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# Mesitylene based azo-coupled chromogenic tripodal receptors—a visual detection of Ag(I) in aqueous medium

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**Abstract**—A series of novel tripodal ligands **3a–d**, based on a mesitylene anchor, containing aza-thioethers as donor atoms and coupled with 4-(4/3/2-nitrophenyl)azophenol or 4-(2-chlorophenyl)azophenol have been synthesized as chromogenic receptors, which are highly selective for silver(I). The complexation behavior of **3a–d** with various metal ions has been evaluated by UV–vis spectrometry in dioxane/water (1:9/v:v) solution at 25 °C. The UV–vis spectra show that the complexation of **3a–c** with $Ag^+$ have pronounced bathochromic shifts accompanied by a unique color change in the solution from yellow to red, which is visible with the naked eye. The ligands do not show any significant change on addition of other metal ions like $Li^+$, $Na^+$, $K^+$, $Sr^{2+}$, $Ca^{2+}$, $Cd^{2+}$, $Zn^{2+}$, $Hg^{2+}$, $Pb^{2+}$, $Ni^{2+}$, and $Cu^{2+}$ and thus are highly specific and selective for $Ag^+$ in the aqueous medium.


## 1. Introduction

Chromogenic sensors provide an informative signal due to the specific color change of a ligand upon metal complexation. This change can be utilized in analyte-sensing systems[1–3] and finds widespread use in environmental and biomedical applications.[4] Receptors specifically designed for sensing purposes are generally called chemosensors.[5] Many of these chemosensors are optical in nature, working on a binding site-signaling subunit approach[6] and usually employ the unspecific interactions with the indicator dyes to generate signal changes.[7] Using this approach a wide variety of cation sensing chemosensors based on crown ethers,[2] calixarenes,[8] azacrown-calixarenes,[9] spherands,[10] cryptands,[11] and podands[3,12] have been reported in literature. This strategy has led to a significant development of a number of chromogenic systems sensing anions,[13] neutral analytes,[14] nucleic acids,[15] and oligonucleotides.[15] As far as metal ion sensing is concerned, the chemosensors may be grouped into three broad categories.[1b] The first category consists of those, which show a color change upon complexation in a totally organic medium. It includes neutral and some anionic species and also those chromoionophores, which work on the basis of skeletal isomerization. The second category comprises anionic species, which are used for metal extraction photometry. The third category includes those chromosensors, which are specially developed for metal photometry in aqueous media. This type of photometry eliminates the use of toxic and volatile organic solvents and also eliminates the phase separation step required in extraction photometry.

Heavy metal ions like $Ag^+$, $Hg^{2+}$ are environmental pollutants for water resources, so their recognition and selective removal forms an important part of chemical research. The existing chemical sensors for the detection of heavy metals include devices based on their films of gold,[16] environmentally sensitive organic molecules,[17] polymeric materials,[18] and bio-composites.[19] These devices have their own limitations. There are numerous reported examples for fluroionophores,[20] which show excellent selectivity for heavy metals. However, the fluorescence quenching nature of the paramagnetic transition metal species via enhancing spin-orbital coupling[21] poses a disadvantage in high signal output upon complexation. The techniques that are available for $Ag^+$ detection are very tedious[22] and involve extraction of $Ag^+$ from aqueous to organic phase.[23] While it is possible to detect other transition metal ions in the aqueous samples by using dithizones in the presence of nonionic surfactants (Triton X-100), $Ag^+$ forms secondary dithizonates, which find no real application in spectroscopic analysis.[24] The development of an optical sensor having high selectivity and sensitivity for $Ag^+$, transducing a visual signal, in the environment friendly aqueous medium, is thus highly desirable.

The above mentioned binding site-signaling subunit[6] approach has been extended to modify one of our acyclic receptors **1**. These chromogenic studies were initiated because such thioether-imine based receptors[25] have been

