DESIGN, SYNTHESIS
AND RECOGNITION STUDIES OF TRIPODAL RECEPTOR

A
Thesis Submitted
In Partial Fulfilment of Requirements
For The Degree of
Master of Science in Chemistry

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Acknowledgment

There are many people who have helped me to make the past such a meaningful time. Most of all I like to express my gratitude to my research mentors Dr. Navneet Kaur and Dr. Susheel Mittal for giving me chance to work on such a interesting topic. They had taken pain to go through the project and make necessary correction as and when needed.

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I must express my deepest appreciation to my family for their encouragement through the entire process.

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Candidate's Declaration

I hereby declare that the work being presented in the dissertation entitled "DESIGN, SYNTHESIS AND RECOGNITION STUDIES OF TRIPODAL RECEPTOR", in partial fulfillment of the requirements for the award of degree of Masters in Chemistry, School of Chemistry and Biochemistry, Thapar University, Patiala, is my own work during the period of Jan 2010 to May 2010, under the supervision of Dr. Navneet Kaur and Dr. Susheel Mittal. I have not submitted the matter embodied in this dissertation for the award of any other degree.

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This is to certify that the above statement made by the candidate is correct and true to the best of our knowledge.

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This is to certify that the project entitled "DESIGN, SYNTHESIS AND RECOGNITION STUDIES OF TRIPODAL RECEPTOR", being submitted by Ms. Jasneet Kaur Dilbar in partial fulfillment of the requirements for the award of degree of Masters in Chemistry in the School of Chemistry and Biochemistry ,Thapar University, Patiala, is a bonafide work carried out under the supervision of Dr. Navneet Kaur and Dr. Susheel Mittal and that no part of this project has been submitted for the award of any other degree.

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INTRODUCTION

The cation recognition chemistry with non-covalent interactions may be traced back to 1967 with the work reported by C. Pedersen. The work was concerned with the first synthesis of crown ether i.e. dibenzo[18]crown-6.[1] The Interest and developments in cation coordination chemistry continued throughout the 1970s and early 1980s, with the synthesis of several hosts of crucial conceptual importance. Now a day the concept of coordination chemistry is an important research arena of molecular recognition chemistry, which refers to the study of non-covalent interactions[2] and encompasses the chemistry of multicomponent molecular assemblies. Currently, selective recognition and sensing of cations and anions by artificial receptors have attracted a considerable research interest in terms of their potential applications in various areas. The development of chemosensor for the estimation of metal ion is an important issue to address. Chromogenic and fluorescent chemosensors are particularly interesting because of the simplicity and sensitivity of the method. The design of chemosensor for metal ion estimation must fulfil some basic criteria[3].

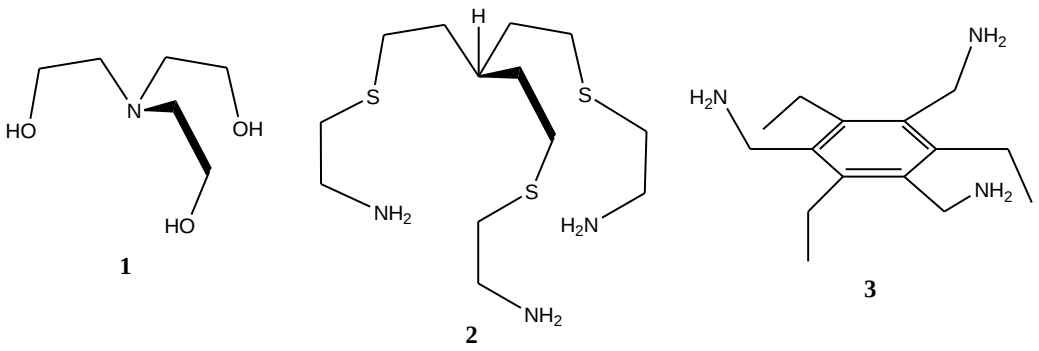
First, for intensity-based measurement, the sensor must not exhibit a signal in the absence of metal ion, and the intensity of signal should change w.r.t the concentration of metal. Second, the response of sensor should be selective for metal ion, means the sensor should not exhibit the same response to other biologically important metal ions and also should not be perturbed by the environment. Third, sensor must explicit the linear relationship between its intensity and the concentration of metal ion. Moreover, this linear

relationship should be valid alone a broad concentration range of metal ion. Fourth, the sensor response should be fast i.e. the complexation of metal ion in the coordination sphere should be very quick and it should not change with time. Fifth, the sensor and its metal complex should have fairly good solubility in a particular solvent system, i.e. sensor should not separate out of the solution on complexation with metal ions. Sixth, the design of sensor for metal is very crucial for those metal ions, which are spectroscopically or magnetically silent due to its configuration. This project aims at designing and synthesizes of tripodal receptor and to examine their binding behaviour towards selected cations.

Design of Tripodal Receptors

Podands are such structures in which arms (or podes) diverge out of some central unit. Cyclic receptors with open end from one side are termed as dipodands and similarly the cryptands with open end from one side are termed as tripodands.[4] So, podands are relatively flexible receptors as compared to cyclic ligands and cryptands; this is because the ends of the podands are not tied simultaneously. However, this flexibility can be decreased either by employing rigid substructural elements at the end of each terminus of the chain or by replacing ether linkages by ester or amide groups. Depending upon the nature of central unit (or platform); the podands exhibit different type of binding affinity towards metal ions[5].

On the basis of central platform, the followings are the some common designs:



The simplest tripodal ligand systems include triethanolamine (**1**) and its derivatives. These tripodal amines in general act as tetradentate ligands towards the hosts such as metal ion. The anchor nitrogen participates in the coordination. These types of nitrogen based receptors are very flexible because of the flipping in the lone pair of nitrogen.[6] The flexibility of central nitrogen can be stopped by putting other relatively rigid central units like sp^3 carbon (**2**) or aromatic platform. This Thus literature also revealed the considerable development in aromatic platform (**3**). To this scaffold side chains having donor atoms can be attached. Depending on the requirement of complexation, the nature, number and placement of donor atoms can be varied.

