Solvent modulated optical tuning for discrimination of Hg$^{2+}$, Zn$^{2+}$ and Cu$^{2+}$ ions by a coumarin-functionalized azine receptor

Subrata Kumar Padhan, Punam Rana, Narayan Murmu, Biswa Ranjan Swain & Satya Narayan Sahu*
School of Chemistry, Sambalpur University, Jyoti Vihar, Burla 768 019, India
E-mail: snsahu.chem@gmail.com; snsahu@suniv.ac.in
Received 28 June 2018

In this work, a coumarin functionalized azine receptor $R$ has been synthesized and evaluated for its metal ion recognition capability via dual mode optical responses. The receptor exhibits a prominent colorimetric response in presence of Hg$^{2+}$, Zn$^{2+}$ and Cu$^{2+}$ ions in acetonitrile solvent medium. While on modulating the working solvent system from acetonitrile to acetonitrile-water (9:1, v/v) medium, the receptor shows a highly selective colorimetric response only with Hg$^{2+}$ ions. On the other hand, the receptor demonstrates a significant fluorogenic response through diagnostic fluorescence “turn-on” behaviour selectively with Cu$^{2+}$ ions in both media. A comprehensive analysis of the binding characteristics and interference studies of receptor $R$ with various metal ions have been carried out by colorimetric, UV-visible and fluorescence experiments. Further, $^1$H NMR titration studies of $R$ with these metal ions indicate a good correlation with those of the spectroscopic experiments. The detection limit of $R$ is found to be in the nanomolar range for Cu$^{2+}$ ion while it detects Hg$^{2+}$ and Zn$^{2+}$ ions in micromolar range indicating a high level of sensitivity. Moreover, the analytical applications of the synthesized receptor $R$ have been found to be excellent for optical discrimination of Hg$^{2+}$, Zn$^{2+}$ and Cu$^{2+}$ ions via solvent modulation in real samples.

Keywords: Coumarin, azine, optical, Hg$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, solvent modulation

The design of abiotic receptors comprising of dual mode detection of multiple analytes via distinct chromoluminescent changes, has become an intriguing and promising research area in past few years. Undoubtedly, receptors exhibiting colorimetric and fluorogenic changes with highly specific recognitions provide an easy and real time monitoring system for essential metal ions in various environmental and biological samples. Tuning the metal ion selectivity of a single receptor by altering the working solvent system is a newly emerged field of chemosensor design concept of type “killing two birds with one stone”. This approach indeed provides the ability of screening multiple targets with a single probe that leads to a cost effective faster analytical tool and also circumvents the tedious job of synthesis of different receptors for different analytes. Further, most of the organic receptors own solvent dependent photophysical properties mainly due to solvent-induced structural modifications by solvent-solute interactions. Hence, different working solvents not only affect the absorption and emission wavelengths of a receptor, but also greatly influence their ion selectivity by the solvation of analytes and solvatochromic nature of the receptor or receptor-analyte complexes.

Alteration of solvent media for a receptor often shows drastic optical changes to different analytes. Thus, such innovative transformation from specific to differential detection with a multi-functional probe by varying the compositions of solvent would open up new avenues for the development of solvent dependent optical sensors. At present, the solvent modulated optical discrimination of transition and heavy transition metal ions from the same source is still quite demanding. Amongst various transition metal ions, the role of Cu$^{2+}$, Hg$^{2+}$ and Zn$^{2+}$ ions are of most significant in the field of environmental, chemical and biological systems. For instance, zinc and copper ion, respectively represents the second and third most abundant transition metal ion in vivo that plays a crucial role in the fundamental physiological processes of living organisms ranging from bacteria to mammals. Although these ions are metabolically beneficial at lower concentrations, they cause serious health hazards such as neurological disorders, kidney and liver damage at higher concentrations. In contrast, mercury is considered as an extremely toxic heavy transition metal ion that causes severe physiological ailment to central nervous system and
other vital tissues even at lower concentrations. Thus the discrimination and real time monitoring of these ions in presence of other interfering species is highly demanding. Moreover, the design of a single receptor that can optically discriminate Cu$^{2+}$, Zn$^{2+}$ and Hg$^{2+}$ ions in presence of each other is quite challenging because of their nearly similar ionic radius (Cu$^{2+}$ = 73 pm, Zn$^{2+}$ = 74 pm and Hg$^{2+}$ = 102 pm), low charge density and very close hydration enthalpies (ΔH$_h$ in kJ/mol$^{-1}$; Cu$^{2+}$ = −2099, Zn$^{2+}$ = −2047 and Hg$^{2+}$ = −1829). Majority of receptors designed for Cu$^{2+}$, Zn$^{2+}$ and Hg$^{2+}$ ions work on the principle of either colorimetric or fluorogenic systems but a paucity of them exhibit the dual mode detection capability. Additionally, most of the fluorogenic Cu$^{2+}$ and Hg$^{2+}$ ion receptors exhibit fluorescence quenching which often mislead the detection of these ions in presence of each other. Therefore, the development of a synthetic receptor that could distinguish these ions both by a colour change and fluorescence enhancement would be more advantageous over the existing ones.

