RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Novel fluorescent chemosensing of CN^- anion with nanomolar detection using Zn^{2+}-isonicotinohydrazide metal complex

Kundan Tayade[a], Nilesh Khairnar[a], Shilpa Bothra[b], Suban K. Sahoo[b], Jasminder Singh[c], Narinder Singh[c], Ratnamala Bendre*[a], Anil Kuwar*[a]

[a]School of Chemical Sciences, North Maharashtra University, Jalgaon, 425001 (MS) India
[b]Department of Applied Chemistry, SV National Institute Technology, Surat-395007 (Gujrat) India.
[c]Department of Chemistry, Indian Institute Technology, Ropar-140 001 (Punjab) India.

Abstract

A novel chemosensor based on Zn^{2+}-isonicotinohydrazide complex **'(ZnL)'** was developed for the selective detection of cyanide (CN^-) over other tested anions, such as HSO_4^-, F^-, Cl^-, Br^-, I^-, NO_3^-, PO_4^{3-}, $SO4^{2-}$, SCN^-, S^{2-}, CH_3COO^- and $H_2PO_4^-$ in 100% aqueous medium. The detection of CN^- with **(ZnL)** can be possible with both UV-visible and fluorescence responses without any interference effects from other anions. This system shows excellent sensitivity with a lower detection limit of 5.49 nM.

Keywords: Chemosensor, Zn^{2+}-complex, Cyanide anion, Fluorescent 'turn-on' sensor.

*Corresponding author -E-mail: kuwaras@gmail.com, bendrers@rediffmail.com

Introduction

In the recent era, molecular recognition of anions by synthetic receptors is an emerging field of research as they play pivotal roles in various fields such as environmental, clinical, chemical, industrial and biological [1-4]. However, the design of chemosensor for anions is a challenging task because of the diversified geometries of anions, lower charge to radius ratio, high hydration energy, and the weak electrostatic interactions between anions and receptors [4]. Among various anions, cyanide serves as an important raw material in various industrial processes such as electroplating, metallurgy, production of organic chemicals and plastics, photographic developing, mining manufacturing and tanning [5]. On the other end, it is extremely toxic to mammals, leading to vomiting, loss of consciousness and adverse effects on central nervous, cardiac, endocrine, and metabolic systems and eventually leads to death [6]. The cyanide toxicity is due to its reaction with the trivalent iron in the cytochrome oxidase (cyt aa3), which inhibits electron transport and thus preventing the cells from consuming oxygen, leading to rapid impairment of the vital functions [7]. Hyperbaric oxygen (HBO), hydroxocobalamin, dicobalt-EDTA and 4-dimethylaminophenol (DMAP) are cyanide antidotes, which are effective in human cyanide poisoning [8]. At pH less than 8, cyanide exists in water as HCN causes more harmful effect to aquatic life than the free cyanide ion [9]. Therefore, the permissible limit for cyanide concentration in drinking water by the World Health Organization (WHO) is lower than 1.9 μM [10].

Various methods such as titrimetric [11], voltammetric [12], potentiometric [13], electrochemical methods [14], ion chromatography [15], etc. employed for the determination of cyanides are time consuming and require the use of sophisticated instrumentation with high detection limits. Hence, optical chemosensors based on chromogenic and fluorescent responses are developed recently due to their simplicity, inexpensive, and rapid online monitoring without the use of sophisticated instruments [16] for the detection of cyanide ions in aqueous media.

As part of our ongoing research on anion recognition [17], In this communication, we have developed an easy-to-prepare Zn^{2+} complex (**'(ZnL)'**) (**Figure 1**) [18] for the selective detection of cyanide ions from 100% aqueous medium. The Zn^{2+} complex **'(ZnL)'** renders two amine groups act as recognition sites for CN^{-} ion.

