Chapter-2

Thiacalix[4]arene based fluorogenic receptors

Abstract

Thiacalix[4]arene derivatives 12, 13 and 15 based on cone and 1,3alternate conformations appended with rhodamine and dimethylaminocinnamyl moieties have been designed and synthesized. The binding behaviour of these receptors was investigated with UV-vis and fluorescence spectroscopy. Chemosensor 12 and 13 having rhodamine moieties undergoes fluorescence enhancement in the presence of Hg$^{2+}$ ions. However, in case of receptor 12 of cone conformation emission enhancement also occurs with Fe$^{2+}$ and Fe$^{3+}$ ions. Thiacalix[4]arene based chemosensor 15 of 1,3alternate conformation having dimethylaminocinnamyl moieties exhibits selective fluorescence emission shift in the presence of Ag$^+$ ions with a detection limit in the nanomolar range.
2.1. Introduction

Metal ions, particularly transition metal ions play an important role in environmental and biological systems. Among various soft metal ions, mercury is one of the most significant cations because of its toxic effects. The exposure to mercury even at very low concentration leads to digestive, kidney and especially neurological diseases as mercury can easily pass through the biological membranes. On the other hand, the use of silver in the electrical, photographic imaging and pharmaceutical industries results in the contamination of environment. Silver ions have a negative effect in biological systems, such as interacting with vital enzymes which results in inactivation of these enzymes, interacting with cell membrane and interfering with electron transport. Hence, the development of fluorescent receptors for simple and rapid detection of these soft metal ions is very important.

Thiacalix[4]arene is a molecular scaffold of particular interest for the design of different types of artificial receptors because of its unique three-dimensional structure in which the bridging methylene groups of the conventional calix[4]arene have been replaced by the sulfur atoms. The presence of sulfur atoms makes thiacalix[4]arene as an efficient host molecule for transition metal ions. Further, the bridging sulfur of thiacalix[4]arene undergoes easy oxidation to sulfoxides (SO) and sulfones (SO$_2$) which changes the properties of the cavity formed by the calix benzene rings. Thiacalix[4]arene exhibits a broad range of interesting functions, chemical behaviour and novel conformational preferences. Thus, there is much more potential in investigating the chemistry of thiacalix[4]arene as an artificial host molecule. The conformational and functionalization control of thiacalix[4]arene scaffold with suitable ligating and signaling units is advantageous to the recognition of metal ions. Thiacalix[4]arenes derivatized with functional groups such as ether 1a, ester 1b and 2, ketone 1c and 1d, and amide 1e and 1f have been reported as host molecules for alkali and transition metal ions. Stoikov et al. synthesized thiacalix[4]arene
Chapter 2: Thiacalix[4]arene based fluorogenic receptors

Based receptors 3a-3d of cone, 3e-3h of partial cone and 3i-3l of 1,3-alternate conformations functionalized with secondary amide and hydrazide groups at the lower rim for metal ions such as Li$^+$, Na$^+$, Fe$^{3+}$, Co$^{3+}$, Cu$^{2+}$, Ag$^+$ and Hg$^{2+}$. Further, thiacalix[4]arene platform can be appended with different types of ligating sites which is difficult to obtain in a single host molecule. In this context, Yamato et al.$^{15}$ reported thiacalix[4]arene based ditopic receptor 4a which forms mononuclear complexes with Li$^+$ and Ag$^+$ ions. In addition, thiacalix[4]arene can be appended with different types of fluorophores such as pyrene anthracene and dansyl for the development of fluorescent chemosensors.$^{16}$ Yamato et al.$^{17}$ reported fluorescent chemosensor 4b based on thiacalix[4]arene of 1,3-alternate conformation with pyrenyl-appended triazole moieties for selective detection of Ag$^+$ ions. Kumar et al.$^{16b}$ reported a thiacalix[4]crown derivative 4c of 1,3-alternate conformation possessing anthracene moieties which exhibits fluorescence enhancement in the presence of Fe$^{3+}$ ions. However, the selectivity and sensitivity of these receptors toward the targeted soft metal ions is relatively poor. Thus, it is very important to design fluorescent chemosensors which exhibit high selectivity and sensitivity toward soft metal ions.

For binding of soft metal ions it is very important to have soft ligating sites like nitrogen and sulfur in the host molecule. We envisaged that thiacalix[4]arene scaffold
which has four soft sulfur atoms, if suitably decorated with soft ligating sites like imino nitrogens might be a good candidate for binding of soft metal ions. Keeping this in mind, in the present work we designed and synthesized fluorescent chemosensors 12 and 13 based on thiacalix[4]arene of cone and 1,3-alternate conformations appended with rhodamine moieties. We have chosen rhodamine as signaling unit because of its good photostability, high extinction coefficient, high fluorescent quantum yield and its tendency to respond mainly transition metal ions.  

Chemosensor 12 of cone conformation appended with rhodamine undergoes fluorescence enhancement in the presence of Fe$^{2+}$, Fe$^{3+}$ and Hg$^{2+}$ ions whereas, chemosensor 13 of 1,3-alternate conformation undergoes selective fluorescence enhancement in the presence of only Hg$^{2+}$ ions with a detection limit up to nanomolar range. In addition, we also designed and synthesized chemosensor 15 based on thiacalix[4]arene of 1,3-alternate conformation appended with dimethylaminocinnamyl moieties through imine units. We have chosen dimethylaminocinnamyl moiety because it exhibits dual fluorescence phenomenon owing to the intramolecular charge transfer (ICT) excited state. Receptor 15 undergoes selective fluorescence shift in the presence of soft Ag$^{+}$ ions. The results of our findings have been divided into two sections and are discussed as follows.

1. Rhodamine appended thiacalix[4]arene of 1,3-alternate conformation for nanomolar detection of Hg$^{2+}$ ions
2. Thiacalix[4]arene-cinnamaldehyde derivative: ICT-induced preferential nanomolar detection of Ag$^{+}$ among different transition metal ions

2.2. Results and discussion

2.2.1. Rhodamine appended thiacalix[4]arene of 1,3-alternate conformation for nanomolar detection of Hg$^{2+}$ ions

Mitsunobu reaction of thiacalix[4]arene 5 with N-(2-hydroxyethyl)phthalimide 6 gave compound 7 in 67% yield (Scheme 2.1). The hydrazinolysis of compound 7 in ethanol gave diamine 5,11,17,23-tetra-tert-butyl-syn-25,27-bis(2-aminoethoxy)-26,28-dihydroxythiaca[4]rene 8 of cone conformation in 74% yield (Scheme 2.1). Similarly, Mitsunobu reaction of compound 7 with propanol gave compound 9 in 79% yield and which on hydrazinolysis gave diamine 5,11,17,23-tetra-tert-butyl-
syn-25,27-bis(2-aminoethoxy)-26,28-dipropoxythiacalix[4]arene 10 of 1,3-\textit{alternate} conformation in 71% yield (Scheme 2.1).

