RESEARCH PAPER

A partial review on Zn^{2+} fluorescence chemosensor

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Abstract: Between all the sensing methods, UV-visible and fluorescence spectroscopy take hold of the most attention of sensor research laboratories owing to its highly selective and sensitive nature, simple in operation method and low cost. Besides zinc plays a vital role in restoring white blood cell function, protein synthaesis, regulation of neurotransmitters function, functions of various enzymes and development of sex organs. Several diseases like, infantile diarrhoea, epilepsy, Alzheimer's disease and ischemic stroke are identified as a result of zinc deficiency. Other side due to modernization zinc pollution became threatening issues. So identification of different metals like, zinc by fluorescence technology has become a vital subject in research areas

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Introduction

Chemistry is the central science and opens doors to wide views of science, environment and social development. Chemistry is involved in our everyday lives and there is a vast range of opportunities both inside and outside the lab.[1] Chemistry is trying to solve global challenges such as human health, energy and the environment.[2] Current research in Chemistry is targeting oriented design, synthesis and exploration of multidimensional properties. Basic idea focuses to characterise a product that could show some optical/electrical/magnetic/biological/medicinal activities or could improve mechanical strength, environmentally benign, economically cheap and so on. Lot of different analytical techniques fulfilling these demands are available. Proposed procedures for metal analyses include flame or graphite furnaces atomic absorption spectroscopy (AAS),[3] photometric methods, inductively coupled plasma emission or mass spectrometry (ICP-ES, ICP-MS),[4] total reflection X-Ray fluorimetry (TXRF)[5] and anodic stripping voltammetry (ASV).[6] Photometry and AAS are single element(one specific element) methods, ICP-ES, ICP-MS and TXRF are used for multi-element (more than one specific element)analysis, and voltammetry is an oligo-element method. These techniques recommend quality limits of detection (LOD) and broad linear ranges, but expensive analytical instruments developed for the utilization in the laboratories. In the last decade chemical sensors are developing for different of applications. Chemical sensors can be a useful tool to monitoring all matters.

1. Chemical sensors

Chemical sensor is "*a portable miniaturized analytical device, which can deliver real-time and on-line information in presence of specific compounds or ions in complex samples*". Discriminating and delicate sensors for monitoring different elements in clinical , biological, environmental issues is a up growing challenging task.The development of various tools and computer software's makes it possible to design various sensors utilizing most of the known chemical, physical and biological properties that have been made used in chemistry.

Fluorescence-based approaches and various parameters such as, fluorescence intensity ,Stokes shift, anisotropy, excitation ,emission spectra and fluorescence lifetime can impart considerable flexibility as an analytical approach for qualitative recognition and quantitative estimation of various cations, anions , H^+ and molecules.[7]

2. Fluorescent chemosensors

Fluorescent chemosensors one of the most commonly used chemosensors.[8,9] Several methods, such as atomic spectrometry,[3] inductively coupled plasma mass spectrometry,[4] reversed-phase high-performance liquid chromatography,[10] electrochemistry,[11] and anodic stripping voltammetry (ASV),[6] have been progressed to sense different in vitro and in vivo biologically salient elements such as various metal ions and anions. But, these methods are extensive, time consuming procedures, high cost or the use of sophisticated instrumentation.[12] But fluorescent chemosensors is highly selective and sensitive towards metal ions even the analyte to be studied is exists in very minute amounts. It is rapidly performed, nondestructive, suitable for high-throughput screening applications. Fluorescence sensor accomplished in solid , liquid and gaseous mediums. So, fluorescent chemosensors are highly convenient in a variety of fields including bio-medicinal , analytical chemistry and environmental chemistry.

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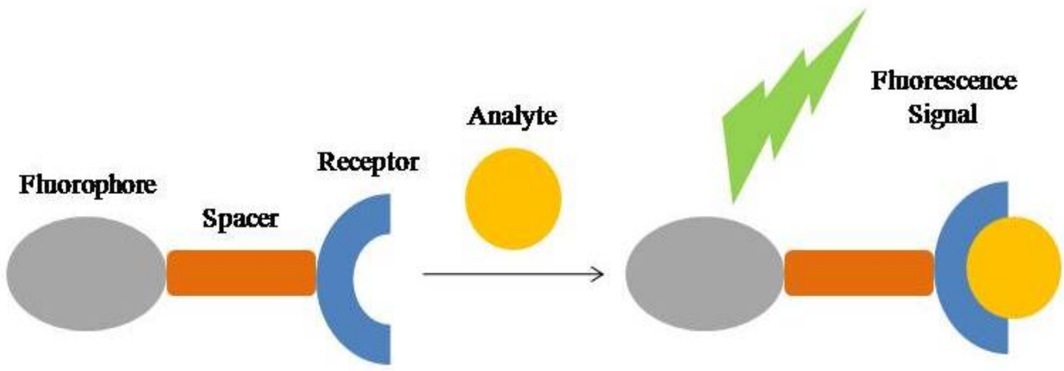


Fig. 1. Main aspects of fluorescent molecular sensors for cation recognition

Fluorescent sensors consist of a fluorophore linked to a receptor **(Fig. 1.**). In the design of such sensors, attention should be paid to both receptor and reporter or signaling moieties. The *signaling moiety* is a signal transducer, i.e. it converts the information (recognition event) into an optical signal expressed as the changes in the photophysical characteristics of the fluorophore. The concept of soft-hard acid base principle of interaction of ionic centres is the fundamental bases of selection followed by the principle of coordination theory, size of chelate ring, space in chelate cavity etc. monitor the specificity of the sensing activity. Receptors are designed based on the coordination chemistry principle and integrated or attached through spacer with transducer unit. Binding of cation to the receptor has developed a strain over the transducer unit which would be responsible for fluorogenic activity enhancement or quenching. Design of receptor may be acyclic or cyclic/macrocyclic with specific binding or chelating centres. The cationic complex of fluoroionophore may interact with external anions who may selectively extract cation from
the binding pocket which depends on relative binding strength and may be responsible for specific change in fluorescence intensity. This would help to indirect sensitivity of anions and also logic operation may be demonstrated.

