

# Nano-molar Detection of Al<sup>3+</sup> in Aqueous Medium with Imine-Coupled Scaffold Containing Mixed N and O Binding Sites

**Kamalpreet Kaur<sup>b</sup>, Sunita Rani<sup>a</sup>, Amritpal Singh<sup>a</sup>, Kiran<sup>a</sup>, Narinder Singh<sup>b</sup>**

<sup>a</sup>Department of Chemistry, Mata Gujri College, Fatehgarh Sahib, Punjab

<sup>b</sup>Department of Chemistry, Indian Institute of Technology Ropar, Rupnagar, Punjab, INDIA

## Abstract

Imine linked chemosensor is prepared through condensation reaction between dipodal amine (**1**) and an aldehyde comprised of nitro group. Chemosensor **2** demonstrated selectivity for Al<sup>3+</sup> by the enhancement of fluorescence intensity at 423 nm. Upon binding of **2** with Al<sup>3+</sup>, approximately 8 fold enhancement in fluorescence intensity was observed due to the combinational effect of ESIPT, C=N isomerisation and quenching of PET. The investigation of photophysical properties of **2** revealed that the sensor is unaffected by the acidic or alkaline p . The receptor **2** is able to detect Al<sup>3+</sup> ion through changes in fluorescence intensity with high sensitivity and selectivity. The receptor is able to detect Al<sup>3+</sup> concentrations ranging from 0-30 nM with detection limit of 9 nM.

**Keywords:** Al<sup>3+</sup> ion sensing, Schiff base, Fluorescence detection, pH effect

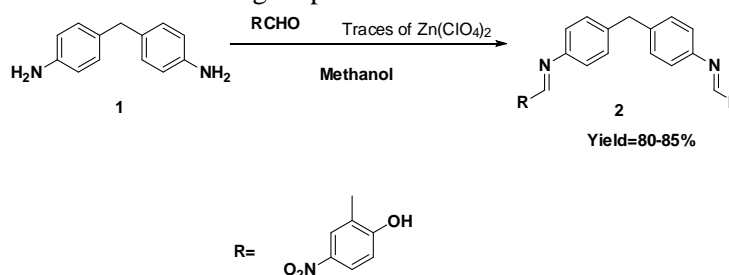
## 1. Introduction

The metal complexes with Schiff base ligands find vital role in the fields of molecular modeling, synthesis of metal-supramolecular assemblies, catalysis, as oxygen carriers and magnetochemistry etc.<sup>1</sup> Literature is replete with the reports of utilizing diverse Schiff base receptors which can be prepared by changing the binding subunit and the signaling sub units.<sup>2</sup> Such receptors contain divergent binding sites that are directed in opposite directions. In addition, the recognition of cations in aqueous and semi- aqueous medium is difficult from the sensors consisting of pure H-bonding sites.<sup>3,4</sup> Keeping these points in mind, herein a chemosensor is designed having imine nitrogen and hydroxyl groups at the optimum distance required for hydrogen bonding, a condition necessary to show ESIPT phenomenon.<sup>5-7</sup>

## 2. Result and Discussion

### 2.1. Synthesis

The dipodal imine linked Schiff base is prepared by following an already published method<sup>8</sup> (Scheme 1). The reaction of 4, 4'-diaminodiphenylmethane (**1**) with nitro group containing aldehyde yielded the receptor **2** having C=N linkage and mixed nitrogen and oxygen donor sites with 85% yield. The yellow colored crude product was recrystallized from methanol to give pure Schiff base.