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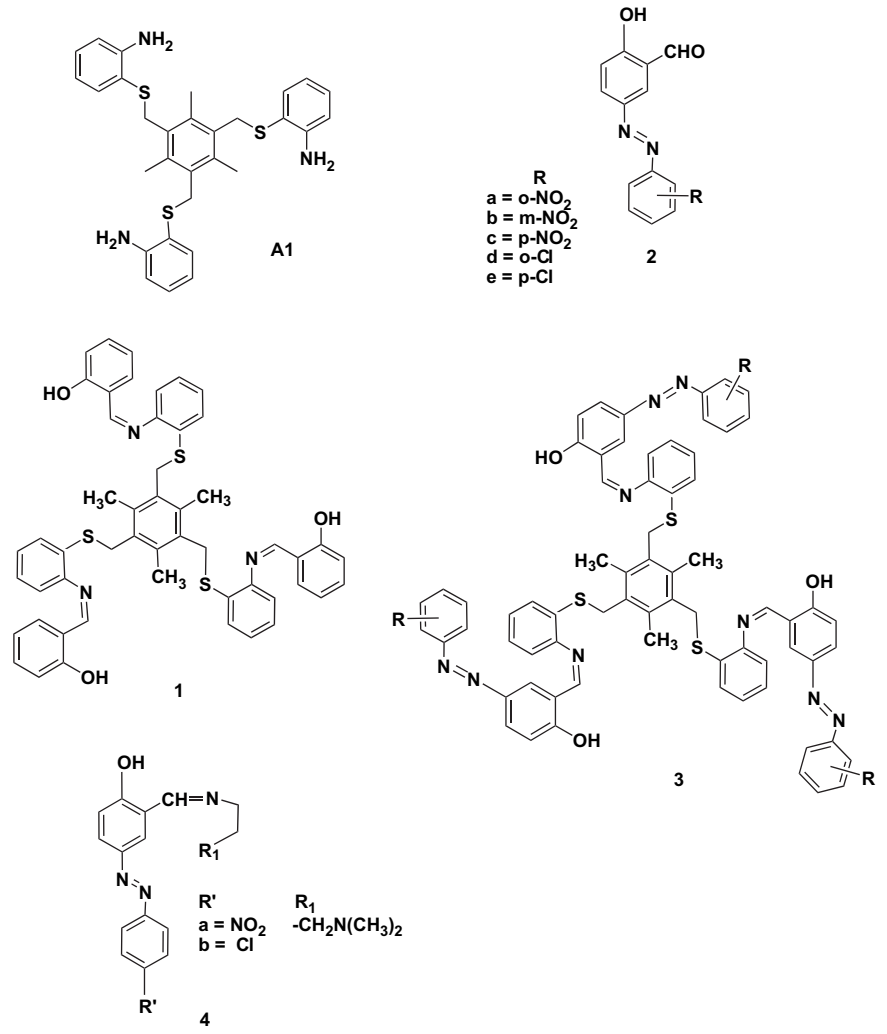
seen to be highly responsive toward $Ag^+$. In order to optically sense this binding of $Ag^+$, a sensing unit **2** was introduced to the receptor **1**. The idea was to check whether the former transduces the chemical change brought about by the interaction of the latter with the metal ion. The appendage of the signaling unit to the lower part of the receptor **1** is shown in Scheme 1, gives new chromogenic receptors **3**. While various 1,3,5-substituted 2,4,6-ethylbenzene based tripodands have been used[26] in IDA (indicator displacement assays) and as anion receptors, to the best of our knowledge there have been hardly any reports where mesitylene based tripodands have been used as binding units transmitting optical signals to show metal recognition. We report here the synthesis of **3** possessing multiple chromogenic donors and the binding ability for $Li^+$, $Na^+$, $K^+$, $Sr^{2+}$, $Ca^{2+}$, $Cd^{2+}$, $Zn^{2+}$, $Hg^{2+}$, $Pb^{2+}$, $Ni^{2+}$, $Cu^{2+}$, and $Ag^+$ metal ions.




**Scheme 1**.

## 2. Results and discussion

Compounds **2a–e** were prepared by the literature method[8v] while **A1** and **1** were prepared as already reported by us.[25a] Compounds **3a–d** were prepared by the reaction of 1 mmol of **A1** in dry acetonitrile with 3 mmol aldehydes **2a–d** in chloroform (see Section 4). Compounds **4a**,**b** were synthesized by reacting **2c** and **2e** with *N*,*N*′-dimethylethylenediamine and characterized by $^1H$ and $^{13}C$ NMR (Supplementary data). Compounds **3a–d** were characterized by various spectroscopic techniques. A band around 1613–1625 $cm^{-1}$ characterized the presence of imine linkages in IR spectra. The $^1H$ NMR spectra of **3a–d** either show two clear peaks each (in the intensity ratio 2:1) for the methyl, methylene, and OH protons or relatively broad signals corresponding to them. In $^{13}C$ NMR spectra also there are two peaks corresponding to methylene carbons. This shows that the conformation of the ligands[27] is II, i.e., cis, trans, trans instead of I, i.e., cis, cis, cis conformation as found in **1** in the solution form[25a] (Fig. 1). The imine units were characterized from signals lying in the range ~ $\delta$ 8.43–8.60 in the $^1H$ NMR spectrum and at ~ $\delta$ 160 in the $^{13}C$ NMR spectra and also from the absence of any signal at ~ $\delta$ 10.0 in the $^1H$ NMR, which corresponds to the aldehyde group. The FAB mass spectra and CHN data are also in accordance with the molecular formulae.

