# CHAPTER-I

## PHOTOPHYSICAL & CATALYTIC BEHAVIOUR OF POLYDENTATE LIGANDS AND THEIR METAL COMPLEXES

# CHAPTER I

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### I. 1. Polydentate ligands and coordination complexes

A large number of organic and inorganic ions/molecules have unshared pair(s) of electrons and can bind variety of metal ions. The neutral molecule or ion (usually anion) that binds metal ion is called ligand and the combination of metal-ligand is termed as coordination complex. The binding of variety of metal ions with large number of ligands results in limitless number of combinations/coordination complexes. Such diverse combinations are found in natural water/water bodies, in biological fluids or in industrial process effluent/waste. Most important aspect is the emergence of new or modification of existing properties of the metal ions like solubility, toxicity, catalytic behavior *etc.* resulting from specific metal-ligand combination out of the countless number of possible metal-ligand combinations. The specific role of metal ions in biochemical reactions is also dictated by the coordination of one or more metal ions to organic groups of great variety and complexity.

The ligands (electron pair donors) act as Lewis bases and metal ions (electron acceptor) act as Lewis acids. Ligands that can bind a metal ion through only one donor atom at a time are called monodentate ligands. A ligand that donates more than one electron pair to more than one metal ion is known as *bridging ligand*. Those ligands which use either of two or more different donor atoms are called *ambidentate* ligands. The ligands possessing more than one donor atom have geometries such that they can form more than one coordinate covalent bond with the same metal ion would result in a ring formation (*chelate ring*) and are called as *chelating ligands.* Such ligands are also called *polydentate ligands.* The polydentate ligands, those bind metal ion through two, three, four, five or six donor atoms are termed as bidentate, tridentate, tetradentate, pentadentate and hexadentate, respectively.

The intrinsic affinity of metal ions for polydente *versus* unidentate ligands is explained in terms of chelate effect. The stabilization of a metal complex is

generally explained through entropic and enthalpic consideration. However, enthalpy contributions resulting from ligand pre-organization are decisive related to metal ion selectivity. The relative differences in complexation enthalpy between unidentate and polydentate ligands is due to the fact that, in the latter molecules, electrostatic and steric repulsion between the coordinating groups including conformational energy may already be built into some extent (ligand preorganization) [1] therefore increasing the enthalpy of the free ligands. This results in a favored complex formation of polydentate relative to unidentate ligands. A detailed analysis of the expected magnitude of such selectivity-modifying effects augmented in polydentate system has been undertaken [2].

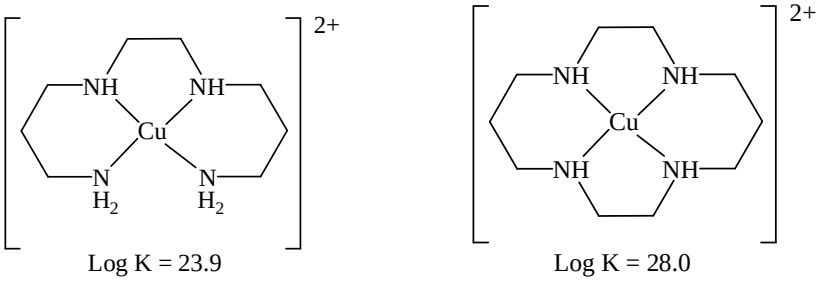



Figure I. 1. Difference in the stability constants.

An impressive large additional stabilization occurs from linking the terminal donors into a ring; this phenomenon is termed as *macrocyclic effect*. Macrocyclic ligands are polydentate ligands with their donor atoms incorporated in a cyclic backbone (Figure I.1). Very high stability of a macrocyclic complex arises primarily from the intricacy in dissociation of the complex in addition to the highly associative chelate effect.

$$Ni\,(trien)^{2+} + H^{+} \xrightarrow{t_{1/2} = 2\ sec} Ni^{2+} + H_4(trien)^{2+}$$

$$Ni\,(cyclam)^{2+} + H^{+} \xrightarrow{t_{1/2} = 2\ years} Ni^{2+} + H_4\,(cyclam)^{2+}$$

Scheme I. 1. Half life of dissociation.

Absence of end group in a macrocyclic ligand hinders dissociation of the macrocyclic complex. Macrocyclic chelate complexes are up $10^7$ times more stable than non-cyclic chelates with the same number of donors (Scheme I.1).

Chemically macrocyclic ligands are of great interest because of their wide versatility as ligands, due to presence of several potential donor atoms, their flexibility and ability to coordinate in either neutral or deprotonated form. In Nature, chlorophyll, heme, vitamin $B_{12}$ all contains tetradentate macrocyclic ligands. Particularly 3*d* transition metal complexes with such ligands have a wide range of biological relevance.

## I. 2. Application of polydentate ligands

The variety and scope of the applications of metal ligand combination have continued to multiply. A particularly insightful treatment is found in the Nobel Lecture of Jean-Marie Lehn [3], where he described the concept of supramolecular chemistry from simple cation and anion recognition, to multiple recognition, catalysis, transport and molecular devices. Polydentate ligands have attracted widespread attention for the following reasons:

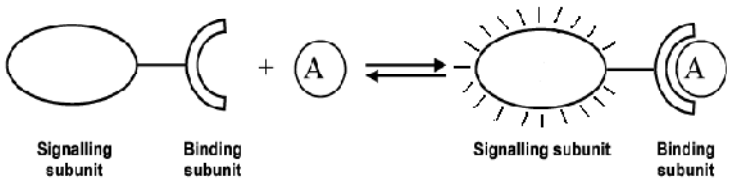
(a) Their ability to discriminate closely related metal ions, (b) the ability to offer environment dependent variation of structure, (c) the significant enhancement of stability constant and d) the inherent ability to mimic important biological ligands developed by nature, for example the porphyrin prosthetic group of many metalloproteins. However, our discussion would be focused on their applications in the field of metal ion selective chemosensors and oxidation catalysis.

