

# SMALL MOLECULE FLUORESCENT CHEMOSENSORS : A REVIEW

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## **Abstract**

A functional fluorescent molecule would be formed when a receptor molecule interacts with the proper analyte and exhibits fluorescence. This formed fluorophore can act as a chemosensors which perform the function like recognition of a particular analyte, detection and analysis. Besides being highly specific, this method also has a rapid response time, a low detection limit, and it is technically straightforward. In these devices, light is emitted by a material (fluorophore) after it is excited at a lower wavelength. In addition to being used as sensor devices, fluorescence-based sensors can also be used for monitoring metal ions. The different molecular entities presented here are well characterized for their sensitivity, selectivity, and low detection limits. So this method plays a significant role as an effective analytical technique.

**Keywords:** *Fluorescence, Fluorophore, Chemosensors, Selectivity, Analytical technique*

## INTRODUCTION

A sensor is a device that detects and responds to electrical or optical signals. Physical parameters such as temperature, blood pressure, humidity, and speed can be measured by converting them into electrical signals. The general working of a sensor and some characteristics of a sensor is given below:



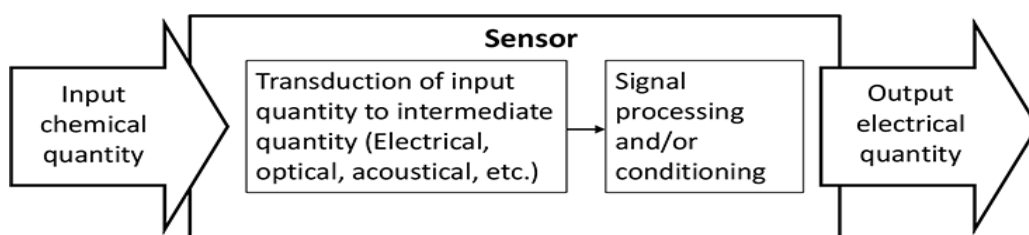
**Figure 1.1 General working of a sensor**

In general, sensors are classified based on primary input quantity (Measurand), physical and chemical transduction principles, material and technology, property and its application. Sensors can be classified in terms of their properties. For example, temperature includes thermistors, thermocouples, pressure includes fibre optics, vacuum, elastic liquid based manometers and electronic sensors. Furthermore, sensors are also categorized on the basis of their applications, such as industrial process control, measurement, and automation; and non-industrial use such as aircraft, medical items, automobiles, consumer electronics, other type of sensors.

Additionally, sensors can be basically categorized into two types depending on their power supply - active and passive. The active sensor requires power, whereas the passive one does not. The active sensors include LiDAR (Light Detection and Ranging) and photoconductive cells, while the passive ones include radiometers and film photography [1].

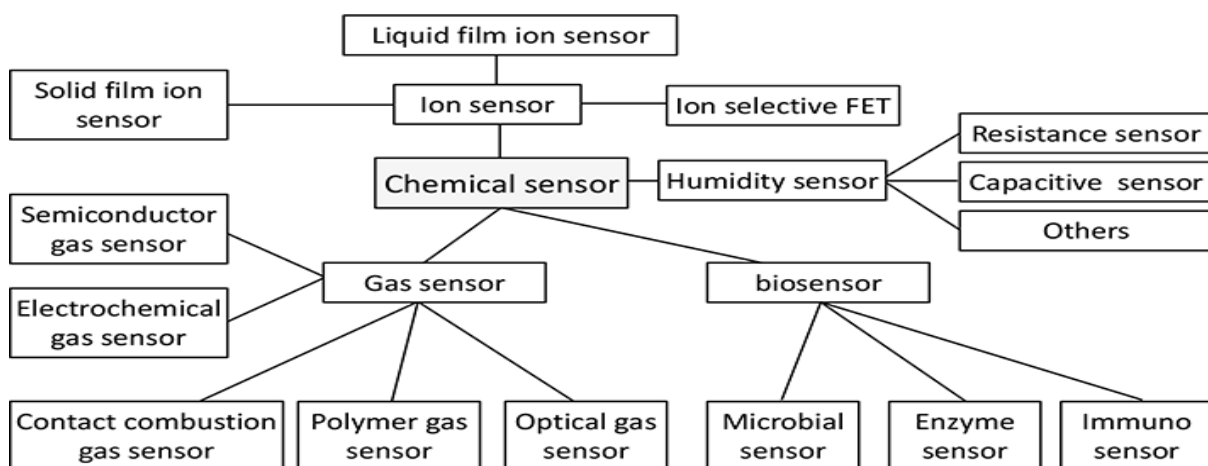
A chemosensor identifies a molecule originating from an abiotic source that can detect matter or energy. According to the International Union of Pure and Applied Chemistry (IUPAC) a chemosensor is defined as “a device that transforms information, ranging from the concentration of a specific sample component to total composition

analysis, into an analytically useful signal”[2]. General working of a chemosensor is given below:



**Figure 1.2 Working of a chemosensor**

*In general, chemical sensors are instruments that measure the concentration, amount, or presence of analytes. In addition to gas, liquid, and solid phases, the analyte can be found in different dimensional scales from nanoscopic to monomolecular ranging from bulk volumes from litres to picolitres. Direct-reading sensors usually respond within milliseconds [3].* For the construction of fluorescent sensors, two main components are required: a fluorophore (signalling motif) and a receptor (recognition motif). An optical response is produced when the signalling moiety function as a signal transducer and transfer the data (recognition event) into an optical signal [4]. Different types of chemical sensors, otherwise known as chemosensors, are given below:

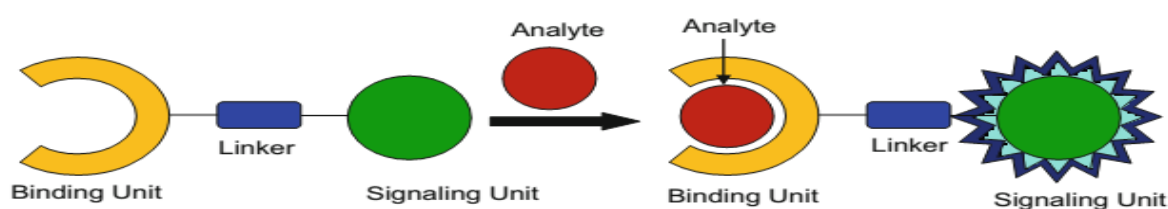


**Figure 1.3 Types of chemosensors**

During the design of a chemosensor, it is necessary to coordinate host-guest interactions or to trigger a chemical reaction that will cause a change in the reporter's properties. The probe is termed a chemosensor if the hosts and guests bind non-covalently and reversibly. Whenever there is an irreversible chemical reaction between the host and guest, it is called

a chemidesimeter (reaction based)[5]. The two separate response techniques that a chemosensor can employ are colorimetric detection and fluorometric detection. [6].

