Review Article

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Trace Level Determination of Various Types of Analyte Using Selective Chemosensor: A General Survey

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Trace level determination of analyte is an extremely important phenomenon and highly relevant area of environmental science, biology, medicine and pharmacology. In this review we have described different type of chemosensor that have been used so far for trace level determination of different types of analyte. Applications of chemo sensor in the arsenic determination have been discussed here. Determination of amino acid by fluorescence spectroscopy has been depicted. Detection of poisonous organic analytes by chemosensor have been made. Some chemosensors have been found to be effective to the determination of selective cations. Various techniques used for determination of analyte by using chemo sensor as well as probable sensing mechanism have been explained here.

Key words: Chemosensor, As(III) determination, Amino acid sensing, Poisonous organic analytes, Cation sensing

1. Introduction

Development of chemosensor for specific analyte is current research interest for the facile monitoring of analytes [1–2] . Chemical sensor is an analytical device which can analysis the information about the chemical composition of substance present in environment, living system and other various system [3–4]. Chemical sensor has widely applicability in the versatile fields like environmental science, biology, medicine and pharmacology. The importances of fluorescent chemosensors are increasing in the field of environmental monitoring, food processing biomedical technology and clinical analysis. The information about the sample is collected in the form of a measurable physical signal that is interrelated with the concentration of the substances. In general fluorescent chemosensors are widely used for the detection of analytes through real time analysis using optical instrument [5–6]. Determination of analytes by fluorescence spectroscopy has become popular due to its operational simplicity, rapidity, selectivity, sensitivity and less expensive methodology. It has several advantages like high selectivity and sensitivity, in vivo or in vitro testing facility and very low detection limit [7–8]. Fluorescence intensity or emission wavelength of designed chemo sensor is changed upon interaction with the analytes. When fluorescent chemosensor interacts with analytes, the change in fluorescent intensities will be occurred due to the perturbation processes like photoinduced electron or energy transfer (PET), formation or disappearance of excimers or exciplexes [9–10].

2. Arsenic Sensing Agent

In recent time Arsenic pollution in ground water is a major problem. More than 100 million peoples are affected by arsenic contamination in drinking water. It causes several health related problem including dermal changes, respiratory, cardiovascular gastrointestinal and carcinogenic effects [11]. Determination of arsenic in drinking water is essential requirements in our society. Varieties of instrumental methods like atomic absorption spectroscopy and X-ray fluorescence spectroscopy are utilized for arsenic sensing. But such techniques are time consuming as well as costly. To overcome this problem, fluorometric determination provides cheap and safe method for arsenic determination. As(III) is the most toxic among the different oxidation states of arsenic. As(III) likes to bind with O-donor ligand due to its large ionic potential. Dey et. al. have reported a water soluble metal–organic complex, $\{[Cu(n\text{-}BuM)(2,2\text{-bipyridine})(H_2O)]_2[Cu_2(n\text{-}BuM)_2(2,20\text{-bipyridine})_2]6H_2O\}$ [where n-$BuMH_2$ = n-butylmalonic acid]. It is an example of inorganic co-crystal (ICC) of one monomeric and one dimeric units of Cu(II) (Figure 1) and this complex shows selective As^{3+} sensing ability in aqueous medium in the pico-molar concentration range [12].

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This inorganic co crystal exhibits selectivity and sensitivity towards arsenic (III) in water. When the aqueous solution of arsenic (III) is added to the copper complex ranging from 49 pico-molar to 4440 pico molar, the fluorescence intensity of the resulting solutions increases gradually (Figure 2). The sensitivity of the water solution of this compounds towards As^{3+} can not be affected in presence of other metal ions like Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Hg^{2+} and Zn^{2+} ion.

