Chapter 1

Chemosensors for ions: A review of literature

In the host guest chemistry the term chemosensor is more closely associated with a molecular event. Sensor is a system that on stimulation by any form of energy undergoes change in its own state and thus one or more of its characteristics.\textsuperscript{1} This change is used to analyze the stimulant both qualitatively and quantitatively. The optical and photo-physical changes in a molecule are found more valuable in this regard. These receptor molecules exhibit selective response to specific ions or neutral species to be used as chromosensors. An appropriate definition of a chemical sensor is the “Cambridge definition”\textsuperscript{2} Chemical sensors are miniaturized devices that can deliver real time and on-line information on the presence of specific compounds or ions in even complex samples. Chemical sensors employ specific transduction techniques to yield analyte information. The most widely used techniques employed in chemical sensors are optical absorption, luminescence, redox potential etc. but sensors based on other spectroscopies as well as on optical parameters, such as refractive index and reflectivity, have also been developed.\textsuperscript{3}

Need for chemosensors

Various neutral and ionic species find widespread use in physiology, medical diagnostics, catalysis and environmental chemistry.\textsuperscript{4,5} As cations and anions are prevalent in both heavy industry and in farming and as such in the environment, chemosensors are beginning to find many applications more so because the role of ions is being better understood now. Different cations such as \(\text{Ag}^+\), \(\text{Cu}^{2+}\), \(\text{Co}^{2+}\), \(\text{Hg}^{2+}\) etc. are relevant in different fields. Just to cite a few examples, \(\text{Ag}^+\) is useful in radio-immunotherapy and photographic technology. It inhibits the growth of bacteria and fungi and reduces the risk of bacterial and fungal infection and also finds use in cancer immunotherapy, deodorizing clothes and agricultural sterilizing agent. \(\text{Hg}^{2+}\) causes environmental and health problems. A wide variety of symptoms are observed upon exposure including digestive, kidney and especially neurological diseases. The level of this ion is therefore an object of strict regulation and should not exceed \(1 \mu g \text{ L}^{-1}\). Cobalt
is an essential element, required for the coenzyme vitamin B$_{12}$ and also believed to be cardiotoxic and may cause lung damage. Copper is necessary for the growth, development, and maintenance of bone, connective tissue, brain, heart and many other body organs. It is involved in the formation of red blood cells, the absorption and utilization of iron and the synthesis and release of life-sustaining proteins and enzymes. These enzymes in turn produce cellular energy and regulate nerve transmission, blood clotting and oxygen transport. It stimulates the immune system to fight infections, repair injured tissues and promote healing. It also helps to neutralize "free-radicals" which can cause severe damage to cells.

Similarly in case of anions few examples may include chloride sensing which is now being used for environmental monitoring. Chloride ion measurements can aid the monitoring of landfills for leaks, tracing the movement of pollutants within a natural water body and detection of salt water intrusion into drinkable ground or surface waters. The monitoring of nitrate levels is used to trace pollution from agriculture (nitrate fertilizers), for checking fish farms and other aquaculture for waste build-up and for surveying nutrient levels in natural water bodies. The excess of fluoride can lead to fluorosis which is fluoride toxicity and results in increase in bone density. The F$^{-}$ ion is important in clinical treatment for osteoporosis and detection of fluoride toxicity resulting from over accumulation of F$^{-}$ in bone.$^{6}$ There are many anions either used as, or are the products of, the degradation or hydrolysis of chemical warfare agents for example fluoride, which is the decomposition product of Sarin gas found in many nerve agents.$^{7}$ Cyanide is highly toxic to animals any type of release into the environment can lead to serious problems.$^{8,9}$ But it is used in various industrial processes, including gold mining and electroplating, production of organic chemicals and polymers, such as nitriles, nylon, and acrylic plastics enhancing the chance of unwanted release.$^{10}$

From the above it is clear that detection of ions is vital as many industrial and agricultural processes can lead to the release of ions to the environment, if left unchecked these can have devastating effects. A major research effort is being focused towards finding inexpensive, reliable and simple ways of detecting ions in solution. Therefore finding new selective ion receptor systems is an important goal which involves sensor
development, environmental remediation, selective separation and extraction of chemical species. The future envisages that greater interest and legal requirements for environmental, food and water monitoring will increase the need of detection of anionic species, selectively at more and more lower concentrations.

**Cation vs. anion sensing** - Though booming in a big way, the research in anion-selective receptors design is still less developed than that reported for its cation counterpart. This lack of development can be related to the following differences that exist between anions and cations.

- **Ionic size** – The anionic sizes are generally larger than cations and consequently necessitate larger binding sites. For e.g. 0.167 nm ionic radius of Cl\(^-\) is much larger than 0.133 nm of K\(^+\). The latter is same as the smallest F\(^-\) anion.

- **Shapes**- Anions come in different geometrical shapes e.g. spherical (Cl\(^-\)), linear (CN\(^-\)), tetrahedral (SO\(_4^{2-}\)) and trigonal planar (NO\(_3^-\)).

– The pH range for existence of anions is narrower in comparison to cations as in the case of phosphate and also ionization states can be variable, e.g. carbonate vs bicarbonate.

- Anions are more heavily hydrated than the cations of comparable sizes.

Design of the chemosensors consist of three components as shown in Fig. 1; a chemical receptor capable of recognizing the guest of interest usually with high selectivity; a transducer or signaling unit which converts that binding event into a measureable physical change and finally a method of measuring this change and converting it to useful information.

![Figure 1](image.png)

**Figure 1.** Schematic diagram showing binding of an analyte (guest) by a chemosensor (host), producing a complex with altered optical properties.
There are three different approaches\textsuperscript{11} which have been used by various groups in pursuing the synthetic receptors, which differ in the way the first two units are arranged with respect to each other.

- Binding site-signalling approach
- Displacement approach
- Chemodosimeter approach

These differ in the way the first two units are arranged with respect to each other. In the “binding site-signalling subunit” approach the two parts are linked through a covalent bond.\textsuperscript{12} The interaction of the analyte with the binding site induces changes in the electronic properties of the signalling subunit resulting in sensing of the target anion. The displacement approach is based in the formation of molecular assemblies of binding site-signalling subunit, which on coordination of a certain anion with the binding site results in the release of the signaling subunit into the solution with a concomitant change in their optical properties.\textsuperscript{13} In the chemodosimeter approach a specific anion-induced chemical reaction occurs which results in an optical signal.\textsuperscript{14} Out of these three approaches the first one has been widely exploited and this is the one which would be pursued in the present review.

Depending on the type of signals produced on the binding event, sensors may be put into two categories; Electronic sensors or Optical sensors.\textsuperscript{15} The former produce signals in the form of changes in the electrochemical properties whereas the latter bring changes in the optical properties.

**Electronic Sensors**

These sensors are mainly categorized into five categories.

1. Ion-Selective Electrodes (ISEs)
2. Field-effect transistors (FETs)
3. Electroactive Sensors
4. Biosensors
5. Microelectrodes
Optical sensors

The optical sensors further can be classified into two categories.

(A) Chromogenic chemosensors. In such type of chemosensors the coordination site binds the guest in such a way that signaling unit shows the changes in color.

