NAKED-EYE ANALYTE SENSING THROUGH STRATEGICALLY DESIGNED CHEMOSENSORS

K. K. Upadhyay,*[a] Virendra Kumar,[a] Priyanka Rai,[a] Santosh Srivastava,[b] K. K. Singh[a] and Shubhra Singh[a]

Introduction

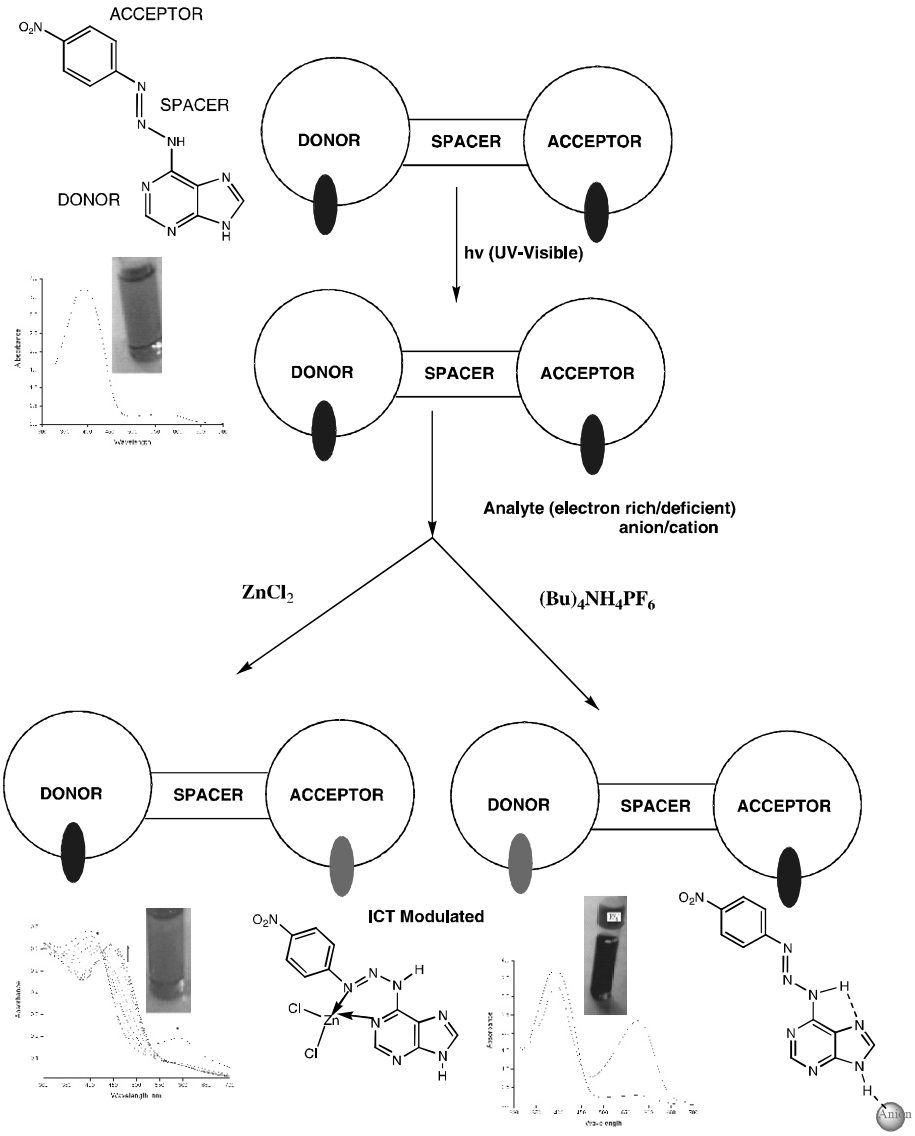
The basis of human civilization on this planet is based upon social interaction and mutual recognition. For mutual recognition some sort of mutual relations are must. This macroscopic behavior of living beings is also exhibited in its microscopic form in the realm of atoms and molecules. For executing any function at the level of atoms and molecules mutual interaction is must. Chemists specially supramolecular chemists have been trying to understand the details of chemical processes in terms of recognition of chemical species through strategically designed chemosensors also known as chemoreceptors.[1] These chemoreceptors are also being used as dosimeters for the quantitative estimation of a particular analyte.[2] The first naked eye chemoreceptor was synthesized by Park and Simmons in 1968 for chloride ion.[3] Since then a variety of colorimetric receptors have been synthesized.[4] These colorimetric receptors are actually molecules incorporating electron rich and deficient pockets simultaneously within the same molecular framework hence capable to produce charge transfer absorption spectra on their UV-visible scanning. This type of charge transfer from donor to acceptor within the same molecule on absorption of UV-visible light by the receptor is known as intramolecular charge transfer (ICT).[5] If an analyte is able to modulate this ICT of the receptor in a characteristic way which is not possible by any other analyte in the same way then that particular analyte is recognized by the receptor through a naked eye change in color of the receptor.[6] That is why molecules with capability of exhibiting ICT may be used as a probe for the naked eye sensing of those analytes which are able to bind with these probes in a selective way. The receptors having binding centres on donor and acceptor both are able to function as ditopic receptors. On the other hand if it possesses binding center on only one then it is known as monotopic one. In recent years there has been an upsurge in the tailor made design and synthesis of such receptors which are highly specific for a particular analyte. Peoples are doing recognition of some tedious analytes like chiral molecules. The recognition of analytes finds applications in many fields like synthetic organic chemistry,[7] catalysis,[8] kinetics[9] and in abetting environmental pollution[10] etc.