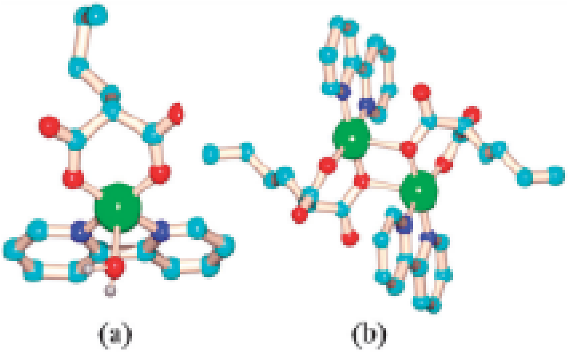


Figure 1. Molecular diagram of the monomeric (a) and dimeric (b) units in $\{[Cu(n\text{-}BuM)(2,2\text{-}bipyridine)(H_2O)]_2[Cu_2(n\text{-}BuM)_2(2,20\text{-}bipyridine)_2]6H_2O\}$(ICC) (C = cyan, N = blue, O = red, Cu = green).

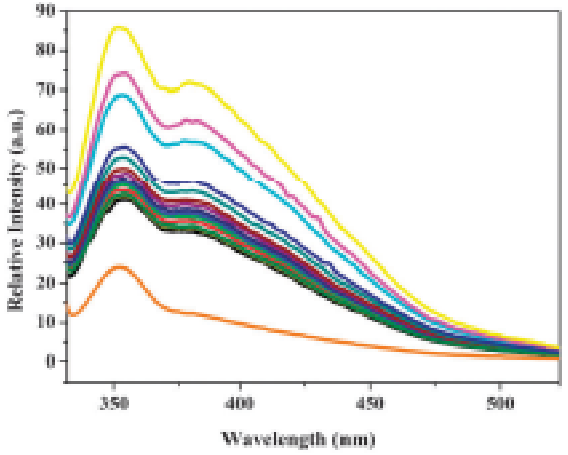


Figure 2. Fluorescence spectra of copper complex in the presence of As^{3+} at different concentrations (initial orange colored spectra only for copper complex in water).

The sensing mechanism can be explained by weak non covalent interaction of the electronically dense lone-pair on free carbonyl oxygen atoms of carboxylate groups of the copper complex with As^{3+}.

3. Fluorescent Probes for Amino Acids

Amino acids are essential component for living organisms as they are the main unit of proteins and peptides. Histidine is useful for human growth and repair of human tissues and its deficiency creates several diseases in human beings [13–14]. Glutamic acid plays a crucial role in brain function as the level of neuronal excitability depends on the relative balance of glutamic acid [15–16]. The abnormal level of glutamic acid may be responsible for several neurological disorders. Several research groups are working in the field of development of chemical sensors for the investigation of various amino acids having significant role in human life [17–19]. In recent time, metal complexes with suitable ligand environment have been utilized as fluorescence and colorimetric probes for amino acids [20–21].

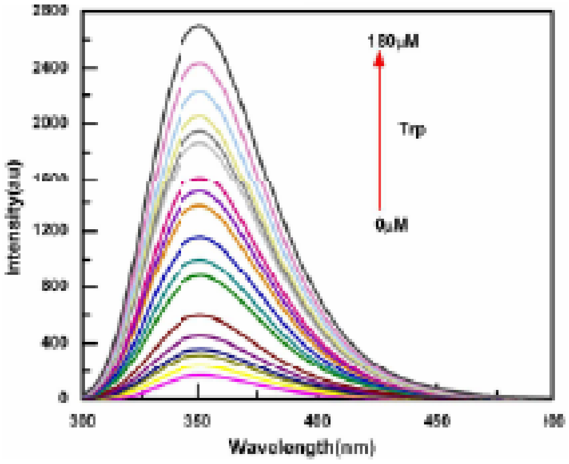


Figure 3. Fluorescence emission spectra of cobalt complex in presence of increasing amount of tryptophan in PBS buffer (pH 7.4). The arrow represents the change in the emission intensity with the increased tryptophan concentration.

A non-toxic, fluorescent probe as cobalt(II) based complex $[Co(PS)_4](ClO_4)_2$ (PS: N-Pyridylsalicylaldimine) was synthesized and characterized by Jana et. al and the reported complex become a convenient luminescent sensor for the recognition of tryptophan (Trp) and Bovine serum albumin (BSA) [22].