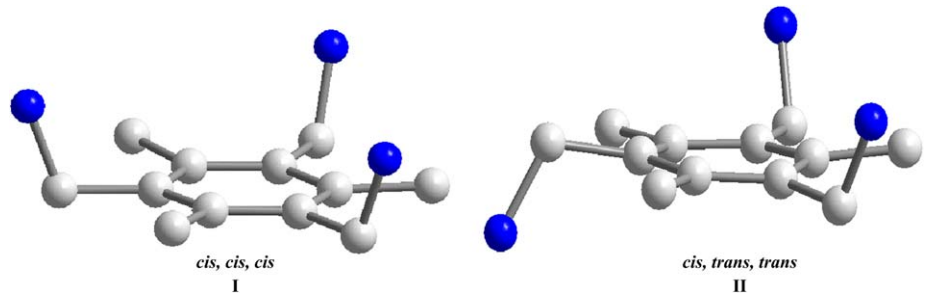



**Figure 1**. Two possible conformations of mesitylene based tripodands.

Most of the phenolic chromoionophores, including azobenzene based molecules, show the role of the phenolic groups in metal–ligand interaction.[28] Therefore, for investigation of the chromogenic behavior of **3** and to find out the origin of the color change, pH dependent UV–vis spectral titrations were performed in the presence of 0.1 M potassium nitrate (to maintain a constant ionic strength). The spectral changes obtained on titration of an acidic solution of **3c** with alkali are shown in Figure 2a. At pH 1.6 the ligand shows a band at ~ $\lambda_{max}$ 387 nm, which was assigned as an internal charge-transfer transition of the chromophore from OH to electron withdrawing nitro group. The absorption value of this band increases gradually as the pH is raised from 1.6 to 6.9. After which an increase of pH from 7.0 to 7.5 brings about a slight decrease in absorption of this band. Further increase of 1 unit of pH is accompanied by a slight red shift (~9 nm) in this band and simultaneous appearance of a new band at $\lambda_{max}$~510 nm. Any further increase in the pH produces a gradual increase in the absorption of the latter band. Deprotonation of the phenolic group in the basic conditions causes a charge density shift in the direction of the acceptor nitro substituents of the chromogenic receptor. This increases the dipole moments, which ultimately leads to a bathochromic shift[29] due to the stabilization of the photoexcited state more than the ground state. These spectral changes are completely reversible, i.e., by titrating an alkaline solution of **3c** with an acid similar changes were observed in the reverse direction as shown in Figure 2b and are brought about by the protonation of the phenolic group.

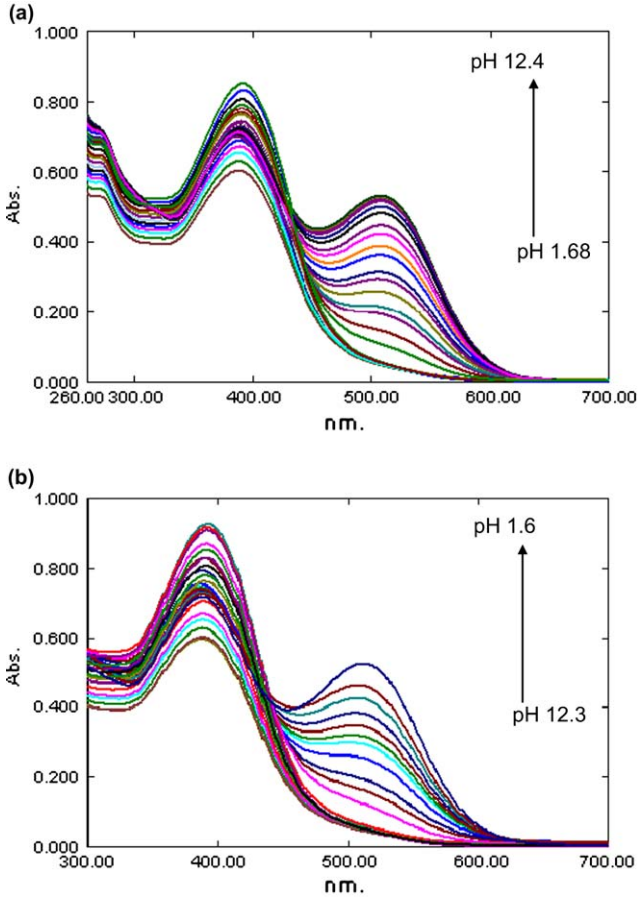



**Figure 2**. Changes in the UV–vis spectra of **3c** upon pH titration of (a) an acidic solution of **3c** with alkali and (b) an alkaline solution of **3c** with acid.

To obtain a quantitative insight into the metal affinity of the chromogenic tripodal ligands, the wavelength changes upon complexation of various metal ions were determined. The solvent system used was dioxane/water in 1:9 (V:V) ratio, so that all the studies were performed virtually in an aqueous system at 25 °C at neutral pH. Typically, receptor **3c** shows a band at $\lambda_{max}$=371 nm ($\varepsilon$=17,000 $M^{-1}$ $cm^{-1}$) in chloroform/acetonitrile (9:1) and at $\lambda_{max}$=384 nm ($\varepsilon$=16,500 $M^{-1}$ $cm^{-1}$) in water/dioxane (9:1). Figure 3 shows the changes in $\lambda_{max}$ upon addition of various metal ions. It was found that there were no significant changes in the spectra upon addition of $Li^+$, $Na^+$, $K^+$, $Sr^{2+}$, $Ca^{2+}$, $Cd^{2+}$, $Zn^{2+}$, $Hg^{2+}$, $Pb^{2+}$, $Ni^{2+}$, and $Cu^{2+}$ metal ion solutions. However, there is a marked change in $\lambda_{max}$ on addition of $Ag^+$ ion solution to the chromogenic receptor **3c** where the band at 384 nm splits into two at 394 and 510 nm. One of them showing slight and other one a marked bathochromic shift. The latter is responsible for the distinct color change (Fig. 4) of the solution from yellow ($\lambda_{max}$=384 nm) to red

