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ORIGINAL ARTICLE

Colorimetric and *turn-on* Fluorescence Chemosensor for Hg^{2+} Ion Detection in Aqueous Media

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Abstract

A new rhodamine 6G based fluorescent and colorimetric chemosensor, containing N-methyl imidazole nucleus, for the selective detection of Hg^{2+} ion was designed and synthesized. The results of UV-Vis and fluorescence spectral study indicated that the receptor is selective and sensitive towards Hg^{2+} with no noticeable interference with other competitive metal ions. The addition of Hg^{2+} to the receptor induced a rapid color change to pink from colorless and the *turn-on* fluorescence response toward Hg^{2+} among different cations was studied. The stoichiometric ratio of 1:1 between the receptor and Hg^{2+} was supported by Job's plot. The color change and *turn-on* fluorescence response upon addition of Hg^{2+} ion was ascribed by the spirolactam ring-opening mechanism. The probable mode of binding between the receptor and Hg^{2+} was confirmed by ^{1}H NMR and Mass spectral study. For the practical application, its electrospun nanofiber test strips successfully applied to recognize Hg^{2+} ion in aqueous media.

Keywords Mercury ion · Sensing · Fluorescent · Nanofiber

Introduction

Fluorescent sensing probes are highly selective and sensitive, cost effective and suitable for real-time monitoring, so they play vital role in the field of heavy metal ions signalling [1–3]. The accurate detection and sensing of heavy transition metal ions are of essential need because of their substantial role in chemical, biological and environmental fields [4]. The heavy metal ions are the main reason for the most of the environmental pollutions [5]. Among those heavy transition metal ions, Hg^{2+} is one of the most toxic metals. World Health Organization (WHO) has set a maximum tolerable level of Hg^{2+} in drinking water is 30 ppb [6], whereas dissolved total mercury concentrations in pristine natural water range between sub-ng L^{-1} levels for seawater up to about 10 ng L^{-1} for coastal water and fresh wates [7]. It is evidenced that Hg^{2+} ion easily passes through skin, respiratory and gastrointestinal tissues and gathers in the living organisms by the process of food chain, resulting in many complaints in human beings such as damage in neurological system and in DNA, numerous cognitive and motion disorders [8–11].

In the fast few years, several methods have been reported to sensitive and reliable detection of the toxic Hg^{2+}, including X-ray fluorescence spectrometry [12], atomic absorption and emission spectroscopy [13], inductively coupled plasma mass spectrometry [14] and capillary electrophoresis [15]. Besides, various strategies have also been explored for the detection of Hg^{2+} using photo electrochemical, surface resonance raman scattering, surface plasmon resonance, electrochemical methods [16, 17]. Though, these techniques are available for detecting mercury ions, these has limitations like more expensive, difficult and time consuming process and sometimes ppb level of Hg^{2+} ion detection is difficult. Compared with all these, a colorimetric and fluorescent sensor has received much attention because of their advantages such as low cost, easy detection by naked eye and good sensitivity [4, 18–20]. In numerous colorimetric and fluorescent probes, rhodamine based receptors are highly favored due to their visible color change in both normal and UV light. Besides, these rhodamine based sensors tend to show remarkable photo-physical

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properties with high quantum yields, long wavelength emission and excellent photo stability [21–23]. In general, rhodamine nucleus can change from ring-close to ring-open form with metal ion complexations by inducing strong emissions and color change for the receptor [24–29].

In the present study, we designed and synthesized a new **R**hodamine derivative functionalized with *N*-methyl **IM**idazole unit (**RIM**). After investigating the properties of **RIM**, we found that the receptor has worked as an efficient, as well as selective and sensitive towards the recognition of Hg^{2+} over other metal ions with significant fluorescence-on with striking color change.

Experimental Section

Reagents and Apparatus

Required Chemicals and solvents for the synthesis of chemosensor **RIM** and metal salts for the analysis were purchased from Sigma-Aldrich and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 600 spectrometer, using tetramethylsilane as internal standard. The chemical shifts for the proton NMR spectra were expressed in ppm units and J value in Hz. ESI-MS spectra were obtained using a 4000 Q TRAP mass spectrometer. UV − Vis spectra recorded using an Agilent 8453 spectrophotometer (1 cm quartz cell) at room temperature. Fluorescence spectra recorded using Cary Eclipse fluorescence spectrophotometer (1 cm quartz cell) at room temperature. The excitation and emission slit widths (3 nm) kept constant for all the measurements.