Tryptophan selectivity of the cobalt (II) complex was monitored through by noticing the changes in fluorescence emission intensity. Fluorescence Intensity of the mixture is increased by increasing amount of tryptophan as depicted in the Figure 3. The enhancement of fluorescence intensity occurs due to the interaction of NH^{3+} group of tryptophan with methoxy group of cobalt complex.

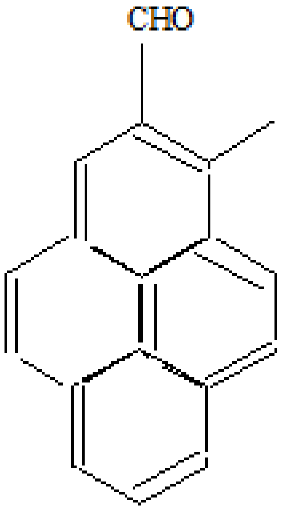
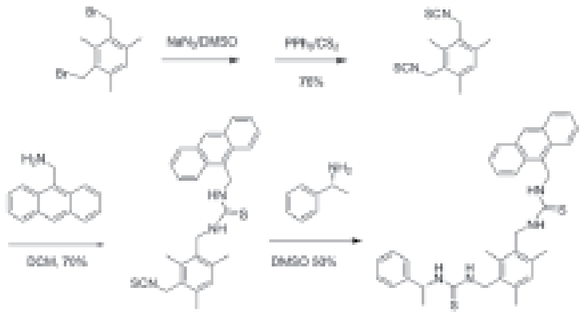


Figure 4. Pyrene based chemosensor for lysine determination.

Another important amino acid, lysine plays a crucial role in krebs cycle and polyamine synthesis. Zhou et al. have synthesized a pyrene based chemo sensor (Figure 4) which has been used as a suitable fluorescent sensor for lysine under neutral conditions [23]. This chemo sensor detected lysine by colormetrically. Here a schiff base is formed upon addition of lysine to the chemo sensor and consequently yellow color is developed.

Xiao-bo Zhou have reported mesitylene based neutral receptors containing thiourea binding sites were designed (Scheme 1) as fluorescent probes for sensing asparate and glutamate. Their binding affinities toward asparate and glutamate have been established in acetonitrile solution by fluorescence titration experiments [24]. In this case, the fluorescent band of the host at 413 nm decreases upon gradual addition of the guest molecule as depicted in Figure 5.



Scheme 1. Synthesis of mesitylene based chemo sensor.

The recognition and sensing of anionic substrates by synthetic receptive molecular systems have been developed by Liu et. al. They prepared a fluorescent di-carboxylate receptor (Figure 6) derived from cholic acid which had great affinity for glutamate [25]. The binding affinities of this fluorescent neutral receptor toward dicarboxylate anions and amino acids have been monitored in a CH_3OH/H_2O system (1 : 1, 0.01 M HEPES buffer, pH 7.4) by fluorescence titration experiments (Figure 7).

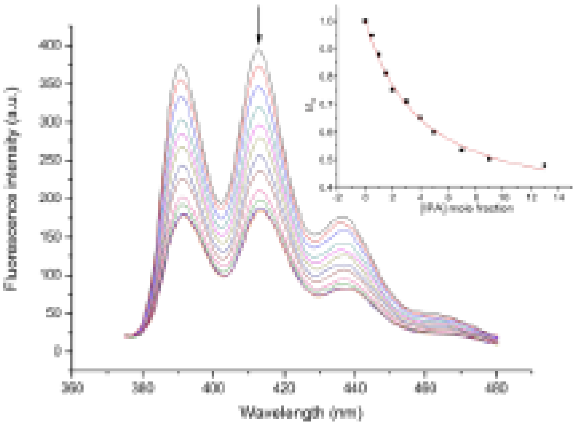


Figure 5. The changes in the fluorescence emission spectra of sensor upon addition of guest in acetonitrile. $\lambda_{ex} = 366$ nm. (Inset) Quenching ratio of sensor as a function of (guest)/(host).

