Chapter VI

An Efficient Colorimetric and Ratiometric Sensor for Fe$^{3+}$, Ru$^{3+}$ and Bi$^{3+}$ using per-6-Amino-β-Cyclodextrin as a Supramolecular Host: Naked-Eye Detection of Cations in Water

6.1 Introduction

Molecular recognition is a crucial process in biological systems such as enzymes, antibodies or genes and is also fundamental to supramolecular chemistry. The development of molecular systems and probes for sensing anions, cations, or neutral molecules using concepts such as photoinduced electron transfer (PET), host-guest chemistry or metal ion induced changes in aggregation behavior has attained prime significance due to their biological and environmental applications. Chemical sensing, which combines a recognition element with an optical or electronic transduction element, has received much attention as an efficient analytical technique for the detection of particular species. Such systems generally contain combination of substrate recognition functionality (receptor) and optical-signaling capacity (chromophore), either directly linked or appropriately associated in a noncovalent manner and are designed to permit the detection of substrates by binding induced changes in absorption or emission properties (termed colorimetric and fluorescence sensors respectively).

Several techniques are currently available for detecting metal cations. Despite this, there has been great interest in developing more sensitive, real-time and inexpensive methods for monitoring cations particularly in water. Though a number of fluorescence-based sensors have been reported, most of them exhibit fluorescence quenching when bound to metal ions and suffer from applicability in aqueous medium due to their poor solubility. And in the absence a fluorophore unit, it fails to detect the cations. Consequently, among the available methods,
colorimetric sensors\textsuperscript{11,21,23,24} are especially promising due to their simple naked-eye applications requiring less labor and expensive equipments than closely related methods such as fluorescent sensors. These sensors in general, contain combination of receptor and chromophore, either directly linked\textsuperscript{12} or appropriately associated in a covalent manner\textsuperscript{13,38} and are designed to permit the detection of substrates \textit{via} binding-induced changes in absorption.

Various synthetic organic moieties are used as optical sensor probes for colorimetric detection of metal ions. Squarylium and dithiosquarylium\textsuperscript{14} dyes are used to selectively detect Cu\textsuperscript{2+} and Ag\textsuperscript{+} spectrophotometrically by cation complexation. Congo-red linked alkylamide polymer\textsuperscript{15} is used for detecting trace amount of metal cations such as Ca\textsuperscript{2+}, Fe\textsuperscript{3+}, UO\textsubscript{2}\textsuperscript{2+}, Ba\textsuperscript{2+}, Cu\textsuperscript{2+} and K\textsuperscript{+} in aqueous media. The polymer shows sensitivity to Ca\textsuperscript{2+} and Fe\textsuperscript{3+}. Lipophilic ionophore \(N,N,N',N'\)-tetradodecyl-3,6-dioxaoctane-1-thio-8-oxodiamide\textsuperscript{16} sufficiently discriminates all the alkali and alkaline earth metal ions and is used for environmental monitoring of Pb\textsuperscript{2+}. Nickel and copper complexes functionalized with flexible crown ether moieties are synthesized and behave as spectroscopic probe for Al\textsuperscript{3+} and lanthanide cations\textsuperscript{17} in organic media by making use of spectral changes in the charge transfer and naphthaldehyde intraligand based bands. \(N\)-Butyl-4,5-di[2-(phenylamino)ethylamino]-1,8-naphthalimide\textsuperscript{18} is used as a probe for easy detection of Cu(II) ion and displays a colorimetric response with very high selectivity among heavy and transition metal (HTM) ions (Scheme 6.1). The solution color change from primrose yellow to pink and red-shift of fluorescence spectra from green to red are attributed to the deprotonation of the two secondary amines conjugated to the naphthalene ring.
Molina et al., have synthesized anthryl and pyrenyl modified 3-aza-1,3-diene, which selectively detect Cu$^{2+}$ ion colorimetrically by visual color change from yellow to orange and a remarkable enhancement of fluorescence (Scheme 6.2). Pyrenyl moiety behaves as a fluorescent sensor for Cu$^{2+}$ and Hg$^{2+}$ in aqueous environment.\cite{19}