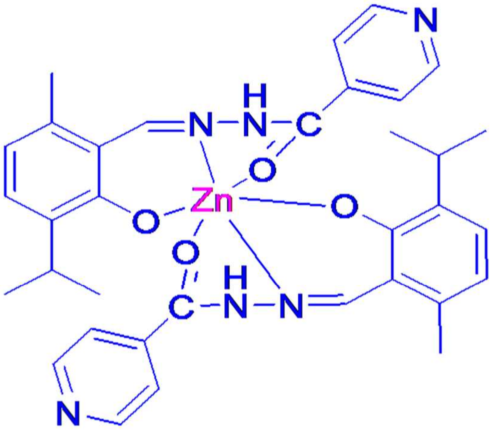

Figure 1. Molecular structure of **'(ZnL)'** developed for the recognition of CN^{-}ions.

Experimental

Materials and reagents

All commercial grade chemicals and solvents were procured from Sigma Aldrich, S.d fine Chemicals, India and Merck Ltd India and were used without any further purification. The anions were added in the form of tetra-n-butyl ammonium (TBA) salts. The Zn^{2+} complex **'(ZnL)'** was synthesized by following our recently reported method [18]. The fluorescence and UV-visible spectra were recorded respectively on a fluoromax-4 spectrofluorometer and Shimadzu UV-2450 in the range of 200-600 nm, respectively at room temperature using 1 cm path length cuvette.

Anion sensing ability of '(ZnL)'

The recognition studies were performed at room temperature, and the solution was shaken well before recording the reading to ensure uniformity. The selective colorimetric sensing ability of **'(ZnL)'** (1×10^{-5} M) towards different anions (1×10^{-4} M) were monitored by naked-eye observation, UV–Vis and fluorescence spectra.

Results and discussion

The anions recognition ability of **'(ZnL)'** was examined by both UV-visible and fluorescence spectroscopic methods in the absence and presence of TBA salts of different anions such as HSO_4^-, F^-, Cl^-, Br^-, I^-, NO_3^-, PO_4^{3-}, $SO4^{2-}$, SCN^-, S^{2-}, CH_3COO^- and $H_2PO_4^-$ in aqueous medium (**Figure 2**). The complex **'(ZnL)'** showed two main absorptions at 307 nm and 351 nm due to multiple transitions (π-π^* and n-π^*) from the coordinated ligand. No significant spectral changes of **'(ZnL)'** were observed upon addition of anions, except CN^-. Upon addition of one equivalent of CN^-, the absorption maximum of **'(ZnL)'** at 307 nm was disappeared and shifted hyperchromically at 351 nm. The absence of bathochromic shift, suggesting the anion-receptor complexation occurred due to the interactions of amine protons with the cyanide anions. The **'(ZnL)'.**CN^- complex structure is theoretically predicted in the gas phases by applying the density functional theory (DFT) method using Gaussian 09W software [19] is shown in **Figure 3**. For this calculation, the exchange-correlation functional B3LYP was used and the basis sets 6-31G(d,p) for C, H, N and O atoms, and LANL2DZ for the Zn atom.