In this context, functionalized Schiff bases are reported as very good chelating ligands for binding of transition and heavy transition metal ions. Further, Schiff bases show solvatophoric properties via excited-state intramolecular proton transfer (ESIPT), aggregation induced emission (AIE), photochromism and solvatochromism processes. On the other hand, coumarin functionality serve as an excellent chromoluminophores that exhibit distinguish optical response on specific events. With this vision we have envisaged to assemble the coumarin units in an azine based Schiff base framework that could provide vivid optical response on metal ion binding. Although some reports have been published on azine based metal ion sensors but few of them exhibit multiple metal ion recognition capability. In continuation to our efforts toward the development of dual mode ion sensors, we have synthesized a coumarin functionalized azine receptor and investigated its metal ion binding properties in organic (acetonitrile, AcN) and aqueous-organic (AcN-water) solvent media. In AcN medium the receptor show a prominent colour change from yellow to orange with a diagnostic cyan colour fluorescence “turn-on” response only in presence of Cu$^{2+}$ ion. On the other hand it shows a bright colour change from yellow to purple and red respectively in presence of Hg$^{2+}$ and Zn$^{2+}$ ions in the same solvent medium. Further, the enthalpies of hydration of various metal ions have been exploited to tune the optical response of the receptor for discriminating detection of Cu$^{2+}$, Hg$^{2+}$ and Zn$^{2+}$ ions in an aqueous-organic medium via solvent modulation. In AcN-water (9:1 v/v) medium, the colorimetric behaviour of the receptor Cu$^{2+}$ and Zn$^{2+}$ complex was significantly suppressed while the Hg$^{2+}$ complex solution still exhibits a purple colour change even in presence of competitive metal ions. In contrast, the receptor exhibits a highly selective fluorogenic response towards Cu$^{2+}$ ions both in organic and aqueous-organic mixture solvents. The analytical applications of the receptor for chromofluorogenic discrimination of Cu$^{2+}$, Hg$^{2+}$ and Zn$^{2+}$ ions have also been evaluated in a real sample models using tap water as the medium of analysis.

**Experimental Section**

**Materials**

All the chemicals and solvents (analytical grade and spectroscopic grade) were obtained from Merck (India) and Spectrochem Pvt. Limited (India) and were used without further purification. The desired synthetic precursor 3-acetyl-7(diethylamino)-2H-chromene-2-one (3) was prepared according to the literature procedure published earlier. The azine based Schiff base receptor Bis(3-acetyl-7(diethylamino)-2H-chromene-2-one)azine (R) was prepared by the condensation of hydrazine hydrate and 3-acetyl-7(diethylamino)-2H-chromene-2-one in ethanol medium at reflux condition as given in Scheme I. Various metal ions such as Ag$^+$, Ba$^{2+}$, Ca$^{2+}$, Cd$^{2+}$, Co$^{2+}$, Cr$^{3+}$, Cu$^{2+}$, Fe$^{3+}$, Hg$^{2+}$, Mg$^{2+}$, Mn$^{2+}$, Ni$^{2+}$, Pd$^{2+}$, Pb$^{2+}$, Zn$^{2+}$, Zr$^{4+}$ ions were used in the form of their perchlorate, nitrate or chloride salts. For UV-visible and fluorescence experiments, the stock solution of the receptor R was prepared at a concentration of 10 μM in UV-grade AcN or UV-grade AcN-Water (Milli-Q) in 9:1 v/v. The various equivalents of guest ions were added in micro-litres from their respective stock solutions of strength ranging from 10$^{-3}$ to 10$^{-4}$ M prepared in UV-grade AcN unless otherwise mentioned.

