
In section 2a irreversible switching of metal ion recognition was observed using allosteric regulation. However, organic molecules which can undergo reversible ‘on-off’ switchable behaviour under the influence of appropriate stimulations are foreseen to open new perspectives for the realization of artificial functions at the molecular level. The controlling of these processes at molecular level using external stimuli is an interesting scientific challenge. Thus, in this part of the investigation, we designed and synthesized imino linked pyrene appended thiacalix[4]crown based chemosensor 11 which triggers a reversible ‘on-off’ switchable behaviour with Cu$^{2+}$ and K$^+$ ions (vide infra). Pyrene has been utilized as fluorophore because of its efficient and sensitive monomer emission at 370-430 nm and excimer emission around 480 nm. The intensity ratio of excimer to monomer emission ($I_E/I_M$) is very sensitive to conformational change and guest ion (cation and anion) concentration, hence it is very informative tool used in sensing systems.

Thus, condensation of diamine 3 with 2.1 mol equiv. of 1-pyrene carboxaldehyde 10 in a mixture of refluxing chloroform and ethanol (1:1) gave thiacalix[4]arene receptor 11 (70%), mp. 260 °C, FAB-MS m/z 1390 (M+1)$^+$ (Scheme 2.3). Likewise condensation of known precursor diamine 12 with 1-pyrene carboxaldehyde 10 furnished model compound 13 without incorporating crown moiety (74%), mp. 260 °C, FAB-MS m/z 1315 (M+1)$^+$ (Scheme 2.4). The structures of thiacalix[4]arene receptors 11 and 13 were confirmed from their spectroscopic and analytical data. The $^1$H NMR spectra of compounds 11 and 13 showed two singlets (18H each) at 1.35, 1.28 and 1.39, 1.37 ppm corresponding to the tert-butyl protons, two triplets (4H each) at 3.08, 3.45 and 3.34, 3.90 ppm.

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ppm corresponding to the NCH$_2$ and OCH$_2$ protons and two singlets (4H each) at 7.42, 7.37 and 7.55, 7.58 ppm corresponding to the aromatic protons of thiacalix[4]arene, a multiplet (18 H) from 7.55-8.5, 7.62-8.64 ppm corresponding to the protons of pyrene moieties and a singlet (2H) appear at 9.16, 9.23 ppm corresponding to imino protons respectively. In addition to this two broad signals and two triplets (4H each) at 3.42, 3.64, 4.02 and 4.05 corresponding to OCH$_2$ protons of crown ring were observed in case of compound 11. A triplet (6H) at 0.66 ppm corresponding to CH$_3$ protons, multiplet (4H) from 0.96-1.10 ppm corresponding to CH$_2$ protons and a triplet (4H) at 4.41 ppm corresponding to OCH$_2$ protons were observed in the case of compound 13. The IR spectra of compounds 11 and 13 showed C=N stretching bands at 1650 cm$^{-1}$ and 1635 cm$^{-1}$ respectively and there was no absorption bands corresponding to free aldehyde and amino groups, indicating that the condensation has taken place.

The cation binding behaviour of compounds 11 and 13 was investigated by UV-vis and fluorescence spectroscopy. The titration experiments were carried out in MeCN:CH$_2$Cl$_2$ (1:1) by adding aliquots of different metal ions. The absorption spectrum of 11 (1 X 10$^{-5}$ M) is characterized by typical absorption bands of pyrene at $\lambda_\text{max}$ = 286, 306, 344, 360 and 395 nm in MeCN/CH$_2$Cl$_2$ (1:1). Among all the metal ions tested (Cu$^{2+}$, Hg$^{2+}$, Pb$^{2+}$, Zn$^{2+}$,
Ni\(^{2+}\), Cd\(^{2+}\), Ag\(^{+}\), K\(^{+}\), Na\(^{+}\), Li\(^{+}\)) a new band is formed at 457 nm on addition of Cu\(^{2+}\) ions (figure 2.18), Hg\(^{2+}\) ions (figure 2.19) and Pb\(^{2+}\) ions (figure 2.20). The formation of new band at 457 nm is attributed to the interaction of these ions with the imino nitrogen atoms leading to the intramolecular charge transfer (ICT) phenomenon from the pyrene moiety to the imino group.

