Fluorescent based chemosensors and its applications: A Review

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Abstract:
There has been extensive use of fluorescent chemosensors for ions and neutral biomolecule in a wide range of disciplines, including biology, physiology, pharmacology, and environmental sciences. Including, fluorescent based sensors are frequently used for the detection of biomolecules or metal ions due to their excellent sensitivity, high precision, immunity to light scattering, and ease of use as well as In addition to measuring dissolved oxygen levels, fluorescence sensors may be used to examine chlorophyll. Fluorescent sensors built on conventional organic and polymeric fluorophores have become more prevalent in recent years. For sensing and biological imaging, a variety of fluorescent probes having AIE characteristics have been quickly developed. Fluorescence imaging as a powerful tool for monitoring biomolecules within the living systems. For the detection of physiologically and/or ecologically significant organisms, a wide variety of fluorescent chemosensors have been made in recent years. Many issues and difficulties still occur in this subject, regardless the advancements achieved. This review article covers the background and offers a broad summary of how the study of fluorescent-based chemosensors has advanced. This will be accomplished by emphasizing certain innovative and exemplary works that have significantly advanced this field. The fundamental ideas behind designing chemosensors for particular analytes, issues and difficulties encountered in the field, as well as potential future research avenues, are all explored. In the current literature review, a brief discussion of the application of fluorescent-based chemosensors in diverse sectors is also provided.

Keywords: *Chemosensors, fluorescent, biomolecules, chlorophyll, metal ions.*

Published in IJIRMPS (E-ISSN: 2349-7300), Volume 11, Issue 1, January-February 2023

1. Introduction:

Researchers have integrated the field of fluorescent-based sensors because they have been employed inconsistently and erratically during the previous few decades [1]. F. Goppelsröder described the first fluorescent chemosensor in 1867 [2], which used the formation of a highly fluorescent chelate of the morin ion to measure the aluminum ion (Al^{3+}). Over the following few years, this resulted in the invention of other fluorescent chemosensors for the detection of numerous different metal ions, which served as the precursor of analytical chemistry as we today recognize it. Rather than focusing on the identification of anions or neutral species, the early fluorescence chemosensors were really primarily focused on the detection of metal ions. This is because metal ions selectively bond to water far more readily than anions or neutral species. The two founder scientists of modern chemosensors, de Silva and Czarnik, encouraged and paved the way for the area's spectacular expansion and growth in more past years, beginning about 1980. Since those early days, fluorescent chemosensors have undergone tremendous development, and their range of use has been expanded to encompass a wide range of biologically significant analytes [1-3].

Fluorescent chemosensors have now been frequently used in a range of domains, including biology, medicine, pharmaceuticals, and environmental engineering, because of their high levels of sensitivity and, in especially, their capacity to be used for both spatial and temporal sampling for in vivo imaging applications.

Researchers shall witness an ever-increasing necessity highly sensitive and selective chemosensors for in vivo biomedical application [4, 5].

In the field of environmental science chemo sensor play a vital role to sustain ecology for that purpose environmentalists and geologists have been very interested in the development of sensors that can identify heavy metal ions in recent times. Due to its capacity to enable naked eye detection of color change and simplify the entire process, colorimetric receptors were designed for the selective recognition of heavy metal ions. Chemosensors, however, continued to be a dependable method for the accurate detection of mercury toxicity. Because of the ratio between two absorption spectra that can aid in adjusting the sensor analytic concentration as well as environmental factors like polarity, photo-bleaching, and temperature, fluorescent chemo-sensors are recommended for a ratiometric response. As a result of the expectations, reversible ratiometric chemosensors that can detect Hg^{2+} were developed [6].

There is a constant need for chemosensors with selectivity for particular metal ions. Chemosensors that target the dangerous heavy metal ions continue to be essential. Work to create compounds that selectively respond to particular metal ions for use as ion sensors has, in part, been motivated by recognition of the harmful effects of some transition and post-transition metal ions on people and animals. Due to major advancements in the synthesis of novel fluorophores and the creation of affordable yet effective techniques, research on fluorescence sensors capable of detecting the heavy and transition metal ions has attracted attention. In the molecular recognition and contemporary uses of chemosensors, benefits such high sensitivity, selectivity, quick response times, naked-eye detection, and fluorescence detection have been recognized as attractive possibilities [7].

