jadon, K. Radhapyari, *Analytical Biochemistry*, 407 (2010) 79–88
66. R.N..Goyal, V.K. Gupta, S. Chatterjee, *Sensors and Actuators*, B: 149 (2010)252-258.
67. V. K. Gupta, A. K. Jain, L. P. Singh, U. Khurana, *Anal. Chim. Acta*, 355(1997)33-41 (1997).
68. A. K. Jain, V. K.Gupta, U. Khurana, L. P. Singh, *Electroanalysis*, 9(1997) 857-860.
69. S. K. Srivastava, V. K. Gupta, S. Jain, *Analyst*, 120(1995)495-498.
70. S. K. Srivastava, V. K. Gupta, M. K. Dwivedi, S. Jain, *Analytical Proceedings including Analytical Communications*, 32, 21-23 (1995).
71. V. K. Gupta, Shilpi Agarwal, Barkha Singhal, *Combinatorial Chemistry & High Throughput Screening*, 14(4)(2011) 284-302.
72. H. Khani, M. K. Rofouei, P. Arab, V. K. Gupta, Z. Vafaei, *J. Hazardous Materials*, 183 (2010)402-409.
73. S. K. Srivastava, V. K. Gupta, S. Jain, *Anal. Chem*., 68(1996)1272-1275.