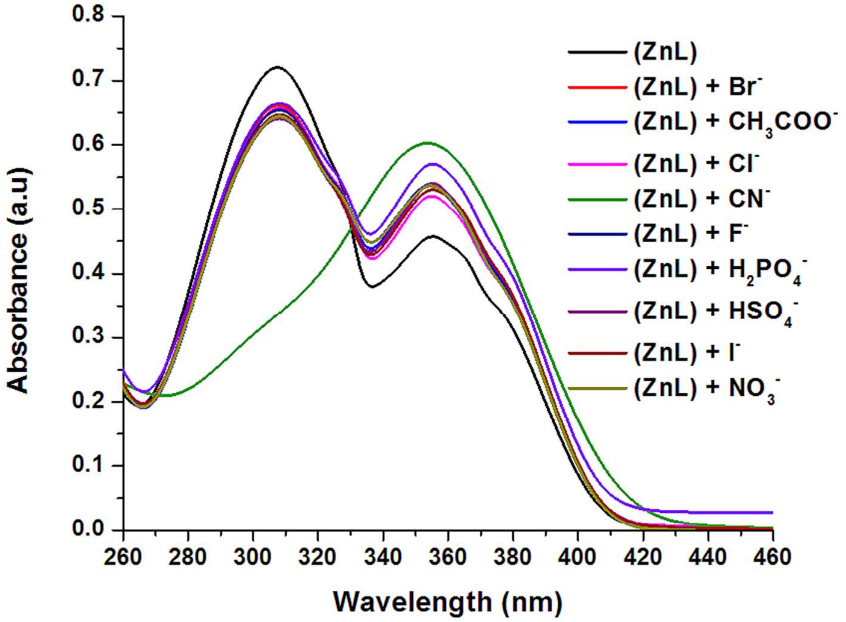

Figure 2. The absorption spectral changes of **'(ZnL)'** (1×10^{-5} M) in the absence and presence of one equivalent of various anions.

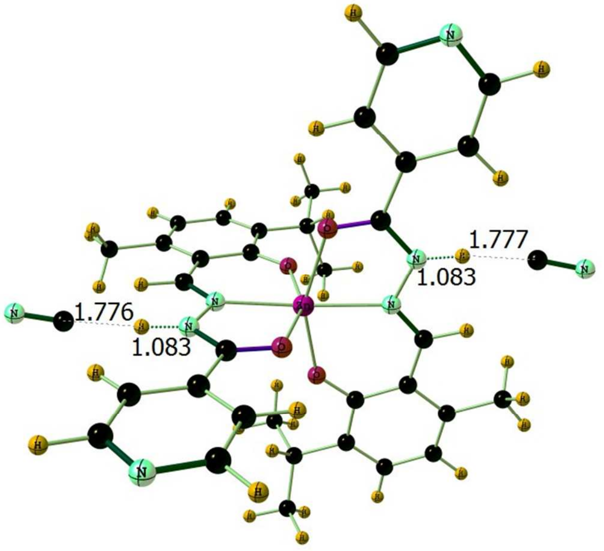

Figure 3. The DFT computed optimized structure of **'(ZnL)'**.CN^- Complex.

Under optimized conditions, we next evaluated the sensitivity of the proposed sensor towards CN^-. Upon addition of increasing concentrations of CN^-, it was observed that the absorption maxima exhibited by the free receptor **'(ZnL)'** at 307 nm was decreased and a concomitant rise in the absorption intensity at 351 nm with the appearance of a well-defined isosbestic point at 326 nm, which indicates the formation of a new species upon interaction of **'(ZnL)'** with CN$^-$ (**Figure 4**). The absorption intensity at 351 nm increases with the continuous increase of CN$^-$ concentrations showing the potential application of **'(ZnL)'** as a ratiometric chromogenic sensor for the detection of CN$^-$.