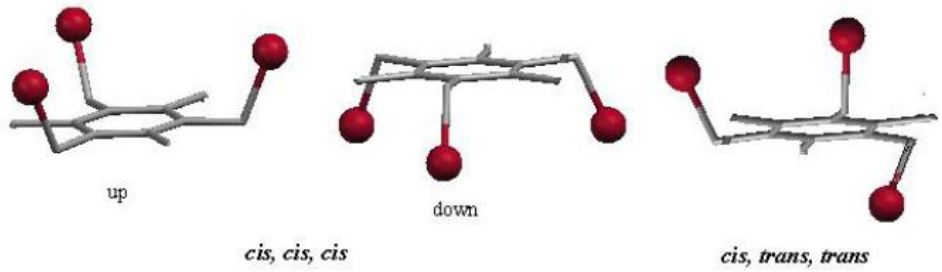


Fig 1: Conformations of 1,3,5 substituted trimethylbenzene derivative

The 1,3,5 substituted trimethylbenzene derivatives (Fig 1) can adopt two types of conformations, (i.e. *cis, cis, cis* or *cis, trans, trans*) when these ligands react with metal ions. The length of the side arm also determines the conformation of the ligand.

Various calix[4] arene based receptors are also reported with functionalization of three – OH groups, that available at the lower rim of calix[4] arene.[7] On functionalization of calix[4] arene, the framework may offer any of following types of conformations:

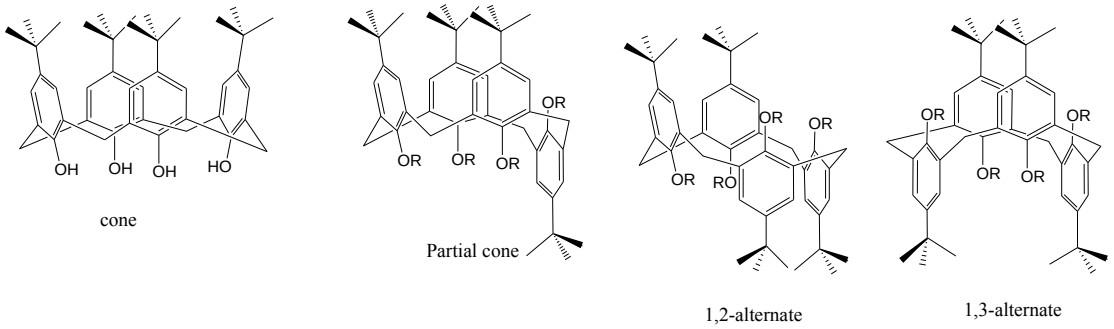


Fig 1: Conformations of calix[4] arene derivative.

Cation Recognition by Tripodal Receptors

The main requirement for the design of chemosensor for cation is a receptor unit ot ligand,that should be selectively interact with cation, and a method to read-out the binding using a change in a physical signal. In the red to the special structure of their three flexible donor-atom-containing chains, tripodal receptors can form complexes with many cations ranging from alkali and alkaline earth metals to transition metals.[8] By chemical amendment of the arms (e.g. changing the chain length or the donor-atom) and under definite experimental conditions, a tripodal receptor can selectively complex metal ions.

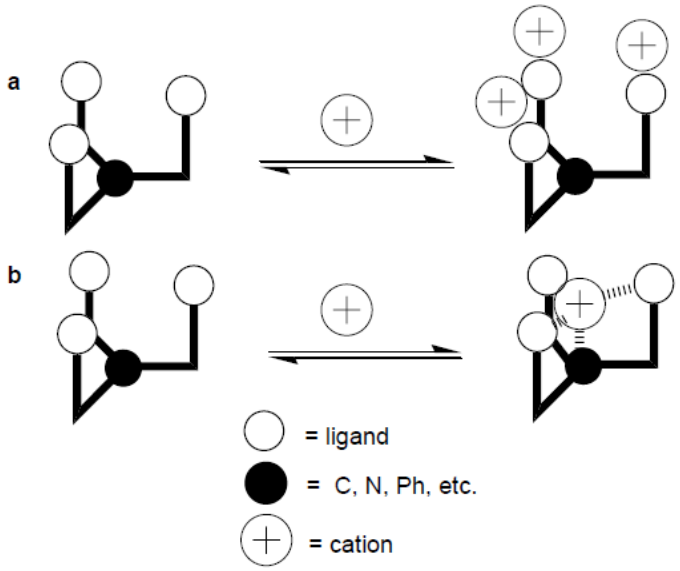
The main features to design a tripodal cation receptor are:

(i) There is a adequate number of donor atoms in the ligand in order to counterpart the coordination number.

(ii) The size of the cavity is large enough to accommodate the metal cation.

(iii) The donor atom containing arms are satisfactorily flexible to match the shape of the coordination sphere.

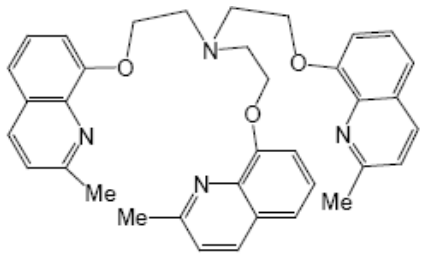
(iv) Since, chelation or solvating donor groups are combined within one tripodal receptor, the complexation mechanism has also to be considered, viz. ion exchange or ion pairing. Tripodal receptors are proficient of forming complexes with metal ions, which exhibit unusual coordination features, a high thermodynamic stability, and kinetic inertness. A tripodal receptor can coordinate in a facial manner to a single metal centre, to form octahedral complexes by packaging roughly just about the metal ions, or in a three dimensional manner to form polynuclear complexes.[9-10]



Tripodal receptors can coordinate either in a three dimensional manner to form polynuclear complexes (a) or in a facial manner to a single metal centre (b)

Vögtle et al have reported a number of tripodes **4-7** based on the derivatization of triethanolamine[11] They have been found to exhibit cation complexation or phase transfer

properties. These ligands with a central triethanolamine type core and bearing end groups or long chains having suitably spaced donor atoms, can be made to have higher complexation capacity by increasing the number of donor atoms. This however, cannot be carried out beyond a certain limit because as the number of donor atoms increase the tendency to form pseudocavity on complexation decreases. This results in a weaker contact between donor atoms and the metal ions.