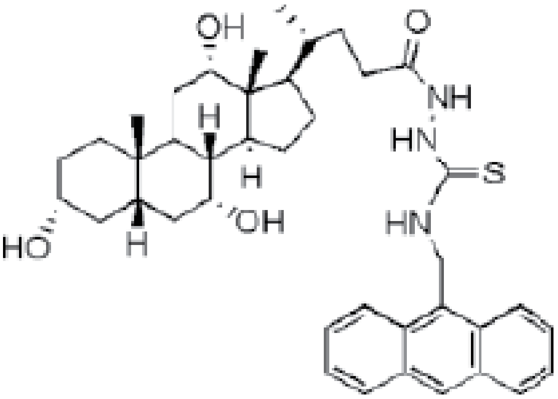


Figure 6. Chemosensor developed from cholic acid.

Another important amino acid for human growth, particularly for children's growth is histidin (His). Deficiency of His-rich protein causes several diseases in human being. There are several method have been applied for its recognition. In recent time, Recognition of His by fluorescence spectroscopy technique has been developed due to the operational simplicity of the process. Das et al have synthesized polymeric copper(II) complex of the ligand L(2-(((2-(phenylamino)ethyl)imino)methyl)phenol) and it has been utilized as a chemosensor for His recognition. The reported compound specifically senses histidine (His) with high selectivity and sensitivity under physiological conditions [26].

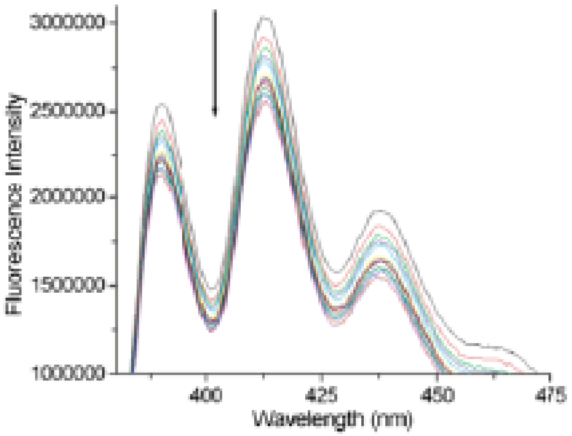
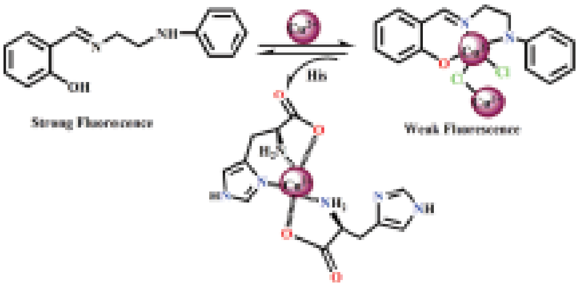


Figure 7. Emission spectra of cholic acid based chemosensor with different concentrations of N-acetyl-L-glutamate in aqueous solution (CH_3OH/H_2O) 1 : 1, 0.01 M HEPES buffer).

When Histidine is added to the copper complex solution, it removes Cu(II) ion from complexes with subsequent release of free ligand (Scheme 2). Enhancement of emission intensity of the resulting solution occurs at 440 nm due to the presence of free ligand.



Scheme 2. Probable mechanism for Histidine recognition.

4. Poisonous Organic Analyte Sensitive Sensors

In recent time, Researchers are involved for the development of synthesis of chemical sensors for the specific detection of metal ions, anions, various poisonous organic analytes and explosives due to their significant role on environment and human life [27–30].

Among various organic analytes, nitroaromatic compounds are serious pollution sources of environment and other security applications because of explosivity and high toxicity. Ghosh et. al have designed and synthesized dinuclear zinc complexes, $[Zn_2LCl_2(H_2O)]$ (1), $[Zn_2L(SCN)_2(H_2O)]\cdot H_2O$ (2), $[Zn_2L(N_3)(CH_3CO_2)]$ (H_2L = N,N′-dimethyl-N,N′-bis(2-hydroxy-3-methoxy-5-methylbenzyl)ethylenediamine) in presence of bridging co-ligands, chloride, thiocyanate/acetate or azide/acetate (Figure 8). The Zn(II) complexes sense nitroaromatic explosives in solution via turn off florescence responses [31].