A benzothiazolium hemicyanine dye\cite{20} is used as a colorimetric and fluorometric mercury ion sensor in aqueous solution. The selective sensing towards mercury is due to the presence of sulfur atom and mercury ions induce a geometric change of the trans isomer to cis form. A diamide-diamine based sensor possessing anthracene-9,10-dione\cite{21} is used as a chromogenic moiety for selective and visual sensing of Cu$^{2+}$ in aqueous medium. Unsymmetrical cationic squaraine dye (USqH$^+$) is used to detect Hg$^{2+}$ and Pb$^{2+}$ colorimetrically.\cite{22} Macrocyclic dioxotetraamine-1,8-naphthalimide derivative,\cite{23} and 4-fluoro-7-mercapto-2,1,3-benzoxadiazole\cite{24} are used to detect Hg$^{2+}$ and Cu$^{2+}$ colorimetrically in aqueous medium.
Iron is widely distributed in nature and is one of the most important elements in biological systems. It plays an important role in the transport and storage of oxygen and also in electron transport. Fe$^{III}$ ion also plays an indispensable role in many biochemical processes at cellular level, and both its deficiency and excess can induce a variety of diseases. If iron concentration exceeds the normal level it may become a potential health hazard. Iron deficiency leads to anemia, as iron trafficking, storage and balance being tightly regulated in an organism. As a consequence, intense research efforts have been directed to develop sensitive and selective sensors for Fe$^{3+}$. However, due to the paramagnetic nature of iron(III) ion, the fluorescent indication for Fe$^{3+}$ is marred by fluorescence quenching. Also colorimetric sensing for Fe$^{3+}$ is scarcely reported. However, despite the urgent need for Fe$^{3+}$ selective sensors, there have been only limited reports on Fe$^{3+}$ ion selective electrodes in literature.

Bi$^{3+}$ is widely used in cosmetics and medicines. It is utilized industrially as a constituent of many kinds of alloys and semiconductors and also as a coolant in atomic reactors. The Bi$^{3+}$ content in the environment has been regarded as one of the indicators of industrial pollution. The concentration of Bi$^{3+}$ in nature, however, is low and the exact detection of Bi$^{3+}$ is difficult. Traces of Bi$^{3+}$ in environmental samples are determined by graphite furnace atomic absorption spectroscopy (GFAAS) after extractive separation with trioctylmethylammonium nitrate. Spectrophotometry and neutron activation analysis combined with liquid-liquid extraction of chelate complexes of Bi(III) with dithiazone, xanthates, amidines and xylene orange have been studied for determination of Bi$^{3+}$ at µg g$^{-1}$ levels and below. Flow-injection analysis with liquid-liquid extraction and spectrophotometry has also been reported.

Similarly Ru$^{3+}$ also is one of the most important transition metal ions and it is widely used as luminescent material in various metal complexes. Often ruthenium complexes are combined with polymers and have been utilized as pH, CO$_2$, metal ion and temperature sensors. However, methods for sensing Ru$^{3+}$ are
very rare. It is also relevant to note that selective chemosensors for transition metal ions in aqueous environment are relatively rare because though transition metal ions are relatively easy to chelate and detect in organic solvents, they are difficult to recognize directly in aqueous environments due to their strong hydration.\textsuperscript{29}