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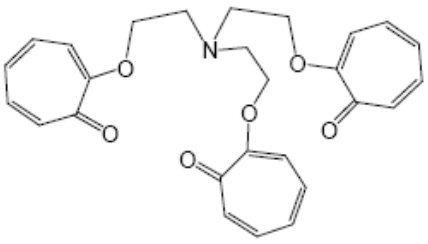

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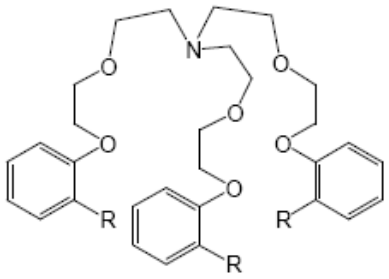

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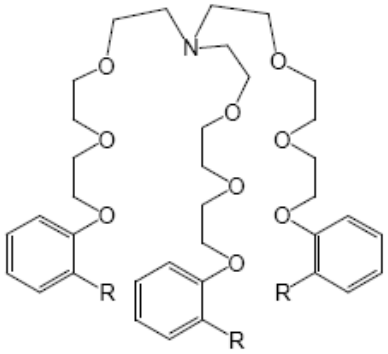

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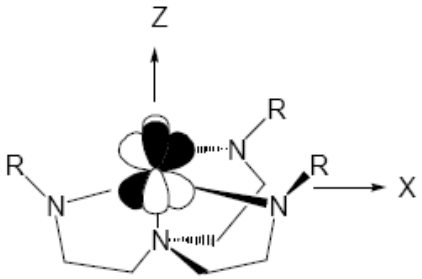
Unlike the triethanolamine**1**, tris(2-aminoethyl)amine **TREN** prefers to coordinate with transition metal ions and main block metal ions.[12-15] This ligand produces five coordinate, high-spin complexes with the divalent, 3d transition metal ions. However in **TREN** the structure of the complex is apparently more sensitive to the size and electronic configuration of the metal ion as well as the availability of other donor groups, and both five and six coordinate complexes have been identified. Triamidoamine ligand **4** $[(RNCH_2CH_2)_3N]^{3-}$ in which R is a bulky substituent attached to **TREN**, also binds to a variety of transition metals in oxidation states trivalent or higher. They usually bind to a

transition metal in a tetradentate manner, thereby creating a sterically protected, 3-fold symmetric "pocket" in which only three orbitals are available to bond to additional ligands in that pocket, two p orbitals (approximately dxz and dyz) and a σ orbital (approximately dz^2)[12-17].



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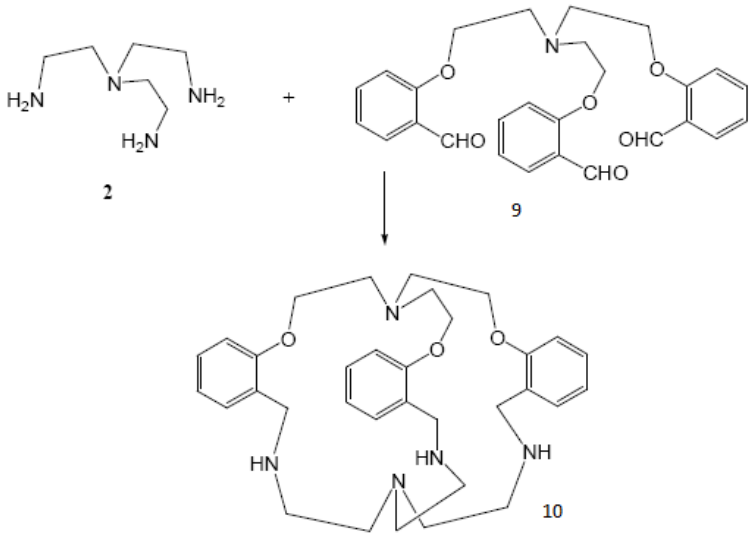
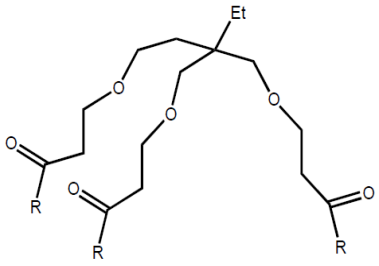
Bharadwaj, et al. performed the condensation of **TREN** with a tripodal aldehyde **9** and generated an aza cryptand **10**. Further many variations in this cryptand have been reported [18-21]



The number of tripodal ligands for alkali and alkaline earth metal ions recognition reported in literature is limited. Some of the works have been addressed to Shanzer and

coworkers used tripodal structures with flexible arms, based on trimethylolpropane, for the complexation of Ca^{2+} The same skeleton is also used in the commercially available Na+ ionophore [$\mathbf{NH_4^+}$](Na^+,K^+,Mg^+ as interference). The C_3-symmetric lipophilic tripodal ionophores **11** R_1 = Et, R_2 = R_3 = R_4 = $N(CH_3)C_6H_5$, 4 R_1 = Et, R_2 = R_3 = R_4 = $N(C_2H_5)C_6H_5$,5 R_1 = Et, R_2 = R_3 = R_4 = $N(C_5H_{10})$ have been prepared and their binding abilities for alkali and alkaline earth metal cations evaluated by extraction experiments and cation transport through bulk liquid membranes.[22]



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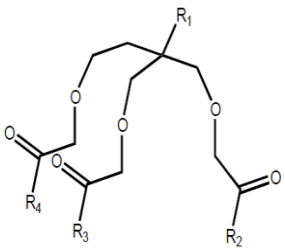

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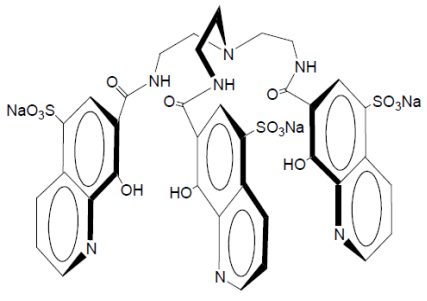
Freshly, the sensing behaviour toward metal ions of simple C_3-symmetrical trimethylolpropane based ionophores with *N*-acyl(thio)urea and picolin(thio)amide ligating sites has been reported. Different metal ions have different binding properties with different tripods. For eg: The hexadentate tripodal ligand shown, incorporating three 8-hydroxy-5-sulfoquinoline subunits is an efficient receptor for Al^{3+} [23].



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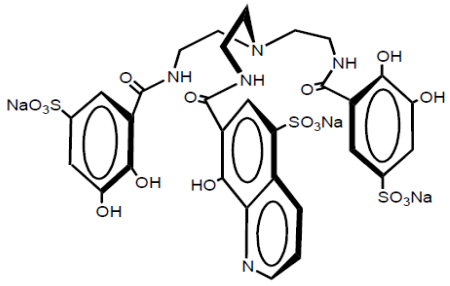
This ligand quantitatively gave the 1:1 chelate under stoichiometric conditions even at 10^{-5} mol L^{-1}. However, the 1:1 Al chelate turned out to be not significantly more fluorescent than the free ligand, whereas fluorescence enhancement by factors of at least 100 occurred with the 1:3 Al chelate. Time-resolved fluorescence measurements, and additional complexation[24] experiments carried out with the tripod given below (one 8-HQS and two 5-sulfocatechol subunits), showed that the stoichiometry between Al^{3+} and the bound bidentate subunits determines the fluorescence enhancement[25].