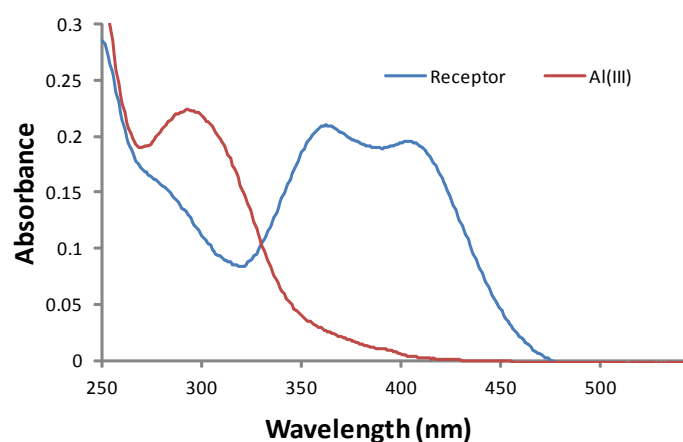


Scheme 1

The receptor **2** was characterized by the IR peak at  $1637\text{ cm}^{-1}$  due to  $-\text{CH}=\text{N}$  group. The mass spectrum of the receptor indicated MS  $m/z$  at 496.  $^1\text{H}$  NMR spectrum exhibited a singlet at 4.05 (2H,  $-\text{CH}_2$ ), four doublets at 7.29 (2H, Ar-H), 7.38 (4H, Ar-H), 7.45 (4H, Ar-H) and 8.23 (2H, Ar-H) and two sharp singlets at 8.64 (2H, Ar-H) and 9.15 (2H,  $-\text{CH}=\text{N}$ ).

## 2.2. Recognition studies

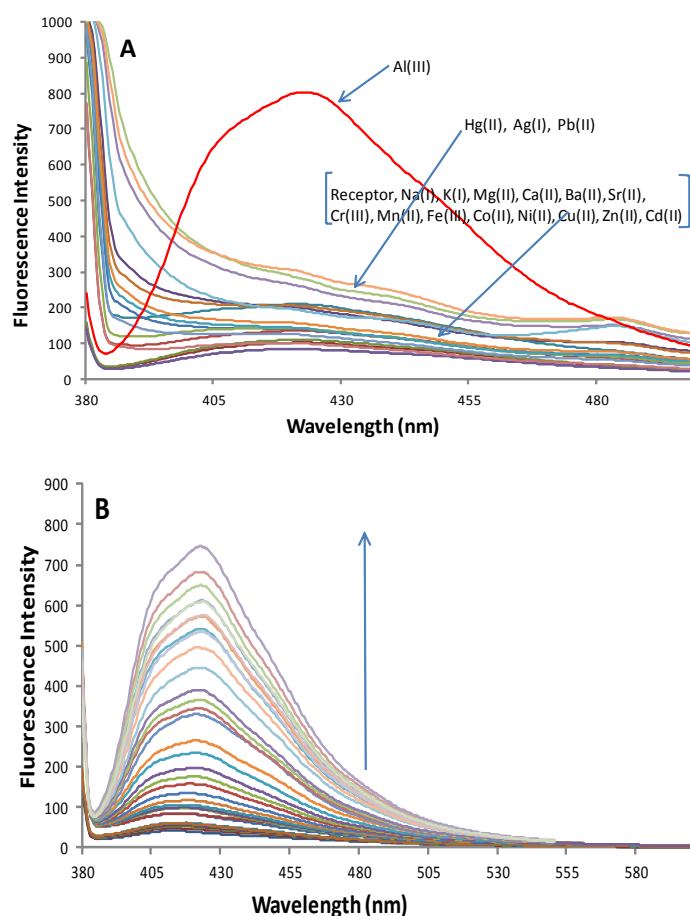
The recognition properties of the dipodal receptor **2** have been evaluated with the help of UV-Vis and/or fluorescence spectroscopy. The recognition behavior of sensor **2** was investigated by recording the UV-Vis absorption spectra in HEPES buffered DMF/ $\text{H}_2\text{O}$  (7:3, v/v) solvent system as indicated in Figure 1. The UV-Vis absorption spectra of receptor **2** displayed strong absorption bands at 366 nm and 404 nm which were the consequences of charge transfer transitions in the imine linkages.



**Figure 1.** UV-Vis absorption spectrum of  $10\ \mu\text{M}$  of **2** upon addition of  $50\ \mu\text{M}$  of aluminium nitrate in HEPES buffered DMF/ $\text{H}_2\text{O}$  (7:3, v/v) solvent system.