### I. 2. 1. *Chemosensors for metal ion*

The chemistry of cation complexation has played an important role in the origin of the field of molecular recognition. A wide range of selective receptors for metal ion has been prepared by coupling those receptors (ionophores) to adequate chromophore/fluorophores. The choice of polydentate linear and macrocyclic ligands becomes obvious as they provide higher binding affinity and selectivity

through its better preorganized cavity. However, other non-covalent interactions such as charge-charge interaction, charge-dipole interaction, dipole-dipole interaction, hydrogen bonding, cation-π interaction, π-π stacking, Van der Waals forces, and hydrophobic effects are to be taken into consideration for designing a new polydentate ion selective motif [4]. Chemical sensor is defined by IUPAC as "*a device that transforms chemical information, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful* signal" [5].

An optical chemosensor consists of a molecule incorporating a binding site, a chromophore or fluorophore, and a mechanism for communication between the two. When analyte binds, there is a change in their optical properties (absorption or fluorescence). The synthesis of new chemosensors capable of sensing metal ions in solution is a prosperous and emerging field.



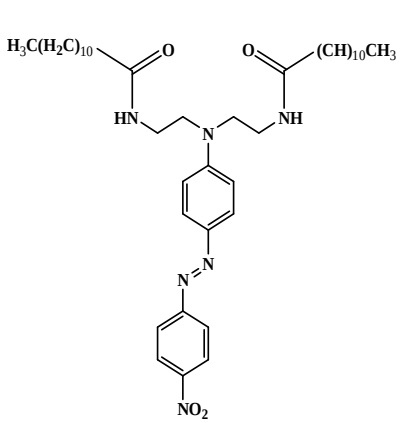

Scheme I. 2. Schematic diagram showing binding of an analyte (guest) by a chemosensor (host), producing a complex with altered optical properties.

Design of the chemosensors consist of three components as shown in Scheme I. 2; 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.

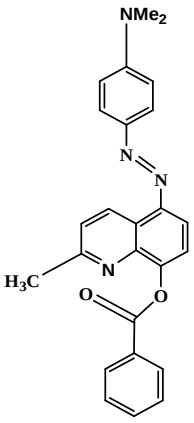
With better understanding of host-guest chemistry of crown ethers, it has become easier to develop chromogenic sensors for metal ions. Later many excellent examples of chromophoric and fluorophoric receptors for different cations have been prepared and studied. The coordination site of a chromogenic chemosensor binds the guest in such a way that signaling unit shows the changes in colour,

whereas fluorogenic chemosensors detect the interaction between the coordination site and the guest moiety with a change in fluorescence behavior of the signaling unit. Based upon the principle of paramagnetic fluorescence quenching (PFQ), photoinduced electron transfer (PET), photoinduced charge transfer (PCT), fluorescence resonance energy transfer (FRET), excimer or exciplex formation, chemodosimeters, etc., excellent examples of receptors for various analytes have been designed and studied for application in physiology, medical diagnostics and in environmental chemistry. Large number of chromogenic and fluorogenic polydentate receptors based on crown ethers, calixarenes; thiacalixarenes; azacrown-calixarenes, podands, etc., have been reported in literature. Extensive work on the metal ion sensing is going on as evident from recent reviews [6–12]. A brief outline of the work done in this area is given below.

Chromogenic receptors as chemosensors are especially attractive because guest detection can be done even in absence of sophisticated instruments. A number of azobenzene based colorimetric receptors have been synthesized and their ion recognition properties were studied. In solution, receptor **1** gives rise to a large cation-induced hypsochromic shift for Cu(II) resulting in a change from red to pale-yellow [13]. Azo 8-hydroxyquinoline benzoate **2** gives [14] distinct color change in the presence of Hg(II) in $CH_3CN$, which enables visual detection of Hg(II).




**1**

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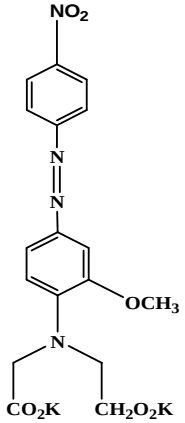
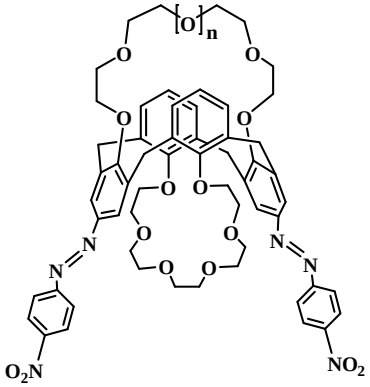



**3**

Highly selective and reversible colorimetric detection of Cu(II)has been achieved with **3** under physiological condition. The Cu(II) recognition gives rise to red to

yellow colour change and reversible upon addition of EDTA. No such changes are observed when *o*-methoxy chelating group is replaced with H.

Calixarenes and crown ethers have proven to be particularly successful for their highly specific metal cation binding in organic solvents. Size complementarity between hosts and guest ions are found to control the metal ion recognition even within a similar group of polydentate calix[4]biscrowns ligands.



**4**

For example, in a study of a series of 1,3-alternate chromogenic azo-coupled calix[4]biscrowns **4, c**alix-[4]bis(crown-5)(crown-6) show $K^+$ ion selectivity while calix[4]bis-(crown-6) give $Cs^+$ ion selectivity. The regioselectivity is controlled by size induced through π-metal complexation.

