Summary

Introduction

The greater understanding of the structural and functional properties of living systems is a key challenge in chemical and biological sciences. In living systems, the non-covalent interactions are very significant in sustaining the two and three-dimensional structure of bio-molecules, such as proteins in which they bind specifically but transiently to one another. Supramolecular chemistry which is “chemistry beyond a molecule” provides one such platform to study the non-covalent interactions of biological systems. This is the chemistry where molecules are able to self-organize, self-assemble, and self-control into systems and the components are often analogues to biological molecules. From last few decades, there have been significant developments in the areas of supramolecular chemistry which includes molecular recognition, catalysis, molecular devices, self-organization, ensembles and nanochemistry. Among these, molecular recognition chemistry aims at the design and synthesis of molecular receptors which are useful to understand and mimic nature’s specific interactions towards various guest molecules by non-covalent interactions. Since the origin of the concept of molecular recognition chemistry (host-guest chemistry), a wide variety of synthetic organic receptors like crown ethers, cryptands, spherands, porphyrins, calixarenes, thiacalixarenes, and cyclodextrins have been used as molecular receptors.

In the present investigation we have designed, synthesized and evaluated a number of receptors based on thiacalix[4]arene. Thiacalix[4]arene is a cyclic oligomer obtained from p-tert-butylphenol and elemental Sulfur (S8) under alkaline conditions. Like calix[4]arene, it adopts four conformations i.e. ‘Cone’, ‘Partial cone’, ‘1,2-Alternate’ and ‘1,3-Alternate’ as shown in figure 1. The results of our finding have been divided into following four chapters.

1. Chapter 1. Introduction and review of literature
Chapter 1. Introduction and review of literature

The versatility of thiacalix[4]arene as host molecule is due to its chemical modifications at wider rim, narrow rim and on the bridging sulfide group. The chemical modifications of narrow and wider rim of thiacalix[4]arene is intrinsic to phenols i.e. modification at the phenolic hydroxyl group and/ or the p-position. Therefore, a variety of thiacalix[4]arene derivatives can be prepared according to well known calix[4]arene chemistry. However presence of sulfide bonds brings steric and electronic effects into account of thiacalix[4]arene chemistry, particularly oxidation of sulfide bonds to sulfoxide and sulfone. The reaction conditions used for the synthesis of a particular thiacalix[4]arenes derivatives may considerably differ from those used for the methylene-bridged calix[4]arene counterpart. Thus, in this chapter, we have discussed the recent developments in derivatization and applications of thiacalix[4]arene chemistry.


The development of synthetic receptors for detection of environmentally or biologically important transition metal ions like Fe$^{3+}$, Cu$^{2+}$, Hg$^{2+}$, Ag$^+$ etc and anions like F, CN$^-$ etc need attention because of their potential applications in many fields like chemistry, medicine, biology and environment. Keeping in view of significance of transition metal ions and anions, in the present chapter, we have designed and synthesized various thiacalix[4]arene derivatives such as bisthiaacalix[4]arenes and thiacalix[4]podands of cone and 1,3-alternate conformations possessing amido and
(thio)uriedo moieties as binding units. The results of our findings are divided into following sections.

2. Anion recognition based on thiacalix[4]arene possessing (thio)urea units

2.1 Cation recognition based on thiacalix[4]arene possessing amide units

In the present section, we have designed and synthesized various bisthiacalix[4]arenes 4a-b and 5a-b and thiacalix[4]podands 7a-d containing amide groups (Chart 1). The binding abilities of bisthiacalix[4]arenes 4a-b, 5a-b and thiacalix[4]podands 7a-d toward different metal ions were evaluated by two-phase solvent extraction of metal picrates (Li⁺, Na⁺, K⁺, Ca²⁺, Sr²⁺, Ba²⁺, Pb²⁺, Hg²⁺, Zn²⁺, Ni²⁺, Ag⁺, Cu²⁺ and Co²⁺). The results showed poor ion extractability of these bisthiacalix[4]arenes 4a-b, 5a-b and thiacalix[4]podands 7a-d of different metal ions.