Water quality is also detected using fluorescent-based chemosensors. The development of a selective and specific chemosensor for cation detection in drinking water is a current issue for researchers. The association site is described as a safe hydrophobic microenvironment where, in the presence of biological anions receptors, anionic species can be encapsulated by hydrogen bonds. Fluorescent cation detection, which has mostly been used to non-aqueous media, is still being promoted, which is advantageous for biomolecules study. By developing several new chemosensors for recognizing cations in drinking water and agricultural crops, this work addresses the Algohary, A.M. in 2021 [8]. The investigation introduced by Algohary, A.M strong is on pyridine chemosensors or the quantitative detection of CuII, COII at specific wavelengths in water and agricultural samples. Because of this, chemosensors have been made and their structural details have been determined utilizing spectral and elemental studies. By displaying colormetric responses, the synthesized chemosensors demonstrated good selectivity and specificity for the detection of copper (CuII) and cobalt (CoII) cations.

Due to their distinctive advantages in high sensitivity, convenience, ease of measurement, low cost, easily performed, and versatility, offering sub nanometers spatial resolution with submicron visualization and submilli second temporal resolution, fluorescent chemosensors have garnered a lot of attention. Fluorescent based chemosensors have demonstrated enormous promise in a variety of real-world scenarios and applications, including the detection of chemical warfare agents, insufficient sewage pollutants, fluorescence guided surgery, whole body diagnostic imaging, in vivo flow cytometry, and e-Health medical tools [1, 9, 10].

2. Types of chemosensors:

The chemosensors also known as chemoreceptors are divided on their type of signal generation [11]. Chemosensors are broadly divided into four types as shown in Figure 1.

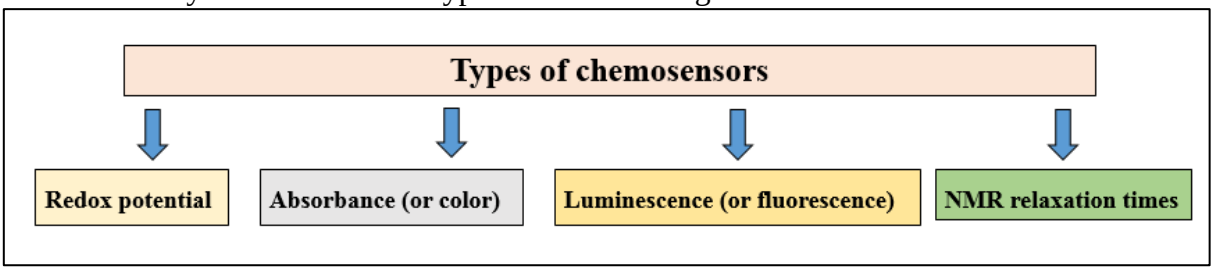

Figure 1: Types of chemosensors

Figure 1 reveals types of chemosensor based on their working principle. The fluorescence based chemosensor work on the luminescence. The luminescence is one types of light energy having different wavelengths. Chemosensors are further divided into three categories: "on-off," "off-on," and "ratiometric"

[11]. An electrically or vibrationally stimulated species that is not in thermal equilibrium with its surroundings will spontaneously emit radiation; this emission usually take the form of either fluorescence or phosphorescence. The term "luminescence" refers to a number of methods where radiation is emitted by atoms or molecules, but the process by which the emission is caused differs. The sensor industry is especially interested in optical spectroscopy, such as UV-Vis and fluorescence. The ability for the scientist to manipulate various fluorescent pathways makes fluorescence spectroscopy particularly appealing [12]. These categories are based on variations in fluorescence signal, and each category is further divided into various divisions based on aspects of molecular structure and/or recognition methods. The early definitions of fluorescent chemosensors stated that they were compounds having a binding site, a fluorophore, and a mechanism for communication between the two sites [11, 13].

3. Literature Review:

Every part of contemporary living involves the usage of sensors; for instance, a smoke or carbon monoxide detector is likely installed in many contemporary homes. Fiber-optic sensors are used in industry to measure process factors like temperature, pressure flow, and liquid level. Sensors are needed in the environment to monitor air pollution and harmful chemicals, as well as in healthcare settings to identify medical disorders. Over the past few decades, sensor technology has grown incredibly quickly. Whereas biosensors integrate a biological component, such as bacteria, tissue, cells, organelles, nucleic acids, enzymes, or antibodies, chemical sensors measure, monitor, and identify chemical molecules. Because of the many advantages they provide, research into the design of fluorescent-based chemosensors with high sensitivity and selectivity for heavy- and transition metal cations that are significant to both the environment and human health is expanding [10-12]. In this article, major developments in chemosensors have been reviewed.