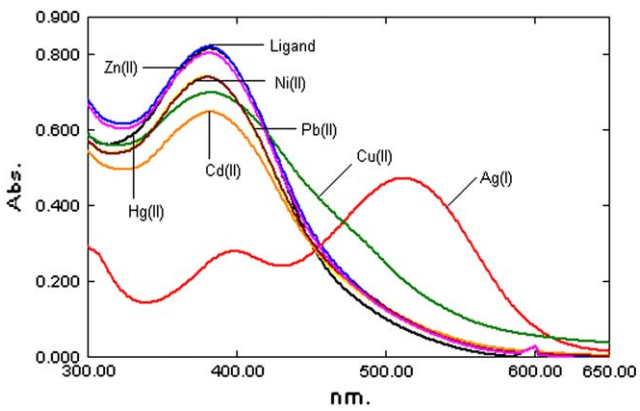



**Figure 3**. Changes in $\lambda_{max}$ of **3c** upon addition of metal ions.

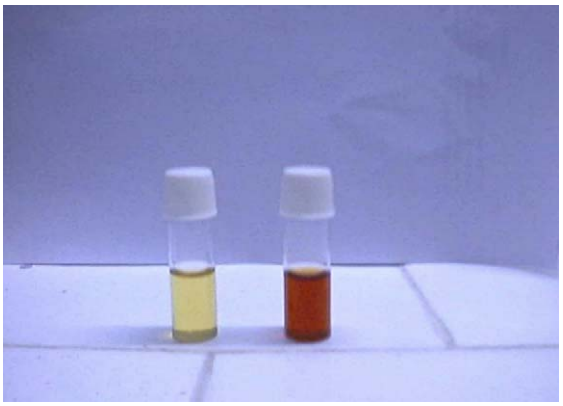


**Figure 4**. A visual change in color upon addition of $Ag^+$ salt.

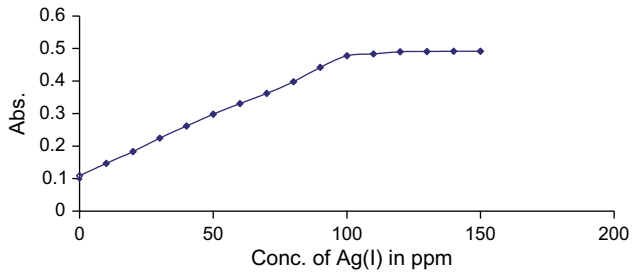



**Figure 5**. A mole-ratio plot for **3c** showing changes in absorption intensity at $\lambda_{max}$=510 nm upon addition of increased amounts of $Ag^+$ in water samples.

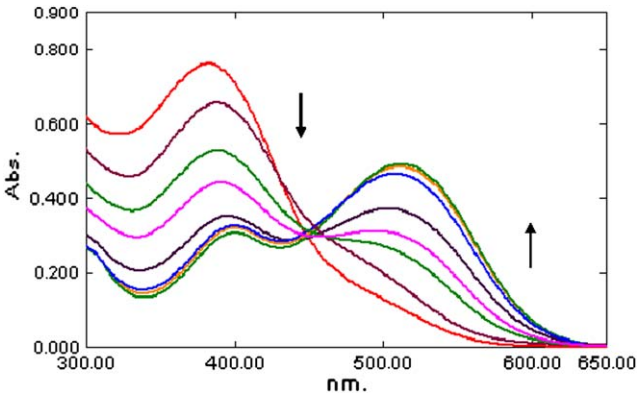



**Figure 6**. Gradual addition of $Ag^+$ into a solution of receptor **3c** shows decrease in the intensity of band at 384 nm and a new peak at 510 nm intensifies leading to an isobestic point at 450 nm.

($\lambda_{max}$=510 nm) upon addition of Ag(I), which is visible even with the naked eye.

Table 1 gives an account of the changes in $\lambda_{max.}$ in different ligands **3a–d** with various metal ions. It shows that the results for the recognition of $Ag^+$ are spectacular in the cases of ortho- and para-substituted **3a** and **3c** products and relatively less pronounced in **3b** and **3d**. These changes in the spectra have been interpreted as a consequence of 1:1 complex formation between the ligands **3** and the Ag(I) ion. The stoichiometry of the **3c** complex was determined by a titration method. The plot between absorption and concentration of Ag(I) reaches a maximum when *L*/*M* ratio is 1:1. Further addition of $Ag^+$ does not cause any change in the absorption (Fig. 5).

A gradual decrease in the intensity of band at 384 nm with a simultaneous increase in the intensity at 510 nm was seen (Fig. 6) when the concentration of metal ion solution was increased stepwise to a solution of **3c**, giving an isobestic point at 450 nm. The association constant $K_s$ for the inclusion complexes of **3** and **4** with different metal ions was determined on the basis of Benesi–Hilderbrand plots[8a,30] for 1:1 stoichiometry and are given in Table 2. The $K_a$s have not been determined with some of the metal ions because their metal ion-induced absorption changes were too small to be evaluated. It is worth noting that for receptors **3**, especially for **3c**, the association constants were the highest. This is in agreement with the observation that their metal ion-induced changes in the spectra are maximum with $Ag^+$, in the form of a new band at 510 nm. The measurements for $K_a$s of Ag complexes were made at $\lambda_{max}$~500 nm. On the other hand, no other metal ion shows the appearance of any such new band with **3**. Some of them, however, show changes only in the absorption values of the band at $\lambda_{max}$~400 nm. Their association constants were determined from measurements at these wavelengths. This shows that the ligands (**3a** and **3c**) are highly selective in their response to $Ag^+$ in comparison to other metal ions at $\lambda_{max}$~500 nm. Thus they may be used for selective recognition of $Ag^+$, which is even visually realized with these chromogenic compounds. By using these chromogenic receptors, $Ag^+$ may be detected spectrophotometrically at a low concentration of $1\times10^{-5}$M and up to a concentration of $5\times10^{-5}$M visually from the color change. More important, however, is the fact that these studies are performed in aqueous solution. On decomplexation of $Ag^+$ by thiourea the spectral changes were be totally reversible as shown in Figure 7. This suggests the reusability of the compound as a reversible chemosensor for Ag(I). The system was further extended to estimate $Ag^+$ in the presence of other soft metal ions, which cause interference in the estimation of $Ag^+$. Experiments were performed

