

Colorimetric and Fluorogenic Recognition of Hg^{2+} and Cr^{3+} in Acetonitrile and their Test Paper Recognition in Aqueous Media with the Aid of Rhodamine Based Sensors

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Abstract Two new rhodamine derivatives (L_1 and L_2) were synthesized, characterized and their ion recognition property has been investigated. Both of the ionophores exhibit colorimetric and fluorogenic response for Hg^{2+} and Cr^{3+} ions among large number of alkali, alkaline earth and transition metal ions tested in acetonitrile. Detail studies on determination of binding constant, binding mode, reversibility of binding, lower detection limit have been carried out. Detection of metal ions in aqueous media has also been demonstrated by preparation of simple, convenient and disposable test paper sensors with two approaches viz. filter paper and membrane filter loaded with these ionophores. Both of these methods responded sharply to both the metal ions (Hg^{2+} and Cr^{3+}) in aqueous solution, detectable by bare-eye. For better sensing at low concentration of metal ions, reprecipitation followed by filtration enrichment of ligands on membrane filter was employed.

Keywords Rhodamine · Ionophore · Sensing · Hg^{2+} · Cr^{3+}

Introduction

The Hg^{2+} ion is considered as highly dangerous to the mankind since its bioaccumulation causes various disorders [1–4].

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Cr^{3+} ion is essential for good health in moderate intake; however it is toxic at high concentration [5–7]. Ion recognition, particularly of toxic heavy metal ions is a matter of intense interest as it has implications in the fields like environment, medicine, biology etc. [8–10]. Chemosensors for on-site selective and sensitive detection of these metal ions in aqueous phase is always endeavored. Sophisticated analytical techniques such as atomic absorption spectroscopy, inductively-coupled plasma-optical emission spectroscopy, inductively-coupled plasma-mass spectroscopy, instrumental neutron activation analysis and x-ray fluorescence spectroscopy are available for quantitative analysis of these metal ions found in various sources such as geological, food, biological and industrial effluent. However, these require tedious sample preparation procedures at one hand while on the other hand these instruments are not only costly but also require high maintenance cost and skilled person to operate.

Electronic Supplementary Information (ESI) available: Fig. S1-S26.

With the aid of suitable molecular probes, metal ions have been sensed in organic medium, mixed organic solvents, aqueous-organic medium with the help of instruments like spectrophotometer, spectrofluorimeter etc. [11–21]. However, it is highly relevant to sense them in aqueous medium.

There are reports in the literature for specific sensing of metal ions like Hg^{2+} and Cr^{3+} in aqueous solution/living cell with the aid of analytical instruments like spectrophotometer, spectrofluorimeter, confocal microscope etc. [22–29]. The potent toxicity of Hg^{2+} and Cr^{3+} drive the need of simple, convenient and bare-eye visualization method of their detection in aqueous solution so that a common man can conduct testing. Progress has been made towards the detection of these two metal ions by test paper sensing with the detection upto 10 ppm concentration in water [30]. However, in this direction

there is a desire to develop system, which can detect at lower level in aqueous solution. Fixation of the colorimetric and fluorometric sensors on some solid substrates like membranes, Langmuir-Blodgett films, covalent immobilization/anchoring with polymers and alternate deposition of oppositely charged polyelectrolyte's have been attempted for sensing of metal ions [31–33]. However, uniformity of signaling reagent over entire surface, control over its concentration, complicated synthetic procedures and less sensitivity are some of the limiting factors with these methods. To obtain aqueous dispersion/suspensions of dyes with small particles, a reprecipitation method was reported [34, 35]. Reprecipitation followed by filtration enrichment of signaling reagent was used for heavy metal detection in the literature [36].

In this study, we have synthesized and characterized two new rhodamine-6G derivatives, **L**₁ and **L**₂. The sensing property of these two ionophores was tested with a series of alkali, alkaline earth and transition metal ions in acetonitrile. Both of these ionophores exhibited high selectivity towards Hg²⁺ and Cr³⁺. Sensing of these two metal ions in aqueous media was also carried out with the aid of filter paper and membrane. Filter paper testing is quite simple, disposable and sensing using membrane involves reprecipitation and filtration enrichment of ionophores and by this method better lower detection limit for the metal ions is achieved.

Experimental section

Materials

Perchlorate salts of Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Cr³⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Hg²⁺, Pb²⁺, rhodamine 6G, ethylenediamine, 9-anthracenecarboxaldehyde, biphenyl-4-carboxaldehyde, were purchased from Aldrich and used as received. Analytical grade ethanol and acetonitrile were purchased from S.D. fine chemicals and used without purification. WhatmanTM filter paper and cellulose acetate membrane filter were used to prepare test paper strip for sensing purpose.