From these results it is clear that development of a selective and sensitive method which can detect, monitor and convert the binding of specific analyte into optical signal is important. Fluorescence signaling is one of the best choices due to its high detection sensitivity and simplicity, “on-off” switchability and applicable for logic gates which translates molecular recognition into tangible fluorescence signals. Thus, developments of fluorogenic chemosensors for metal ions based on ion-induced changes in fluorescence are particularly attractive due to their simplicity, high
sensitivity, and instantaneous response. In fact a variety of effective fluorescent sensors for alkali and alkaline earth metal ions have already been reported.\textsuperscript{10} The development of chemosensors for soft transition metal ions particularly iron need attention. Among transition metal ions, Fe\textsuperscript{3+} ions\textsuperscript{12} have received considerable attention. The trivalent form of iron is an essential element in human body and provides the oxygen-carrying capacity of heme, acts as a cofactor in many enzymatic reactions, plays an important role in oxygen metabolism, electron-transfer processes and DNA-RNA synthesis. The deficiency and excess of iron result in various pathological disorders as it is essential for most organisms. Thus, the diversity of their functions, both beneficial and otherwise, makes the monitoring and detection of iron important.

Thus, we have designed and synthesized a fluorogenic chemosensor 10 based on thiacalix[4]arene of cone conformation bearing pyrene moieties for selective detection of Fe\textsuperscript{3+} ions (Chart 2). The fluorogenic chemosensor 10 shows high selectivity towards Fe\textsuperscript{3+} among all the metal ions (Li\textsuperscript{+}, Na\textsuperscript{+}, K\textsuperscript{+}, Ba\textsuperscript{2+}, Mg\textsuperscript{2+}, Ni\textsuperscript{2+}, Cu\textsuperscript{2+}, Cu\textsuperscript{2+}, Zn\textsuperscript{2+}, Cd\textsuperscript{2+}, Hg\textsuperscript{2+}, Ag\textsuperscript{+}, Pb\textsuperscript{2+}, Co\textsuperscript{2+}, Mn\textsuperscript{2+} and Fe\textsuperscript{2+}) tested. The addition of Fe\textsuperscript{3+} ions to the solution of compound 10 results in fluorescence quenching of excimer emission in mixed aqueous media. Further, biological application of receptor 10 has been addressed by carrying out fluorescent titrations of \textit{in situ} prepared 10.Fe\textsuperscript{3+} complex towards different amino acids, bovine serum albumin (BSA) protein and blood serum. Upon the addition of amino acids or bovine serum albumin (BSA) protein or blood serum to the solution of 10.Fe\textsuperscript{3+} complex, no change in the fluorescence emission of 10.Fe\textsuperscript{3+} complex was observed.

![Chart 2](image-url)
The receptor 10 was suitable amphiphilic for its dissolution in aqueous organic media for better cell permeability; therefore, receptor 10 was explored for possible detection of iron in the living cells. The prostate cancer (PC3) cell lines treated with compound 10 and then with Fe$^{3+}$ were imaged by confocal fluorescence microscope. The PC3 cell lines treated with receptor 10 display strong blue fluorescence emission indicating its high permeability into living cells. However, cells treated with both receptor 10 and Fe$^{3+}$ showed quenched intracellular fluorescence emission. This indicates that compound 10 has high selectivity towards Fe$^{3+}$ ions in the biological systems.

2.2 Anion recognition based on thiacalix[4]arene possessing (thio)urea units

Anions play an important role in our daily life; being crucial to physiological functions as well as various industrial process. Anions are crucial to many processes as they help regulate cellular pH, maintain cell volume and osmotic balance, and serve as cellular signals. Basically, the anion receptors can be positively charged or neutral molecules. The positively charged molecules interact with anions through electrostatic interaction. On the other hand, the neutral anion receptors containing amide, (thio)urea and pyrrole groups binds anions via favourable hydrogen bonding. With respect to the amide group, which can donate a single hydrogen bond, (thio)urea can donate two parallel H-bonds, to two oxygen atoms of an oxoanion, possibly displaying geometrical complementarity or to a spherical anion in a bifurcate mode. Therefore, (thio)ureas have been taken as good hydrogen bond donors for the construction of anion receptors that may bind anions by two hydrogen bonds of the (thio)urea-NH.