(B) Fluorogenic chemosensors. In fluorogenic chemosensors the interaction between the coordination site and the guest moiety shows the changes in fluorescence behavior of the signaling unit.

The development of colorimetric sensors is increasingly appreciated since naked eye detection can offer qualitative and quantitative information without resort to any spectroscopic instrumentation. The fluorescence measurement on the other hand is usually very sensitive, versatile and offer sub-micromolar estimation of guest species. A wide variety of optical chemosensors have been reported for the cation, anion and neutral molecules. Based on the nature of analyte being detected, irrespective of the photophysical phenomenon the receptors follows, the chemosensors may be broadly classified into 3 categories; Cations sensors, Anions sensors, Neutral sensors. The present review is restricted to the optical chemosensors for cations and anions, which can be further classified as:

1. Cation sensors:

Optical cation sensing, which was originally started for metal ions not having a spectra of their own in the visible region, has been extensively studied. With the better understanding of host-guest chemistry of crown ethers, it became easier to develop chromogenic sensors for metal ions. Later many excellent examples of chromophoric and fluorophoric receptors for different cations have been prepared and studied.

(I) Chromogenic cation sensors. The chromogenic cation sensors may be grouped into three broad categories.16

i) Chemosensors for photometry in organic media: Such types of chemosensors function only in organic media. This category includes neutral and some protonic species depending on their molecular charge when they form complex with metal ions. Neutral chemosensors cause a net electronic charge transfer from the donor end to the acceptor
Such type of chemosensors involves intramolecular and intermolecular electron donor acceptor interactions, resulting in metal induced hypsochromic or bathochromic spectral shifts. Thus the metal binding to the chemosensor affects the electronic ground and excited state of chromophore with respect to the corresponding electronic state of the uncomplexed chromophore. In case of protonic chemosensors, the groups such as nitrophenol, azophenol having acidic protons form an integral part of the chemosensor skeleton. The color change is attributed to the deprotonation in these receptors. Although the organic base is not enough to cause the color change by itself, it facilitates the metal induced proton dissociation of the chromophore, which is followed by the intramolecular charge transfer through conjugation leading to color change.

ii) Chemosensors for extraction photometry: This type includes the anionic type chemosensors in which a proton-dissociable group is a part of the chromophore. In the presence of metal ion the interaction of the particular chemosensor is displayed in the form of optical properties. If the anion produced upon deprotonation is singly charged, the ionophore formed is a charge-neutralized complex with monovalent metal ion which is extractable from aqueous solution to a water-immiscible organic solvent. Sometimes receptors contain two anionic side arms the resulting molecules extracts the divalent metal ions. The performance of such chemosensors depends upon the steric orientation of the anionic group and cavity of the receptor to accommodate the particular metal ion.

iii) Chemosensors for photometry in aqueous media: Such types of chemosensors are specially designed for the metal photometry in aqueous media. This type of photometry eliminates the use of toxic and volatile organic solvents and also eliminates the phase separation step required in extraction photometry.

II. Fluorogenic cation sensors; A large number of fluorescent signaling systems exploiting the photo induced intramolecular electron transfer (PET) mechanism and metal ions as input are known. These systems are designed to covalently link fluorophores to electron donating atoms of acyclic or macrocyclic receptors. In guest free state, the binding subunit of the receptor donates a lone pair to the excited fluorophore via PET (Figure 2) and the excited fluorophore comes to the ground state through a non-radiative
pathway, causing quenching of fluorescence. The presence of a metal ion engages this lone pair through bonding, the PET is blocked, leading to the recovery of fluorescence. A system with fluorescent on/off capability can potentially act as a molecular photonic switch, which is the most important component of any true photonic device.

![Figure 2](image.png)

**Figure 2.** Schematic diagram showing mechanism of ion recognition by fluorescent PET sensors

Based upon the above techniques, excellent examples of receptors for various analytes have been prepared and studied for application in physiology, medical diagnostics and in environmental chemistry. A number of chromogenic receptors based on crown ethers, calixarenes; thiacalixarenes; azacrown-calixarenes, and podands have been reported in literature.

**(a) Podand based azo-coupled colorimetric cation sensors**

A number of azobenzene-based colorimetric receptors have been synthesized and its ion recognition studies were performed. In solution, receptor 1 gives rise to a large cation-induced hypsochromic shift for Cu\(^{2+}\) resulting in a change from red to pale-yellow that was clearly visible to the naked eye.\(^{20}\)

Azo 8-hydroxyquinoline benzoate 2a gives\(^{21}\) distinct color change in the presence of Hg\(^{2+}\) in CH\(_3\)CN, which produces naked eye detection of Hg(II). In order to investigate the effect of substituents, the receptor 2a has been modified to synthesize a series of 8-hydroxyquinoline benzoates with diverse azo groups. Bathochromic effect of 2 a-c occurs as substituent changes from -H, -OCH\(_3\), to -N(CH\(_3\))\(_2\) in CH\(_3\)CN solution upon complexation with Hg\(^{2+}\) ion.
A naked eye, highly selective and reversible colorimetric detection of Cu$^{2+}$ has been achieved with 3 under physiological condition. The internal charge transfer (ICT) sensors are highly colored, absorbing in the green. For 3a, the Cu$^{2+}$ recognition gives rise to red-to-yellow color changes that are visible to the naked-eye and reversible upon addition of EDTA, whereas for 3b, which lacks the aromatic o-methoxy chelating group, no such changes were observed.

Callan et al. has reported Quantum Dot–Schiff base conjugate 4 whereby the incorporation of a receptor onto the surface of a Quantum Dot (QD) alters its selectivity. The three-dimensional surfaces of the nanoparticle provide a particular organization to the receptor, which can recognize the Cu (II) and Fe(III) simultaneously, at physiological pH in a buffered solution. A significant shift in the absorption spectrum was observed in 4 on the addition of Cu(II) and Fe(III) in semi aqueous medium, in contrast the Schiff base itself displayed no selectivity.
(b) *Calix based azo-coupled colorimetric cation sensors*

The metal ion induced deprotonation of azophenol moieties\(^{23}\) produces visual optical changes in the electronic spectra of the ligands 5, 6, 7, 8, 9. Upon the addition of 100 equiv. of Hg\(^{2+}\) the color of the solution changed distinctly from yellow to red. In another series 1,3-alternate chromogenic azo-coupled calix[4]biscrowns 6 there is a regioselective complexation of metal ion. From the results of UV/vis band shift upon metal ion complexation, it was concluded that the metal ions were entrapped only by the upper crown loop, causing the hypsochromic shift on the UV/vis spectra. Calix\-[4]bis(crown-5)(crown-6) revealed K\(^+\) ion selectivity while calix [4]bis(crown-6)(crown-6) showed Cs\(^+\) ion selectivity caused by a size complementarity between hosts and guest ions.