Synthesis of RIM

Step1: Synthesis of Rhodamine 6G Hydrazide

To a solution of Rhodamine 6G (2 g, 4.2 mmol) in ethanol 40 mL was added Hydrazine hydrate (0.21 g, 2.3 mmol) and the reaction mixture stirred at ambient temperature for 18 h. The solid precipitated was filtered and washed with water, a small trace of impurities present in the solid were purified by silica gel column chromatography with gradual increase of ethyl acetate in hexane (1.5 g, yield = 83%). ^{1}H NMR ($CDCl_3$, 600 MHz), δ(ppm): 1.24 (t, 6H, J = 7.2 Hz), 1.85 (s, 6H), 3.14 (m, 4H), 3.45 (s, 2H), 3.51 (s, 2H), 6.19 (s, 2H, 6.32 (s, 2H), 6.98 (m, 1H), 7.38 (m, 2H), 7.88 (m, 1H) (Fig. S1). ^{13}C-NMR ($CDCl_3$, 600 MHz) δ(ppm): 13.74, 15.69, 37.34, 95.82, 103.90, 116.97, 122.02, 122.79, 126.68, 127.11, 128.84, 131.56, 146.52, 150.72, 151.21, 165.19 (Fig. S2). ESI-MS (m/z) calcd. 428.54, found 429.9 ($M + H^+$) (Fig. S3).

Step2: Synthesis of 3′,6′-Bis(Ethylamino) -2′,7′-Dimethyl-2-(((1-Methyl-1H-Imidazol-2-Yl)Methylene) Amino)Spiro[Isoindoline-1,9′-Xanthen]-3-One (RIM)

To a solution of 1-methyl-1H-imidazole-2-carbaldehyde (0.26 g, 2.3 mmol) in ethanol (20 mL) was added Rhodamine 6G Hydrazide (1 g, 2.3 mmol) and stirred at under 80 °C for 12 h. Solid was precipitated from the reaction mixture when cooled to room temperature and the obtained solid was filtered and washed thoroughly with cold ethanol to obtain pale pink pure product (0.98 g, yield = 79%). ^{1}H NMR (600 MHz, DMSO-d_6), δ (ppm): 1.19 (t, 6H, J = 7.2 Hz), 1.86 (s, 6H), 3.12 (m, 4H), 3.59 (s, 3H), 5.08 (t, 2H, J = 5.4 Hz), 6.19 (s, 2H), 6.31 (s, 2H), 6.92 (s, 1H), 7.09 (d, 1H, J = 7.2 Hz), 7.18 (s, 1H), 7.57 (m, 1H), 7.62 (m, 1H), 7.91 (d, 1H, J = 7.2 Hz), 8.77 (s, 1H) (Fig. S4); ^{13}C NMR (150 MHz, DMSO-d_6), δ (ppm): 14.59, 17.45, 35.40, 37.91, 66.08, 96.06, 105.22, 118.79, 123.49, 124.37, 126.09, 127.37, 129.32, 129.41, 129.48, 134.43, 139.67, 141.60, 148.32, 151.47, 151.53, 164.19 (Fig. S5). ESI-MS *m/z*: Calcd. 520.2, found: 521.3 ($M + H^+$) (Fig. S6).

Polyurethane Electrospun Nanofiber Preparation

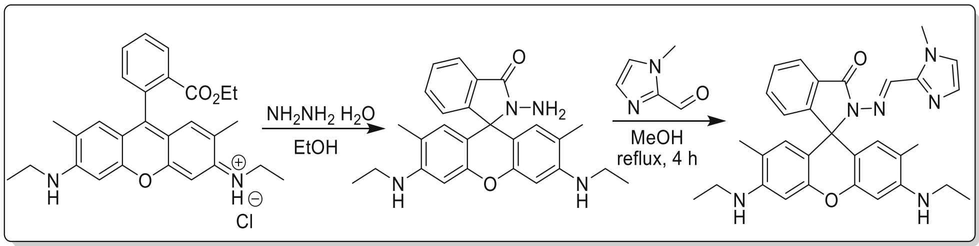
Electospun nanofiber imbedded **RIM** sample was prepared by mixing 30 g of dimethylacetamide, 20 mL of acetone and 10 g polyurethane and the mixture was stirred well at room temperature for 12 h to obtain a homogeneous mixture and then added **RIM** (0.1 mmol) to it and stirred for another 12 h, this homogenous solution was used to obtain the required electrospin nanofiber.