Instrumentation

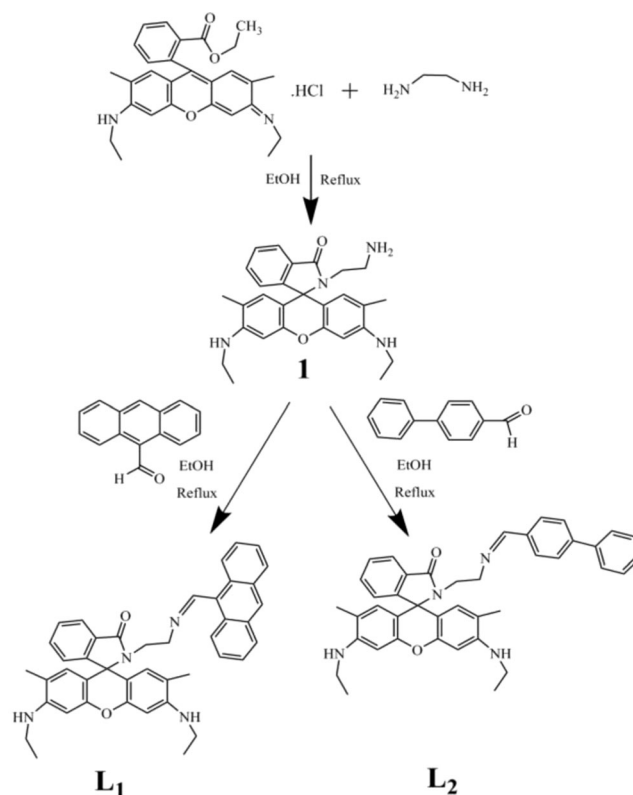
¹H and ¹³C NMR spectra were recorded on a Bruker 200 MHz (DPX-200) and 500 MHz (Avance II) FT-NMR spectrometers, using tetramethylsilane as an internal reference in CDCl₃ solvent. ¹H NMR titration was carried out at 500 MHz in mixed solvent medium (CD₃CN and CDCl₃). ESI-MS was recorded on a LC-MS instrument, LC (Waters), MS (Micromass). MALDI TOF/TOF analyzer (AB MDS Sciex, 4800 plus) was used to record mass spectra of the complexes. The absorption spectra were recorded with a Varian (carry 500) UV–vis-NIR spectrophotometer. Fluorescence spectra were recorded with Edinburgh (F900) spectrophotometer. Elemental analysis was

done with Elementar (Vario Micro Cube) elemental analyzer. Atomic Force Microscope (NT-MDT, Ntegra Aura) was used to record images of ligand-incorporated membrane filters.

Synthesis

The intermediate compound **1** was synthesized following the literature method, as shown in Scheme 1 [37, 38]. In a typical procedure, rhodamine 6G (1.92 g, 4 mM) dissolved in hot ethanol and ethylenediamine (1.34 mL, 20 mM) was added into it. The reaction mixture was refluxed for 8 h till the fluorescence of the solution was disappeared. The precipitate, which was separated during reflux, was collected and washed with 20 mL of cold ethanol and then recrystallized from acetonitrile. Yield: 70 %. The ionophores **L**₁ and **L**₂ were synthesized from compound **1** following a modified published procedure used for other compound. In a typical procedure, compound **1** (600 mg, 1.3 mM) was dissolved in hot ethanol (40 mL) and then 9-anthracenecarboxaldehyde (310 mg, 1.5 mM) was added into it. The reaction was allowed to reflux for about 12 h. On cooling to room temperature, the precipitate separated was filtered off and washed with ethanol, which gave **L**₁ as dull green compound, yield 73 %. Similarly, biphenyl-4-carboxaldehyde (273 mg, 1.5 mM) was treated with **1** (500 mg, 1.1 mM) to obtain **L**₂ as off-white compound, yield 77 %.

Characterization data for 1: ¹H NMR (200 MHz, CDCl₃, δ (ppm)): δ 7.92 (d, 1H), 7.46 (t, 2H), 7.05 (d, 1H), 6.34 (s,



Scheme 1 Synthesis of **L**₁ and **L**₂

2H), 6.22 (s, 2H), 3.51 (t, 2H), 3.20 (t, 4H), 2.39 (t, 2H), 1.90 (s, 6H), 1.32 (t, 6H). ^{13}C NMR (500 MHz, CDCl_3 , δ (ppm)): δ 168.73, 153.50, 151.65, 147.44, 132.52, 131.07, 128.24, 128.07, 123.82, 122.79, 118.02, 105.95, 96.49, 65.11, 43.60, 40.71, 38.33, 16.69, 14.70. ESI-MS (m/z): found 457.20, calculated for $[\text{M}+\text{H}]^+$ 457.58. Elemental analysis: C, 73.61; H, 7.28; N, 11.92 %, calculated values for $\text{C}_{28}\text{H}_{32}\text{N}_4\text{O}_2$: C, 73.68; H, 7.00; N, 12.26 %.