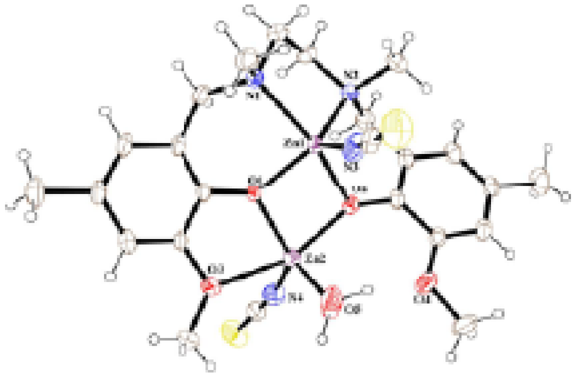


Figure 8. ORTEP view of zinc complex with 30% ellipsoid probability.

Quenching of fluorescence intensity of zinc complex is noticed upon addition of picric acid to the zinc complex with gradual increase in concentration as shown in Figure 9. Fluoroscence intensity decreases by the addition of picric acid. Such quenching phenomenon can be explained due to the polarsibility of the picric acid in methanol and also the π–π interaction between analytes and the host materials. Such interaction may induces the electron transfer from zinc complex to electron deficient picric acid.

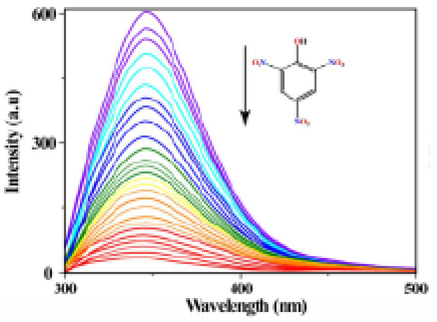


Figure 9. Fluorescence spectra of zinc complex in methanol upon increasing concentration of picric acid.

5. Cation Sensor Activity

Fluorescent chemosensors are also very useful for the detection of cations with high selectivity and sensitivity and very low detection limit even up to nanomolar scale. Various researcher are involved in this research field.

Kundu et al. have designed and synthesized schiff based molecule having fixable aliphatic propyl arm (Figure 10). These molecule bind with Al^{3+} and Zn^{2+} selectively in MeOH-H_2O solvent system. The fluorescence enhancement was observed as depicted in Figure 11. The reported schiff base remains non-fluorescent in solution due to photo-induced electron transfer (PET), excited state intramolecular proton transfer (ESIPT) and C=N bond isomerization. However, after binding with metal ion, chelation-induced enhanced fluorescence (CHEF) comes into play to prevent all the processes and induce dramatic fluorescence increase in the adduct [32]. The sensing mechanism are presented in Scheme 3.

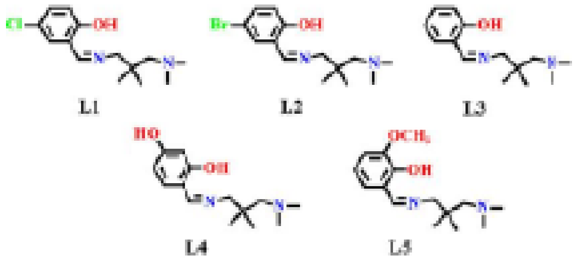


Figure 10. Various type of chemosensor **L1-L5** for cation sensing.

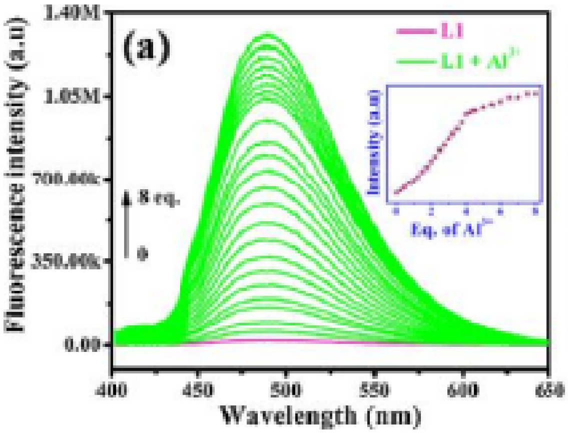
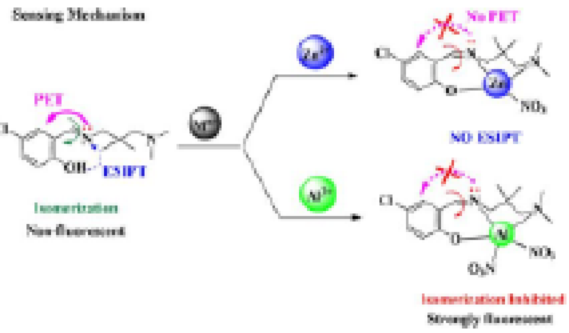


