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ORGANIC MOLECULAR FRAMEWORKS AS FLUORESCENT SENSORS TO DETECT CADMIUM AND MERCURY IONS FROM AQUEOUS MEDIUM: A REVIEW

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ABSTRACT

Exposure to heavy metal ions, even at very mild concentration limits is very hazardous to all living creatures on earth. The development of reliable and sensitive molecules to detect these toxic ions is of considerable interest. Great efforts have been done by researchers to develop chemosensors, especially fluorescent probes to detect these toxic ions. In this review, the recently reported cadmium and mercury ion sensors are briefly discussed and summarized. Chemosensors are categorized based upon the nature of fluorophoric unit as well as receptor moiety.

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INTRODUCTION

Quality of ground, surface and drinking water is deteriorating day by day with the rapid growth of industrialization in developing countries in order to reduce the scarcity of resources as a result of growing population (1-2). The extensive use of natural resources to develop urbanization and industrialization are the main sources of release of various contaminants in water. Among the various types of water pollutants; such as fertilizers, pesticides, plastics, oils, other organic and inorganic wastes, the heavy metal ions are highly toxic and problematic (3-5). Although some metals like iron, zinc and cobalt are essential nutrients, but their higher concentrations can be hazardous to humans (6). Heavy metals such as mercury and cadmium are on the top of the toxicity level and are highly poisonous even at very low concentration level. These metals are closely associated with deadly cancer and neurodegenerative diseases (7-10). Cadmium exhibits carcinogenic effects on humans. Although it naturally exists in the environment at very low concentration, the level of Cd has been considerably increased by anthropogenic activities. Zn and Pb refineries, disposal of industrial wastes contaminated with Cd, Ni/Cd batteries, electronic products, fertilizers and pesticides are the main sources of Cd exposure. Cd has the highest solubility in water as compared to the other heavy metals. Therefore the rate of Cd spread in nature is very high and it is not an essential element for human life. Due to its water-soluble properties, Cd is taken into living systems by plants and marine species. Cd exhibits long-term persistence in the environment and easily accumulates in vegetables, crustaceans, and mollusks over time. The removal of Cd is extremely difficult when it enters the human body. The toxicity of Cd affects the kidneys which can cause kidney dysfunction. Its toxicity also affects respiratory and skeletal systems (11-13).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 (14-15). Therefore, developing a highly sensitive, selective and rapid method for detecting these ions is still a vital need in order to solve the problems of increasing mercury and cadmium

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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 (16-20).

Fig 1. Graphical design of fluorescent chemosensor

Sensing behavior of fluorescent chemosensors is based upon host-guest relationship, which is well shown in the graphical design (Fig 1). The sensing probe is basically consisting of two unit; receptor unit and fluorescent moiety. The receptor unit holds the analytic ion and this binding causes observable changes in the absorption or emission frequencies of fluorescent moiety (21). This report summarizes recent advances in the designing and development of organic molecules used as fluorescent chemosensors to detect highly toxic heavy metal ions of mercury and cadmium.

Fluorescent Chemosensors of Cadmium: A report by T. Gunnlaugsson *et al* describes the synthesis and photochemical evaluation of two fluorescent chemosensors1and 2(Fig 2) for the selective detection of Cd(II) ions in aqueous solutions at pH 7.4. Both sensors have good selectivity for Cd(II) over competitive ions like Zn(II), Cu(II) or Co(II) ions. Weak emission bands were observed for free sensors at pH 7.4, while the broad emission with significant shifting toward higher wavelength was observed in the presence of Cd (II) ions (22). In 2017, a report described the synthesis of semicarbazone derivative of a pyrene-appended piperidin-4-one 3(Fig 2), a fluorescent chemosensor of cadmium and studied its metal ion sensing behavior in water and aqueous β-cyclodextrin medium. Pyrene unit provides good fluorescence qualities to the assembled sensor. In β-cyclodextrin medium, the sensor molecule gets binded with cyclodextrin unit and provides non-toxicity to system as well as improves the sensing ability of chemosensor. Sensing results explains that formation of cyclodextrin complex does not affect the sensitivity and selectivity of probe (23).