Characterization data for L_1 : ^1H NMR (200 MHz, CDCl_3 , δ (ppm)): δ 8.94 (s, 1H), 8.44 (d, 1H), 8.40 (d, 3H), 7.99 (d, 3H), 7.48 (m, 6H), 7.08 (d, 1H), 6.35 (s, 2H), 6.24 (s, 2H), 3.69 (s, 4H), 3.36 (b, 2H), 3.18 (b, 4H), 1.67 (s, 4H), 1.56 (s, 6H), 1.27 (t, 6H). ^{13}C NMR (500 MHz, CDCl_3 , δ (ppm)): δ 167.94, 161.15, 153.16, 151.25, 146.8, 131.92, 130.73, 130.60, 129.33, 128.67, 128.10, 127.50, 127.34, 126.02, 124.79, 124.62, 124.44, 123.30, 122.22, 117.34, 105.69, 96.02, 64.53, 60.07, 40.89, 37.75, 15.91, 14.13. ESI-MS (m/z): found 645.47, calculated for $[\text{M}+\text{H}]^+$ is 645.82. Elemental analysis: C, 80.20; H, 6.36; N, 8.65 %, calculated values for $\text{C}_{43}\text{H}_{40}\text{N}_4\text{O}_2$: C, 80.13; H, 6.24; N, 8.69 %.

Characterization data for L_2 : ^1H NMR (200 MHz, CDCl_3 , δ (ppm)): δ 8.03 (s, 1H), 7.94 (t, 1H), 7.62 (t, 5H), 7.4 (m, 4H), 7.03 (b, 1H), 6.35 (s, 2H), 6.24 (s, 2H), 3.44 (s, 4H), 3.21 (b, 4H), 1.86 (s, 4H), 1.58 (s, 6H), 1.32 (t, 6H). ^{13}C NMR: (500 MHz, CDCl_3 , δ (ppm)): 168.45, 161.96, 153.90, 151.75, 147.38, 143.12, 140.42, 135.09, 132.44, 131.06, 130.28, 129.02, 128.81, 128.57, 128.52, 128.34, 128.15, 127.97, 127.86, 127.67, 127.37, 127.10, 123.81, 122.78, 117.87, 106.10, 96.65, 65.08, 59.09, 41.29, 38.37, 16.69, 14.76. ES-MS (m/z): found 621.19, calculated for $[\text{M}+\text{H}]^+$ 621.79. Elemental analysis: C, 78.70; H, 6.42; N, 8.63 %. Calculated for $\text{C}_{41}\text{H}_{40}\text{N}_4\text{O}_2$: C, 79.35; H, 6.45; N, 9.03 %.

Detection of metal ion: Stock solutions of L_1 and L_2 (2×10^{-5} M) and perchlorate salts (2×10^{-4} M) of various metal ions (Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cr^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , and Pb^{2+}) were prepared in acetonitrile. Then, 2 mL solution of each metal perchlorate solution was added into 2 mL solution of each ionophore (L_1 and L_2) and the absorption and emission spectra of the resulting solutions were recorded. For the emission titration study, the spectra were recorded as a function of progressive addition of the standard solutions of strongly interacting metal ions (Cr^{3+} and Hg^{2+}) while maintaining the constant concentration of ionophore (2×10^{-5} M).

Results and discussion

Characterization of L_1 and L_2

Characterization data for **1**, L_1 and L_2 are given in the “Experimental section”. The ^1H , ^{13}C NMR and mass spectra for **1** are submitted as ESI (Figs. S1–S3) and the data are

similar to that reported previously [37], confirming its formation. The elemental analysis and mass data for L_1 and L_2 are in excellent agreement with the proposed composition. The mass spectra of L_1 and L_2 are submitted as ESI (Figs. S4 and S5). The ^1H and ^{13}C NMR spectra for L_1 and L_2 are also submitted as ESI (Figs. S6–S9). In the ^1H NMR spectra, the peak at δ 2.39 for **1**, which is due to $-\text{NH}_2$ protons, could not be observed in the spectra of L_1 and L_2 , on the other hand new peaks at δ 8.94 for L_1 and δ 8.03 for L_2 were noted, and they can be assigned to the proton of azomethine group ($-\text{CH}=\text{N}-$). The observation therefore suggests the formation of Schiff bases, L_1 and L_2 . In the aromatic region of the ^1H NMR spectra of L_1 and L_2 , there are some additional peaks at positions expected from anthracene and biphenyl moieties, respectively, which suggest the presence of these moieties in the new ligand (L_1 and L_2). The ^{13}C NMR data, given in the “Experimental section”, is consistent to the structures of L_1 and L_2 . The signals at δ 161.15 and 161.96 for L_1 and L_2 , respectively are due to the carbon atom of azomethine moiety, which further confirmed the formation of Schiff bases L_1 and L_2 .