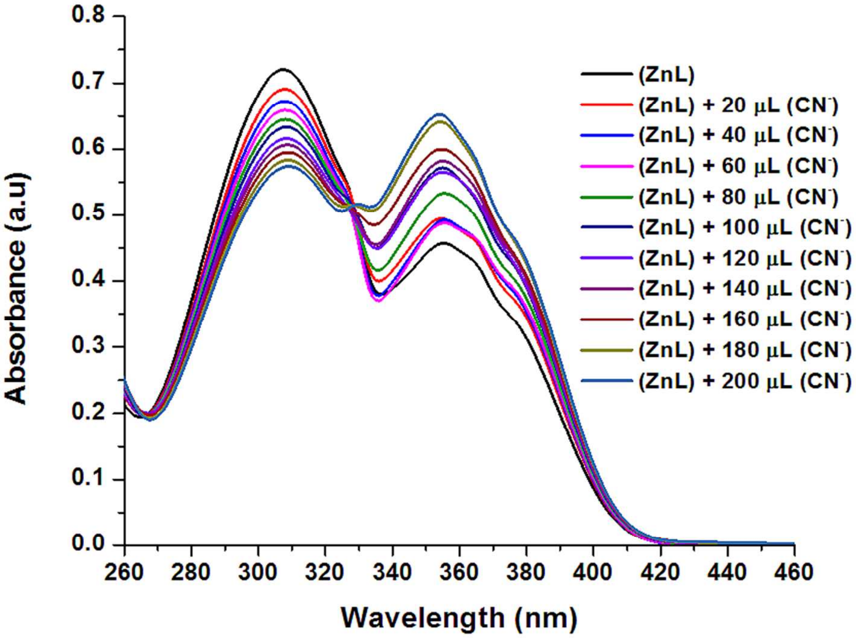

Figure 4. The absorption spectral changes of **(ZnL)** (1×10^{-5} M) with the successive addition of CN$^-$ (1×10^{-4} M) in aqueous medium.

The fluorescence study of **'(ZnL)'** was also investigated in the absence and presence of various TBA salts (1×10^{-4} M) of HSO$_4^-$, F$^-$, Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, PO$_4^{3-}$, SO4^{2-}, SCN$^-$, S^{2-}, CH$_3$COO$^-$ and H$_2$PO$_4^-$ anions. The receptor **'(ZnL)'** showed a weak fluorescence emission at 545 nm upon excitation at 351 nm. It was observed that on addition of CN$^-$, the emission of **'(ZnL)'** at 545 nm was significantly enhanced and also shifted to 535 nm ($\Delta\lambda_{em}$ = 10 nm) making it easier to distinguish CN$^-$ ions from other tested anions (**Figure 5**). The sensing mechanism for the blue shift could be attributed due to induces charge transfer (ICT) interaction between CN$^-$ having a weaker negative charge density and the electron rich donor array of amines and carbonyl groups of **'(ZnL)'**. The CN^{-} ion shows high binding affinity because of its tendency to undergo protonation.

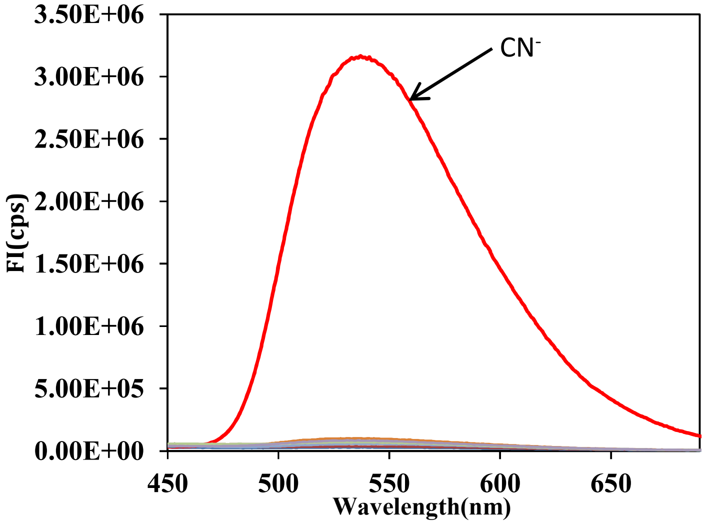

Figure 5. Fluorescence spectra of **(ZnL)** (1×10^{-5} M) in the absence and presence of different anions in aqueous medium.

In addition to selective recognition of CN^{-} ion with **(ZnL)**, it gives remarkable fluorescent color which can be visually detected by the naked-eye and under UV irradiation. Visual detection studies of receptor **(ZnL)** (1×10^{-5} M) were conducted with all anion (CN^{-}, HSO_4^{-}, F^{-}, Cl^{-}, Br^{-}, I^{-}, NO_3^{-}, CH_3COO^{-} and $H_2PO_4^{-}$). The receptor **(ZnL)** solution does not show any significant fluorescence at room temperature. But, it was observed that in presence of anions (10.0 equivalents) the receptor **(ZnL)** showed spectacular fluorescent color selectively for CN^{-} ions, which is also supported by fluorescence spectral changes (**Figure 5**).

