Chemosensors for Hg Ions: A Review of Literature
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Abstract
In this review, recently reported Hg ion sensors are briefly discussed. We also summarized selectivity and sensitivity of various chemosensors for mercury ions. The basic principle for emission of radiation, pH limit, suitable solvent, detection limit, mode of binding, ratio between metal and ligand are detailed in this paper.

Keywords: Mercury ion; Naked eye; Quantum yield; Fluorescent sensor; Bathochromic shift; Dosimeter

Introduction
Chemosensors have been playing a crucial role in the analytical chemistry, bio-medicinal science and environmental chemistry [1]. Chemosensors offer an accurate and low-cost finding of anions, enzymes and toxic heavy metal ions with high selectivity and sensitivity [2]. 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. Hence, the effective and selective detection of Hg ions is of great importance. In this regard, many organic compounds have been synthesized and are being used as a successful chemosensors. Hence we would like to provide the overall summary of the design and application of Hg ion selective chemosensors.

Song et.al utilized an irreversible desulfurization reaction to build up a new fluorescent ratiometric chemosensor (Figure 1) based on the FRET, which would be used to the detection of Hg2+ in aqueous medium [3]. The colorimetric and fluorescent response to Hg2+ can be easily detected even by the naked eye. Chemosensor, compound 1 shown high selectivity and sensitivity for Hg2+ with a wide pH range (1.0-8.0) and can be utilized to set up the fluorescence assay for Hg2+ in living cells.

A novel "turn-on" fluorescent sensor (Figure 2) based on glucose and rhodamine B for finding of Hg2+ ions was designed and synthesized by Li et al. [4]. The fluorescent sensor showed a great specificity for Hg2+ ions than for other metal ions in aqueous medium. On the addition of Hg2+ 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 Hg2+ ions showed 1:1 stoichiometric reaction. Furthermore, glucose-based rhodamine B sensor can be used for the detection of the limited Hg2+ ions in drinking water.

Udhayakumari and Co-workers have designed and synthesized a series of novel azo linked polycyclic aromatic hydrocarbons based sensors (Figures 3a-3c) in single step. Compound 3a and 3b were developed for the selective and sensitive detection of Hg2+ ions over the other transition metal ions. These sensors exhibit fluorescence enhancement with a detectable naked-eye color changes in presence of Hg2+ ions in aqueous solution [5].

Velmurugan et al. have successfully designed and synthesized a novel BINOL based fluorescent chemosensor (Figure 4) which exhibited a very selective "turn-on" fluorescent chemosensor for Hg2+ ion in the existence of all other metal ions (transition, heavy and alkali metal ions) at neutral pH [6]. The significant enhancement with high emission selectivity of compound 4 toward Hg2+ is due to PET inhibition process. Moreover, the finding limit of receptor compound 4...
Hosseini et al. have designed and synthesized magnetic core-shell Fe₃O₄@SiO₂ nanoparticles functionalized by BTC which acts as a fluorescent chemosensor (Figure 8) for Hg²⁺ ion [10]. The enhancement of fluorescence is attributed to the strong covalent binding of Hg²⁺ ions with the binding constant value of 1.7×10⁵/M. Sensor compound 8 can be utilized for analysis of Hg²⁺ ions in environmental sample.

Liu et al. have reported a new rhodamine-based fluorescent probe (Figure 9) for Hg²⁺ [11]. The colorimetric and fluorescent response to Hg²⁺ can be easily detected by the naked eye. The selectivity of this system for Hg²⁺ over other metal ions is admirable.

An easy, facile, low-cost and efficient semicarbazone-based chemosensor (Figure 10) with extremely selectivity for Hg²⁺ has been toward Hg²⁺ was 4.4 × 10⁻⁷ M, which shows that the sensor Figure 4 can be utilized in toxicological, biological, and environmental applications.

Jing et al. synthesized a highly selective ratiometric fluorescent chemosensor (Figure 5) for Hg²⁺ ions. It was prepared by joining terpyridine and photochromic perfluoro-diarylethene via a stilbene linkage [7]. When triggered by Hg²⁺, 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.

By intramolecular charge transfer blocking mechanism, Zhang and co-workers have developed a highly selective dual channel chemosensor (Figure 6) for Hg²⁺ ions based on a non-sulfur, easily prepared Schiff base compound [8]. Particularly, the high selectivity experiments showed that the fluorescent sensor is specific for Hg²⁺ even after interference by high concentrations of other metal ions.

