WORLD JOURNAL OF PHARMACEUTICAL RESEARCH
SJIF Impact Factor 7.523
Volume 6, Issue 15, 296-340. Review Article ISSN 2277–7105

A THESAURUS COMPRISING BRIEF INTRODUCTION OF CHEMOSENSOR FOR RECOGNITION OF METAL CATIONS AND ANIONS

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Article Received on
26 Sept. 2017,

Revised on 16 October 2017,
Accepted on 06 Nov. 2017

DOI: 10.20959/wjpr201715-10087

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ABSTRACT

The development of sensitive chemosensors capable of selective recognition of metal ions, especially for cations and anions with biological interest, has always been of particular significance, chemosensors find wide applications in many disciplines such as biochemistry, clinical and medical sciences, cell biology, analytical chemistry and environmental sciences. In this review, we first summarize the colorimetric and fluoroscence chemosensors for sensing of cations including transition metal cations and cations of s-block and p-block elements with the mechanism of analyte detection. The second part of this review highlights the chemosensors both colorimetric and fluoroscence for anion sensing. In this contest, special interest has been devoted to covers all the chemosensors for transition metal ions and cations of s & p-block elements and also the anions in a single review because in the literature, no report on the reviews covering the simultaneous detection of transition metal ions and cations of s & p-block elements and anions. In this contribution we review the chemical systems able to act as colorimetric and luminescent chemosensors for this class of metal cations and anions. This review also summarizes an important or biological as well as hazardous role played by these metal cations and anions in environment and human being. We hope, this review article is quite helpful for those researchers who are working in the field of sensors and switches for getting the brief introduction about sensors for metal cations and anions by referring this single review article.

KEYWORDS: Photoinduced electron transfer, Electron energy transfer, Chemosensors, Transition metal ions, Ions of s & p-block elements and Anions.

1.1 INTRODUCTION

Nowadays the motto of the scientists inclined towards the design and synthesis of newer nitrogen containing heterocyclic compound and utilization of these heterocyclic compounds as colorimetric and fluorescent chemosensor for the recognition and sensing of biologically and environmentally important species such as metal cations and anions has emerged as a significant goal in the field of chemical sensors in recent years.[1-3] A chemosensor is an organic heterocyclic molecule that gives a visible response in the presence of a target substrate (analyte). Generally, sensors can be derived from small organic molecules appended with various functionalities for detection of chemical species through non-covalent interactions is referred to as chemosensors.[3] Literature survey demonstrates that an enormous efforts have been devoted on design, synthesis and study of these chemosensor on living cells, accelerate an interesting pathways for the accurately identify and quantify toxic-metal ions and allow the probing of cell activity, as these elements cause severe damage to human health and environment.[4,5] In this way, a chemosensor device is conceived to avoid classical expensive and laborious analytical methodologies and to allowing in situ and real time detections and quantification of analytes at the lowest cost possible. In a world of fast and unpredictable changes it is extremely necessary to develop new chemosensors; applications cover from process control, environmental monitoring, food control and food analysis, medical diagnosis and treatment, and many other disciplines need more sophisticated and specific sensing systems for their development, including chemistry, biology, medicine, military security, new materials, nano-devices and environmental science.[6],[7] The list of attractive analytes to be detected is extensive, however, among all possible analytes, metal ions and anions occupy a central task in all aspects of human life and development. The development of the chemosensor for specific analyte, three factors are most important, which are affinity, selectivity and readout. A chemosensor must have a dissociation constant *Kd* that matches the concentration of the analyte being detected; this allows minor changes in analyte concentration to be detected. The issue of selectivity is crucial in that the chemosensor must be designed so as to bind only with the desired analyte and no other competitors.[6,7] The choice of readout is contingent on both the application of the chemosensor and the availability of instrumentation. Possible signaling methods include UV-visible spectroscopy, and fluorescent spectroscopy which is preferred due to its sensitivity, allowing low concentrations of the analyte to produce large changes in output.[8] In particular, chemical sensing driven by desired analyte through molecular recognition has been recognized as a powerful tool to accurately identify and quantify toxic-metal ions, explosives, carbohydrates, nucleosides or nucleotides, amino acids, and various chemical entities and also allow the probing of their cell activity.[9] This study will lead to fabricate chemical material which will make bridge between organic synthesis and material chemistry.

Chemosensors are the molecules of abiotic origin that bind selectively and reversibly with the analyte with concomitant change in one or more properties of the system, such as color (colorimetric chemosensors) or fluorescence (fluorescent chemosensors) or redox potentials (electrochemical sensors) (Fig. 1).[10, 11]

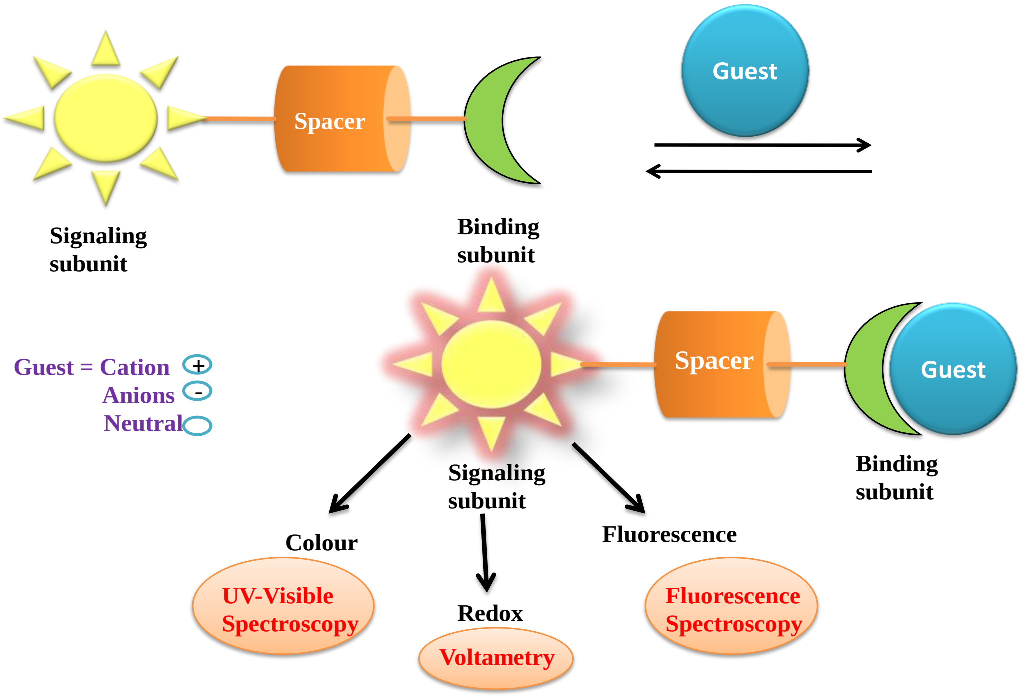


Fig 1: Schematic presentation of interaction of chemosensor with guest analyte.

A chemical sensor is a device that qualitatively or quantitatively detects the presence of specific chemical substances. Generally, a sensor device contains three elements such as a receptor or binding subunit, a signal transducer or spacer and a read-out or signaling subunit (Fig. 1). The receptor should have the ability to differentiate and binds selectively to a specific target substance known as the analyte. The formation of selective receptor–analyte complex were depends on the size, shape and binding energy of the receptor and analyte molecules. The signal transducer or spacer is an active unit whose properties should change upon complexation and eventually a spacer that can change the geometry of the system and tune the electronic interaction between the two former moieties.[12] Signal transduction is the process through which an interaction of receptor with analyte yields a measurable form of energy change and is converted to a signal change that can be read and quantified by the signaling subunit. The read-out domain or signaling subunit is the part responsible for reporting the binding event.[7] The read-out or signaling subunit of chemosensor usually measures the change in fluorescence intensity, intensity decay lifetime, or a shift of the emission wavelength, change in the absorption intensity or shift of absorption wavelength.[13] There are two types of sensors as fluorescence and colorimetric chemosensors. The chemosensors generally based on fluorescence signal changes are commonly referred to as fluorescent chemosensors[11], whereas the chemosensors involving the change in colour upon binding with the specific analyte are termed as chromogenic or colorimetric chemosensors.[14, 15] The fluorescent chemosensors has attracted great deals of attention due to their distinct advantages in high sensitivity, simplicity, ease of measurement, low cost, easily performed, and versatile, offering subnanometer spatial resolution with submicron visualization and submilli second temporal resolution.[16-21] The fluorescence sensors have been developed by utilizing organic heterocyclic molecule appended with fluorophore moiety such as pyrene, cyanine, naphthalimide, fluorescein, rhodamine, coumarin, quinolone and BODIPY, which provide a wide range of emission from ultraviolet to near infrared, by using various sensing mechanisms as photoinduced electron transfer (PET), fluorescence resonance energy transfer (FRET), internal charge transfer (ICT), chelation enhanced fluorescence quenching (CHEQ), and dimerization fluorescence.[22-27] The fluorescence methods depend upon the change of fluorescence intensity and/or a shift in the fluorescence band of the sensor upon interaction with the metal ion. Although such a methodology has been successful for diamagnetic metal ions, its application to paramagnetic metal ions is fraught with difficulties in view of the fact that the latter quench fluorescence either via energy or electron transfer which renders low signal output.[28-31] Only in some cases a fluorescence enhancement has been observed.[32-34]

On the other hand; absorption-based colorimetric chemosensors are desirable, which could be widely used owing to the low cost, less labor-intensive, highly sensitive and lack of equipment required, and a color change that can easily be observed by the naked eyes, even at very low analyte concentration.[35-37] Generally, colorimetric chemosensors were designed by employing intramolecular charge transfer (ICT) mechanism, which consisted of donor–acceptor conjugation systems. Interactions between electron-rich donors and electron-poor acceptors tend to have a well-defined geometry due to a combination of charge transfer, electrostatic, van der Waals and solvophobic effects; for convenience, these effects are determined as donor–acceptor (D–A) interactions. And the strength of the D–A interactions would vary delicately with the change of the electron donor or electron-acceptor abilities of the D or A moieties, which directly led to the variation of the absorption spectra.[37]

1.2. Mechanism of analyte detection

There are numerous fluorescence sensing mechanisms such as Photoinduced electron transfer (PET) and electronic energy transfer (EET). These mechanisms result in changes in fluorescence intensity and have been extensively studied and widely used in the design of the chemosensors.[13]

1.2.1. Photoinduced electron transfer[13]

The sensors comprising of photoinduced electron transfer process can be classified into two categories such as fluorescence “turn-on” or fluorescence “turn-off” upon binding with metal cations. In the former case, the receptors usually contain a relatively high-energy non-bonding electron pair or loan pair localized on donating atom in the receptor. In the absence of analytes or metal cation which is to be detected, this electron pair quenches the emission by rapid intramolecular electron transfer from the receptor to the excited fluorophore, as shown in Fig. 2. When this electron pair coordinates to Lewis acid cations in solution, the HOMO of the receptor is lowered. This decreases the driving force for the PET process effectively stopping the quenching event and turning on the fluorescence of the chromophore. In some cases, the receptor takes part only indirectly in the photophysical process.

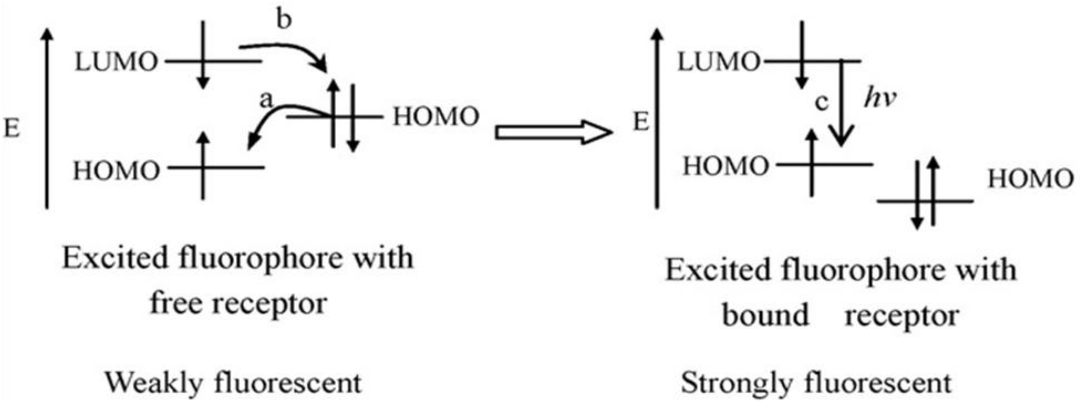


Fig 2: Orbital energy level diagrams for fluorescence "turn-on" PET sensors before and after binding to cation where (a) forward electron transfer; (b) backward electron transfer; (c) fluorescence emission processes.