**Table 1**. Optical response of ligands **3a–d**, **4a–b** ($10^{-4}$ M) to different metal nitrate salts ($10^{-3}$ M) in 1:9 dioxane/water

| Compd | $\lambda_{max}$ (nm) | $\varepsilon$ (l cm$^{-1}$ mol$^{-1}$) | $Ag^+$ | $Cu^{2+}$ | $Ni^{2+}$ | $Zn^{2+}$ | $Cd^{2+}$ | $Hg^{2+}$ | $Pb^{2+}$ | $Li^+$ | $Na^+$ | $K^+$ | $Ca^{2+}$ | $Sr^{2+}$ | $Co^{2+}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **3a** | 394 | $10.9\times10^3$ | +66 | +6 | +3 | +7 | −1 | 0 | −2 | −1 | +2 | 0 | 0 | +1 | — |
| **3b** | 425 | $6.2\times10^3$ | +57 | +18 | +19 | +3 | +14 | +5 | −20 | 0 | +1 | 0 | 0 | 0 | — |
| **3c** | 384 | $8.2\times10^3$ | +126 | +2 | −5 | −1 | +1 | −1 | −4 | +2 | +3 | −1 | 0 | 0 | — |
| **3d** | 364 | $13.2\times10^3$ | +9 | +2 | +3 | +1 | −1 | −22 | +1 | 0 | 0 | 0 | 0 | 0 | — |
| **4a** | 400 | $17.6\times10^3$ | −10 | −15 | −45 | — | — | — | — | — | — | — | — | — | −20 |
| **4b** | 397 | $18.2\times10^3$ | −3 | −5.0 | −10 | — | — | — | — | — | — | — | — | — | −5 |

(+) and (−) in wavelength changes denote red and blue shifts. Samples were prepared by mixing 1 ml of $10^{-3}$ M ligand solution in dioxane and 1 ml of $10^{-2}$ M metal nitrate solution in water and making 10.0 ml of the total solution.

**Table 2**. Association constants ($K_s$, $M^{-1}$) of various metal nitrates with different ligands

| Receptor | $Ag^+$ | $Cu^{2+}$ | $Ni^{2+}$ | $Zn^{2+}$ | $Cd^{2+}$ | $Hg^{2+}$ | $Pb^{2+}$ | $Na^+$ | $Co^{2+}$ |
|---|---|---|---|---|---|---|---|---|---|
| **3a** | $2.7\times10^3$ | $8.9\times10^2$ | $1.12\times10^2$ | $3.8\times10^2$ | — | — | — | | — |
| **3b** | $1.2\times10^3$ | $8.3\times10^2$ | $8.15\times10^2$ | — | $5.8\times10^2$ | — | $8.5\times10^2$ | — | — |
| **3c** | $1.8\times10^4$ | $3.2\times10^2$ | — | — | — | — | $3.5\times10^1$ | $2.3\times10^2$ | — |
| **3d** | $4.2\times10^2$ | $2.9\times10^2$ | $2.4\times10^2$ | — | — | $6.6\times10^2$ | — | — | — |
| **4a** | $4.1\times10^2$ | — | $1.4\times10^3$ | — | — | — | — | — | $9.9\times10^2$ |
| **4b** | — | $2.5\times10^2$ | $5.7\times10^2$ | — | — | — | — | — | — |

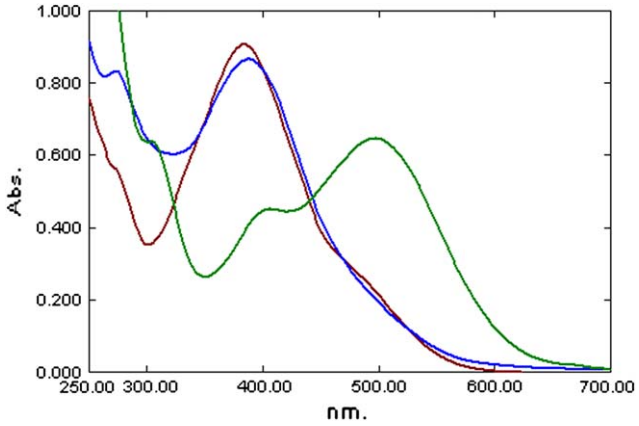



**Figure 7**. UV–vis spectra of **3c** before and after addition of Ag(I) and reversed changes upon addition of thiourea. Blue [**3c** (0.1 mM)], green [**3c**+Ag(I) (both 0.1 mM)], brown [**3c**+Ag(I) (both 0.1 mM)+thiourea (excess)].

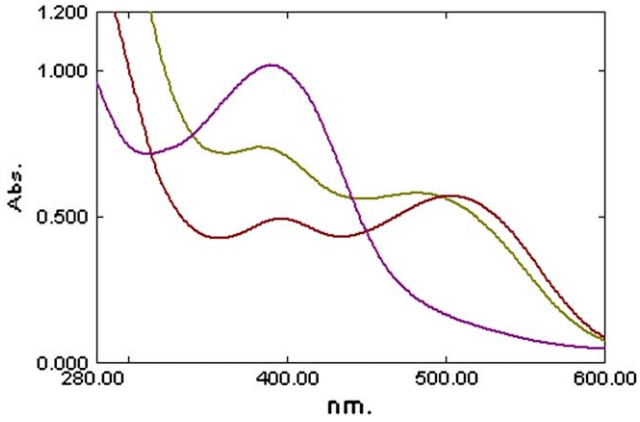



**Figure 9**. Spectra of ligand **3c**·**Ag** at different pH: purple (pH 1.6), brown (pH 7), dark green (pH 12). The aqueous phase of pH 1 and 12 was adjusted by HCl and triethylamine, respectively.

to measure absorption in the UV–vis spectra of a series of solutions containing **3c**, different amounts of Ag(I) and one other metal ion having concentrations 100–500 times more than Ag(I). The plot of absorption vs concentration of Ag(I) (Fig. 8) shows that $Cd^{2+}$, $Zn^{2+}$, $Hg^{2+}$, $Pb^{2+}$, $Ni^{2+}$ do not make any difference in the absorption value for the band at 510 nm. Hence, these metal ions do not cause any interference in the estimation of $Ag^+$, even when they are present in a concentration 500 times larger than $Ag^+$, except for $Cu^{2+}$, which causes a small interference when water samples contain $Ag^+$ at very low concentrations (less than 50 μM) and $[Cu^{2+}]/[Ag^+]$ ratio is 500.