Shuo_Liu el at. [13] Reported the fluorescent chemosensors for copper (II) ion. In this article author mainly focused on the structure, mechanism and application of fluorescent chemosensors for copper ion detection. Because In the human body, copper is the third most commonly found important trace metal element. It is also necessary for many living things to function normally, but excessive amounts of Cu^{2+} are extremely hazardous to living things and cause massive amounts of pollution in our environment. Hence, developing more precise and focused fluorescent chemosensors is crucial for accurately assessing the amounts of Cu^{2+} in biological and environmental systems.

Yun-Bao Jiang et al. [14] developed a simple yet highly selective and sensitive Cu^{2+} ion chemosensor. In the addition of Cu^{2+}, there was a blue shift and a substantial increase in the CT fluorescence of in ACN and aqueous ACN solutions. The transition metal ion acts as a fluorescence quencher, and the sensor responds to Cu^{2+} with a highly selective fluorescent response. Because both the electron donor ($-N(CH_3)_2$) and the ionophore in the electron acceptor in may be used to create turn-on CT fluorophores for transition metal ions, a new technique for manufacturing turn-on CT fluorophores for transition metal ions has been developed. He reported the principle similar to PET inhibition, with the metal ionophore incorporated in both the electron donor and acceptor. Cu^{2+} fluoroionophores showing enhanced excimer emission were recently reported. Herein is described a new CT dual fluorescent fluoroionophore that shows a highly selective and sensitive fluorescent response toward Cu^{2+}.

H. Cao et al. [15] developed three anthracene-based fluorescence sensors with a Schiff base moiety for Cu^{2+} detection. Two of the three derivatives had a Cu^{2+}-induced fluorescence Turn-On with great sensitivity and selectivity over other metal ions. In the presence of Cu^{2+} in the range of 1.2106 to 4.8105M, a 120-fold significant fluorescence amplification was seen for 2 in acetonitrile media, allowing to detect Cu^{2+} in drinking water or biological samples. 2 also presented a simple but effective identification unit for Cu^{2+} based on the PET mechanism, which could be relevant for future chemosensor development. The author mentioned containing a Schiff base moiety were synthesized and investigated as chemosensors for the detection of Cu^{2+}. Authors also reported extremely high selectivity to Cu^{2+} over other 12 interference ions with 120-fold fluorescence enhancement at 468 nm in the acetonitrile media. The nitrogen atom in Schiff base and sulfur atom of 1a provided a binding scaffold for recognition of Cu^{2+} with high affinity (Ka = 4.35 × 104 M−1). The formation of Cu^{2+} complex caused a decrease of electron density on nitrogen atom and sequentially led to fluorescence enhancement based on the photoinduced electron transfer (PET) mechanism.

Chunwei Yu [16] et al. designed and manufactured a novel "off-on" fluorescent chemosensor based on the equilibrium between the spirolactam (non-fluorescence) and the ring-opened amide for Cu^{2+} detection

using naphthalimide modified rhodamine B. (fluorescence). In neutral aqueous conditions, the chemosensor displayed high Cu^{2+}-selective fluorescence amplification over a variety of other metal ions or anions. The limit of detection (LOD) for Cu^{2+} was determined to be as low as 0.18 M, and the 1:1 binding stoichiometry for 8 and Cu^{2+} was discovered. In addition, the demonstrated its usefulness in biological systems for measuring Cu^{2+} in living cells.

Song et.al [17] utilized an irreversible desulfurization reaction to build up a new fluorescent ratiometric chemosensor based on the FRET, which would be used to the detection of Hg^{2+} in aqueous medium.

Velmurugan et al. [18] have successfully designed and synthesized a novel BINOL based fluorescent chemosensor which exhibited a very selective "turn-on" fluorescent chemosensor for Hg^{2+} ion in the existence of all other metal ions (transition, heavy and alkali metal ions) at neutral pH. The significant enhancement with high emission selectivity of compound 4 toward Hg^{2+} is due to PET inhibition process. A simple dimeric binol-based fluorescent chemosensor capable of detecting Hg^{2+} in aqueous media is designed and synthesized. The Hg^{2+} recognition processes follow a photo induced electron transfer (PET) mechanism and are scarcely influenced by other coexisting metal ions. In addition, determination of mercury in waste water samples was also analysed by authors.