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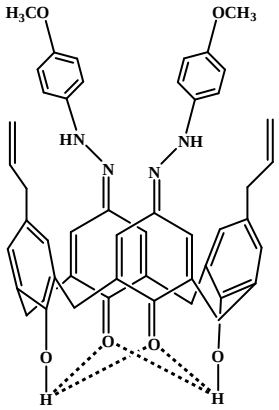
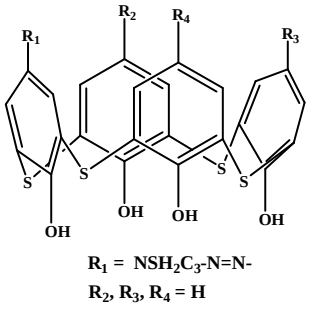


**5**



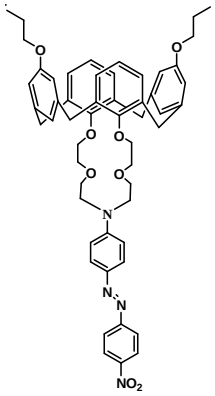
**6**

Upper rim allyl- and arylazo-coupled calix[4] arenes based chromogenic sensors **5** is highly selective for Hg(II) ion [15]. A marked bathochromic shift in the UV/ visible spectra from $\lambda_{max}$ 359 nm to 520 nm ($\Delta\ \lambda_{max}$ = 161 nm) is observed upon

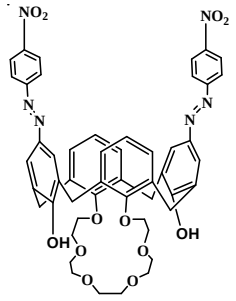
titration by $Hg(ClO_4)_2$ in a methanol-chloroform solvent system. Upper rim modification of tetrathiacalix[4]arenes bearing various azo groups have been reported **6** and their ionic recognition has been studied with an expectation to obtain new molecular filters and devices for specific use [16].

Kim *et al.* have synthesized azo-coupled calix[4]azacrown-5 **7** having an azo chromophoric pendant group [17]. Absorption spectra show 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 $K^+\cdots\pi$ interaction between the two aromatic rings and the $K^+$ ion. The shift in UV absorption band is also dependent on the lipophilicity of the species of counter anion used.

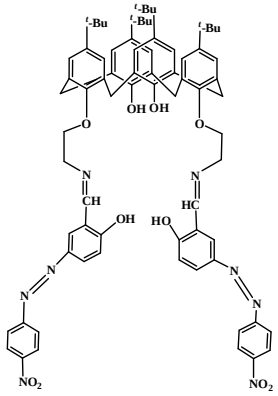
Azo-coupled calix [4] crown based receptors **8** show visual color change on the addition of $Ca^{2+}$ and $Mg^{2+}$ in the cone conformation [18]. However cesium and other alkali metals metal ions are not entrapped in the crown-6-ring due to non availability of 1,3- alternate conformation. Metal ions entrapped by the crown loop induce deprotonation of the receptor easily even at neutral pH causing a charge density shift in the direction of the acceptor substituent (nitro group) of the chromoionophore.



**7**



**8**

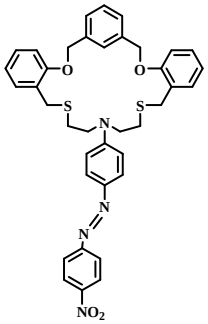


**9**

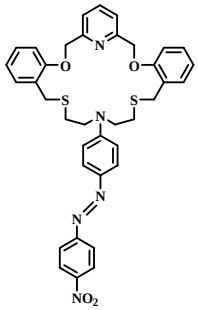
A dipodal calix[4]arene derivative [19] **9** is found to be highly selective for $Na^+$. A bathochromic shift in the UV–Vis spectra is observed in the presence of $Na^+$ with a visual color change in the solution from yellow to red. The binding ability and photophysical behavior of alkali cations by calix[4]arene derivative **9** is explained

on the basis of substituent effects at the lower rim of parent calix[4]arene and size-fit concept between host calix[4]arenes and guest cations.

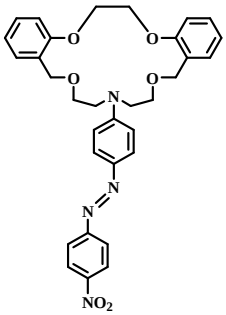
An azo-coupled macrocyclic chromoionophores were synthesized by incorporating phenyl **10** and pyridyl **11** subunits [20] for selective detection of Hg(II) ion. Polydentate ligand **10** exhibits a larger cation-induced hypsochromic shift than **11**, suggesting that the presence of the pyridine unit in **11** may inhibit the Hg···*N*-azo interaction. The observed color changes for Hg(II) in **10** and **11** are found to be controlled by anion-coordination ability.



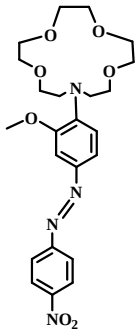
**10**



**11**

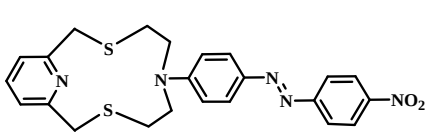


**12**

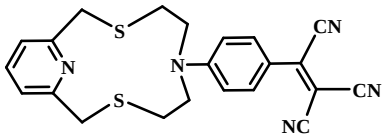


**13**

An N-azo-coupled macrocycle **12** as a chromoionophore [21] exhibits Hg(II) 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 are attributed to *endo* and *exo* complex respectively. The azo dye based chemosensor [22] **13** displays extremely good sensitivity and selectivity for $Na^+$ as compared to other physiologically important alkali and alkaline earth metal ions. The sensitivity is in the same range of $Na^+$ ion concentration found in the blood sample. Receptor shows absorption band at $\lambda_{max}$ 485 nm, which displays a hypsochromic shifts with $\Delta\ \lambda_{max}$ 110 nm on addition of $Na^+$. A strong color change from red to yellow in aqueous solution even at low metal ion concentrations is observed. Chromogenic $N_2S_2$-donor macrocycles functionalized with p-nitroazobenzene **14** and phenyltricyanovinyl **15** units were synthesized [23]. These two receptors exhibit excellent Hg(II) selectivity by metal-induced color change from red to colorless ($\Delta\ \lambda_{max}$ = 137 - 140 nm).