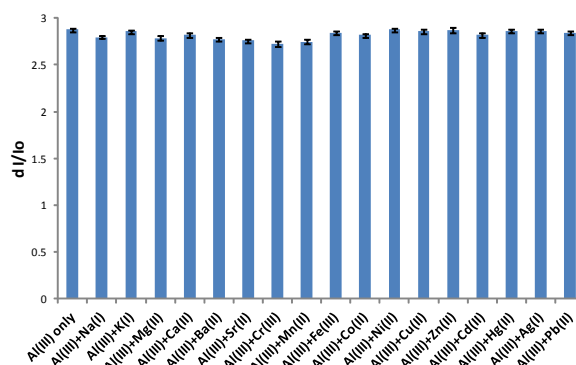
The fluorescence spectrum of receptor **2** displayed a weak fluorescence emission band at  $\lambda_{\text{max}}=417\text{ nm}$  (Figure 2), when excited at  $366\text{ nm}$  (at room temperature) with  $10\ \mu\text{M}$  concentration of **2** in HEPES buffered DMF/ $\text{H}_2\text{O}$  (7:3, v/v) solvent system. The receptor **2** was not able to exhibit the dual channel emission due to excited state intramolecular proton transfer (ESIPT) phenomenon. The metal binding studies of sensor **2** was assessed from the modulation in fluorescence intensity of receptor **2** upon addition of a particular metal salt (Figure 2A). The addition of  $30\ \mu\text{M}$  solution of  $\text{Al}^{3+}$  to the  $10\ \mu\text{M}$  solution of **2** results in the emergence of a new band at  $\lambda_{\text{max}}=423\text{ nm}$ . Under the similar conditions (as used for  $\text{Al}^{3+}$ ), the fluorescence profile of receptor **2** was checked for other metal ions such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$  (Figure 2A). No major noticeable change in the fluorescence signature of sensor **2** was noticed in the presence of any of the tested metal ions. Upon addition of  $\text{Al}^{3+}$  to the receptor **2**, a significance increase in the fluorescence intensity is observed. Furthermore; the increase is not detected exactly at  $417\text{ nm}$  because the binding of  $\text{Al}^{3+}$  close to fluorophore influences the ring current and therefore modulates the charge transfer (CT) band.<sup>9</sup>

To get more insight into the binding behavior of receptor **2** as a sensor for  $\text{Al}^{3+}$ , a fluorescence titration experiment was performed by adding incremental quantity of  $\text{Al}^{3+}$  ( $0\text{--}30\ \mu\text{M}$ ) to the solution of receptor **2** in HEPES buffered DMF/ $\text{H}_2\text{O}$  (7:3, v/v) solvent system as shown in Figure 2B. A considerable enhancement in the fluorescence intensity at  $423\text{ nm}$  is observed upon the successive addition of  $\text{Al}^{3+}$  ( $0\text{--}30\ \mu\text{M}$ ) to the solution of receptor **2**.



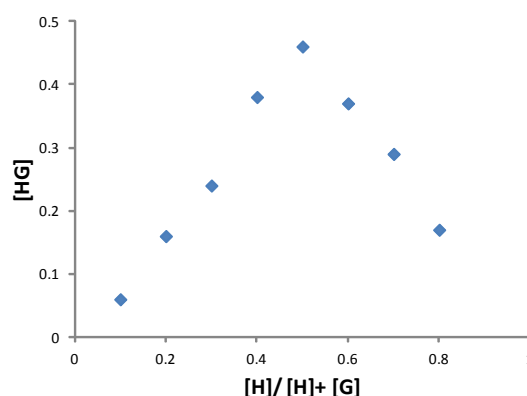
**Figure 2.** (A) Changes in fluorescence intensity of **2** ( $10\ \mu\text{M}$ ) upon addition of  $30\ \mu\text{M}$  of a particular metal nitrate salts in HEPES buffered DMF/ $\text{H}_2\text{O}$  (7:3, v/v) solvent system; (B) Fluorescence emission profile of **2** ( $10\ \mu\text{M}$ ) upon successive addition of  $\text{Al}^{3+}$  (0- $30\ \mu\text{M}$ ) in HEPES buffered DMF/ $\text{H}_2\text{O}$  (7:3, v/v) solvent system.

In order to discover the practical application of receptor **2** as a selective sensor for  $\text{Al}^{3+}$  ion, the competitive experiments were executed for the estimation of 3 equiv. of  $\text{Al}^{3+}$  in the presence of any one of the  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ag}^+$  or  $\text{Pb}^{2+}$  (3 equiv.). No considerable differences in the fluorescence intensity were examined by comparing the intensity with and without other metal ions (Figure 3). Therefore, the receptor **2** acts as a selective sensor of  $\text{Al}^{3+}$  even in the presence of other competitive metal ions.



**Figure 3.** Fluorescence response of receptor **2** ( $10\ \mu\text{M}$ ) to  $\text{Al}^{3+}$  (3 equiv.) over other selected metal ions (3 equiv.) at 423 nm.