Upon binding with a metal ions or anions, two processes can occur: Chelation Enhancement of Quenching (CHEQ), which means that the fluorescence emission is quenched, and Chelation Enhancement of Fluorescence (CHEF), where the emission intensity is increased. Several types of quenching processes observed which include collisional and static quenching, as well as Fluorescence Resonance Energy Transfer (FRET). Collisional or dynamic quenching can be considered as a reduction in fluorescence intensity due to a collision of the quencher with the fluorophore in the excited state. Upon contact the fluorophore returns to the ground state without light emission. One of the best known collisional quenchers which quench almost all known fluorophores is molecular oxygen. It is therefore often required to remove dissolved oxygen to obtain consistent measurements. In static quenching a non-fluorescent complex is formed between the quencher and the fluorophore. In contrast to both of these quenching processes, FRET does not require contact of the quencher with the fluorophore. The energy transfer occurs without the appearance of a photon. Different fluorescence mechanisms for metal sensing are given below.

For example the specific identification by using chromogenic or fluorogenic sensors of Cr^{3+} ,[13] Mn^{2+},[14] Fe^{3+} ,[15] Co^{2+},[16] Ni^{2+},[17] Cu^{2+},[18] Zn^{2+},[19] are reported in literature. Nontransition metal ions identification by fluorogenic sensor is a scope of intensive research and reports available for Cd^{2+},[20] Hg^{2+},[21] Pb^{2+},[22] Al^{3+} [23,24] etc. Classical complexometric indicators (many of which are natural products also used as histological stains and some of which date back to the early 1800s) may have greater or lesser degrees of specificity: for example, calcein and Eriochrome Black T are used to detect Ca^{2+}, Mg^{2+}, and Al^{3+}; hematoxylin for Fe^{3+} and Al^{3+}; murexide for Ca^{2+}, Cu^{2+}, Ni^{2+}, and Transition Metal ions. The design of sensor for f-block metal ions are up healing task and are approaching fast.[25]

The use of dyes for the detection of anions has been an active area of research and has been extensively studied recently.[26-36] Anion receptors can be neutral or positively charged and in general anion-receptor interactions are dominated by electrostatics and hydrogen bonding. It is common to link a chromogenic or fluorescent reporter moiety to a specific chelating receptor, but one may also use fluorescent Lewis acids directly. Dyes with urea, thiourea, or naphthalimide sites, or metal ion containing dyes have been used heavily as anion binding sites for both colorimetric and luminescent detection. Electrostatic attraction brings anion and sensor very close and then selectivity of the interaction is directed by choice of soft-acid base property, hydrogen bonding efficiency, size of the cavity or binding site, efficiency of anion---π interaction etc. These interactions associated with collisional effect may enhance or quench the emissivity of the sensor. Different sensors for identification of CO_3^{2-},[27] HSO_4^-,[28] NO_2^-,[29] CN^-,[30] S^{2-},[31] F^-,[32] I^-,[33] PO_4^{3-}

,[34] $H_2PO_4^-$,[35] acetate [36] etc are well reported in recent literature.

Prominent areas of molecular sensor research are the detection of biomolecules for disease diagnosis, the detection of volatile components for air pollutant characterization, and the detection of chemical analytes for evaluation of physiological activity.

Small molecules like environmental pollutant (CO, HCN, H_2S, SO_2, NO_x), Green House Gases (CO_2, CH_4, vapour, CFC, Cl_2 etc.), Amino acids, Alcohols, low molecular weight Carboxylic Acids, Aldehydes, thiols, aromatic amines, pesticides, herbicides, etc. have been required to be detected at very low concentration for analytical, environmental and health reasons. Many dyes (permitted or nonpermitted) are used as food colours and most of them are restricted or not permitted by FDA; quality of food control for health and safety and very accurate concentration measurement are most urgent. Among the many biologically important thiols such as cysteine (Cys), homocysteine (Hcy), and glutathione (GSH), GSH is well-known as the most important and abundant antioxidant in plants, animals, fungi, and some bacteria and archaea.[37,38] Many groups are tirelessly working for the design of molecular sensor for Alcohols,[39] pesticides and herbicides,[40] NO_x,[41] H_2S,[42] Glutathione,[43] Galactyl.[44]

2.1. Photoinduced electron transfer (PET)

Photoinduced electron transfer is a quenching process which occurs between organic fluorophore and suitable electron donating moieties mainly observed in a fluorofore which linked with a amine moiety via a methylene spacer. This process has huge application in the design of cation sensor and pH indicators. Such as anthracene– amino acid,[45] After absorption of a photon by the flurophore, an electron is transferred from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) (**Fig. 2**),