![Scheme 2.1 Synthesis of thiacalix[4]arene derivatives 8 and 10.]

The reaction of rhodamine acid chloride 11 (prepared by the reaction of rhodamine B and phosphorus oxychloride) with diamine 8 furnished compound 12 in 44% yield (Scheme 2.2). Similarly, the reaction of rhodamine acid chloride 11 with diamine 10 furnished compound 13 in 53% yield (Scheme 2.2). The structures of compounds 12 and 13 were confirmed from their spectroscopic and analytical data. The \textsuperscript{1}H NMR spectrum of compound 12/13 showed four singlets (18H, 18H, 4H and 4H) at 0.76/0.97, 1.28/1.15, 6.83/7.26 and 7.52/7.30 ppm corresponding to the tert-butyl and aromatic protons, a triplet (24H each) at 1.12/1.10 ppm corresponding to the CH\textsubscript{3} protons, a quartet/multiplet (16H each) at 3.25-3.32/3.21-3.32 ppm corresponding to the NCH\textsubscript{2} protons of rhodamine moiety, a triplet/multiplet (4/8H) at 3.66/349-3.60 ppm corresponding to the NCH\textsubscript{2} and OCH\textsubscript{2} protons, a triplet (4H) at 3.79/3.85 ppm corresponding to the OCH\textsubscript{2} protons, five multiplets (4/4H, 8/8H, 4/2H, 4/4H and 2/2H) at 6.19-6.23/6.17-6.21, 6.34-6.39/6.37-6.41, 7.02-7.07/7.04-7.07, 7.38-7.41/7.38-7.41 and 7.84-7.87/7.88-7.91 ppm corresponding to the aromatic and OH protons. In addition to the above signals, compound 13 also showed a triplet and a multiplet (6H and 4H) at 0.90 and 1.60-1.70 ppm corresponding to the CH\textsubscript{3} and CH\textsubscript{2}
protons. In the mass spectra, the parent ion peaks for compounds 12 and 13 were observed at $m/z$ $(M+2)^+$ 1656 and 1740, respectively. These spectroscopic data corroborate with structures 12 and 13 for these compounds.

![Scheme 2.2 Synthesis of thiacalix[4]arene-rhodamine derivatives 12 and 13.](image)

The binding behaviour of compound 12/13 was studied toward different metal ions ($\text{Hg}^{2+}$, $\text{Fe}^{2+}$, $\text{Fe}^{3+}$, $\text{Cu}^{2+}$, $\text{Ni}^{2+}$, $\text{Cd}^{2+}$, $\text{Co}^{2+}$, $\text{Pb}^{2+}$, $\text{Zn}^{2+}$, $\text{Ba}^{2+}$, $\text{Ag}^+$, $\text{K}^+$, $\text{Na}^+$ and $\text{Li}^+$) as their perchlorate salts by UV-vis and fluorescence spectroscopy. The absorption spectrum of 12/13 (5 μM) in THF did not exhibit any absorption of rhodamine moiety as the spirolactam ring of rhodamine moiety is in ring closed form (Figure 2.1/2.2). However, with gradual addition of $\text{Hg}^{2+}$ ions, a new absorption band appeared at 554 nm in both cases along with a colour change from colourless to pink (Inset of Figure 2.1/2.2). The formation of new absorption band at 554 nm is attributed to the opening of the spirolactam ring upon addition of $\text{Hg}^{2+}$ ions. The additions of other transition and alkali metal ions did not alter the absorption spectrum of compound 12/13 (Figure 2.3/2.4) except the addition of $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ ions to the solution of compound 12 which results in the formation of a absorption band at ~550 nm (Figure 2.3) along with the appearance of pink colour (Inset of Figure 2.3). Thus, receptor 13 is more selective toward $\text{Hg}^{2+}$ ions and acts as an efficient colorimetric chemosensor for detection of $\text{Hg}^{2+}$ ions.
In the fluorescence spectrum, receptor 12/13 (1 μM) exhibited no fluorescence emission when excited at 530 nm in THF (Figure 2.5/2.6). Upon addition of increasing amounts of Hg$^{2+}$ ions to the solution of receptor 12/13, a remarkable enhancement in emission intensity was observed at 572/576 nm (Figure 2.5/2.6). Fluorescence enhancement observed for receptor 12/13 upon addition of Hg$^{2+}$ ions is attributed to the formation of the 12-Hg$^{2+}$/13-Hg$^{2+}$ complex resulting in the opening of spirolactam ring of rhodamine to amide form that enhances the fluorescence emission. Thus, the addition of Hg$^{2+}$ ions ‘Turns On’ the fluorescence whereby the colourless, non-fluorescent and spirolactam form of compound 12/13 changes to coloured, highly fluorescent (orange) with spirolactam ring-opened form (Inset of Figure 2.5/2.6). Under the same conditions as used for Hg$^{2+}$, we also tested the fluorescence response of receptor 12/13 toward other metal ions. A negligible change in fluorescence occurred in the presence of other metal ions in the case of receptor 13 (Figure 2.7) whereas in the case of receptor 12 fluorescence enhancement also occurred in the presence of Fe$^{2+}$ and Fe$^{3+}$ ions in addition to the Hg$^{2+}$ ions. The reason
for fluorescence enhancement of 12 in the presence of Fe$^{2+}$ and Fe$^{3+}$ ions might be due to the participation of hydroxyl oxygens as binding sites in binding toward the Fe$^{2+}$ and Fe$^{3+}$ ions, which in the case of receptor 13 being in 1,3-*alternate* conformation are oriented away from Fe$^{2+}$ and Fe$^{3+}$ ions. Thus, receptor 13 is more selective to Hg$^{2+}$ ions in comparison to receptor 12 (Figure 2.8).
Further, to check the practical applicability of receptor 13 as Hg\(^{2+}\) selective fluorescent sensor, we also carried out competitive experiments in the presence of Hg\(^{2+}\) at 30 µM mixed with other metal ions at 30 µM. As shows in Figure 2.9, no significant variation was found in the fluorescence intensity with or without the other metal ions. It was found that 13 has a detection limit of 16 nanomolar for Hg\(^{2+}\) which is sufficiently low for the detection of nanomolar concentration range of Hg\(^{2+}\) ions. By considering the ratio of the fluorescence intensity (I/I\(_o\)) at 576 nm, we observed 136-fold fluorescence increase in the case of 13-Hg\(^{2+}\) complex. Fitting the changes in fluorescence spectra of compound 13 with Hg\(^{2+}\) ions, the nonlinear regression analysis program SPECFIT\(^{24}\) gave a good fit and demonstrated that 1:2 stoichiometry (host:guest) was the most stable species in the solution with a binding constant (log \(\beta\)) of 8.20 with ± 0.07 error. The method of continuous variation\(^25\) (Job’s plot) was also used to prove the 1:2 stoichiometry (Figure 2.10). The binding of Hg\(^{2+}\) with the spirolactam ring of receptor 13 is proved by \(^1\)H NMR spectroscopy (Figure 2.11). The aromatic protons H\(^a\), H\(^b\), H\(^c\) and NCH\(_2\) protons corresponding to the rhodamine