*The process of fluorescence is characterized by molecules absorbing photons of light at a certain wavelength and emitting photons at different longer wavelengths and the difference is termed as Stokes shift[7]. A fluorescent chemosensor utilizes a guest binding unit (receptor), a guest signalling unit (fluorophores/chromophores) and a mechanism that communicates between the two units[8]. Fluorescence-based chemosensors detect ions by detecting a change in fluorescence properties, such as wavelength or intensity, or by identifying a new fluorescence band[9].* At that time, fluorescent chemosensors were defined as "compounds incorporating a binding site or a receptor, a fluorophore, and a mechanism for communicating between the two sites"[10]. With the use of a highly luminous morin chelate, F. Goppelsroder reported the creation of the first fluorescent chemosensor in 1867 for the detection of aluminium ion ( $Al^{3+}$ ) [11]. It is crucial to consider factors such as pH, ionic strength, and polarity of the solvent, which can have significant impacts on the ability of the receptor to bind and recognize analytes.

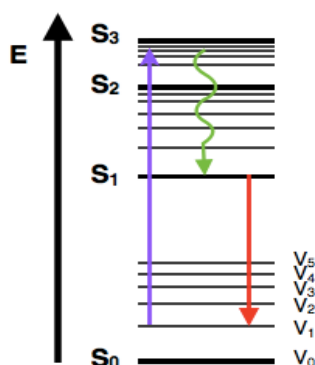


**Figure 1.4 Generalized representation of a fluorochemosensor**

The intensity and fluorescence lifetime is the basis of the measurement of a sensor. [12]. Analytes can be selectively detected and recognized by a variety of sensing mechanisms including Forster resonance energy transfer (FRET), photoinduced electron transfer (PET), Photoinduced charge transfer (PCT), Excited state intramolecular proton transfer (ESIPT), Aggregation induced emission (AIE), and monomer excimer formation [13]. Fluorescence is often used to analyse molecules, and adding a fluorescing agent to detergents that emits blue light causes fabrics to appear whiter in the sun. Minerals can be analysed using X-ray fluorescence, and there are other applications as well. This review explains in detail about the different metal ion detection using fluorescent sensors, different types of instrumental techniques involved, various schemes for the construction of chemosensors with high selectivity for specific analytes, numerous fluorophores, their applications and spectral properties

## EXPERIMENTAL STUDIES

In fluorescent chemosensors, the combination of a fluorophore (transducer) and a receptor is obtained by attaching electron donating and electron accepting groups to a conjugated system. The concept of fluorescence is usually explained using Jablonski diagram as shown in Figure 2.1. In a Jablonski diagram, energy is represented on a vertical axis. Fluorescence is the process by which molecules emit photons using the energy they receive from photons. Jablonski diagrams show a straight line between electronic states going down on the energy axis.



**Figure 2.1** Jablonski diagram - Possible scenario with **absorption**, **internal conversion** and **vibrational relaxation** and **fluorescence** processes

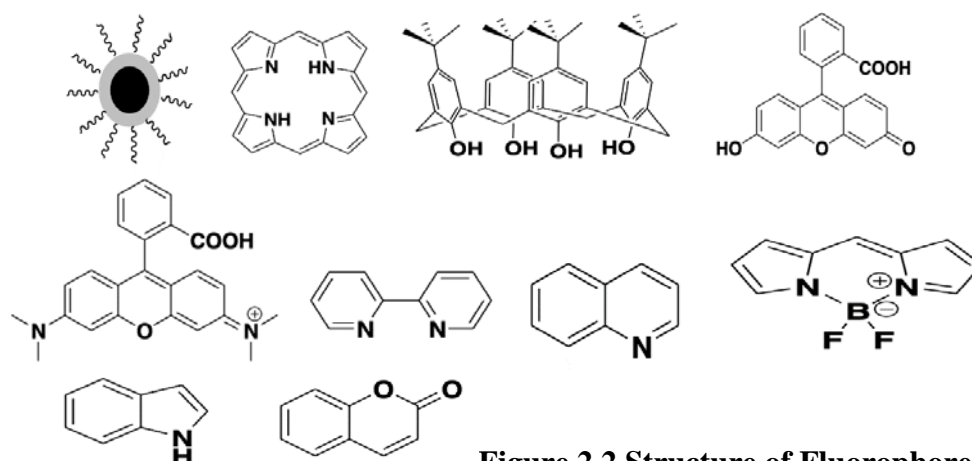
Generally, fluorescence is observed in compounds with a rigid framework and not many loosely coupled substituent through which vibronic energy can be emitted. They are called fluorophores, analogously to chromophores, and contain a system of double bonds conjugated within them. The fluorochromes are analogous to auxochromes because they tend to enhance fluorescence. Intrinsic and extrinsic are two main classes of fluorophores. Natural fluorophores are intrinsic, which includes the aromatic amino acids, NADH, flavins, derivatives of pyridoxyl, and chlorophyll. In contrast, a sample is mixed with fluorophores to give fluorescence or to alter its spectral properties are defined as extrinsic fluorophores, which includes dansyl, fluorescein, rhodamine, and other substances [14]. Various fluorophores were studied in detail for detecting various analytes.

Molecular devices such as fluorescent nanosensors are interesting molecule sensors which detects heavy metal ions in the environment. Fluorescence-based nanosensors work by causing specific changes in the fluorescence properties of nanomaterials because of the interaction between recognition components (nanomaterials) and target analytes (metal ions), such as quenching, enhancement/recovery, wavelength shifts, and anisotropy.