Among the biologically important anions, fluoride and cyanide are of particular interest owing to their significant role in biological system. Fluoride ions plays important role in preventing dental caries, and in the treatment for osteoporosis. An excess of fluoride can lead to thyroid activity depression and immune system disruption and fluorosis, which is a type of fluoride toxicity that generally manifests itself clinically in terms of an increase in bone density. On the other hand, CN$^-$ ion is among the most toxic inorganic anions. It strongly interact with active site of cytochrome $a_3$ and inhibits the cellular respiration in mammalian cells, as a result even its small amount is very lethal to human body. Unfortunately cyanide does not easily decompose in the environment. However, it is still a challenge to find a suitable chromogenic sensor for cyanide which is one of the most toxic
inorganic anions known so far. Thus, due to its wide range of applications and serious toxicity, the development of new chemosensors for fluoride and cyanide determination or sensing may be of interest.

During the last few decades, a large number of anion receptors\textsuperscript{13,14} in different structural scaffolds bearing different binding units. However, there are only few reports for anion recognition based on thiacalixarene.\textsuperscript{20} Thus, in the present section, we have designed, synthesized and evaluated different optical chemosensors based on thiacalix[4]arene possessing (thio)urea moieties. For facility in presentation, the results have been divided into following two subsections.

2.2.1 Fluorogenic receptors based on thiacalix[4]arene possessing (thio)urea units

2.2.2 Chromogenic receptors based on thiacalix[4]arene possessing (thio)urea units

2.2.1 Fluorogenic receptors based on thiacalix[4]arene possessing (thio)urea units

The selective recognition and sensing of anions by artificial fluorogenic receptors has emerged as a key research theme within the host guest chemistry involving different fluorogenic behaviour such as fluorescence quenching, fluorescence enhancement, ratiometric response etc on interaction with anions.

In this part of investigation, the pyrene-appended fluorogenic chemosensors 12, 13, 15, 16, and naphthyl-appended fluorogenic chemosensors 18 and 19 based on thiacalix[4]arene of 1,3-\textit{alternate} conformation have been synthesized possessing (thio)urea moieties (Chart 3). The compounds 12 and 13 containing urea as binding units showed high selectivity towards fluoride ions by quenching the fluorescence emission of pyrene groups. However, the thiourea compounds 15 and 16 showed response towards fluoride ions and cyanide ions in different modes. The addition of 5.0 equiv of F\textsuperscript{-} ions to the solution of compounds 15 and 16 results in red shift (δ14 nm) of monomer emission with simultaneous formation of excimer emission at 500 nm which is ascribed to intramolecular excimer formation between two pyrene moieties. Further addition of F\textsuperscript{-} ions (6-80 equiv) enhances the fluorescence emission at 413 nm due to intramolecular charge transfer (ICT) between thiourea nitrogen (N-H) and fluoride/cyanide ions. On the other hand, the addition of increasing amounts of CN\textsuperscript{-} ions to the solution of compounds 15 and 16 results in ratiometric response with significant quenching in the monomer emission at 399 nm and formation of excimer emission at 500 nm which is due to intramolecular π-π interactions of pyrene groups which lead to excimer formation with monomer quenching.
However, compounds 18 and 19 bearing two naphthyl moieties are selective for fluoride ions. In the absence of fluoride ion, these receptors 18 and 19 were in “off-state” showing no fluorescence emission band. With the addition of fluoride ion, the fluorescence emission of compounds 18 and 19 turned to “on-state” due to excimer formation between two naphthyl groups. The intermolecular binding interactions of F⁻ ion with NH protons of thiourea moieties trigger the intramolecular π-π interactions of naphthyl groups which lead to excimer formation and “off-state” of free ligands 18 and 19 turns to “on-state” with the addition of F⁻ ion. There was no change in the fluorescence of compounds 18 and 19 in the presence of other anions (Cl⁻, Br⁻, I⁻, OAc⁻, HSO₄⁻, NO₃⁻, H₂PO₄⁻, malonate, fumarate, tartrate, adipate, phthalate).