Results and Discussion

The rhodamine 6G-imidazole based receptor (**RIM**) was synthesized according to the synthetic steps delineated in Scheme 1. It is well known that addition of metal ions to the spirolactam ring of rhodamine forms a complex by ring opening and induces colorimetric and fluorescence response [23, 30]. The binding ability of probe (**RIM**) towards various metal ions (Hg^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+}, Fe^{2+}, Al^{3+}, Ni^{2+}, Ag^{+}, Pb^{2+} and K^{+}) was examined in 50% aq. DMF solution by using UV-Vis absorption, fluorescence emission and ^{1}H NMR and ESI-MS spectroscopic techniques at room temperature.

Colorimetric Response to Metal Ions

The sensing ability of probe **RIM** (5×10^{-5} M) towards several metal ions such as Hg^{2+}, Ag^{+}, Al^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cs^{+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, K^{+}, Li^{+}, Mg^{2+}, Na^{+}, Ni^{2+}, and Zn^{2+} was examined in 50% aq. DMF by visual detection method and was shown in Fig. 1. As seen from the figure, the synthesized



Scheme 1 Synthetic route for chemosensor **RIM**

receptor (**RIM**) displayed a change in color from colorless to pink instantaneously in day light (Fig. 1, top) with the addition of Hg^{2+} in 50% aq. DMF solution (pH 7.3), whereas, the other chosen metal ions to the receptor solution not producing such color change. Besides, under UV light, the receptor solution in presence of Hg^{2+} ions showed a fluorescent yellow color from non-fluorescent that could also be detected with the naked eye (Fig. 1, bottom). This color variation in both visible and UV light is ascribed to the formation of **RIM-**Hg^{2+} complex. Further to validate the selectivity of the probe, other metal ions were also tested by adding it to the receptor solution under the same conditions, exhibited no noticeable change in color, even upon the addition of 10 eqv. of the respective metal ions. Thus the probe **RIM** can serve as a selective naked-eye colorimetric and fluorescent receptor for Hg^{2+} ions without any additional device assistance.

Absorption Spectral Response

The UV-Vis spectral changes for the probe **RIM** (5×10^{-5} M) with various cations (above mentioned) were investigated in 50% aq. DMF solvent (pH 7.3). As shown in Fig. 2, the absorption spectrum of **RIM** exhibited two peaks at the shorter wavelengths of 267 nm and 309 nm. At the same time, no clear absorption peak appeared around 530 nm for the acceptor unit. This is because the probe is in a colorless spirolactam (closed-ring) form. The addition of cations such as Ag^+, Al^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cs^+, Cu^{2+}, Fe^{2+}, Fe^{3+}, K^+, Li^+, Mg^{2+}, Na^+, Ni^{2+}, and Zn^{2+} did not produce any spectral change while with the addition of Hg^{2+} (5×10^{-5} M), a new peak appeared at 538 nm and the intensities of the absorption bands gets increased with increase in the concentration of mercury ion. The appearance of a new peak at 538 nm is might be due to the opening of the spirolactam ring of **RIM** with Hg^{2+} interaction.

To gain further insight into the sensing behaviour of **RIM**, a titration study was conducted with the gradual addition of Hg^{2+} (1 eqv.) to the probe (Fig. 3). Upon addition of incremental amounts of Hg^{2+} ions, the new absorption peak centered at 538 nm observed with increasing intensity with a noticeable color change from colorless to pink. Also the plot of absorbance maxima against Hg^{2+} concentration is shown in Fig. S7. The enhancement of the absorbance peak at 538 nm can be attributed to the ring-opened form of the spirolactam present in the receptor **RIM** upon binding with Hg^{2+} ions. This is due to complexation of the receptor with Hg^{2+} ion.

Fluorescence Emission Studies

The fluorescence emission spectrum of probe (1.5×10^{-6} M) was recorded in the absence and presence of Hg^{2+} ions (1 eqv.) by excitation at 520 nm. As shown in Fig. 4, the free receptor **RIM** showed no emission peak when excited at 520 nm. When Hg^{2+} is added to **RIM** in 50% aq. DMF solution (pH 7.3), a significant development of a new intense peak is observed at 562 nm. The binding ability of probe towards Hg^{2+} was studied by fluorescence spectra with the gradual addition of Hg^{2+} to the solution of probe. Besides, the plot