It was also observed that there was a moderately small change in the emission spectra of **(ZnL)**, when 1 equivalent of other anions were introduced into the sensing ensemble, whereas CN^{-} showed fairly good intensity indicating selectivity of receptor **(ZnL)** towards CN^{-} (**Figure 6**). Specificity is a very important parameter to evaluate the performance of a sensor. Therefore, the interference of various anions in the detection of CN^- by **(ZnL)** was investigated. The competitive experiments of **(ZnL)** were conducted in the presence of 1 equiv. of CN^- mixed with excess of other interfering anions (2 equiv.). No interference was shown by any anions in the receptor **(ZnL)** system containing CN^- ions (**Figure 7**). These results indicate that the receptor **(ZnL)** shows a good selectivity and specificity towards CN^- over other competitive anions.

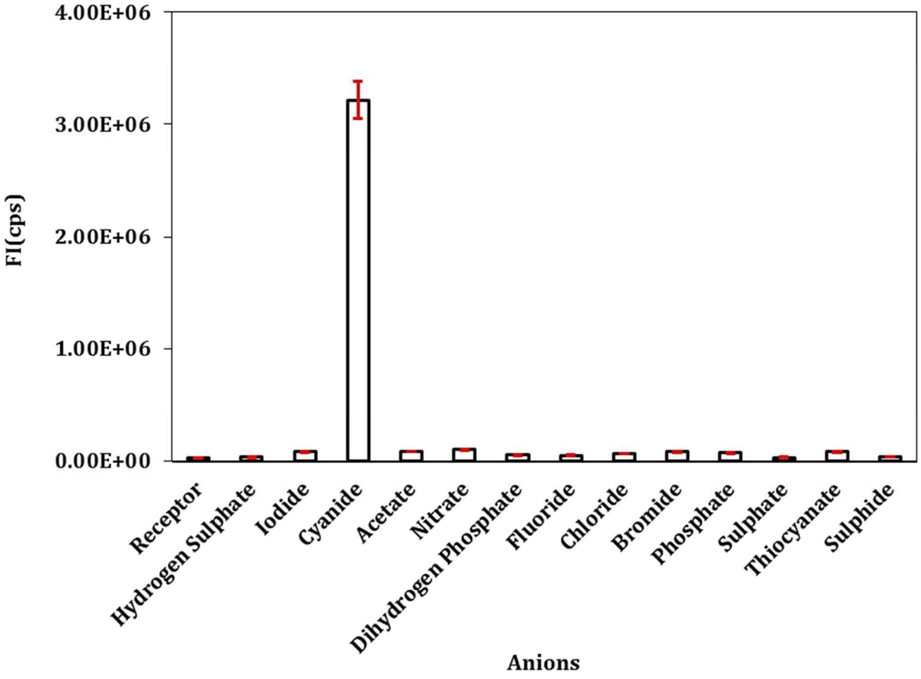

Figure 6. Response of receptor **(ZnL)** towards various anions.