Because of their easy synthesis, biocompatibility, high specificity, surface functionalization, and optical properties, metal nanoparticles (NPs) have gained much attention in the fluorescent sensing of heavy metals. By synthesizing diphenylamine-based Schiff bases, a novel high-selectivity chemosensor was developed which detects Cu(II)s[15]. A major reason for porphyrin popularity is their high absorption coefficients at 400–450nm (visible range), tuneable fluorescence emission with subsequent modification of molecular structures, and large Stokes shift that minimizes background fluorescence. Using UV-vis spectroscopy, it has developed a cationic 5,10,15,20-tetrakis (N-methyl-4-pyridyl) porphyrin tetrachloride as an optical sensor for measuring  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Cd}^{2+}$  simultaneously. [16]. Using the traditional phenol chemistry, calix [n] arene is chemically modified by alternating phenol and methylene groups [17]. Leray et al. For the detection of  $\text{Al}^{3+}$  ions, the 1,3-alternate conformation of calixarene with dansyl-attachment was used. [18]. Fluorescein exhibits excellent photophysical properties, including quantum yield and strong absorption properties. Fluorescein can also be used with Ar laser lines and filter sets are available [19]

. For the selective detection of  $\text{Hg}^{2+}$ , a versatile sensor based on FRET technique constituting rhodamine and terthiophene was reported by Kaewtong et al. and its minimum detection ability was recorded to be  $1.34 \times 10^{-6}$  M[20]

Bipyridine-based fluorescent receptors have been developed for copper ion detection [21]. Boradiazindacene (BODIPY) fluorescent dyes have diverse applications because they exhibit high fluorescence quantum yields, good photo-stability, sharp absorption and emission spectra, and high absorption coefficients. [22]. In addition, the properties of its fluorescence can be regulated via forster resonance energy transfer (FRET) or photo-induced electron transfer (PET).[23]. The use of boron-dipyrromethene (BODIPY) as a fluorescent sensor for copper ion detection has been reported [21]. An indole-based fluorescent chemosensor was also reported that is capable of selectively detecting mercuric ions. This fluorescent chemosensor utilizes indole as the fluorescent agent and triaminoethylene as the linker. There is a study that describes the development of a fluorescent chemosensor made up of the coumarindithioate derivative that can detect mercuric ions after chelation. This sensor material exhibited an off-on type fluorescent response enabling detection of  $\text{Hg}^{2+}$  ions upon mercuric ion induction [20].



**Figure 2.2 Structure of Fluorophore-Nanoparticle, Porphyrin, Calixarene, Fluorescein, Rhodamine, Bipyridine, Quinoline, BODIPY, Indole, Coumarin.**

The use of metals in the environment, industry, and biochemistry is immense. Some metals on earth can be detected using fluorescent sensors. *There are two essential features in fluorescent metal sensors:* a fluorophore with light-emitting and light-absorbing properties and a metal chelating or binding moiety. The molecular or electrical structure of the sensor must be changed by the metal binding to enable it to work as a sensor. Chemosensors detect metal ions qualitatively and quantitatively via fluorescence changes (intensity and/or band shift) due to the reactions between metal ions and the chemosensor. Binding mechanisms include the transfer of fluorescence energy and electron between metal and fluorophore. *This results in either a "turn-on" or "turn-off" fluorescence response resulting from increased or decreased fluorescence [24].* In the case that their fluorescence is quenched (cut off) by interaction with metal ions, these kinds of chemosensors are called 'on-off' fluorescent chemosensors. Normally in fluorescent sensor systems, the ionophore binds to a target ion selectively, while the fluorophore determines the sensitivity [25].

In this study, fluorescent chemosensors were used to detect different ions of metal. Mercury (II) ion ( $\text{Hg}^{2+}$ ) is one of the widely commonly utilised heavy metal ions in industrial and agricultural processes. It has been demonstrated that semiconductor quantum dots such as CdS, ZnS and CdTe is employable to construct fluorescent sensors for  $\text{Hg}^{2+}$ . To carry out the detection of  $\text{Hg}^{2+}$  ions, fluorescent 2, 3-diamino phenazine (DAP) nanoparticles (NPs) were synthesized by irradiating o-phenylenediamine (o-PD) aqueous solution with UV radiation [26].

The second most prevalent metal ion is Zinc (concentration ranging from sub-nM to 0.3 mM) which plays a crucial part in the control of metalloenzymes, the transcription of genes, the transmission of brain signals, and apoptosis. On the basis of salicylate azo derivatives, a fluorescent chemosensor was synthesized. Interestingly,  $Zn^{2+}$  exhibits a stronger fluorescence response in aqueous medium than the other metal ions in competition is due to a charge transfer process within the receptors.[27]. Copper, which has a very important role in biomolecules and dietary copper is essential for proper haemoglobin synthesis, for the avoidance of anaemia, and for the functioning of redox enzymes. [24][28]. Soma Mukherjee et al. developed a coumarin based chemosensor for selective fluorescent recognition of  $Cu^{2+}$  in MeOH/H<sub>2</sub>O medium with 1:1 binding stoichiometry[29]. The most significant and fourth-most prevalent type by mass in the earth's crust is the perplexing metal iron. Pyrene TEMPO and DansSQ, two early probes of  $Fe^{2+}$ , both turn on in response to  $Fe^{2+}$  through various mechanisms. A  $Ca^{2+}$  fluorescent sensor was developed based on diarylethene and triazoloyl hydrazine unit. In the presence of  $Ca^{2+}$  ion a color change was observed from dark purple to light blue[24]. Magnesium is fourth most abundant cation found in the human body. A new diarylethene and 4-methylphenol Fluorescent was synthesized for the detection of  $Mg^{2+}$  ion, which show a colour change from dark purple to green[30]. Based on a functionalized porphyrin, an effective colorimetric and fluorometric Cd (II) chemosensor has been designed. In addition to a significant colour change, in response to Cd (II) ions, the chemosensor also exhibited substantial ratiometric changes in the absorption and fluorescent emission spectra[31]. A rhodamine-alkyne conjugate probe for  $Au^{3+}$  was synthesized, and its detection limit was 10.5 nM. Using tetramethyl substituted bis(difluoroboron 1,2-bis[(1H-pyrrol-2-yl)methylene] hydrazine as a fluorescent sensor for  $Cd^{2+}$  ions has been reported. Arsenic, a group 15 element ubiquitous in nature, is a teratogenic and carcinogenic toxin which is known to bring about serious skin diseases, neurodegenerative disorders and cardiovascular conditions. An excellent biofriendly selective sensor for  $As^{3+}$ , especially in  $AsO_3^{3-}$  form, was reported. [32].