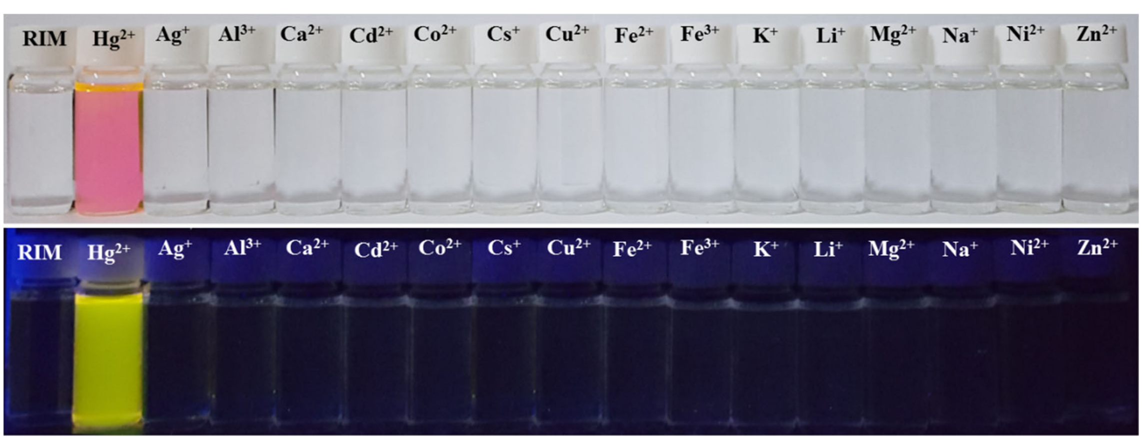


Fig. 1 Photographs of **RIM** (5×10^{-5} M) upon addition of various metal ions (1 eqv.) in 50% aq. DMF (Top) normal light (Bottom) UV light

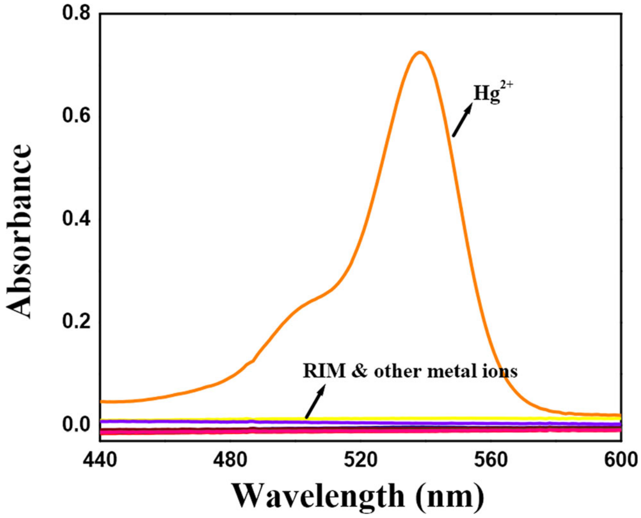


Fig. 2 Changes in absorption spectra of **RIM** (5×10^{-5} M) upon addition of various cations in 50% aq. DMF (pH 7.3)

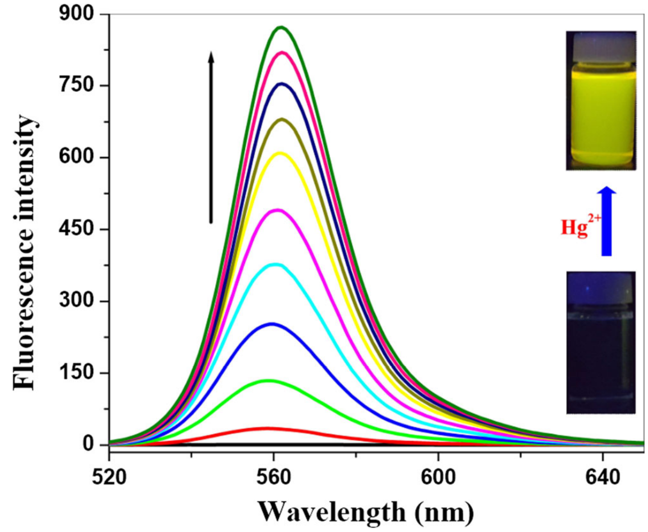


Fig. 4 Fluorescence emission spectral changes of **RIM** (1.5×10^{-6} M) at increasing concentration of Hg^{2+} ion (0–1.5×10^{-6} M) in 50% aq. DMF (pH 7.3)

of fluorescence maxima against Hg^{2+} concentration is shown in Fig. S8. Upon incremental addition of Hg^{2+}, **RIM** showed dramatic increase of fluorescence intensity with the dramatic change of fluorescent yellow color viewed under UV lamp. The color under UV lamp indicates "OFF–ON" signal upon addition of Hg^{2+} ion to the receptor. To know the binding ability of the receptor with mercury ion, the binding constant was calculated using Benesi-Hildebrand equation [31].