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Tripodal azacrown ether calix[4]arenes, and , bind transition metal ions such as Co^{2+}, Ni^{2+} and Cu^{2+} in a 1:1 mode. Though, the ligands outline the nearly all stable complexes with Cu^{2+} ions. Consequently, these receptors may be potentially worn as switchable receptors for metal ions. The binding capability of the receptor can be switched by changeable pH of the solution.Three arms of tripodal ligands indicate the cooperative effect to form stronger complex with various metal ions. The complexation is controlled by pH: at neutral . It has been suggesting a possible use of it as a luminescence chemosensor for these various metal ions.[26]

Sometimes the large augment of the short wavelength emission and the fading of the TICT (twisted intramolecular charge transfer) emission is observed during complexation

of ions. The use of a molecular platform to position ligating sites for actinide/lanthanide complexation has first been reportedl. Reaction of tripodal ligand tris(2-benzimidazolylmethyl)amine with lanthanides(III) in the presence of the counterions ClO_4^-, OTf^- or Cl^- resulted, even for ligand to metal ratios smaller than 2, in the formation of bisligand complexes screening strong π-π interactions are flanked by the benzimidazole rings both in solution and in the solid state. The receptors with electron-donating alkoxy groups endow with a similar potentiometric performance, particularly the NH^+ ion selectivities over Na^+ and K^+ ions, as that of nonactin in PVC-based, ion-selective membrane electrodes. This may entail that the cation size-selective binding sites fashioned by the oxygen atoms in the receptors have assured curb in discriminating alkali metal cations over ammonium ion. The electron-donating nature of the alkoxy substituents increases the electron density of the aryloxy rings, resulting in enhanced cation-π interactions[27-28].

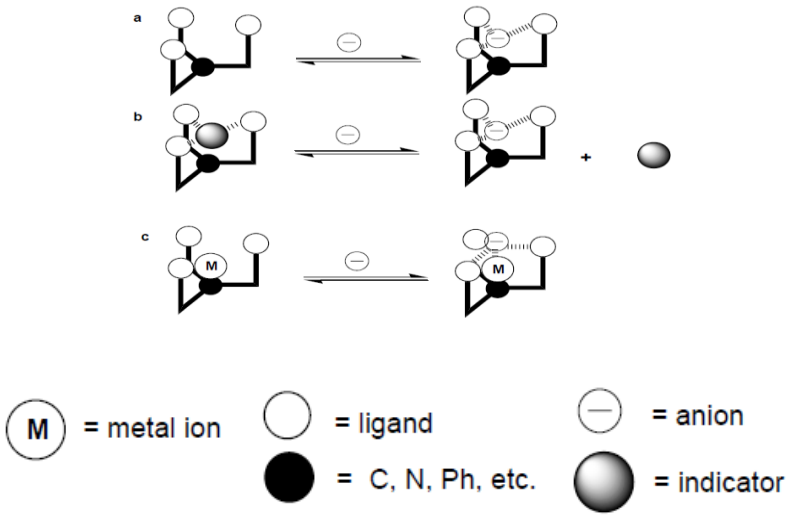
Anion Recognition by Tripodal Receptors

For anions sensing the various aspects that deal with are with the use of fluorogenic and chromogenic reagents.[29] With regards to this it has been sensed that, it is remarkable that there are relatively few examples on anion sensing when compared with the literature devoted to anion detection or when compared to cation sensing. Only the inclusive analysis has been done about signalling of small anions using changes in fluorescence, luminescence, or color (no changes in fluorescence or color using anionic macromolecules such as DNA are included) and how the use of relatively simple molecules is leading to the development of new systems for the selective sensing of target

anionic guests will be pointed out and will lead to further research work and innovation techniques. [30]

Metal complexes have also been used as anion binding sites. Using electrostatic or hydrogen bonding connections can form stronger bonds that make metal complexes to bind anions strongly.[31] Displacement reaction takes place when a target anion is added to the solution containing the binding site signalling unit ensemble; the binding site coordinates the anion whereas the signalling subunit returns to the solution retrieving its non-coordinated spectroscopic behaviour. If there is a difference between spectroscopic characteristics of the signalling subunit in the molecular ensemble than to those in its non-coordinated state, then the anion binding process is coupled to a signalling event.

As it can be inferred, the stability constant for the formation of the complex between the binding site and the signalling subunit has to be lower than that between the binding site and the target anion. [32] Only in this way will the displacement reaction take place; hence, the target anion will be observed in the presence of target anion(the signalling event). Additionally, selectivity can be achieved by choosing an indicator binding site couple with a formation stability constant larger than that between the signalling unit and the potentially intrusive anions. [33]

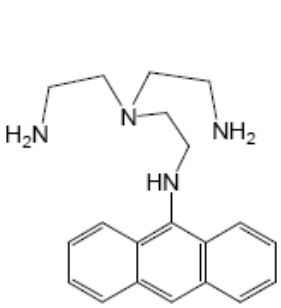


Types of the interaction of tripodal receptors with anions: directly using noncovalent interaction, viz. hydrogen bonds or hydrophobic effect (a) or indicator displacement (b) or electrostatic interaction with metal complex (c)

A general ballpark figure to the development of anion chemosensors is the coupling of at least two units, each one displaying a accurate function: the binding site and the signalling subunit. Many chemical sensors has been follow the latest approach of the covalent attachment of signalling subunits and binding sites and so in the development of anion chemosensors this has been resulted out into the most widely used approach and so is definitely be elemental approach in upcoming developments. [34] Various changes have been arised in such a way. This can has been seen as a change in colour or the change in its properties. and these changes has been arised in such manner as the coordination site binds the anion in such a line of attack that the properties of the signalling subunit are transformed giving rise to variations either in the color (chromogenic chemosensor) or in its fluorescence behaviour (fluorogenic chemosensor) on making the choice of a receptor of the various firm anions. It has been pragmatic that amines can also give electrostatic

interactions with anions as they are usually protonated and therefore charged at neutral and acidic aqueous solutions. [35]

The first explicitly intended anion chemosensor hold anthracene was testimony by Czarnik[34] in 1989 who in print the behaviour of two receptors, which were proficient of sensing the existence of definite anionic species in aqueous environments by changes in the fluorescence of the anthracene signalling subunit.