In the later case, if the energy level of the cation LUMO is between the energy levels of the fluorophore HOMO and LUMO, the binding of the cations by the receptor provides a non-radiative path to dissipate the excitation energy, resulting in a quenching of the fluorescence of the chemosensor as shown in Fig. 3.

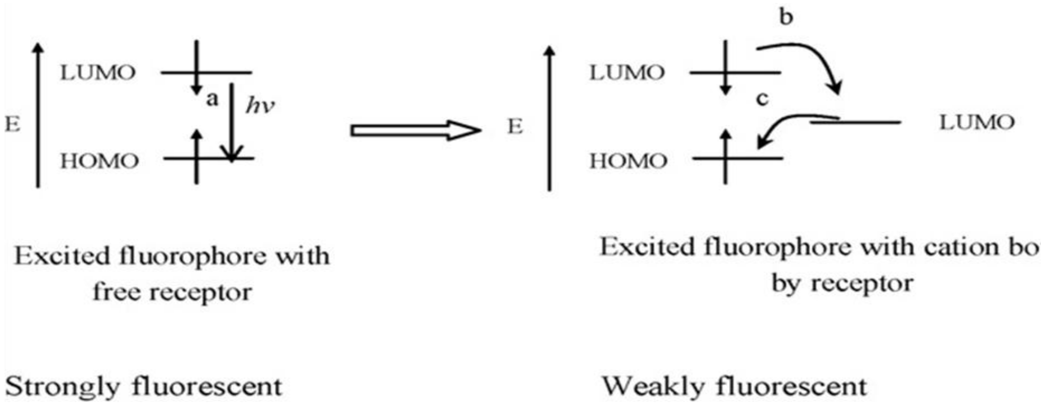


Fig 3: Orbital energy level diagrams for fluorescent "turn-off" PET sensors before and after binding to cation where (a) fluorescence emission; (b) forward electron transfer; (c) backward electron transfer processes.

1.2.2. Electronic energy transfer[13]

Electronic Energy transfer is a new mechanism for the fluorescence quenching upon binding cations. There are two types of EET mechanisms such as the double electron exchange energy transfer (Dexter) or the dipole–dipole coupling (Forster) energy transfer.[21, 38] In the organic fluorophore–cation system, usually the Dexter energy transfer dominates as shown is Fig. 4. In this case, the fluorophore return back to its ground state by non-radiative decay.

The Dexter energy transfer requires close contact between the fluorophore and the cations and also direct orbital overlap. This type of fluorescence quenching not only requires the appropriate relative energy levels between fluorophore and cation, but also requires some specific characteristics of the spacer, such as flexibility and a shorter distance between the donor and acceptor. The Forster energy transfer mechanism comprising the long range coupling of dipoles, for allowing the exchange of excitation energy through space, i.e. without a path of direct orbital overlap.[39, 40]

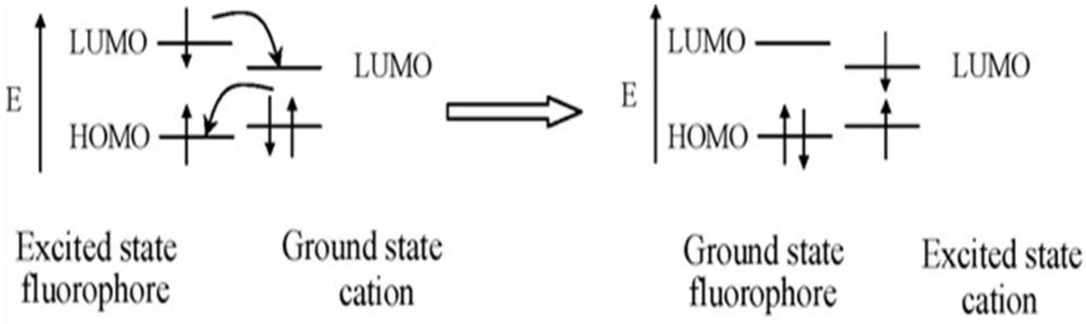


Fig 4: Orbital energy level diagrams for double exchange transfer between the excited fluorophore to the cation bound by receptor followed by cation return to the ground state by non-radiative decay.

1.3 Chemosensors for detection of metal cations

In the past few decades and upto now various chemosensors are reported in the literature for the detection of metal cations in aqueous or semi aqueous and in the living cell. In the contest of this thesis, we wish to divide these chemosensors in separate class: chemosensors for metal cations of S & P-block element, chemosensors for transition metal ions and chemosensors for anions and summarize these chemosensors briefly by taking various examples. Due to the significant nature of the field, this chapter is proposed as a brief discussion of specific subjects and a few recent literature examples which are appropriate for understanding of the work described in the later chapters of this dissertation.

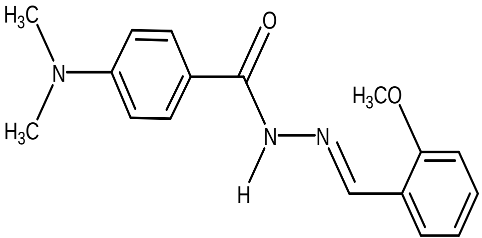
1.3.1. Fluorescent and colorimetric chemosensors for detection of transition metal cations

There is growing interest in the design and development of molecular sensors that can detect analyte even at very low concentration.[41, 42] Among the different analytes, special attention is devoted to develop chemosensors for transition metal ions such as iron, zinc, copper, and cobalt ion, because these are essential elements in environmental and biological systems, but at the same time some of them can cause severe damage to environment and living system, when present in uncontrolled amounts. In our contribution, we will review the chemical systems according to the receptor moiety present in the chemosensor that were able to act as colorimetric and fluorescent chemosensors for this class of metal ions.

Among the transition metal ion, Copper is the third most abundant transition metal in human body.[43] The Cu^{2+} ion play crucial role in many biological and environmental processes.[44] It also plays a vital role as a catalytic co-factor for a variety of metallo-enzymes and transcriptional events such as superoxide dismutase, cytochrome c oxidase and tyrosinase.[45, 46] It is an environmental pollutant at high concentrations[47] and leads to various neurodegenerative diseases in human being such as Alzheimer's disease, prion disease, Wilson's disease, Menkes disease, amyotrophic sclerosis, gastrointestinal disorders, kidney damage, lipid metabolism, and inflammatory disorders.[48-50] Therefore, the rapid and easy detection of Cu^{2+} is very important in environmental and biological systems. The past and present literature report tells that various colorimetric and fluorescent sensors based on receptor moiety available for Cu^{2+} recognition.

The Yun-Bao Jiang[51] et al. reported a simple yet highly selective and sensitive chemosensor 1 for Cu^{2+} ion. A blue shift and dramatic enhancement in the CT fluorescence of 1 in ACN and aqueous ACN solutions were observed in the presence of Cu^{2+}. The transition metal ion act as an efficient fluorescence quencher, the sensor 1 gives highly selective fluorescent response toward Cu^{2+}. As both the electron donor ($-N(CH_3)_2$) and the ionophore in the electron acceptor in 1 can be provide a new strategy for constructing turn-on CT fluorophores for transition metal ions.

H. Cao[52] et al. three anthracene-based fluorescence sensors bearing a Schiff base moiety for detection of Cu^{2+}. Among the three derivatives, 2 displayed a fluorescence Turn-On in response to Cu^{2+} with high sensitivity and selectivity over 12 other metal ions. The 120-fold strong fluorescence enhancement has been observed for 2 in acetonitrile media in the presence of Cu^{2+} in the range of 1.2×10^{-6} to 4.8×10^{-5}M that allowed 2 to detect Cu^{2+} in drinking water or biological samples. 2 also provided a simple but efficient recognition unit to Cu^{2+} based on PET mechanism that may be useful for developing chemosensors in the future.



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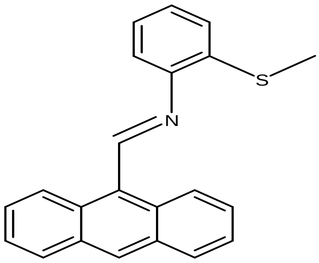

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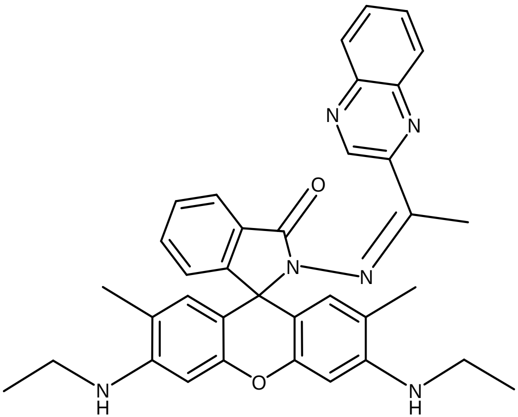
The B. Tang[53] et al. reported the synthesis, chemosensing properties and cellular applications of a new fluorescent sensor 3 with rhodamine 6 G as the fluorophore and 2-acetyl-(1,4)-benzodiazine, a Cu^{2+}-selective ligand, to monitor intracellular Cu^{2+} levels in living cells. The fluorescent probe 3 is highly selective for Cu^{2+} over other metal cations. The weakly fluorescent probe 3 showed a fluorescence enhancement response upon binding with Cu^{2+}. The 3 also facilitate naked-eye detection of Cu^{2+}.

P. Xie and co-workers[54] reported new chemosensor based on spirolactam form of rhodamine 101 hydrazone 4 for the recognition of copper ion in aqueous solutions. The 4 displays a selective and sensitive colorimetric change with rapid response upon addition of Cu^{2+}, due to formation of Cu^{2+}.4. As fluorescent maximum of this chemosensor to Cu^{2+} can be red-shifted to above 600 nm. But Cu^{2+} in high concentration will quench the fluorescence of the Cu^{2+}.4 complex of delocalized form of 4.



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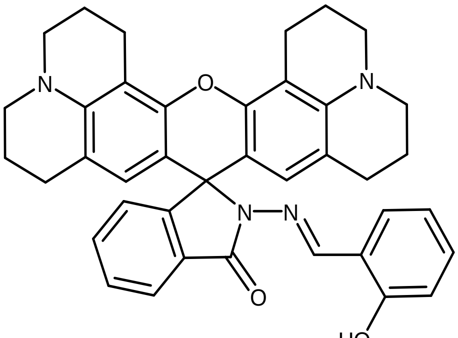

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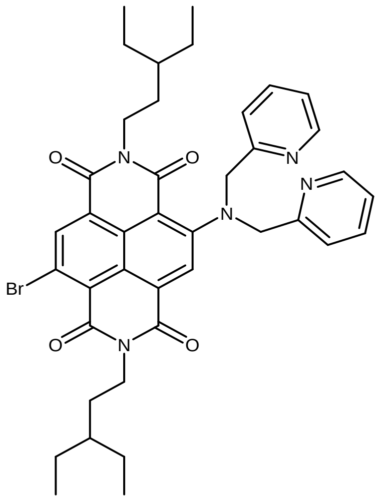
Zen Li and Co-workers[55] established naphthalendiimide (NDI)-based chemosensor (5) for naked-eye detection of Cu^{2+}, 5 displayed high selectivity in the presence of other competitive metal ions. The Cu^{2+} recognition gave rise to apparent red-to-yellow color change with the blue-shift maximum absorption wavelength as large as 80 nm, through the intramolecular charge transfer mechanism (ICT). The pH effect studies indicated that 5 can be applied to the analysis of samples from mildly acidic to basic environments. The stoichiometry of the 5-Cu^{2+} was determined by the Job plot, which was performed at room temperature in methanol. The plot of absorption versus X [5]([5]/([5] + [Cu^{2+}])) showed that the absorption value arrived at its maximum at a molar fraction of ca. 0.50, which confirmed the 1:1 binding mode between 5 and Cu^{2+}.

The X. Peng and Co-worker[56] designed new ratiometric fluorescent probe N-butyl-4, 5-di [N-(phenyl)-2-(amino)-acetamino]-1, 8-naphthalimide (6) on the basis of the mechanism of internal charge transfer (ICT). The probe 6 showed excellent selectivity for Cu^{2+} in the presence of a variety of other metal ions in aqueous ethanol solutions. The 1:1 binding mode of probe 6 with Cu^{2+} was observed for complexation of 6 with Cu^{2+}. Fluorescent emission spectra of probe 6 in the presence of Cu^{2+} showed a 50nm blue shift, which is from 521 nm to 471 nm. Furthermore, 6 show the same fluorescent change with the Cu^{2+} in living cells.