2.2.2 Chromogenic receptors based on thiacalix[4]arene possessing (thio)urea units

Among the various types of optical chemosensors, the chromogenic chemosensors are very attractive because they which convert binding signal of ionophore unit into a highly sensitive and visible signal through intramolecular charge transfer process which leads to change of colour, visible to naked eye. Traditionally, chromogenic anion sensing has been more difficult to achieve in comparison to that
of cations. This is mostly due to their wide range of geometries, which are often pH sensitive, as in the case of phosphate, which therefore renders them sensitive to spatial arrangements and orientation of binding groups.

Thus, in this section, we have designed and synthesized chromogenic chemosensors 21-23 based on thiacalix[4]arene possessing (thio)urea as binding units and p-nitrophenyl as Signaling unit (Chart 4). The receptor 21 showed response towards fluoride, cyanide and acetate ions among all the anions (Cl\(^-\), Br\(^-\), I\(^-\), OAc\(^-\), HSO\(_4\)^-, NO\(_3\)^-, H\(_2\)PO\(_4\)^-, malonate, fumarate, tartrate, adipate, phthalate) tested. The addition of increasing amounts of fluoride, cyanide and acetate ions to the solution of 21 results in ratiometric response with decrease in absorbance at 315 nm and formation of red shifted absorption band 365 nm/ 355 nm (δ 50 nm for fluoride and δ 40 for cyanide and acetate). However, compound 22 was selective towards CN\(^-\) ions over other anions. The addition of CN\(^-\) ions to the solution of compound 22 result in ratiometric response with decrease in absorbance at 353 nm and formation of new absorption band at 472 nm. The compound 22 showed effective ‘naked eye’ detection of CN\(^-\) ions over the other anions due to intramolecular charge transfer (ICT) between thiourea nitrogen (N-H) and cyanide ions.

![Chart 4](chart4.png)

On the other hand, the receptors 23a and 23b showed response towards fluoride and cyanide ions over other anions (Cl\(^-\), Br\(^-\), I\(^-\), OAc\(^-\), HSO\(_4\)^-, NO\(_3\)^-, H\(_2\)PO\(_4\)^-, malonate, fumarate, tartrate, adipate, phthalate) tested. The additions of fluoride or cyanide ions to the solution of compounds 23a and 23b resulted in decrease of absorption at 332 nm and formation of two red shifted absorption bands at 369 nm and 447 nm. The color of the solutions of compounds 23a and 23b change from colorless to dark yellow and orange red with addition of fluoride and cyanide ions due.
to intramolecular charge transfer (ICT) between (thio)urea nitrogen (N-H) and fluoride/cyanide ions.


The development of optical chemosensors for soft transition-metal ions and anions based on ion-induced changes in fluorescence are particularly attractive due to their simplicity, high sensitivity, and instantaneous response. Among the soft metal ions, copper is important heavy metal ion which is third most abundant element present in human body after Zn$^{2+}$ and Fe$^{2+}$. It plays an important role in fundamental physiological processes in organisms ranging from bacteria to mammals. However, copper can be toxic if the level exceeds cellular needs. Copper is also capable of displacing other metals which act as co-factors in enzyme-catalyzed reactions. Alteration in copper concentration at cellular level is related to serious neurodegenerative diseases like Menkes and Wilson diseases, Alzheimer’s disease and prion diseases. Mercury is another important soft metal ion due to its widespread contamination which arises from a variety of natural and anthropogenic sources including oceanic and volcanic emission, gold mining, and combustion of fossil fuels. The exposure to mercury even at very low concentration leads to digestive, kidney, and especially neurological diseases. On the other hand, among the biologically important anions, fluoride and cyanide are of particular interest owing to their significant role in biological systems (vide supra).

For the selective binding of soft metal ions such as Cu$^{2+}$ and Hg$^{2+}$, nitrogen and sulfur binding sites are desirable. It has been reported that amide groups complex cations through nitrogen and oxygen, but also anions through hydrogen bonding between anions and amide N-H.$^{24}$ Thus, we envisaged that derivatizing thiacalix[4]arene framework with amide group possessing suitable signaling unit should give a host capable of interacting with both cations and anions. Thus, in the present chapter, we have designed and synthesized fluorogenic chemosensors 14-17 (Chart 5) for selective detection of soft metal ions and anions. The results of our investigations are divided into following two sections.