![Figure 2.9](image)

**Figure 2.9** Fluorescence competitive selectivity (I-I\(_o\)/I\(_o\)) of 13 (1 µM) toward Hg\(^{2+}\) ions (30 µM) in the presence of other metal ions (30 µM) in THF; \(\lambda_{\text{ex}} = 530\) nm. (I-I\(_o\)/I\(_o\)); I\(_o\) = initial emission intensity at 576 nm; I = final emission intensity at 576 nm after addition of metal ions.

![Figure 2.10](image)

**Figure 2.10** Job’s plot for determining the stoichiometry (1:2) of 13 and Hg\(^{2+}\) ions.
moeity of receptor 13 undergo downfield shift of $\Delta \delta = 0.16, 0.20, 0.18$ and 0.13 ppm, respectively in the presence of 2.0 equiv of Hg$^{2+}$ ions which indicates transformation of non-fluorescent spirocyclic form of rhodamine moiety in receptor 13 to the fluorescent ring opened amide form. The fluorescence quantum yield$^{26}$ ($\Phi_f$) of compound 13 in the free and Hg$^{2+}$ bound state was found to be 0.06 and 0.51 respectively.

![Image](image1.png)

**Figure 2.11** $^1$H NMR spectra of 13 in CDCl$_3$/CD$_3$CN (8:2); (A) Free ligand 13; (B) 13 + 2.0 equiv of Hg(ClO$_4$)$_2$.

The substantial increase in the quantum yield of receptor 13 in the presence of Hg$^{2+}$ ions and its high Hg$^{2+}$ ions selectivity showed its credibility as a good Hg$^{2+}$ ion sensor. We also carried out reversibility experiment which proved that binding of Hg$^{2+}$ ions with compound 13 was reversible. In the presence of KI, the iodide ion because of its strong affinity for Hg$^{2+}$ ions forms a complex with it, which results in the decomplexation of the receptor-Hg$^{2+}$ complex. On further addition of Hg$^{2+}$ ions the fluorescence intensity was revived again indicating the reversible behaviour of the receptor 13 for the Hg$^{2+}$ ions (Figure 2.12).

![Image](image2.png)

**Figure 2.12** Fluorescence spectra showing reversibility of Hg$^{2+}$ coordination to receptor 13 by KI; blue line, free 13 (1 µM), green line, 13 + 20 µM Hg$^{2+}$, red line, 13 + 20 µM Hg$^{2+}$ + 200 µM KI, orange line, 13 + 20 µM Hg$^{2+}$ + 200 µM KI + 100 µM Hg$^{2+}$, in THF; $\lambda_{ex} = 530$ nm.
In conclusion, we synthesized new thiacalix[4]arene appended rhodamine based chemosensors 12 and 13. Chemosensor 13 of 1,3-\textit{alternate} conformation selectively senses Hg$^{2+}$ ions among various metal ions tested with a detection limit up to nanomolar range.

2.2.2. Thiacalix[4]arene-cinnamaldehyde derivative: ICT-induced preferential nanomolar detection of Ag$^+$ among different transition metal ions

In the section 2.2.1, we discussed about chemosensors 12 and 13 which undergo fluorescence enhancement in the presence of Hg$^{2+}$/Fe$^{3+}$/Fe$^{2+}$ and Hg$^{2+}$ ions, respectively. For high sensitivity and simplicity, a significant spectral shift in either the absorption or emission spectra becomes very important. However, fluorescence enhancement with spectral shift for silver ions is limited till now because silver ions usually quench fluorescence emission via the electron transfer and intersystem crossing processes. Thus, it is extremely advantageous to design a sensor which exhibits spectral shifts in the presence of silver ions. The most fundamental way to assure such a spectral change is to design a molecule exhibiting intramolecular charge transfer (ICT) mechanism which involves the observation of changes in the ratio of the intensities of the absorption or the emission at two wavelengths. Keeping this point in view, we have designed and synthesized receptor 15 based on thiacalix[4]arene of 1,3-\textit{alternate} conformation bearing dimethylaminocinnamyl moieties which exhibits selective fluorescence emission shift in the presence of Ag$^+$ ions as a consequence of enhanced intramolecular charge transfer (ICT) process.

The condensation of diamine 10 with $N,N$-dimethylaminocinnamaldehyde 14 furnished compound 15 in 78% yield (Scheme 2.3). The structure of compound 15 was confirmed from its spectroscopic and analytical data. The IR spectrum of compound 15 showed -HC=N- group stretching band at 1602 cm$^{-1}$. There is no absorption band corresponding to free aldehyde and amino groups, which indicates

![Scheme 2.3 Synthesis of receptor 15.](image-url)
that the condensation has taken place. The $^1$H NMR spectrum of compound 15 showed four triplets (6H, 4H, 4H and 4H) at 0.62, 3.05, 3.82 and 4.14 ppm corresponding to the CH$_3$, NCH$_2$, OCH$_2$ and OCH$_2$ protons, three multiplets (4H, 8H and 8H) at 1.02-1.09, 6.63-6.74 and 7.31-7.34 ppm corresponding to the methylene, aromatic and CH protons, four singlets (18H, 18H, 12H and 4H) at 1.26, 1.28, 2.99 and 7.41 ppm corresponding to the tert-butyl, NCH$_3$ and aromatic protons and a doublet (2H) at 7.87 ppm corresponding to the imino protons. The mass spectrum showed a parent ion peak at $m/z$ 1205 (M+1)$^+$ corresponding to the compound 15. These spectroscopic data corroborate the structure 15 for this compound.