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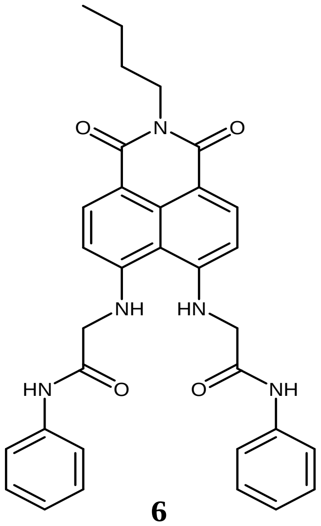
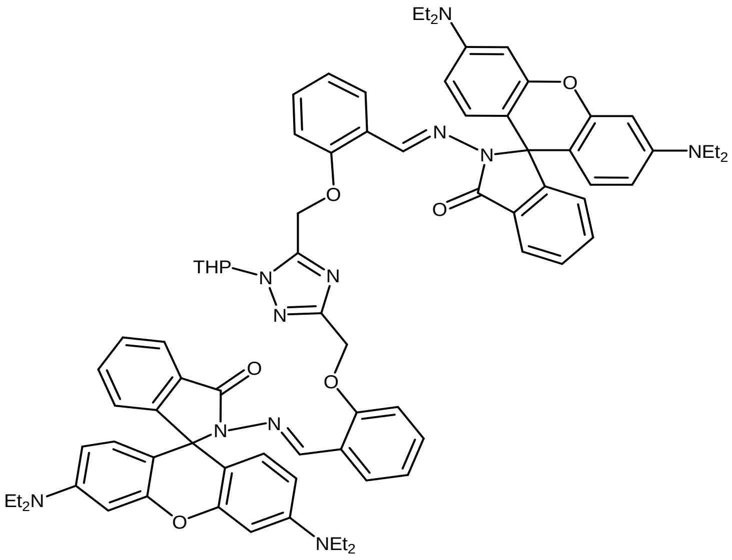


6

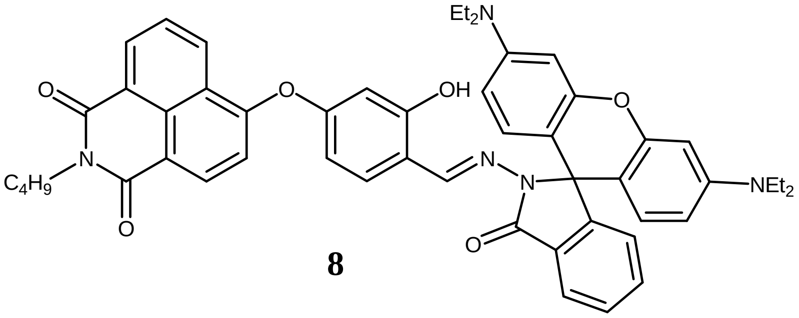
J. Zhang[57] et al. chemosensor **7** based on rhodamine B with 1, 2, 4-triazole as subunit. **7** exhibits high selectivity and sensitivity toward Cu^{2+} in ethanol/water (6:4, v:v) using pH 7.0 HEPES buffer solution. The **7** binds with Cu^{2+} by undergoing ring opening mechanism in 2:1 binding mode. The chemosensor displays a linear response to Cu^{2+} in the range between 1×10^{-7} M and 1×10^{-6} M with a detection limit of 4.5×10^{-8} M. The 7 could be successfully employed as selective chemosensor in the fluorescence imaging of living cells.

Chunwei Yu[58] et al. Designed and synthesized a novel “off-on” fluorescent chemosensor (8) by naphthalimide modified rhodamine B for Cu^{2+} detection, based on the equilibrium between the spirolactam (non-fluorescence) and the ring-opened amide (fluorescence). The chemosensor 8 showed high Cu^{2+}-selective fluorescence enhancement over variety of other metal ions or anions in neutral aqueous media. The limit of detection (LOD) was obtained as low as 0.18 µM of Cu^{2+}, the 1:1 binding stoichiometry was found for 8 and Cu^{2+}. The 8 further displayed its valuable applications in biological systems for the measurement of Cu^{2+} in living cells.



7

Iron is the most abundant essential transition metal ion in human body and act as catalytic co-factor for many proteins in a wide range of biochemical processes such as oxygen transport, oxidoreductase catalysis and electron transport.[59, 60] Iron deficiency in human leads to low oxygen delivery to cells, resulting in anaemia, low blood pressure, diabetes, liver and kidney damage and ultimately decreased immunity[61], whereas excessive loading of iron in living cells leads to formation of reactive oxygen species (ROS) by free radical reaction. These ROS can damage nucleic acid, proteins and lipids. This cellular toxicity due to iron ions leads to various diseases such as Alzheimer’s, Parkinson’s, Huntington’s diseases.[62] A current literature report tells that varieties of chemosensors are available for Fe^{3+}. Due to fluorescence quenching nature of Fe^{3+}, the development of ‘Turn-on’ chemosensor is the challenging task.



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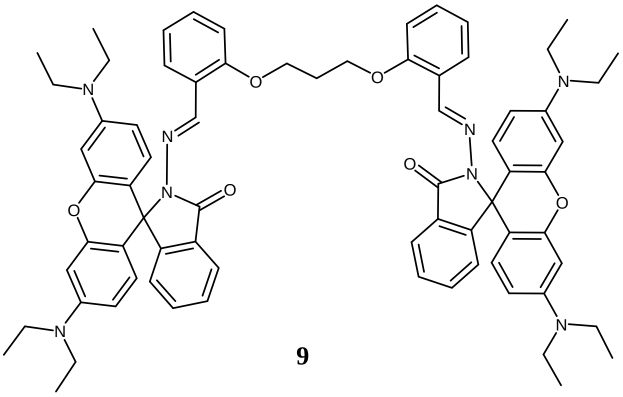
N.R. Chereddy[63] et al. reported rhodamine based chemosensor for detection of Fe^{3+} ion. The chemosensor 9 upon complex formation with Fe^{3+} ions at pH 7.4 gave rise an intense pink color and enhancement in fluorescence emission intensity enabled the detection of Fe^{3+} in the presence of other competitive metal ions. Moreover the sensor 9 can be employed to detect Fe^{3+} ions in the fibroblast living cells. D.Y. Lee[64] et al., fabricated novel benzimidazole-based, anthracene-coupled fluorescent receptor 10 capable of recognizing and estimating the concentrations of Fe^{3+} in semi-aqueous solution. Receptor 10 displayed a well defined maximum at 414 nm in the fluorescence spectrum recorded at a concentration of 10 µM in pure acetonitrile, when excited at 367 nm. The sensor 10 could be made very selective for Fe^{3+} over other metal ions by making use of the solvatochromic behavior of the receptor.

V. Bhalla[65] and Co-worker develop triazole appended pentacenequinone derivative 11. Compound 11 exhibits selective response towards Fe^{3+} ions. Interestingly 11.Fe^{3+} exhibits ‘‘turn-on’’ response towards fluoride ions and thus, makes the 11.Fe^{3+} ensemble a novel probe for the selective detection of fluoride ions.

Further, 11 coated test strip can detect traces of Fe^{3+} and F^- ions and provide a simple, portable and low cost method for detection of Fe^{3+} and F^- ions in aqueous solution.



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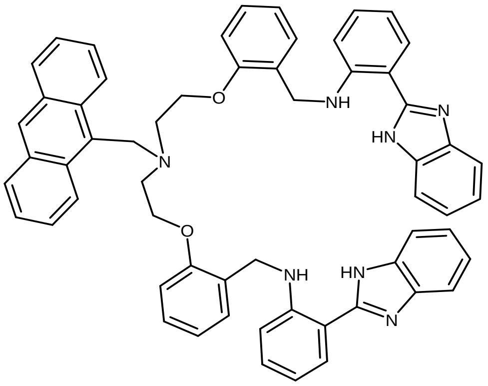

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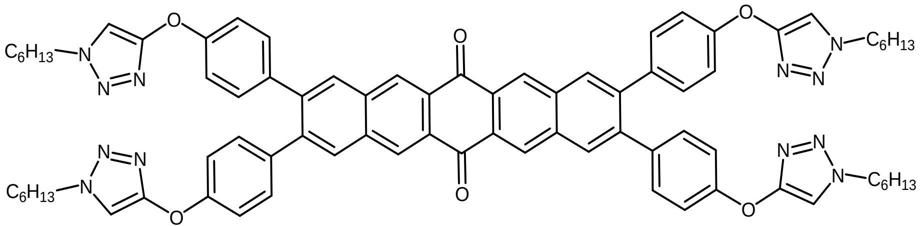
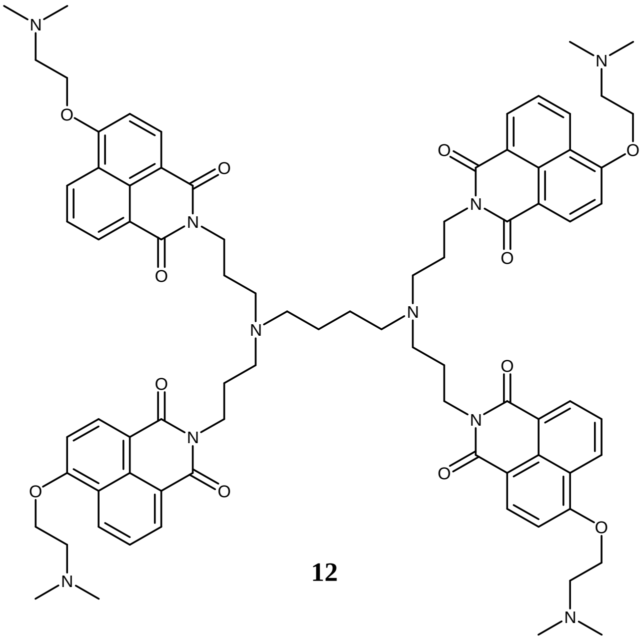


11

Ivo Grabchev[66] laboratory reported for the first time the 4-nitro-1,8-naphthalimide bonded to poly(propylene amine) dendrimer 12. The photophysical properties of new blue fluorescent dendrimer 12 have been investigated in organic solvents of different polarity. The influence of various metal cations (Pb^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Fe^{3+}) on the fluorescence intensity of the new dendrimer 12 has been investigated in acetonitrile solution with regard to its potential application as a fluorescent sensor for metal ions detection. The new dendrimer allows development of a new selective fluorescent sensor for Fe^{3+} based on 1, 8-aphthalimide modified first generation PPA dendrimer.

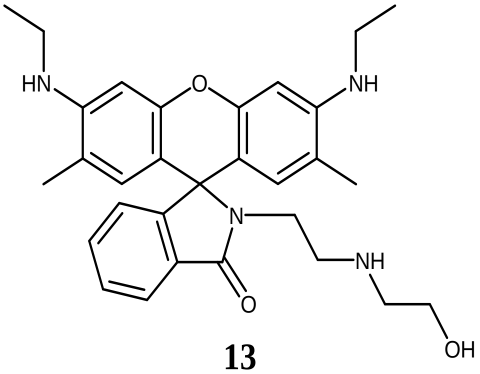


12

Zinc is the second most abundant transition metal ion present in the body[67, 68] play an important role in numerous biological processes such as catalytic activity, brain activity, immune function, gene transcription, cellular transport.[69-71] The excessive overload leads to apoptosis, epilepsy, ischemia and Alzheimer's disease while its deficiency in the body leads to several malfunctions like growth retardation, diarrhea, impotence and delayed sexual maturation.[72-78] In recent years the development of fluorescent and colorimetric sensors for zinc ions has become a very popular area of research.

G. Sivaraman and D. Chellapa[79] developed new rhodamine based selective and sensitive fluorescent turn-on chemosensor 13 for detection of Zn^{2+}. A prominent fluorescence enhancement was found in the presence of Zn^{2+}, which was accompanied by changes in the absorption spectrum. The sensor 13 showed 'naked-eye' detection of Zn^{2+} ions by color change of the solution from colorless to pink. Furthermore, the sensor 13 effectively used as a fluorescent probe for monitoring Zn^{2+} in living cells by means of confocal laser scanning microscopy experiments.

J.Y. Choi and J. Yoon[80] designed and synthesized a new hydroxypyrene-based selective colorimetric and fluorescent sensor 14. Chemosensor 14 showed a new UV-Vis absorption peak at $\lambda max_{=}$ 498 nm with Zn^{2+}, which can be attributed to an internal charge transfer (ICT) mechanism. The sensor 14 with Zn^{2+} displays highly selective fluorescence "turn-on" enhancement at long wavelength $\lambda max_{=}$ 588 nm in a buffered system. The combination of two phenol groups on the pyrene and phenyl moieties as well as a conjugated hydrazone group can make a binding pocket for Zn^{2+}.



