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Research Paper

Fluorescent Chemosensors to Detect Mercury Ions: A Review

Mrs. ParveenSaini
Department of chemistry, SDAM College Dinanagar, Punjab-143531, India

ABSTRACT
Exposure to mercury ions, even at very low concentration is very hazardous to all living organisms on earth. Great efforts have been done by researchers to develop chemosensors, especially fluorescent probes to detect these toxic ions. In this review, the recently reported Hg ion sensors are briefly discussed and summarized. Chemosensors are categorized based upon the nature of fluorophoric unit as well as moiety binding to mercury ion.
Keywords: Mercury ion, fluorescent sensors, Chemo-sensing, Heavy metals, host-guest chemistry

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I. INTRODUCTION

Chemosensors are the molecular frameworks that have a wide range of applications in the field of analytical chemistry, environmental chemistry and medical diagnosis [1-2]. These molecules provide an accurate, conducive and low-cost determination of various organic and inorganic anions, enzymes and toxic heavy metal ions with high selectivity and sensitivity [3]. The selective detection of metal ions by these molecules has attracted researcher's attention towards the human health and environment protection. It is well seen that rapid growth of industrialization in developing countries and extensive use of natural resources are the main components of environmental contamination [4-5]. The contamination of heavy metals is a major environmental problem due to their accumulation and strong toxicity that lead to severe health issues even at low concentration limits [6-8].

Mercury or Mercury ion Hg^{2+} is one of the most prevalent toxic heavy metals is considerably harmful to the environment and the human health. Mercury is considered as highly hazardous, lethal and easily changed into most toxic form like methyl mercury by bacteria and it is extensively scattered in the environment owing to the numerous human deeds and later bio accumulates through the food chain. Excessive deposition of mercury in human body can cause multiple diseases such as deafness, headache, visual impairment, serious effect on central nervous system and even permanent damage of the brain [9-10]. Therefore, developing a highly selective and rapid method for detecting mercury ions is still a vital need in order to solve the problem of increasing mercury pollution in water and the environment. In this regard, many organic compounds have been synthesized and are being used as successful chemosensors. Above all, the fluorescent chemosensors have drawn greater attention due to the advantages of fast response, signal visibility, and application for on-site and high throughput measurement [11-15].

A fluorescent chemosensor typically consists of two units, one receptor unit that selectively binds metal ion and second unit for output message that results from photoluminescence changes in the probe after binding with the analyte ion. Among numerous kinds of luminescent chemosensors, organic fluorescent materials are most widely used and studied because of their chemical structures. Their functional groups can be easily modified through various chemical processes to enhance their binding ability and fluorescent quantum yield. Chemosensing by these probes is based upon host–guest relationship where target species gets bonded with receptor unit linked to the fluorescent unit (fluorophore) results into changes in either position or intensity of emission or absorption band upon binding with metal ion [16-21]. This report summarizes few organic frameworks developed during past few years used to detect highly toxic mercury metal with great sensitivity and selectivity.

II. Review of literature

Rhodaminebased fluorescent chemosensors:

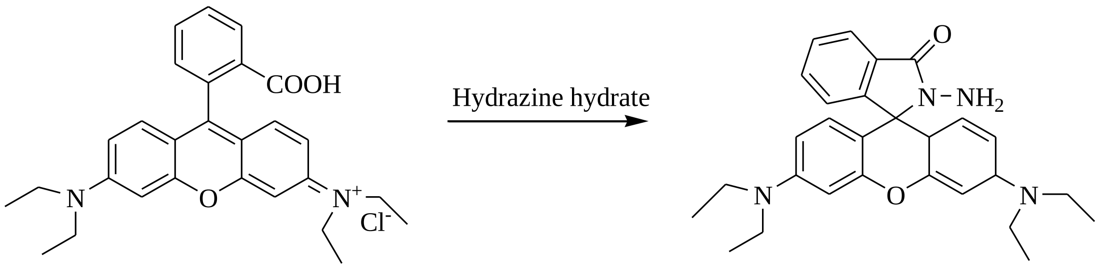
Rhodamine appended fluorophores gained considerable attention due to their high fluorescent quantum yield, broad absorption and excellent enhancement in emission wavelength on complexation with metal ions [22].