To see the effect of pH on the metal–ligand complex the spectra of the ligand **3c** in the presence of $Ag^+$ were taken at three different pH values as shown in Figure 9. At pH 7 the complex showed two bands of different intensities, at 396 and 503 nm, just as was found for the free ligand at basic pH. In basic conditions, i.e., at pH 12, both the free ligand as well as the complex showed two bands at 384 and 484 nm, having different absorption values. The bathochromic shift at pH 12 is as expected since the phenolate ions produced in the basic conditions result in stronger interaction between **3** and $Ag^+$ leading to the absorption at 484 nm. Also two bands at different $\lambda_{max.}$ values, are indicative of two types of phenolic groups both in the free ligand (in alkaline pH) as well as in the complex (in neutral and alkaline pH). Such a band splitting has earlier been reported in the chromogenic azo-coupled calix[4]crown compounds[9a,d] with two types of -oxy units, having nonequivalent interactions with the metal ion. From this it may be inferred that the complexation does not entail complete deprotonation of all the phenolic groups to form an ion pair but is more of covalent in nature. This is in accordance with suggestions[31] made by Takagi that less basic, more charge-delocalized phenolates preferentially bind to large metal ions (with low charge densities) by forming intramolecular complexes similar to ion pairs whereas more basic, less charge-delocalized phenolates extract smaller ions (with high charge densities) preferentially by forming covalent complexes. In contrast, the UV–vis absorption peaks in the acidic solution (pH∼1) remain almost invariant (∼390 nm) both in the free ligand as well as in the complex. It may be concluded from above that there is a metal ion-induced deprotonation of the phenolic group at neutral pH in the presence of Ag(I) ions.

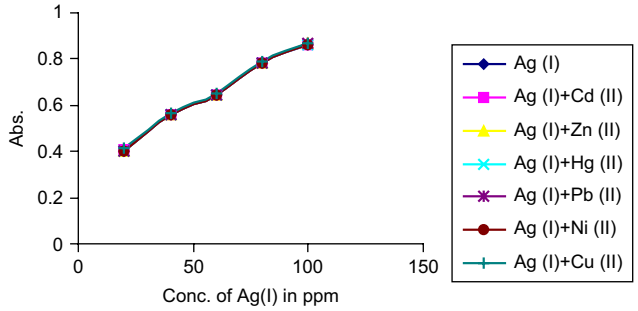



**Figure 8**. Changes in absorption intensity when $Ag^+$ is present along with other interfering cations.

The mode of binding by the receptors was inferred from the $^1H$ NMR spectra of **3a** and **3a**·$Ag^+$ taken in DMSO since ligand as well as metal ion are soluble in it. Though the peaks are broader, they showed clear and significant shifts in the chemical shift values on complexation. NMR spectra of

the complex also showed that the ligand is in conformation II as found in the free ligand. An upfield shift of $\Delta\delta$ 0.186, 0.022 in imine, 0.151 in OH, 0.016, 0.064 in methyl protons, and a downfield shift of 0.122, 0.173 in methylene protons, respectively, indicate participation of S, imine N, and hydroxyl group in coordination toward $Ag^+$ ion. The color changes accompanying interactions of **3** with $Ag^+$, demonstrate a significant chromogenic effect taking place on metal-induced cooperative binding by the phenol group. In both free state and the complex, the ligand is found in conformation II, hence one of the phenolic groups, which is pointing in the other direction may be participating cooperatively in coordination with the metal ion. This also explains the splitting of the 384 nm band of the free ligand into two bands (Fig. 3) at 394 and 510 nm in the UV–vis spectrum. Thus the observed chromogenic effect could be explained in terms of the protonable receptors undergoing complete or partial, metal-induced deprotonation of the phenolic groups. On addition of an aqueous solution of $Ag^+$ to the solution of receptor **3c**, the coordination of $Ag^+$ occurs through soft donors S and imine nitrogens and is further facilitated by cooperative binding from a polar OH group. Such cooperative, sidearm binding by phenolic groups has been seen in all phenolic chromoionophores.[28]

It has been seen that the availability of a 2-dimensional pseudo-cavity provided by soft S and imine N of the tripodal ligands in conformation II, augmented by chelation through –OH group, has an important role in cation binding and selectivity. Both are working cooperatively with each other and one would not show the chromogenic behavior in the absence of other. This was inferred by making similar UV–vis studies on **4** in 1:9 (v/v) mixture of dioxane and water. The responses in the electronic spectra of **4** for $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, and $Ag^+$ were studied (Table 1). It was seen that **4a** shows a considerable shift of 45 nm with $Ni^{2+}$ whereas $Ag^+$ shows only a small shift, both of which are hypsochromic in nature. On the other hand, **4b** hardly shows any response toward any of these metal ions. As the binding sites available in **4a** are more appropriate for the borderline transition metal ions than softer $Ag^+$, it shows better response toward $Ni^{2+}$ ion. The strong electron withdrawing nitro group at the para position to the hydroxyl group facilitates deprotonation of the latter resulting in chelation to the metal ion. The sensing units **2** (aldehydes of the dye component) do not show any significant change in their electronic spectra with $Ag^+$ ions at neutral pH (Supplementary data). This suggests that the chelation by the podand molecule, having metal specific soft binding sites and favorable disposition of the signaling unit helping in ionization of hydroxyl group, is required for the efficient chromogenic response of these chemosensors toward Ag(I) ions.