![Diagram 5](image1)

![Diagram 6](image2)

![Diagram 7](image3)

Upper rim allyl- and arylazo-coupled calix[4] arenes based chromogenic sensors 8 is highly selective for Hg(II) ion.\(^{24}\) This shows visual color change in the presence of Hg(II) ion. A marked bathochromic shift in the UV/vis spectra from \(\lambda_{\text{max}}\) 359 nm to 520 nm (\(\Delta \lambda_{\text{max}}\) = 161 nm) was observed upon titration by Hg(ClO\(_4\))\(_2\) in a methanol-chloroform solvent system. Job’s plot shows 1:1 stoichiometry between 8 and Hg(II) ion. Upper rim modification of tetrathiacalix[4]arenes bearing various azo groups have been reported 9 and their ionic recognition has been studied in a hope to obtain new molecular filters and devices for specific use.\(^{25}\)
Kim et al. has synthesized azo-coupled calix[4]azacrown-5 10 having an azo chromophoric pendant group. Absorption spectra showed hypsochromic shift upon cation complexation, alkali and alkaline metal ions. Receptor has selectivity for K⁺ not only due to the size compatability between the K⁺ ion and the azacrown-5 loop but also due to a significant K⁺⋯π interaction between the two aromatic rings and the K⁺ ion. The UV band shifting is also dependent on the lipophilicity of the species of counter anion used. Azo-coupled calix [4] crown based receptors 11 showed visual color change on the addition of Ca²⁺ and Mg²⁺ in the cone conformation. However cesium and other alkali metals metal ions were not entrapped in the crown-6-ring because ligand was not in 1,3-alternate conformation. Metal ions entrapped by the crown loop induced deprotonation of the receptor easily even at neutral pH causing a charge density shift in the direction of the acceptor substituent’s (nitro group) of the chromoionophore.

A dipodal calix[4]arene derivative 12 was found to be highly selective for Na⁺. A bathochromic shift in the UV–Vis spectra was shown in the presence of Na⁺ with a visual color change in the solution from yellow to red. The binding ability and photophysical behavior of alkali cations by calix[4]arene derivative 12 was explained on the basis of substituted effects at the lower rim of parent calix[4]arene and size-fit concept between host calix[4]arenes and guest cations.
(c) Crown based azo-coupled colorimetric cation sensors

In literature Hg²⁺ selective azo-coupled macrocyclic chroinoionophores were synthesized by incorporating benzene 13 and pyridine 14 subunits. In a cation induced color change experiment, 13 gave a larger cation-induced hypsochromic shift than 14, suggesting that the presence of the pyridine unit in 14 may inhibit the Hg···N-azo interaction. The observed color changes for Hg²⁺ in 13 and 14 were found to be controlled by anion-coordination ability.
An N-azo-coupled macrocycle 15 has been used as a chromoionophore\textsuperscript{30} and shown to exhibit Hg\textsuperscript{2+} selectivity where the color of the metal complex is controlled by the anion. The two different colors for the complexes with iodide and perchlorate anions have been attributed to two different types of \textit{endo} and \textit{exo} complexes. The azo dye based chemosensor\textsuperscript{31} 16 displays extremely good sensitivity and selectivity for Na\textsuperscript{+} as compared to other physiologically important alkali and alkaline earth metal ions, which is pH independent above pH 3.9. This sensitivity is in the same range as found in blood for Na\textsuperscript{+} ion concentration. Receptor showed an absorption band at $\lambda_{\text{max}}$ 485 nm, which showed a hypsochromic shifts with $\Delta\lambda_{\text{max}}$ 110 nm on addition of Na\textsuperscript{+}. This also showed a strong visual color change from red to yellow in aqueous solution even at low metal ion concentrations.

Chromogenic N\textsubscript{2}S\textsubscript{2}-donor macrocycles functionalized with p-nitroazobenzene 17 and phenyltricyanovinyl 18 units were synthesized.\textsuperscript{32} These two receptors exhibit excellent Hg\textsuperscript{2+} selectivity by showing the drastic metal-induced color change from red to colorless ($\lambda_{\text{max}} = 137 - 140$ nm). The sensing ability for Hg\textsuperscript{2+} with the proposed chromoionophores is due to the stable 1:1 metal-ligand complexation formation.

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\text{17} \\
\text{18}
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\textbf{(d) Acyclic fluorescent cation receptors}

Duan \textit{et al.} have synthesized a new Ag(I) selective fluorescent chemodosimeter 19 by incorporating imidazolium units and naphthyl lumophores into a two-arm dipodand.\textsuperscript{33} A conformational switching “off–on” signalling process was shown by the receptor in the presence of Ag (I), through a combined signaling by both PET and excimer formation mechanisms.
A 1,8-diaminonaphthalene based Cu$^{2+}$ selective ratiometric and colorimetric fluoroionophore receptor 20 recognizes Cu$^{2+}$ selectively on the basis of ICT in which the metal has been incorporated in the electron donor moiety of the deprotonated fluorophore. UV-vis and emission spectra of the chemosensor showed remarkable red shift in acetonitrile-water solution upon Cu$^{2+}$ complexation. A dual color change from colorless (receptor) to purple followed by blue and large red shifts in emission were also observed.$^{34}$

Molecule 21 is a chromogenic and off-on fluorogenic probe$^{35}$ for the naked-eye detection of copper (II) in water-acetonitrile. The receptor can detect Cu$^{2+}$ from environmental samples by UV and fluorescence spectroscopy, in the range of trace amounts ($\mu$gL$^{-1}$), as required by organisms. With the stepwise addition of Cu$^{2+}$ the absorption band at 550 nm disappeared with simultaneous appearance of a new band at 393 nm. Similarly fluorescence titration of receptor showed 5-fold enhancement in the intensity of emission at 650 nm upon the addition of Cu$^{2+}$ solution.

Pyrene-based Cu$^{2+}$ indicator 22 that functions both as a naked-eyed and fluorogenic probe$^{36}$ for Cu$^{2+}$ with 2:1 complex stoichiometries. Upon addition of Cu$^{2+}$ the receptor shows a strong static excimer emission at 460 nm, along with a weak monomer emission at 388 nm. The excimer emission intensity induced by the Cu$^{2+}$ ion depends on the spacer length between the pyrene and quinolinylamide unit. For Cu$^{2+}$ ion sensing the intramolecular distance between the pyrene and quinoline amide groups should be less, this allows for eminent $\pi\cdots\pi$ interactions.
A Cu$^{2+}$ sensing fluorescent sensor 23 senses the metal ion on the basis of the mechanism of internal charge transfer (ICT ) with high sensitivity and selectivity. This resulted in the reduction of electron donating ability of the two amino groups conjugated to the naphthalene ring. This molecule detects the Cu$^{2+}$ ratiometrically with blue shifts of 50 nm. In ethanol water solutions it exhibits a strong fluorescent emission at 525 nm. The formation of 1:1 metal-ligand complex has been observed with a shift in the emission band from 525 nm to 475 nm. Dithiadicarbamates have been used to create the metal ion receptor 24 that has a high affinity towards Hg$^{2+}$. More attention has been paid to carbamodithioate and related structures for the molecular recognition of heavy metals. These sensors add novel interesting tools for environmental and biological detection of Hg$^{2+}$.