Rhodamine B derivatives also show significant color variations during coordination with metal ions, so has been widely used to design on-off fluorescent probes.

Li. et al. group of researchers reported the synthesis of rhodamine linked triazoleas chemosensor1 by introducing rhodamine B to 5-methyl-2-phenyl-2H-1,2,3-triazole-4- carboxylic acid. In first step, rhodaminehydrazide was synthesized using proper reaction procedure (Fig 1). After that, the fluorescent sensor 1(Fig 2) was generated on treatment of rhodaminehydrazide with triazole derivative. Synthesized molecule found to have specific chromogenic response on binding with Hg^{2+} ion in DMF-H_2O (v:v =1:1) at pH =7.4, the colourlessrhodamine appended triazole turned pink in the presence of mercury ion that enabled naked eye detection of ion. The probe displayed high selectivity to Hg^{2+} ion, supported by UV-Visible and fluorescence spectroscopy along with TD-DFT calculations. The fluorescence signal was not affected with the presence of other metal ions. Binding of triazoleunit with Hg^{2+} ion in 1:2 molar ratio causes ring opening of spirolactum (colourless) to ring opened amide with pink colour with significant enhancement in fluorescence intensity [23].

In 2020, Ding et al. described the synthesis of rhodaminebased chemosensor2(Fig 2) by introducing rhodamine B to Ethyl 2,5-diphenyl-2H-1,2,3-triazole-4- carboxylate. The probe displayed distinct enhancement in fluorescence at 577nm on complexation with Hg^{2+} in water-dimethyl formamide solution at pH=7.4. Also, the colourlessrhodamine appended triazole turned pink in the presence of mercury ion that enabled naked eye detection of ion. This turn on/off fluorescence well explained the ring opening of rhodamine moiety on coordination of mercury ion with probe [24].

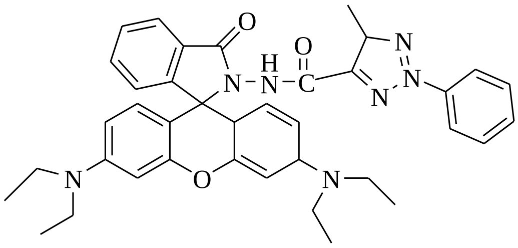
Another rhodamine linked triazole fluorescent chemosensor3 (Fig 2) for Hg^{2+} was produced by reacting rhodaminehydrazide with previously synthesized triazole derivative, 5-methyl-1-phenyl-1H-1,2,3-triazole-4-carboxylic acid. On complexation with Hg^{2+} Ion, chemosensor 3 exhibited about 4000-times increase in fluorescence intensity in comparison to other metal ions in competition. Complexation of molecule 3 with Hg^{2+} ion in 1:2 molar ratioproduces colour changes [25].



Rhodamine B

Rhodamine hydrazide

Fig 1: Synthesis of rhodaminehydrazide from rhodamine B



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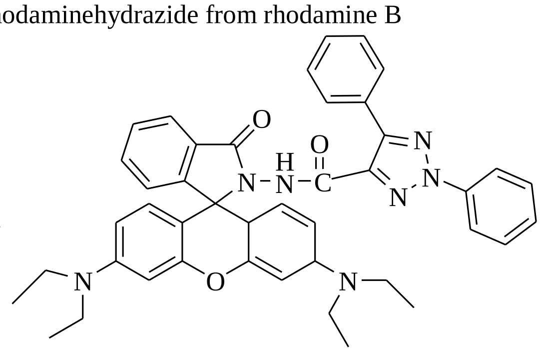