A non-sulfur sensor (Figure 7) of mercury ions has been reported by Wu and co-workers [9]. This sensor has 1, 5-diaminonaphthalene Schiff base derivatives which showed brilliant fluorescent and UV-vis responses for Hg²⁺ ions by the direct cleavage of carbon-nitrogen double bond changing an ICT state mechanism.
reported by Qu, and co-workers [12]. Compound 10 gives an instant answer to the Hg$^{2+}$ ions by fluorescence quenching response. The distinct color changes in UV light and speedy fluorescence extinction can be detected by naked eyes. It is found that this sensor totally free of interference from any other ions. In addition, this sensor acts as a recyclable component in sensing materials. It can be repeated use above 10 times.

A simple and easy-to-prepare coumarin dithioate derivative has been reported by El-Shekheby et al. as a new, highly selective and sensitive chemosensor (Figure 11) for sensing trace amounts of Hg$^{2+}$ ions [13]. Compared with some other Hg$^{2+}$ chemosensors, coumarin dithioate derivative shows advantages such as low finding limits, quick response and high selectivity. It shows effective enhances fluorescence upon complexation with Hg$^{2+}$ ions. The spectral response towards Hg$^{2+}$ is reversible making it of great potential use in straight recognition.

New azocalix[4]arene based chemosensors (Figure 12) that are mainly selective for Hg$^{2+}$ due to presence of azo groups at the upper rim as the metal binding sites was designed and reported by Elçin et al. [14]. These compounds could be used for the selective extraction of Hg$^{2+}$ ions from particular samples such as industrial effluents or environmental surface waters.

Kavitha et al. have reported a simple, efficient, low price and water soluble chemosensor (Figure 13) that utilizes for exact recognition of Hg$^{2+}$ ions [15]. High selectivity and sensitivity for toxic Hg$^{2+}$ ions in neutral aqueous solution was revealed by this chemosensor. This sensor also displays an on-off fluorescent signaling pattern. The emission spectra can be quenched between pH ranging from 6.0 to 12.0. This gives strong confirmation that sensor compound 13 could be used as a fluorescent probe for pH monitoring.

He et al. have designed and synthesized a new chemosensor (Figure 14), having a BODIPY signal moiety and a bis[2-(phenylseleno)ethyl]...
amine detection site \[16\]. It was shown remarkable color changes and fluorescence enhancement upon the binding with Hg\(^{2+}\) in CH\(_3\)CN, which make compound 14 be used as a colorimetric fluorescent sensor. More amusingly, the Hg\(^{2+}\) induced chromogenic process could be reversed by addition of EDTA or cysteine. Based on the "off-on-off" fluorescence of compound 14 induced by Hg\(^{2+}\) and cysteine, compound 14 may be engaged to design molecular switches.

Wang et al. prepared a novel single molecular FRET based fluorescent sensor (Figure 15) for the ratiometric and reversible detection of Hg\(^{2+}\) in aqueous medium \[17\]. It was shown high sensitivity and selectivity toward Hg\(^{2+}\) and could be suitably identified even by naked eye. Sensor compound 15 was fit in a broad pH range 1.0–10.0 and permitted the ratiometric detection of intracellular Hg\(^{2+}\) levels in live EC 109 cells. Furthermore, sensor compound 15 for the ratiometric fluorescent detection of Hg\(^{2+}\) was speedy and the identifying event could complete in 13 min in practical detection.

Yang et al. have designed a novel bifunctional colorimetric and fluorescent chemosensor (Figure 16). It shows significant "off-on" fluorescence accompanied with color changes from colorless to red upon binding to Hg\(^{2+}\) ions \[18\]. The spectral response of compound 16 toward Hg\(^{2+}\) was demonstrated to be reversible and robust against interference from other metal ions.

An (E)-2-(2-(2-(1H-indol-3-yl) vinyl)-4H-chromen-4-ylidene) malononitrile (Figure 17) was synthesized by Lee et al. and its cation detecting properties in DMSO were examined by UV–vis spectroscopy \[19\]. On the addition of Hg\(^{2+}\) to dye compound 17 showed color change and the absorption band indicates a formation of a 1:1 dye compound 17-Hg\(^{2+}\) coordination compound. The dye compound 17 displayed high selectivity for Hg\(^{2+}\) ions as compared with other cations.