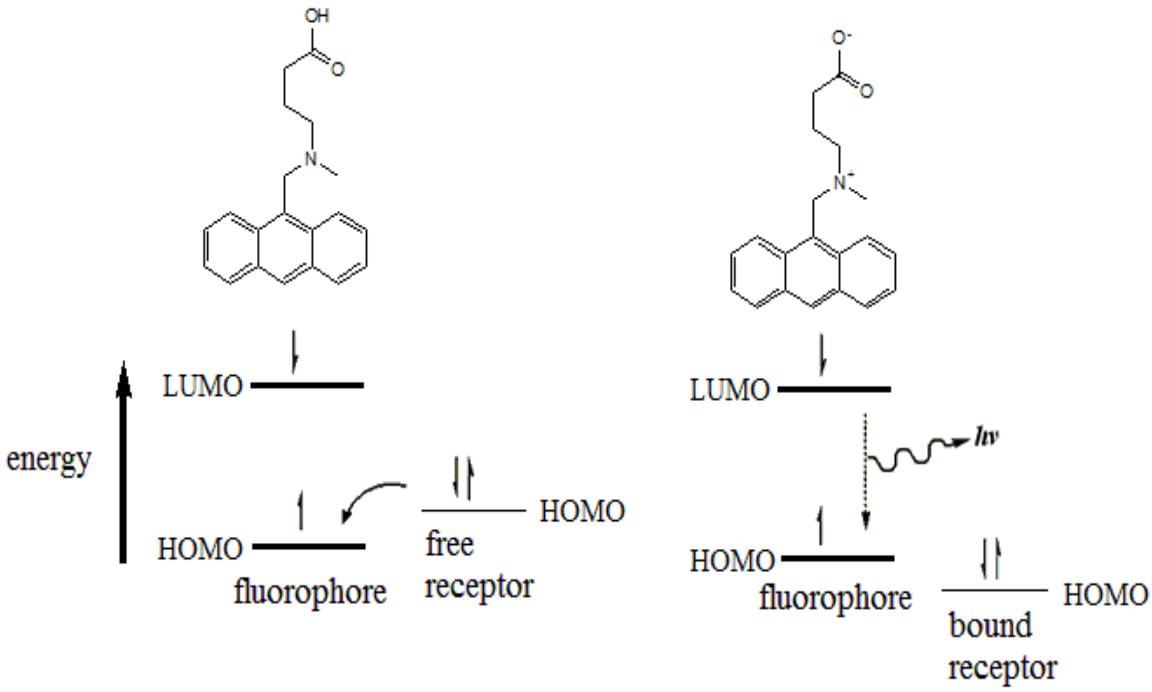


Fig. 2. Principle of cation sensing by PET

i.e. electron transfer from amino groups (HOMO of the donor) to aromatic hydrocarbons, as a result fluorescence quenching occurs. But, If the amino group is protonated (or strongly interacts with a cation), HOMO of the donor is much more stabilised than HOMO of the fluorophore moieties, so, electron transfer is hindered and a very large enhancement of fluorescence is observed. There are no spectroscopic shifts for emission band upon binding with the metal ion in case of PET inhibition mechanism.

2.2. Excited-state intramolecular proton transfer (ESIPT)

Photoinduced proton transfer through an intramolecular hydrogen bond is termed excited-state intramolecular proton transfer (ESIPT).[46] Many molecules contain a proton donor, hydroxyl group and proton acceptor, heterocyclic-N or a carbonyl-O in close proximity. In the ground state, ESIPT molecule generally prefer *enol* form which is stable by intramolecular hydrogen bonding, Upon photoexcitation, proton transfer from the excited enol (E*) to the excited keto (K*) form. Consequentlyt, we get a dual fluorescence spectra with large Stokes shift (≈ 10 000 cm^{-1}) and it is remarkably fast process (rate constant k ≈ 1 × 1013 s^{-1}.[47] The basic photophysical process of the ESIPT chromophores is illustrated by 2-(2-hydroxyphenyl)-benzothiazole. in (**Fig. 3**).[48]