Sensing of metal ions by absorption spectroscopy

The interaction of metal ions with the ionophores was followed by UV–vis spectral change. A detail of experimental procedure is given in the “Experimental section” and the spectral changes are shown in Fig. 1. It may be noted that upon addition of 10 equivalents of metal ions, a strong band appears at 527 nm (Fig. 1) for both Cr^{3+} and Hg^{2+} , this band was absent for the solution of L_1 and L_2 . The other metal ions tested (Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+}) did not exhibit formation of any new band even after addition of 100 molar equivalent of metal ions. This observation suggests binding of these two metal ions over the others tested. The appearance of the absorption band at 527 nm indicates the delocalization in the xanthane moiety of rhodamine due to spirolactam ring opening induced by strong binding of the metal ions [38]. The colour change noted after 10 min upon addition of all the metal ions tested were photographed and shown in Fig. 2. It may be noted that the ionophore L_1 shows distinct reddish-pink color with both of these metal ions whereas L_2 shows pink color with the same metal ions (Fig. 2) and the colour is detectable by bared-eye in both the cases. The stoichiometries of the complexes formed were determined by Job’s plot (Figs. S10–S13) and the data show 1:1 complex formation for both the ionophores with both the metal ions.

Mass spectroscopy

The mass spectra of the ionophores after addition of Hg^{2+} and Cr^{3+} were recorded and the spectra are submitted as ESI

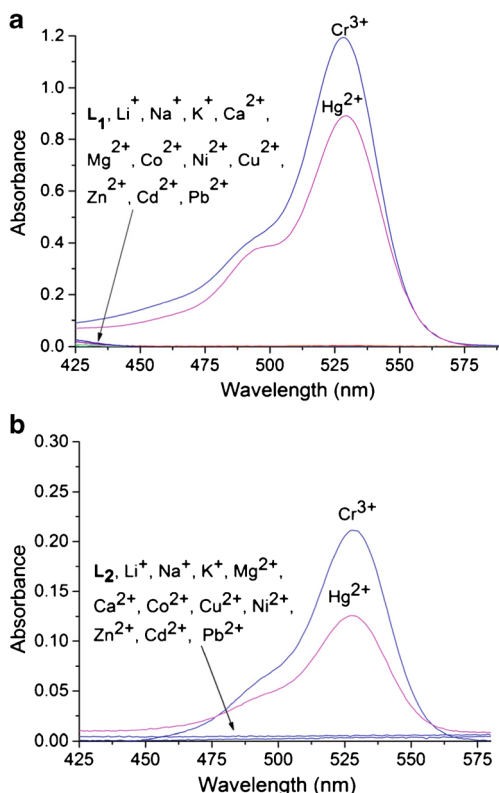


Fig. 1 UV-vis spectra of L₁ (a) and L₂ (b) in CH₃CN (2×10^{-5} M) upon addition of 10 equivalents of different metal ions

(Figs. S14–S17). For L₁, the observed m/z values for Hg²⁺ and Cr³⁺ are 846.27 and 711.93, respectively, which correspond to the compositions [L₁⁻¹+Hg²⁺]⁺ (calculated: 844.41) and [L₁⁻¹+Cr³⁺+H₂O-H⁺]⁺ (calculated: 713.82). For L₂, the observed m/z values 821.42, 839.45, 855.44, 894.47 and 911.50 for Hg²⁺ correspond to the compositions [L₂⁻¹+Hg²⁺+XH₂O]⁺ (calculated values are 820.38 (X=0), 838.39 (X=1), 856.40 (X=2), 892.44 (X=4) and 910.45 (X=5)).

Fig. 2 Colour changes of L₁ and L₂ (2×10^{-5} M) in presence of 10 equivalents of different metal ion in CH₃CN