A triphenyl amine semicarbazone derivative (Figure 18) serving as chemosensor for Hg\(^{2+}\) ions using two different discovery modes have been designed by Malkondu et al. \[20\]. Compound 18 can be utilized as a selective naked eye chemosensor for Hg\(^{2+}\). Besides, TOCAZOL got from the reaction of compound 18 with Cu(ClO\(_4\))\(_2\) shown a selective fluorescent sensing behavior towards Hg\(^{2+}\) ions. For practical metal ion finding, the investigational conditions were conducted in a binary mixture of MeCN/H\(_2\)O (9/1).

Ghosh and co-workers have reported that rhodamine-labelled receptor (Figure 19) is capable of sensing Hg\(^{2+}\) ions in aq. CH\(_3\)CN \[21\]. Concurrent involvement of amide parts of the rhodamines with the polyether chain favours the robust chelation Hg\(^{2+}\) ions. Additionally, the chemosensor compound 19 is found to be effective in reporting the existence of Hg\(^{2+}\) ions inside the cell.

Chan et al. have synthesized and characterized a new non-reaction based luminescent iridium(III) complex (Figure 20) for the quick, selective and direct detection of Hg\(^{2+}\) ions in aqueous medium \[22\]. This chemosensor shows a robust luminescence "switch-on" response to Hg\(^{2+}\) with a detection limit in low-micromolar range and is extremely selective for Hg\(^{2+}\) over other metal ions. Besides, the addition of
cysteine to the system can return the luminescence signal of compound 20 to the "off" state.

Two new rhodamine hydrazone derivatives bearing one (Figure 21a) and two (Figure 21b) thiophene units have been reported by S. Park and co-workers [23]. The X-ray crystal structure of compound 21a was also got, in which the unique spirolactam ring was clearly shown. Compound 21a and compound 21b exhibited highly selective fluorescence changes with Hg\(^{2+}\) among the various metal ions. These selective changes were attributed to the spirolactam ring opening methods and following hydrolysis. The selectivity for Hg\(^{2+}\) ions can be attributed to the affinity of the thiophene group towards Hg\(^{2+}\) and the rigid hydrazone binding site.

A novel rhodamine B based fluorescent probe (Figure 22) was prepared and characterized by Zhang et al. Probe compound 22 displayed good sensitivity and selectivity recognition to Hg\(^{2+}\) ions over other metal ions and anions [24]. On the addition of Hg\(^{2+}\) ions, compound 22 revealed remarkably improved fluorescent intensity and color alteration from colorless to pink in Tris–HCl (10 mM, pH = 7.2) aqueous buffer medium. The intra cellular fluorescent imaging renders it a capable probe to analyze Hg\(^{2+}\) ions in living cells, highly selective and sensitive detection method for Hg\(^{2+}\) was effectively applied to water samples analysis.

A new red fluorescent sensor (Figure 23) for Hg\(^{2+}\) was designed by using of the specific binding of thymine with Hg\(^{2+}\) ions as well as the AIE feature of triphenylamine–triazines motif [25]. The aggregation was confirmed by TEM analyses, absorption and \(^1\)H NMR spectral of compound 23 in the presence of Hg\(^{2+}\) ions. This test revealed that the probe is highly selective and sensitive for Hg\(^{2+}\) ions even in the presence of other metal ions. Additionally, compound 23 showed large two photon absorption cross-section (3328 GM), telling that the targeted two-photon imaging is highly suitable for biological applications.

Pandey et al. have designed and synthesized some new quinazolines (Figure 24a-24c). Strong fluorescence at RT was shown by these probes. Absorption, fluorescence, \(^1\)H NMR, HRMS and FAB-MS spectral studies have been utilized for the Hg\(^{2+}\) detection. Fluorescence intensity of compound 24a-24c quenches selectively in the presence of Hg\(^{2+}\) ions. Job’s plot study shown that compound 24a and 24b interact with Hg\(^{2+}\) ions in 1:1, while compound 24c in 1:2 (probe/metal) stoichiometries [26].

Hamid et al. have synthesized dye (Figure 25). This probe works
efficiently with amazing high selectivity and sensitivity [27]. The interaction taking place between Hg(II) ions and compound 25 complex (through thiol groups) was responsible for the spectral changes. It can be used for highly selective and sensitive chemosensor for Hg^{2+} ions in alcoholic–aqueous medium even in the presence of comparatively high concentrations of competing other metal ions. Moreover, and in terms of sensitivity, the limit of quantification of the probe was estimated to be lesser than 0.4 ppm.