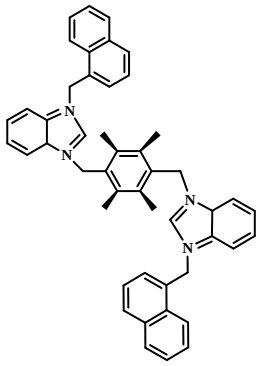


**14**

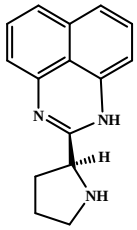


**15**

Duan *et al.* have synthesized a new Ag(I) selective fluorescent chemodosimeter **16** by incorporating imidazolium units and naphthyl lumophores into a two-arm dipodand [24]. 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.

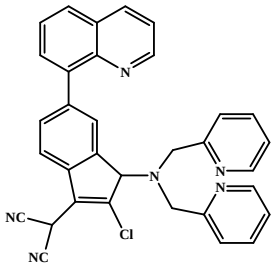


**16**

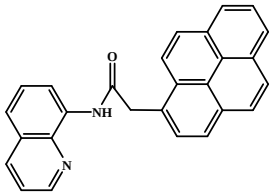


**17**

A 1,8-diaminonaphthalene based Cu(II) selective ratiometric and colorimetric fluoroionophore receptor **17** recognizes Cu(II) selectively on the basis of ICT with metal bound deprotonated fluorophore. Absorption and emission spectra of the chemosensor show remarkable red shift in acetonitrile-water solution upon Cu(II) complexation [25]. Compound **18** is a chromogenic and *off-on* fluorogenic probe [26] for visual detection of copper (II) in water-acetonitrile. The receptor can detect Cu(II) in the range of $\mu gL^{-1}$ similar to Cu(II) concentration in living organisms. With the stepwise addition of Cu(II) the absorption band at 550 nm disappeared with simultaneous appearance of a new band at 393 nm. Fluorescence titration of receptor exhibit 5-fold enhancement of the emission intensity at 650 nm upon the addition of Cu(II) solution. Pyrene-based **19** functions both as visual and fluorogenic probe [27] for Cu(II) with 2:1 stoichiometry. Upon addition of Cu(II) 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 Cu(II)



**18**



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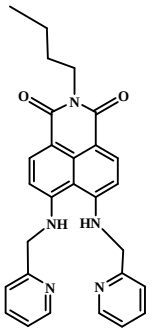
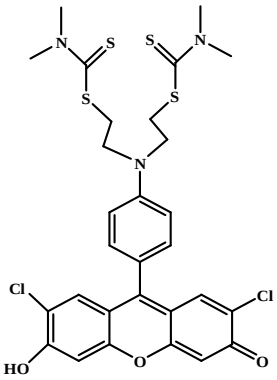


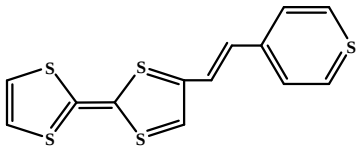
**20**

ion depends on the spacer length between the pyrene and quinolinylamide unit. For Cu(II) ion sensing, shorter intramolecular distance between the pyrene and quinoline amide augments higher degree of $\pi\cdots\pi$ interactions.

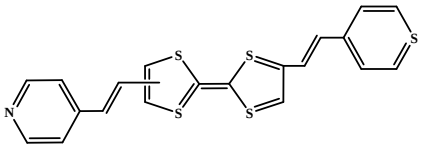


**21**

Another Cu(II) sensing fluorescent sensor **20** detects the metal ion on the basis of the mechanism of internal charge transfer (ICT ) with high sensitivity and selectivity [28]. This results in the reduction of electron donating ability of the two amino groups conjugated to the naphthalene ring. This molecule detects the Cu(II) ratiometrically with blue shift of 50 nm. It exhibits a strong fluorescent emission at 525 nm in ethanol water medium. The formation of 1:1 metal-ligand complex has been observed with a shift in the emission band from 525 nm to 475 nm. Dithiadicarbamate **21** has a high affinity towards Hg(II) [29]. 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 $Hg^{2+}$.



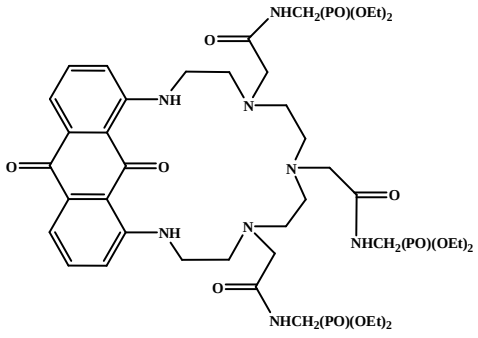
**22 a**



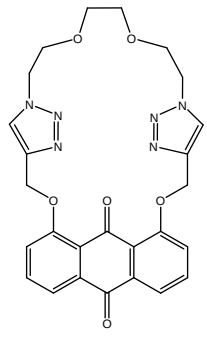
**22 b**

TTF-pyridyl derivatives **22a** and **22b** along with their phenyl analogues have been designed and synthesized (where TTF = tetrathiafulvalene) [30]. The TTF moiety and pyridyl group or phenyl group are bridged *via* a double bond, which has been 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. The compound **22** show remarkable sensing and coordinating properties towards $Pb^{2+}$ in comparison to their phenyl analogues**,** The color changes from yellow to deep purple**.**

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 the ligand backbone can be tuned to be metal specific. In addition, the modification of solubility properties of the chosen receptor by suitable substitution is important to develop water-soluble receptors.

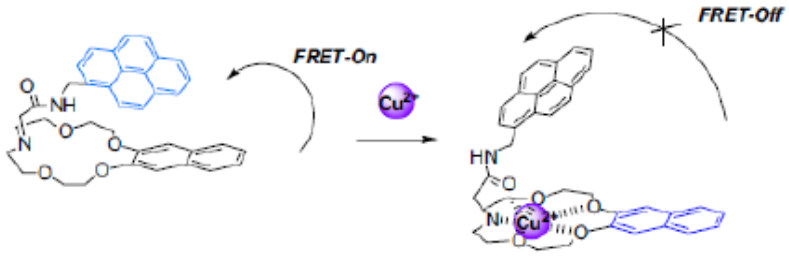


**23**



**24**

A new anthraquinone-based colorimetric molecular sensor **23** exhibits efficient binding for lead ion in water and allows visual detection [31]. A 1, 2, 3-triazole based $Al^{3+}$ selective chemosensor **24** was synthesized and studied for its optical/ electrochemical properties [32]. A significant enhancement in fluorescence intensity is observed at 556 nm on 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.