How naked eye receptors work:

A naked-eye receptor must have potential to exhibit intramolecular charge transfer (ICT) spectrum on its scanning through UV-visible light. Hence it must have the electron rich and deficient pockets within the same species. At the same time it must have some suitable centers on donor/ acceptor or both so that its ICT may be modulated by a suitable analyte resulting into naked-eye change. This modulation of ICT may be either in terms of $\in_{max}$ or λ_{max} leading to naked-eye change in the receptor. In the light of wide distribution of ions from biological system

[a]*Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi - 221 005, India,*
[b]*Department of Chemistry, Udai Pratap College (Autonomuos),Varanasi - 221 002, India,*

to material ones the ions (cations and anions) constitute a very important class of analyte.[11] For last few years we have been involved in design, synthesis and evaluation of suitable naked-eye receptors which are appropriate binder of cations and anions.[12-14] Either of these species may bind with donor or acceptor pockets of the receptor. If the cation binds with the donor pocket than it reduces the flow of electron from donor to acceptor increasing HOMO-LUMO gap which results into hypsochromic or blue shift while there will be bathochromic shift if the cation binds with acceptor pocket of the receptor leading to decrease in the HOMO-LUMO gap. These shifts will be in vice-versa order if the anion is the analyte.



Scheme - 1 Showing modulation in ICT after interaction of cation/ anion with a particular receptor (*p*-nitrophenyltriazenyl purine; PNTP)

On the other hand the modulation of ICT in terms of $\in_{max}$ may be understood in terms of different extent of approach of equilibrium on the right hand side which may further be understood in terms of different binding ability of receptor with different analytes leading to different binding constants.

$$RH + X^- \rightleftharpoons [R\text{-----}H\text{------}X] \rightleftharpoons R^- + HX$$

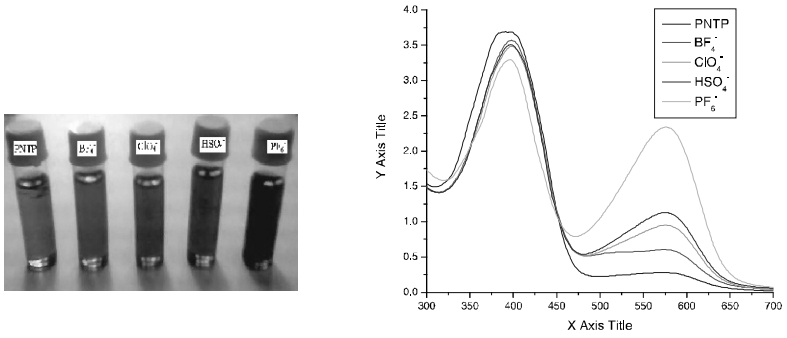


Figure-1 Color changes of PNTP upon interaction with anions and UV-Visible changes of PNTP upon addition of anions

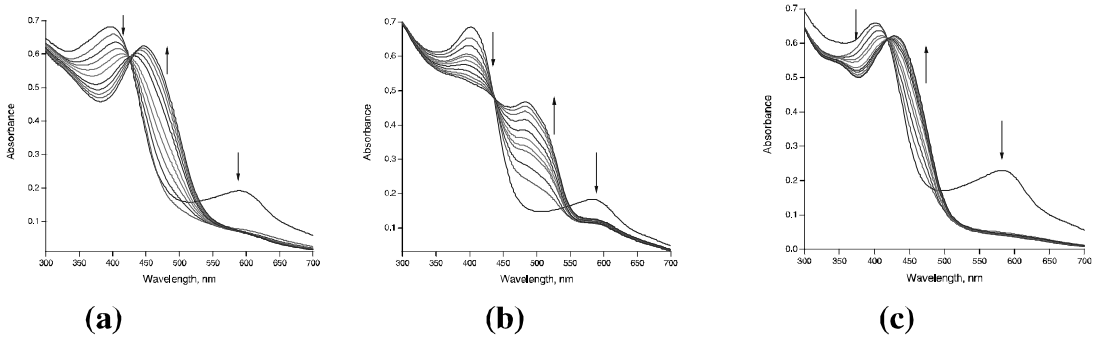


Figure - 2 Titration Curves of receptor 1 with d^{10} metal ions: (a) Zn^{II} (b) Cd^{II} (c) Hg^{II}