The binding behaviour of compound 15 toward different cations was studied by UV-vis and fluorescence spectroscopy. The titration experiments were carried out in dry THF by adding aliquots of different metal ions. The absorption spectrum of 15 (10 µM) is characterized by typical absorption bands of dimethylaminocinnamyl moiety at 265 and 352 nm (Figure 2.13A) assigned to the transition from S$_0$ to S$_2$ and S$_1$ states, respectively. Low energy absorption at 352 nm indicates that this is a $\pi-\pi^*$ type of transition. Addition of Ag$^+$ ions up to one equivalent result in the red shift of the band centered at 352 nm to 396 nm with an isosbestic point at 370 nm (Figure 2.13A). The formation of new band at 396 nm is due to the interaction of Ag$^+$ ions with imino nitrogen atoms leading to weak intramolecular charge transfer (ICT) from the nitrogen atom of the dimethylamino moiety to the imino nitrogen atom. On further addition of Ag$^+$ ions (1-100 equiv) the absorption band at 396 nm decreases with simultaneous appearance of a new absorption band at 466 nm (Figure 2.13B). The variations in the absorption bands at 396 and 466 nm on addition of Ag$^+$ ions led to a
clear isosbestic point at 432 nm. We believe that as the amount of Ag$^+$ ions increases, the interaction between Ag$^+$ ions and imino nitrogen atoms induces an enhanced ICT from the nitrogen atom of the dimethylamino moiety to the imino nitrogen atom, of which the electron density is diminished on interaction with Ag$^+$ ions which results in a large red shift with appearance of a new band at 466 nm accompanied by visible colour change (Inset of Figure 2.13B). In the presence of 100 equivalents of other metal ions like Hg$^{2+}$, Fe$^{2+}$, Fe$^{3+}$, Zn$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Cd$^{2+}$, Pb$^{2+}$, Ba$^{2+}$ and Mg$^{2+}$ the absorption band at 352 nm decreases accompanied by red shift to 466 nm (Figure 2.14). The addition of K$^+$, Li$^+$ and Na$^+$ ions result in the small decrease in absorbance at 352 nm with slight red shift (Figure 2.14). The addition of just one equivalent of divalent metal ions shifted the absorption of 15 from 352 nm to 466 nm as divalent metal ions have more affinity toward electrons and this immediately induced a strong intramolecular charge transfer in comparison to Ag$^+$ ions, being of monovalent nature.

![Figure 2.14](image)

**Figure 2.14** UV-vis spectra of 15 (10 μM) with various metal ions (100 equiv each) in THF.

From these UV-vis studies it is clear that compound 15 is interacting with different metal ions in the ground state. Fitting the changes in the absorbance spectra of compound 15 with different metal ions that changes the absorption spectrum of 15, the nonlinear regression analysis program SPECFIT demonstrated that 1:1 stoichiometry (host:guest) was the most stable species in the solution with different binding constants (Table 2.1). From the binding constant data it is clear that the binding of Ag$^+$ with compound 15 is relatively strong in comparison to the binding of other metal ions with compound 15.

The fluorescence spectrum of compound 15 (1 μM) in THF exhibits a strong emission at 418 nm when excited at 360 nm (Figure 2.15). The intense fluorescence emission of 15 at 418 nm is due to the extended conjugated system which involves the

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<th>log β</th>
<th>Metal ions</th>
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<td>5.02 ± 0.44</td>
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<td>Fe$^{2+}$</td>
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<td>Fe$^{3+}$</td>
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<td>Ba$^{2+}$</td>
<td>3.34 ± 0.05</td>
<td>Mg$^{2+}$</td>
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Table 2.1 Binding constants of different metal ions with compound 15.
redistribution of charge in the excited state and makes a twisted intramolecular charge transfer (TICT) state responsible for the emission of receptor 15. To confirm that the emission observed for receptor 15 in THF is based on the twisted intramolecular charge transfer, we studied the fluorescence behaviour of receptor 15 in various polar and non-polar solvents (Figure 2.15). In non-polar solvents (benzene and toluene) receptor 15 shows unresolved emission corresponding to both delocalized excited (DE) state at short wavelength (402 nm) and twisted intramolecular charge transfer (TICT) state at longer wavelength (414 nm). Any increase in polarity of the solvents did not affect the position of delocalized excited band. In comparison to delocalized excited band, TICT band shows a large red shift while moving from non-polar to polar solvents. For example, in THF a red shift of TICT band (4 nm) was observed in comparison to non-polar solvents, while the presence of delocalized excited band is hardly observed as in this case the delocalized excited band goes underneath the envelop of TICT emission band. Thus, the appearance of red shifted emission band in polar solvents clearly indicates that the emission of the receptor 15 in THF is due to the twisted intramolecular charge transfer state. Further, upon addition of just two equivalents (0-2 μM) of Ag⁺ ions to the receptor 15 in THF, the emission band centered at 418 nm quenches completely and a new emission band appears at 488 nm with a bathochromic shift of about 70 nm (Figure 2.16A). With further additions of Ag⁺ ions (2-30 μM) the emission band at 488 nm shows significant fluorescence enhancement (Figure 2.16B) also visible by naked eye (Inset of Figure 2.16B). The fluorescence behaviour of compound 15 in the presence of Ag⁺ ions is attributed to the alteration in the electronic properties of 15 i.e. increased intramolecular charge.

![Figure 2.15](image-url) Fluorescence spectra of 15 (1 μM) in polar and non-polar solvents; λex = 360 nm.
transfer (ICT) on metal ion complexation. The nitrogen atoms of the imino moieties got involved in the coordination with silver ions which enhances the electron withdrawing ability of imino nitrogen atoms which leads to an enhanced intramolecular charge transfer process and consequently results in a large red shift.

![Figure 2.16](image)

**Figure 2.16** Fluorescence spectra of 15 (1 µM) with Ag⁺ ions in THF; λₑₓ = 360 nm; (A) in the presence of 0-2 equiv of Ag⁺ ions; (B) in the presence of 0-30 equiv of Ag⁺ ions; inset of (B) showing the fluorescence change: (a) before; (b) after the addition of Ag⁺ ions.