A simple and low-cost post-functionalization policy was used to synthesize a new fluorescent Hg^{2+} polymeric chemosensor (Figure 26) by covalent coupling of organic fluorescent molecular RhBH to a water-soluble copolymer poly (VP-co-GMA). This RhBH-functionalized polymer poly (VP-co-GMA-g-RhBH) showed outstanding selectivity and high sensitivity towards the finding of Hg^{2+} in polar protic solvent MeOH/CHCl_{3} (v/v, 98:2) [29].

Yari et al reported (Figure 28), the ability of a ligand containing...
crown sub-units to coordinate Hg\(^{2+}\) ion in the sol–gel derived film [30]. As the ligand having a suitable light sensitive moiety, its changes at the electronic level upon interaction with metal centers. Furthermore, probe has many advantages including outstanding extensive dynamic range, very low detection limit, high selectivity and better reproducibility.

Wang et al. have synthesized Dipyrido[3,2-a:20,30-c]phenazine (L) which was employed as a selectively fluorescent chemosensor (Figure 29) for Hg\(^{2+}\) in DMF [31]. The fluorescence increasing was attributed to the formation of compound 29 Hg\(^{2+}\) by 1:1 complex ratio. The experiment results also showed that the response behavior of compound 29 to Hg\(^{2+}\) is pH independent in the range of pH 6.0-9.0 and show outstanding sensitivity and selectivity for Hg\(^{2+}\) over other examined metal ions.

Ma et al. have designed and reported a binaphthyl-based fluorescent chemosensor (Figure 30) which could be used as a highly selective and sensitive chemosensor, and specifically identify Hg\(^{2+}\) ion [32]. The high emission selectivity of compound 30 to Hg\(^{2+}\) was purely driven by the selective creation of 1:2 complex.

A simple and easy-to-prepare fluorescent chemosensor (Figure 31) for Hg\(^{2+}\) based on 1,8-anthracenedisulfonamide has been designed and reported by Hu et al. [33]. The selectivity of this chemosensor for Hg\(^{2+}\) ions in aqueous medium over other metal ions is high. The spectral response to Hg\(^{2+}\) is reversible.

Bingol et al. have designed and synthesized a novel calix[4]arene chemosensor (Figure 32) with benzothiazole azo groups at the upper rim as the metal ion binding sites [34]. It showed high selectivity for Hg\(^{2+}\) in DMF. The Hg\(^{2+}\) ion detection provides a large bathochromic shift in the absorption spectrum (from light orange colour to reddish colour), which is clearly visible to the naked eye. This probe may be very useful for rapid detection of Hg\(^{2+}\) ion.

Ramesh et al. designed, a simple nanocomposite thin film sensor based on silver nanoparticles embedded in poly(vinyl alcohol) fabricated through a facile in situ assembly procedure [35]. It was shown fast, sensitive and selective detection of mercury in all its oxidation states. It can be used in situ and ex situ analysis and also shows Low-cost, linear response over a wide range of concentrations.

A new Hg\(^{2+}\) chemodosimeter DT-ABD (Figure 33) was designed and synthesized by Chem et al. which displays specific Hg\(^{2+}\)-induced
A novel naphthalene diimide-dithiocarbaminate based fluorescence probe (Figure 35) was synthesized by Pal et al. [38]. On the addition of various metal ions, the probe gave an irreversible change only for Hg\(^{2+}\) ions. The detection limit of the sensor is 2.1X10^{-7} M. It can also probe Hg\(^{2+}\) ions in cells by using the dosimeter exploiting its high cell permeability.

A novel rhodamine-based chemodosimeter (Figure 36) has been prepared for the detection of Hg\(^{2+}\) in aqueous medium by Quy et al. [39]. Compound 36 shows good selectivity and sensitivity to Hg\(^{2+}\) ions over other ions. The solution of compound 37 with Hg\(^{2+}\) can cause OFF-ON fluorescence which is a visible color change from colorless to pink. The low detection limit is 0.04 µM which make it a promising for the determination of Hg\(^{2+}\) ions.

Yao et al. [40] have demonstrated the construction of magnetic silica yolk–shell structure nanoparticles (Figure 37). Filling of N719 endowed the nanocomposites with detecting and eliminating functions towards mercury ions. This probe response to mercury ions within 1 minute and eliminate more than 97% of Hg\(^{2+}\) ions.

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