An entirely new type of sensing through which we came across recently is the solvent assisted sensing of Hg^{II} where a particular ICT which was not observed in the nujol mull of the receptor but was observed in a polar solvent where X=O (X=C/ S) like DMSO, DMF or acetone. This solvent assisted peak was modulated by cation or anion.[12-14] In the cation one we did naked-eye sensing of an obnoxious metal ion like Hg^{II} at the milimolar level in DMSO/aq. DMSO through strategically designed receptors by the coupling of diazonium salts of a few sulfonamides over a series of active methylene compounds like ethylacetoaceatate, diethyl malonate, acetyl acetone etc. The experimental observations of Hg^{II} naked-eye sensing with one such receptor involving ethylacetoacetate as the active methylene compound (OSPBE)[12] has been presented below.

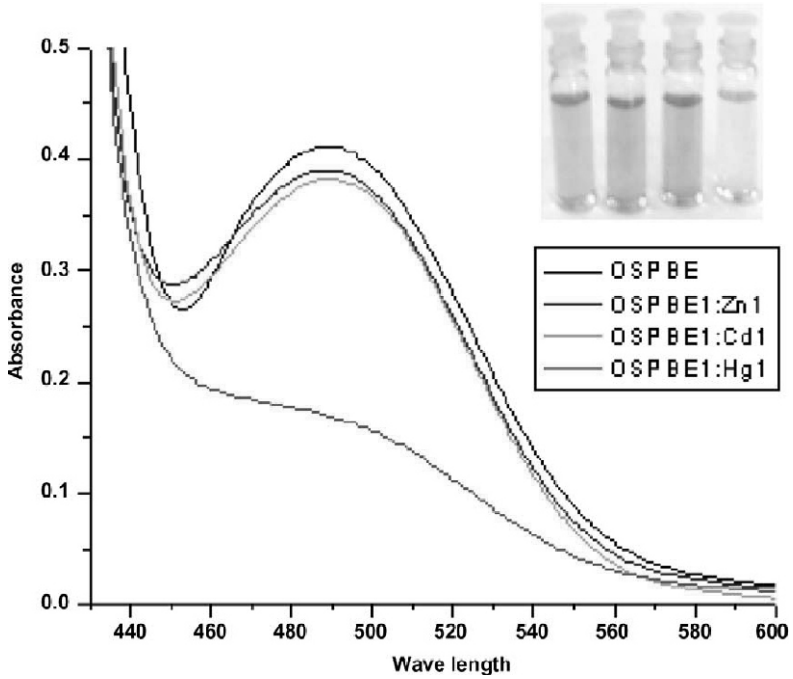


Figure - 3 Absorption spectra of 1x10^{-3} M DMSO solution of OSPBE on addition of 1 equiv. of Zn^{II}, Cd^{II} and Hg^{II} (420–600 nm)