This type of emission shift is not observed by the addition of any other metal ions (Figure 2.17). The addition of metal ions like Hg²⁺, Fe²⁺, Fe³⁺, Zn²⁺, Cu²⁺, Cd²⁺ and Pb²⁺ shows linear decrease of the emission at 418 nm (Figure 2.18). Fluorescence quenching in case of Hg²⁺ and Pb²⁺ may be attributed to spin-orbit coupling, in the presence of Cu²⁺ and Fe³⁺ ions may be due to the paramagnetic nature of these ions and in the presence of Fe²⁺, Zn²⁺ and Cd²⁺ ions may be due to photoinduced electron transfer from the photoexcited dimethylamino phenyl moiety to the coordinated metal ions. However, the preferred ICT process from nitrogen atom of dimethylamino moiety (donor) to the metal bound imino nitrogen atom (acceptor) may also contribute to the observed fluorescence quenching. The addition of other metal ions such as...
Ba$^{2+}$, Mg$^{2+}$, K$^+$, Li$^+$, Na$^+$, Ni$^{2+}$ and Co$^{2+}$ did not alter the fluorescence emission of compound 15.

**Figure 2.18** Fluorescence spectra of 15 (1 µM) with different metal ions (30 equiv each) showing the linear decrease of the emission at 418 nm in THF; $\lambda_{ex} = 360$ nm.

Further, by considering the ratio of the fluorescence intensity at 488 nm ($I_{488}$) to that of 418 nm ($I_{418}$), we observed 13-fold fluorescence enhancement in the case of 15-Ag$^+$ complex in comparison to the free receptor (0.11). The fluorescence quantum yield of 15-Ag$^+$ complex is 0.32 (at $\lambda_{em} = 488$ nm) as compared to that of free 15 (0.47, at $\lambda_{em} = 418$ nm) which shows good agreement with fluorescence spectra obtained for receptor 15 in the presence of Ag$^+$ ions. To check the practical ability of compound 15 as a Ag$^+$ ions selective fluorescent sensor, we carried out competitive experiments in the presence of Ag$^+$ at 30 µM mixed with the other metal ions at 30 µM. As shown in the Figure 2.19, no significant variation in emission was observed by comparison with or without the other metal ions. It was found that 15 has a detection limit of $70 \times 10^{-9}$ mol L$^{-1}$ for Ag$^+$ ions which is sufficiently low for the detection of nanomolar concentration range of Ag$^+$ ions. Fitting the changes in the fluorescence spectra of compound 15 with Ag$^+$ ions, the nonlinear regression analysis program SPECFIT gave a good fit and demonstrated that 1:1 stoichiometry

**Figure 2.19** Competitive selectivity ($I/I_0$) of receptor 15 (1 µM) toward Ag$^+$ ions (30 µM) in the presence of other metal ions (30 µM each) in THF; $\lambda_{ex} = 360$ nm. Bars represent the emission intensity ratio ($I/I_0$) ($I_0$ = initial fluorescence intensity at 488 nm; $I$ = final fluorescence intensity at 488 nm after the addition of metal ions).
(host:guest) was the most stable species in the solution with a binding constant (log $\beta$) of 6.73 with ± 0.17 error which is comparable with that determined by the absorbance method. The method of continuous variation (Job’s plot) was also used to prove the 1:1 stoichiometry (Figure 2.20). The binding mode of receptor 15 with Ag$^+$ ions is proved by $^1$H and $^{13}$C NMR spectroscopy. The imino protons of receptor 15 undergo a downfield shift of $\Delta \delta = 0.18$ ppm on addition of 1.0 equiv of Ag$^+$ ions proving interaction of 15 with Ag$^+$ ions through nitrogen atoms of imino moiety (Figure 2.21). The participation of sulfur atoms of thiacalix[4]arene ring toward Ag$^+$ ions coordination is proved by $^{13}$C NMR studies of compounds 10 and 15 in the presence of Ag$^+$ ions. In the presence of 1.0 equiv of Ag$^+$ ions compounds 10 and 15 undergo downfield shift of signals corresponding to the carbons of the aromatic ring of thiacalixarene moiety from 126.16-128.68 ppm to 126.23-131.32 ppm and 123.23-

**Figure 2.20** Job’s plot of 15 with Ag$^+$ ions in THF representing 1:1 stoichiometry.

**Figure 2.21** $^1$H NMR (300 MHz) spectra of 15 in CDCl$_3$/CD$_3$CN (8:2); (a) Free 15; (b) 15 + 1.0 equiv of AgClO$_4$.

**Figure 2.22** Fluorescence spectra showing reversibility of Ag$^+$ coordination to 15 by Cl$^-$ ions; blue line, free 15 (1 $\mu$M), red line, 15 + 30 $\mu$M Ag$^+$, green line, 15 + 30 $\mu$M Ag$^+$ + 30 $\mu$M Cl$^-$, orange line, 15 + 30 $\mu$M Ag$^+$ + 30 $\mu$M Cl$^-$ + 80 $\mu$M Ag$^+$ in THF; $\lambda_{ex} = 360$ nm.
130.67 ppm to 126.30-131.40 ppm, respectively. The downfield shifts of signals corresponding to the carbons of the aromatic ring of the thiacalixarene moiety in both cases elucidate the role of sulfur atoms of thiacalix[4]arene ring in the coordination toward Ag$^+$ ions. The binding of Ag$^+$ ions with receptor 15 is also proved by mass spectroscopy. The mass spectrum showed a peak at $m/z$ 1412.7 corresponds to the 15-AgClO$_4$ complex which not only confirms the binding of Ag$^+$ ions with receptor 15 but also prove 1:1 stoichiometry of host and guest species. In addition to this, we also carried out reversibility experiment, which proves that binding of Ag$^+$ ions to receptor 15 is reversible (Figure 2.22). The addition of tetrabutylammonium chloride to the solution of 15-Ag$^+$ complex restored the fluorescence signal of 15 to its original level. Further, addition of Ag$^+$ ions to the same solution gives the outcome of 15-Ag$^+$ complex indicating the reversible behaviour of the chemosensor 15.

In conclusion, we synthesized chemosensors 12, 13 and 15 based on thiacalix[4]arene. Chemosensor 13 exhibits selective fluorescence enhancement in the presence of Hg$^{2+}$ ions ascribed to the ring-opening of rhodamine moiety in the presence of these ions. Chemosensor 15 based on the thiacalix[4]arene of 1,3-alternate conformation appended with dimethylaminocinnamyl moieties bind with Ag$^+$ ions and thus, preferentially enhances intramolecular charge transfer process from nitrogen atoms of the dimethylamino moiety to the Ag$^+$-coordinated imino moiety resulting in significant emission shift which allowed the nanomolar level detection limit of silver ions.