In supramolecular chemistry, the recognition of ions and molecules is an essential part and the first step in the design of molecular sensors. Cyclodextrins, are well known to encapsulate various organic guests within their hydrophobic cavities.\textsuperscript{30} This fascinating property enables them to be used successfully in various applications such as catalysis and enzyme mimics to sensors. Upon specific functionalization, it can act as an excellent platform for sensing of various moieties. Various modified photoactive metallocyclodextrins are used as molecular sensors.\textsuperscript{31} Many chromophore-modified CDs are used as chemosensors for detecting molecules.\textsuperscript{32} Colorless neutral molecules can be detected with changes in the intensities of the fluorescence, absorption or circular dichroism using chemosensors based on such chromophore-modified CDs. Liu et al., have synthesized number of fluorophore modified CDs, that can act as supramolecular sensors for various molecules and metal ions.\textsuperscript{33} Recently aminobenzenesulfonamidoquinolino-β-CD\textsuperscript{34a} and 8-aminoquinolino-β-CD\textsuperscript{34b} are used to sense Zn\textsuperscript{2+} ion. Amino-CDs are homogeneous CD derivatives modified by persubstitution at the primary face with amino pendant groups and this manifests combined hydrophobic and electrostatic binding of guest molecules relative to native CDs. For example, the binding constant of 1 for \textit{p}-isopropylbenzenephosphate\textsuperscript{35} is three times larger than that for native β-CD, while for \textit{p}-isopropylphenol the binding constant is only 2\% of that of β-CD. Amino CDs are employed as biomimetic catalysts in Kemp elimination,\textsuperscript{36a} deprotonation\textsuperscript{36b} and chiral recognition processes.\textsuperscript{36c} Polyamino-modified β-CDs also form stable complexes with metal cations in presence of guest molecules.\textsuperscript{37} However, use of per-6-amino-β-cyclodextrin (per-6-ABCD), for sensing studies, has not received enough attention.
In the present work, using a simple colorimetric method, per-6-ABCD 1 is employed as a supramolecular host for detecting metal cations such as Fe\(^{3+}\), Ru\(^{3+}\) and Bi\(^{3+}\) using \(p\)-nitrophenol 2 as a spectroscopic probe in water medium. It is relevant to note that \(p\)-nitrophenol 2 as its phenolate anion has been used as a probe for anion sensing with calix[4]pyrrrole.\(^{38}\)

### 6.2 Results and Discussion

The amino group present in the primary side of per-6-amino-\(\beta\)-cyclodextrin (per-6-ABCD, 1) is basic in nature (pKa 6.6-8.5).\(^{39a}\) \(p\)-Nitrophenol 2 is colorless (\(\lambda_{\text{max}}\) 318 nm) in pure water medium (pKa 7.14).\(^{39b}\) When equimolar amounts (5 x 10\(^{-5}\) M of each) of 1 and 2 are mixed, 2 forms an inclusion complex 3 with 1 (binding constant of 2 with 1 is 1855 M\(^{-1}\) calculated by non-linear curve fit method), gets ionized by abstraction of a proton from 2 by the amino groups present in 1 and forms \(p\)-nitrophenolate anion resulting in an intense yellow color (\(\lambda_{\text{max}}\) 402 nm). It is known that amino groups are useful ligands and can form complexes with cations. The presence of polyamino groups in 1 has also resulted in formation of strong complexes with metal cations.\(^{37}\) These unique features prompted us to develop a simple colorimetric sensor for metal cations using 3 (formed from 1 and 2) and its water solubility in aqueous medium. As mentioned above, addition of \(p\)-nitrophenol 2 (5 x 10\(^{-5}\) M) to per-6-ABCD 1 (5 x 10\(^{-5}\) M) forms an inclusion complex 3 (Scheme 6.3) and the color has changed from colorless to intense yellow. The \(\lambda_{\text{max}}\) of 2 at 318 nm has disappeared and a new absorption peak, due to \(p\)-nitrophenolate ion appears at 402 nm.