Figure 11. Fluorescence titration spectra of schiff based ligand (10 μM) in CH_3OH/HEPES buffer (at pH ~ 7.4) with addition of $Al(NO_3)_3$.

Kirpik et. al. have synthesized a tridentate bisbenzimidazole-pyridine ligand with two pentyl side units (Figure 12) [33]. This ligand was also used for its colorimetric and fluorometric sensing ability of several metal ions [Na^+, K^+, Mg^{2+}, Al^{3+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+}, Pb^{2+}]. Free ligand is highly fluorescent but when it is bonded with metal ions quenching of the emission band occurs as depicted in Figure 13.



Scheme 3. Proposed sensing mechanism for the increase in fluorescence intensity upon addition of metal ion to the chemosensor L1.

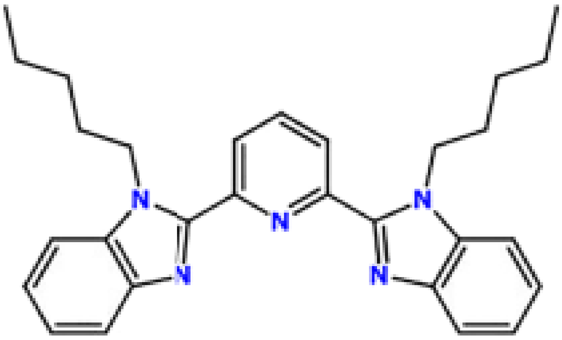


Figure 12. Tridentate bis benzimidazole-pyridine ligand

Saha et. al. have synthesized a new cocrystalline dynamic framework $\{[Cu(ina)_2(H_2O)][Cu(bpy)(ina)]\cdot 2H_2O\}_n$ (ina = isonicotinate, bpy = 4,4 bipyridine) that contains both open metal sites (OMSs) and free functional organic sites (FOSs) (Figure 14). Pyridyl groups and carboxylate oxygen atoms are efficient in binding cations, and hence the cation sensing activity of the framework was investigated. The evacuated framework was immersed in solutions that contained different metal ions, namely, Mg^{2+}, Ni^{2+}, Zn^{2+}, Hg^{2+}, and Pb^{2+}, in DMF with a concentration of 0.1 mmol each to form a metal-ion-incorporated microcrystalline solid. The framework shows selectivity toward the Ag^+ ion over the other tested cations (Figure 15) [34].

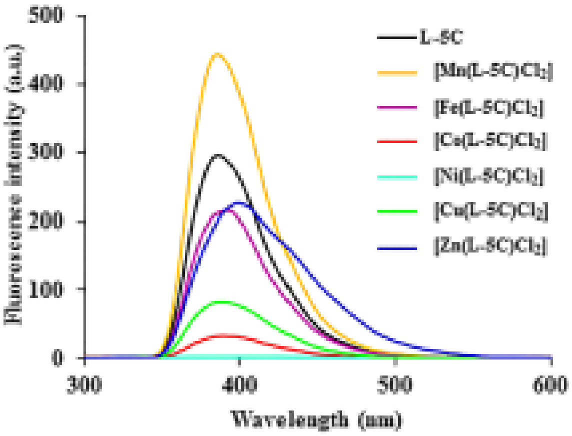


Figure 13. Emission spectra of Ligand and its complexes in MeOH (5×10^{-5} M).