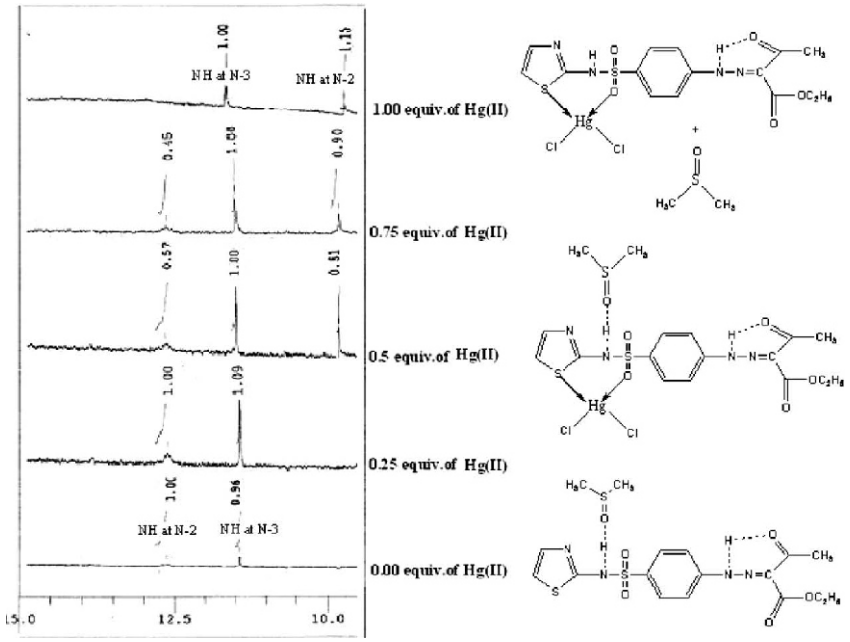


Figure - 4 Truncated ^{1}H NMR spectra (9.5–15.0 ä ppm) of OSPBE on the concomitant addition of 0–1 equiv. of Hg^{II} as its chloride salt to the 1x10^{-3} M DMSO-d_6 solution of OSPBE.

The receptor OSPBE selectively binds with Hg^{II} as its chloride salt among the d^{10} metal ions and produces olive green color. As it can be seen that receptor's absorption peak in the form of a broad band at 489 nm gets vanished on binding with Hg^{II}. The 1H NMR titration spectra shown above narrates the entire process of binding of Hg^{II} with receptor i.e. OSPBE.

Conclusion

Recognition of analytes through purposely designed receptors is an emerging area for last few decades. Many receptors having different potential towards the recognition of analytes have been synthesized by different groups. One of the major bottle neck in this field is the solubility of receptors in aqueous medium. Most of the receptors which have been synthesized and used are in non-aqueous medium like DMSO, acetonitrile etc. That is why the real use of these naked eye receptors has not been percolated to common man for day to day uses. Hence it is the urgent need of hours to do suitable changes at suitable places in preexisting receptors so that they may become water soluble and could be exploited towards analyte sensing particularly for cations and anions to its full potential.

References

1. Examples of chemoreceptors: **(a)** T. Gunnlaugsson, M. Glynn, G.M. Tocci (née Hussey), P.E. Kruger, F.M. Pfeffer, *Coord. Chem. Rev.* **2006**, 250, 3094. **(b)** R. Martinez-Manez, F. Sancenon, *Chem. Rev.* **2003**, 103, 4419. **(c)** K. Ghosh, A.R. Sarkar, G. Masanta, *Tetrahedron Lett.* **2007**, 48, 8725.
2. (a) C. Liu, X. Qian, G. Sun, L. Zhao and Z. Li, *New J. Chem.,* **2008**, 32, 472. (b)
3. 1968 park: C. H. Park, H. E. Simmons, J. Am. Chem. Soc. **1968**, 90, 2431.
4. colorimetric receptors
5. J. Shao, H. Lin, Huakuan Lin, *Talanta* **2008**, 77, 273.
6. ICT based selective receptor S. H. Mashraqui, S. Sundaram and A. C. Bhasikuttan, *Tetrahedron* **2007**, 63, 1680.
7. P. D. Beer, P. A. Gale, *Angew. Chem., Int. Ed.* **2001**, 40, 486.
8. J. L. Sessler, J. M. Davis, *Acc. Chem. Res. 2001*, 34, 989
9. A. Bianchi, K. B. James, E. G. Espana, Supramolecular Chemistry of Anions, Wiley-VCH, New York, 1997.
10. M. Grunder, J. F. Dozol, Z. Asfari, J. Vicens, J. Radioanal. Nucl. Chem. 1999, 241, 59.
11. (a) N. T. V. Le, D. R. Richardson, *Biochim. Biophys. Acta* **2002**, 1603, 31. **(b)** D. H. Saavedra, H. Zhou. J. M. McCord, *Biomed. Pharmacother.* **2005**, 59, 204. **(c)** A. F. Parisi, B.L. Vallee, *Am. J. Clin. Nutr.* **1969**, 22, 1222. (d) R. Uauy, M. Olivares, M. Gonzalez, *Am. J. Clin. Nutr.* **1998,** 67, 952. **(e)** E. D. J. Harris, *Trace Elem. Exp. Med.* **2001**, 14, 207.
12. K.K. Upadhyay, S. Upadhyay, K. Kumar, R. Prasad, *J. Mol. Struct.* **2009**, 927, 60.
13. K. K. Upadhyay, A. Kumar, S. Upadhyay, R. K. Mishra, P. K. Roychoudhuary, *Chem. Lett.* **2008**, 37, 186.
14. K. K. Upadhyay, A. Kumar, R. K. Mishra, R. Prasad, *Bull. Chem. Soc. Jpn.* **2009**, 82, 813.