TTF-pyridyl derivatives 25a and 25b along with their phenyl analogues have been designed and synthesized (where TTF = tetraphiafulvalene). In these compounds, the TTF moiety and pyridyl group or phenyl group are bridged via a double
bond, which was designed to optimize the communication between the TTF unit and the pyridyl or phenyl group. All these compounds exhibit strong absorption bands in the range of 370 to 550 nm, which are assigned to the ICT from the HOMO in TTF to the LUMO in the pyridyl or phenyl group. The interaction between pyridyl group and Pb\(^{2+}\) enhances the electron-accepting ability of the pyridyl group. 25 show remarkable sensing and coordinating properties to Pb\(^{2+}\) as compared to their phenyl analogues, with visual color change from yellow to deep purple.

(e) Cyclic fluorescent cation receptors

Chromogenic sensors based on chromogenic macrocyclic backbone are particularly convenient for the development of selective sensors for different metal ions. In fact, by changing the nature and the number of side arms this backbone can be adapted to the nature of the metal analyte. In addition, the modification of solubility properties of the chosen receptor by the introduction of a neutral (diethoxyphosphoryl) methyl group is also interesting and can be widely applied for creating water-soluble receptors. A new anthraquinone-based colorimetric molecular sensor 26 exhibits efficient binding for lead ion in water and allows naked-eye detection. 40

A 1,2,3-triazole based Al\(^{3+}\) selective chemosensor 27 was synthesized and studied for its optical/ electrochemical properties. 41 A significant enhancement in fluorescence intensity was seen at 556 nm, on the addition of Al\(^{3+}\) ions due to the combined effect of ICT and CHEF caused by 1,2,3-triazole ring and carbonyl groups within a 2:1 complex mode.
An On-Off fluorescent chemosensor 28 for Cu^{2+} works via intramolecular fluorescence resonance energy transfer (FRET-On). In the presence of Cu^{2+} fluorescence of pyrene is strongly quenched (FRET-Off) whereas that of naphthalene group is revived.\(^{42}\)

(f) Calix based fluorescent cation receptors

The calix[4]arene derivate 29 carrying two spirobenzopyran moieties have been reported\(^{43}\) as lanthanide ions sensor. Significant shifts in UV–vis spectrum and the emission spectra have been observed in the presence of lanthanide ions. An apparent color change could be observed with the ‘naked eye’ over other cations including Na\(^+\), K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), Fe\(^{3+}\), Cu\(^{2+}\) and Zn\(^{2+}\). A triazole-modified calix[4]crown in the 1,3-alternate conformation based fluorescent on-off switchable chemosensor 30 with two different types of cationic binding sites has been synthesized by Chung et al.\(^{44}\) Fluorescence studies showed strong quenching by Hg\(^{2+}\), Cu\(^{2+}\), Cr\(^{3+}\), and Pb\(^{2+}\); however,
the revival of emission from the strongly quenched Pb$^{2+}$ complex was observed by the addition of K$^+$, Ba$^{2+}$, or Zn$^{2+}$ ions.

(g) **Metal based cation sensors**

Two ferrocene derivatives 31, 32 bearing two donor-acceptor systems are capable of selectively sensing cations by cooperative binding of the two $\alpha,\alpha'$ groups bonded to the ferrocene nucleus, thus permitting the naked-eye selective colorimetric detection of Cu$^{2+}$ cation. A novel colorimetric detection of Hg$^{2+}$ based on a mesoporous nanocrystalline TiO$_2$ film sensitized with a ruthenium dye 33 has been affected in aqueous solution with high selectivity. Using an entirely different approach Hg$^{2+}$ has been sensed by using a coordination complex of Ru(III) with substituted bipyridine and thiocyanate ions.

Based on ruthenium complexes mercury selective colorimetric sensors 34 has been reported. Hg$^{2+}$ coordinates reversibly to the sulfur atom of the dye’s NCS groups and a color change was observed even at submicromolar level concentration of mercury.
Moreover, by adsorbing the sensor molecules onto high-surface-area mesoporous metal oxide films, an easy-to-use system for the dip sensing of mercury (II) in aqueous solution has been developed. These films can be reused for sensing if they are washed with an aqueous solution of KI which presumably removes the mercury from the surface by forming a stable iodide complex of it.

(h) Miscellaneous examples of cation sensors

A coumarin-based copper selective colorimetric chemosensor 35 shows good sensitivity and selectivity for the Cu$^{2+}$ both in aqueous solution and on paper-made test kits. The quantitative detection of Cu$^{2+}$ was preliminarily examined. A phosphorodithionate-based ligand 36 communicates a color change with Hg$^{2+}$ owing to a charge transfer and a solubility change. The receptor 37 is colorimetric mercury selective ion sensor. It was observed that when commercially available 2-amino isoquinoline was mixed with mercuric ion no color changes were observed, whereas in case of receptor 37 color and fluorescence changes upon binding. A base/buffer was required to bind with mercury ion in a 1:1 stoichiometry.

Recently an inexpensive, OMP (organic molecular probe) 38 consisting of a charge-transfer complex, has been developed for the detection of small quantities of mercury. OMP is a hemicyanine dye composed of an electron-donor aniline moiety and an electron acceptor benzothiazolium species, showing a detection limit of 100 ppb for mercury.
2. **Anion sensors**

Confining here to chromogenic anion sensors, these may be broadly divided into two main categories, following the classification put forth by both P. A. Gale and Tuntulani et al.\(^5^3\)

(I) **Metal and Lewis acid based chromogenic hosts**

(II) **Nonmetal based chromogenic hosts**

(I) **Metal and Lewis acid based chromogenic hosts**: As put forth by Gale\(^5^2\) for metal-involved chromogenic hosts, the changing color comes from the color of metals or metal complexes, especially transition metal ions, whose electronic properties are changed upon coordination to anions. The anions may also displace the coordinated chromophore to produce a colorimetric response. Besides coordination aspects, the color change can originate from reactions between chromogenic hosts or indicators and anions. This type of chromogenic anion sensor can be called a “chromoreactand”. When the reaction occurs, the conformed host will definitely change its electronic properties. This, therefore, results in an observable color change. Metal ions in these receptors can play one or many out of the following roles; act as a coordination site for the anions, as non-coordinating moiety but changing its physical properties in the presence of anion or as an electron withdrawing component in a \(\pi\)-electron system so as to facilitate attack of anion on it. It may also preorganize the receptor for the anion or behave as a co-guest in an ion pair receptor.\(^5^4\)-\(^5^6\) Many excellent reviews are also available in the literature on metal ions based\(^5^7\)-\(^6^1\) anionic sensors.