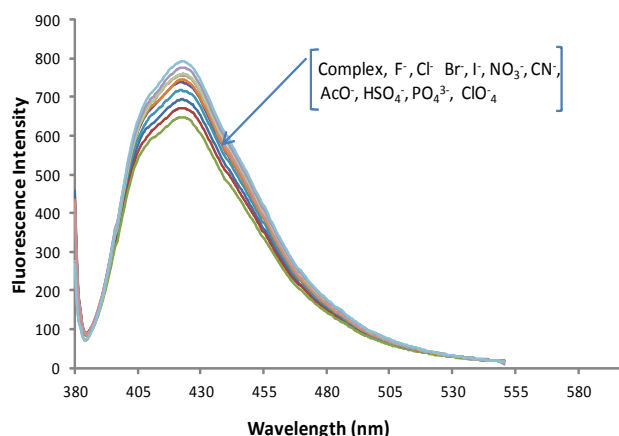
The effect of changing p on receptor **2** was evaluated in DMF/H<sub>2</sub>O (7:3, v/v) solvent system. The lowering in p of the solution of **2** from 9.66 to 3.0 led to insignificant increase in fluorescence intensity at 417 nm. The effect of base on the fluorescence profile of **2** led to conclude that receptor **2** was less susceptible to get influenced under the basic conditions and the increase in p from 9.66 to 13.05 resulted in a small increase in the fluorescence intensity. The detection limit of receptor **2** for the analysis of Al<sup>3+</sup> was established from the plot of normalized fluorescence intensity as a function of the concentration of the added metal ion.<sup>10</sup> Receptor **2** has a detection limit of 9 nM for Al<sup>3+</sup> ion. The association constant  $K_a$  of sensor **2** for Al<sup>3+</sup> has been calculated from Benesi-Hildebrand plot<sup>11</sup> and was found to be  $1.45 \times 10^4 \text{ M}^{-1}$ . The Job's plot<sup>12</sup> at 423 nm indicated 1:1 stoichiometry of the complex (Figure 4). The response time of sensor **2** was found to be 50 s.



**Figure 4.** Job's plot for the complex formed between receptor **1d** and Al<sup>3+</sup>. The fluorescence intensity at 423 nm was used for calculations. The concentration of [HG] was calculated by the equation  $[HG] = I/I_0 \times [H]$ .

In order to synthesize the aluminium complex of receptor **2**, an aqueous solution of aluminium nitrate was refluxed with a solution of **2** in THF. The **2**.Al<sup>3+</sup> complex has been characterized by ESI Mass, IR and compared through fluorescence spectroscopy. The stretching band of **2** due to  $\nu_{C=N}$  in IR spectrum was shifted by  $70 \text{ cm}^{-1}$  upon the complex formation of **2** with Al<sup>3+</sup>; indicating the involvement of imine linkages in coordination.

The anion binding affinity of **2**.Al<sup>3+</sup> complex was investigated by the changes in the fluorescence signature of **2**.Al<sup>3+</sup> complex (10  $\mu\text{M}$ ) upon addition of 10  $\mu\text{M}$  solution of tetrabutyl ammonium salts of different anions in HEPES buffered DMF/H<sub>2</sub>O (7:3, v/v) solvent system. The fluorescence profile of **2**.Al<sup>3+</sup> complex was unperturbed by the presence of any of the anions F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, CN<sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, NO<sub>3</sub><sup>-</sup>, AcO<sup>-</sup> or ClO<sub>4</sub><sup>-</sup> as shown in Figure 5.



**Figure 5.** Changes in fluorescence intensity of **2**.Al<sup>3+</sup> (10  $\mu\text{M}$ ) upon addition of 10  $\mu\text{M}$  of tetrabutyl ammonium salts of different anions in HEPES buffered DMF/H<sub>2</sub>O (7:3, v/v) solvent system.

The receptor **2** is able to detect  $\text{Al}^{3+}$  ion through changes in fluorescence intensity with high sensitivity and selectivity. The receptor is able to detect  $\text{Al}^{3+}$  concentrations ranging from 0 to 30  $\mu\text{M}$  with detection limit of 19  $\mu\text{M}$ . This receptor has an added advantage that the metal complex is not influenced by the presence of any anion.