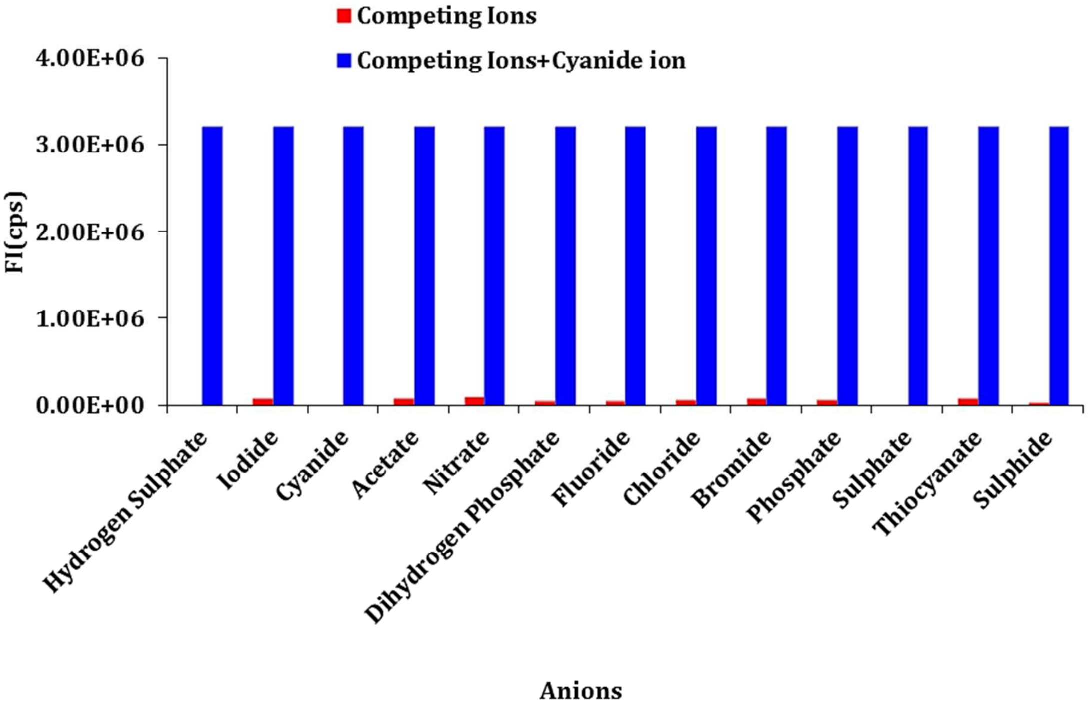

Figure 7. Specificity of the receptor **(ZnL)** towards various anions (2 equivalents) in the presence of CN^{-} (1 equivalents).

The binding study of **(ZnL)** towards CN^{-} was further investigated by emission spectroscopy titration. Upon progressive addition of CN^{-} (0 to 10 equiv.) in the aqueous solution of **(ZnL)**, a gradual enhancement of the fluorescence at 535 nm was observed (**Figure 8**). Linear fitting of the titration curves were done using Benesi-Hildebrand Plot ((1/Δ*F*) vs 1/ [*G*]) [20] (**Figure S1**), Scatchard plot (Δ*F*/ *[G] vs* Δ*F*) [21] (**Figure S2**) and Connor plot (*(1-F/F$_0$)/ [G]* vs *F/F$_0$*) [22] (**Figure S3**). The association constant (K) was calculated to be $3.35 \pm 0.2 \times 10^5$ M^{-1} using the following equations:

$$\mathbf{1/F - F_0 = (1/F_\infty - F_0)\,K[G] + 1/F_\infty - F_0} \tag{2}$$

$$\mathbf{F_\infty - F_0/[G] = (F_\infty - F_0)K - (F - F_0)K} \tag{3}$$

$$\mathbf{1 - (F/F_0)/[F] = K\,(F/F_0) - \propto K} \tag{4}$$

Where, F_0 represents the fluorescence intensity in the absence of guest ion, F represents the fluorescence intensity in the presence of guest ion, F_∞ represents fluorescence intensity after titration and [G] represents the concentration of guest.

The detection limit was also determined by using the emission titration data (**Figure S4**). The developed receptor **(ZnL)** can be used for the sensitive recognition of CN^- with the detection limit down to a low concentration of 5.49 nM, which is lower than the previously reported detection limit as depicted in Table S1.This estimation done by using the equation:

$$[\boldsymbol{G}]_{\boldsymbol{Total}} = \boldsymbol{a}/\mathbf{2}\boldsymbol{K}\,(\mathbf{1}-\boldsymbol{a})^{\mathbf{2}}\,[\boldsymbol{H}]_{\boldsymbol{tot}} + \boldsymbol{a}[\boldsymbol{H}]_{\boldsymbol{tot}}/\mathbf{2}$$

Where $[G]_{tot}$ is the total concentration of guest, $[H]_{tot}$ is the total concentration of host, a = (F-F_0)/ (F_i- F_0).