In the fluorescence spectra, compound 11 exhibited typical excimer emission band of the pyrene groups centred at 490 nm and a weak monomer emission at 396 nm. The formation of excimer band indicates that compound 11 exist in stacked or folded conformation with the two pyrene units very close to each other. On adding various metal ions i.e. Cu\(^{2+}\), Hg\(^{2+}\), Pb\(^{2+}\), Zn\(^{2+}\), Ni\(^{2+}\), Cd\(^{2+}\), Ag\(^{+}\), K\(^{+}\), Na\(^{+}\) and Li\(^{+}\) as their perchlorate salts to the solutions of compound 11, a change in the fluorescence behaviour was observed.

The results are shown in figure 2.21. It was observed that the fluorescence of receptor 11 (2.5 µM) was strongly quenched by the addition of Hg\(^{2+}\), Pb\(^{2+}\) and Cu\(^{2+}\) ions. However, it showed enhancement with K\(^{+}\) ions. These results confirm that Hg\(^{2+}\), Pb\(^{2+}\) and Cu\(^{2+}\) are recognized by pyrenyl nitrogen atoms. The fluorescence quenching of monomer emission induced by Hg\(^{2+}\), Pb\(^{2+}\) and Cu\(^{2+}\) in chemosensor 11 is ascribed to reverse PET,\(^{63}\) from pyrene unit to the nitrogen atom of which the electron density is diminished by metal ion complexation. The excimer quenching is due to conformational change that occurs during

![Figure 2.18 UV-vis spectra of 11 (1X 10^{-5} M) in the presence of Cu\(^{2+}\) ions (0-15.0 equiv.) in MeCN/CH\(_2\)Cl\(_2\) (1:1).](image)

![Figure 2.19 UV-vis spectra of 11 (1X 10^{-5} M) in the presence of Hg\(^{2+}\) ions (0-10.0 equiv.) in MeCN/CH\(_2\)Cl\(_2\) (1:1).](image)
**Figure 2.20** UV-visible spectra of 11 (1X 10⁻⁵ M) in the presence of Pb²⁺ ions (0-10.0 equiv.) in MeCN/CH₂Cl₂ (1:1).

**Figure 2.21** Fluorescence intensity changes [(I-I₀)/I₀ x 100] of receptor 11 and 13 (each of 2.5 µM) in MeCN/CH₂Cl₂ (1:1) upon addition of 100.0 equiv. of various metal perchlorates. Excitation wavelength was 343 nm. I₀ is the fluorescence intensity at 490 nm of each free host, and I is the fluorescence intensity after adding metal ions.

**Figure 2.22** Changes in fluorescence emission spectra of 11 upon addition of Cu²⁺ (8.0 equiv.) ions in MeCN/CH₂Cl₂ (1:1), λₑₓ = 343 nm.