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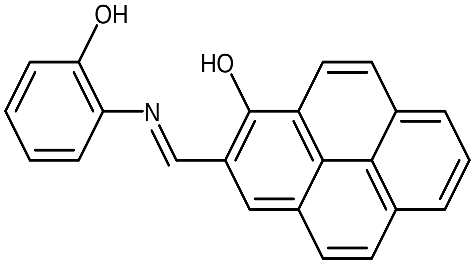
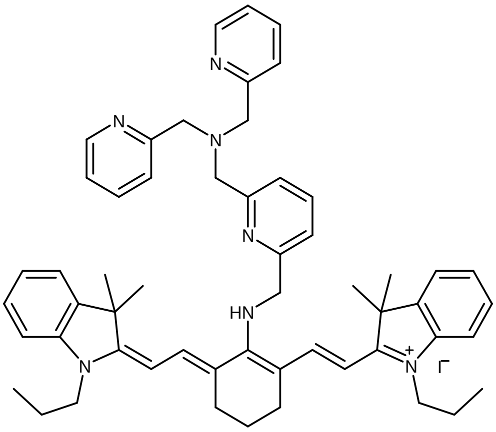


14

Z. Guo and J. Yoon[81] et al. designed cyanine-based highly selective and sensitive fluorescent sensor 15, to monitor endogenous Zn^{2+} in live cells and organisms. The chemosensor 15 shows remarkable color change from blue to light red upon addition of Zn^{2+} to 15. The recognition profile of sensor 15 was investigated by using UV-Vis and fluorescence spectroscopy. A remarkable hypsochromic shift (ca.140 nm) in the emission maximum of 15 takes place from 730 nm to 590 nm.

V. Bhalla and M. Kumar[82] designed and synthesized a pentaquinone based fluorogenic receptor 16 for Zn^{2+} ions. 16 shows fluorescence enhancement in the presence of Zn^{2+} ions with a detection limit up to a nanomolar range under the F-triggered synergistic effect. In addition, 16 behave as a molecular keypad with sequential chemical inputs of Zn^{2+} and F$^-$ ions.

The Silver ion, like other heavy metals cadmium, chromium, copper and mercury etc. is one of the poisonous categories of toxic ions. Ag$^+$ ion plays significant roles such as microelements in the human tissue and possesses antimicrobial activity. Ag$^+$ has been widely used commercially in the electrical, photographic imaging and in the pharmaceutical industry.[84] Hence, Ag$^+$ also gets accumulated in the environment due to human activity, which may lead to toxicity.[85] Excessive intake and long-term accumulation of Ag$^+$ can lead to insoluble precipitates in skin and eyes also lead to toxicity to environment benign bacteria, amphibian, and fishes in waters.[86, 87]



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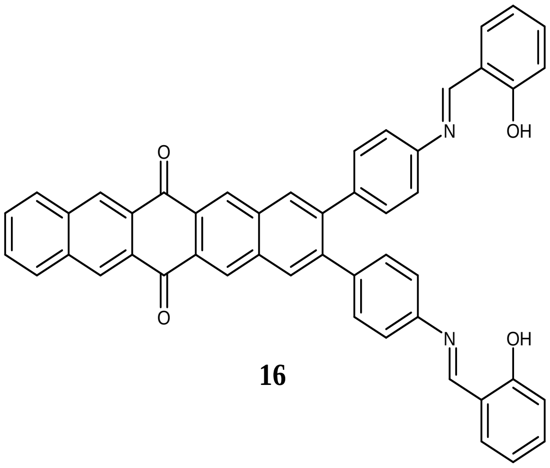
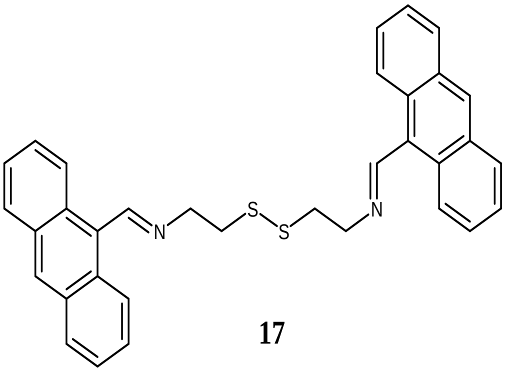


16

D. Chellapa[88] team reported a new probe 2,-2-disulfediyl bis-(N-anthracen-9-ylmethylene) ethanamine (Cysan) 17 based on anthracene platform. 17 show high selectivity towards Ag$^+$ metal ions. The fluorescence enhancement at 440 nm was observed for probe 17 upon complexation with Ag$^+$ ions over other metal ions. These photophysical studies indicate that the probe 17 can be adopted as a selective, sensitive and reversible fluorescent chemosensor for Ag$^+$ ions. The compound 18 from H.

Yang[89] laboratory is anthraquinone derivative having two thiourea groups that can selectively sense Hg^{2+} and Ag$^+$ through different color change, which was visually discernible by a 58 nm blue shift in the presence of Hg^{2+} and a broadening of the band in the presence of Ag^+.



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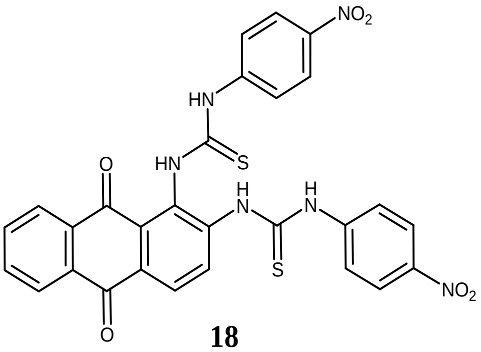
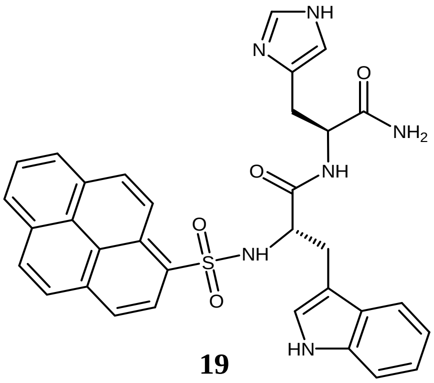


18

S. Jang[90] and Co-worker develop pyrene derivative chemosensor 19 based on a dipeptide shows a highly sensitive ratiometric response to Ag^+ as well as silver nanoparticles in aqueous solution at physiological pH. 19 can be effectively employed for Ag^+ recognition in living cell. A novel conjugated polymer 20 containing fluorene and ethyl 2-(2-(pyridin-2-yl)-1Hbenzo[d]imidazol-1-yl) acetate was designed by D. Cao[91] group. 20 show high sensitivity and selectivity for Ag^+ detection in the presence of other metal cations. Upon addition of Ag+, the fluorescent emission of the polymer solution in THF was quenched dramatically, accompanying the color changed from blue to green.



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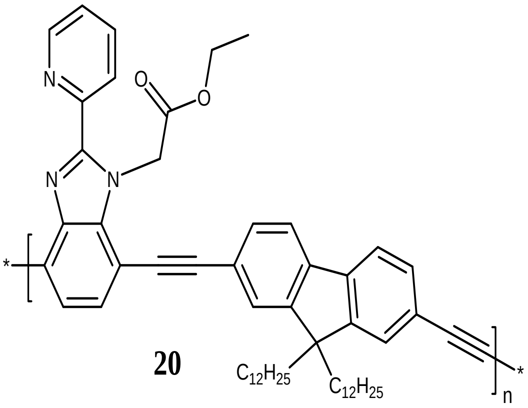

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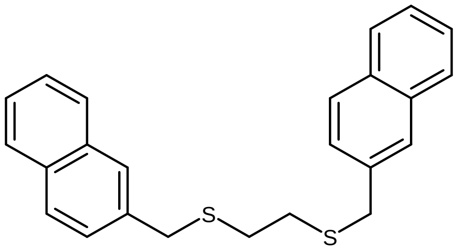
Nickel, among various transition metals, is an important metal nutrient for supporting life. Due to its widespread use in many industries, catalytic processes, it is added to environment and shows toxic effect to environment. Overexposure to nickel ion can cause acute asthma, stomachaches, pneumonitis, dermatitis, eczema, disorders of central nervous system and cancer of the nasal cavity, sinus and lungs, excess nickel accumulation can abnormally affect blood (increases red blood cells), kidney (increases protein in urine), respiratory and immune systems.[92] The International Agency for Research on Cancer (IARC) realized nickel compounds as group-I carcinogenic to humans in 1990.[93] Nickel plays crucial role in many biological processes occurs in variety of microorganisms and plants.[94] The enzymes and coenzymes containing Ni^{2+}: urease, Ni−Fe hydrogenases, F430 etc. play a noteworthy role in human life.[95]

A. Banerjee[96] et al. design naphthalene-based novel fluorescent probe, 1-[(naphthalen-3-yl) methylthio]-2-[(naphthalen-6-yl) methylthio]-ethane 21. The addition of Ni^{2+} to a solution of 21 (DMSO: water = 1:1, v/v; λmax=345 nm, λmax=280 nm) quenched its monomer emission, with subsequent enhancement of the excimer intensity (at 430 nm) with an isoemissive point at 381 nm. The 21 could detect Ni^{2+} as low as 1×10^{-6} M with a fairly strong binding constant, 2.0×10^{4} M^{-1}. Fruther 21 can be applied to detect Ni^{2+} in the living cells of plant origin by using a fluorescence microscope.

J. Jiang[97] team reported a novel colorimetric chemosensor 22 based on coumarin derivative for selective and sensitive recognition of Ni^{2+} ion in solution. The recognition of Ni^{2+} ion gave rise to color change from colorless to pink in ethanol which was clearly visible to the naked eye. Moreover, 22 can be applied to detect Ni^{2+} ion by test strips which also exhibits an obvious color change from colorless to red only with Ni^{2+} ion aqueous solution..



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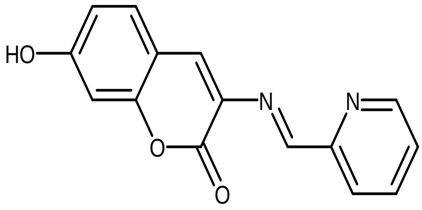
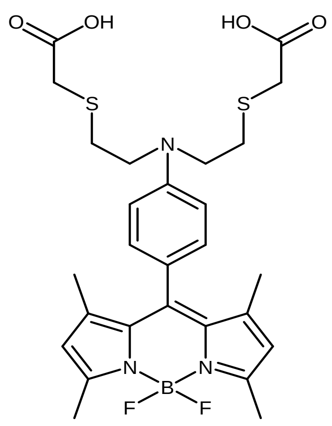


22

C.J. Chang[98] develop BODIPY based fluorescent turn-on sensor 23 for detecting nickel in living cells. 23 exhibit a selective turn-on fluorescence response to Ni^{2+} in water. Confocal microscopy experiments show that 23 can be used for detecting changes in Ni^{2+} levels within living cells.



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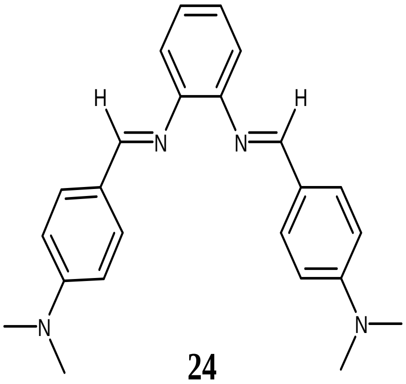
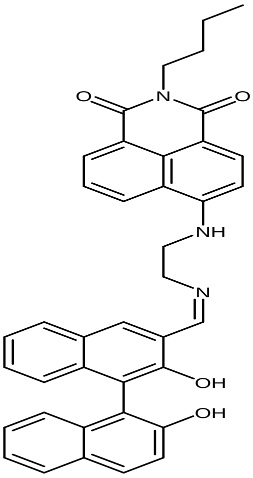


24

The compound 24 from M.H. Mashhadizadeh[99] group, a new PVC membrane electrode that is highly selective to Ni^{2+} ions. The sensor shows fairly a good discriminating ability towards Ni^{2+} ion. The electrode was used in the direct determination of Ni^{2+} in aqueous solution and as an indicator electrode in potentiometric titration of nickel ions.

Cr^{3+} in the class of transition metal ions plays critical role in the metabolism of carbohydrates, proteins, lipids and nucleic acids.[100] The deficiency of Cr^{3+} would cause disturbances in the glucose level and lipid metabolism in human and lead to increase the risk for diabetes and cardiovascular diseases, whereas excessive intake causes genotoxic effects.[101] Cr^{4+} has harmful effect on liver, lung, and kidney[102] and causes cancer by oxidizing the biological species such as DNA and some proteins.[103] Cr^{3+} is an essential trace element for the proper functioning of human metabolism: Cr^{3+} and insulin makes the correct level of glucose in the human body, through glucose tolerance factors (GTF), thereby activating certain enzymes, hormones, nucleic acids and stabilizing proteins.[104, 105] However Cr^{3+} is added into environment due to various industrial and agricultural activities and acts as an environmental pollutant.[106]

The L. Wang[107] laboratory report nnaphthalimide and BINOL framework based fluorescent probe 25. The 25 exhibited fluorescence ‘turn-on’ response for Cr^{3+} and high selectivity over other metal ions. The binding mode between 25 and Cr^{3+} was found to be 1:1 was verified through MALDI-TOF mass spectrum. The detection limit for Cr^{3+} was calculated to be 0.20 μM, which indicated the good sensitivity sensor for Cr^{3+}. Y. Wan[108] et al., introduce a new rhodamine-based fluorescent chemosensor 26, which exhibits a distinct two photon excited fluorescence (TPEF) on/off characteristic upon binding Cr^{3+} ions. The broad excitation wavelength, on/off fluorescence and high selectivity to Cr^{3+} enable 26 to be a powerful Cr^{3+} cation sensor with potential application, especially in biological detection.