A selective colorimetric and fluorometric chemosensor 4 (Fig 2) based on conjugated polydiacetylenes has been synthesized by T.C. Pham *et al* in 2019 that displayed a selective colorimetric and fluorometric change in the presence of Cd (II) at pH 7.4. A rapid fluorescent turn on response with visual detection (blue to violet) on successive addition of aqueous solution of cadmium was shown by the sensor with significant selectivity to Cd (II) in comparison to other metal cations. The minimum detection limit of 1.85x10^{-5} M was found for cadmium ions (24). In 2019, a fluorene based fluorescent chemosensor 5(Fig 2) was prepared and explored for detection of metal ions. Out of various metal ions tested, the sensor was found to be highly sensitive and selective for Cd (II) ions, which illustrated red-shifted fluorescence spectra at pH 7. An increase in cadmium ion concentration caused increase in fluorescence intensity also. Limit of detection of Cd (II) ions was 0.289 mg/L .To increase the efficiency of fluorescence detection, the probe was functionalized with PMMA/SPIONs.

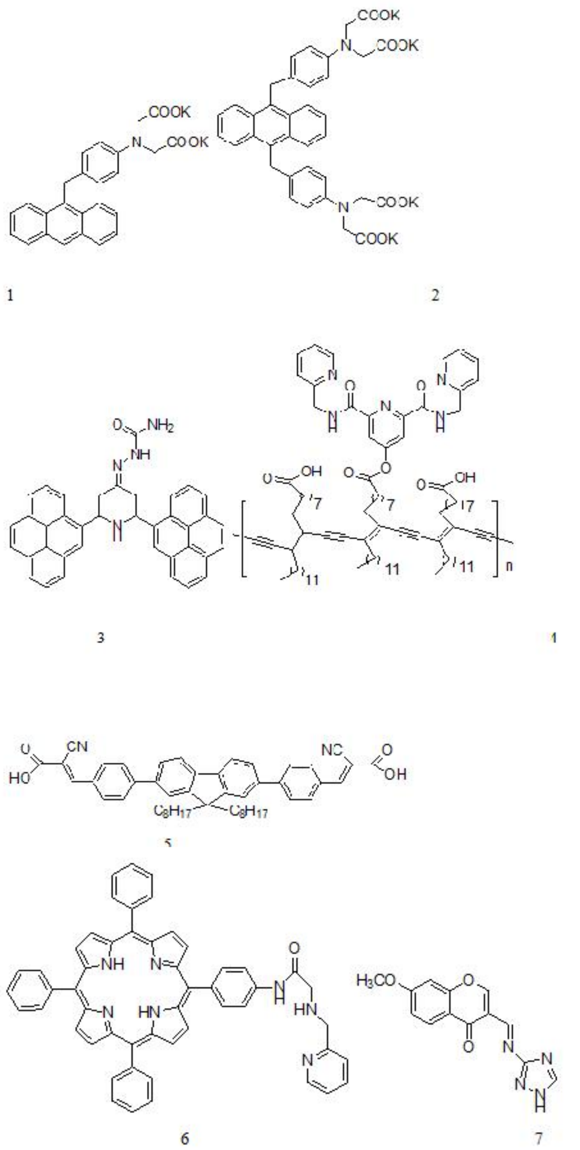

Fig 2. Fluorescent chemosensors for selective detection of Cd(II)

The fluorescent magnetic nanoparticles have also been investigated with the successive addition of Cd (II) ions. They indicated the detection of Cd(II) ions in the limit of detection at 0.184 mg/L that is lower than the simple chemosensor 5. Moreover, the functionalized fluorescent magnetic nanoparticles found to have improved sensing qualities (25). A new chemosensor 6(Fig 2) based on a functionalized porphyrin was generated that exhibits efficient colorimetric and fluorometric detection of Cd (II). Chemosensor displayed a distinct color change, as well as significant ratiometric variations in the absorption and fluorescent emission spectra upon exposure to Cd (II) ions. The dual chromo- and fluorogenic responses of the probe are attributed to the formation of a 1:1 complex of Cd (II) and chemosensor, which ultimately affects its optical properties. The sensor also exhibited high selectivity and sensitivity toward Cd (II) over other common metal ions in a moderate pH range, leading to potential fabrication of both “naked-eye” and ratiometric fluorescent detection of Cd(II) (26). In 2016, a novel chromone Schiff-base linked fluorescent chemosensor 7(Fig 2) named as 7-methoxychromone-3-methylidene-1,2,4-triazole-3-imine was designed and generated for selective detection of Cd(II) ions.