**Figure 2.23** Job’s plot showing 1:1 stoichiometry of 11 with Cu²⁺ ions.
the binding of these metal ions to the two nitrogen atoms. In this changed conformation, it is no longer possible for the pyrene groups to have parallel stacking. The fluorescence spectra of 11 (2.5 µM) at various concentrations of Cu$^{2+}$ are shown in figure 2.22. The fluorescence intensity of both monomer and excimer bands gradually decreased as the concentration of Cu$^{2+}$ increased from 0-8.0 equivalents. The binding constant (log $\beta_1$) of compound 11 with copper ions, was found as 5.70. The stoichiometry of the complex was 1:1 as proved by the Job’s plot (figure 2.23). Similar fluorescence behaviour (figures 2.24 and 2.25) and 1:1 stoichiometry (host: guest) was observed in case of Pb$^{2+}$ and Hg$^{2+}$ complexes (figures 2.26 and 2.27) with receptor 11 respectively. The binding of Hg$^{2+}$ and Pb$^{2+}$ with 11 has also been proved by NMR spectroscopy. The imine protons undergo a downfield shift ($\Delta$δ) of 1.64 and 1.65 ppm respectively. The log $\beta_1$ values for 11.Pb$^{2+}$ and 11.Hg$^{2+}$ complexes were found to be 6.15 and 6.54 respectively. However in contrast, the addition of 94.0 equiv. of K$^+$ to solution of 11 in MeCN/CH$_2$Cl$_2$ (1:1) gave 21% fluorescence enhancement (figure 2.28). The reason for the increase in the intensity of the excimer band at 490 nm is due to the fact that the K$^+$ ions binds to the polyether chain and as a result of which, the photo induced electron transfer to the photo excited pyrene dimer is suppressed. The binding of the K$^+$ ions with crown-5 is also supported by $^1$H NMR study where the protons of the crown-5 ring are shifted downfield by 0.22, 0.35, 0.32 and 0.18 ppm. The binding constant (log $\beta_1$) of compound 11 with K$^+$ ions is found to be 2.90. Selective K$^+$ binding by crown-5 ring of 11 is also proved by an experiment where K$^+$ was titrated into 11.Cu$^{2+}$ complex (vide infra). The increase in the fluorescence is supported by quantum yield which increased from ($\phi_f = 0.49$) to ($\phi_f = 0.60$) in dry THF. As the compound 11 contains two different metal ion binding sites, a metal ion will choose more favourable one when added to the solution of 11. The two nitrogen atoms of the imines prefer to bind Cu$^{2+}$, Pb$^{2+}$ and Hg$^{2+}$ resulting in fluorescence quenching while crown-5 ring bind K$^+$ ions which results in small fluorescence enhancement.
We observed an interesting ‘on-off’ switching process with regard to cation exchange based upon discrimination between K\(^+\) and Cu\(^{2+}\) ions (figure 2.29). When K\(^+\) was added to solution of 11.Cu\(^{2+}\) complex the fluorescence intensities of both excimer and monomer
bands were gradually enhanced and reached a plateau after adding about 698.0 equiv. of K\(^+\) ions to 11.Cu\(^{2+}\) complex (figure 2.30). However, on addition of K\(^+\) ions to 11.Cu\(^{2+}\) complex, typical shape and full intensity of excimer emission could not be obtained which may be the result of less overlapping pyrene dimer to provide the less effective HOMO-LUMO interaction in the excited state. The revived fluorescence intensity on addition of K\(^+\) ions is attributed to negative heterotropic allosteric effect.

![Figure 2.29](image)  
**Figure 2.29** Receptor 11 showing allosteric behaviour with Cu\(^{2+}\) and K\(^+\) ions.

![Figure 2.30](image)  
**Figure 2.30** Fluorescence emission changes with addition of K\(^+\) ions to the solution of 11.Cu\(^{2+}\) complex in MeCN/CH\(_2\)Cl\(_2\) (1:1); \(\lambda_{ex} = 343\) nm.

In the reverse of this metal ion exchange process, when the Cu\(^{2+}\) was gradually added to the solution of 11.K\(^+\) complex, the fluorescence was again shown to be quenched by the Cu\(^{2+}\) (figure 2.31) showing that the Cu\(^{2+}\) moves in and the K\(^+\) moves out from...
11. On the other hand the fluorescence intensity of the quenched complexes 11.Hg$^{2+}$ and 11.Pb$^{2+}$ could not be revived even after the addition of 1000.0 equiv. of K$^+$ which indicates that the complexation of K$^+$ in the crown ether site of 11 is unable to carry out decomplexation of Hg$^{2+}$ and Pb$^{2+}$ ions. The reason for observing such an allosteric behaviour with Cu$^{2+}$ only and not with Hg$^{2+}$ and Pb$^{2+}$ is due to the fact that the complexation of Cu$^{2+}$ with 11 is weak in comparison to the complexation of Pb$^{2+}$ and Hg$^{2+}$ with 11 as it is clear from the stability constant data (vide supra). We have also carried experiments using Na$^+$ and Li$^+$ ions to affect fluorescence of 11.Cu$^{2+}$ but found that the K$^+$ ions is the only effective cation to revive the fluorescence intensity. This suggests that the size of crown ring is suitable for the binding of only K$^+$ ions. It was observed that addition of K$^+$ slowly liberates Cu$^{2+}$ from the imino binding site of 11.Cu$^{2+}$ complex compared to release of K$^+$ upon addition of Cu$^{2+}$ with 11.K$^+$ complex. In the former the revival of fluorescence continued to increase even after more than 500.0 equiv. of K$^+$ were added. This suggests that Cu$^{2+}$ is complexed stronger and faster by imino nitrogen than is K$^+$ by polyether oxygen atoms.