(II) **Nonmetal based chromogenic hosts**: Anion sensors based on nonmetal chromogenic hosts employ H-bonding and/or electrostatic interactions for carrying out the job. Confining here to this category of anion sensors, many such systems have been reported which are based upon amide,\(^6^2\) pyrrole,\(^6^3\)-\(^6^4\) urea/thiourea,\(^6^5\)-\(^6^6\) azo dye units,\(^6^7\) naphthalene/naphthalimide units,\(^6^8\) porphyrin units containing neutral hosts,\(^6^9\) polyammonium and ammonium containing,\(^7^0\) guanidinium, amidinium or thiouronium\(^7^1\) containing cationic hosts. Many excellent reviews are also available in the literature on fluorogenic/chromogenic,\(^1^1\),\(^5^2\),\(^5^3\),\(^7^2\) pyrrole based,\(^6^3\) guanidinium based,\(^7^3\) calixarene...
based, and urea based receptors. In all of these neutral or positively charged receptors, polarized N-H fragments are there which behave as H-bond donors towards anions. According to Amendola and coworkers there is a remarkable correspondence between transition metal coordination chemistry and anion coordination chemistry. Neutral ligands donate electron pairs to the metal and neutral receptors donate H-bonds to the anion. Thus, whereas formation of metal-ligand complex can be studied in any solvent, which ensures solubility of the reactants, the study of the anions is preferably carried out in aprotic media to avoid competition for the anion by the H-bonding solvent. The recognition phenomenon in these systems typically involves either H-bonding (incipient proton transfer) or complete deprotonation of -N-H protons (frozen proton transfer) or a stepwise process leading from H-bonding to proton dissociation. Sometimes it leads to the stepwise deprotonation of two protons, excluding the intermediate step corresponding to the H-bonding. As proposed by Fabbrizzi et al. during this host-guest complexation, following consecutive equilibria may take place in solution, involving a neutral receptor LH₂ and the anion X.

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\text{LH}_2 + X^{-} \rightleftharpoons [\text{LH}_2 \cdots X]^{-} \quad 1
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\[
[\text{LH}_2 \cdots X]^{-} + X^{-} \rightleftharpoons [\text{LH}]^{-} + [\text{HX}_2]^{-} \quad 2
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\[
[\text{LH}]^{-} + 2X^{-} \rightleftharpoons \text{L}^{-} + [\text{HX}_2]^{-} \quad 3
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Here the first step corresponds to a genuine H-bonded complex and the second step involves abstraction of a proton from the complex to leave a mono deprotonated derivative LH⁻ which may further get fully deprotonated according to step 3 at higher concentrations of the anion. The second step, akin to the Bronsted acid-base reaction takes the recognition process out of the realm of the supramolecular chemistry. Nevertheless it is an efficient and sensitive method of anion sensing and has been amply employed for this purpose. The occurrence of deprotonation is highly dependent on the intrinsic acidity of LH, stability of [HX₂]⁻ and the polarity of the solvent and thus is not observed in all the cases. Hence based upon above interactions, the efforts have been directed toward the design and implementation of new tools for the anion sensing. Anion
sensors can be classified into 2 categories: neutral receptors and positively charged receptors.

(i) Neutral non-metal based anion receptors

(a) Amide-based receptors. Amide NH groups have been employed to design a wide range of receptors for anion recognition. Recently receptors 39a,b possessing nitroaromatic moieties as signaling units and amide and/or amines as binding units have been reported.\(^7^8\) The receptor gives a spectacular naked eye detection of F\(^-\) at ppm level and is highly selective for it even in the presence of other halide ions. An addition of a few drops of a protic solvent reverses the color change thus establishing the role of H-bonding interaction in the recognition.

Szumna et al. prepared an acetate selective macrocyclic receptor 40 containing two linked Pyridine clefts.\(^7^9\) The receptor showed 1:1 stoichiometry in solution form whereas a 2:1 complex formed in solid state, which was confirmed by X-ray crystal structure.

Anion binding properties of a series of macrocyclic tetraamides 41a-d containing two 2,6- diamidopyridine groups linked via short aliphatic chains, were compared by Chmielewski and co-workers.\(^8^0\) It was observed that receptor’s size play a significant role in the strength and selectivity of its anion complexes. It was found that binding constant for chloride increases with increase in the size of ring. Further increase in the size of ring causes a decrease in binding constant for chloride. A good size complementarity between chloride and 41b was found as compared to 41d, later showed strong binding affinity for large sized anions such as phosphate, sulfate or carboxylate anions. An isophthalic acid based amide receptor 42 shows significant selectivity for sulfate and phosphate.\(^8^1\) Both
amide and bridging amine sites are responsible for anion recognition. Complementarity between the receptor and oxo-anion as well deprotonation of the anion by the amine groups of receptor play a significant role in the binding strength.

Neutral receptors 43 with six amide groups in a pseudotetrahedral cleft arrangement and optically fluorescent moieties pyrene groups have been designed which display a high selectivity for phosphates. In a macrobicyclic ion-pair receptor 44 with adjacent anion and cation binding sites, it was found that steric selectivity of the receptor for alkylammonium cations increases with simultaneous binding of the anion.

A series of sulfonamides based receptors have been designed by Kondo et al. The role of hydroxyl group in sulfonamide cleft receptors 45 and 47 have been investigated and their recognition behavior was compared with the non-hydroxyl containing compounds 46 and 48. \(^4\) H NMR titration experiments have been performed to calculate the association
constants. The higher affinity of the hydroxyl functionalized compounds 45 for anionic guests was observed as compared to non-hydroxyl containing compounds 46. Thus it was evident that -OH group is involved in the anion complexation.\textsuperscript{85} 

(b) **Urea-thiourea based receptors.** Receptors based on urea and thiourea are good hydrogen bond donors and are excellent receptors for anions such as fluoride, carboxylates and phosphates ions. These receptors can form strongly hydrogen bonded complexes with biologically important anions because of high hydrogen-bonding ability of these functional groups. Anions such as fluoride and acetate cause the deprotonation of urea and thiourea NH by the formation of stable species like HF\textsubscript{2}\textsuperscript{-}. A new chromogenic azophenol-thiourea based anion sensor 49 has been developed.\textsuperscript{67a} This system allows for the selective visual colorimetric detection of F\textsuperscript{-}, H\textsubscript{2}PO\textsubscript{4}\textsuperscript{-}, and AcO\textsuperscript{-} by means of hydrogen bonding interactions. In \textsuperscript{1}H NMR, large downfield shifts in thiourea NH protons were seen upon complexation. Broadening of phenolic OH indicated its involvement in the hydrogen-bonding interactions. These selectivity trends turned out to be dependent upon guest basicity and conformational complementarity between ligand and the guest.

A dual-chromophore sensor 50 with two chromophoric moieties, azophenol and \textit{p}-nitrophenyl has been developed. A colorimetric differentiation was seen for different anions such as H\textsubscript{2}PO\textsubscript{4}\textsuperscript{-}, F\textsuperscript{-}, CH\textsubscript{3}COO\textsuperscript{-} of similar basicity, whereas there was no colorimetric differentiation in case of receptors 51 with only one chromophoric moiety (azophenol group only). Thus the cooperativity of two chromophoric moieties in a dual-chromophore receptor plays a significant role in color discrimination of anions of similar basicity. It has been noticed that both the chromophores have been affected with four oxygens of H\textsubscript{2}PO\textsubscript{4}\textsuperscript{-} via multitopic hydrogen bonding interaction. This causes a significant color change with H\textsubscript{2}PO\textsubscript{4}\textsuperscript{-} as compared to F\textsuperscript{-} and CH\textsubscript{3}COO\textsuperscript{-}, which have a relatively
weaker effect on the $p$-nitrophenyl group. This enables the color discrimination between $\text{H}_2\text{PO}_4^-$, $\text{F}^-$ and $\text{CH}_3\text{COO}^-$.