$$(F_\alpha - F_o)/(F_x - F_o) = 1/K[Hg^{2+}]$$

Where F_o, F_x and F_α are the fluorescence intensities of the receptor in the absence of mercury ions, at a given concentration and concentration for complete interaction, respectively [29]. The binding constant (K) was calculated from the slope of the $(F_\alpha – F_o)/ (F_x – F_o)$ versus $1/[Hg^{2+}]$. The obtained plot is linear ($r > 0.97$; Fig. S9) and binding constant was found to be 5.12×10^5 M. The binding constant is in the range of 10^5 indicates the strong interaction between the receptor and mercury ion.

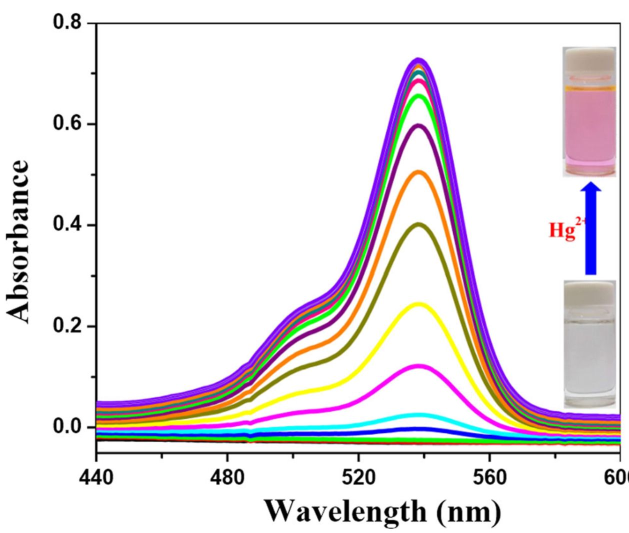


Fig. 3 UV-Vis absorbance spectral changes of **RIM** (5×10^{-5} M) at increasing concentration of Hg^{2+} ion (0-5×10^{-5} M)in 50% aq. DMF (pH 7.3)

Competitive Study of RIM toward Hg^{2+} over Other Metal Ions

Selectivity is the most important factor for ion sensing. To validate the competitivety of receptor, we performed competition experiments using fluorescence measurements. The fluorescence emission response at 562 nm was examined by adding receptor **RIM** to a Hg^{2+} solution (1 eqv.) in presence of other individual metal ions, such as Ag^+, Al^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cs^+, Cu^{2+}, Fe^{2+}, Fe^{3+}, K^+, Li^+, Mg^{2+}, Na^+, Ni^{2+}, and Zn^{2+} (1 eqv.), as shown in Fig. 5. The addition of 1 eqv. of Hg^{2+} prompted a significant emission response with **RIM**, whereas the other metal ions did not produce any change in the emission peak at the same concentration. In addition, the emission of the solution of **RIM** and Hg^{2+} was not influenced when the measurement is carried out with or without other competing metal ions. Thus, the receptor is highly selective towards Hg^{2+} over other metal ions.

Stoichiometry through Job's Plot

The binding stoichiometry of **RIM**-Hg^{2+} was determined using Job's continuous variation method [32] by fluorescence technique. As shown in Fig. 6, the curve with a maximum at 0.5 mol fraction indicates that a 1:1 stoichiometric ratio existing between **RIM** and Hg^{2+}.