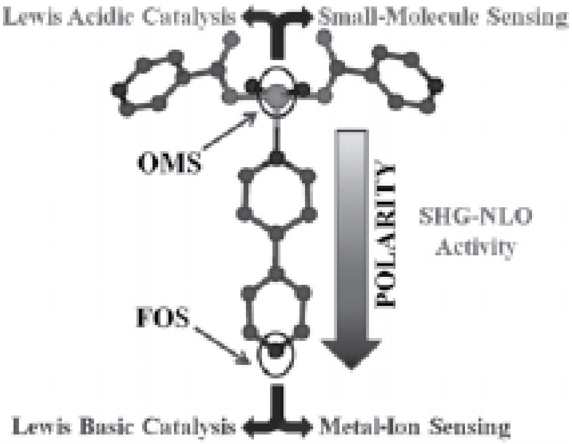


Figure 14. The presence of both open metal sites and free functional organic sites.

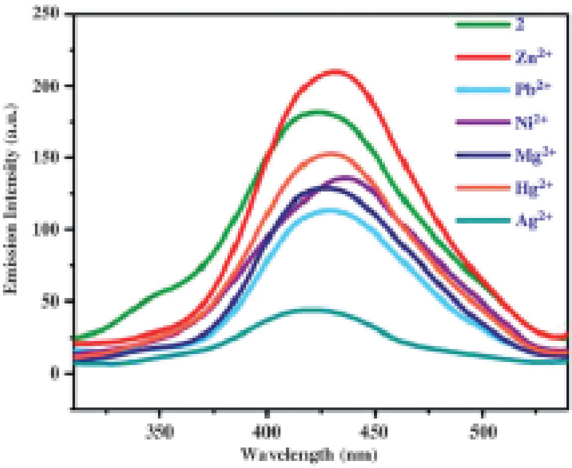


Figure 15. Fluorescence spectra of complex with different cations.

Conclusion

A general survey of trace level determination of various types of analytes by chemo sensor has been discussed here. Importances of use of chemosensors are widely illustrated here. Trace level of arsenic (III) are determined selectively by choosing suitable chemo sensor. Synthesis and design of chemical sensors for the detection of various amino acids having significant influences on human life have been depicted here. Development of synthesis of chemical sensors for the specific detection of metal ions, various poisonous organic analytes and explosives which have significant role on environment and human life are mentioned in this review work. Development of such sensors will help to solve many challenges in our society to some extent.

References

[1] (a) A. P. de Silva, D. B. Fox, A. J. M. Huxley, T. S. Moody, *Coord. Chem. Rev.* 205, 2000, 241; (b) L. Prodi, F. Bolletta, M. Montaliti, N. Zaccheroni, *Coord. Chem. Rev.* 205, 2000, 59.

[2] (a) J. R. Lakowicz, *Priciples of Fluorescence Spectroscopy*, 2nd ed., Plenum, New York, 1999.

[3] (a) V. Amendola, L. Fabbrizzi, M. Licchelli, C. Mangano, P. Pallavicini, L. Parodi, A. Poggi, *Coord. Chem. Rev.* 192, 2000, 649; (b) J. P. Desvergne, A. W. Czarnik, *NATO ASI Ser. Ser.* C 1997, 492.

[4] J. L. Kolanowski, F. Liu, E. J. New Chem. Soc. Rev. 47, 2018, 195.

[5] J. C. Saha, A. K. Dikshit, M. Bandyopadhyay and K. C. Saha, Crit. Rev. Environ. Sci. Technol., 29, 1999, 281.

[6] W. R. Cullen and K. J. Reimer, Chem. Rev., 89, 1989, 713.

[7] M. E. A. Fegley, S. S. Pinnock, C. N. Malele, W. E. Jones, Inorg. Chim. Acta. 381, 2012, 78.

[8] M. E. A. Fegley, S. S. Pinnock, C. N. Malele, W. E. Jones, Sensor, 10, 2010, 7018.

[9] M. Ali, M. Jha, S. K. Das, S.K.Saha, J. Phys, Chem (B), 113, 2009, 15563.

[10] L. Pu, Chem. Rev., 104, 2004, 1687.