2.3. Experimental

2.3.1. General methods and instrumentations

2.3.1.1. Physical measurements

Most of the chemicals and reagents were purchased from Sigma-Aldrich and were used as such without further purification. Solvents for carrying out reactions and studies were dried prior to use. Tetrahydrofuran was dried by refluxing it over sodium metal and benzophenone for 5 h and then fractionally distilled. Melting points were determined in capillaries and are uncorrected. $^1$H NMR and $^{13}$C NMR spectra were recorded on JOEL-FT NMR-AL 300 MHz spectrophotometer using CDCl$_3$/CD$_3$CN/DMSO-d$_6$ as solvent and tetramethylsilane (TMS) as internal standards. Data are recorded as follow: chemical shifts in ppm (δ), multiplicity (s =
singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal, dd = doublet of doublet), coupling constants (Hz), integration and interpretation. Elemental analysis was done using Flash EA 1112 CHNS-O analyzer of Thermo Electron Corporation. IR spectra were recorded with Shimadzu FTIR 8400S IR spectrophotometer by using KBr as medium. UV-vis spectra were recorded on SHIMADZU UV-2450 PC spectrophotometer with a quartz cuvette (path length 1 cm). The cell holder was thermostatted at 25°C. All the fluorescence spectra were recorded on SHIMADZU RF-5301 PC spectrofluorimeter.

2.3.1.2. UV-vis and fluorescence titrations

For UV-vis and fluorescence titrations stock solutions (0.1 mM) of ligands (chapter 2: 12, 13 and 15 in THF; chapter 3: 4, 5 and 8 in THF; EtOH:H$_2$O; 8:2; v/v and THF:H$_2$O; 9:1; v/v, respectively; chapter 4: 3 and 13 in THF and THF:H$_2$O; 95:05; v/v, respectively; chapter 5: 2, 8 and 11 in CH$_3$CN:H$_2$O; 8:2; v/v, CH$_3$CN:H$_2$O; 1:1; v/v and H$_2$O:EtOH; 8:2; v/v; chapter 6: 3 in CH$_3$CN:H$_2$O; 8:2; v/v) were freshly prepared. Metal perchlorates (Li$^+$, Na$^+$, K$^+$, Mg$^{2+}$, Ba$^{2+}$, Mn$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, Ag$^+$, Pb$^{2+}$, Fe$^{2+}$, Fe$^{3+}$, Cu$^{2+}$, Co$^{2+}$, Ni$^{2+}$ and Hg$^{2+}$); inorganic anions (HP$_2$O$_7^{3-}$, HPO$_4^{2-}$, H$_2$PO$_4^{-}$, Cl$^-$, Br$^-$, I$^-$, OAc$^-$, HSO$_4^-$, NO$_3^-$ and CN$^-$) as their tetrabutylammonium salts in THF; THF:H$_2$O; EtOH:H$_2$O; CH$_3$CN:H$_2$O; CO$_3^{2-}$ as K$_2$CO$_3$ in double distilled water; Pd$^{2+}$ ions as PdCl$_2$ in brine:MeOH; Pt$^{4+}$ as H$_2$PtCl$_6$.6H$_2$O in double distilled water; PdCl$_2$(PPh$_3$)$_2$ in DMSO; Pd(OAc)$_2$ in brine:MeOH; PdCl$_2$(dppf)$_2$ in DMSO; cysteine and homocysteine in CH$_3$CN:H$_2$O were freshly prepared as 10$^{-1}$ M to 10$^{-3}$ M standard solutions. Hydrogen peroxide (H$_2$O$_2$), tert-butyl hydroperoxide (t-BuOOH) and hypochlorite (OCl$^-$) were delivered from 30%, 70%, and 5% aqueous solutions, respectively. Hydroxyl radical (•OH) and tert-butoxy radical (•O'Bu) were generated by the reaction of 1 mM Fe$^{2+}$ with 100 $\mu$M of H$_2$O$_2$ or 100 $\mu$M of t-BuOOH, respectively. In titration experiments, each time a 3 mL solution of ligands (1/2/5/10 $\mu$M) were filled in a quartz cuvette (path length, 1 cm) and metal ions/anions/reactive oxygen species were added into the quartz cuvette by using a micro-pipette.

2.3.1.3. Stoichiometry of complexes

The stoichiometry of various complexes of receptors (chapter 2: 13 and 15; chapter 3: 4, 5 and 8; chapter 4: 3 and 13; chapter 5: 2; chapter 6: 3) designated as “molecular hosts” with cations as “guests” were determined by using the method of continuous variation (Job’s plot). The total concentration of molecular host “H” and
guest “G” was constant (2.5 × 10⁻⁵ M) with a continuous variable molar fraction of guest [G]/([H] + [G]). For 1:1 (H:G) stoichiometry, molar fraction of guest should be 0.5, for 1:2 stoichiometry, molar fraction of guest should be 0.7 and for 2:1 stoichiometry, molar fraction of guest should be 0.3.

2.3.1.4. Binding constants of complexes

The binding constants (log $\beta$) of different receptors (chapter 2: 13 and 15; chapter 3: 4, 5 and 8; chapter 4: 3 and 13; chapter 5: 2; chapter 6: 3) with cations were calculated from UV-vis/fluorescence titration experiments by means of SPECFIT programme (global analysis system V3.0 for 32-bit Window system), which uses singular value decomposition and nonlinear regression modelling by the Leverberg–Marquardt method.

2.3.1.5. $^1$H NMR titrations

Stock solutions (10 mM) of ligands (chapter 2: 13 and 15; chapter 3: 4; chapter 4: 13; (chapter 5: 2; chapter 6: 3) and cations were prepared in CDCl₃/CD₂CN; CD₂CN/D₂O for the $^1$H NMR experiments.