To further confirm negative allosteric behaviour between Cu$^{2+}$ and K$^+$ ions, we studied the binding behaviour of compound 13 under same conditions as used for the compound 11. The results were same in the case of UV-vis studies of compound 13 as were observed for compound 11. The absorption spectrum of
13 (1 X 10^{-5} M) is characterized by typical absorption bands of pyrene at \( \lambda = 288, 307, 360, 396 \) nm in MeCN/CH$_2$Cl$_2$ (1:1). Among all the metal ions tested (\( Cu^{2+}, Hg^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, Ag^{+}, K^+, Na^+, Li^+ \)), a new band is formed at 461 nm on addition of \( Cu^{2+}, Hg^{2+} \) and \( Pb^{2+} \) ions (figure 2.32, 2.33 and 2.34 respectively).

The fluorescence spectra of 13 exhibited typical excimer emission band of the pyrene groups centred at 490 nm. The fluorescence emission of receptor 13 (2.5 \( \mu \)M) was quenched by the addition of \( Hg^{2+}, Pb^{2+} \) and \( Cu^{2+} \) ions. The quenching of fluorescence intensity of 13 with \( Cu^{2+}, Hg^{2+} \) and \( Pb^{2+} \) ions is shown in figure 2.35, 2.36 and 2.37 respectively. However, no change in fluorescence intensity of 13 was observed with \( K^+ \) ions. Moreover, when 94.0 equiv. of \( K^+ \) ions were added to the solutions of \( Hg^{2+} \),

![Figure 2.34](image_url)

**Figure 2.34** UV-vis spectra of 13 (1X 10^{-5} M) in the presence of \( Pb^{2+} \) ions (0-10.0 equiv.) in MeCN/CH$_2$Cl$_2$ (1:1).

![Figure 2.35](image_url)

**Figure 2.35** Changes in fluorescence emission spectra of 13 upon addition of \( Cu^{2+} \) (10.0 equiv.) ions in MeCN/CH$_2$Cl$_2$ (1:1), \( \lambda_{ex} = 343 \) nm.

![Figure 2.36](image_url)

**Figure 2.36** Changes in fluorescence emission spectra of 13 upon addition of \( Hg^{2+} \) (7.0 equiv.) ions in MeCN/CH$_2$Cl$_2$ (1:1), \( \lambda_{ex} = 343 \) nm.

![Figure 2.37](image_url)

**Figure 2.37** Changes in fluorescence emission spectra of 13 upon addition of \( Pb^{2+} \) (7.0 equiv.) ions in MeCN/CH$_2$Cl$_2$ (1:1), \( \lambda_{ex} = 343 \) nm.
**Pb**²⁺ and **Cu**²⁺ complexes of receptor 13, the fluorescence intensity did not changed which indicates that no cation exchange occurred in the case of 13 as there is no binding site available for **K**⁺ ions in receptor 13 (figure 2.38). Hence, the fluorescence intensity is not revived in case of receptor 13. This observation indicates that for ‘on-off’ switching based on cation exchange the presence of more than one cation binding site is very important.

To summarize, we have synthesized novel fluorescent chemosensor 11 with two different cation binding sites on lower rim of thiacalix[4]arene framework of 1, 3-**alternate** conformation. In the free ligand, two pyrene moieties linked to cation recognition units composed of imine units form a strong excimer. The changes induced in the emission spectra by addition of metal cations indicate that the 11 respond to **Hg**²⁺, **Pb**²⁺, **Cu**²⁺ and **K**⁺ over other metal ions investigated, while 13 with propyl groups instead of crown-5 ring shows response with **Hg**²⁺, **Pb**²⁺ and **Cu**²⁺ ions. The fluorescence quenching of monomer emission induced by **Hg**²⁺, **Pb**²⁺, **Cu**²⁺ in the case of both the receptors 11 and 13 is ascribed to reverse PET and excimer quenching is due to conformational change that occurs during the binding of these metal ions to the two nitrogen atoms. On the other hand addition of **K**⁺ ions to the solution of 11 showed a small enhancement in emission intensity because **K**⁺ is entrapped by the crown-5 unit. Interestingly, the fluorescence is quenched by **Cu**²⁺ but can be revived by the addition of excess **K**⁺ ions in to the 11.**Cu**²⁺
complex. Thus the metal ion exchanges trigger an ‘on-off’ switchable fluorescent chemosensor.