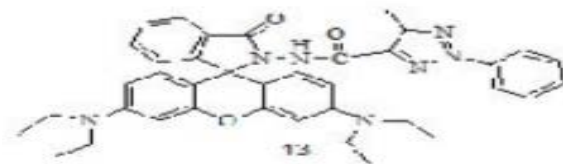
In its bivalent state ( $Ni^{2+}$ ), nickel is an important transition metal for biological systems due to its role in metabolism, respiration, and biosynthesis. Nickelsensor-1 (NS1) was developed by the Chang group was the first fluorescent sensors for cellular  $Ni^{2+}$ . NS1 consists of a fluorophore derived from BODIPY bound to a mixed N/O/S receptor. When this probe binds  $Ni^{2+}$ , its fluorescence increases by 25 times. Cobalt ( $Co^{2+}$ ) is an important nutrient for plants and animals. CP1 (Cobalt probe 1) exploits the redox activity of  $Co^{2+}$  by means of a reaction-based strategy. In absence of  $Co^{2+}$ , the fluorescein dye in CP1 is only weakly fluorescent. CP1 detected both aqueous and endogenous  $Co^{2+}$ . The



fluorescent sensor named Leadfluor-1 (LF1), which detects lead levels by using a dicarboxylatepseudocrown ether that is  $Pb^{2+}$ -selective and a fluorescein-like xanthenone reporter, experiences an 18-fold increase in fluorescence when bound to lead. [24]. In recent years, fluoride ion sensor technology has attracted considerable attention due to its potential usefulness for biological applications like dental treatment and osteoporosis treatment. Anthrone-based ratiometric turn-on chemosensor for F- analysis using real-time samples was developed by Soma Mukherjee et al. [33]. In particular, fluorescent polymers can detect explosives based on nitro-aromatic compounds [34]. Detection of small neutral molecules by fluorescent chemosensors: Thiols (Cysteine (Cys) and homocysteine (Hcy)) are key components of biological systems. In a study by Martinez-Manez and co-workers, fluorescent chemosensors based upon squaraine were developed for the detection of thiols [3]. A vast range of biological analytes were detected with sensors based on graphene nanomaterials, including glucose, cholesterol, heavy metal ions, hydrogen peroxide, NAs, cancer biomarkers, pesticides, and food pathogens. These sensors demonstrated good sensitivity, low detection limits, and scalability. [35]. As a result of their significance in biology, the environment, and chemical chemistry, there is considerable interest in the development of strategies that lead to multiple ion detection[36]. Researchers have developed synthetic chemosensors that have been designed to detect individual ions such as  $Cu^{2+}$ ,  $Al^{3+}$ ,  $Cd^{2+}$  and  $S^{2-}$ . Martinez-Manez and co-workers have used a single fluorescent chemosensor and demonstrated numerous ion detection [37].

Soma Mukherjee et al. synthesised a novel turn-on type chromofluorogenic anthracene based sensor comprising Schiff base as a probe for successful detection of chromium(III) and aluminium(III) ions in an aqueous environment. Bis(N,N-dimethylamine methylene)acridine, the new acridine derivative, exhibits prominent selectivity and sensitivity towards bivalent  $Zn^{2+}$  and  $Cd^{2+}$  ions in both water and methanol [39]. A new class of colorimetric and fluorescent chemosensors for fluoride and cyanide ion detection that contains anthraquinone and imidazole as binding as well as signalling moieties has been developed [38].

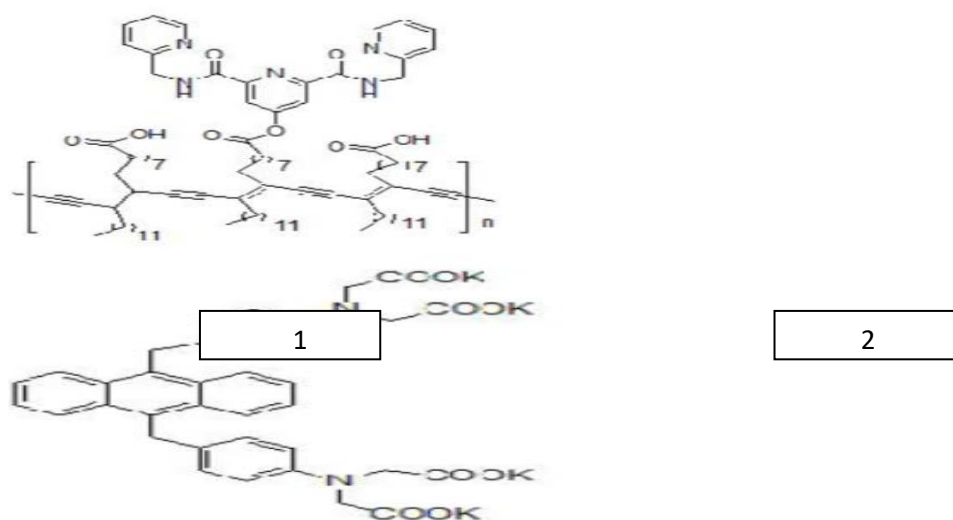
Fluorescent chemosensor for mercury: Researchers Li et al. outlined a process for rhodamine-linked triazole synthesis as a fluorescent chemosensing system by incorporating rhodamine B to 5-methyl-2-phenyl-2H-1,2,3-triazole-4- carboxylic acid (Fig 2.3). Upon binding with the mercury ion in DMF-H<sub>2</sub>O (v:v =1:1) at pH =7.4, the colourless triazole with rhodamine appended turned pink enabling naked eye detection of the ion. Moreover, UV-Visible and fluorescence spectroscopy along with TD-DFT calculations revealed the probe's high selectivity for Hg (II) ions. In addition, no effect of other metal ions was observed on fluorescence signal.