[11] (a) A. C. D. Kozul, T. H. Hampton, J. C. Davey, J. A. Gosse, A. P. Nomikos, P. L. Eisenhauer, D. J. Weiss, J. E. Thorpe, M. A. Ihnat and J. W. Hamilton, Environ. Health Perspect.,117, 2009, 1108. (b) J. C. Saha, A. K. Dikshit, M. Bandyopadhyay and K. C. Saha, Crit. Rev. Environ. Sci. Technol., 29, 1999, 281.

[12] B. Dey, R. Saha, P. Mukherjee, Commun. 49, 2013, 7064.

[13] Du, Z. Huang, X. Q. Yu and L. Pu, Chemical Communications, 49, 2013, 5399.

[14] B. Kumari, S. Kundu, K. Ghosh, M. Banerjee, S. K. Pradhan, S. M. Islam, P. Brandão, V. Félix and D. Das, Dalton Transactions, 47, 2018, 14008.

[15] A. Banerjee, R. Singh, E. Colacio and K. K. Rajak, European Journal of Inorganic Chemistry, 2009, 2009, 277.

[16] H. Benveniste, M. B. Jørgensen, N. H. Diemer and A. J. Hansen, Acta Neurologica Scandinavica, 78, 1988, 529.

[17] M. Friedman, *Journal of Agricultural and Food Chemistry*, 47, 1999, 3457.

[18] H. Akitomi, Y. Tahara, M. Yasuura, Y. Kobayashi, H. Ikezaki and K. Toko, *Sensors and Actuators, B: Chemical*, 179, 2013, 276.

[19] R. E. Ionescu, S. Cosnier and R. S. Marks, Analytical Chemistry, 78, 2006, 6327.

[20] M. A. Hortala, L. Fabbrizzi, N. Marcotte, F. Stomeo and A. Taglietti, Journal of the American Chemical Society, 125, 2003, 20.

[21] A. Buryak, Infoscine, 2007, 3886, 1.

[22] S. K. Jana, A. K. Mandal, A. Kumar, H. Puschmann, M. Hossain, S. Dalai, RSC. Advance, DOI: 10.1039/C6RA16086G.

[23] Y. Zhou, J. Won, L. Y. Lee, J. Youn, Chem. Commun., 47, 2011, 1997.

[24] X. Zhou, Y. W. Yip, W. H. Chan , A. W. M. Lee, Beilstein J. Org. Chem., 7, 2011, 75.

[25] S. Y. Liu, L. Fang, Y. B. He, W. H. Chan, K. T. Yeung, Y. K. Cheng, R. H. Yang, Org. Lett. 7, 2005, 5825.

[26] B. Kumari, S. Kundu, K. Ghosh, M. Banerjee, S. K. Pradhan, Sk. M. Islam, P. Brandão, V. Félix , D. Das, Dalton, Trans, DOI: 10.1039/c8dt03007c

[27] S.K. Asthana, A. Kumar, S. K. Hira, P. P. Manna, Inorg. Chem. 56, 2017, 3315.

[28] P. S. Yao, Z. Liu, J. Z. Ge, Y. Chenb, Q. Y. Cao, Dalton Trans. 44, 2015, 7470.

[29] Z. Hu, B. J. Deibert, J. Li, Chem. Soc. Rev., 43, 2014, 5815 .

[30] P. A. Gale, C. Caltagirone, C. Chem. Soc. Rev., 44, 2015, 4212.

[31] A. Das, S. Jana, A. Ghosh, Crystal Growth Design, 2018, DOI: 10.1021/acs.cgd.7b01752

[32] B. K. Kundu, P. Mandal, B. Ghosh Mukhopadhyay, R. Tiwari, D. Nayak, R. Ganguly, S. Mukhopadhyay, Sensors & Accutators: B Chemical 282 (2019) 347.

[33] H. Kirpik, M. Kose, J. N. Ball, Appl. Organomet. Chem. DOI: 10.1002/aoc.5992

[34] R. Saha, B. Joarder, A. Singha Roy, Sk. M. Islam, S. Kumar, Chem. Eur. J. 2013, 19, 16607