The ability of this per-6-ABCD complexed \(p\)-nitrophenolate anion 3 to detect metal cations has been tested in water in the presence of various metal cations such as Ag\(^{+}\), Cu\(^{+}\), Mn\(^{2+}\), Fe\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\), Hg\(^{2+}\), Pb\(^{2+}\), Bi\(^{3+}\), Fe\(^{3+}\), Ru\(^{3+}\), Cr\(^{3+}\), Ln\(^{3+}\) and Eu\(^{3+}\) in order to assess its potential sensor applications. Water is chosen as solvent for all spectral measurements in the presence of metal cations since it guarantees a good solubility of 1 (< 5 x 10\(^{-4}\) M), their complexes with metal
cations and respective metal salts which are the source for the metal cations. The sensing ability of 3 is checked for different metals based on their oxidation states starting from monovalent metal ions. When 0.1 equivalent ($5 \times 10^{-6}$ M) of monovalent cations like Cu$^+$ and Ag$^+$ (Fig. 6.1) is added to a solution of 3 ($5 \times 10^{-5}$ M) in water, there is only a small decrease in the absorbance at 402 nm. Though

**Fig. 6.1** UV-Vis spectra of 3 ($5 \times 10^{-5}$ M) upon addition of a) Ag$^+$ ($5 \times 10^{-6}$ to $5 \times 10^{-5}$ M)

**Fig. 6.2** UV-Vis spectra of 3 ($5 \times 10^{-5}$ M) upon addition of a) Cd$^{2+}$ ($5 \times 10^{-6}$ to $5 \times 10^{-5}$ M)
the concentration of the metal ion is increased up to 1 equiv (5 x 10^{-5} M), no sensing of metal ion is noticed for the both metal ions as there is only a small decrease in 402 nm absorption. The sensing study is also extended to divalent metal cations like Mn^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} (Fig. 6.2), Hg^{2+} and Pb^{2+}. Here too all the divalent metal ions show poor response to 3 even at equimolar concentrations (5 x 10^{-5} M) of metal ions.

Sensing studies are also extended to trivalent metal ions such as Cr^{3+}, Fe^{3+}, Ru^{3+}, Ln^{3+}, Eu^{3+} and Bi^{3+}. When 0.1 equiv (5 x 10^{-6} M) of Fe^{3+} is added to a solution of 3 (5 x 10^{-5} M) in water, the absorbance at \( \lambda_{\text{max}} \) 402 nm has decreased significantly with the emergence of a band at 318 nm (corresponding to 2). Further addition of Fe^{3+} has led to a decrease in the intensity of the 402 nm peak and a concomitant increase in the intensity of 318 nm band (Fig.6.3), resulting in a change in the color of the solution from intense yellow to colorless. At equimolar concentration of Fe^{3+} (5 x 10^{-5} M), the disappearance of \( p \)-nitrophenolate anion and appearance of \( p \)-nitrophenol (in 3) is almost complete marked by presence of a well-defined isobestic point at 358 nm. This disappearance of 402 nm band (\( p \)-nitrophenolate anion) shows clearly the sensing of Fe^{3+} cation in water.

Further to increase the scope of 3 for sensing applications, a series of other trivalent transition metal cations and rare earth metal cations are examined. Among these, similar observations (as in Fe^{3+}), are noticed in addition of trivalent cations Ru^{3+} (Fig. 6.4) and Bi^{3+} (Fig. 6.5). In both the cases a similar trend, \( i.e., \) the disappearance of 402 nm band and appearance of 318 nm band, is noticed as in Fe^{3+}. Addition of other trivalent cations such as Cr^{3+}, Ln^{3+} and Eu^{3+} has led to very weak relatively negligible changes in the absorbance of 3 when compared with Fe^{3+}, Ru^{3+} and Bi^{3+} cations.
Fig. 6.3 UV-Vis spectra of 3 ($5 \times 10^{-5}$ M) upon addition of Fe$^{3+}$ ($5 \times 10^{-6}$ to $5 \times 10^{-5}$ M)

Fig. 6.4 UV-Vis spectra of 3 ($5 \times 10^{-5}$ M) upon addition of Ru$^{3+}$ ($5 \times 10^{-6}$ to $5 \times 10^{-5}$ M)
Fig. 6.5 UV-Vis. spectra of 3 (5 x 10^{-5} M) upon addition Bi^{3+} (5 x 10^{-6} to 5 x 10^{-5} M)

The absorbance response A_0/A of 3 to various metal cations at different concentrations is plotted (Fig. 6.6) and this shows clearly that Fe^{3+}, Ru^{3+} and Bi^{3+} exhibit good response than other metal cations.