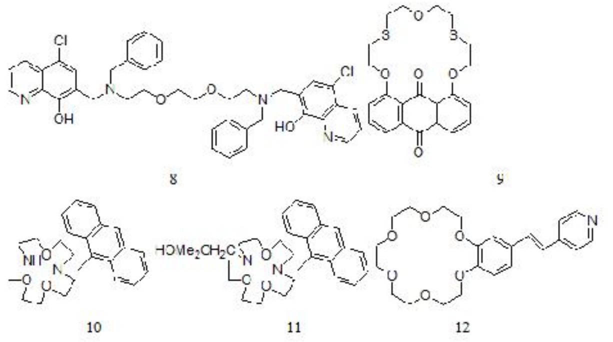

Fig 3. Fluorescent chemosensors of Cd (II)

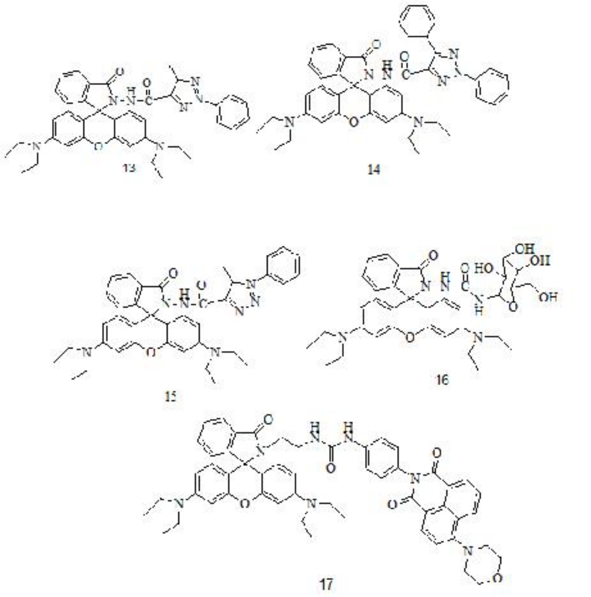

Fig 4. Rhodamine linked molecules as fluorescent chemosensors of mercury

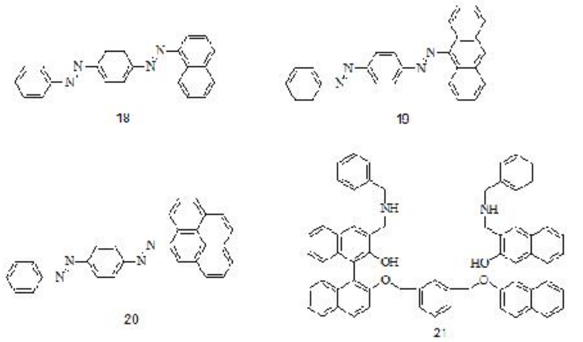

Fig 5. Chemosensors of Hg(II) with polycyclic aromatic hydrocarbons as fluorophore

The synthesized sensor gave strong absorption band at 409nm and emission at 462 with the addition of Cd (II) ion solution using ethanol as solvent. The probe exhibited high selectivity for Cd (II) ions over other metal ions with a strong fluorescence enhancement and high sensitivity with the detection limit reaching at 10^{-6} M (27). J. Kawakami *et al* synthesized two 8-Hydroxyquinoline based ligands, found to have fluorescent chemosensing qualities towards detection of Zn(II) and Cd(II) ions. The ligand 8(Fig 3) synthesized from 5-chloro-8-hydroxyquinoline on treatment with 1,2-bis (2-benzylaminoethoxy) ethane showed significant fluorescence intensity change with Cd(II) (28).