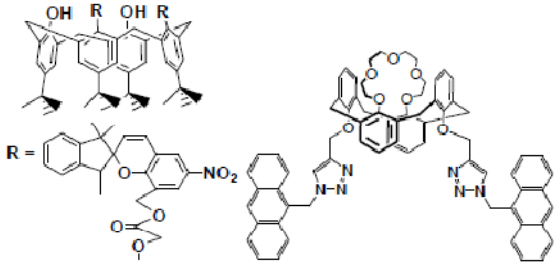


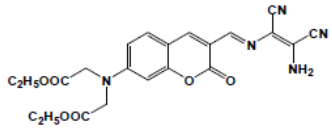

**25**

Scheme I. 3. *On-Off* fluorescent chemosensor **25 (** adapted from ref 33).

An *On-Off* fluorescent chemosensor **25** for Cu(II) (Scheme I. 3) works via intramolecular fluorescence resonance energy transfer (FRET-On). In the presence of Cu(II) fluorescence of pyrene is strongly quenched (FRET-Off) whereas that of naphthalene group is revived [33].

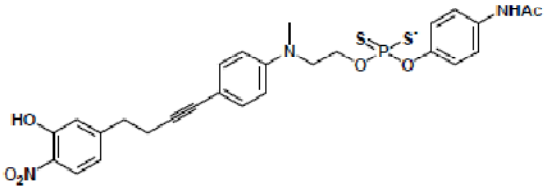
The calix[4]arene derivate **26** carrying two spirobenzopyran moieties have been reported [34] as lanthanide ions sensor. Significant shifts in UV–vis spectrum and the emission spectra have been observed in the presence of lanthanide ions. The colour change can be visually detected for $Na^+$, $K^+$, Mg(II), Ca(II), Fe (III), Cu(II) and Zn(II) cation. A triazole-modified calix[4]crown in the 1, 3-alternate conformation based fluorescent *on-off* switchable chemosensor **27** with two different types of cationic binding sites has been synthesized by Chung *et al*. [35]. Fluorescence studies showed strong quenching by Hg(II), Cu(II), Cr(III), and Pb(II); however, the emission from the strongly quenched Pb(II) complex is restored by the addition of $K^+$, Ba(II), or Zn(II) ions.

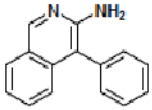


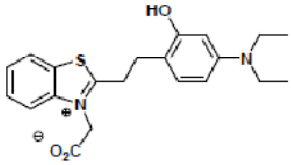


**26** **27** **28**

A coumarin-based copper selective colorimetric chemosensor **28** shows good sensitivity and selectivity for the Cu(II) both in aqueous solution and on paper-made test kits [36]. A phosphorodithionate-based ligand **29** communicates a color change with Hg(II) owing to a charge transfer and a solubility change [37]. The receptor **30** is colorimetric mercury selective ion sensor [38].







**29** **30** **31**

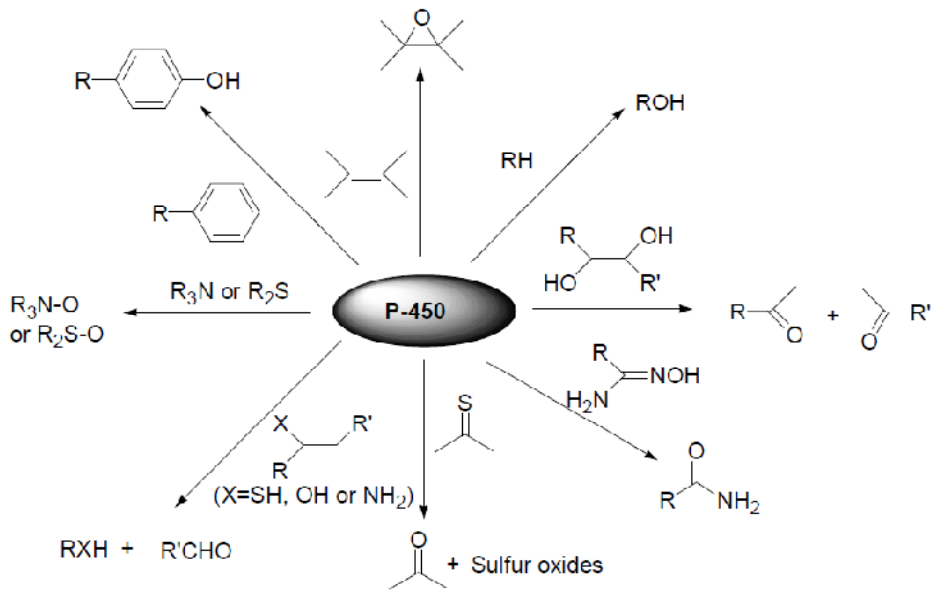
It is observed that commercially available 2-amino isoquinoline mixed with mercuric ion show no color change but the receptor **30** detects Hg(II) by change in colour and fluorescence upon binding. Recently an inexpensive, OMP (organic molecular probe) **31** consisting of a charge-transfer complex, has been developed for the detection of small quantities of mercury [39]. 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.

Although great efforts have been devoted to the development of fluorescent and colorimetric sensors based on polydentate ligand system, which can selectively detect heavy metal ions mainly mercury ions, available in the recent reviews [7, 40], the field is of great potential for development of better detection system. Many of the intelligently designed receptors fulfil the required WHO's detection limit of 1 µg $L^{-1}$ for $Hg^{2+}$, but only few of them are successfully applied to track the

changes within living cells. The area of selective metal ion sensing is emerging as a prosperous field in chemical, biological, material and analytical sciences.