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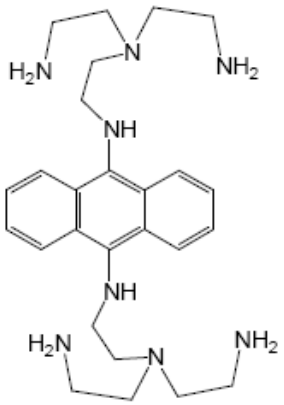

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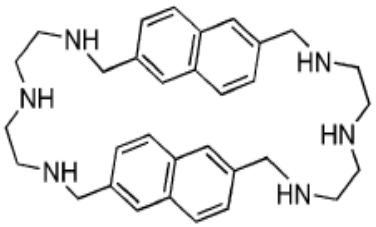
In the view of this fact that the previous work that it has occasionally intimated to the anthryl-functionalized polyazaalkanes have been deliberated as anion sensing fluorophores. For case in point, the revealed compound exemplify how without altering the signalling subunit (anthracene), the selectivity in opposition to anions is inhibited by the topology of the binding site. Naphthalene and naphthalene derivatives generally show no well shaped and poor structured bands centered 275 nm that upon excitation display an emission broadband at 350 nm. [36] In wide-ranging, naphthalene derivatives are less fluorescent than alike compounds containing anthracene. Analogous derivatives to those

found with anthracene have in common been described with naphthalene. Compound is the only naphthalene-containing case with a polyamine as an anion binding site. [37]



At present, molecular recognition of anions by synthetic receptors is an mounting ground to explore. [38] Classically, synthetic anions receptors consist of a variety of combinations of macrocyclic polyammonium/guanidiniums , pyrrols , Lewis acids , calix[n]arenes , amides and urea/thiourea moieties. Intended for the devise of a selective anion receptor the geometry and the basicity of the anion and the nature of the solvent have to be well thought-out.

The key features for the design of tripodal anion receptors are:

(i) A ample number of positively charged or neutral electron-deficient groups in the ligand to dole out as interaction sites is there.

(ii) Receptors with a supple(flexible) tripodal structure have a strapping(strong) affinity for trigonal oxoanions, such as carbonate, phosphate and chlorate, for the reason that the geometry and the orientation of the host molecules favour the formation of a stable host-guest complex .

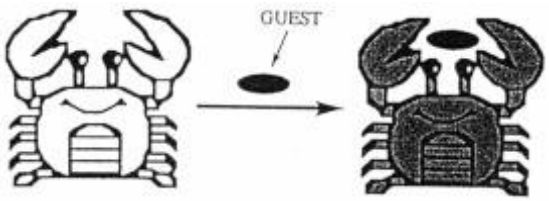
(iii) The classical complexation mechanism can also be applied. At this juncture, the interactions occur based on non-covalent interactions. The non-covalent

interactions comprises electrostatic interactions, hydrogen bonding, hydrophobicity, coordination to a metal ion, and a amalgamation of these interactions. On the other hand, for the anions itselves, the size, shape, H-bonding capability, acid/base properties and the number of interaction sites should also be well thought-out.

Chromogenic Chemosensor: The specific color change of a receptor upon guest binding is an informative signal that is utilized in guest-sensing systems.[4] The concept is now well extended to supramolecular chemistry by the development of a wide variety of chromoionophores. [1] Podands based chromogenic receptors have been described in the literature and comprehensive studies on this idea are required to allow sensing of target ions by colour change. Expansion of anion binding sensors is the recently advanced and emerging research area in the various fields of chemistry for significant importance if we compared it to the well-developed cation chemosensors. [8]

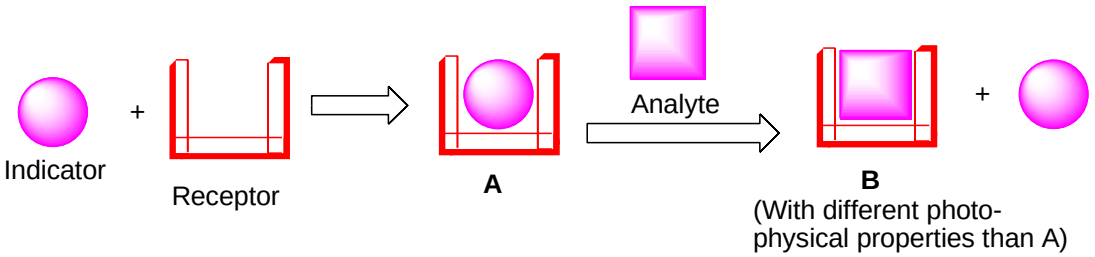
For scheming a chemosensor there are several approaches that one follows:

(**a**) A chemosensor is usually consisting of receptor subunit and signalling subunit. These two subunits are designed in such a way that any analyte binding at receptor subunit must modulate the signalling subunit. This modulation of signalling subunit leads to the change in photo-physical properties of chemsensor and from the extent of these changes, the concentration of analyte is determined.



Synthetic Chromogenic Receptors

(**b**) Although the technique (a) is marvellous, however some time, it is synthetically tedious to engineer a clear and significant chemsensor. To counter such problems of long organic synthesis, recently another strategy is devised and popularized by Prof. E.V. Ansyln under the title of indicator displacement assay.



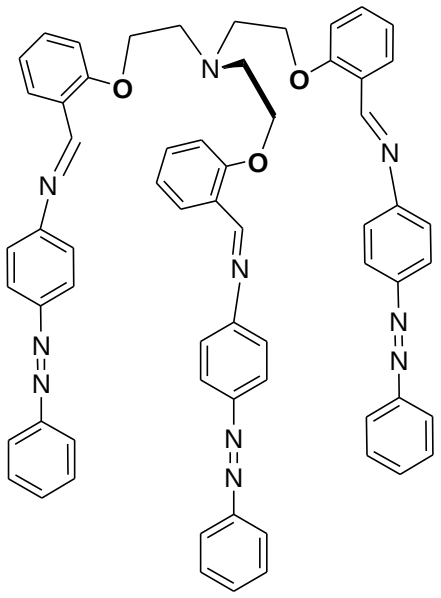
Scheme 1: Indicator Displacement Assay

The concept is a simple one and makes use of a three-component system, namely host (receptor), a guest (coloured or fluorescent) as an indicator and the target analyte. The indicator is bound by the host giving rise to a characteristic colour and/or fluorescence signature for that molecule in the solvent of choice. The indicator is chosen in such a way that it binds to the host more weakly then the target analyte. Hence when the analyte is added, the indicator is released and the colour and/or fluorescence signature changes by a characteristic pattern.