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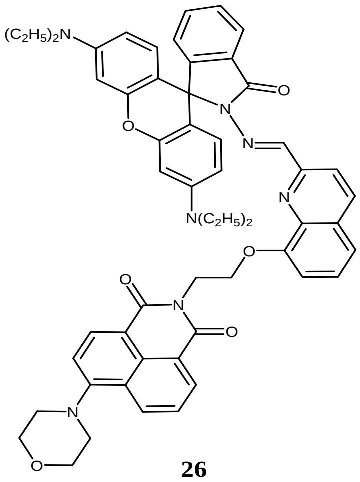

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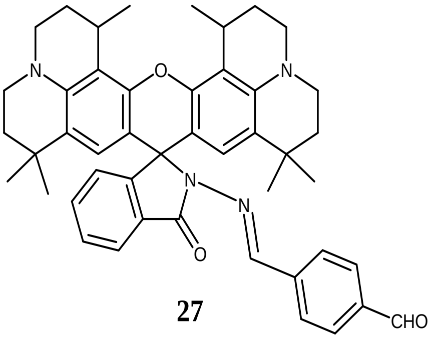

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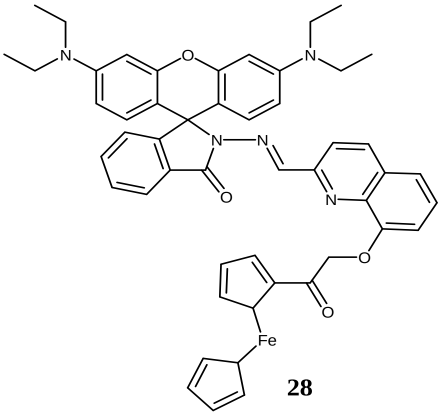


28

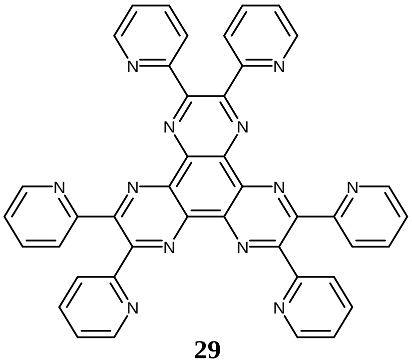
P. Xie[109] designs a new rhodamine-based derivative 27 as a colorimetric and fluorescent “off–on” chemosensor for Cr^{3+} in aqueous solutions. The sensing behaviors of 27 toward Cr^{3+} in neutral aqueous solutions were investigated by UV–Vis absorption and fluorescence spectroscopy. 27 is found to exhibit a significant increase in absorbance at 581 nm and an amplified fluorescence at 600 nm toward Cr^{3+} in a preferential, sensitive and rapid manner. The chemosensor has been used for imaging of Cr^{3+} in living Hela cells with satisfying results.

K. Huang[110] team develop sensor 28 based on rhodamine B with a ferrocene substituent for Cr^{3+}. A significant fluorescence enhancement was occurring in the presence of Cr^{3+}, which was accompanied by changes in the absorption spectrum and the electrochemical parameters.

Furthermore, 28 can be used as a fluorescent probe for monitoring Cr^{3+} in living cells by means of confocal laser scanning microscopy experiments.

Cadmium is a very toxic element and easily absorbed and accumulated by plants and other organisms.[111] Cadmium is an important metal which has widespread use in several industries[112] such as metal alloys, batteries, paint, pigments, plastic, and electroplating and microelectronics devices. It is also used for making phosphate fertilizers in agriculture.[113] Human activity and industrial processes add cadmium to the environment and it serves as toxic pollutant. Excessive intake of cadmium lead to several physiological effects as it can accumulate in organs such as the kidney, thyroid gland and spleen[114], consequently resulting in renal dysfunction, calcium metabolism disorders and increases incidence of certain forms of cancers[115] such as pulmonary, lung, breast, endometrial, nonpulmonary cancers, prostatic, renal cancers. Due to intensive toxic nature of cadmium there is urgent demand for developing excellent methods to monitor cadmium both in the environment and in vivo living cell.

X.H. Bu[116] laboratory design polypyridyl ligand, 2,3,6,7,10,11-hexakis(2-pyridyl)dipyrazino[2,3-f:20,30-h]quinoxaline 29, was found to have excellent fluorescent selectivity for Cd^{2+} over many other metal ions based on the intramolecular charge-transfer mechanism, which makes 29 as a potential fluorescence sensor or probe for Cd^{2+}. An obvious color change from dark to bright blue for 29 upon adding Cd^{2+} which can be visually observed by the naked eye. The fluorescent chemosensor 30 based on the 4, 5-diamino-1, 8-naphthalimide as the fluorophore for exact discrimination between Cd^{2+} and Zn^{2+} reported from X. Qian and J. Cui[117] laboratory. The di-2-picolylamine (DPA) was introduced as part of the receptor, which has a higher affinity to Zn^{2+} and Cd^{2+}. To distinguish between Zn^{2+} and Cd^{2+}, another pyridine moiety was involved as the supplemental group in 30.



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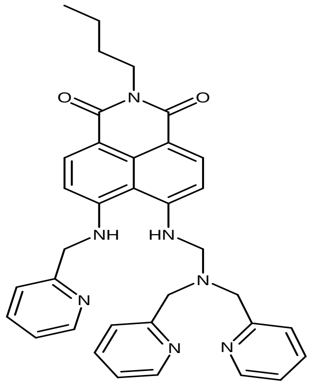
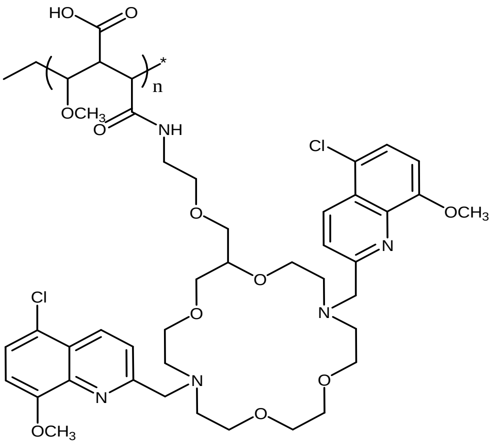


30

R.T. Bronson[118] et al., Develop an ion-selective chemosensor 31 for Cd^{2+}. Immobilization of the chemosensor 31 on quartz was achieved in a simple monolayer and in a thin film using a polymer intermediary the thin film contains much more chemosensor than the monolayer and provides measurable responses to aqueous Cd^{2+} concentrations below 1 µM. T. Gunnlaugsson[119] develop new fluorescent chemosensors 32 which have good water solubility, pH-independent in the physiological pH range and show sufficient selectivity for the selective sensing of Cd^{2+}over Zn^{2+} at pH 7.4. The fluorescence emission of 32 was pH-independent and switched off between pH 3-11 in 100% water.



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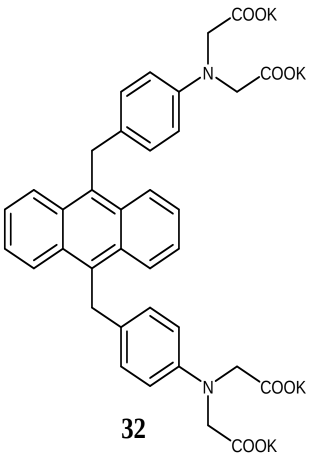
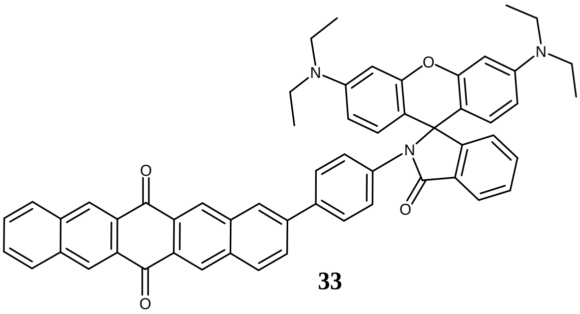


32

Mercury is one of the most hazardous and dangerous species in the nature due to its high affinity for thiol groups in proteins and enzymes, leading to the dysfunction of cells and consequently causing many health problems such as prenatal brain damage, kidney damage, cognitive motion disorder, vision and hearing loss, disorder of central nervous system and even death.[120-122] The release of mercury and its compound into the environment originates from a variety of man-made, industrial and natural sources such as agriculture, paper, pharmaceutical, electronics industry, gold mining, and fossil fuel combustion, burning of coal, oceanic and volcanic eruption.[123-124] Both elemental and ionic form of mercury can be converted to methyl mercury by bacteria in the environment, which subsequently bioaccumulates through the food chain.[125]

When absorbed in the human body, mercury causes damage to the central nervous, DNA, mitosis, and endocrine system.[126]

V.Bhalla[127] et al., synthesized rhodamine−pentaquinone dyad 33 and rhodamine−pentaquinone−rhodamine triad 34 that show TBET in the presence of Hg^{2+} ions. Complexation of the Hg^{2+} ion opens the spirolactam ring of rhodamine moieties to give specific color change as well as fluorescence enhancement at 572 and 582 nm, respectively. In addition, in vitro properties of compound 34 showed good selectivity toward Hg^{2+} ions with “on” fluorescence response.



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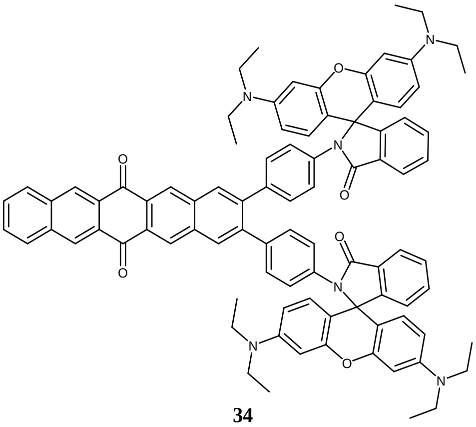
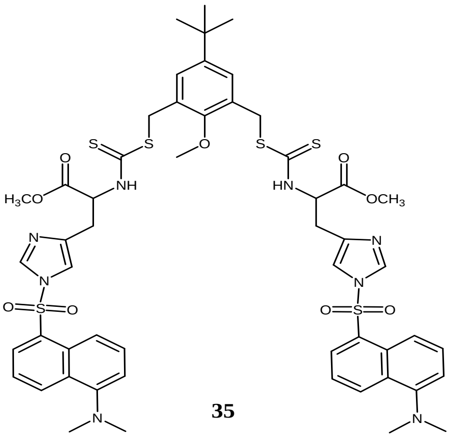


34

S. Bandyopadhyay[128] team reported chemosensor 35 having a bipodal thiocarbamate scaffold attached to histidine moieties senses Hg^{2+} with a remarkable selectivity. In addition to the detection of Hg^{2+} visually under UV light in solution, the chemosensor was used for fabrication of paper strips that detected Hg^{2+} in aqueous samples. The sensor 35 was also used for imaging Hg^{2+} in adult zebrafish and in human epithelial carcinoma HeLa S3 cells. The Z. Li[129] and Co-worker designed 36 according to the TICT mechanism, which exhibited “turn-on” fluorescence response for Hg^{2+} ions. The long wavelength fluorescence, cell-permeability coupled with its function in the wide range of pH, 36 can be applied to image Hg^{2+} ions in living cells.



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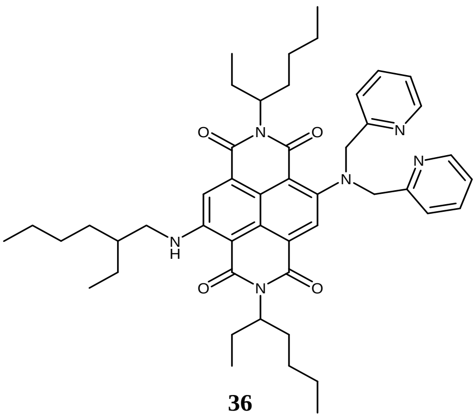


36

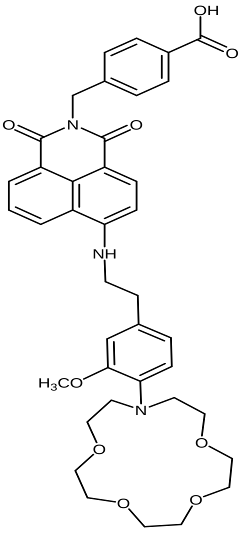
1.3.2. Fluorescent and colorimetric chemosensors for detection of metal cations of S & P-block element.