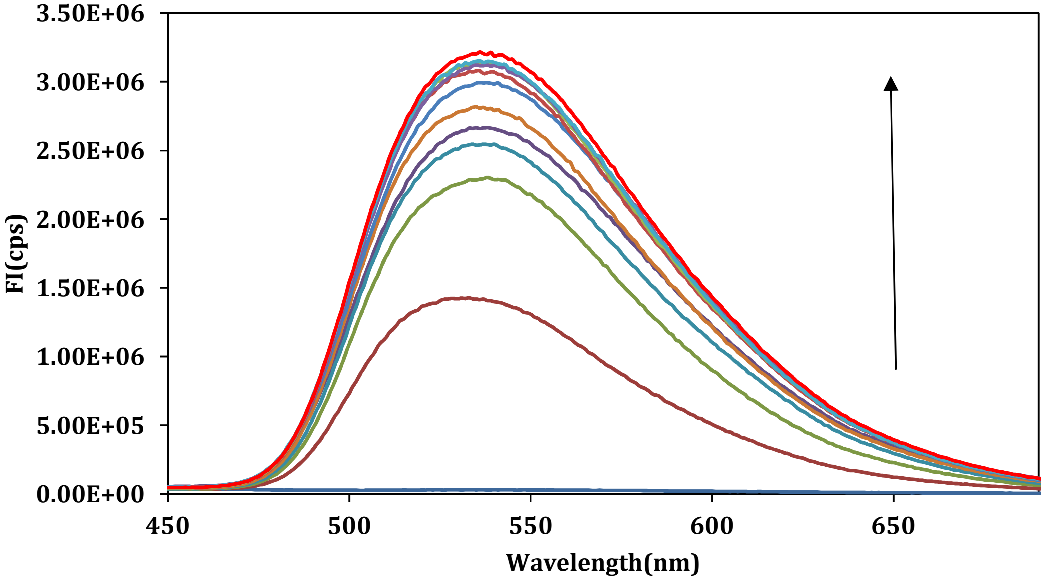

Figure 8. Fluorescence spectra of **(ZnL)** (1 × 10^{-5} M) after the successive addition of CN^- (1 × 10^{-4} M) in aqueous medium.

The proposed receptor can also be used for visual or naked eye determination of cyanide in aqueous media. As cyanide ion is being introduced into the solution of (ZnL), its fluorescent yellow colour changes to dark orange (**Figure 9**). Hence it can be said that the proposed zinc complex can be used determination of cyanide in aqueous samples using UV-Visible, fluorescence and naked eye determination.

Figure 9. Naked eye determination of cyanide ion in aqueous sample using (ZnL)

Conclusions

A colorimetric and fluorescent sensing ensemble complex **(ZnL)** was developed for the highly selective and sensitive detection of cyanide ion in 100% aqueous medium. The ensemble is extremely easy-to-prepare and simple for qualitative and quantitative detection of cyanide using the donor–acceptor type of sensor with a remarkable turn-ON fluorescence response. This system can be used to detect CN^- either visually or spectrophotometrically, with unprecedented high selectivity towards cyanide over a wide range of other mono- and di-anions. Also, this system allows detection of cyanide at a concentration down to 5.49 nM.