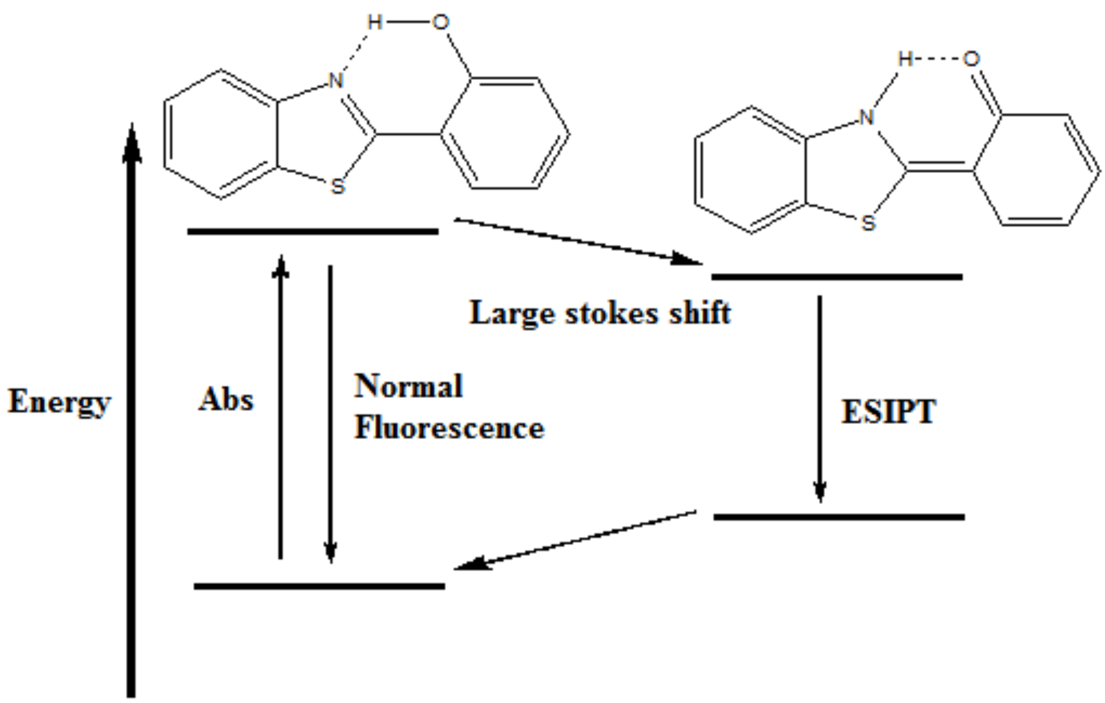


Fig. 3. Principle of Excited-state intramolecular proton transfer (ESIPT)

2.3. Fluorescence resonance energy transfer (FRET)

Förster (Flourescence) Resonance Energy Transfer (FRET) is a energy transfer phenomenon that occurs from an excited molecular fluorophore (the donor) to another fluorophore (the acceptor) through a non-radiative process. When the absorption spectrum of acceptor (A) molecule overlap with the emission spectrum of a donor (D or fluorophore), energy transfer occurs (**Fig. 4**).[49] However, FRET is a highly distance-dependent phenomenon between donor and acceptor. Its efficiency is inversely proportional to the sixth power of the distance between both molecules. Accordingly FRET can be used to determine distances between donor to acceptor fluorophores called "molecular ruler".[50]

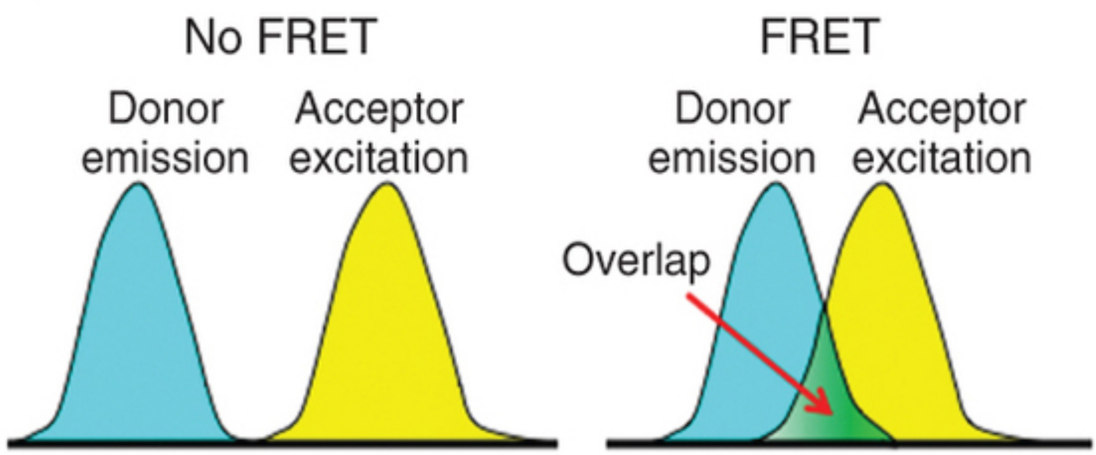


Fig. 4. Principle of cation sensing by FRET

2.4. Excimer or exciplex formation

Excimer is formed between the interaction of a excited state molecule and a ground state molecule with same chemical identity. but, exciplex is formed between the interaction of a excited state molecule and a ground state molecule with different chemical identity. Two processes i.e. the formation of Excimer and exciplex are a reversible and have been characterised by decreased normal fluorescence emission associated with a new broad and structureless emission at longer wavelength.[51] The amount of metal ion present in solution can be identified from the ratio between the emission intensity of monomer and excimer. Sensors based on this concept are called "ratiometric sensors".[52]

2.5. Photo induced Charge Transfer (PCT)

An electron transfer from electron donor to acceptor moieties. From absorption and emission spectra, it can be easily distinguished between PET and PCT.[53] PET process is generally quenching and here, generally no shifting of spectral. But in PCT process, fluorescene is ovserved with large Stokes shift, because due to electron transfer dipole moment changes. A typical example of PCT based Fluorescent sensor is azocrown appended merocyanine fluorophore (**Fig. 5**).[54] In PET, there is a spacer between fluorophore and receptor but in PCT , fluorophore and receptor are intregated with π-conjugated. On complexation with metal ions, PCT sensors show fluorescence "turn-on" and"turn-off" with a different absorption and emission wavelengths, based on the type of metal ion , anion, fluorophore and complexation mode.[55]