Along the same line it is interesting to develop sensors for metal ions like Na^+, K^+, Mg^{2+}, and Ca^{2+} which are involved in several biological processes such as transmission of nerve pulses, muscle contraction and regulation of cell activity, stabilization of DNA conformation, ion transport through membranes, maintenance of cell shape and signal transduction, as enzyme cofactor.

Magnesium in macronutrient quantities is found in the bone, it plays a key role in bone remodeling and skeletal development.[130] Mg^{2+} play critical role to regulate and controls over 300 enzyme reactivities including oxidative phosphorylation, glycolysis and DNA and protein synthesis.[131] Magnesium is a cofactor in the phosphorylation of glucose during carbohydrate metabolism.[132]

Calcium play bigger role in the formation of healthy bones and teeth, about 99% of calcium is concentrated in the teeth and bones and about 1% is present in biological fluids and soft tissues, in which the calcium cation plays a key role in, e.g. cell signaling.[133] Ca^{2+} plays an essential role in a variety of cellular processes, including cell proliferation, cell growth, cell death, hormone secretion, muscle contraction, gene transcription and neurotransmitter release.[134-136] Moreover, disturb in calcium levels in serum leads to several diseases such as hyperthyroidism, hyperparathyroidism, osteoporosis and malignant tumors.[137]

H. He[138,139] et al., chemosensor 37 and 38 are employed in determination of blood electrolyte level for simultaneous recognition of Na^+ and k^+ in it. The sensing of Li^+ in aqueous medium was very difficult job due to higher hydration of small Li^+ in water. Gunnlaugsson[140] et al. did this job by developing sensor 39 uses in acetonitrile as solvent.



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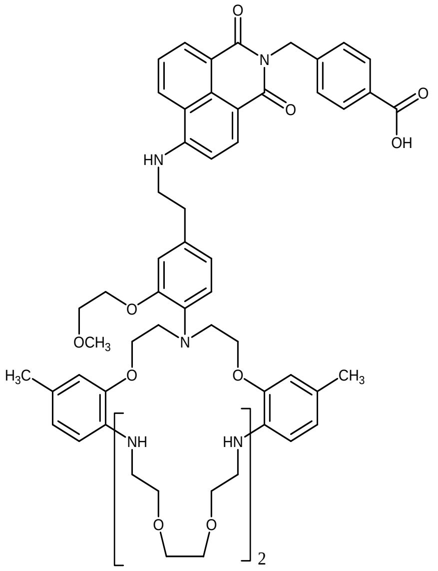

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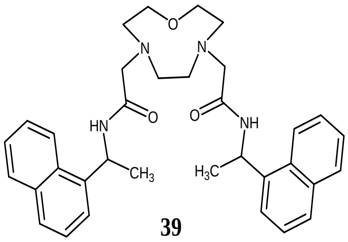

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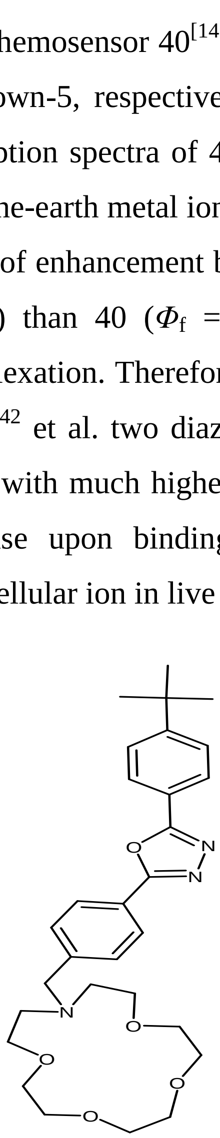
The chemosensor 40[141] and 41 was designed for Mg^{2+}, consisting of one and two monoaza-15-crown-5, respectively, on photoemittive diaryl-1,3,4-oxadiazoles. The fluorescence and absorption spectra of 40 and 41 were significantly distorted by alkali metal ions. However, alkaline-earth metal ions, Mg^{2+}, Ca^{2+} and Ba^{2+} produced high fluorescence enhancements, the order of enhancement being $Mg^{2+} > Ca^{2+} > Ba^{2+}$. The sensor 41, which is a poor emitter (Φ_f = 0.039) than 40 (Φ_f = 0.065) experienced the highest emission by 24-folds upon Mg^{2+} complexation. Therefore sensor 41 is employed to recognize Mg^{2+} in biological systems. F.I. Wolf142 et al. two diaza-18-crown-6 hydroxyquinoline derivatives 42 (R= H, Cl), that bind Mg^{2+} with much higher affinity than other available probes and show a strong fluorescence increase upon binding. Furthermore, sensor 42 can be effectively employed to map intracellular ion in live cells by confocal microscopy.



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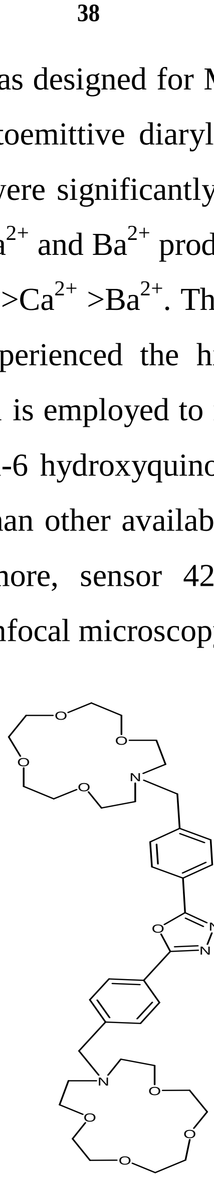

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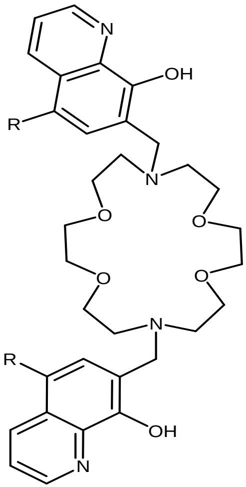
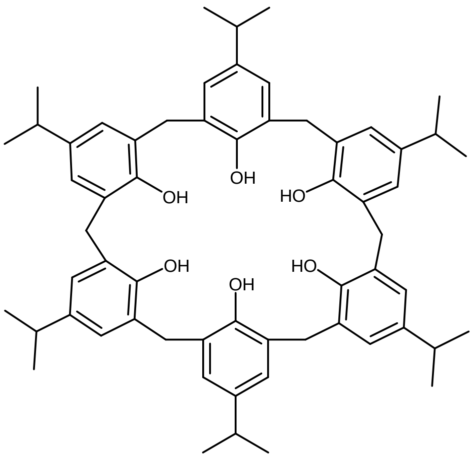


R=H & Cl **42**

A. K. Jain[143] develops new PVC-based membrane using p-isopropylcalix [6] arene 43 as an ionophore has been as a calcium-ion-selective sensor. The sensor 43 exhibits a good potentiometric response to Ca^{2+} ion. The 43 can be used for a period of 3 months without any drift in potential. The useful pH range for the electrode was found to be 2.5–6.0, and it works well in mixtures with non-aqueous content up to 25% (v/v). The 43 can also be used successfully as an indicator electrode in the potentiometric titration of Ca^{2+} against EDTA.

K.Suzuki[144] et al., designed the first Ca^{2+}-Mg^{2+} multifluorescent probe, 44 by combining in a single molecule a coumarin moiety as a stable fluorophore BAPTA (*O*,*O*´-bis(2-aminophenyl)ethyleneglycol-*N*,*N*,*N*´,*N*´-tetraacetic acid) as the Ca^{2+} selective binding site. The electron-donor site of the chromophore and a charged β-diketone as the Mg^{2+} selective binding site as the electron-accepting site. Moreover 44 employed for simultaneous imaging of intracellular Ca^{2+} and Mg^{2+}.

X. Zhang[145] synthesized new fluorescent Ca^{2+} probe 45, which consists of 1,2-bis(2-aminophenoxy)ethane-N,N,N′,N′-tetraacetic acid as a Ca^{2+}-chelating moiety and two benzothiazolium hemicyanine dyes as fluorophores. Upon addition of Ca^{2+}, the fluorescence spectra of 45 displayed a significant enhancement in fluorescence intensity and blue shift of 20 nm in the emission spectrum. The 45 can be used as a double targetable Ca^{2+} probe that can be used to report cytoplasmic Ca^{2+} and nuclear Ca^{2+} simultaneously.



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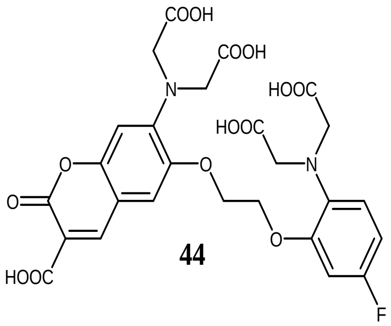

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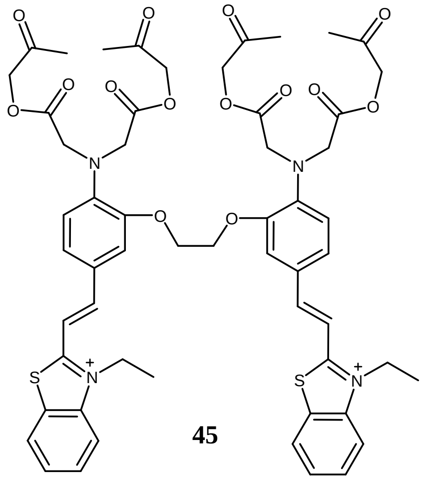
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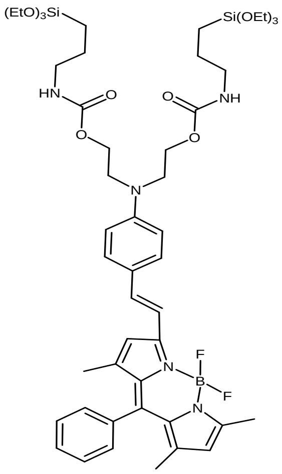
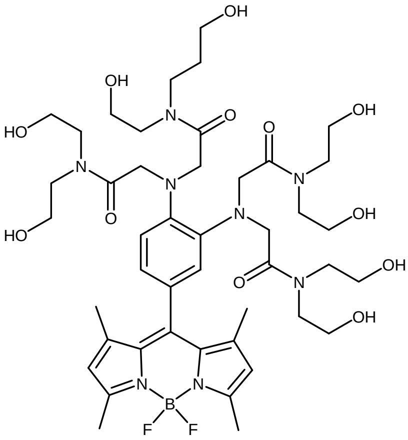

46

Among heavy metal ions, Pb^{2+} is one of the most dangerous and highly toxic metal causing adverse effects on human health and environment.[146] Lead is largely distributed in the environment such as in air, soil and water due to its widespread use in batteries, gasoline, and pigments.[147] The main sources of lead pollution are coal combustion, petrol and diesel burning, mining, metal smelting, use of Pb based paint, leaded gasoline and use of Pb-containing pipes in water sup- ply systems.[148, 149] The accumulation of Pb^{2+} in the body may leads to many serious human health problems, including neurological, reproductive, cardiovascular and developmental disorders, muscle paralysis, mental confusion, memory loss, anaemia, abdominal pain and vomiting, physical growth impairments, nerve disorders, kidney disorders and reduced IQ.[150-152]

J.H. Jung and D.D. Kang[153] readily prepared BODIPY-functionalized $Fe_3O_4@SiO_2$ core/shell nanoparticles 46. The 46 behave as fluorogenic and chromogenic chemosensor shows a high affinity and high selectivity for Pb^{2+} over other competing metal ions. Fruther, 46 tested for imaging Pb^{2+} ion in living cells. X. Li[154] and Y. Han team design and synthesize a new fluorescent sensor 47 based on the BODIPY fluorophore and the polyamide receptor for Pb^{2+}. The sensor 47 is highly selective and sensitive for Pb^{2+} upto ppb levels in water.

J. Chang[155] develops a new fluorescent turn-on sensor 48 based on fluorescein as fluorophore for selective detection of Pb^{2+} in water and in living cells. The 48 demonstrate visible wavelength excitation and emission profiles and 18-fold fluorescence enhancement upon Pb^{2+} binding. Additionally, confocal microscopy experiments prove that 48 can monitor changes in Pb^{2+} levels within living mammalian cells. H. Cao and co-workers[156] report a ratiometric fluorescent sensor 49 that shows considerable selectivity and high affinity to Pb^{2+} in aqueous media. Binding induces excimer formation, given that a highly sensitive ratiometric measurement of lead concentrations.