## 3. Conclusions

Silver ion selectivity and specificity of the binding unit of Schiff base **1** was optically transduced by the sensing unit **2**. Appendage of **2** to **1** has resulted in a fully reversible, chromogenic response to the binding of Ag(I) metal ion. The metal ion recognition is detectable spectrophotometrically up to a metal ion concentration of $1\times10^{-5}$ M and visually up to a concentration of $5\times10^{-5}$ M. The results are highly useful as these chromogenic compounds are developed for metal photometry in environment friendly aqueous medium. The compounds are highly Ag(I) selective and do not show any interference from common contaminants even when they are present in concentrations 500 times larger than Ag(I) ion, except for $Cu^{2+}$, which shows small interference when water samples contain Ag(I) at a very low concentration, i.e., less that 50 μM.

## 4. Experimental

### 4.1. General

Melting points are uncorrected. Most chemicals were purchased from Aldrich Co. and used as received without further purification. Organic solvents were purified by standard procedures. The elemental analyses were performed on a Flash EA 1112 elemental analyzer and FAB mass spectra were recorded at RSIC at Central Drug Research Institute, Lucknow, India. The $^1H$ and $^{13}C$ NMR were taken on a 200 MHz Bruker or a 300 MHz JEOL spectrometers using TMS as a standard reference. IR spectra were recorded on a PYE Unicam IR spectrometer for the compounds in the solid state as KBr discs or as neat samples. UV–vis absorption spectra were taken on a Shimadzu Pharamaspec UV-1700 UV–vis spectrophotometer. The compounds **2a–e** were prepared by the literature method.[8v] The tripodal amine **A1** was prepared as already reported by us.[25a]

### 4.2. General method of preparation

Compounds **3a–d** were prepared by taking tripodal amine **A1** (531 mg, 1.0 mmol) in dry acetonitrile and the aldehyde **2a–c** (1.084 g, 4.0 mmol) or **2d** (1.020 g, 4.0 mmol) in chloroform. The two solutions were mixed and the reaction mixture refluxed for 2 h. The progress of the reaction was monitored by TLC. At completion the solvent was evaporated and the product recrystallized in methanol to give reddish orange solids.

**4.2.1. Compound 3a.** Yield=64%; mp=160 °C; IR (KBr, $cm^{-1}$) 1622; FABMS $[M+1]^+$=1291; $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 1.24 (s, –OH of solvent methanol), 1.56 (br s, $-CH_3$ of solvent methanol), 1.99, 2.14 (s, 9H, $-CH_3$), 3.69, 3.74 (br s, 6H, $-CH_2$); 7.04 (d, 3H, Ar, $J$=8.0 Hz), 7.14–7.29 (m, 6H, Ar), 7.41–7.52 (m, 6H, Ar), 7.59–7.66 (m, 6H, Ar), 7.68–7.83 (m, 6H, Ar), 7.87–7.97 (m, 6H, Ar) 8.50 (s, 3H, CH=N), 14.03 (s, 3H, OH); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 15.61 ($CH_3$), 29.68 ($CH_2$), 118.13 (Ar), 118.39 (Ar), 118.58 (Ar), 119.05 (Ar), 123.94 (Ar), 124.12 (Ar), 127.70 (Ar), 128.09 (Ar), 128.57 (Ar), 129.91 (Ar), 130.31 (Ar), 131.32 (Ar), 132.33 (Ar), 132.88 (Ar), 145.25 (Ar), 146.95 (Ar), 147.42 (Ar), 160.75 (–CH=N), 165.49 (ArOH); Anal. Calcd $C_{69}H_{54}N_{12}O_9S_3$: C 64.18, H 4.18, N 13.02, S 7.44; found: C 63.89, H 4.38, N 13.64, S 6.98.

**4.2.2. Compound 3b.** Yield=63%; mp=185 °C; IR (KBr, $cm^{-1}$) 1616; FABMS $[M+1]^+$=1291; $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 1.26 (s, –OH of solvent methanol), 1.57 (br s, $-CH_3$ of solvent methanol), 2.00, 2.17 (s, 9H, $-CH_3$), 3.72,

3.97 (s, 6H, –$CH_2$), 7.06 (d, 3H, Ar, $J$=8.0 Hz), 7.09–7.30 (m, 12H, Ar), 7.33–7.40 (m, 3H, Ar), 7.62–7.66 (m, 6H, Ar), 7.95–8.55 (m, 9H, Ar), 8.55–8.60 (m, 3H, CH═N), 13.87, 13.98 (s, 3H, OH); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$15.65 ($CH_3$), 15.79 ($CH_3$), 29.68 ($CH_2$), 33.64 ($CH_2$), 116.61 (Ar), 118.13 (Ar), 118.60 (Ar), 119.05 (Ar), 124.35 (Ar), 127.27 (Ar), 127.67 (Ar), 128.05 (Ar), 129.05 (Ar), 129.25 (Ar), 129.84 (Ar), 130.64 (Ar), 131.28 (Ar), 132.42 (Ar), 136.46 (Ar), 144.88 (Ar), 146.93 (Ar), 148.94 (Ar), 152.89 (Ar), 160.79 (CH═N), 165.28 (ArOH); Anal. Calcd $C_{69}H_{54}N_{12}O_9S_3$: C 64.18, H 4.18, N 13.02, S 7.44; found: C 63.78, H 3.97, N 12.89, S 6.89.