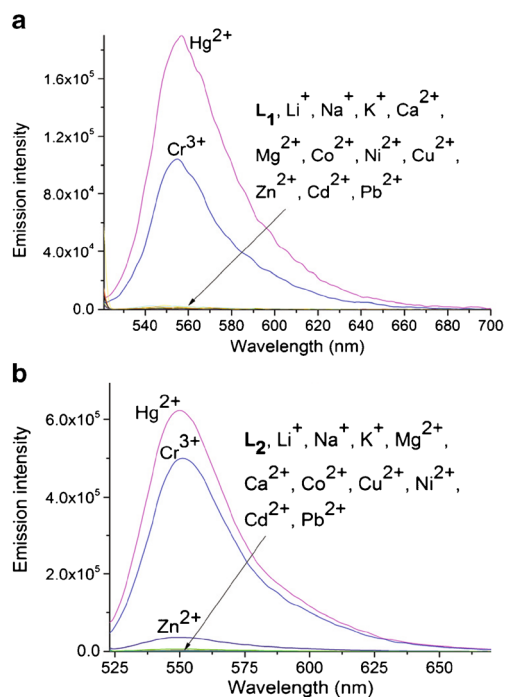
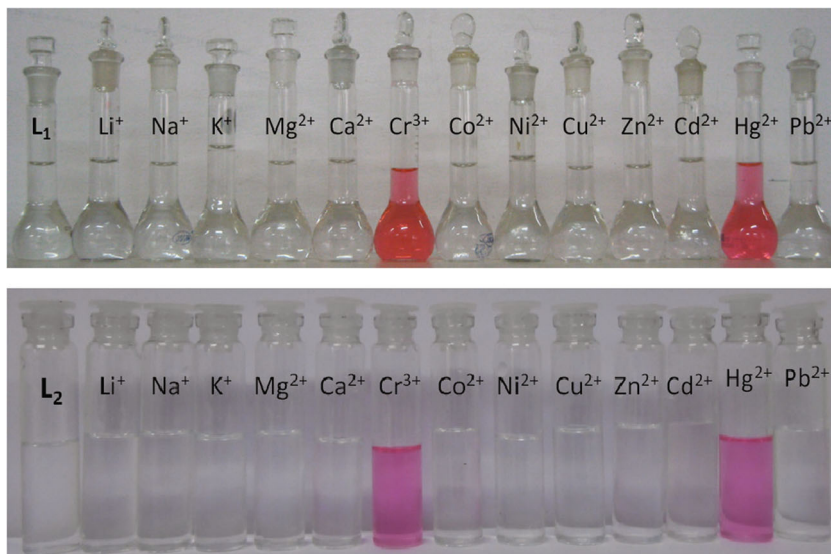


Fig. 3 Emission spectra of L₁ (a) and L₂ (b) in CH₃CN (2×10^{-5} M) upon addition of 10 equivalents of different metal ions by exciting at 520 nm

For Cr³⁺, the observed m/z value is 825.47, which matched well with the composition [L₂⁻¹+Cr³⁺+ClO₄⁻+3H₂O]⁺ (calculated: 825.33). The mass data therefore confirmed the binding of metal ions with the ionophores.

Fluorescence study

The emission spectra of L₁ and L₂ were recorded in CH₃CN (2×10^{-5} M) in the absence and presence of various metal ions (10 equivalents), as mentioned for absorption spectroscopy,

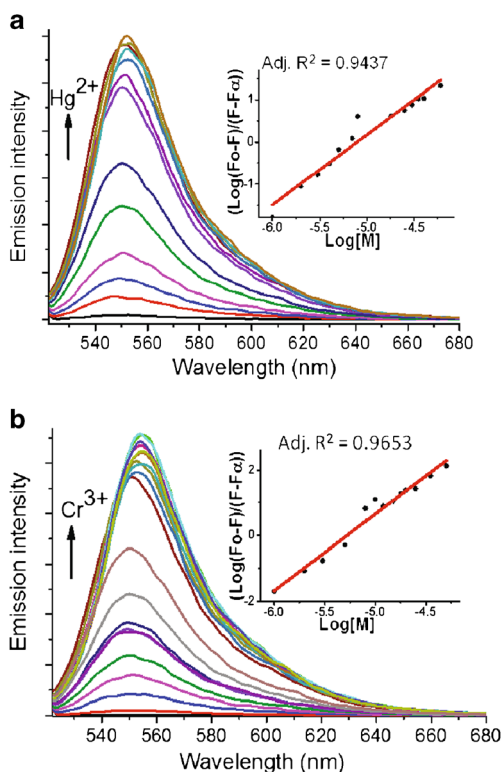


Fig. 4 Fluorescence spectral changes of L_2 (2×10^{-5} M) in CH_3CN upon incremental addition of Hg^{2+} (a) and Cr^{3+} (b)

upon excitation at 520 nm. The ionophores L_1 and L_2 did not show any emission band, however after addition of metal ions it exhibited a strong band at 550 nm for Cr^{3+} and Hg^{2+} (Fig. 3). For other metal ions, no emission band was observed. This suggests that both Cr^{3+} and Hg^{2+} formed strong complexes with the ionophores and these metal ions induced opening of spirolactam ring making strongly fluorescent complexes. The induction of delocalization in the xanthane moiety of rhodamine gives strong emission [38]. Fluorescence titration experiments for both the ionophores were carried out with Cr^{3+} and Hg^{2+} ions, details of which is given in the “Experimental section” and the spectral changes for L_2 is shown in Fig. 4 and the same for L_1 is submitted as ESI (Fig. S18). Binding constants were calculated using fluorescence titration data following the literature procedure [39]. The plots $\log[(F_0-F)/(F-F_\infty)]$ versus $\log[M]$ are shown as the insets of the Figs. 4 and S18. The titration data

Table 1 Binding constants and lower detection limit from fluorescence titration

Complex	Binding constant (K_s) M^{-1}	Limit of detection (μM)
$L_1.Hg^{2+}$	7.91×10^4	4
$L_1.Cr^{3+}$	7.32×10^4	2
$L_2.Hg^{2+}$	1.26×10^5	2
$L_2.Cr^{3+}$	1.89×10^5	2