A chromogenic indoaniline-thiourea-based sensor 52 has been reported for the recognition of different tetrahedral oxoanions ($\text{H}_2\text{PO}_4^-$, $\text{HSO}_4^-$) in an organic solvent through complementary intermolecular hydrogen bonding. A selective colorimetric response was shown by these oxoanions by disturbing the intramolecular hydrogen-bonded structure of the sensor. A hypsochromic band shifts was observed from 678 nm to 632 nm upon the addition of $\text{H}_2\text{PO}_4^-$. However a less intense color change was observed in the presence of $\text{AcO}^-$ or $\text{F}^-$ with higher basicity, while no color change was seen in case of $\text{Cl}^-$, $\text{Br}^-$ and $\text{I}^-$ even upon the addition of excess of anions to receptor.

A remarkable anion and cation induced $\text{On-Off}$ colour switching was shown by a ferrocene-based ditopic receptor 53 having a urea and a benzocrown ether unit. The receptor showed absorption Maxima at $\lambda_{\text{max}}$ 304, 332 nm, after 10 molar equivalents addition of $\text{F}^-$ a new a band appeared at 472 with a significant color change from
colorless to yellow. However upon the addition of K\(^+\) the chromogenic process reversed and the yellow colour induced by the presence of fluoride was now no longer observable and the absorption maximum at 472 nm had disappeared. Thus the ditopic inputs of cation and anion color changes in the receptor controlled by switching \(\text{on}\) (in the presence of F\(^-\)) and \(\text{off}\) (in the presence of K\(^+\)) the optical outputs.

Callan and co-worker have designed ferrocenyl urea receptor 54, attached to the surface of a pre-formed CdSe/ZnS Quantum dot (QD) via a dihydrolipoic acid linker,\(^{87}\) in which QD fluorescence is quenched by an electron transfer mechanism. The receptor showed good selectivity for fluoride over other monovalent anions. In the presence of fluoride ion, the fluorescence of receptor again enhanced due to the change in the PET between the ferrocene units and the QD.

![Chemical structures](image)

Fabbrizzi \textit{et al.} have reported bright yellow 1:1 complexes\(^{75}\) of 1,3-bis(4-nitrophenyl) urea based receptor 55 with a variety of oxoanions in an CH\(_3\)CN solution, the stability of these anions decreases with the decreasing basicity of the anion. Fluoride displays a more intricate behavior; upon the stepwise addition of F\(^-\) the absorption band of receptor at 345 nm disappeared, with a simultaneous appearance of a new band at 370 nm which reached its limiting value after the addition of 1 equiv. of F\(^-\) to give the stable 1:1 complex through a hydrogen-bonding interaction. Upon the further addition of a second equivalent of F\(^-\), a new band at 475 nm (orange red color) was obtained which could be assigned to urea deprotonation, due to the formation of HF\(_2^-\). Another Urea-based receptor 56 has been reported having napthalimide like electron-withdrawing chromogenic substituents.\(^{88}\) Upon the addition of fluoride stepwise deprotonation of the \textit{two} N-H fragments was observed with significant color change, whereas only one N-H fragment deprotonated in the presence of less basic anions such as CH\(_3\)COO\(^-\) and H\(_2\)PO\(_4^-\) . In the presence of F\(^-\) ion the band at 400 nm decreased and a new band developed at 540
nm with a visual color change from yellow to red, which was assigned to the deprotonation of one of the N-H fragments of urea subunit. On further addition of F⁻ ion the color of the solution turned red to blue and the band at 540 nm disappeared with the simultaneous appearance of a new band at 600 nm. This was assigned to the double deprotonation of the N-H fragments of receptor. A similar deprotonation behavior was also observed in the presence of OH⁻ ion.

Ortho-phenylenediamine based bis-urea compounds 57 have been synthesized²⁹ for the recognition of carboxylate anions in DMSO- water solution. This is also supported by the crystal structure of benzoate complex of receptor 57 a, which shows that receptor bound to carboxylates via four hydrogen bonds. The binding affinity for anions could be increased by introducing an electron withdrawing group to the bis –urea skeleton of the receptor and by converting urea group to thiourea the carboxylate / dihydrogen selectivity could be tuned further.
Anthraquinone based thiourea receptors 58 have been used to give good sensitivity and selectivity for discrimination of maleate vs. fumarate or malate vs tartrate. Receptor 58a can also distinguish cis-aconitate or trans-aconitate with a unique colour change and can be used as colorimetric sensors for recognition of chiral dicarboxylates. Gunnlaugsson and co-workers have synthesized PET based chemosensor 59 for the recognition of anions having two binding sides such as dicarboxylates and pyrophosphate. Thiourea receptor sites with concomitant PET quenching of the anthracene moiety were responsible for anion recognition.

A fluoride selective, urea-activated phthalimide based anion sensor 60 with a stereogenic centre was synthesized. Upon the addition of fluoride a new CT complex emission at a longer wavelength was observed with no changes in the singlet lifetime of the receptor. This suggests a fluorescence static quenching mechanism in the presence of fluoride. In order to study the binding behavior of receptor with fluoride 1H-NMR titration experiments were also performed in CD$_3$CN. Two signals at 5.89 ppm and 7.81 ppm appeared corresponding to urea protons, which shifted to downfield by 2 ppm and 4.5–5 ppm respectively, suggesting H-bonding interactions between the receptor and anion rather than receptor deprotonation. Upon addition of a protic solvent the reversibility of this process was also confirmed.

\[
\begin{align*}
\text{60} & \\
n = 1 & \quad X = O & R = H \\
n = 1 & \quad X = S & R = \text{CF}_3 \\
n = 5 & \quad X = S & R =\text{NO}_2
\end{align*}
\]

Indole based receptors 61a-c with amide and urea or thiourea moieties as additional NH donor groups have been reported by Pfeffer and co-workers. All four N–H bond donors in these receptors strongly interact with the anions. 1H NMR titrations suggest that all the receptors show deprotonation in the presence of F$^-$ in DMSO-d$_6$ and weak interactions with chloride. In the presence of chloride a large shift in proton
resonances was observed in the urea or thiourea NH groups as compared to indole and amide NH groups. This suggests that urea or thiourea NH groups predominantly interact with the chloride ion. Whereas in the presence of oxo-anions in particular dihydrogen phosphate a co-operative binding behavior was observed, in which protons of the entire hydrogen bond donor i.e. urea or thiourea, indole and amide show a significant downfield shift in the proton resonances.

Gunnlaugsson and co-workers reported the amidourea-based compound 62 bearing a 4-hydrazine 1,8-naphthalimides that is able to act as colorimetric sensor\(^9^4\) for different anion. The receptors showed bathochromic shifts in the absorption spectra upon the addition of various anions such as acetate, dihydrogenphosphate and fluoride, either due to hydrogen bonding or deprotonation of, the amidourea. Unique changes in the absorption spectra were shown with each of the three anions. This can be considered as a ‘fingerprint’ identity for different anions.