3.1 Dansyl-appended thiacalix[4]arene based bifunctional receptor for Cu$^{2+}$ and F$^-$. ions

3.2 Pyrene-appended thiacalix[4]arene based bifunctional receptors for Cu$^{2+}$/Hg$^{2+}$ and CN$^-$ ions
3.1 Dansyl-appended thiacalix[4]arene based bifunctional receptor for Cu$^{2+}$ and F$^{-}$ ions

The fluorescent chemosensor 25 based on thiacalix[4]arene of cone conformation have been synthesized bearing dansyl groups (Chart 5). The binding abilities of the sensor 25 towards different cations such as lithium, sodium, potassium, nickel, cadmium, copper, zinc, lead, silver, mercury and anions like fluoride, chloride, bromide, iodide, cyanide, acetate, hydrogen sulphate and nitrate have been examined by UV-vis, fluorescence and $^1$H NMR spectroscopy. The fluorescent chemosensor 25 behave as bifunctional receptor showing high selectivity for Cu$^{2+}$ and F$^{-}$ ions. The addition of Cu$^{2+}$ ions to the solution of compound 25 results in ratiometric response with increasing fluorescence emission at 433 nm at the expense of the fluorescence emission centered at 504 nm. However, addition of fluoride ions to the solution of compound 25 results in fluorescence quenching at 504 nm. There was no change in the fluorescence emission of compound 25 in the presence of other cations (Li$^+$, Na$^+$, K$^+$, Ba$^{2+}$, Mg$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, Hg$^{2+}$, Ag$^+$ and Pb$^{2+}$) and anions (Cl$^-$, Br$^-$, I$^-$, OAc$^-$, CN$^-$, HSO$_4$-$, NO$_3^-$ and H$_2$PO$_4$-$). Thus, compound 25 may be considered as a potential bifunctional fluorescent chemosensor for Cu$^{2+}$ and F$^{-}$ ions.

![Chart 5](image.png)

3.2 Pyrene-appended thiacalix[4]arene based bifunctional receptors for Cu$^{2+}$/Hg$^{2+}$ and CN$^-$ ions

In the next part of our research work, we have synthesized fluorogenic chemosensors 30-32 bearing pyrene moieties (Chart 5). The compounds 30 and 32 exhibit monomer emission indicating that pyrene units are not stacked together. However, compound 31 showed both monomer and excimer emission due to stacking
of two pyrene units. Among all the metal ions (Li$^+$, Na$^+$, K$^+$, Ba$^{2+}$, Mg$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, Hg$^{2+}$, Ag$^+$, Pb$^{2+}$), compounds 30 and 31 were selective for Cu$^{2+}$ ions while compound 32 was selective for Hg$^{2+}$ ions. The addition of Cu$^{2+}$ ions resulted in significant quenching in monomer emission of compound 30 and ratiometric response with monomer enhancement and excimer quenching of compound 31. On the other hand, compound 32 showed significant quenching in monomer emission with Hg$^{2+}$ ions. Among all the anions tested (F$^-$, Cl$^-$, Br$^-$, I$^-$, OAc$^-$, CN$^-$, HSO$_4^-$, NO$_3^-$ and H$_2$PO$_4^-$), compounds 30-32 were selective towards CN$^-$ ions with quenching in fluorescence emission. Thus, compounds 30-32 may be considered as a potential bifunctional fluorescent chemosensors for Cu$^{2+}$/CN$^-$, Cu$^{2+}$/CN$^-$ and Hg$^{2+}$/CN$^-$ respectively.