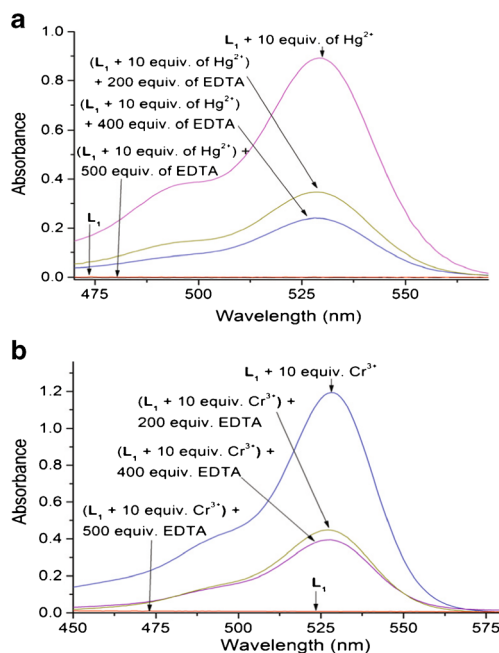


Fig. 5 Absorption spectral changes after addition of EDTA for L_1 with Hg^{2+} (a) and Cr^{3+} (b)

shows good linear fit ($R^2=0.94-0.97$) for all the four complexes and the binding constants thus obtained are shown in Table 1. The data in Table 1 suggests moderate to strong binding with both the metal ions and L_2 binds stronger than L_1 .

Lower detection limit was calculated on the basis of measurable fluorescence enhancement on addition of very low concentration of metal ions given in Table 1

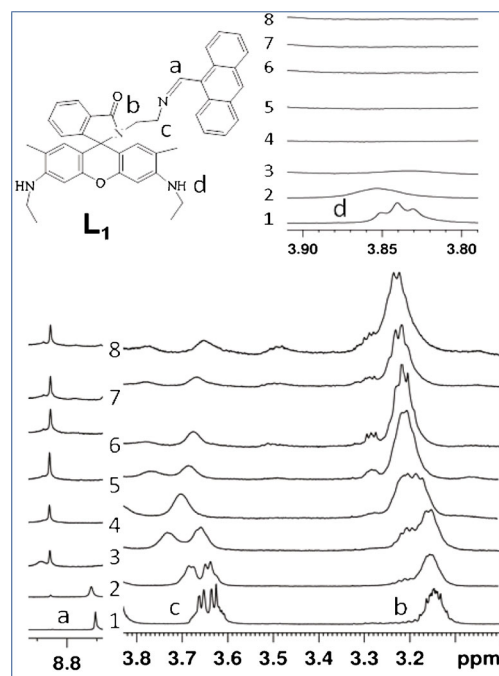
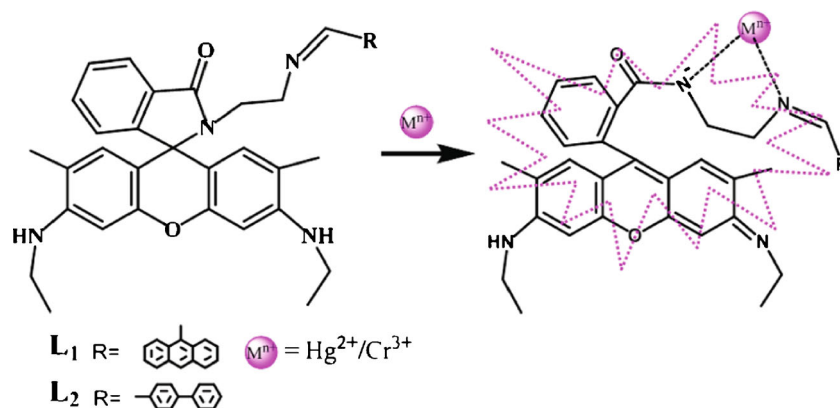


Fig. 6 1H NMR spectral change for L_1 in $CD_3CN-CDCl_3$ (x axis: δ ppm, y: intensity) with incremental addition of Hg^{2+} (0.2 to 1.6 equivalents).

Fig. 7 Probable binding mode of metal ions with the ionophores



and Figs. S19 to S22. These detection limits are found comparable to the molecular sensors reported in the literature [40, 41].

Reversible demetalation study

Reversible binding of metal ions with the ionophores was examined with the aid of EDTA. To the solution containing ionophore and 10 molar equivalent of metal ion ($\text{Cr}^{3+}/\text{Hg}^{2+}$) was added incremental amount of EDTA. The intensity of the absorption band decreased proportional to the amount of EDTA added and the band at 527 nm and also colour of the solution disappeared upon addition of 500 molar equivalent of EDTA (Figs. 5 and S23). EDTA is a well-known ligand for complexation with most of the transition metal ions and in this case demetalation of the metal-ionophore complexes took place and consequently the absorption band appeared after complexation with metal ion is again disappeared. Further addition of metal ion gives reappearance of the absorbance band and respective colours, which shows reversibility.