2.3.1.6. Fluorescence quantum yield

Fluorescence quantum yield ($\phi_{fs}$) was determined in analytical grade THF or CH₃CN or absolute EtOH using optically matching solution of rhodamine B ($\phi_{fr} = 0.65$ in ethanol) as standard at an excitation wavelength of 540 nm for compounds (chapter 2: 13; chapter 4: 13; chapter 5: 2); naphthalene ($\phi_{fr} = 0.23$ in ethanol) as standard at an excitation wavelength of 300 nm for compounds (chapter 2: 15; chapter 3: 8; chapter 5: 11; chapter 6: 3); pyrene ($\phi_{fr} = 0.65$ in ethanol) as standard at an excitation wavelength of 340 nm for compounds (chapter 3: 5; chapter 5: 8) and the quantum yield was calculated using the following equation:

$$\phi_{fs} = \phi_{fr} \times \frac{1-10^{-A_{fs}}} {1-10^{-A_{fr}}} \times \frac{N_{fs}^2}{N_{fr}^2} \times \frac{D_s}{D_r}$$

The quantum yield is measured at room temperature by a single excitation wavelength coming from Xenon lamp of the spectrofluorimeter and calculated according to the above equation. $\phi_{fs}$ is the radiative quantum yield of the sample, $\phi_{fr}$ radiative quantum yield of reference, $A_s$ and $A_r$ are the absorbance of the sample and the reference respectively, $D_s$ and $D_r$ the respective areas of emission for sample and reference respectively. $L_s$ and $L_r$ are the lengths of the absorption cells respectively.
N_s and N_r are the index of refraction of the sample and reference solutions (pure solvents were assumed respectively).

2.3.2. Synthesis of thiacalix[4]arene derivatives

Compounds 5, 7, 8, 9 and 10 were synthesized according to literature procedures.


A mixture of p-tert-butylphenol (64.5 g, 0.43 mol), elemental sulfur (27.5 g, 0.86 mol), and NaOH (8.86 g, 0.21 mol) in tetraethylene glycol dimethyl ether (19 mL) was stirred under nitrogen. The stirred mixture was heated gradually to 230°C over a period of 4 h and kept at this temperature for further 3 h with concomitant removal of evolving hydrogen sulfide with a slow stream of nitrogen. The resulting dark red product was cooled to ambient temperature and diluted with toluene (35 mL) and then 4 M aqueous sulfuric acid solution (140 mL) followed by the addition of acetone (500 mL) to give a suspension. The precipitate was collected by filtration, recrystallized from CHCl_3/CH_3OH and dried to give compound 5 in 22% yield (70 g). Mp: 320°C. 1H NMR (300 MHz, CDCl_3): δ = 1.22 (s, 36H, C(CH_3)_3), 7.63 (s, 8H, ArH) and 9.59 (s, 4H, OH) ppm.


To a mixture of compound 5 (4.0 g, 5.55 mmol), N-(2-hydroxyethyl)phthalimide 6 (7.35 g, 38.5 mmol) and triphenylphosphine (10.08 g, 38.5 mmol) in dry THF (100 mL) was added dropwise diethyl azodicarboxylate (6.75 g, 38.5 mmol) and the mixture was stirred at room temperature for 48 h. The solvent was evaporated and the residue was triturated with methanol to give a solid and column chromatography over silica gel (hexane/ethyl acetate; 8/2; v/v) was carried out to obtain compound 7 in 67% yield (4.0 g). Mp: 290°C. 1H NMR (300 MHz, CDCl_3): δ = 0.72 (s, 36H, C(CH_3)_3), 1.27 (s, 18H, C(CH_3)_3), 4.44 (t, J = 5.6 Hz, 4H, NCH_2), 4.87 (t, J = 5.6 Hz, 4H, OCH_2), 6.81 (s, 4H, ArH), 7.24 (s, 2H, OH), 7.47 (s, 4H, ArH), 7.55-7.57 (m, 4H, ArH) and 7.82-7.84 (m, 4H, ArH) ppm.

A solution of compound 7 (0.5 g, 0.46 mmol) and hydrazine monohydrate (0.06 g, 1.84 mmol) in ethanol (40 mL) was refluxed for 12 h. After completion of the reaction a solid separated out, which was filtered, dissolved in chloroform and washed with 20% ammonium hydroxide solution. The organic layer was dried with anhydrous sodium sulfate and solvent removed to give compound 8 as white solid in 74% yield (0.25 g). Mp: 300°C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 0.88\) (s, 18H, C(CH\(_3\))\(_3\)), 1.30 (s, 18H, C(CH\(_3\))\(_3\)), 3.32 (t, J = 6 Hz, 4H, NCH\(_2\)), 4.51 (t, J = 6 Hz, 4H, OCH\(_2\)), 7.11 (s, 4H, ArH) and 7.65 (s, 4H, ArH) ppm.


To a mixture of compound 7 (0.5 g, 0.46 mmol), propanol (0.11 g, 1.84 mmol), triphenylphosphine (0.48 g, 1.84 mmol) in dry THF (50 mL) was added dropwise diethyl azodicarboxylate (0.32 g, 1.84 mmol) and the mixture was stirred at room temperature for 48 h. The solvent was evaporated and the residue left was crystallized with methanol to give compound 9 in 79% yield (0.42 g). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 0.69\) (t, J = 7.6 Hz, 6H, CH\(_3\)), 1.12-1.18 (m, 4H, CH\(_2\)), 1.24 (s, 18H, C(CH\(_3\))\(_3\)), 1.37 (s, 18H, C(CH\(_3\))\(_3\)), 3.60 (t, J = 8.0 Hz, 4H, NCH\(_2\)), 3.87 (t, J = 8.0 Hz, 4H, OCH\(_2\)), 4.13 (t, J = 8.0 Hz, 4H, OCH\(_2\)), 7.35 (s, 4H, ArH), 7.62-7.69 (m, 4H, ArH), 7.73 (s, 4H, ArH) and 7.83-7.86 (m, 4H, ArH) ppm.


A solution of compound 9 (0.2 g, 0.17 mmol) and hydrazine monohydrate (0.03 g, 0.68 mmol) in ethanol (40 mL) was heated at 110°C for 12 h. After completion of the reaction a solid separated out, which was filtered, dissolved in chloroform and washed with 20% ammonium hydroxide solution. The organic layer was dried with anhydrous sodium sulfate and solvent removed to give compound 10 as white solid in 71% yield (0.11 g). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 0.63\) (t, J = 7.6 Hz, 6H, CH\(_3\)), 0.86-0.92
(m, 4H, CH$_2$), 1.26 (s, 18H, C(CH$_3$)$_3$), 1.28 (s, 18H, C(CH$_3$)$_3$), 2.42 (t, J = 5.2 Hz, 4H, NCH$_2$), 3.74 (t, J = 7.6 Hz, 4H, OCH$_2$), 3.95 (t, J = 5.2 Hz, 4H, OCH$_2$), 7.29 (s, 4H, ArH) and 7.36 (s, 4H, ArH) ppm.