Chapter 4. Molecular switches and logic devices based on thiacalix[4]arene

Recent advances in molecular computing$^{25}$ based on chemical reactions performed either in solution or at functionalised interfaces have stimulated interest in the development of molecular electronic and photonic devices$^{26}$ for information processing, sensing and computation. Molecular computing is an attractive research subarea of unconventional computing,$^{25}$ involving integration of molecular information processes using various Boolean logic operations such as AND, OR, INH, XOR, XNOR, and NOR gates at the molecular level which is related to the integration and processing of binary data of microprocessor systems. The conventional silicon based devices have limitation of their miniaturization down to the nanoscale. Therefore, development of materials for information storage and retrieval at the molecular level is promising choice for this limitation.$^{27}$

Various molecular logic gates were constructed exclusively by chemical inputs, while the output was observed as changes in optical signal using different scaffolds. However, there are only few reports of molecular switches and photonic logic gates based on calix[4]arene but none on thiacalix[4]arene. Thus, keeping in view the above significance, we have designed and synthesized thiacalix[4]arene based fluorogenic receptors for development of molecular switches, logic gates and logic devices. The results of our findings have been divided in three sections.

4.1 Reversible switches and logic gates based on thiacalix[4]arene
4.2 Molecular keypad lock and crossword puzzle based on thiacalix[4]arene
4.3 Molecular information storage devices based on thiacalix[4]arene
4.1 Reversible switches and logic gates based on thiacalix[4]arene

Within the past decade, many fluorescent chemosensors showing NOT, AND, OR, XOR, NAND, XNOR, INHIBIT logic operations, and combinational logic circuits have been reported. Among these logic gates, the particularly important one is XNOR gate. The XNOR (exclusive NOR) gates have gained an intense attention as it is an important logic system in most digital circuits as well as in more complex devices. In the XNOR gate, there are two independent meanings: ‘exclusive’ for NOR or ‘NOT’ for XOR. Accordingly, the XNOR can be represented by the situation where the output is 1 only if none (A=B: 0) or both of two inputs (A=B: 1) are operated. In literature, there are only few reports where fluorogenic receptors have been mimicked as XNOR logic gate.

Keeping in view the importance of the XNOR logic gate, the development of receptors behaving as XNOR logic gate is very important in supramolecular chemistry. Thus, in this part of investigation, we have designed and synthesized new pyrene and naphthyl-appended chemosensor 37, 40, 42-44 based on thiacalix[4]arene of cone and 1,3-alternate conformation (Chart 6). The compounds 37 and 40 gave strong monomer emission at 386 nm when excited at 344 nm showed high selectivity towards $\text{Fe}^{3+}$ ions and $\text{F}^-$ in two contrasting modes. The addition of increasing amounts of $\text{Fe}^{3+}$ as its perchlorate salt to the solution of receptors 37 and 40, there were significant quenching in the fluorescence emission. However, addition of $\text{F}^-$ to the solution of compounds 37 and 40 leads to ratiometric response with monomer quenching and small excimer formation. On the other hand, addition of $\text{F}^-$ ions to the solutions of iron complex of compounds 37 and 40 results in revival of fluorescence emission. Thus, chemosensors 37 and 40 behaves as a bifunctional fluorescent switch which mimics the performance of an exclusive-NOR (XNOR) logic gate with chemical inputs of $\text{Fe}^{3+}$ and $\text{F}^-$ ions.

However, the photophysical properties of chemosensors 42-44 demonstrate selective optical recognition of $\text{Fe}^{3+}$ and $\text{CN}^-$ ions. The addition of $\text{Fe}^{3+}$ ions to the solution of compounds 42-44 results in quenching of fluorescence emission. However, addition of $\text{CN}^-$ ions to leads to fluorescence quenching of compound 42 and ratiometric response with formation of small emission band at 454 nm and decrease in emission band at 350 nm of compounds 43 and 44. On the other hand, addition of $\text{CN}^-$ to the solution of iron complexes of compounds 42-44 results in revival of fluorescence emission. Thus, chemosensors 42-44 behaves as a bifunctional
fluorescent switches which mimics the performance of an exclusive-NOR (XNOR) logic gate with chemical inputs of Fe$^{3+}$ and CN$^{-}$ ions.