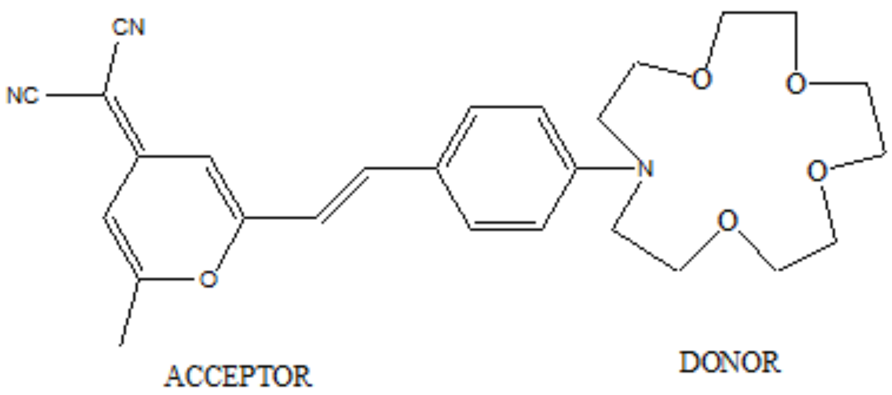


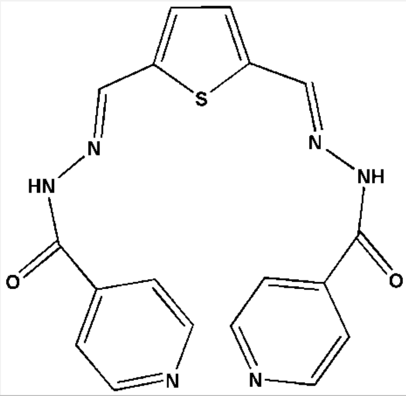
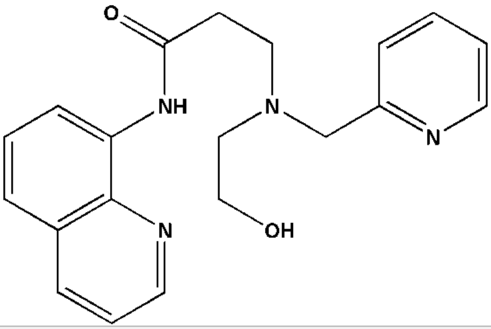
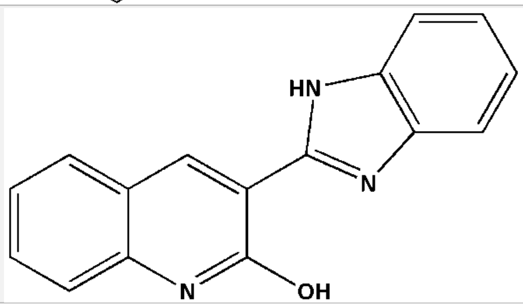
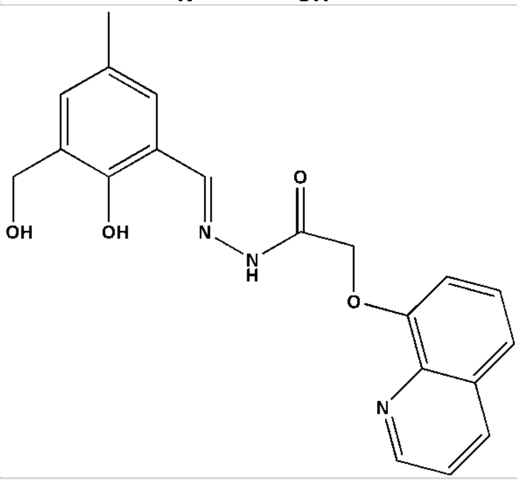
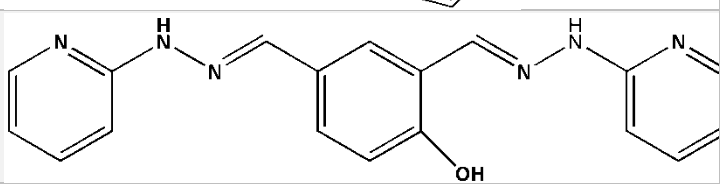
Fig. 5. Principle of cation sensing by FRET

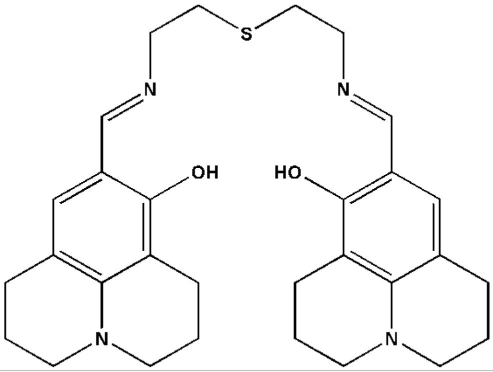
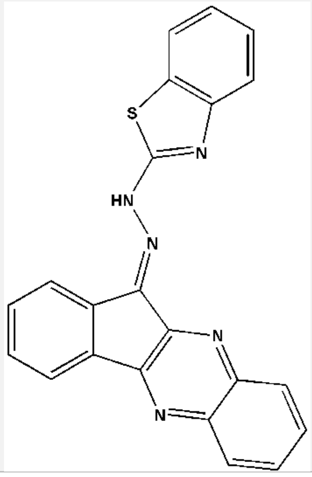
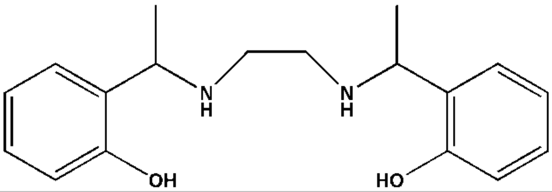
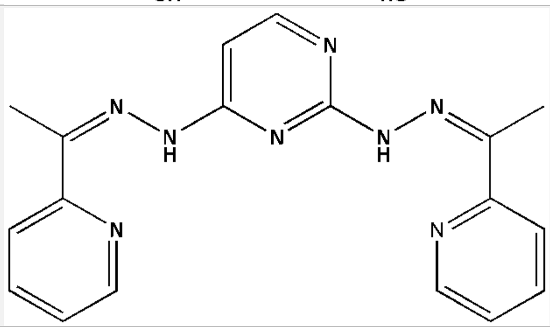
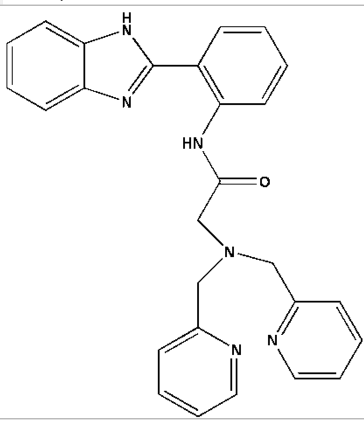
4. Importance of Zinc