AIMS AND OBJECTIVES

The specific color change of a receptor upon guest binding is an informative signal that is utilized in guest-sensing systems. The concept is now well extended to supramolecular chemistry by the development of a wide variety of chromoionophores. Tripodal and tetrapodal chromogenic receptors have rarely been described in the literature and comprehensive studies on this idea are required to allow sensing of target ions by colour change.

Design of receptor 4 as Chromogenic probe



4

In this project new chromogenic receptor (**4**) has been developed by inserting the azo dye to the side arms of the receptors. Many alternative scaffolds i.e. aromatic platform and tren derivatives are also possible by substituting with similar side arms. In receptor (**4**), chromophores are directly attached to the binding groups, so that a signal will be provided upon binding the target guest molecules.

EXPERIMENTAL

All the commercial chemicals were of reagent grade and were used without further purification. NMR spectra were recorded on a Bruker AVANCE 400 MHz spectrometer. Chemical shifts are reported in parts per million, downfield of TMS. Multiplicity is indicated by the following abbreviations: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad (b). IR spectroscopy data was obtained from a Perkin Elmer Spectrum 100 FT-IR spectrometer. Elemental analyses were recorded on an Elementar Vario EL spectrometer. Absorbance measurements were recorded on Agilent UV–Vis spectrometer using 10 mm quartz cuvettes. All the measurements were carried out at room temperature.

A. Synthesis of target compounds

(1) Synthesis of Triethanol amine hydrochloride (1)

In the 100 ml Round bottom flask took 20 ml of triethanol amine,to it added 25ml of absolute ethanol and slowly added 35ml of conc.HCl, White colour precipitates formed. The precipitates were filtered under vacuum pump and air dried. Yield= 65%

(2) Synthesis of trischloroethylamine hydrochloride (2).

In 250ml round bottom flask 22.13g (0.016moles) of the **1** is taken and to this added 13.83ml of chloroform. The suspension is stirred for 5-10 min. Slowly to it added thionyl chloride (55.32 mL, 0.046moles) with the help of dropping funnel at room temperature. The reaction mixture is refluxed for 6 hrs and then stirred at room temprature overnight. The product separated out, filtered and washed with chloroform. (yield=65%) Product was characterized by melting point only. Mp 126 ^{o}C (Literature value 127 ^{o}C)

(3) Synthesis tripodal aldehyde (3)

In 250ml round bottom flask 50 ml propanol is taken, to it added 6 equiv. of crushed NaOH (4g, 0.0041 moles), and then reflux it for 10 min at 80˚C till clear solution is obtained. Then 6equiv. of salicyaldehyde was added dropwise (9 ml, 0.0246 moles) and refluxed it vigorously till fine suspension is formed. At this point 1 g of compound **2** was

added, and refluxed it for 8hrs at 80˚C. The reaction mixture was then cooled down and the evaporated to reduce its volume to 1/3rd. Then crushed ice was added to separate the product as grey-green solid and filtered, washed with cold water and air dried. ^{1}H (400 MHz, $CDCl_3$): 10.44 (3 x 1H, s,-CH=O), 7.75 (3 x 1H, d, ArH), 7.52 (3 x 1H, t, ArH), 7.03 (3 x 1H, t, ArH), 6.95 (3 x 1H, d, ArH), 4.21 (3 x 2H, t, OCH_2), 3.15 (3 x 2H, t, NCH_2), IR (cm^{-1}): 1725 (C=O)

(4) Synthesis tripodal receptor (4)

500 mg of the **3** is taken in 100 ml round bottom flask,and to it added 5 ml of methanol. The solution was heated at 50˚C for 10 min and then added solution of 8 eq of 4- amino azo benzene (6.8 g, 0.0067 moles) in 5ml of methanol. It was allowed to stir at 50˚C for 30 min. The product separated as yellow-orange colored solid. It was filtered, washed with methanol and dried to afford the product in 67% yield (23.22 mg)

Mp 136 ^{o}C

1H (400 MHz, CDCl3): 8.70 (3 x 1H, s,-CH=N), 8.02 (6 x 1H, d, ArH), 7.95 (6 x 1H, d, ArH), 7.54 (9H, m, ArH), 7.42 (12H, m, ArH), 7.15 (3 x 1H, d, ArH), 6.98 (3 x 1H, t, ArH), 4.96 (3 x 2H, t, OCH_2), 4.28 (3 x 2H, t, NCH_2), IR (cm-1): 1610 (C=N), CHN analysis: Theoretical C (75.73), H(5.45), N(14.02); Found C (74.5), H(5.2), N(14.9).

B. Recognition studies

(1) Cation recognition studies

The cation binding ability of **4** was determined by preparing solutions containing 10 μM solution of receptor along with standard solution of a particular metal salt in THF:H_2O (9:1, v/v). The absorption spectrum of each solution was recorded at λ_{max} = 365 nm. The cation recognition behaviour of any receptor for the binding of a particular cation was evaluated from the changes in absorption spectrum of receptor upon addition of that metal salt.

(2) Receptor vs metal ion titration

Volumetric flasks were taken each containing 10 μM of **4** along with varied amounts of a particular metal salt in THF:H_2O (9:1, v/v). The solutions were shaken thoroughly and their absorption spectra were recorded with excitation at λ_{max} = 365 nm.