References

1. (a) M. M. G. Antonisse, D. N. Reinhoudt, Electroanalysis, 1999, 11, 1035; (b) F. P. Schmidtchen, M. Berger, Chem. Rev., 1997, 97, 1609.
2. (a) A. Bianchi, K. B. James, E. G. Espana, Supramolecular Chemistry of Anions ed. Wiley-VCH: New York, NY, 1997; (b) J. L. Sessler, P. A. Gale, W. S. Cho, In Anion Receptor Chemistry; J. F. Stoddart, ed. Monographs in Supramolecular Chemistry, RSC: Cambridge, UK, 2006.
3. (a) R. Dutzler, E. B. Campbell, R. Mackinnon, Science, 2003, 300, 108; (b) C. Miller, Nature, 2006, 440, 484; (c) X. H. Cheng, Y. Zhou, J. G. Qin, Z. Li, ACS Appl. Mater. Interfaces, 2012, 4, 2133; (d) S. Xu, B. Liu, H. Tian, Prog. Chem., 2006, 6, 688.
4. (a) D. Sharma, A. R. Mistry, R. K. Bera, S. K. Sahoo, Supramol. Chem., 2013, 25, 212; (b) D. Sharma, S. K. Sahoo, S. Chaudhary, R. K. Bera, J. F. Callan, Analyst, 2013, 138, 3646; (c) D. Sharma, A. Kumar SK, S. K. Sahoo, Tetrahedron lett., 2014, 55, 927; (d) D. Sharma, S. K. Sahoo, R. K. Bera, R. Kamal, J. Fluoresc., 2013, 23, 387.
5. (a) G. Qian, X. Li, Z. Wang, J. Mater. Chem., 2009, 19, 522; (b) L. Peng, M. Wang, G. Zhang, D. Zhang, D. Zhu, Org. Lett., 2009, 11, 1943.
6. (a) S. I. Baskin, T. G. Brewer, Medical Aspects of Chemical and Biological Warfare, ed. F. Sidell, E. T. Takafuji, D. R. Franz, TMM Publication, Washington, DC, 1997, 10, 271; (b) R. W. Mayes, J. Forensic Sci., 1991, 36, 179; (c) J. Zamecnik, J. Tam, J. Anal. Toxicol., 1987, 11, 47; (d) B. C. Levin, P. R. Rechani, J. L. Gurman, F. Landron, H. M. Clark, M. F. Yoklavich, J. R. Rodriguez, L. Dros, F. Mattos de Cabrera, S. Kaye, J. Forensic Sci., 1990, 35, 151.
7. M. Noroozifar, M. K. Motlagh, R. Z. Dorabei, Talanta, 2007, 72, 1773.
8. K. K. Lam, F. L. Lau., Am. J. Emerg Med., 2000, 18, 172.

9. Guidelines for Interpreting Water Quality Data, British Columbia, Canada: The Resources Inventory Committee; 1998.
10. Guidelines for Drinking-Water Quality; World Health Organization: Geneva, 1996.
11. T. Suzuki, A. Hiolki, M. Kurahashi, Anal. Chim. Acta, 2003, 476, 159.
12. A. Safavi, N. Maleki, H. R. Shahbaazi, Anal. Chim. Acta, 2004, 503, 213.
13. D. Shan, C. Mousty, S. Cosnier, Anal. Chem., 2004, 76, 178.
14. V. K. Rao, S. R. Suresh, N. B. S. N. Rao, P. Rajaram, Bull. Electrochem., 1997, 13, 327.
15. T. T. Christison, J. S. Rohrer, J. Chromatogr., A, 2007, 31, 1155.
16. (a) Z. Xu, X. Chen, H. N. Kim and J. Yoon, Chem. Soc. Rev., 2010, 39, 127; (b) F. Wang, L. Wang, X. Chen and J. Yoon, Chem. Soc. Rev., 2014, 43, 4312.
17. (a) U. Fegade, S. K. Sahoo, A. Singh, P. Mahulikar, S. Attarde, N. Singh and A Kuwar, RSC Adv., 2014, 4, 15288; (b) R Patil, K Tayade, S. K. Sahoo, J. Singh, N. Singh, D. Hundiwale and A. Kuwar, J. Mol. Recognit., 2014, DOI: 10.1002/jmr.2392.
18. K. Tayade, S. K Sahoo, B. Bondhopadhyay, V. K. Bhardwaj, N. Singh, A. Basu, R. Bendre, A. Kuwar, Biosensor and Bioelectronics, 2014, 61, 429.
19. M. J. Frisch, Gaussian 09, Revision A.1, Gaussian Incorp., Wallingford, CT, 2009.
20. H. A. Benesi, J. H. Hildebrand, J Am Chem Soc. 1949, 71, 2703.
21. G. Scatchard, Annals of the New York Academy of Sciences, 1949, 51, 660.
22. K. A. Connors, The measurements of molecular complex stability. Wiley, New York 1987.