**Figure 2.3 Rhodamine linked fluorescent chemosensor for Mercury**

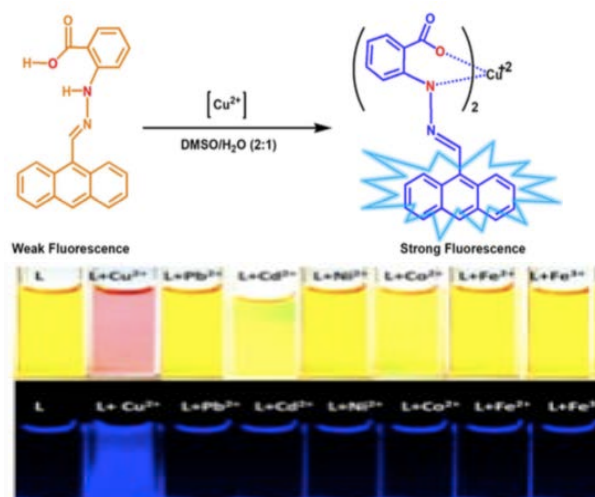
Fluorescent Chemosensor for  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$ : (Wang et al., 2019) A novel fluorescence sensor was created using negatively charged gold nanoclusters and positively charged N-CDs with an excitation wavelength of 380 nm (AuNCs). The sensor has dual emission peaks at 440 and 565 nm. The study shows that the stable blue fluorescence of N-CDs has been used to quantify the presence of  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$ , while the red fluorescence of AuNCs was amplified by  $\text{Pb}^{2+}$  and quenched by  $\text{Cu}^{2+}$ . [40].

Fluorescent Chemosensor for Cadmium: Pham et al. in 2019 synthesized a selective fluorometric and colorimetric chemosensor based on conjugated polydiacetylenes that responded selectively to  $\text{Cd}(\text{II})$  in the presence of pH 7.4 (Fig 2.4-1). The sensor was demonstrated to create a quick fluorescence switch on effect with visual detection (blue to violet) and considerable selectivity to  $\text{Cd}(\text{II})$  as compared to other metal cations upon repeated addition of aqueous cadmium solution. For cadmium ions, a minimum detection limit of  $1.85 \times 10^{-8} \text{ M}$  was discovered. Toward the detection of metal ions, a fluorene-based fluorescent chemosensor was developed in 2019 (Fig 2.4-2). At pH 7, the sensor exhibited red-shifted fluorescence spectra for  $\text{Cd}(\text{II})$  ions, which demonstrated high selectivity and sensitivity for these ions. As the concentration of cadmium ions increased, so did the intensity of fluorescence and the detection limit for  $\text{Cd}(\text{II})$  ions was 0.2889 mg/L. In order to enhance the fluorescence detection efficiency, the probe was functionalized with PMMA/SPIONs [31].



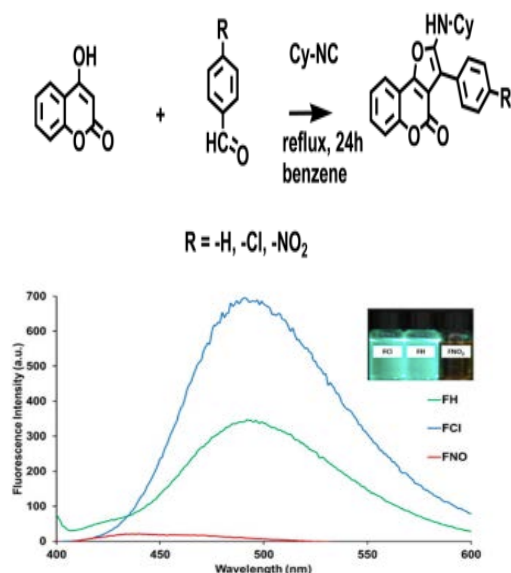
**Figure 2.4 Fluorescent chemosensor for selective detection of Cd(II)**

Fluorescent Chemosensors of Copper: A novel luminescent hydrazone ligand was synthesized through the 1:1 condensation of 2-hydrazinobenzoic acid with 9-anthracene aldehyde. It was then characterized using absorption, emission, FTIR, NMR and mass spectrometry. In aqueous solution, its potential as a turn-on, ratiometric, and reversible luminescent chemosensor for  $\text{Cu}^{2+}$  was studied. When exposed to  $\text{Cu}^{2+}$ , the receptor's colour in DMSO- $\text{H}_2\text{O}$  (2:1) medium shifts from yellow to reddish brown.  $\text{Cu}^{2+}$  caused a remarkable increase in emission intensity ( $\Phi = 0.091$ , 11 fold) perhaps as a result of intra-ligand charge transfer (ILCT). This chemosensor's capacity to selectively extract  $\text{Cu}^{2+}$  from aqueous metal ion mixtures with dichloromethane solvent is an intriguing characteristic. Extraction efficiency increased from 85% (L: $\text{Cu}^{2+}$ , 1:1) to 95% (L: $\text{Cu}^{2+}$ , 2:1) in the pH range of 6.5–10.0. In order to monitor the extraction behaviour of  $\text{Cu}^{2+}$ , UV-Vis spectroscopy and an easily portable smartphone were utilized to collect RGB data, which may prove useful for field-based analysis. No significant interference has been observed in presence of  $\text{Cu}^{2+}$  ( $1.0 \times 10^{-5}$  M) after addition of 5-fold excess of other metal ions ( $\text{Zn}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ) in DMSO- $\text{H}_2\text{O}$  (2:1) medium. It was further demonstrated that the pH adjustment could regenerate (> 98%) the ligand up to 4 cycles and exhibit a high recyclability and reusability, which might serve as a useful tool in extracting  $\text{Cu}^{2+}$  efficiently from aqueous media [41].



**Fig. 2.5 Fluorescent chemosensor for copper and fluorescence studies**

Fluorescent Chemosensors of  $Fe^{2+}$ : Furocoumarin (furo[3,2-c]coumarin) derivatives (FH, FCl and FNO<sub>2</sub>) have been synthesized by mixing 4-hydrocoumarin, benzaldehyde derivatives, and cyclohexylisocyanide. Recrystallization is used to purify the compounds instead of time-consuming column chromatography which also demonstrates the possibilities of automated high throughput synthesis and screening. Due to electron withdrawal from  $-NO_2$  resulting in fluorescence quenching of furocoumarin, FNO<sub>2</sub> does not exhibit considerable fluorescence intensity, while FH and FCl do. Additionally, the fluorescence study led to the demonstration of a new fluorescent (FH) ratio metric chemosensor based on coumarin that is attributed to  $Fe^{3+}$  recognition in methanol as well as in water/methanol (9:1, v/v). With  $Fe^{3+}$ , FH produced 1:2 complexes and exhibited a fluorescence turn-off response. While the probe selectivity reduces in aqueous environments, the "turn off" effect still operates, proving that fluorescence is not completely quenched by water. An excitation wavelength of 374 nm was used to measure the fluorescence emission spectra from 430 to 700 nm. Emission and excitation slit widths were both set to 1nm [42].