Fig. 6.6 Plot of absorbance (A_0/A at 402 nm) of 3 (5 x 10^{-5} M) against concentration variation (5 x 10^{-6} to 5 x 10^{-5} M) of different metal cations
A similar trend is also observed when the absorbance data \( A/A_0 \) at 318 nm is plotted against various concentrations \((5 \times 10^{-6} \text{ M to } 5 \times 10^{-5} \text{ M})\) of metal cations (Fig. 6.7).

Fig. 6.7 Plot of absorbance \((A/A_0 \text{ at } 318 \text{ nm})\) of 3 \((5 \times 10^{-5} \text{ M})\) against concentration variation \((5 \times 10^{-6} \text{ to } 5 \times 10^{-5} \text{ M})\) of different metal cations.

The absorbance response \((A_0/A)\) of different metal cations \((5 \times 10^{-5} \text{ M, equimolar to per-6-ABCD})\) at 402 and 318 nm are presented in figs. 6.8 and 6.9.

Fig. 6.8 Absorbance response \((A_0/A)\) at equimolar concentration of 3 \((5 \times 10^{-5} \text{ M})\) with various cations \((5 \times 10^{-5} \text{ M})\) at 402 nm
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Fig. 6.9 Absorbance response \((A/A_0)\) at equimolar concentration of 3 \((5 \times 10^{-5} \text{ M})\) with various cations\((5 \times 10^{-5} \text{M})\) at 318 nm

The perceived absorbance and color changes of 3 with \(\text{Fe}^{3+}\), \(\text{Ru}^{3+}\) and \(\text{Bi}^{3+}\) ions, useful for rapid visual sensing, is also evident in a ratiometric method of detection of \(\text{Fe}^{3+}\), \(\text{Ru}^{3+}\) and \(\text{Bi}^{3+}\). Ratiometric measurements have the important feature that they permit signal rationing and thus increase the dynamic range and

Fig. 6.10 Ratiometric response \((A_{318}/A_{402})\) of 3 \((5 \times 10^{-5} \text{ M})\) with various cations \((5 \times 10^{-5} \text{ M})\)
provide built-in correction for environmental effects. The dependence of absorption ratio at $A_{318}/A_{402}$ at equimolar concentrations of $3$ and various metal ions (Fig. 6.10) shows that here too, changes in the absorption spectrum of $3$-$Fe^{3+}$, $3$-$Ru^{3+}$ and $3$-$Bi^{3+}$ is very significant when compared with other cations.

This selective complexation and much more improved sensing response of trivalent cations $Fe^{3+}$, $Ru^{3+}$ and $Bi^{3+}$ may be rationalized in principle by various factors like ionic radius of cations, electronegativity as well as HSAB theory of the cations. To understand better the various factors responsible for metal cation sensing, the data at 402 nm are plotted (Fig. 6.11) as a function of ionic radius (Table 6.3). Absence of any meaningful correlation indicates that ionic radii of cations is not the deciding factor in this sensing study.