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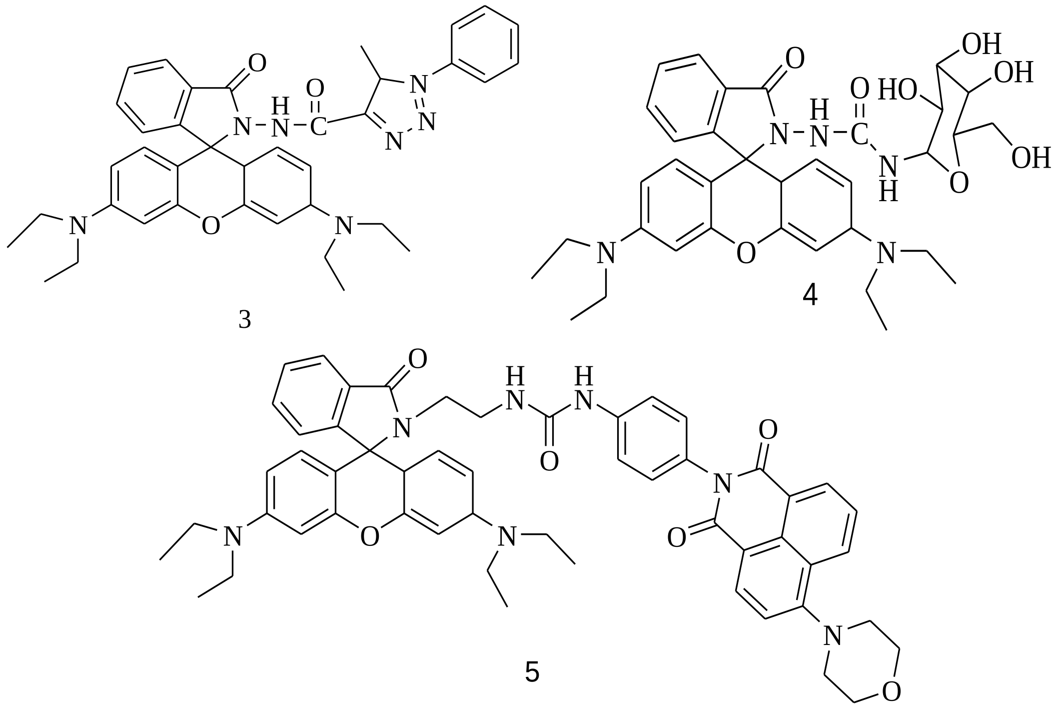


Fig 2: Rhodamine linked molecules as fluorescent chemosensors

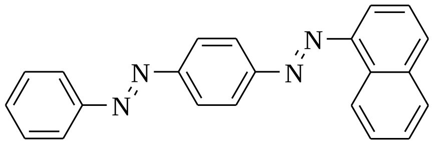
A novel ‘‘turn-on’’ fluorescent sensor 4 (Fig 2) based on glucose and rhodamine B for finding of Hg^{2+} ions was designed and synthesized by Li et al. The fluorescent sensor showed a great specificity for Hg^{2+} ions than for other metal ions in aqueous medium. On the addition of Hg^{2+} ions to the solution of glucose-based rhodamine B sensor, the absorption and fluorescence signals enhanced remarkably at 567 and 587 nm respectively. Titration of sensor with Hg^{2+} ions showed 1:1 stoichiometric reaction. Furthermore, glucose-based rhodamine B sensor can be used for the detection of the limited Hg^{2+} ions in drinking water [26].

Fluorescent chemosensor 5 was synthesized by an irreversible desulfurization reaction and used for the detection of Hg^{2+} in aqueous medium. The colorimetric and fluorescent response to Hg^{2+} can be easily detected even by the naked eye. Chemosensor, shown high selectivity and sensitivity for Hg^{2+} with a wide pH range (1.0-8.0) and can be utilized to set up the fluorescence assay for Hg^{2+} in living cells [27].

Polycyclic aromatic hydrocarbon based sensors:

A series of novel azo linked polycyclic aromatic hydrocarbons based sensors 6-8(Fig 3) were designed and synthesizedin a single step. Compound 6 and 7 were developed for the selective and sensitive detection of Hg^{2+} ions over the other transition metal ions. These sensors exhibit fluorescence enhancement with a detectable naked-eye color changes in presence of Hg^{2+} ions in aqueous solution [28].