**General Methods**

$^1$H NMR spectra were taken from an Avance III-400 MHz Bruker spectrometer. Chemical shifts are reported in parts per million (δ, ppm) from tetramethylsilane with the solvent resonance (DMSO-d$_6$: 2.5 ppm; CDCl$_3$: 7.26 ppm) as the internal standard. Data are reported as follows: chemical
Synthesis of the azine based Schiff base receptor (R)

The receptor R was synthesised according to the facile synthetic protocol as depicted in Scheme I. Refluxing 3-acetyl-7(diethylamino)-2H-chromene-2-one (3) with hydrazine hydrate in ethanolic medium for 72 h affords the bis(3-acetyl-7(diethylamino)-2H-chromene-2-one) azine receptor (R) through condensation reaction. Synthetic details of receptor R is given in electronic supplementary information (ESI). The spectroscopic data were found to be well supportive and consistent with the indicated structure of the receptor (Figure S1-S7). In the $^1$H NMR spectra of the receptor R (Figure S3), methyl proton of N,N-diethyl unit of the receptor shows a triplet at δ 1.23 integrating to twelve protons. Methyl protons of acetyl group shows a singlet at δ 2.32 due to six protons while the –CH$_2$– proton signals of N,N-diethyl unit shows a quartet at δ 3.43. Out of the three aromatic protons, one shows singlet at δ 6.50 and two doublets at δ 6.58-6.61 and 7.33-7.35 integrating to a sum of six protons while the coumarin ring proton shows a prominent singlet at δ 8.11 integrating to two protons. The $^{13}$C NMR signals at δ 161.3 and 157.4 of the receptor could be attributed to the imine (–C=N−) and coumarin carbonyl (–C=O) carbons respectively which is evidence for the formation of coumarin conjugated azine receptor (Figure S5). In the FT-IR spectra, the peak at 2954 cm$^{-1}$ corresponds C–H$_{ar}$ of –CH$_{ar}$, peak at 1706 cm$^{-1}$ which corresponds to lactone ring C=O$_{ar}$ and the peak at 1618 and 1508 cm$^{-1}$ corresponds to C=N$_{ar}$ and N–N$_{ar}$ respectively, which is evidence for the formation of the receptor R (Figure S6). The ESI-MS (Figure S7) spectrum shows a major peak at m/z 515.29 [M+H$^+$] which completely matches the calculated molecular weight of the receptor [M$^+$].

Results and Discussion

Colorimetric, UV-visible and fluorescence analysis of receptor R with various metal ions in organic (AcN) solvent medium

The binding interactions of receptor R towards various metal ions were evaluated by the colorimetric and fluorogenic optical response of the receptor (10 µM) in AcN medium. Addition of 5 equivalents of various metal ions (from 10$^{-3}$ M stock solution in AcN) exhibited a significant colorimetric response in presence of Hg$^{2+}$, Zn$^{2+}$ and Cu$^{2+}$ ions via a visual colour change from yellow to purple, red and orange colour respectively in the receptor solution (Figure 1A). However, a brownish yellow colouration was observed in case of 5 equivalents of Cd$^{2+}$ ions, which was very insignificant at smaller equivalents.

These colorimetric observations were further examined by the UV-visible spectral readings. The
receptor $R$ shows an $n\rightarrow\pi^*$ transition band at 416 nm in its UV-visible spectrum that corresponds to its yellow colour. Upon addition of 5 equivalents of $\text{Hg}^{2+}$, $\text{Zn}^{2+}$ and $\text{Cu}^{2+}$ ion, the absorption band at 416 nm decreases dramatically with the appearance of longer wavelength absorption bands at 536, 534 and 518 nm, respectively (Figure 1B). Addition of 5 equivalents of $\text{Cd}^{2+}$ ion exhibited a shoulder band at 450 nm which was insignificant at lower equivalents. The normalized absorbance of the respective solutions when analyzed at 536 nm, exhibited a significantly high optical response in case of $\text{Hg}^{2+}$, $\text{Zn}^{2+}$ and $\text{Cu}^{2+}$ ions in comparison to other metal ions (inset of Figure 1B).