![Graph showing absorbance response ($A_0/A$) of $3$ (5 x 10^-5 M) at 402 nm plotted against ionic radii (pm) of cations in increasing order](image)

**Fig. 6.11** Absorbance response ($A_0/A$) of $3$ (5 x 10^-5 M) at 402 nm plotted against ionic radii (pm) of cations in increasing order

**Table 6.1** Ionic radii (pm) of various metal cations

<table>
<thead>
<tr>
<th>$M^{+}$</th>
<th>$Cr^{3+}$</th>
<th>$Fe^{3+}$</th>
<th>$Mn^{2+}$</th>
<th>$Ru^{3+}$</th>
<th>$Cu^{2+}$</th>
<th>$Zn^{2+}$</th>
<th>$Cu^{+}$</th>
<th>$Fe^{2+}$</th>
<th>$Eu^{3+}$</th>
<th>$Cd^{2+}$</th>
<th>$Hg^{2+}$</th>
<th>$Bi^{3+}$</th>
<th>$La^{3+}$</th>
<th>$Pb^{2+}$</th>
<th>$Ag^{+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic radii</td>
<td>61.5</td>
<td>64.5</td>
<td>67.0</td>
<td>68.0</td>
<td>73.0</td>
<td>74.0</td>
<td>77.0</td>
<td>78.0</td>
<td>94.7</td>
<td>95.0</td>
<td>102.0</td>
<td>103.0</td>
<td>103.2</td>
<td>112.0</td>
<td>115.0</td>
</tr>
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</table>
The data are also plotted against electronegativity (Table 6.2) of the various metal cations. Electronegativity values reported by Xue\textsuperscript{42} are taken into consideration for the various ions (calculated on the basis of an effective ionic potential defined by ionization energy and ionic radii) in their most common coordination number (six for all the ions in the present study). For Fe\textsuperscript{2+} and Fe\textsuperscript{3+} average values of low spin and high spin states are taken. It is interesting to note that cations with higher electronegativity bind more readily with metal cations (Fig. 6.12). Trivalent cations bind readily then divalent and univalent cations. However, discrepancies are noticed with Eu\textsuperscript{3+} and Cr\textsuperscript{3+}. In spite of their high electronegativities, absorbance changes are small in these two cases.

![Fig. 6.12 Absorbance response (A0/A) at 402 nm plotted against increasing electronegativity of cations](image)

**Table 6.2** Electronegativities of various metal cations\textsuperscript{42}

<table>
<thead>
<tr>
<th>M\textsuperscript{+}</th>
<th>Ag\textsuperscript{+}</th>
<th>Cu\textsuperscript{2+}</th>
<th>Pb\textsuperscript{2+}</th>
<th>Cd\textsuperscript{2+}</th>
<th>Mn\textsuperscript{2+}</th>
<th>Hg\textsuperscript{2+}</th>
<th>La\textsuperscript{3+}</th>
<th>Zn\textsuperscript{2+}</th>
<th>Fe\textsuperscript{2+}</th>
<th>Cu\textsuperscript{2+}</th>
<th>Bi\textsuperscript{3+}</th>
<th>Eu\textsuperscript{3+}</th>
<th>Ru\textsuperscript{3+}</th>
<th>Cr\textsuperscript{3+}</th>
<th>Fe\textsuperscript{3+}</th>
</tr>
</thead>
</table>

Survey of literature shows that the Lewis acid strength of a cation depends on its oxidation state and coordination number. A cation with a higher value of
electronegativity attracts electrons more strongly and as a consequence, the electron cloud of anion penetrates that of the cations and thus a more covalent bond is formed. A good linear correlation is thus expected to exist between Lewis acid strength and the corresponding electronegativity. This prompted us to correlate the acidity of the metal cations to their corresponding sensing by 3.

A closer look at the data show that the results can be more readily explained on the basis of Pearson’s hard-soft acid base (HSAB) theory. Amino group can be considered as a relatively harder base (but not as hard as F⁻ and O⁻). Analysis of the hardness and softness of various cations show that much more harder acids like ‘Cr³⁺’ and also more softer acids like Ag⁺, Cd²⁺, Pb²⁺, Cu²⁺ and Hg²⁺ have much weaker affinity towards 3. The remaining various borderline acids studied here can be classified into two categories. Those (namely Fe³⁺ and Ru³⁺) which are closer to harder acids bind much more readily to 3. On the other hand, borderline acids such as Zn²⁺, Hg²⁺ etc., which are more oriented towards softer acids have very low affinity. The trend also holds good for Ln³⁺ and Eu³⁺, which are considered as harder acids and hence do not have any binding preference for 3. The above aspects clearly explain why Cr³⁺ and Cu²⁺, in spite of their high electronegativities have weaker affinity towards 3.