**Figure 2.6** Fluorescent chemo sensor for Fe<sup>2+</sup> and fluorescence studies

Fluorescent Chemosensors of Al<sup>3+</sup> and Cr<sup>3+</sup>: For the detection of chromium(III) ions (Cr<sup>3+</sup>) and aluminium(III) ions (Al<sup>3+</sup>) in water, a novel anthracene containing Schiff base (L) was created as a chromo fluorogenic switch. Additionally, absorption, emission, NMR, FTIR, and mass studies have been carried out. Under UV light, the colour of the receptor changes from blue to green when Al<sup>3+</sup> and Cr<sup>3+</sup> are present, with association constants (K<sub>a</sub>) and limits of detection (LOD) of 10<sup>5</sup> M<sup>-1</sup> and 10<sup>-11</sup> M respectively. Their spectral patterns have not undergone any significant changes in the presence of monovalent and divalent ions (Na<sup>+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup> and Zn<sup>2+</sup>). DFT/TDDFT experiments confirms that the ligand exhibits a turn-on emission in the presence of Al<sup>3+</sup> and Cr<sup>3+</sup>, which may be caused by chelation-enhanced fluorescence (CHEF). Here, an advanced level combinational INHIBIT gate was designed by using Al<sup>3+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup> and EDTA. This ligand also exhibits the ability to preferentially extract Al<sup>3+</sup> and Cr<sup>3+</sup> from an aqueous mixture of other metal ions by the liquid-liquid extraction technique. The first derivative normal fluorescence spectroscopy was employed to simultaneously estimate the concentrations of Al<sup>3+</sup> and Cr<sup>3+</sup> in the mixture without prior separation [38].



**Figure 2.7** Fluorescent chemo sensor for Al<sup>3+</sup> and Cr<sup>3+</sup>

Fluoride based fluorescent Chemosensor: Anthrone and 2-hydrazinobenzoic acids were condensed in 1:1 fashion to form hydrazone, a simple, small molecule. In addition to absorption, emission, NMR, FTIR, and mass spectrometry measurements, it was investigated in the red region (550–700 nm) as a luminescent, ratio metric, turn-on chemosensor for fluoride ions ( $F^-$ ). Fluoride ions are highly selective in the DMSO medium with a detection limit of  $\sim 10^{-5}$  M. Fluoride caused the color of this chromofluorogenic sensor to change instantly from pale orange to red as seen clearly by the naked eye while emitting red fluorescence when exposed to UV radiation. In presence of  $F^-$ , the ligand was observed to have a significant red shift, which is of great interest. Studies using DFT and TDDFT offered support for the electronic transitions involved in the absorption and emission spectroscopy and the energy-optimized structure. Using a smart phone's RGB grabber application to capture this color change, it might be possible to monitor concentration of the fluoride ion in non-aqueous environments. Additionally, the sensor was utilised to detect and estimate  $F^-$  in real samples with the help of UV–vis spectroscopy. These findings were consistent with the results obtained by the fluoride meter. As a result, the sensor mentioned above can be used for fluoride analysis in practical applications.[42].

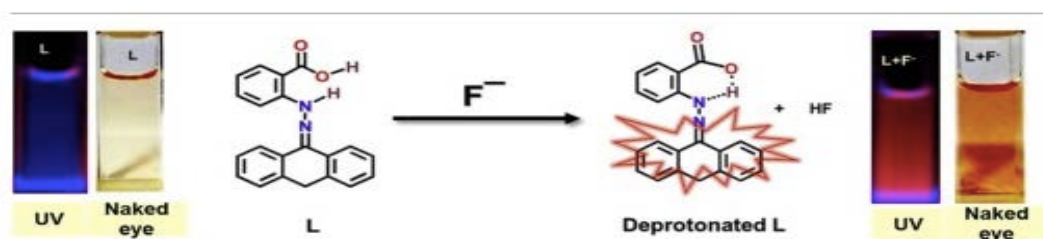


Figure 2.8 Fluorescent chemosensor for Fluoride

## INSTRUMENTATION

Fluorescence detection systems are comprised of four essential elements: i) a fluorophore ii) an excitation light source, iii) wavelength filters to isolate emission photons from excitation photons, iv) a detector that registers emission photons and produces a recordable output, usually as an electrical signal [43]. Modern fluorimeters can detect particles as small as one photon and a fluorescence microscope can distinguish particles separated by less than 10 nm. Instruments that measure fluorescence parameters can be classified into several types. The oldest fluorescence-based instrument is the filter-based fluorometer. Typically, this type is used in applications requiring periodic quantitative analysis of a single analyte in a simple, compact system. Additionally, optical filters are

often used to reduce autofluorescence noise. Autofluorescence is the emission of fluorescence from materials other than the target analytes. Monitoring the water quality, detecting the dissolved organic matter, and detecting heavy metal ions can be done through this device [7].

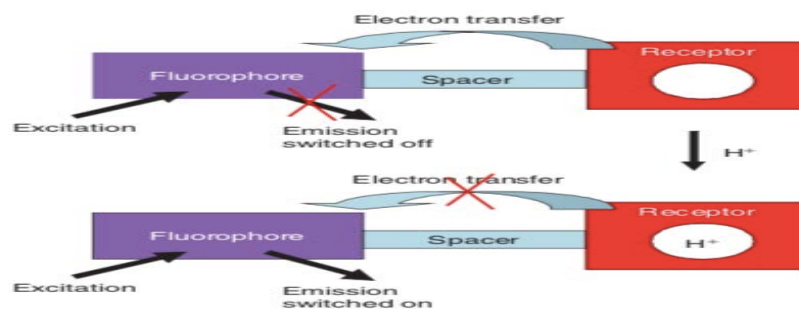
**Multi ion selective sensors:** Multiple ion detection strategies have got a lot of attention since their importance in biological, environmental, and chemical assays [36]. AgInS<sub>2</sub>-based sensors were used for detection of heavy metal ions such as Co<sup>2+</sup>, Pb<sup>2+</sup> and Ni<sup>2+</sup>, which cause acute or chronic diseases. These sensors can record the absorption spectra of the samples by using a spectrophotometer UV-3600 and spectrofluorometer FP-8200. It consists of microspheres of calcium carbonate doped by microspheres of porous matrix. The CaCO<sub>3</sub>-Fe<sub>3</sub>O<sub>4</sub>-AgInS<sub>2</sub>/ZnS microspheres were placed in aqueous solutions containing Co<sup>2+</sup>, Ni<sup>2+</sup>, and Pb<sup>2+</sup> ions at varied concentrations to show the microspheres' capacity to detect heavy metal ions. Sensors based on CaCO<sub>3</sub>-Fe<sub>3</sub>O<sub>4</sub>-AgInS<sub>2</sub>/ZnS offer prospects for developing methods to monitor environmental heavy metal ions. [8].