Jing et al. [19] synthesized a highly selective ratiometric fluorescent chemosensor for Hg^{2+} ions. It was prepared by joining terpyridine and photochromic perfluoro-diarylethene via a stilbene linkage. When triggered by Hg^{2+}, a 1:2 metal/ligand complex was formed, with the result that its emission intensity enhanced considerably by three fold larger fluorescence quantum yield and the emission peak shown a remarkable bathochromic-shift from 454 nm to 514 nm with clear color change from light blue to bright green.

Hosseini et al. [20] have designed and synthesized magnetic core-shell $Fe_3O_4@SiO_2$ nanoparticles functionalized by BTC which acts as a fluorescent chemosensor for Hg^{2+} ion. The enhancement of fluorescence is attributed to the strong covalent binding of Hg^{2+} ions with the binding constant value of 1.7×105/M. Sensor compound 8 can be utilized for analysis of Hg^{2+} ions in environmental sample.

He et al. [21] have designed and synthesized a new chemosensor having a BODIPY signal moiety and a bis [2-(phenyls leno) ethyl] amine detection site. It was shown remarkable color changes and fluorescence enhancement upon the binding with Hg^{2+} in CH_3CN, which make compound 14 be used as a colorimetric fluorescent sensor. Developed novel BODIPY-based colorimetric fluorescent sensor shows high selectivity and sensitivity toward Hg^{2+} and Cu^{2+} over alkali and transition metal ions. Se-1shows a significant red-shift in the absorption spectra from 525 to 571 nm for Hg^{2+} and 590 nm for Cu^{2+}, which induces color changes from pink to purple and blue. Upon excitation at 570 nm, upon interaction with Hg^{2+} ions displays a 5-fold fluorescence enhancement with a 2 nm blue-shift, while with Cu^{2+} exhibits a 13-fold fluorescence enhancement and red-shifts from 595 to 610 nm. The binding mode of with Hg^{2+} or Cu^{2+} has been investigated by Job's plot, ESI and 1H NMR experiments. Authors also investigated that, the absorption and fluorescence of the Hg^{2+} complex can be reversibly restored to that of the uncomplexed ligand by using EDTA.

4. Characterization techniques of fluorescent based sensors:

The characterization of any sensor is very important parameter in the research. The chemosensor can be characterized by conventional methods such as- Inductively coupled plasma atomic emission spectrometry (ICP-AES), Inductively coupled plasma mass spectrometry (ICP-MS), Atomic absorption spectroscopy (AAS) and electrochemical methods are costly and require professional characterization techniques [12, 16, 22]. Compared to sophisticated instrumentation, fluorescent chemosensors for analyte detection and analysis have shown to be promising alternatives due to the simple equipment required, cost-effective synthetic procedures and analysis, rapid response times, low detection limits, high resolution and good selectivity and sensitivity.

Aptamers can be isolated from oligonucleotide libraries using SELEX (Systematic Evolution of Ligands by EXponential enrichment). Cell-SELEX, capillary electrophoresis-based SELEX, microfluidics-based SELEX, FACS-based SELEX, microtiter plate-based SELEX, magnetic bead-based SELEX, and in vivo SELEX are only a few of the newly developed SELEX variants. Biosensors primarily employ optical, electrochemical, and piezoelectric methods. These biosensors are further divided into labeled and label-free aptasensors based on various transduction methodologies. The most popular technique for label-free optical sensors is surface plasmon resonance (SPR), whereas fluorescent dyes (fluorescein) are utilized for label-

based optical aptasensors. Fluorescent nanoparticles, like QDs, offer significant advantages over conventional fluorescent dyes for tracking biological systems in real time [23, 24].

5. Applications of fluorescent chemosensors:

Due to the ease of use, high selectivity, and sensitivity in fluorescence tests, fluorescent chemosensors have grown significantly and applicable over the past few years into a various area. In this topic the applications of fluorescent chemosensors is described in brief. The hazardous elements like Cu^{2+}, Fe^{3+}, Fe^{2+}, Cd^{2+}, Hg^{2+}, and Zn^{2+} can be detect by using fluorescent chemosensors [20- 22]. Even though by developing the probe of fluorescent chemosensors various hazardous element can be detect in water as well as other drinking liquors to maintain the quality of product and reduce the health effects on human health. The fluorescent chemosensor based on β-diketone for detecting Th^{4+} ions in aqueous solution and application in living cell imaging is also one of the reported work by researchers [23]. The fluorescent chemosensors is also used in biological imaging applications. The Figure 2 shows that the various applications of fluorescent chemosensors [23-25].