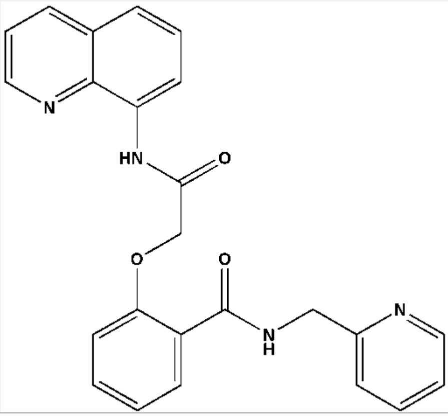
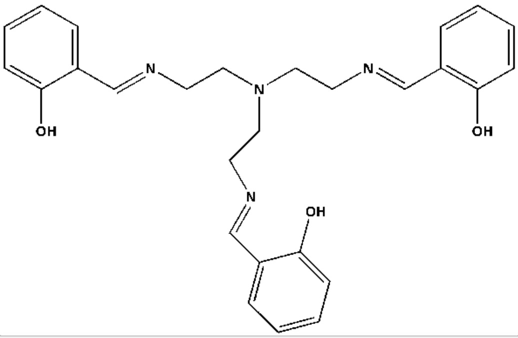
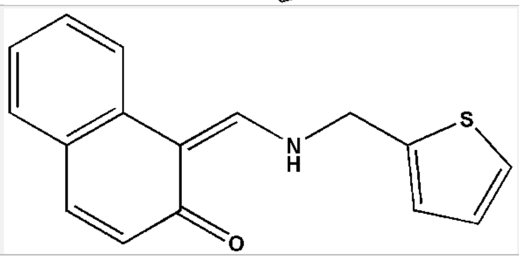
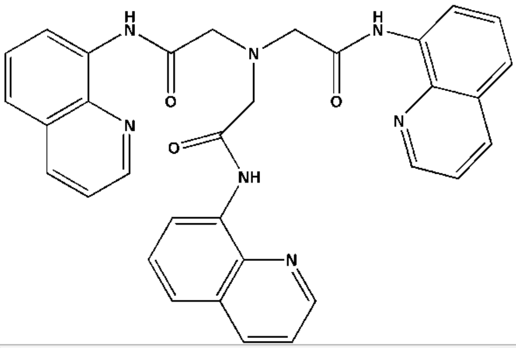
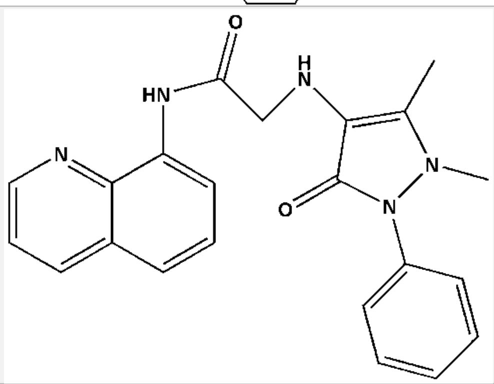
Among the heavy transition metal ions, Zinc is the second most abundant heavy metal ion exist in the human body with a total content of 2–3 gm and almost 90% is found in bones and muscle.[56] Besides, Other organs such as skin, brain, prostate, liver, lung, white and red blood cells, heart, gastrointestinal tract, kidney, and pancreas contained estimable concentrations of zinc.[57,58] Zinc plays a vital role in protein synthesis and helps regulate the cell production in the immune system of the human body.[59,60] one of zinc's most vital functions is to restoring white blood cell function which defend the body opposed to lot of infections and help for the synthesis of collagen and regrowth.[61,62] Zinc deficiency gland enlargement which is susceptible to cancer.[63] Vitamin B6 and Zn together regulate the function of neurotransmitters that communicate with the body.[64] Taste buds and olfactory cells are zinc regulating organs and improvement of the senses of taste, smell zinc is obligatory. Vitamin-A stimulating enzymes could not function without zinc monitoring night vision.[65] Bone matrix became hard and strong due to presence of sufficient zinc- hydroxyapatite component. Zinc assists in spermatogenesis and the development of the sex organs.[66] Alzheimer's disease[67,68] infantile diarrhoea ,epilepsy and ischemic stroke[69,70] are results of zinc deficiency. Zinc is a cofactor of almost 300 critical enzymes. (This "cofactor" status of zinc means that zinc participates directly in the activity of the enzymes.) such as DNA and RNA polymerases,[71] carbonic anhydrases,[72] alkaline phosphatises (AP),[73] Alcohol dehydrogenases (ADH),[74] peptidases[75] and they help in regulating various cell functions . So, Zinc is very important for human body as its has multiple function and an adequate amount of zinc is necessary in our daily diet. Beside, with the expansion of the modern chemical industry, the environmental pollution caused by different transition metal ions like Zn^{2+} ions has become more serious and pose a threat to the environment and public health.[76] Soil microbial activity reduces by excess zinc which results in a phytotoxic effect at excess level.[77,78]