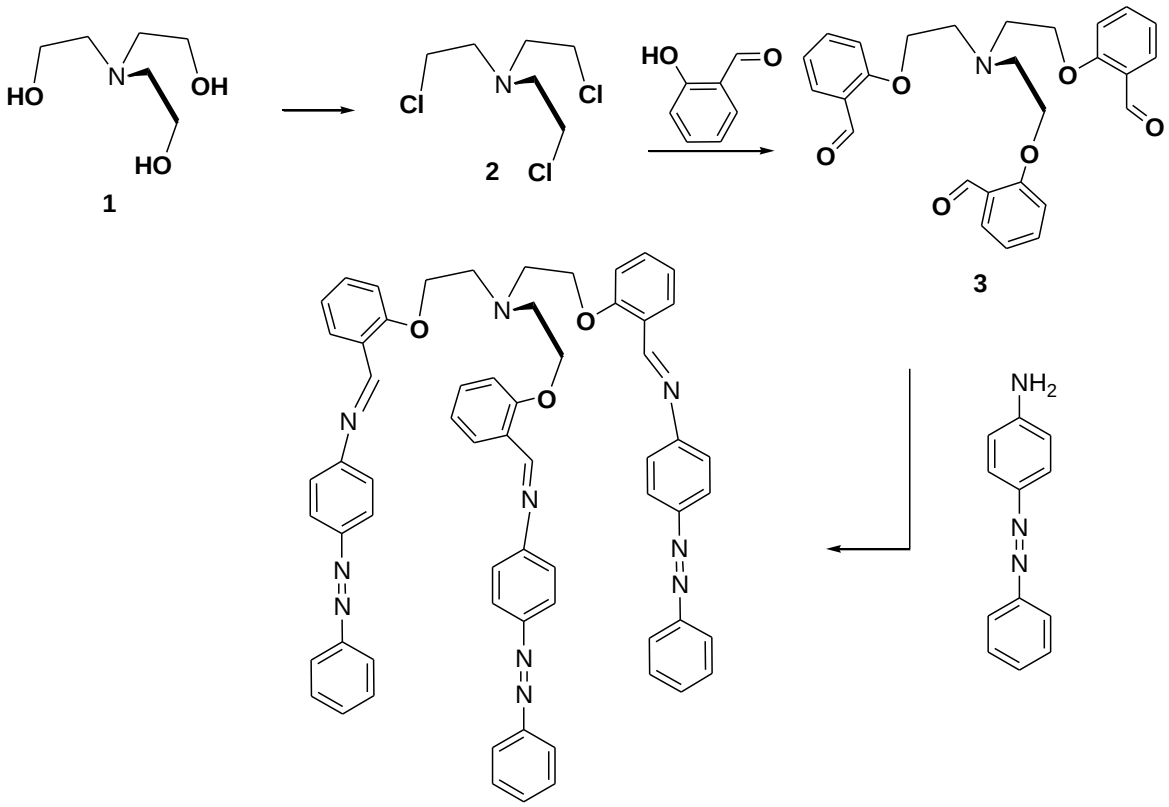
(3) Stoichiometry determination

In order to determine stoichiometry of the complex formed from receptor **4** and particular metal ion, solutions of **4** and metal salt were prepared as 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2 and 9:1 (in THF:H2O (9:1, v/v). These solutions were kept at 25±1 ºC for 3 h, and were shaken occasionally. Their absorption spectra were recorded at λ_{max} = 365 nm and intensity at λ_{max} = 365 nm was used for calculations. The concentration of [HG] was calculated by the equation $[HG] = \Delta I/I_o \times [H]$.It was done with the help of job plot .

RESULTS & DISCUSSION

Synthesis of Tripodal Receptor

The compound **2-4** were synthesised by following the slightly modified literature procedure.[9]



Scheme 2

The triethanolamine (**1**) was purified by making its hydrochloride salt. The trischloroethylamine (2) was prepared by suspending the hydrochloride salt of triethanolamine (45 g) in $CHCl_3$ and treated with $SOCl_2$ (120 ml). Upon completion of reaction, the reaction mixture was chilled in ice bath and white coloured crystals

separated out. This crystalline material was separated with simple filtration and its melting point was compared with literature value. The tripodal aldehyde (**3**) was prepared by taking salicylaldehyde (3.0 mol) along with NaOH (5.0 mol) in 2-propanol. The mixture was refluxed for 1 h and yellow coloured viscous material was formed. To the reaction mixture compound **2** (1.0 mol) was added and refluxing was continued for another 10 h. Upon completion of reaction the reaction mixture was poured into the ice chilled water and ppts were separated out. These ppts were filtered and dried. The compound was characterized by melting point as well as with ^{1}H NMR spectroscopy. The final compound **4** was prepared by taking tripodal aldehyde **3** (1 mmol) in dry methanol. The solution was warmed to dissolve it and azo dye (3.0 mmol) was added to it. Stirred the reaction mixture for two hours, a solid material was obtained with yellowish orange color. The final compound was characterized with ^{1}H NMR; product also shows the band for imine linkages (-CH=N-) in its IR spectrum and the purity of product was checked with elemental analysis.

The specific color change of a receptor upon guest binding is an informative signal that is utilized in guest-sensing systems. The concept is now well extended to supramolecular chemistry by the development of a wide variety of chromoionophores. Tripodal and tetrapodal chromogenic receptors have rarely been described in the literature and comprehensive studies on this idea are required to allow sensing of target ions by colour change.

Metal binding affinity of receptor 4

The metal binding affinity of receptor **4** was established from the changes in UV-Vis signature of **4** upon addition of different metal salts as shown in Fig. 7.

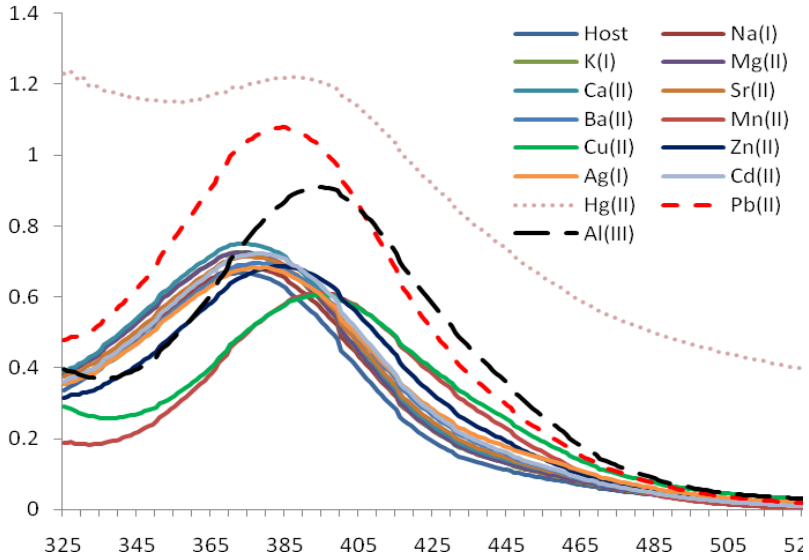


Figure 7. Changes in UV-Vis spectra of **4** (10μM) upon addition of standard solution of a particular metal ion salt in THF/H_2O (9:1, v/v) solvent system.