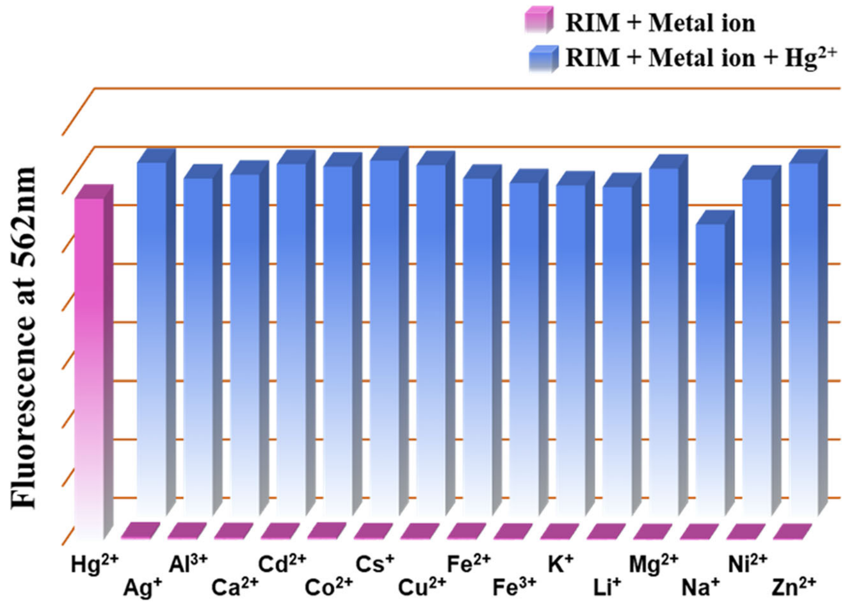


Fig. 5 Competetive experiment of **RIM** upon addition of Hg^{2+} in the presence of other interfered metal ions by fluorescence technique

pH Effect on Interaction of Probe with Hg^{2+}

To validate the utility of the probe in environmental and biological needs, the effect of pH on the interaction of receptor toward Hg^{2+} was carried out by fluorescence study. The response of **RIM** in the absence and presence of Hg^{2+} at different pH (from 2 to 10) conditions were shown in Fig. 7. At acidic conditions (pH 2–6), without Hg^{2+}, the color of the receptor changed to pink due to protonation leading to a little ring opening of spirolactam of **RIM** and the solution is almost colorless while the figure showed no fluorescence signal in the pH range from 7 to 10, suggesting that the **RIM** molecules prefer the ring-closed form. With the addition of Hg^{2+} to **RIM** solution, under acidic and neutral conditions (pH 2–7), strong protonation led to the ring opening in spirolactam and observed fluorescence emission at 562 nm. However, a weak fluorescence intensity exist at pH 8–10. These results reveal that the **RIM** exhibited a excellent sensing ability under acidic and neutral condition as a fluorescent probe for detection of Hg^{2+}.

Binding Mechanism: ^{1}H NMR and Mass Analysis

From the above discussion, we expected that a binding mode of **RIM** with Hg^{2+} is as shown in Scheme 2. The receptor **RIM** has three binding positions (O, imine-N, and imidazole N atoms), which can form a complex with Hg^{2+}. The addition of mercury ion to the receptor makes a coordination to the carbonyl O, imine N and imidazole N atoms [33–35], thus

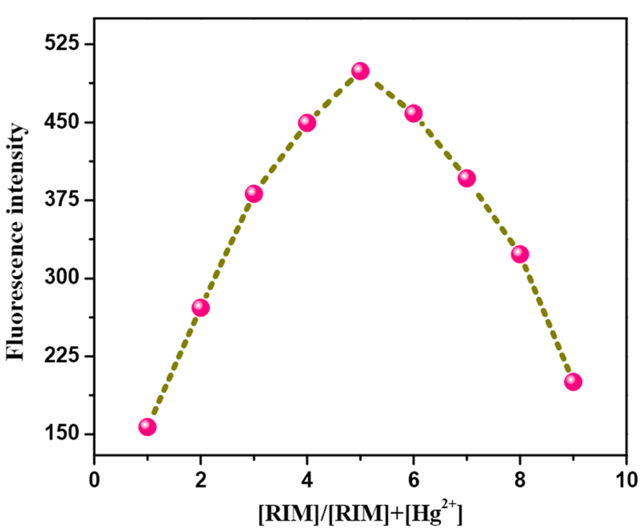


Fig. 6 Job's plot of **RIM** with Hg^{2+} ion

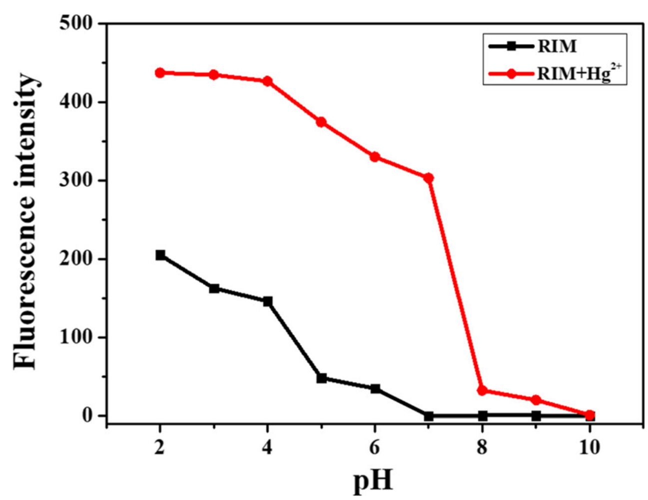
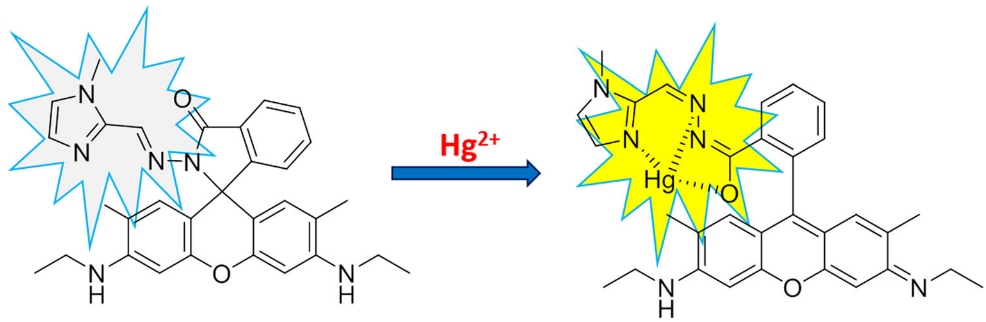