### I. 2. 2. *Oxidation catalyst*

The selective insertion of one oxygen atom from oxygen donors into various hydrocarbon molecules under mild conditions remains a challenge in chemical science. The chemical transformation of C–H → C–OH of hydrocarbons, especially alkanes, is an energy intensive process reflected by the inertness of alkanes toward chemical conversion. While selective oxidation of C–H bond under mild condition represents a major challenge in industrial and synthetic chemistry, nature has evolved several metalloenzymes to accomplish such transformation selectively under very mild conditions. For example, cytochrome P-450 is a ubiquitous membrane bound monooxygenase that catalyzes the hydroxylation of membrane-entrapped nonpolar substrates including drugs, steroids, and pollutants, yielding partially water-soluble products that can be further metabolized [41]. Several other types of oxygen transfer reactions are also catalyzed by this enzyme, including epoxidation, N-dealkylation, O-dealkyaltion and sulfoxidation (Scheme I. 4).

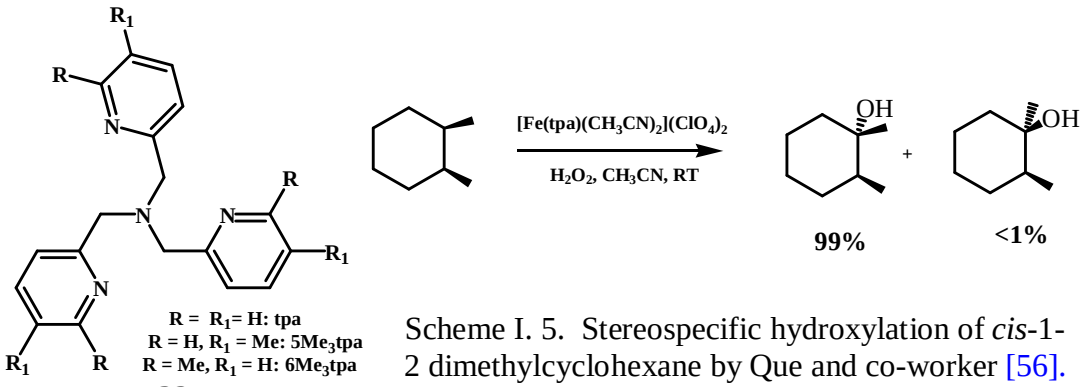



Scheme I. 4. Oxidations of organic compounds by cytochrome P-450.

The extensive effort to understand the catalytic mechanism of these enzymes gives rise to the field of biomimetic catalysis. In this background, extensive efforts have been devoted to develop functional models of enzymes with an emphasis on oxyfunctionalization of hydrocarbons.

Porphyrins complexes of iron(III) as well as manganese(III), chromium(III) and ruthenium (III) are the most physiologically relevant models for cytochrome P-450 enzymes. Much effort has been focused on metalloporphyrins in the search of efficient catalyst to promote oxygenation of hydrocarbons under mild conditions. The first oxidation system with synthetic metalloporphyrin as a catalyst was developed by Grooves and co-workers in 1979 [42]. This oxidation system, which consists of terminal oxidant iodosylbenzene (PhIO) and catalyst [$Fe^{III}$(TPP)Cl] (TPP = tetraphenylporphyrin), was shown to effect both epoxidation of styrene and cyclohexene, and hydroxylation of cyclohexane and adamantane. Subsequently, numerous reports on metalloporphyrin-catalyzed oxidation systems have appeared in the literature [43-53]. Among the most extensively studied systems are the epoxidation of alkenes and hydroxylation of alkanes catalyzed by iron, manganese and ruthenium porphyrins with different terminal oxidants. Metalloporphyrins are also well explored for catalyzing the oxygenation of alcohols, nitroso compounds and sulfides. Several oxidation systems containing iron ions have been described as mimics for nonheme mono and dioxygenases. Although mononuclear iron derivatives have been reported as models for methane monooxygenase [54], binuclear iron complexes have been more widely investigated and are commonly employed as MMO active-site models [55].

In the course of developing functional models for non-heme iron oxygenases, Professor Que and his research group discovered a family of non-heme iron catalysts, represented by $[Fe(II)(tpa)(CH_3CN)_2]^{2+}$ (tpa = tris (2-pyridylmethyl) amine **32**), those are capable of stereospecific hydrocarbon oxidations using $H_2O_2$ as oxidant (Scheme I. 5) [56]. The oxidation of *cis*- and trans-1,2-dimethylcyclohexane afforded tertiary alcohol products with >99% retention of stereochemistry and, furthermore, the system allowed oxygen insertion into




**32**

Scheme I. 5. Stereospecific hydroxylation of *cis*-1-2 dimethylcyclohexane by Que and co-worker [56].

olefins, affording only epoxide products with complete retention of stereochemistry [56]. In this direction, several non-heme mononuclear iron complexes have been developed which are capable of performing stereoselective alkane oxidation to give alcohols (R-H to R-OH). A schematic representation of important polydentate ligands are given in Figure I. 2. In this context, it may be noted that the most effective non-heme iron catalysts are those iron centre coordinated with nitrogen based tripodal or linear tetradentate ligands leaving two *cis* labile sites available for coordination with exogeneous ligands (the oxidant and/or the substrate).