**4.2.3. Compound 3c.** Yield=63%; mp=210 °C; IR (KBr, $cm^{-1}$) 1625; FABMS $[M+1]^+$=1291; $^1$H NMR ($CDCl_3$, 200 MHz) $\delta$ 1.26 (s, –OH of solvent methanol), 1.58 (br s, –$CH_3$ of solvent methanol), 2.01 (br s, 9H, –$CH_3$), 3.71–3.79 (m, 6H, –$CH_2$), 6.91–7.46 (m, 18H, Ar), 7.57 (d, 3H, Ar, $J$=8.0 Hz), 7.94 (d, 3H, Ar, $J$=8.0 Hz), 8.07 (s, 3H, Ar), 8.29–8.37 (m, 6H, Ar), 8.43–8.56 (m, 3H, –CH═N), 13.17, 14.07 (s, 3H, OH); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 15.60 ($CH_3$), 26.99 ($CH_2$), 29.67 ($CH_2$), 117.27 (Ar), 118.07 (Ar), 119.03 (Ar), 123.12 (Ar), 124.70 (Ar), 125.45 (Ar), 127.37 (Ar), 128.15 (Ar), 129.94 (Ar), 130.36 (Ar), 131.38 (Ar), 132.35 (Ar), 136.52 (Ar), 146.90 (Ar), 147.42 (Ar), 160.75 (CH═N), 165.58 (ArOH); Anal. Calcd $C_{69}H_{54}N_{12}O_9S_3$: C 64.18, H 4.18, N 13.02, S 7.44; found: C 64.56, H 4.56, N 12.88, S 6.93.

**4.2.4. Compound 3d.** Yield=64%; mp=165 °C; IR (KBr, $cm^{-1}$) 1614; FABMS $[M+1]^+$=1258, 1260 (isotopic peaks); $^1$H NMR ($CDCl_3$, 200 MHz) $\delta$ 1.25 (s, –OH of solvent methanol), 1.59 (br s, –$CH_3$ of solvent methanol), 2.00, 2.14 (s, 9H, –$CH_3$), 3.74, 3.95 (s, 6H, –$CH_2$), 7.07 (d, 3H, Ar, $J$=8.0 Hz), 7.16–7.33 (m, 12H, Ar), 7.40–7.56 (m, 6H, Ar), 7.60–7.66 (m, 6H, Ar), 8.00–8.06 (m, 6H, Ar), 8.53 (s, 3H, –CH═N), 13.89 (s, 3H, OH); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 15.62 ($CH_3$), 29.73 ($CH_2$), 33.66 ($CH_2$), 117.52 (Ar), 118.20 (Ar), 118.32 (Ar), 119.05 (Ar), 127.21 (Ar), 127.90 (Ar), 128.10 (Ar), 128.19 (Ar), 130.08 (Ar), 130.57 (Ar), 130.70 (Ar), 131.98 (Ar), 132.10 (Ar), 134.02 (Ar), 136.44 (Ar), 145.61 (Ar), 147.24 (Ar), 148.57 (Ar), 161.05 (CH═N), 164.64 (ArOH); Anal. Calcd $C_{69}H_{54}N_9O_3S_3Cl_3$: C 65.87, H 4.29, N 10.02, S 7.63; found: C 65.32, H 4.53, N 10.37, S 7.97.

### 4.3. Stability constant determination

Fifteen measuring flasks were taken each containing 1 ml of ligand solution ($1\times10^{-3}$ M, in dioxane) along with varied amounts (0.1–1.5 ml) of metal nitrate solution ($1\times10^{-3}$ M, in water). Then the measuring flasks were filled to make 10 ml, with a stock solution of a commercially available buffer of pH 7 and 1 M $KNO_3$. The measurements for Ag(I) were made at $\lambda_{max}$~510 nm and for the remaining metals at $\lambda_{max}$~400 nm.

### 4.4. Mole-ratio method

Fifteen solutions were made by varying *L*/*M* ratio and keeping the total volume of the solution constant as 10 ml in water/dioxane 9:1. The concentration of the receptor was kept at $10^{-4}$ M in all the solutions, while the metal ion concentration was varied from $1\times10^{-5}$ to $1.5\times10^{-4}$ M in different solutions. A stock solution of a commercially available buffer solution of pH 7 and 1 M $KNO_3$ was used to maintain a constant pH and ionic strength. The absorption was measured at 510 nm as it showed the maximum and the cleanest variation upon addition of $Ag^+$.

### 4.5. Ion interference studies

For every interfering ion, five 10 ml measuring flasks each containing 1 ml of ligand solution ($1\times10^{-3}$ M, in dioxane) were taken. To these varied amounts of water solution of $Ag^+$ (0.20–1.0 ml of $1\times10^{-3}$ M) were added. Then 1 ml solution of one interfering metal ion ($1\times10^{-1}$ M) was added to all of them. The measuring flasks were then filled up to the mark with buffered solution of pH 7 and 1 M $KNO_3$ in water so as to keep the composition of solution in each flask as constant. The respective flasks thus contained interfering metal ion in concentrations 100–500 times more than Ag(I). The absorption of each solution was recorded at $\lambda_{max}$=510 nm.

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## Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2006.05.047.

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