Fig. 7 The pH effect of **RIM** and **RIM**-Hg^{2+} ion using fluorescence technique

Scheme 2 Plausible binding mode of chemosensor **RIM** with Hg^{2+} ion



influencing a change in the spirolactam ring by ring opening. ^{1}H NMR spectra of probe **RIM** and **RIM**-Hg^{2+} were recorded in DMSO-d_6 at room temperature are shown in Fig. 8. Upon addition of 1 eqv. of mercury ions to the probe causes a downfield shift in the imine protons that is the imine hydrogen (–N=CH–) next to the "N" group displays a noticeable shift in the proton from 8.77 ppm to 8.92 ppm. This downfield shift in the peak indicates mercury ions binds well with the "N" atom resulting in a reduction of electronic density on the imine proton [36] and also aromatic protons adjacent to imine group shifted downfield due to the chelation with Hg^{2+}. In addition, the disappearance of peak corresponds to NH protons at 5.08 ppm is observed due to the tautomeric electron and proton flow from NH group to the spirocyclic ring led to spirolactam ring opening. Further to confirm the complexation of receptor **RIM** with Hg^{2+} ion, ESI-MS spectra was recorded with and without adding mercury ion to the receptor solution. For the free receptor, peak appeared at 521.3 (M + H^+) and for the receptor-Hg^{2+} a peak at 722.2 (M + Hg^{2+}) confirms the complexation. (Fig. S10).

Practical Application

To inspect the practical utility of probe **RIM**, alginate beads with receptor was prepared to monitor the detection of mercury ion in real time, the beads were prepared by mixing **RIM** (2%) and sodium alginate (1 g) in deionized water (10 mL). The mixture was heated for 2 h with vigorous stirring; the obtained clear solution was added drop wise to the saturated solution of $CaCl_2$. The beads were formed immediately in the $CaCl_2$ solution which was collected and further it was used to sense mercury (Fig. 9). A striking pink color appeared with pre dissolved mercury in 100% water. Therefore, the **RIM** imbedded to alginate bead can be used in real field for the rapid detection of mercury ion spontaneously.

For another application of receptor **RIM**, we synthesised polyurethane electrospun nanofibers blended with receptor for rapid on-site detection of Hg^{2+}. The colorimetric sensing behavior of the electro spun