Non-heme diiron complexes, involving (-)-4,5-pinenebipyridine ligand **33** and alkylhydroperoxides have been intensively studied by various groups [55] and emerged as a new class of catalysts for oxidation. Among the active systems reported so far, the $Fe_2(tpa)_2$/ROOH studied by Que and co-workers [57], the $Fe_2O$(tmima)/ROOH investigated by Fish and co-workers [58] and more recently the $Fe_2$(hexpy)/*m*-CPBA [59] proposed by Kodera and co-workers are noteworthy. The major limitation of these systems is the relative instability of the catalysts, which are slowly deactivated during the course of the reaction [60]. Moreover, the performance of hydrogen peroxide as terminal oxidant was not impressive until recently, because of the strong ability of non-heme iron complexes to catalyse the dismutation of $H_2O_2$. The catalytic activity for $H_2O_2$ dependent oxidation of alkanes with bipyridine and phenanthroline-based iron complexes are reported Fontecave and co-workers [61]. Although, high turnover number was obtained, the

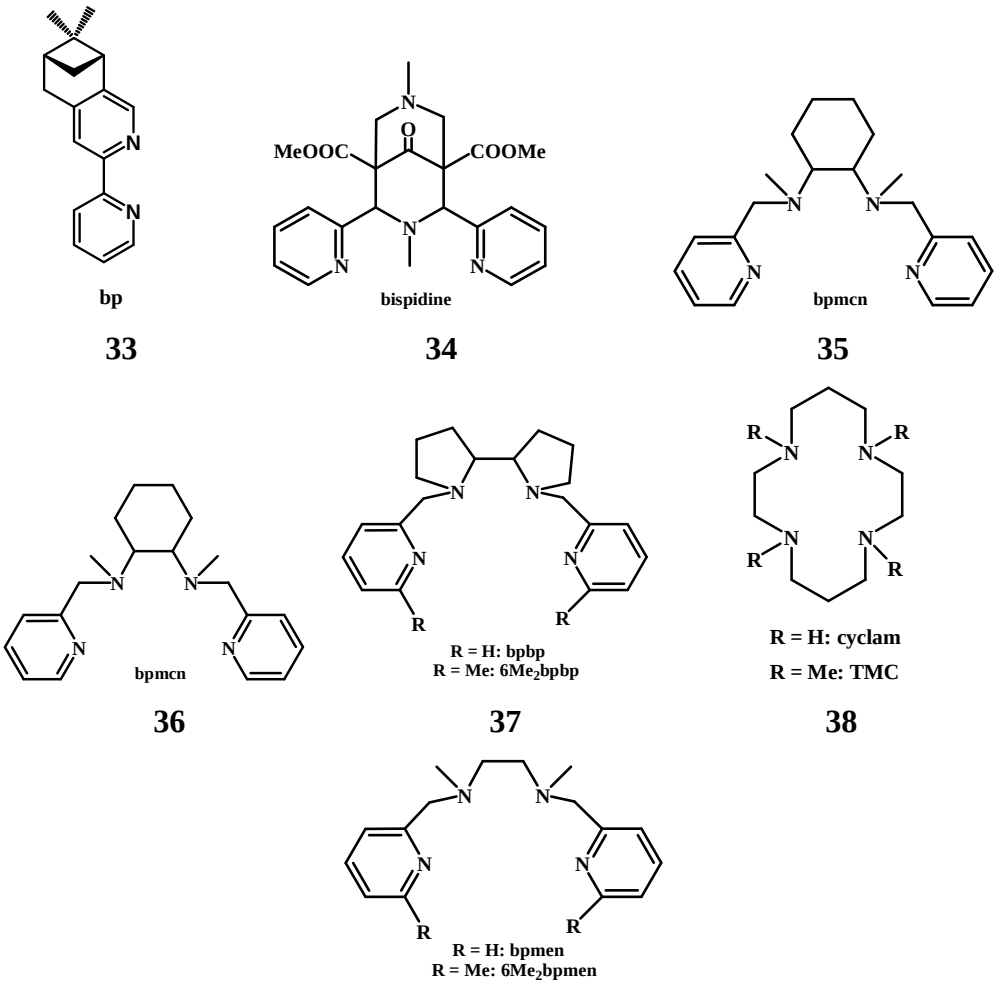
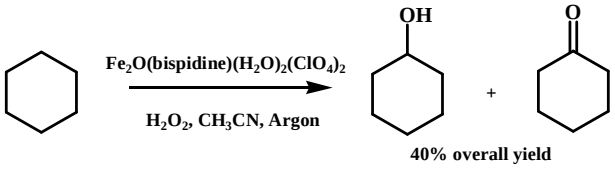


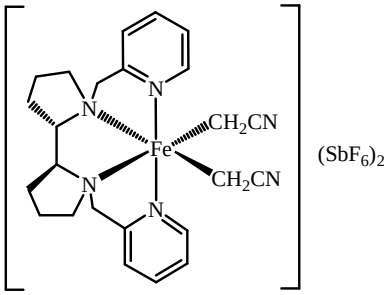

Figure I. 2. Structures of polydentate ligands

yield was low (based on the oxidant). Later on, the same research group described the synthesis of chiral bipyridine **35**, and its application as a ligand in the Fe-catalysed oxidation of alkanes (Scheme I. 6) and sulphides [62]. The moderate enantiomeric excess (40%) obtained in the case of *p*-bromophenylmethylsulfide provided the first direct evidence that oxidation reactions catalysed by non-heme iron do not proceed exclusively through radical chain autoxidation.




Scheme I. 6. Cyclohexane oxidation by chiral Fe-bispidine [62].

Shul'pin and co-workers [63] devoted several studies to the C-H activation of unreactive substrates and described various systems involving, among the others, hydrogen peroxide and oxygen as oxidising agents and several transition metals complexes as catalysts. For example, they recently reported the use of 2,2'-bipyridine as co-catalyst in the $FeCl_3$-catalysed oxidation of alkanes with hydrogen peroxide in acetonitrile solution at 60 °C [64]. The presence of the additive dramatically accelerated the oxidative process and TONs up to 400 after 1 hour were obtained.




**40**

Recent review by Talsi *et al.* [65] presents a comprehensive list of polydentate ligands based on N-donor set for chemo and stereoselective C-H oxidation by iron and manganese complexes. Furthermore, Chen *et al.* have recently discovers a highly reactive mononuclear non-heme iron catalyst **40** that stereoselectively hydroxylates $sp^3$ C–H bond [66]. The findings have contributed to redefining how C–H bonds are viewed in synthetic planning, future methods development, and in the exploration of molecular diversity through catalysis.