![Chart 6]

In the first part of this section, we have synthesized a thiacalix[4]arene based receptor which mimics the function of XNOR logic gate. Another important logic system is INHIBIT logic gate which is frequently used in complex digital circuits. An INHIBIT (INH) logic gate is a result of concatenation of AND and NOT gates, but in contrast to other gates with concatenated NOT, the logic inversion concerns not the output but one of the inputs. Numerous chemically driven INH gates have been developed based on fluorogenic systems but none on thiacalix[4]arene chemistry.

Thus, we have designed and synthesized a new fluorogenic chemosensor 46 based on thiacalix[4]arene of cone conformation. Among the different cations and anions, compound 46 showed high selectivity towards Fe$^{3+}$ and F$^{-}$ ions. The fluorogenic chemosensor 46 behave as “Turn-On” optical chemosensor for Fe$^{3+}$ at 428 nm due to excimer formation and for F$^{-}$ ions at 352 nm due to monomer of naphthyl moieties. The simultaneous presence of Fe$^{3+}$ and F$^{-}$ ions results in reversible “Off-On” switch at 428 nm and 352 nm. The reversible “Off-On” switch mimics as an INHIBIT logic gate with chemical inputs of Fe$^{3+}$ and F$^{-}$ ions.
4.2 Molecular keypad lock and crossword puzzle based on thiacalix[4]arene

In the next part of investigation, we were interested in using various logic gates to formulate molecular level devices. Numerous chemical systems have been developed which mimic various electronic devices such as identification tags for small objects, memory units, molecular keypad lock, laboratory on molecule and demultiplexer performing digital operations. Among these, molecular keypad lock is an important electronic logic device used for numerous applications in which an access to a device is restricted to a particular person having exact password to open the keypad lock. Such molecular devices, capable of authorizing password entries, are of high significance for information protection at molecular scale. The most important feature of the keypad lock system is the dependence of the output signal not only on the proper combination but also on the correct order of the input signals. In other words one should know the exact password to open the lock and this prevents access to an unauthorized user.

In view of the importance of molecular keypad devices, in the present section, we have designed and synthesized fluorogenic receptor based on thiacalix[4]arene of 1,3-alternate conformation bearing two dansyl groups and a crown-5 ring (Chart 7) which mimics the function of molecular keypad lock. Among all cations and anions tested, the compound showed high selectivity towards Hg and F ions. In the presence of Hg ions, the fluorescence emission of compound is quenched. The addition of increasing amount of F ion to the solution of compound results in ratiometric response with significant decrease in emission at 493 nm and formation of new blue shifted bands centered at 410 nm and 436 nm. However, addition of K or F ions to the solution of compound in the presence of Hg behaves as “On-Off” reversible switch. The reversibility and selectivity of receptor helps us to develop the sequence dependent logic circuit capable of memory functions. The receptor acts as molecular keypad lock with different sequences of three chemical inputs (Hg, F and K ion). The most important feature of the keypad lock system is the dependence of the output signal on the correct order of the input signals. The three chemical inputs Hg, F and K are designated as “H”, “F” and “K”, respectively. Out of six possible input combinations i.e. HKF, HKF, KHF, FHK, FKH, only HKF input combination gave different fluorogenic output signal at 484 nm and that would “opens” a molecular keypad lock only by inserting the right sequences of three input keys H, F and K, respectively. Only one correct order of the input signals (HKF)
resulted in the TRUE output signal “1” with strong fluorescence emission at 484 nm while all others keys produced the FALSE output signal “0” with quenched fluorescence emission. The TRUE output signal “1” can be used to “open” the molecular keypad lock while the FALSE signal “0” failed to open the lock which can result in the “alarm” signal indicating the wrong password.