^1H NMR titration

The ^1H NMR spectra of the ionophores with incremental addition of Hg^{2+} were recorded to ascertain the mode of

interaction with the metal ion. In case of Cr^{3+} , no NMR study was carried out due to its paramagnetic nature. Selected portion of the NMR spectral changes with the addition of increasing amount of Hg^{2+} for L_1 is shown in Fig. 6 and the same for L_2 is submitted as ESI (Fig. S24). In the figure it may be noted that upon addition of Hg^{2+} ions, significant changes in the chemical shift for the Ha, Hb, Hc, and Hd protons (inset of Fig. 6 for naming of protons) occurred. The change in chemical shifts and broadening of the signals suggests involvement of this unit for making interaction with metal ion. The observation is consistent to the literature report for spiro-lactam ring opening induced by metal ion, as shown in Fig. 7 [42, 43]. The splitting and appearance of new signals is probably due to existence of the Hg^{2+} -complex of the ionophore in different geometrical conformation in solution. Similar observation was also noted for the complexation of L_2 .

Sensing studies in aqueous media with paper strips

Ionophores are not soluble in water; therefore a paper strip method has been evolved to detect Cr^{3+} and Hg^{2+} in aqueous media. In this method a strip of the Whatman filter paper no. 42 (pore size 2.5 μm) was immersed in a 2 mM dichloromethane solution of each of the ionophores for about 5 min. The ionophore loaded paper strip was then allowed to air dry at

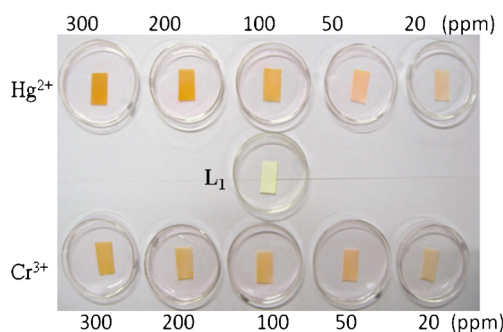


Fig. 8 Colour changes observed for L_1 with the variation in concentration of metal ions detected by paper strip method in aqueous media

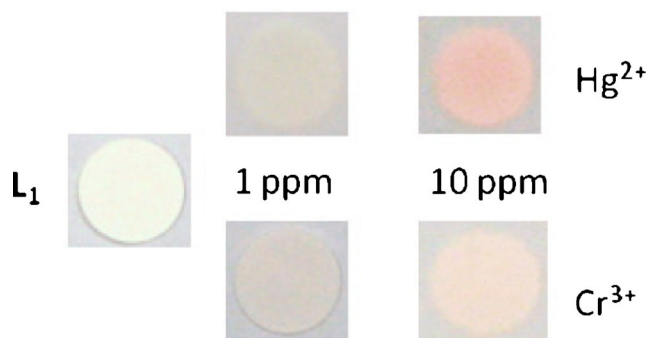


Fig. 9 Colour change observed on membrane surface for L_1 after passing aqueous solution containing metal ions ($\text{Hg}^{2+}/\text{Cr}^{3+}$)

room temperature. The dull white colored paper strip was then dipped in the aqueous solution of Cr^{3+} and Hg^{2+} of various known concentration (20, 50, 100, 200 and 300 ppm) for about 5–7 min. These metal ion dipped paper strips were then dried and their colors were compared to that of the strip without dipping in metal ion and shown in Fig. 8 for L_1 and submitted as ESI for L_2 (Fig. S25). For both of the metal ions, color of the strips changed from dull white to orange and pink for L_1 and L_2 respectively. In case of L_1 , intensity of the orange color increases with the increase of the concentration of metal ion (Fig. 8).