Following the colorimetric and UV-visible spectral investigations, the fluorescence measurements were performed to understand the interaction of $R$ with metal ions. Interestingly, addition of various metal ions to the receptor solution ($10\,\mu\text{M}$ in AcN) exhibited a diagnostic cyan colour fluorescence response only in presence of $\text{Cu}^{2+}$ ion under the UV-lamp at 365 nm (Figure 2A) where the receptor solution was almost non-emissive. In the fluorescence spectra, the receptor $R$ ($10\,\mu\text{M}$ in AcN) is almost non-

![Figure 1](https://via.placeholder.com/150)

Figure 1 — Interaction of $R$ ($10\,\mu\text{M}$) in AcN medium with various metal ions (5 equiv.), (A) Colorimetric response and (B) UV-Visible spectra. Inset show normalized absorbance in presence of various metal ions at 536 nm.

![Figure 2](https://via.placeholder.com/150)

Figure 2 — (A) Fluorescence response of $R$ ($10\,\mu\text{M}$) in AcN upon addition of 5 equiv. of various metal ions under a UV-lamp of 365 nm. (B) Fluorescence spectra of corresponding solutions, inset show the change in emission intensities of corresponding solutions at 468 nm ($\lambda_{ex} = 416$ nm).
emissive in the range of 426-600 nm when excited at 416 nm. On addition of Cu\(^{2+}\) ions, it showed a distinct emission band at 468 nm with the appearance of cyan colour in the receptor solution (Figure 2B). In contrast, addition of other metal ions to \(R\) did not exhibit any significant change in its emission intensity indicating there by a highly selective fluorogenic response with Cu\(^{2+}\) ions.

Further, to understand the binding characteristics of receptor \(R\) towards Hg\(^{2+}\), Zn\(^{2+}\) and Cu\(^{2+}\) ions, UV-visible titration experiments were carried out in AcN medium. Upon incremental addition of various equivalents (0.0-4.0 equiv.) of Hg\(^{2+}\) ions (from a standard solution of 0.4 mM) to 10 \(\mu\)M receptor solution, the absorption band at 416 nm decreases gradually with the appearance of a new absorption band at 536 nm passing through an isobestic point at 446 nm (Figure 3A). Analysis of the titration profile of Hg\(^{2+}\) ions with \(R\) indicates that the increment of the peak at 536 nm was found to be insignificant up to the addition of 0.8 equivalents. However, it exhibits a sudden rise upon addition of 1.0 to 2.0 equiv. of Hg\(^{2+}\) ions. Beyond the addition of more than 2.0 equiv. of Hg\(^{2+}\) ions the absorption intensity get saturated (inset Figure 3A). This observation indicates that some kind of co-operativity exist between the receptor \(R\) and Hg\(^{2+}\) ions during their complexation events. In a similar set of experiment, addition of 0.0 to 4.0 equiv. of Zn\(^{2+}\) ions showed a gradual increase of absorption band at 534 nm with the appearance of an isobestic point at 462 nm. The titration profile of Zn\(^{2+}\) ions with \(R\) exhibits a continuous rise of absorption intensity at 534 nm up to the addition of 2 equivalents of Zn\(^{2+}\) ions and beyond that it gets saturated with very minimal rise in intensity (inset Figure 3B). In contrast, the UV-visible titration spectra for Cu\(^{2+}\) ion were found to be quite different as compared to that of Hg\(^{2+}\) and Zn\(^{2+}\) ions.

Interestingly, incremental addition of Cu\(^{2+}\) ions to the receptor solution exhibits a gradual increase in absorption band at 538 nm up to 2.4 equivalents. However, beyond 2.4 equiv. of Cu\(^{2+}\) ions the