Another electronic device which is less developed at molecular level is “molecular crossword puzzles”. The output signals in this molecular logic system are dependent not only upon the appropriate combination of chemical inputs but also upon the exact sequence of these inputs. However, it is still a great challenge to develop such molecular level devices in a single molecular entity. Thus, we have designed and synthesized a new fluorogenic chemosensor 50 based on thiacalix[4]arene of 1,3-alternate conformation which showed high selectivity towards Fe$^{3+}$ and CN$^-$ ions in contrasting modes in mixed aqueous media (THF: water, 9:1, v/v). Upon addition of small amounts of Fe$^{3+}$ ion to the solution of compound 50, there was significant quenching with small blue shift in fluorescence emission. However, addition of increasing amounts of CN$^-$ ion to the solution of compound 50 results in ratiometric response with decrease in fluorescence emission at 531 nm and formation of a new blue shifted band centered at 460 nm. The sequence dependent addition of Fe$^{3+}$ and CN$^-$ ions leads to formulation of various logic gates. Using these logic gates with two inputs Fe$^{3+}$ and CN$^-$ ions, sequential logic circuits have been constructed which mimics a crossword puzzle with optical memory feature (in feedback loop). The exact sequence would be possible by assigning the correct order of input signals (addition of Fe$^{3+}$ followed by CN$^-$ ions) so that only one sequence would solve the crossword puzzle.
4.3 Molecular information storage devices based on thiacalix[4]arene

In the section 4.2, we have developed molecular logic devices (molecular keypad lock and crossword puzzle) that are dependent upon the correct sequence of chemical inputs. Another important molecular device which has been less developed at molecular level is “memory units or information storage devices (Write-Read-Erase)”. These types of molecular storage devices mainly involve sequential integration of various logic gates into combinatorial circuits which is an important step for the realization of information storage processes (memory devices).\textsuperscript{30} This behaviour is extensively used in microprocessor for memory elements of integrated logic circuits. However, there are only few reports where information storage devices (Write-Read-Erase) have been developed at molecular level.

Thus, in the present investigation, we have designed and synthesized fluorogenic receptors \textit{52-55} based on thiacalix[4]arene which demonstrate switching behaviour with different analytes. The fluorescence spectra of compounds \textit{52} and \textit{53} (Chart 8) bearing two pyrene groups gave dual mode emission i.e. weak monomer at 377 nm and strong excimer emission of pyrene group at 470 nm, respectively when excited at 344 nm. The chemosensors \textit{52} and \textit{53} demonstrates significant selectivity towards Ag\textsuperscript{+} and Fe\textsuperscript{3+} in contrasting modes, among all the metal ions tested. Upon addition of increasing amounts of Ag\textsuperscript{+} as its perchlorate salt to the solution of receptors \textit{52} and \textit{53}, there was ratiometric response with monomer enhancement and significant excimer quenching. On the other hand, the addition of increasing amounts of Fe\textsuperscript{3+} ions to the solution of compounds \textit{52} and \textit{53} results in significant quenching in the fluorescence emission. The ‘\textit{in situ}’ prepared silver and ferric complexes of receptors \textit{52} and \textit{53} were investigated towards different amino acids and found to have pronounced selectivity towards cysteine. Depending on the three chemical inputs (Ag\textsuperscript{+}, Fe\textsuperscript{3+}, cysteine), the receptors \textit{52} and \textit{53} can switch between different fluorescence emission states i.e. “on” (strong fluorescence emission) or “off” (quenched fluorescence emission) which display “Write-Read-Erase-Read” behaviour with the help of binary logic. The molecular logic gates developed in response to molecular switching between chemical inputs (Ag\textsuperscript{+}, Fe\textsuperscript{3+} and cysteine) have been integrated sequentially into combinatorial logic circuits which generate optical memory features in the feedback loop (feeding one of the outputs of the device to be input) through signals transmission at excimer channel. This behaviour is extensively used in microprocessors for memory elements of integrated logic circuits.
Similarly, compounds 54 and 55 (Chart 8) behave as “turn-off” chemosensor for Fe$^{3+}$ and “turn-on” optical chemosensor for Hg$^{2+}$, K$^+$ and F$^-$ ions at 364 nm. The simultaneous presence of Fe$^{3+}$ and Hg$^{2+}$ or K$^+$ or F$^-$ ions, respectively, results in formulation of reversible “On-Off” switch at 364 nm. The molecular logic gates developed in response to Fe$^{3+}$, Hg$^{2+}$, K$^+$ and F$^-$ ions have been integrated sequentially into logic circuits which generate memory features with “Write-Read-Erase-Read” function.
References