1,8-Anthraquinone-18-dithiacrown-5, a macrocyclic luminescent chemosensor 9(Fig 3) was found for selective detection of Cd (II) and Hg(II). Probe shows increase in fluorescence intensity on addition of these ions with no interference of other transition metal ions (29).Two new diazacrown based fluorescent chemosensors 10, 11(Fig 3) were designed and synthesized that shows increase in intensity of fluorescence through photoelectron transfer effect on complexation with Cd(II) ions, although they can form stable complexes with other metal ions also (30). Chemosensor 12(Fig 3), where crown ether is fused with benzene ring joined through conjugation with pyridine moiety has been reported in literature. This assembly consists of two ionophoric units to bind with Cd (II). The coordinated ligand shows increase in fluorescence intensity of 500nm, whereas free ligand shows fluorescence maxima at 430nm (31).

Fluorescent chemosensors of mercury: Li *et al.* group of researchers described the synthesis of rhodamine linked triazole as fluorescent chemosensor 13(Fig 4) by introducing rhodamine B to 5-methyl-2-phenyl-2H-1,2,3-triazole-4-carboxylic acid. Synthesized compound was found to have specific chromogenic response on binding with Hg (II) ion in DMF-H_2O (v:v =1:1) at pH =7.4, the colourless rhodamine appended triazole turned pink in the presence of mercury ion that enabled naked eye detection of ion. The probe displayed high selectivity to Hg (II) ions, 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 (32). Another rhodamine based chemosens or 14(Fig 4) displayed distinct enhancement in fluorescence at 577nm on complexation with Hg (II) in water-dimethyl formamide solution at pH=7.4. Also, the colourless rhodamine 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 (33). More advanced rhodamine linked triazole fluorescent chemosensor15 (Fig 4) has been produced by reacting rhodamine hydrazide with previously synthesized triazole derivative, 5-methyl-1-phenyl-1H-1,2,3-triazole-4-carboxylic acid. On complexation with Hg (II) ion, chemosensor 15 exhibited about 4000-times increase in fluorescence intensity in comparison to other metal ions in competition. Complexation of molecule 15 with Hg (II) ion in 1:2 molar ratios produces color changes (34).

Glucose and Rhodamine B based ‘‘turn-on’’ fluorescent sensor 16 (Fig 4) for detection of Hg (II) ions was designed and synthesized by Li *et al.* The fluorescent sensor showed a significant selectivity for Hg (II) ions than for other metal ions in aqueous medium. On the addition of Hg (II) ions to the solution of sensor molecule, the absorption and fluorescence signals enhanced remarkably at 567 and 587 nm respectively. Titration of sensor with Hg (II) ions showed 1:1 stoichiometric reaction. Furthermore, glucose-based rhodamine B sensor can be used for the detection of the limited Hg (II) ions in drinking water (35). Fluorescent chemosensor 17(Fig 4) was synthesized by an irreversible desulfurization reaction and used for the detection of Hg (II) in aqueous medium. The colorimetric and fluorescent response to Hg (II) can be easily detected even by the naked eye. Chemosensor, shown high selectivity and sensitivity for Hg (II) in a wide pH range (1.0-8.0) (36). A group of novel azo linked polycyclic aromatic hydrocarbons based sensors 18-20 (Fig 5) were designed and synthesized in a single step. These sensors exhibit fluorescence enhancement with a detectable naked-eye color changes in presence of Hg (II) ions in aqueous solution (37). Fluorescent chemosensor 21 (Fig 5) have been successfully designed and synthesized that exhibited a very selective “turn-on” response for Hg (II) ion in the existence of all other metal ions at neutral pH through photoelectron transfer. Moreover, the finding limit of receptor compound 20 toward Hg (II) was 4.4 × 10-7 M, which shows that the sensor can be utilized in toxicological, biological and environmental applications (38).

Conclusion

Present report summarizes recently synthesized fluorescent sensors of cadmium and mercury ions from aqueous medium that exhibited no change in sensitivity and selectivity of chemosensors in the presence of other metal ions. Sensors having aromatic groups with extended conjugation as fluorophoric unit attached to receptor moiety have an excellent fluorescent behavior that can be observed even with naked eye. There is lot of scope to design and develop such type of probes with highly conjugated fluorophors to address environmental as well as health related issues.

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