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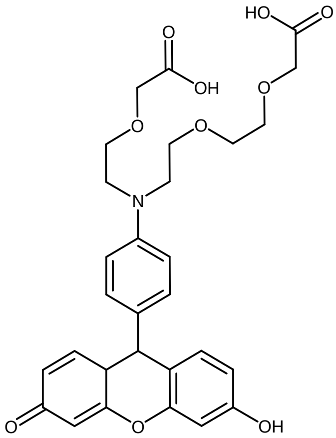

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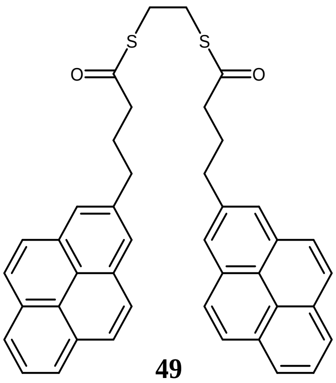
Aluminum is the third most prevalent element and the most abundant metal in the earth’s crust. It is largely dispersed in the environment due to its widespread use in water treatment, as a food additive, aluminum based pharmaceuticals, medicines, occupational dusts, aluminum containers and cooking utensils and use of aluminum foil, vessels and trays results in moderate increases in the Al^{3+} concentration in food.[157] The excessive exposure to aluminum may affect the absorption of calcium in the bowel, causing softening of the bone, atrophy and even aberrance and also affects the absorption of iron in blood, causing anemia.[158] The toxicity of aluminum in humans causes damage of the central nervous system resulting neurodegenerative diseases such as Alzheimer’s and Parkinson’s, dementia and encephalopathy, intoxication in hemodialysis patients, Rickets, gastrointestinal problems, headaches, breast cancer, decreased liver and kidney function.[159-162]



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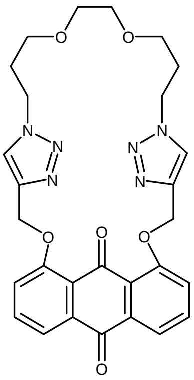

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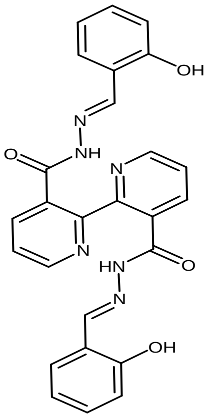

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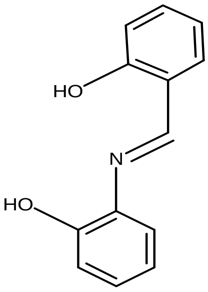

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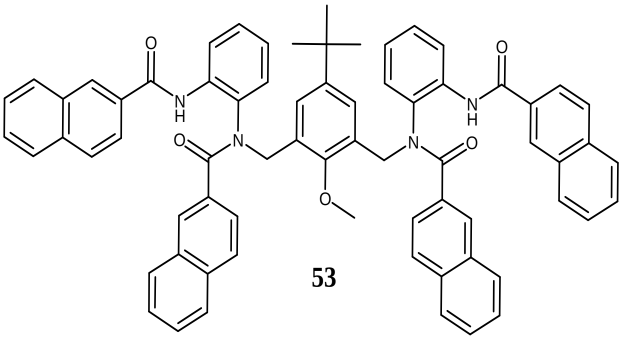

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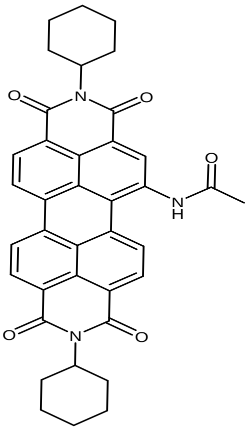
J. Kim and J. S. Kim[163] synthesize chemosensor 50 bearing a 1,2,3-triazole ring spacer for the selective detection of Al^{3+}. The addition of Al^{3+} ions to 50 induced a considerable change in fluorescence intensity, attributable to ICT and CHEF effects from the 1, 2, 3-triazole ring. The electrochemical behavior of 50 in the presence of the Al^{3+} ion was significantly altered compared with those of the other metal cations tested. Y. Guo[164] et al., synthesize and characterize a schiff base-type fluorescent chemosensor 51, 2, 20-bipyridyl-3, 30-bis-(N, N´-disalicylidene)-formyhydrazone. The Al^{3+} induces the fluorescence enhancement of the formyhydrazone and results in “OFF-ON” type sensing with excellent selectivity and high sensitivity in aqueous system. Furthermore, 51 have potential for the detection of Al^{3+} in the biological environment.

S. Kim[165] et al., simple salicylimine-based fluorescence turn-on chemosensor 52 for Al^{3+} ion. Upon treatment with Al^{3+}, the fluorescence enhancement at 510 nm occurs due to formation of a 1:1 complex between the 52 and Al^{3+}. As the concentration of Al^{3+} was increased, the fluorescence gradually increased. In addition, 52 could be used to map intracellular Al^{3+} distribution in live cells by confocal microscopy. S. Bandyopadhyay[166] and Co-workers demonstrates a sensor 53 by incorporating local hydrophobicity around a multidentate receptor to achieve desolvation of a strongly hydrated Al^{3+} ion results in efficient binding of the ion, and consequently elicits a strong fluorescence response. The sensor shows a remarkable detection limit of 57 nM for Al^{3+} which is among one of the lowest reported so far.

1.3.3. Fluorescent and colorimetric chemosensors for detection of anions.

The design and synthesis of molecular probes for sensing and recognition of anions has been a subject of intense research as anions play a major role in many chemical and biological processes and also behave as pollutants in our environment.[167] A deficiency of F^{-} may cause tooth decay, while an excess of F^- might lead to heart disease, fluorosis, acute gastric and kidney problems.[168,169] The chloride Cl^- and nitrate NO_3^- anions are tracers of water pollution.[170] Iodide plays vital role in several biological processes such as neurological activity and thyroid function. The iodide content of urine and milk is often required to provide information for nutritional, metabolic and epidemiological studies of thyroid disorder.[171] However, excessive application of iodide ion and iodine has caused serious environmental pollution and physical diseases in human as hypothyroidism, autoimmune thyroid disease and papillary thyroid cancer.[172] Cyanide anion is highly toxic and dangerous environmental pollutant associated with leakage from electroplating and herbicide industries.[173] The CN^- anion has ability to bind strongly with the active site of cytochrome–oxidase and retards the mitochondrial electron transport chain process, consequently decreases oxidative metabolism.[174] Phosphate anions $H_2PO_4^-$ not only play significant roles in biological processes such as genetic information storage, energy transduction, signal processing and membrane transport, but also are key pollutants.[175] Acetate AcO^- exhibits specific biolochemical behaviors in the enzymes. Combined with coenzyme it becomes the key substance in the metabolism of carbohydrate.[176] The HSO_4^- is important inorganic anion as it is found in many agricultural fertilizers, industrial raw materials, and nuclear fuel waste and has toxic effects as a pollutant when it gets into the environment.[177]



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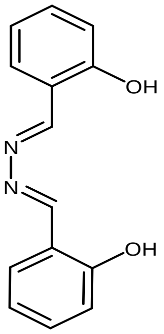

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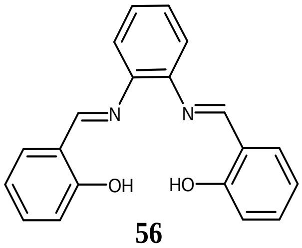

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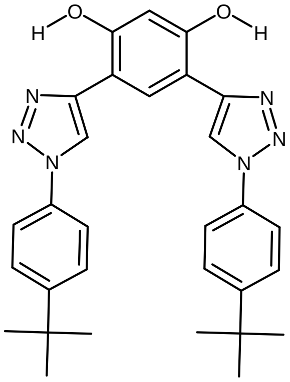
L.M. Wang[178] et al., fabricated new colorimetric and ratiometric fluorescent sensor 54 based on a perylene diimide moiety for naked-eye detection of fluoride ion. Addition of F^- to solution of 54 in dichloromethane (DCM) resulted in an obvious color change (from red to blackish green) because of a large red shift (151 nm) in absorption. The recognition mechanism was attributed to the intermolecular proton transfer between a hydrogen atom on the amide N position of 54 and F^-. The detection limit was calculated to be 0.14 µM. S. Shao[179] and co-workers developed two salicylaldehyde based colorimetric and fluorescent chemosensors 55 and 56, both receptors showed unique selectivity for F^- over other anions in DMSO solution. ^{1}H NMR titration experiments revealed that the F^- induced colorimetric and "turn on" fluorescence response was due to hydrogen bonding interaction between the OH protons and F^-.



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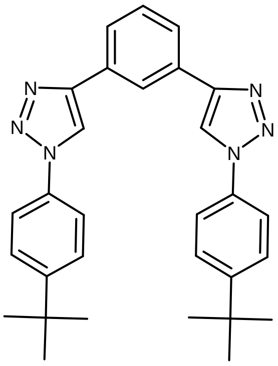

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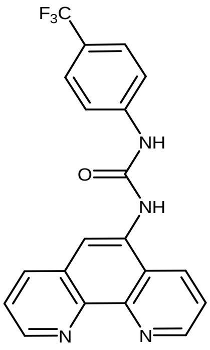

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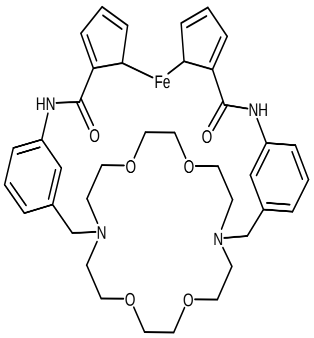
A. H. Flood[180], group design aryl-triazole pentads sensor 57 and 58 with intramolecular hydrogen bonds to enhance chloride binding. Both the sensor has dual hydrogen bond donor and acceptor properties of their 1,2,3-triazoles that helps selective chloride binding. T. Gunnlaugsson[181] et al. fabricated urea functionalized phenanthroline sensor 59. The fluorescence enhancement of 59 observed only in the presence of Cl^- in CH_3CN whereas for the other ions fluorescence quenching was observed. The binding stoichiometry was predicted from non-linear regression analysis and was found to be 1:1 as well as 1:2 as a result of coordination of the chloride to two equivalents of 59.

C. Suksai[182] and co-worker synthesize heteroditopic receptor 60 containing a crown ether and amidoferrocence groups. The 60 showed a switched-on binding for Br^- in the presence of Na^+ and a switched-off binding in the absence of Na^+. Binding affinity were evaluated as Kass = 16,096 M^{-1}. Receptor 60 was sense Cl^- and Br^- electrochemically.



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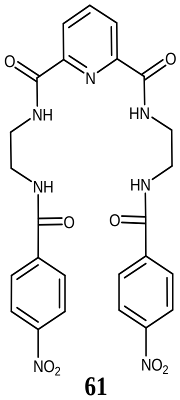

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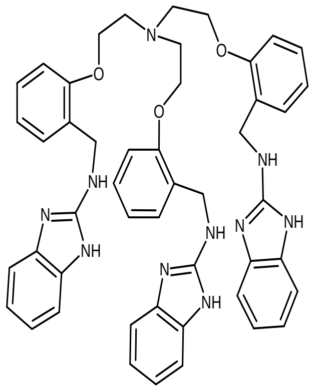

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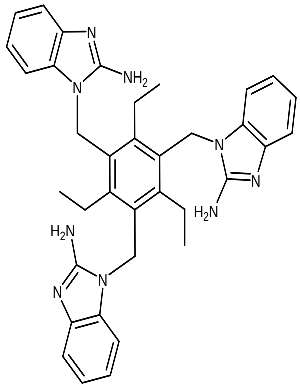

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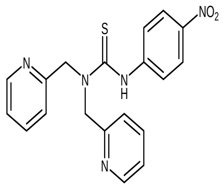

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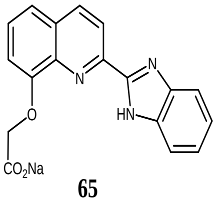

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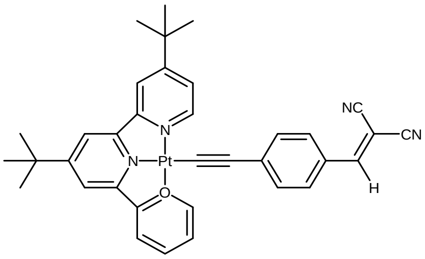

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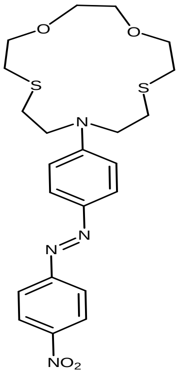

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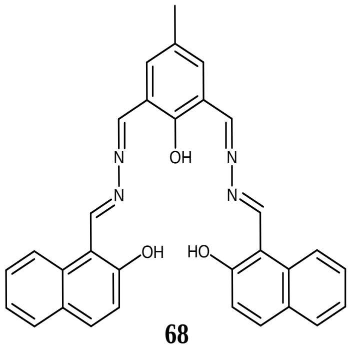


68

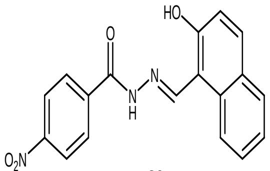
L. Feng[183] and co-worker reported colorimetric and fluorescent sensor N^2,N^6-bis(2-(p-nitrobenzamido) ethyl)pyridine-2,6-dicarboxamide 61, for iodide-sensing. The recognition properties of 61 toward various anions was evaluated in THF/H_2O (4/1, v/v) solution by fluorescence emission and UV–Vis absorption spectroscopy. The detection of iodide ion by 61 was based on intermolecular charge transfer (ICT) and heary atom quenching mechanism. By adding iodide ions, the color of 61 solution changes from colorless to yellow and a red-shift in the absorption and emission spectra can be observed.