### 3. Experimental Section

#### 3.1 Materials and Instrumental Information

The chemicals were purchased from Sigma Aldrich and were used without any further purification. The known procedures were used to purify the organic solvents. The NMR spectra were recorded using a JEOL-ECS instrument which operated at 400 MHz for  $^1\text{H}$  NMR and 100 MHz for  $^{13}\text{C}$  NMR spectra. FT-IR spectra were obtained as KBr pallets on a Bruker Tensor 27 spectrometer for the compounds in the solid state. The mass spectrum was recorded using Waters Micromass Q-ToF Mass Spectrometer. The absorption spectra were recorded on a Specord 250 Plus Analytikjena spectrophotometer. The fluorescence measurements were performed on a Perkin Elmer L55 Fluorescence spectrophotometer.

#### 3.2. Synthesis

The compound **2** has been prepared by stirring 4, 4'-diaminodiphenylmethane (198 mg, 1.0 mmol) along with 2-hydroxy-5-nitrobenzaldehyde (417.5 mg, 2.5 mmol) in methanol. After stirring the reaction mixture for 10 hours at room temperature a yellow colored precipitate was filtered and was washed with MeOH many times. The solid was recrystallized from MeOH. Yield = 85%; IR:  $1637\text{cm}^{-1}$  ( $-\text{CH}=\text{N}$ ); MS m/z 496; Anal. Calcd. for  $\text{C}_{27}\text{H}_{20}\text{N}_4\text{O}_6$ : C, 65.81; H, 4.62; N, 11.65; O, 19.89;  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz): 4.05 (s, 2H,  $-\text{CH}_2$ ), 7.29 (d, 2H, ArH), 7.38 (d, 4H, ArH), 7.45 (d, 4H, ArH), 8.23 (d, 2H, ArH), 8.64 (s, 2H, ArH), 9.15 (s, 2H,  $-\text{CH}=\text{N}$ ).  $^{13}\text{C}$  NMR couldn't be obtained due to solubility problems.

#### 3.3. Cation Recognition studies

All the recognition studies were performed at  $25\pm 1^\circ\text{C}$  and before recording any spectrum a sufficient time was given with shaking to ensure the uniformity of the solution. The cation binding ability of the receptors was determined by preparing standard solutions of known concentrations of the receptors along with fixed amounts of particular metal nitrate salt in a particular solvent system. The cation recognition behavior of the receptors was evaluated from the changes in fluorescence spectra and/or UV-Vis absorption spectra of sensors upon addition of known concentrations of different metal salts. The fluorescence spectrum was recorded at excitation wavelength equal to the wavelength of absorption maximum in the UV-Vis absorption spectra. For titrations, volumetric flasks were taken each containing standard solution of sensors along with varied amounts of a metal nitrate salt with which the receptor is exhibiting high and selective binding affinity. In order to determine the stoichiometry of the complex formed from a particular receptor and a particular metal ion, solutions were prepared as 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2 and 9:1. These solutions were kept for 1 h, and were shaken occasionally. The plot of  $[\text{HG}]$  vs  $[\text{H}] / [\text{H}] + [\text{G}]$  was used to determine the stoichiometry of the complex formed. The concentration of  $[\text{HG}]$  was calculated by the equation  $[\text{HG}] = \Delta I / I_0 \times [\text{H}]$ . To evaluate any possible interference due to different cations for the estimation of metal ion, solutions were prepared containing the receptor and that particular metal ion along with and without other interfering metal ions.

### 4. Conclusions

In comparison to other chemosensors available in literature, a relatively easy synthetic methodology has been utilized for the synthesis of compound **2**. The incorporation of imine linkage and a combination of  $-\text{N}$  and  $-\text{O}$  donor atoms made the receptor a very promising candidate for the metal ions. The chemosensor **2** possesses enormous selectivity for  $\text{Al}^{3+}$  ions as revealed by the fluorescence spectroscopy. In addition, the investigation of photophysical properties of compound **2** depicted that the chemosensor is unaffected by acidic or alkaline p .