This response of 3 towards metal cations and color change from yellow to colorless is due to the complexation of M⁺ with the amino groups present in the 3. A plausible mechanism for this cation sensing is given in scheme 6.3. When p-nitrophenol 2 forms a complex with per-6-ABCD 1, the phenolic proton is abstracted by the amino groups in 1. The complexation of M⁺ with the amino groups of 3 has resulted in simultaneous transfer of the proton from amino groups of
Scheme 6.3 Mechanism for metal cation sensing by 3 in water

3 (which is already abstracted from 2) back to 2. This results in reprotonation of \( p \)-nitrophenolate ion regenerating 2. This proton transfer is responsible for sensing process and color change resulting in naked eye detection of \( \text{Fe}^{3+} \) (5 x 10^{-5} M) as shown in fig. 6.13

Fig. 6.13 Naked eye detection of \( \text{Fe}^{3+} \) (5 x 10^{-5} M) a) pure \( p \)-nitrophenol (colorless)(2) in water, b) per-6-ABCD + \( p \)-nitrophenolate anion (intense yellow color)(3), c) 3 with \( \text{Fe}^{3+} \) (colorless)
6.3 Conclusions

Using per-6-amino-β-cyclodextrin (per-6-ABCD, 1) as a supramolecular host and \( p \)-nitrophenol (\( p \)-PNP) as a spectroscopic probe, a colorimetric and ratiometric sensor for transition metal cations such as \( \text{Fe}^{3+} \), \( \text{Ru}^{3+} \) and a heavy metal \( \text{Bi}^{3+} \) in water has been developed. Other metal ions like \( \text{Ag}^+ \), \( \text{Cu}^+ \), \( \text{Mn}^{2+} \), \( \text{Fe}^{2+} \), \( \text{Cu}^{2+} \), \( \text{Zn}^{2+} \), \( \text{Cd}^{2+} \), \( \text{Hg}^{2+} \), \( \text{Pb}^{2+} \), \( \text{Cr}^{3+} \), \( \text{Ln}^{3+} \) and \( \text{Eu}^{3+} \) are not sensed by this procedure. This metal ions sensing by simple color change from intense yellow to colorless, can be used readily for their naked-eye detection. The selective sensing for the above three metal cations is rationalized based on electronegativity and HSAB concept of acidity and basicity.

6.4 Experimental

Stock solution of per-6-ABCD (\( 5 \times 10^{-4} \) M) in 250 mL was prepared in double distilled water and it was used for all sensing studies. After addition of per-6-ABCD in water, the solution was continuously sonicated for 12 h for complete solubilization after the solution become clear solution. The stock solution is sonicated for 10 min. before every use of metal ion sensing. \( p \)-Nitrophenol (\( 5 \times 10^{-5} \) M, stock 250 mL) was prepared in double distilled water. The water must be free from ions and other. (If not, the stock solution of \( p \)-nitrophenol itself undergoes ionization (formation of \( p \)-nitrophenolate anion) and appears as yellow solution which will disturb the sensing process. Stock solutions (\( 5 \times 10^{-4} \) M) of all the metal ions were also prepared in water and used. For UV titration, a series of solutions with different metal ion concentrations (\( 5 \times 10^{-6} \) M to \( 5 \times 10^{-5} \) M) were prepared in 10 ml SMF (Vensil, class ‘A’) and submitted to UV analysis using JASCO-Spectral manager. The calculations were done in a Microsoft-Excel-2003 software.
References