Figure 7 clearly shows that there is a marked change in UV-Vis signature of **4** upon addition of only poisonous metal ions like Al(III) or Hg(II) or Pb (II). On the other hand, no such significant changes in UV-Vis spectra were observed when receptor **4** was exposed to other metal salts under the same experimental conditions. Again the soft-soft interactions are responsible for complexation of either of Al(III) or Hg(II) or Pb (II) ion by the sp^2 N of the –C=N group.

(a) **Titration of receptor 4 w.r.t. metal ions**

To learn more about the properties of **4** as a receptor for either of Al(III) or Hg(II) or Pb (II), UV-Vis spectroscopy was used along with titration. Figure 8-9 illustrates the absorption response of chemosensor **4** with increase in concentration of Al(III) or Hg(II) or Pb (II) respectively. In all the cases, the absorption of a 10 μM solution of **4** enhanced, while shape of the absorption band changed significantly. The receptor **4** exhibited a highest sensitivity toward Hg(II), first quenching and then enhancing its absorption with the addition of metal salt. The titration is showing no regular pattern in the change of UV-Vis signature; thus receptor has limited application as sensor for Hg(II).

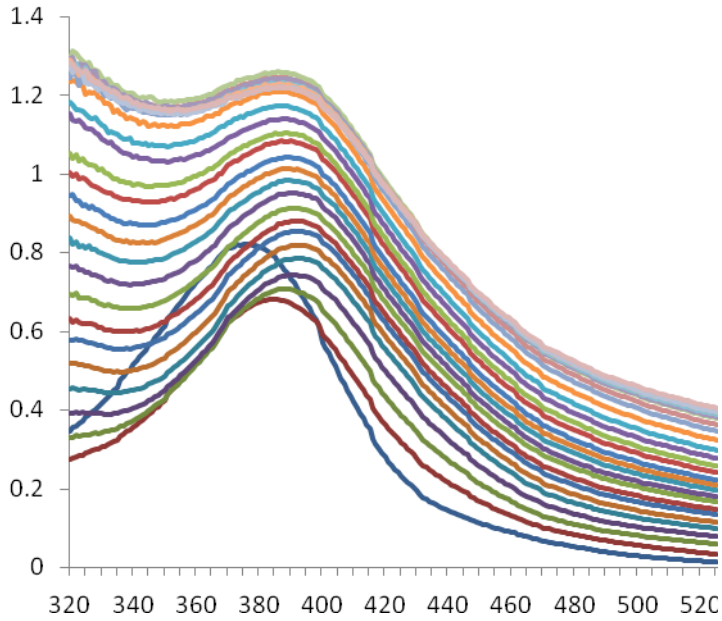


Figure 8. Changes in UV-Vis spectrum of receptor **4** (10 μM) upon addition of Hg(II) salt (0-100 μM) in THF/H_2O (9:1, v/v) solvent system.

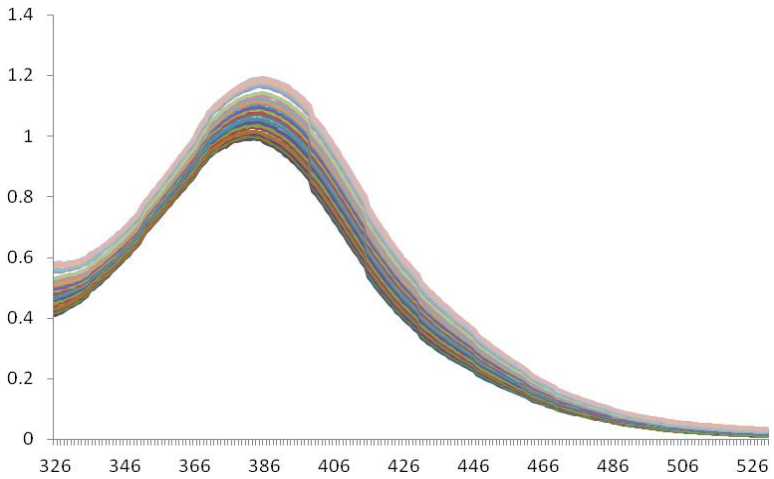


Figure 9. Changes in UV-Vis spectrum of receptor **4** (10 μM) upon addition of Pb(II) salt (0-100 μM) in THF/H_2O (9:1, v/v) solvent system.

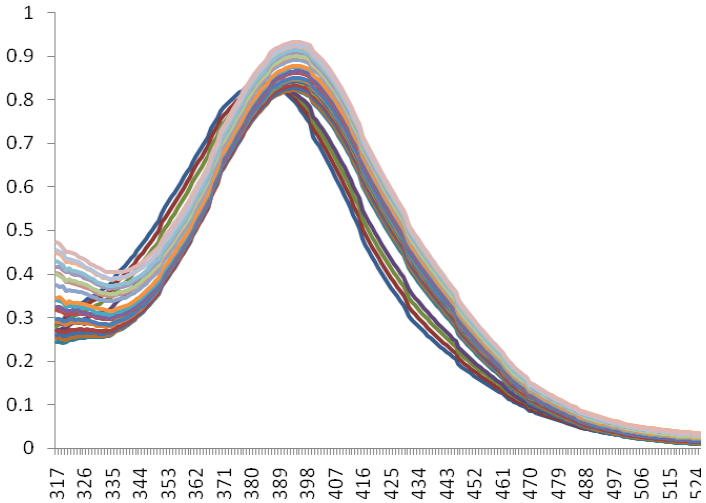


Figure 10. Changes in UV-Vis spectrum of receptor **4** (10 μM) upon addition of Al(II) salt (0-100 μM) in THF/H_2O (9:1, v/v) solvent system.

Unlike to the response of receptor 8 for Hg(II), the response of receptor **4** for Al(III) and Pb (II) is different. In both the cases titration exhibited a continuous increase in absorption with the addition of metal salt. These titrations are showing regular pattern in the change of UV-Vis signature; thus receptor can be used as sensor for both Al(III) and Pb (II).

CONCLUSIONS

A new chromogenic receptor was synthesized. The final receptor was prepared by Schiff's base condensation reactions. These reactions have been performed by reacting a tripodal aldehyde with chromogenic amine.

New chromogenic receptor (4) shows the marked change in UV-Vis signature of 4 upon addition of only poisonous metal ions like Al(III) or Hg(II) or Pb (II). On the other hand, no such significant changes in UV-Vis spectra were observed when receptor 4 was exposed to other metal salts under the same experimental conditions. The soft-soft interactions are responsible for complexation of either of Al(III) or Hg(II) or Pb (II) ion by the sp^2 N of the –C=N group.

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