*Sensors may be used for the detection of the metal ions in various ways. Photophysical mechanisms for the detection of the analyte include charge transfer (CT), photoinduced electron transfer (PET), Förster resonance energy transfer (FRET), a more recent development aggregation induced emission (AIE) or aggregation caused quenching (ACQ), excimer formation, inductively coupled plasma atomic emission spectroscopy (ICP-AES), atomic absorption spectroscopy (AAS), voltammetry, UV-visible absorption spectroscopy, fluorescence spectroscopy and colorimetry. A conventional spectrofluorometer may be used to calculate the concentration (mM-nM) of fluorescent molecules in aqueous solution. A few instrumentation techniques are briefly discussed.*

**Photo induced electron transfer (PET) mechanism-** In the case of photoinduced electron transfer sensors, there are two types, such as fluorescence "on" and fluorescence "off" upon binding with metal cations. In PET, an electron of a photo-excited fluorophore is transferred from the receptor's HOMO to the fluorophore's energetically closed HOMO. The excited electron from the LUMO is returned to HOMO of the receptor instead of the HOMO of the fluorophore because of the presence of filled HOMO of fluorophore, which ceases the fluorescence (the "off" state). When the receptor binds with the cation, its electron is donated to the cation, leading to an increase in the receptor's reduction potential, resulting in a lower energy receptor HOMO compared to the HOMO of the



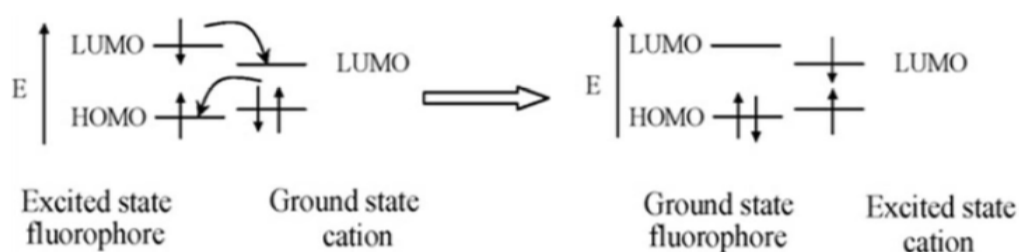
fluorophore. After the PET process is stopped, the excited electron returns to its ground state, producing fluorescence (the 'on' state) [44].



**Figure 3.1 Mechanism of PET**

Electron transfer mechanism (ET) - Energy transfer (ET) can be classified into two types depending on the distance of the energy donor from the energy acceptor: fluorescence resonance energy transfer (FRET) or electronic energy transfer (EET). In this process, always the donor unit absorbs light at relatively short wave length and the acceptor unit fluoresces at longer wavelength. Energy-transfer chemosensors are very distance-dependent.

Dexter electron transfer or electron energy transfer (EET) - In order for the Dexter energy transfer to take place, the fluorophores must be in close contact with the cations, in addition it should also have direct orbital overlap. This kind of quenching needs a particular quality of the spacer, including flexibility and a closer proximity ( $<10^{\circ}$ ) between the donor and acceptor, in addition to the proper relative energy between the fluorophore and cation.[45].

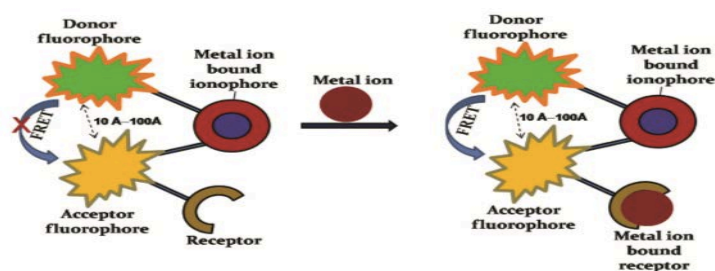


**Figure 3.2. Orbital energy level diagrams for double exchange transfer between the excited fluorophore to the cation bound by receptor followed by cation return to the ground state by non-radiative decay.**

Fluorescence resonance energy transfer (FRET) - Forster type energy transfer is also called fluorescence resonance energy transfer (FRET). In this procedure, a spatially



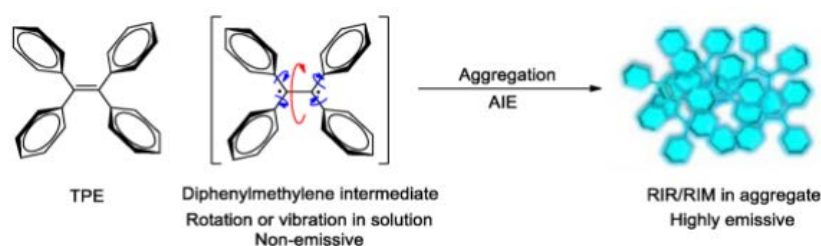
proximate ground state acceptor receives energy from an excited state donor while being monitored for fluorescence. FRET is a non-radiative process. Alternatively, an electron in the acceptor's HOMO is excited to its LUMO using the energy produced when an electron in the LUMO of the donor relaxes to its HOMO. Additionally, the wavelength of energy emitted by the donor and absorbed by the acceptor are identical. Acceptor and donor units of FRET dyes are normally connected by non-conjugated linkers, and they do not depend on the interaction between their orbitals. FRET is therefore still performed although the separate between acceptor and donor groups, the overlap in the spectral lines of acceptor absorption and donor emission, as well as the relative orientations of transition dipoles of the acceptor and donor units are critically important parameters for its efficiency [45].