## 5. References

1. (a) L.F. Lindoy and I.A. Atkinson, Self assembly in Supramolecular Chemistry, *Royal Society of Chemistry, Cambridge, UK*, 2000; (b) L. Lecren, W. Wernsdorfer, Y.-T. Li, A. Vindigni, H. Miyasaka and R. Clérac, *J. Am. Chem. Soc.*, 2007, **129**, 5045–5051; (c) D. Chen, A.E. Martell and Y. Sun, *Inorg. Chem.*, 1989, **28**, 2647–2652; (d) L. Canali and D.C. Sherrington, *Chem. Soc. Rev.*, 1999, **28**, 85–93.
2. (a) Q. Meng, J. K. Clegg, A. J. Brock, K. A. Jolliffe, L. F. Lindoy and G. Wei, *Polyhedron*, 2014, **74**, 113–121; (b) Q.-L. Zhang, B.-X. Zhu, L.F. Lindoy and G. Wei, *Inorganic Chemistry Communications*, 2008, **11**, 678–680.
3. S. Kubik, *Chem Soc. Rev.*, 2010, **39**, 3648–3663; (b) C. Reyheller and S. Kubik, *Org. Lett.*, 2007, **9**, 5271–5274; (c) S. Kubik, C. Reyheller and S. Stüwe, *J. Inclusion Phenom. Macrocyclic Chem.*, 2005, **52**, 137–187.
4. (a) K. Ghosh, A. R. Sarkar, A. Samadder and A. R. Khuda-Bukhsh, *Org. Lett.*, 2012, **14**, 4314–4317; (b) X. Lou, D. Ou, Q. Li and Z. Li, *Chem. Commun.*, 2012, **48**, 8462–8477.
5. (a) V. Amendola, G. Bergamaschi, A. Buttafava, L. Fabbrizzi and E. Monzani, *J. Am. Chem. Soc.*, 2010, **132**, 147–156; (b) S. K. Kim, D.H. Lee, J.-I. Hong and J. Yoon, *Acc. Chem. Res.*, 2009, **42**, 23–31 ; (c) J. H. Lee, J. Park, M. S. Lah, J. Chin and J.-I. Hong, *Org. Lett.*, 2007, **9**, 3729–3731; (d) S. Mizukami, T. Nagano, Y. Urano, A. Odani and K. Kikuchi, *J. Am. Chem. Soc.*, 2002, **124**, 3920–3925; (e) L. Fabbrizzi, N. Marcotte, F. Stomeo and A. Taglietti, *Angew. Chem. Int. Ed.*, 2002, **41**, 3811–3814.
6. (a) H. Wang, L. Xue and H. Jiang, *Org. Lett.*, 2011, **13**, 3844–3847; (b) Z. Xu, J. Pan, D. R. Spring, J. Cui and J. Yoon, *Tetrahedron*, 2010, **66**, 1678–1683; (c) X. Lou, L. Qiang, J. Qin and Z. Li, *Applied materials and interfaces*, 2009, **1**, 2529–2535; (d) P. Saluja, N. Kaur, N. Singh and D. O. Jang, *Tetrahedron Letters*, 2012, **53**, 3292–3295.
7. (a) A. Kaur, H. Sharma, S. Kaur, N. Singh and N. Kaur, *RSC Adv.*, 2013, **3**, 6160–6166; (b) X. He, Q. Zhang, W. Wang, L. Lin, X. Liu, and X. Feng, *Org. Lett.*, 2011, **13**, 804–807.
8. (a) R. M. Patil and S. R. Chaurasiya, *Asian J. Chemistry*, 2008, **20**, 4615–4624; (b) M. Mazloum-Ardakani, M. A. Sheikh Mohsenia and M. Salavati-Niasari, *Canadian Journal of Analytical Sciences and Spectroscopy*, 2008, **53**, 179–188.
9. (a) R. Martínez-Mañez and F. Sancenón, *Chem. Rev.*, 2003, **103**, 4419–4476; (b) Q. Li, M. Peng, H. Li, C. Zhong, L. Zhang, X. Cheng, X. Peng, Q. Wang, J. Qin and Z. Li, *Org. Lett.*, 2012, **14**, 2094–2097; (c) A. Bozdemir, R. Guliyev, O. Buyukcakir, S. Selcuk, S. Kolemen, G. Gulseren, T. Nalbantoglu, H. Boyaci and E. U. Akkaya, *J. Am. Chem. Soc.*, 2010, **132**, 8029–8036.
10. M. Shortreed, R. Kopelman, M. Kuhn and B. Hoyland, *Anal. Chem.*, 1996, **68**, 1414–1418.
11. H.A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703–2707.
12. P. Job, *Ann. Chim.*, 1928, **9**, 113–203.