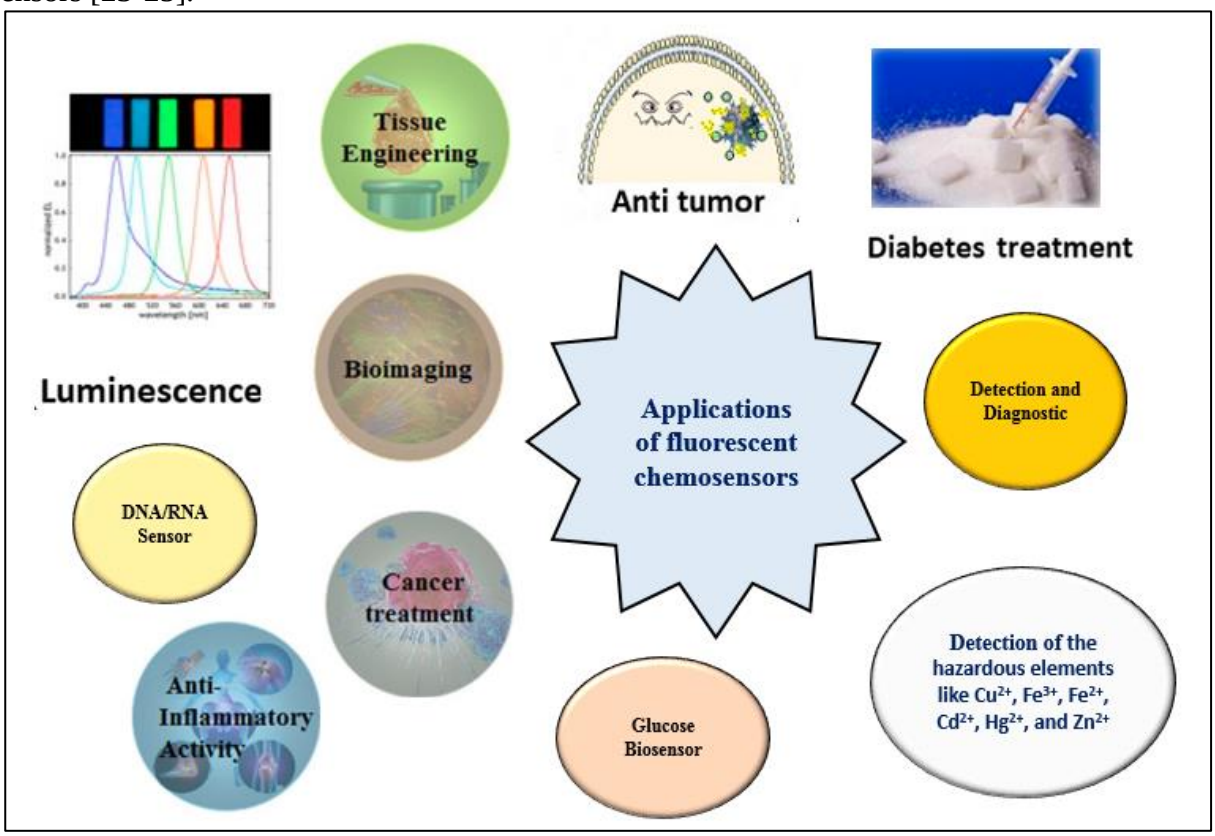

Figure 2: Applications of fluorescent chemosensors

Conclusion and Future Scope

The current review paper provided the brief information of different emerging area of chemosensors. The different types of chemosensors as well as different characterization methods used in analysis and development of chemosensors. Chemosensors have tremendous applications in the field of science and technology as well as biomedical filed. This paper is very helpful in future those researchers will work in the area of chemosensor.

Acknowledgment

Authors are very much thankful to Principal of KTHM College, Nashik for providing lab facility with computer and internet, I would also thanks to Head of Department and research centre Chemistry of KTHM College, Nashik for his constant guidance and extensive support to encourage for this work.

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