Another novel tripodal fluorescent receptor 62 bearing benzimidazole motifs was synthesized from D.O. Jang[184] laboratory for iodide recognition. The receptor 62 showed changes in fluorescence intensity only with I^- over a variety of interfering anions in CH_3CN/H_2O (9:1, v/v) solution. D.O. Jang[185] laboratory again synthesized a novel 1,3,5-substituted triethylbenzene derivative with a 2-aminobenzimidazole moiety 63 as a binding and signaling subunit. The sensor 63 shows high selectivity for iodide ions in a buffered CH_3CN/H_2O (99:1, v/v) solution. The photophysical properties of 63 were obtained from UV-Vis absorption and fluorescence spectroscopy.

J. Kang[186] and co-worker synthesize chemosensor 64, which show high selectivity towards CN^- ion over variety of other competing anions. In aprotic acetonitrile solvent, the selectivity for CN^- anion get disappear whereas the nonselective colour change was observed for strongly basic anions such as F^-, AcO^-, $H_2PO_4^-$. The detection limit of 64 was far below WHO guidelines for drinking water. Y.Y. Guo[187] et al, designed a new fluorescent chemosensor sodium 2-(2-(1H-benzo[d]imidazol-2-yl)quinolin-8-yloxy)acetate 65, based on 8-hydroxyquinoline derivative. 65 displays a fluorescence quenching effect with Hg^{2+} in aqueous solution to form the compound mercury(II) 2-(2-(1H-benzo[d]imidazol-2-yl)quinolin-8-yloxy)acetate chloride 65.Hg^{2+} which could be fast dissociated by the addition of cyanide so that “ON–OFF–ON” type fluorescence change was observed. Furthermore, 65.Hg^{2+} is suitable for the detection of CN^- in biological environment by fluorescence microscopic imaging.

Jean-Luc Fillaut[188] and co-worker describe a rational approach to luminescence turn-on sensing of CN^- by a dicyanovinyl-substituted acetylide Pt (II) complex 66, which underwent nucleophilic addition reaction with cyanide anions to the α-position of the dicyanovinyl group. The charge transfer band from ML′CT to MLCT/L′LCT demonstrates selectivity for cyanide anions in this acetylide Pt (II) sensor. The 66 exhibits strong phosphorescence with CN^- ion. R. M. Manez[189] laboratory designed aza-oxa-thia macrocycle based chemosensor 67 for nitrate ion recognition. The charge transfer band from the 540 nm to 490 nm was observed for 67 with a concomitant change in color from red to yellow.

S. Goswami[190] and co-worker design and synthesize a novel fluorescent probe 68, it ascertains dual channel sensing ability for the Cu^{2+} ion based on fluorescence quenching mechanism with noticeable color change from light to dark yellow and exhibited high selectivity for acetate in acetonitrile over other common anions accompanied with exciting color changes from light yellow to pink. Another naphthalene based receptor 69 came into the literature from S. Goswami[191] group which shows selective binding for acetate anion by remarkable color change from colorless to pink. The anion recognition profile of the receptor 69 via hydrogen bonding interactions was monitored by UV–Vis, fluorescence, and ^{1}H NMR titrations. The X. Shang[192] team fabricates probe 70 containing p-NO_2 group which exhibits strong binding for AcO^- anion. Addition of AcO^- anion to sensor 70 gave rise dramatic color change from colorless to orange and decrease in the fluorescence emission intensity of the 70 was observed due to quenching of PET process from the thiourea NH to –NO_2 group.



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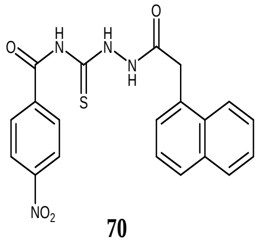

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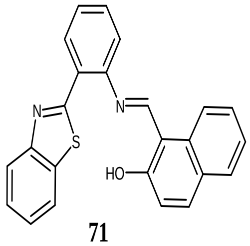

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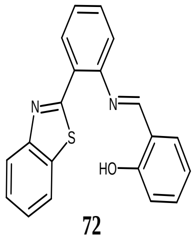

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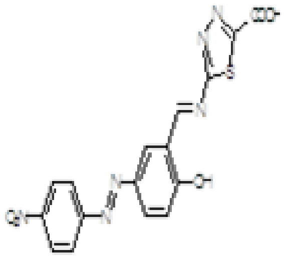

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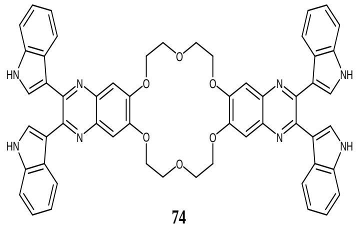

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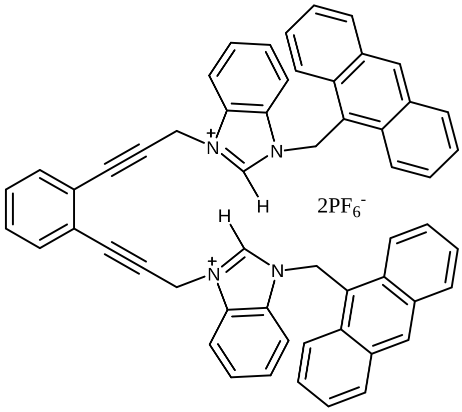
Bhardwaj[193] et al., designed a benzthiazole-based multifunctional chemosensor **71** and **72** with siderophores like hydrogen bond donor and acceptor binding sites for recognition of both Fe^{3+} and oxyanion HSO_4^-. The sensors recognizes Fe^{3+} selectively through enhancement of fluorescence emission intensity at 440 nm and recognizes $HSO4^{-}$ through a bathochromic shift in UV-Vis spectra from 315 nm to 365 nm with clear isosbestic points at 345 nm and 395 nm.

T.B. Wei[194] and co-worker develop a novel chemosensor 73 bearing Schiff base structure, nitrophenyl azobenzol and carboxyl groups for the recognition of $HSO4^{-}$ anion. The chemosensing behavior of 73 was studied by using UV–Vis and ^{1}H NMR titration, which revealed that 73 displayed a remarkable binding ability for the $HSO4^{-}$ with an association constant $Ka = 6.59 \times 10^4 M^{-1}$.

X.-M. Liu[195] et al., fabricated a new ditopic ion pair receptor 74 containing two bis-indole moieties and a bis-benzocrown ether unit and shows a remarkable color switching (ON-and-OFF) function induced by F^- and K^+ recognition. The ditopic receptor 74 binds to HSO_4– in the presence of $74.K^+$.



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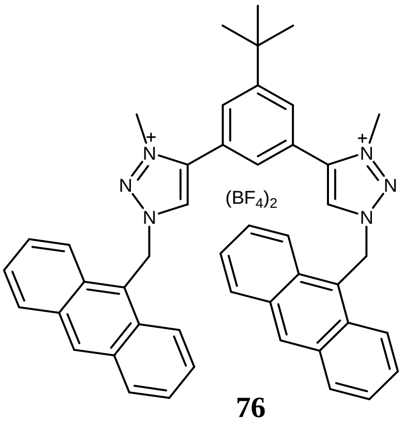

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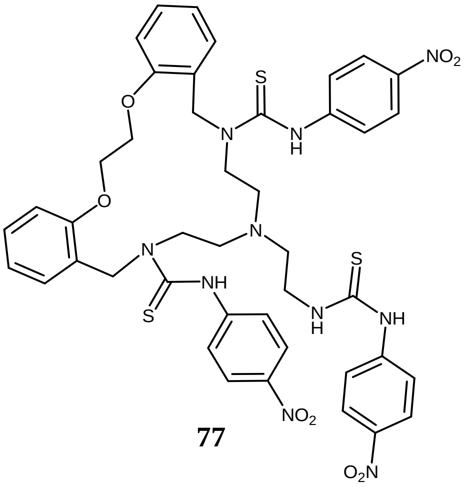

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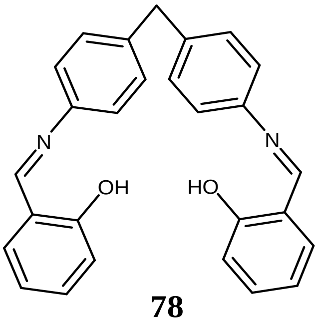

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K. Ghosh[196] et al., design enediyne scaffold-based new chemosensor 75. The sensor 75 recognize $H_2PO_4^-$ in CH_3CN containing 1% DMSO by showing a ratiometric change in fluoroscence emission upon complexation. The association constant of 75 with $H_2PO_4^-$ was calculated as $3.06 \pm 0.6 \times 10^4$ M^{-1}. Q.Y. Cao[197] group designed and synthesized a novel anthracene-based anion receptor 76 bearing two 1,2,3-triazolium donor groups. In competitive solvents, 76 show good selectivity with fluorescence enhancement toward $H_2PO_4^-$ with no interference from other anions. A. Aldrey[198] et al., reported a new H-bond macrocyclic chromogenic chemosensor 77 in organic media, which show excellent selectivity for dihydrogenphosphate over other inorganic anions, such as acetate or fluoride by drastic changes in its UV–Vis spectra.

N. Singh[199] and Co-worker design a dipodal sensor 78 to map Al^{3+} in HEPES buffered THF/H_2O (7:3, v/v) through excited state proton transfer, exhibiting a quenching at 355 nm and enhancement at 480 nm. The 78 binds strongly with Al^{3+} results into the formation of aluminium complex ($78.Al^{3+}$), which displays a highly selective response to perchlorate anion ClO_4^- over other anions by producing a new band at 428 nm. The chemical inputs of Al^{3+} and ClO_4^- satisfies the conditions of AND molecular logic gates and in a sequential manner generates an output which mimics the functions of a security keypad loc.

1.4 Conclusion and Outlooks

The work discussed in this review illustrates that the colorimetric and fluorescence based sensing is an effective approach to recognize the metal cations and anions in the organic and aqueous media with improved sensitivity. In this review, we have reported a large variety of colorimetric and fluorescence chemosensors for transition metal cations and cations of s- & p-block element and anions. An interesting feature of this review is that it consists of lot of information about the important as well as hazardous role played by each metal cation and anions were existing in aqueous, organic and environmental media along with their available colorimetric and fluorescent chemosensors. We believe that by referring this review article the chemistry community devotes strong attention towards the development of sensory systems that will be able to detect or monitor the concentrations of metal cations and anions in real-time and real-space. By this article a wide horizon is therefore open for further investigation and developments in the field of chemosensors. In other words, there is still a great demand for the development of more and more efficient chemosensors for cations and anions. From this work it is obvious that the future of cation and anion sensing is quite intense and many new structures, structural motives and applications are still yet to be fully explored. We hope to be able to participate in those future endeavours.

1.5 ACKNOWLEDGEMENT

S.R.Patil is very grateful to all members of our research group and to our collaborators, all of whose names appear on the reference list and Dr. U. D. Patil is grateful for the financial support from the DST, New Delhi, INDIA, under FAST TRACK scheme for Young Scientists, (Reg. No. CS-088/2013). The SRP is grateful to Professors Suban K. Sahoo, Carl Redshaw, Debasis Das, Chullikkattil P. Pradeep, FabiaoYu, and Lingxin Chen for their helpful discussions and fruitful collaboration. It is a pleasure to acknowledge the support of Dr. U. D. Patil and Dr. A. A. Patil for their inspiration and hard work.

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