**General procedure for synthesis of 12 and 13**

A solution of rhodamine B (0.20 g, 0.41 mmol) in 1,2-dichloroethane (10 mL) was stirred at room temperature and phosphorus oxychloride (0.30 g, 2.05 mmol) was added dropwise. After 4 h the reaction mixture was cooled and evaporated in vacuum to give rhodamine acid chloride 11 which was impure and used in the next step directly. The crude acid chloride was dissolved in the dry dichloromethane (10 mL) and stirred at room temperature. The solution of diamine 8 (0.15 g, 0.18 mmol)/10 (0.15 g, 0.16 mmol) in dry dichloromethane (10 mL) with 0.5 ml of TEA was added dropwise to the solution of 11 in dry dichloromethane (10 mL) at room temperature and allowed to stirred for 12 h. The reaction mixture was treated with water, extracted with dichloromethane and dried over anhydrous sodium sulfate. The organic layer was evaporated under reduced pressure and the crude product was purified by column chromatography (dichloromethane/methanol; 9/1; v/v) to give corresponding product 12/13.

**Compound 12**: (Yield 44%; 0.13 g); Mp: 222°C. $^1$H NMR (300 MHz, CDCl$_3$): δ = 0.76 (s, 18H, C(CH$_3$)$_3$), 1.12 (t, J = 6 Hz, 24H, CH$_3$), 1.28 (s, 18H, C(CH$_3$)$_3$), 3.25-3.32 (q, 16H, NCH$_2$), 3.66 (t, J = 6 Hz, 4H, NCH$_2$), 3.79 (t, J = 6 Hz, 4H, OCH$_2$), 6.19-6.23 (m, 4H, ArH), 6.34-6.39 (m, 8H, ArH), 6.83 (s, 4H, ArH), 7.02-7.07 (m, 4H, ArH and OH), 7.38-7.41 (m, 4H, ArH), 7.52 (s, 4H, ArH) and 7.84-7.87 (m, 2H, ArH) ppm. $^{13}$C NMR (75.45 MHz, CDCl$_3$): δ = 12.67, 30.75, 31.45, 33.83, 38.84, 44.34, 64.85, 73.06, 98.12, 105.35, 108.17, 121.95, 122.71, 123.78, 127.84, 128.27, 128.60, 131.19, 132.24, 133.84, 141.92, 147.08, 148.77, 153.29, 153.65, 155.56, 156.59 and 167.71 ppm. MS ES$^+$ m/z 1656 (M+2). Anal Calcd for C$_{100}$H$_{114}$N$_6$O$_8$S$_4$: C, 72.52%; H, 6.94%; N, 5.07%. Found C, 72.34%; H, 7.28%; N, 4.89%.

**Compound 13**: (Yield 53%; 0.15 g); Mp: 186°C. $^1$H NMR (300 MHz, CDCl$_3$): δ = 0.90 (t, J = 9 Hz, 6H, CH$_3$), 0.97 (s, 18H, C(CH$_3$)$_3$), 1.10 (t, J = 9 Hz, 24H, CH$_3$), 1.15 (s, 18H, C(CH$_3$)$_3$), 1.60-1.70 (m, 4H, CH$_2$), 3.21-3.32 (m, 16H, NCH$_2$), 3.49-3.60 (m,
8H, NCH$_2$ and OCH$_2$), 3.85 (t, J = 6 Hz, 4H, OCH$_2$), 6.17-6.21 (m, 4H, ArH), 6.37-6.41 (m, 8H, ArH), 7.04-7.07 (m, 2H, ArH), 7.26 (s, 4H, ArH), 7.30 (s, 4H, ArH), 7.38-7.41 (m, 4H, ArH) and 7.88-7.91 (m, 2H, ArH) ppm. $^{13}$C NMR (75.45 MHz, CDCl$_3$): $\delta$ = 10.36, 12.62, 23.52, 31.17, 31.30, 33.77, 33.92, 39.65, 44.31, 64.76, 67.81, 72.85, 98.11, 105.62, 108.08, 116.59, 122.75, 123.67, 127.80, 128.40, 128.60, 131.14, 132.04, 132.98, 144.24, 145.03, 148.67, 153.35, 158.64, 167.76 and 185.25 ppm. FAB MS $m/z$ 1740 (M+2)$^+$. Anal Calcd for C$_{106}$H$_{126}$N$_6$O$_8$S$_4$: C, 73.15%; H, 7.30%; N, 4.83%. Found C, 73.22%; H, 7.42%; N, 4.58%.

**Synthesis of compound 15**

A mixture of diamine 10 (0.10 g, 0.08 mmol) and N,N-dimethylaminocinnamaldehyde 14 (0.03 g, 0.17 mmol) in a 1:1 mixture of dry dichloromethane and dry methanol was refluxed for 24 h. After the completion of the reaction solvent was evaporated and the residue left was crystallized from CHCl$_3$/CH$_3$OH to give compound 15 in 78% yield (0.10 g). Mp: 212°C; IR (KBr) $\nu_{max}$ = 1602 cm$^{-1}$. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ = 0.62 (t, J = 9 Hz, 6H, CH$_3$), 1.02-1.09 (m, 4H, CH$_2$), 1.26 (s, 18H, C(CH$_3$)$_3$), 1.28 (s, 18H, C(CH$_3$)$_3$), 2.99 (s, 12H, CH$_3$), 3.05 (t, J = 9 Hz, 4H, NCH$_2$) 3.82 (t, J = 9 Hz, 4H, OCH$_2$), 4.14 (t, J = 6 Hz, 4H, OCH$_2$), 6.63-6.74 (m, 8H, ArH, CH), 7.31-7.34 (m, 8H, ArH), 7.41 (s, 4H, ArH) and 7.87 (d, J = 9 Hz, 2H, HC=N) ppm. $^{13}$C NMR (CDCl$_3$, 75.45 MHz): $\delta$ = 10.08, 22.10, 31.20, 31.50, 34.19, 40.02, 59.00, 67.25, 70.07, 112.06, 123.59, 123.80, 124.29, 127.64, 127.80, 128.01, 128.68, 142.29, 145.03, 148.67, 153.35, 158.64, 167.76 and 185.25 ppm. FAB MS $m/z$ 1205 (M + 1)$^+$. Anal Calcd for C$_{72}$H$_{92}$N$_4$O$_4$S$_4$: C, 71.72%; H, 7.69%; N, 4.65%. Found C, 71.81%; H, 7.42%; N, 4.29%.

**References**