### I. 3. Scope and objectives of the present study

The objective of the present research work is to design polydentate ligands mainly with N-donor sets. The synthesis of ligand frame having multiple donor centres, the study of their interaction with metal ions and the reactivity of the metal complexes are the major objective of the present investigation. The work undertaken in the thesis consists of two broad but closely related areas of metal sensing and catalysis. A brief purpose of the research work is as follows:

1. Chemosensors for different metal ions have attracted much attention because of their convenient use and high sensitivity [67]. In particular, selective detection of Hg (II) ions is of significant importance for environmental and health related issues [68] Therefore, design and development of luminescent chemosensors those are selectively responsive to Hg(II) ions is highly desirable [69]. Several signaling systems based on the principle of concentration quenching, exciton coupling, excimer formation, symmetry breaking, charge transfer and excitation transfer have been developed. In spite of the progress made in this direction, majority of these chemosensors suffer from several drawbacks like the short fluorescent lifetime and small stoke shifts *etc* [70, 71]. Designing Hg (II) ion selective probe with high fluorescent quantum yields, large stoke shifts and longer lifetimes constitute an attractive area of research. It is our endeavour to design new N-donor polydentate ligands with open chain and macrocyclic ligand platform. The pyrrole based linear and macrocyclic conjugated system which additionally act as a fluorophore would be suitable for designing metal sensing system based on monitoring their photophysical changes. Detail photophysical characterization and their interaction with metal ions in solution would suffice the need for the development of novel chemosensor system.

2. The C-H activation or more specifically oxyfunctionalization of hydrocarbons (alkanes/ alkenes) under mild condition is an important goal in chemistry [72]. The catalytic systems *in vitro* often rely on the application of high temperature/pressure and suffer from poor selectivity and production of toxic waste [73]. Nature has evolved several efficient metalloenzymes to carry out alkane hydroxylation, olefin epoxidation, and olefin *cis*-dihydroxylation selectively under physiological conditions [74]. These metalloenzymes have proved useful in the development of model catalytic systems for hydrocarbon oxidation [75].

The design and synthesis of ‘catalytically potent’ first transition metal (iron and copper) complexes with polydentate ligands would be done. The characterization of these newly synthesized metal complexes with conventional spectroscopic

techniques and crystal X-ray crystallography would help us to understand the structural topology and its relationship with reactivity.

3. The design of catalytic system based on the principle of cooperative ligand centred reactivity of the metal complexes as catalyst in bond activation process is on the rise. The cooperative action of ligand frame during ligand based redox process in a transition metal complex not only regulates the steric property but also vastly modulate the electronic and redox property of the metal complex. Therefore, catalytic tuning through the employment of redox active polypyrrolic actor ligands instead of spectator ligands would be undertaken.

4. Furthermore, the combination of 3d transition metal with redox innocent ligand would also be studied. The subsequent effect of steric environment provided by the flexible ligand would enable us to understand the redox behaviour of metal ion in catalytic environment. The iron centre of N-donor redox-innocent 14-membered macrocyclic tetraamine ligand, 1, 4, 8, 11-tetraazacyclotetradecane (cyclam) would be examined for its potential application in catalytic hydroxylation reactions.

5. The selective transformation of hydrocarbons leading to oxygenated products such as alcohols and carbonyl compounds is an important industrial process [76]. Oxidation products of cycloalkanes, cycloalkenes and other olefinic compounds are the starting material of many commercially important products. For example, the controlled oxidation of cyclohexane gives cyclohexanol. Cyclohexanol is used as an important feedstock in the polymer industry, as a precursor to nylons and for the synthesis of various plasticizers [77, 78]. Although hydrocarbon oxidation is a thermodynamically favoured process, it is always a challenge to do so in a controlled and selective way. Therefore, the need for controlled reaction, higher efficiency, and selectivity has always been a feedstock of catalytic reaction. Therefore our effort would be to develop a catalytic system for oxidation of some industrially important organic compounds.

6. Catalytic systems with environmentally benign oxidizing agent operating under ambient conditions would be developed. Hydrocarbon oxidation with traditional oxidants such as $CrO_3$ or $KMnO_4$ produces multiple products and can be

designated as rather inefficient. Replacing stoichiometric oxidants such as $KMnO_4$, $Ag_2O$ and $CrO_3$ by environmentally benign ones is self-evidently a sensible chemical strategy. The use of benign terminal oxidants such as $H_2O_2$ and *t*-BuOOH would be a sincere effort to move towards more congenial catalytic oxidation system.

7. Recent advances in green and clean technology experience an upsurge in the use of ionic liquid as a benign reaction medium. With an aim to develop nontoxic methodologies, room temperature ionic liquids (RTILs) are found to be very useful medium for a wide range of organic and transition-metal catalyzed reactions [79]. Therefore, the examination of the role of ionic liquid in catalytic oxyfunctionalization process is a prerequisite and would be dealt with different terminal oxidants.

8. Although homogenous catalysis has always been the major contribution in catalytic system, the limitations of such systems are quite reminiscent from the literature. Homogenous catalysis is often encountered with poor selectivity, lower turnover number, catalytic bleaching and lower recovery. Comparative studies in selectivity of a product in a catalytic system, in the case of the biomimetic oxidation of hydrocarbons, reveal that selectivity arises not only from the steric effects imposed by the environment of the enzyme active site upon substrate approach [80], but also from specific binding at the active site. The role of protein matrix found in enzymes inspires chemist to incorporate size and shape selective framework of mineral matrix such as clays and zeolites, assuming that the mineral framework may generate sufficient steric environment to provide specific binding site, stability, and flexibility in catalytic systems and to achieve specificity selectivity, stability and efficiency of enzymes [81, 82]. Therefore effort would be given to develop a catalytic system based on grafting or intercalating metal complexes into solids such as clay, silica, *etc*. This would certainly provide a new surface area with limited or selective access to the active centres. The adaptation of this technique would further provide better stability and activity of the metal complexes.

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