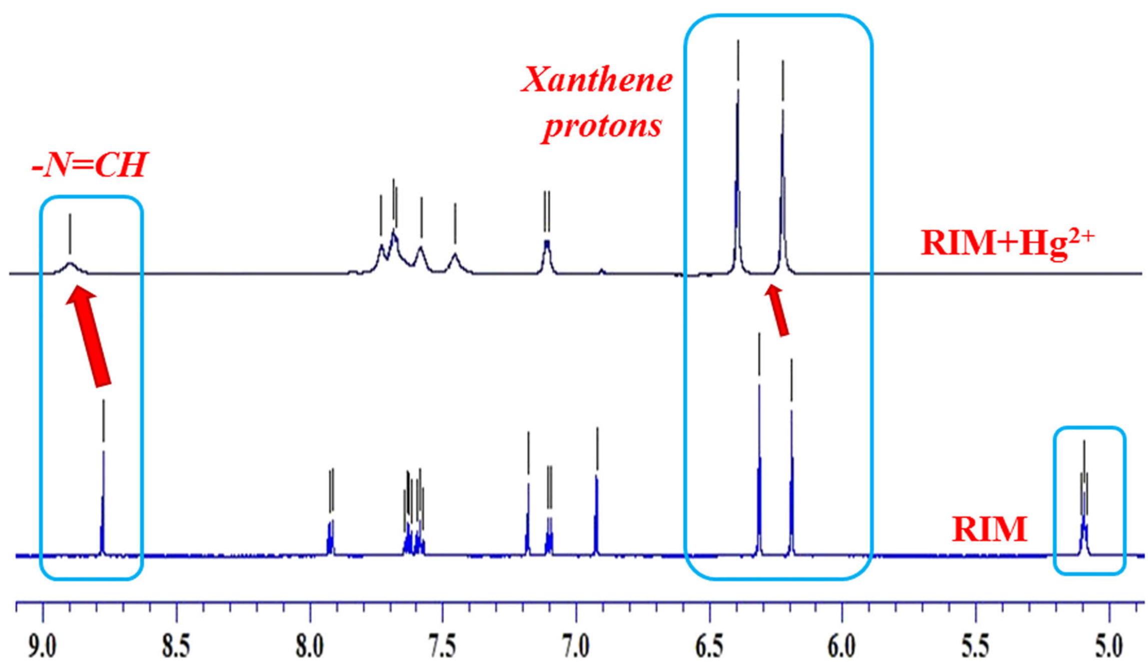


Fig. 8 ^{1}H NMR spetra of **RIM** in the absence and presence of Hg^{2+} ion in DMSO-d_6

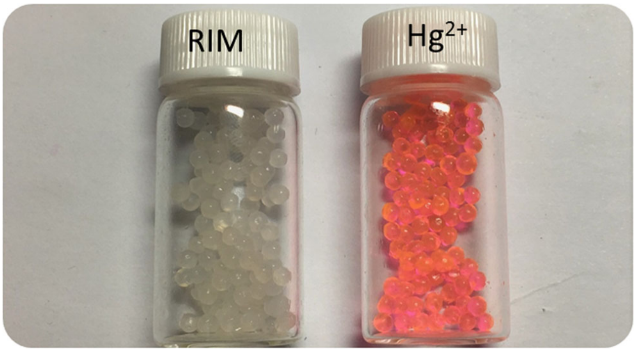


Fig. 9 Color change of Alginate bead with Hg^{2+} solution in water

test strips was examined in 100% water medium. To examine the selectivity, the test strips were sprayed with a solution containing various cations such as Hg^{2+}, Ag^{+}, Al^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cs^{+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, K^{+}, Li^{+}, Mg^{2+}, Na^{+}, Ni^{2+}, and Zn^{2+} (1×10^{-5} M). As shown in Fig. 10, an obvious visible color change of pink color was observed immediately after the addition of Hg^{2+}. However, the addition of other cations produces no change in the nanofiber strips. This experiment makes the receptor quite useful for rapid on-site detection of Hg^{2+}.

Conclusion

In summary, we have designed and synthesized a novel fluorescent-ON chemosensor based on a rhodamine 6G-N-methyl imidazole conjugate. The receptor **RIM** exhibits extraordinary selectivity and high sensitivity toward Hg^{2+} detection in the presence of various other metal ions. The interaction between **RIM** and Hg^{2+} ions enhances the emission at 562 nm and induces a visible color change and yellow fluorescence in day light as well as under UV light respectively. A binding stoichiometry of 1:1 ratio obtained between receptor and Hg^{2+} ions using jobs plot. The ^{1}H NMR and mass spectral data confirmed that the mechanism of sensing of mercury ion by **RIM** is the ring opening of spirolactum. Further, the practical application of this chemosensor revealed that **RIM**-blended electrospun nanofiber test strips and alginate beads showed selective detection of Hg^{2+} ions in aqueous medium with striking color change in UV light.

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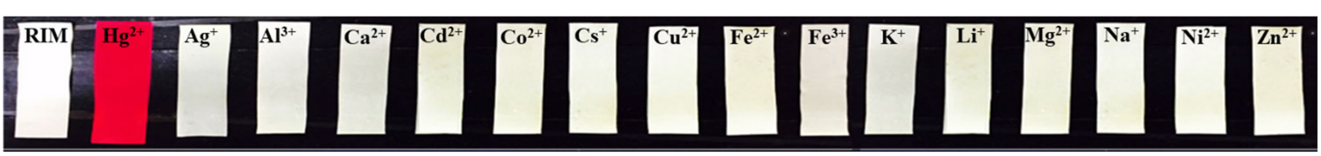

Fig. 10 Photographs of color change of **RIM**-blended electrospun nanofiber test strips after addition of various metal ions under UV light

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