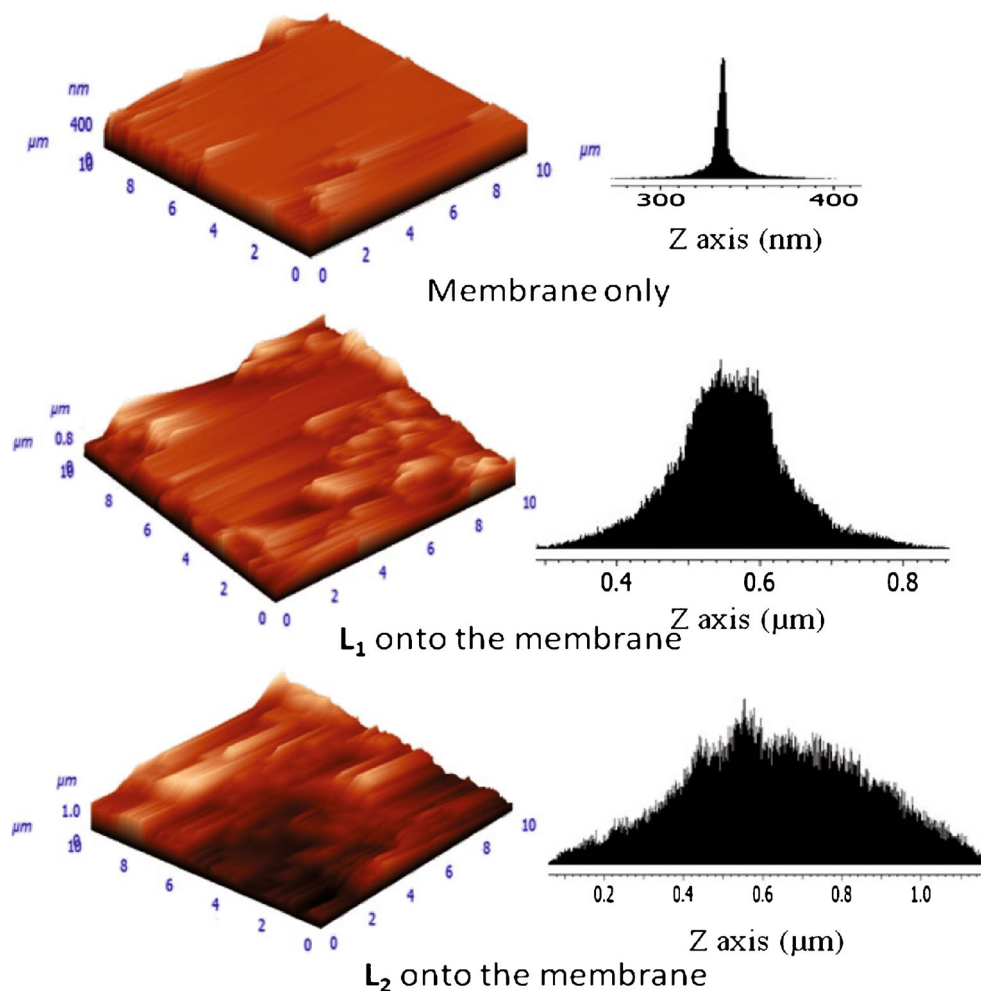
Sensing studies in aqueous media with filtration enrichment technique using membrane filtration

This technique helps to detect metal ions at low concentration. This technique involves formation of a concentrated layer of ionophore onto the membrane so that detection of metal ion passing through the layer of ionophores at low concentration can be achieved. In a typical procedure, solutions of the ionophores (1 mM, 2.5 mL) were prepared by dissolving 1.61 and 1.55 mg of L_1 and L_2 , respectively in acetone and each of

these solutions was added to 122.5 mL of MQ water and the mixture was stirred (850 rpm) at room temperature for 2 h. This aqueous dispersion of ionophore (15 mL) was then passed through the membrane (cellulose acetate, 25 mm) having 0.2 μm porosity applying gentle pressure. The ionophore-loaded membrane was then allowed to air-dry, fixed to filtration apparatus and the aqueous solution (15 mL) containing 10 and 1 ppm of the metal ions ($\text{Hg}^{2+}/\text{Cr}^{3+}$) was passed through the membrane. After drying, the surface of the membrane exhibited colour change from dull white to light pink, it is detectable by bared eye for 1 ppm but prominent for 10 ppm of metal ions (Figs. 9 and S26).

For surface study, atomic force microscopic images (AFM, 3D images) of the membrane with and without loading of ionophores along with their height histograms were recorded (Fig. 10). The images clearly show that the morphology, surface roughness and the height histogram (Z axis) of the ionophore-loaded membrane significantly changed compared to unloaded membrane. The height histogram was increased from 340 nm to 0.5 μm for both the ionophores. Surface roughness also increased significantly with the incorporation of both the ionophores.

Fig. 10 AFM images and their corresponding histograms of the membrane without and with loading of ionophores



Conclusions

Two new rhodamine-6G derivatives having anthracene and biphenyl functionalities have been synthesized and characterized. Metal ion sensing property of these two ionophores has been investigated with a wide range of alkali, alkaline earth and transition metal ions in acetonitrile. Both the ionophores exhibited high selectivity towards Hg^{2+} and Cr^{3+} with sharp colour change from colourless to pink/reddish-pink. Detail fluorescence and NMR studies revealed that spiro lactam ring opening occurred in presence of metal ions forming $\text{Hg}^{2+}/\text{Cr}^{3+}$ -complex. Binding constants were calculated from fluorescence titration data and stoichiometries of the complexes formed were determined from Job's plot. Detection of Hg^{2+} and Cr^{3+} in aqueous media was carried out by colorimetric method using paper strips and membrane filtration techniques. Membrane filtration enrichment technique demonstrated detection at lower concentration. AFM study for surface modification of membrane upon deposition of ionophores has also been carried out.

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