Velmurugan et al. have successfully designed and synthesized a fluorescent chemosensor 9 (Fig 3), that exhibited a very selective “turn-on” response for Hg^{2+} ion in the existence of all other metal ions at neutral pH. The significant enhancement with high emission selectivity of compound 9 toward Hg^{2+} is due to photoelectron transfer process. Moreover, the finding limit of receptor compound 9 toward Hg^{2+} was 4.4×10^{-7} M, which shows that the sensor can be utilized in toxicological, biological, and environmental applications [29].



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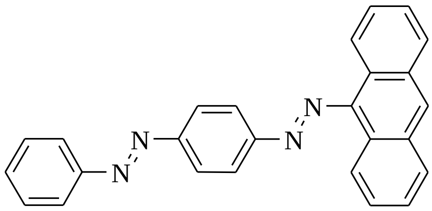

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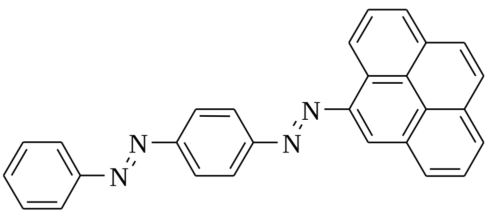

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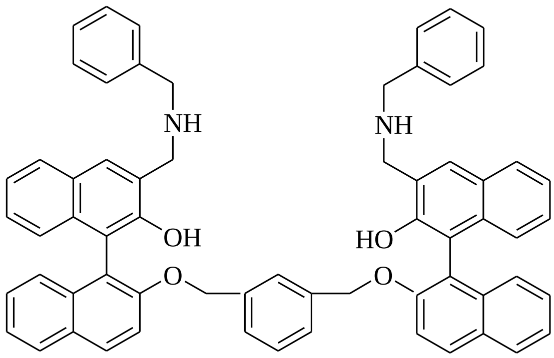

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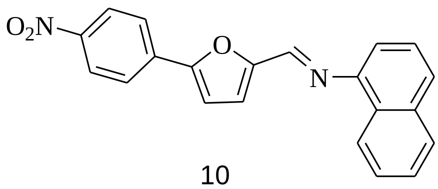
Fig 3: Chemosensors with polycyclic aromatic hydrocarbons as fluorophore

Schiff base linked fluorescent chemosensors:

A highly efficient and selective chemosensor 10 (Fig 4) was designed and developed by Zhang and co-workers to detect Hg^{2+}ions based on a non-sulfur, easily prepared Schiff base compound [30]. Particularly, the high selectivity experiments showed that the fluorescent sensor is specific for Hg^{2+} ions even with the interference by high concentrations of other metal ions.



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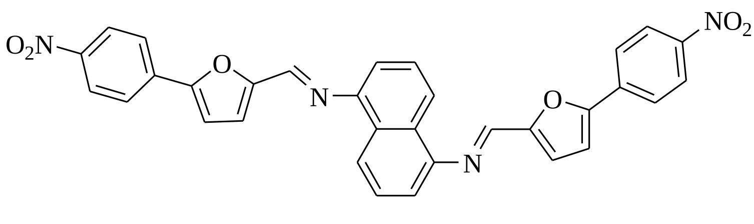

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Fig 4: Schiff base linked fluorescent chemosensors of mercury

Fluorescent sensor 11 (Fig 4) of mercury ions has been reported by Wu and co-workers. This sensor has 1, 5-diaminonaphthalene Schiff base derivatives which showed excellent fluorescent and UV-visible responses on complexation with Hg^{2+} ions by the direct splitting of carbon-nitrogen double bond [31].

III. CONCLUSION:

Present review summarizes recently synthesized fluorescent sensors that selectively recognize mercury ions from aqueous medium and the sensitivity of chemosensors do not changewith the presence of other metal ions. Sensors havingaromatic groups with extended conjugation attached to receptor moiety have an excellent fluorescent behavior that is observed even with naked eye. There is lot of scope to design and develop such type of probes to address environmental as well as health related issues.

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