The amido urea-based colorimetric anion sensors\(^9^5\) 63 and 64 gave rise to red shifts in their absorption spectra upon anion recognition, the sensing of F\(^-\) and hydrogenpyrophosphate gave rise to large changes with concomitant color changes from yellow to purple, which were visible to the naked eye.

(c ) **Indole and pyrrole based anion receptors.** The Indole and pyrrole groups provide a highly effective moiety for anion complexation in synthetic receptor systems. Oxidized bis(indolyl)methane 65 a simple chromophore containing an acidic H-bond donor moiety and a basic H-bond acceptor moiety, can act as a selective colorimetric
sensor either for $F^-$ in aprotic solvent or for $\text{HSO}_4^-$ and weak acidic species in water-containing medium. The deprotonation/protonation of oxidized bis(indolyl)methane 65 is responsible for the dramatic color change.

![Chemical Structures](image)

1, 3-diindolylurea based receptor 66 showed a high affinity for dihydrogen phosphate in polar solvent. The $^1H$ NMR titrations suggest that oxo-anions interact strongly with urea and indole groups as compared to amide group as in 67. Jurczak and co-workers have synthesized diindolylmethane based new acyclic anion receptor 68. The receptors can bind $\text{HPO}_4^{2-}$ via hydrogen bonding interactions even in pure methanol. An unprecedented stable dimer was formed by interaction of two ligand molecules with phosphate anion, which was supported by X-ray structural analysis. Oxygen atoms of the anion form eight complementary hydrogen bonds with NH groups of 68. It was evident from the N-O distances in the X-ray structural that indole moieties bind more strongly with anion than urea groups.

![Chemical Structures](image)

Two indole-based receptors 69 a and 69 b have been designed for sensing of fluoride and acetate anions. Highly flat rigid structure of indole-based system with a large $\pi$ system was responsible for high binding affinity and sensitivity for acetate and
fluoride anions. Combined use of receptors 69a and 69b on the basis of their visual color change in the presence of acetate and fluoride anions offers a simple way for distinguishing these two anions with the naked-eye.

An indole conjugated bisthiocarbonohydrazone based receptor 70 has been developed for the selective recognition of fluoride ion by visual color change along with a near-infrared (NIR) band at 936 nm. Receptor showed an absorption band at 342 nm corresponding to the Ar–CH=N–NH conjugation. Upon the stepwise addition of F⁻ absorption maxima at 342 nm disappeared with simultaneous appearance of new bands at 522, 572, and 936 nm. A large shift in the NIR region is due to the high conjugation and planarity of 70, which favors maximum negative charge distribution of the deprotonated receptor in the presence of fluoride.

![Chemical structures of receptors 70 and 71](image)

Zhu and co-workers have synthesized colorimetric fluoride sensor 71 by combining pyrrole and hemiquinone units. The receptor contains two kinds of NH protons with different chemical environments. Dideprotonation was observed in the presence of fluoride, which was responsible for the selective discrimination of fluoride from other anions. Other anions like CN⁻, CH₃COO⁻ or H₂PO₄⁻ induce monodeprotonation only with the formation of an absorption band at 740 nm. Different deprotonation behavior between these anions and F⁻ is due to the unique stability of [HF₂]⁻.

Two amidopyrroles 72 and 73 containing imidazole groups, have been reported. These receptors have ability to bind and co-transport H⁺/Cl⁻ across vesicle membranes similar to the prodigiosin. X-ray crystal structures showed that in the solid state receptor 72 formed a ‘2+2’ complex with HCl and with each chloride bound by
three hydrogen bonds; two from the pyrrole and amide groups of one receptor and one from the imidazolium group of another receptors in the dimer.

![Chemical Structures](image)

Deprotonation was observed in the pyrrolylamidothiourea receptor 74 upon addition of only one equivalent of anions such as acetate, fluoride and dihydrogen phosphate, which was also confirmed by X-ray crystallography. The receptor 74 showed a significant shift in the absorption band at 430 nm with a distinct color change from yellow to red.\(^{103}\)

**(d) Hydroxyl group containing receptors.** In recent years Hydroxyl groups have been employed to design different anion sensors and have proven to be effective via hydrogen bonding or deprotonation of –OH group. Hong and co-workers used azophenol dyes as an optical-signaling chromophoric unit in the receptors 2-4, which gave a significant color change in the presence of fluoride ion.\(^{104}\) Azophenolic OH of these receptors function as an anion binding site while the steric effects of alkyl groups (H, methyl, tert-butyl) at 2 and 6 positions affect the anion selectivity. Fluoride ion strongly binds to 75, 76 and 77 due to the formation of the salt complex. In the presence of 1 equiv. of fluoride receptor 76 and 77 undergo significant color change from yellow to blue. Steric hindrance by the dimethyl groups at 2 and 6 positions in receptor 76 prohibits the formation of effective hydrogen bonds and salt complexes for the larger anions. This causes the discrimination for fluoride ion in receptor 76 as compared to 75. Although better selectivity for F\(^-\) ion is expected for 77 due to the larger t-Bu groups *ortho* to the phenolic OH, but no color discrimination was observed for the fluoride anion due to the existence of hydrazone–azophenol equilibrium.
A chromogenic receptor 78 containing a nitro group as a signalling unit and OH and NH groups as binding sites has been reported\textsuperscript{105} by Kandaswamy and co-workers for the colorimetric sensing of fluoride ions. Upon the addition of fluoride ion, solutions of the receptor became orange. In $^1$H NMR titrations two signal corresponding to the OH and NH protons were observed at 11.65 and 10.64 ppm respectively. An upfield shift was observed upon the addition of 1 equiv of F$^-$ due to the hydrogen bonding between the fluoride ions and the OH and NH groups of receptor 78. Upon further addition of F$^-$ more than 2 equiv. deprotonation was observed in the receptor with the appearance of a new signal at 16 ppm corresponding to HF$_2^-$.

A selective coloration for F$^-$, H$_2$PO$_4^-$ and AcO$^-$ was shown by an azophenolurea-introduced porphyrin based colorimetric sensor 79.\textsuperscript{106} The binding interactions between the azophenolic OH of the receptor and the different anions as well as the basicity of the anions were responsible for the observed color changes. The absorption intensities of the receptor with different anions were correlated to the intensity of color change, in the
order of $F^-$ > AcO$^-$ > H$_2$PO$_4^-$ . Depending upon the basicity $F^-$, H$_2$PO$_4^-$ and AcO$^-$ form stronger complexes than other anions with significant color changes.

A phosphate selective ortho-hydroxyphenyl oxadiazole based fluorescent chemosensor 80 have been reported by Lee and co-workers. Fluorescent emission bands were observed at 330 nm and around 500 nm in DMF corresponding to the enol form and keto form, respectively. In the presence of dihydrogen phosphate both the fluorescence emission bands are quenched with a slight red shift, due to the intermolecular hydrogen bonding between hydroxyl groups of the receptor and anion. In the presence of basic anion like fluoride ion, the OH group of the receptor was deprotonated with the formation of a new emission band at 450 nm.