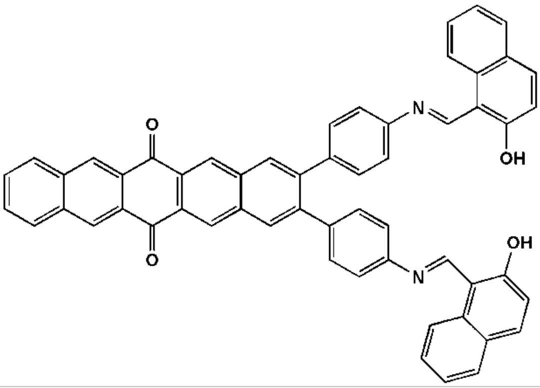
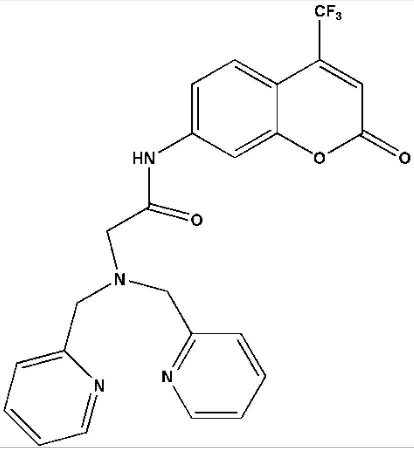
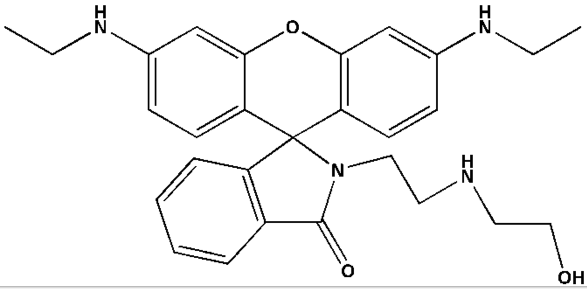
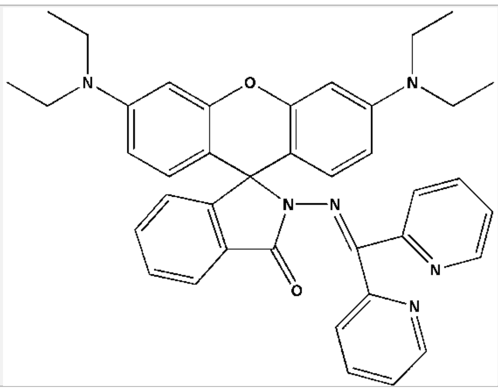
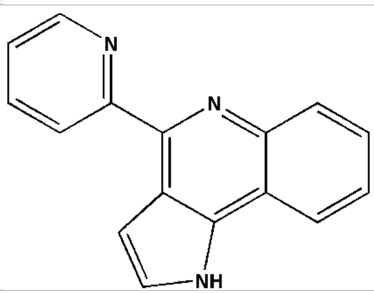
Recently, various fluorescent chemosensors for Zn^{2+} have been developed using quinoline, coumarin, Vanilline, indole, 8-naphthalimide, para-cresol-diformyl, bipyridine, and other fluorophores, which showed excellent selectivity and sensitivity towards Zn^{2+} ions. Some of these are given in **table.1.**

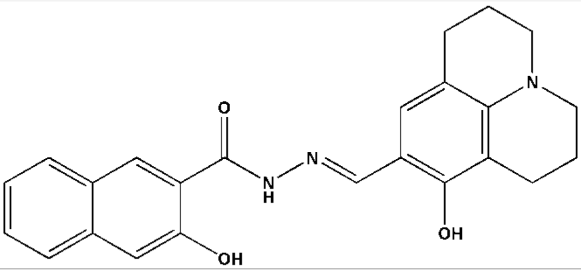
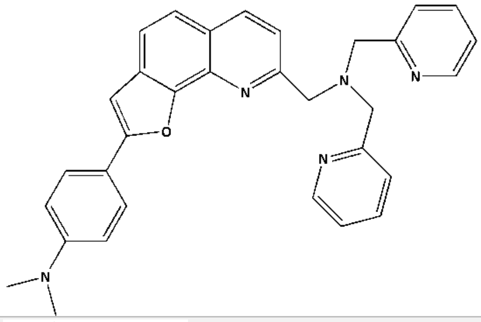
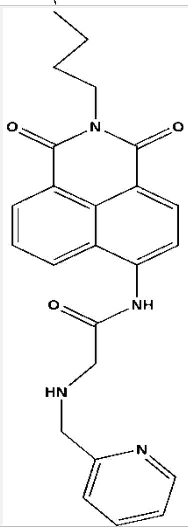
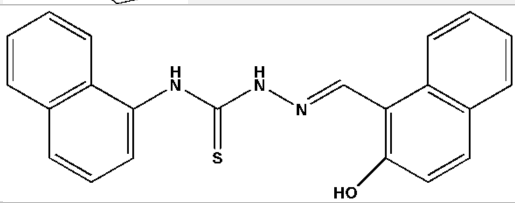
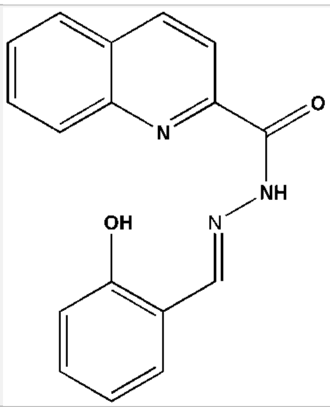
Table.1. Some reported Zn^{2+} fluorescence chemosensor:

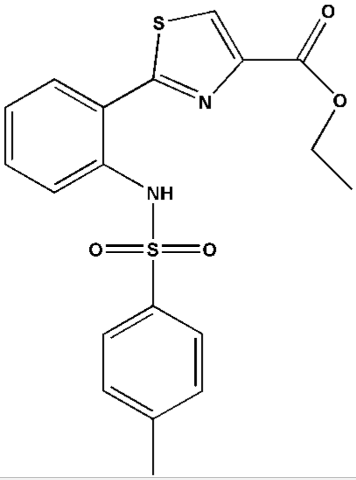
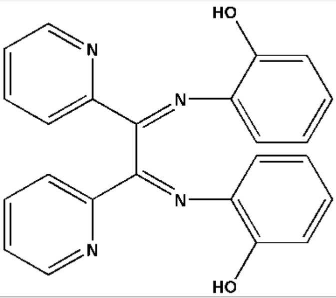
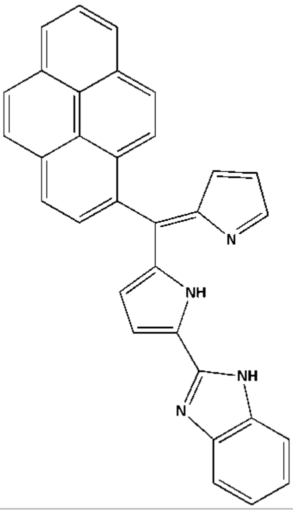
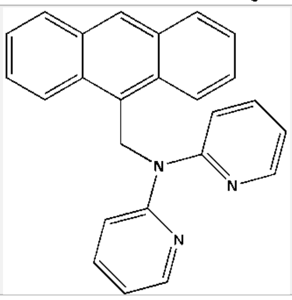
Serial no	**Structure**	**Detection limit**	**References**
1		3.79 nM	79
2		19 nM	80
3		1.5 x 10^{-5} M	81
4		23.5 nM	82
5		13.9 nM	83

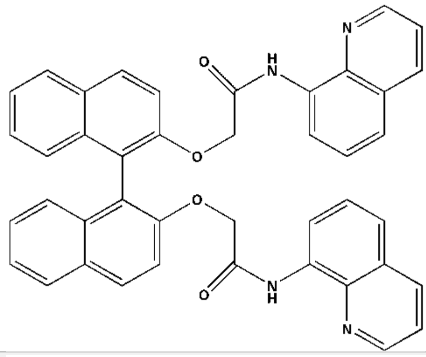
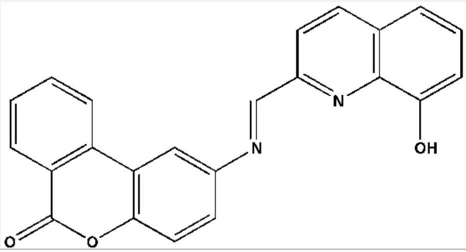
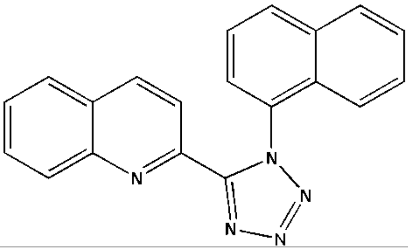
6		1.59 µM	84
7		6 nM.	85
8		650 nM	86
9		141 nM	87
10		621 nM	88

11		49 nM	89
12		1.1 µM	90
13		30 nM	91
14		3.2 mM	92
15		130 nM	93

16		3.5 nM	94
17		18 nM	95
18		150 nM	96
19			97
20		$1.5x\ 10^{-6}$ M	98

21		3.3x 10^{-6} M	99
22			100
23		7.2 nM	101
24		1.03 × 10−6 M	102
25		21 nM	103

26		20 μM	104
27		6.3 × 10−11 M	105
28		236 nM	106
29		2.06 × 10−6 M	107

30		1.51 10^{-6} M	108
31		10 × 10−6 M	109
32		20 nM	110

5. Conclusions

From the above discussion, it reveals that the use of fluorescent probes/sensors is now commonplace in analytical, biological, environmental and clinical applications of a wide range of chemical species, especially zinc as it plays diverse roles in biological processes. Therefore, considerable effort has been devoted to the development of efficient and selective methods to detect Zn^{2+}. For practical applications, it is necessary to develop less expensive, easily prepared, selective and sensitive signalling molecules for quantitative identification of Zn^{2+} ion. Schiff bases (-C=N-) are known as good complexing agents and have been designed to incorporate fluorescent moiety for optical sensing of metal ions.

Reference

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