**Figure 3.3. Metal-complex based fluorescent probes for metal ion sensing via FRET mechanisms**

Photoinduced charge transfer- Because electron excitation is basically a charge transfer process, the microenvironment of the fluorophore, which may include both electron donating and withdrawing couples (donor/acceptor), is often required for internal charge transfer (ICT) and photoinduced charge transfer (PCT). Exhibition of a large Stokes shift and low excitation energy (visible light) is observed in these fluorophores. When a cation binds with a donor, organic probes are known to display a blue shift for the absorption band, whereas contact with an acceptor results in a red shift. When a modified donor (D) or acceptor (A) binds to a cation, the absorption/emission band also exhibits blue or red shift, consequently modifying the PCT excited state. PCT probes based on Metal-complex contain metals that have already been bonded to receptors, yet presence of a fluorophen (F) and an acceptor group (A) in it does not alter its function as PCT probes [46].

Aggregation induced emission (AIE) based chemosensor: In this case, as the water content rises, there is an increase in the intensity of the fluorescence emission, and the intensity reduces as a complex form between the fluorophore and the metal ion in the aggregation state. When organic luminophores are excited, their free-rotating groups (rotational degrees of freedom) relax back down through rotation instead of releasing the energy as light. As Figure 3.4 illustrates, these luminophores can become very fluorescent or emissive when they aggregate or crystallize, which decreases rotational freedom, which increases quantum yield and photoluminescence efficiency. In biological applications, it can be used to detect toxic chemicals.



**Figure 3.4. Representation of AIE**

Laser induced fluorescence (LIF): Environmental monitoring is made possible through this technique. The majority of remote-sensing instruments that use LIF techniques have pulsed lasers with wavelengths ranging between 308 and 355 nm for excitation, and these instruments can also be used for vegetation monitoring and also in the cultural heritage sector. Utilizing specific spectral signatures, laser-induced fluorescence provides an effective method of identifying various types of oil released, as well as for studying the effects of weathering [51].

A nanocrystal called a quantum dot exhibits a broad absorption band and narrow and symmetric emission spectra. These properties can be tuned by modifying the material, shape, and size of the nanocrystals. Due to their outstanding chemical and optical properties, quantum dots (QDs) are widely used in many analytical fields to determine a wide variety of analytes due to their simple synthesis methods, high chemical and photo stability, outstanding aqueous dispersibility, enhanced photoluminescence efficiency, excellent surface reactivity and narrow symmetric emission profile. Their limited selectivity is a major barrier to the use of QD-based fluorescence probes, so to improve specificity, groups or materials should be added to the surface of QDs to enhance the affinity [36].

Luminescence-based analyte detection methods are highly sensitive, thus they are among the most important signal transduction methods for chemical detection. FLIM

(Fluorescence Lifetime Imaging) captures images of living cells. Using this method, one can gather data about changes in the fluorophore's local environment or its energy. Fluorescence correlation spectroscopy (FCS) is a method that measures small variations in unprompted fluorescence intensity of a sample, with the signal providing information on the kinetics of reversible thermodynamic processes.

## **DISCUSSION**

The fluorescence spectroscopy technique is a sensitive and rapid way of characterizing molecular environments and events. This spectroscopy generally involves light being emitted by the excitation source, passing through a unified wave function and colliding with the fluorophore sample, which absorbs some of the incident light and subsequently emitting fluorescence. In comparison with other analytical techniques, fluorometry offers very high sensitivity, specificity, simplicity, economical. It is usually more sensitive than absorbance measurements. The use of fluorescent materials is widely accepted and powerful in environmental, industrial, DNA sequencing, medical diagnostics, genetic analysis, forensics, and biotechnology applications. Both quantitative and qualitative analysis can be done by this tool.

Among the earliest imaging modalities developed was fluorescence imaging, a technique applied most often in the biological sciences. Fluorescence microscopy is commonly used to study dynamic cellular events. As a method that relies on the principle of fluorescence, fluorescent microscopy has revolutionized cell biology and molecular biology. The ability to achieve submicron resolution is one of the benefits of fluorescence imaging. Compared to MRI contrast agents, it is more sensitive and less toxic, but suffers from low depth penetration and light scattering.

Despite the great advances, there are still challenges to overcome such as the limited targeting of metal ions and the need to determine different types of metal ions detection assays with different emission wavelengths for simultaneous on-site detection alongside the need to develop fluorescent materials[40].

## **CONCLUSION**

The field of fluorescent chemosensors has advanced greatly in the 150 years since Goppelsroder published the first fluorescent chemosensor for Al<sup>3+</sup>. Currently, fluorescence is one of the most effective detection tools available due to its low detection limit and its ability to visualize through confocal microscopy. The measurement of absorbance and fluorescence is different, so fluorescence is more sensitive. Numerous

environmental, industrial, and biological uses involve metals. In this review several main principles of fluorescence sensing have been discussed, as well as the various strategies used in sensor design. We reviewed the creation of different fluorescence sensors that use targeted receptor moieties coupled to a spacer or directly coupled to various fluorophores, as well as the photophysical background that contributed to their development. The sensors are able to detect numerous metal ions in a different environmental and biological sample using a number of different of binding modes and various fluorescence response mechanisms.

As a result of molecular recognition, interaction between the receptor and analyte should lead to a marked modification of the photophysical properties of the signal transducer parts via some means of signal transduction mechanisms. A spectroscopic instrument can therefore detect the change in absorption or emission properties. There are a number of signal transduction mechanisms discussed, including excited-state intramolecular proton transfer (ESIPT), internal charge transfer (ICT), fluorescence resonance energy transfer (FRET), and monomer-excimer, etc. Fluorescent probes that enable the detection and imaging of toxic substances and crucial cellular components, including small chemical species linked to various human diseases, have been developed by combining mechanistic modalities with analyte-specific receptors, appropriate fluorophores, or reactive sites. With high sensitivity and specificity, it has been successfully applied for the diagnosis of multisystem cancers. As this technology is widely applicable, it is anticipated to be a crucial research area in the near future. In future in-vivo imaging and detecting more than one analyte at a time will be possible using fluorescent probes with fewer difficulties. In summary, the past guided us in the correct direction, the present presented us with problems to overcome, and the future provides us hope that chemosensors will usher in a more civilised age.

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