(e) **Imidazole and benzimidazole based anion receptors.** NH group of imidazole and benzimidazole provide efficient binding sites for recognition of different anions. Raposo and co-workers have reported bithienyl-imidazo-anthraquinone based chromogenic and fluorescent chemosensor 81. Upon the addition of fluoride ion a red shift was observed in the absorption spectra with an enhancement of the fluorescence emission intensity. The deprotonation of the NH in the imidazole ring with fluoride ion was responsible for a significant color change from yellow to pink. Upon addition of metal ions such as Zn$^{2+}$, Cu$^{2+}$ and Hg$^{2+}$ the original yellow color of receptor-fluoride complex is restored with a quenching in the fluorescence intensity. This reversible colorimetric reaction upon metal complexation gives rise to an *Off-On-Off* (yellow-pink-yellow) system.

![Image of receptors 81 and 82]

Benzimidazole based tripodal fluorescent receptor 82 showed significant changes in its fluorescent behavior in the presence of iodide ion over the other anion such as F$^-$, Cl$^-$, Br$^-$, HSO$_4^-$, NO$_3^-$, CH$_3$COO$^-$, and H$_2$PO$_4^-$ in 10% aqueous CH$_3$CN. A role of
benzylic N-H in the binding with iodide is suggested. The ion recognition behavior of 83 was investigated using UV–vis, fluorescence and $^1$H NMR spectroscopy. In the fluorescence spectra large quenching of intensity of the band at 375 nm was observed on the addition of fluoride ion, the further addition of $F^-$ ion slowly shifted the band to 434 nm.$^{110}$

A benzimidazole-based fluorescent receptor 84 has been developed$^{111}$ for the recognition of the adipate. A 1:1 receptor-adipate complex formed, which restricts the rotation around the single bond between two benzimidazoles. This results in two emitting states responsible for the ratiometric recognition of adipate.

Jang and co-worker have designed benzimidazole based neutral dipodal colorimetric anion chemosensor 85 for the detection of $F$ and $\text{AcO}^-$. In the pure DMSO, receptor can bind to a DMSO molecule and electron-deficient sulfur of bounded DMSO act as a binding site for anion recognition. Han et al. have reported fluoride selective colorimetric and ratiometric fluorescent chemosensors 86.$^{113}$ The anion-induced proton transfer was responsible for the colorimetric and ratiometric properties. In the first step receptor formed a hydrogen bonded complex with the fluoride ion, whereas in the
second step deprotonation of the complex was observed to form L⁻ and FHF⁻. The fluorescence behavior and ion interaction with fluoride depends upon the electron push-pull properties of the substituents on the phenyl para position. Receptor 86a showed the best selectivity for F⁻ ion as compared to other receptors, which was due to the fitness of anion in the acidity of NH-group of receptor.

(ii) Positively charged, non-metal based anion sensors

Anion binding behavior of tren-based tripodal species 87 was studied by Bowman-James and co-workers. The receptor has high affinity for dihydrogen phosphate and hydrogen sulfate with log $K_a = 3.25$ and 3.20 respectively. It was evident from the X-ray crystal structure that the ligand form a triprotonated complex with phosphate.

In the receptor 88 four imidazolium groups are appended to a napthalene scaffold through methylene bridging. The receptor showed high selectivity for iodide as compared to other halides. The selective binding was evident from the $^1$H NMR titrations and fluorescence quenching. A benzimidazole based fluorescent receptor 89 shows a ratiometric fluorescent sensing for acetate ion over a wide range of anions. Upon the addition of acetate ion, quenching in fluorescence intensity at 443 nm was observed, with the appearance of a new band at 339 nm.
By incorporating two tripodal binding domains two viologen-based anion receptors 90 and 91, have been designed.\textsuperscript{117} The receptor 90 has high affinity for carboxylate anions such as acetate, malonate and succinate with a significant color change from colorless to intense purple. These absorption changes arise because of charge-transfer from anion to the bipyridinium unit. In case of receptor 91, initially no color change was seen as the anions bind at the periphery of the receptor, however further addition of more than two equivalents of acetate and more than one equivalent dicarboxylate anions, receptor exhibit significant color change. Thus the identity of the peripheral binding groups plays an important role to select the amount of anion required for particular colorimetric response.

The receptor 92 exhibits good recognition ability towards different anions\textsuperscript{118} such as $\text{H}_2\text{PO}_4^-$, $\text{F}^-$ and $\text{AcO}^-$ through hydrogen bonding and electrostatic interactions.
Dihydrogen phosphate bound selectively to the receptor through strong excimer formation. The combined effects of semi-rigid structures, electrostatic interactions and the participation of both N–H···O and C–H···O hydrogen bonds are responsible for the high affinity and selectivity of receptor. Another anthracene appended o-phenylenediamine-based receptor 93 exhibit strong interaction with dihydrogen phosphate and fluoride ion in CH$_3$CN. In the presence of these anions quenching of anthracene emissions upon complexation was observed as compared to other anions.

A chloride selective fluorescent Off–On chemical sensor 94 exhibits a guest-induced conformational switching process. The benzoimidazolium moieties form hydrogen bonded complex with anion which was evident from $^1$H NMR experiments. In the presence of chloride ion protons attached to the electron-deficient carbon atoms in the benzoimidazolium group shifted downfield, suggesting the formation of CH$^+$···anion hydrogen bonds.

Yoon and co-workers have reported fluorescent receptor 95 the binding properties of which have been studied from the changes in the fluorescent behavior of pyrene. Receptor 95 displayed a quite selective fluorescent quenching effect in the presence of H$_2$PO$_4^-$ due to PET process. By the use of positively charged H-bond donating carbolinium ion 96 and neutral H-bond donating receptors 97, it has been demonstrated that the stability of 1:1 complexes is strictly related to the acidic tendencies of the receptor and to the basic properties of the anion.
For biologically important anions like $\text{HSO}_4^-$ and $\text{H}_2\text{PO}_4^-$, amide groups held on various scaffolds like isophthalamide, dipicolinic and pyrrole bisamide have been reported with the most recent being 98 with azulene bisthioamide moiety. The latter might enhance the anion interaction due to large dipole of azulene. For the detection of micromolar concentration of cyanide ion a receptor containing oxazine ring 99 has been designed which opens to form a 4-nitrophenylazophenolate chromophore in response to cyanide ion.

**Conclusions-**

Among the various types of sensors, optical sensors have very promising future. Since the various cations or anions are the essential part of the environmental, food and water, so their recognition and selective removal with high sensitivity (recognition at
lower concentrations up to µm level) forms an important part of chemical research. The technical problems in the designing of these sensors need to be overcome, which include the following considerations.

The sensor designed for the ion recognition should be stable, having sufficient lifetime and the ability to operate in water and the low sensitivity to the operative pH are important under normal conditions. The sensors having the capability to sense/recognize the various analytes in aerobic and aqueous medium are highly required.

On the other hand to deal with the problem of sensor lifetime is to avoid it completely by using each sensor once. Hence the design and synthesis of inexpensive and disposable sensor such as disposable sensor strips or nanoparticle based optical beads highly desired. These strips or beads display significant color changes in the presence of particular ion solution. The optical sensors show high selectivity for a particular ion in the presence of other ions of similar nature. The design and synthesis of sensors that can detect small concentrations of the ion of interest in the presence of other interfering ions is of considerable interest.
References