![Figure 3 — UV-visible titration spectra of \(R\) (10 \(\mu\)M) in AcN upon addition of 0.0 to 4.0 equiv. of Hg\(^{2+}\)(A), Zn\(^{2+}\)(B) and Cu\(^{2+}\)(C) ions respectively. Insets show the respective absorbance at 536, 534 and 538 nm in presence of 0.0 to 4.0 equiv. of Hg\(^{2+}\), Zn\(^{2+}\) and Cu\(^{2+}\) ions respectively. UV-visible single wavelength time scan (D) at 538 nm for \(R\) (10 \(\mu\)M) in AcN upon addition of 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 and 5.0 equiv. of Cu\(^{2+}\) ions.](image-url)
absorbance at 538 nm decreases dramatically with a hypsochromic shift in the absorbance band towards 518 nm (Figure 3C). This peculiar behaviour of Cu$^{2+}$ ion with the receptor R was further analyzed by UV-visible single wavelength time scan for 500 seconds at 538 nm in presence of different equivalents of Cu$^{2+}$ ions (Figure 3D). It was observed that the absorbance intensity at 538 nm remain stable in presence of 0.5, 1.0, 1.5 and 2.0 equivalents of Cu$^{2+}$ ions up to 500 seconds. However, beyond 2 equivalents of Cu$^{2+}$ ions that is at 3.0, 4.0 and 5.0 equivalents, the absorbance intensity at 538 nm is found to be lower as compared to the absorbance in presence of 2.0 equiv. of Cu$^{2+}$ ions. Further, the absorbance intensity rapidly decreases with time up to 500 seconds as shown in Figure 3D. These experimental findings suggested that the appearance of an absorption band at 538 nm below 2.0 equiv. of Cu$^{2+}$ ions is possibly due to azine’s (=N=N=) nitrogen interactions with Cu$^{2+}$ ions. This kind of interactions of R with metal ions enhances the intramolecular charge transfer (ICT) from the donor (N, N-diethyl amino group) to acceptor binding sites (=N=N=) resulting in a large bathochromic shift in the absorption band$^{47,54,55}$. However, the decrease in absorbance intensity at 538 nm in presence of excess Cu$^{2+}$ ions beyond 2.0 equivalents with a hypsochromic shift from 538 nm to 518 nm may be attributed to the binding of Cu$^{2+}$ ions with nitrogen atoms of N, N-diethyl amino group of the receptor R that perhaps suppress the ICT process.

Since the receptor shows a selective fluorogenic response with Cu$^{2+}$ ions, fluorescence titration studies were conducted between R and Cu$^{2+}$ ion to further emphasize the binding interactions. Figure 4 represents the titration spectra of R (10 µM) upon gradual addition of various equivalents of Cu$^{2+}$ in AcN medium. The receptor was found to be nearly non-emissive when excited at 416 nm but on incremental addition of Cu$^{2+}$ ions, a steady increase in fluorescence intensity was observed at 468 nm up to the addition of 2.4 equivalents of Cu$^{2+}$ ions. Beyond 2.4 equivalents of Cu$^{2+}$ ions, the fluorescence intensity at 468 nm steadily decreases with a bathochromic shift of 10 nm towards 478 nm up to the addition of 4.0 equivalents of Cu$^{2+}$ ions and then gets saturated (inset Figure 4). These findings are well supportive and are in accordance with the UV-visible titration data of R in presence of Cu$^{2+}$ ion. Further, chelation enhanced fluorescence (CHEF) effect could be the reason for the large enhancement of fluorescence and significant bathochromic shift of absorption band of the receptor in presence of copper ions$^{55}$. Thus it is evident that, in AcN medium the optical behaviour of R with Cu$^{2+}$ ions is significantly different than that of Hg$^{2+}$ and Zn$^{2+}$ ions that fluorogenically discriminates Cu$^{2+}$ ions from the other metal ions.

The interference of metal ions during the binding event with receptor R was investigated by the competitive binding assay in presence of each other in

![Figure 4](image-url)
AcN medium. Different sets of experiments were carried out by preparing 50 mL ($[R] = 10 \mu M$) of each $R•M^{2+}$ ($M^{2+} = Hg^{2+}/Zn^{2+}/Cu^{2+}$) complex solution in 1:5 receptor to metal ion ratio. For the fluorescence assay 1:2 ratio of $R$ to $Cu^{2+}$ was taken. Figure 5A shows the variation in absorbance intensity at 536 nm in the UV-visible competitive assay experiment. It was observed that addition of 5 equivalents of various metal ions to $R•Hg^{2+}$ (1:5) complex solution, the absorbance intensity at 536 nm decreases only in presence of $Cu^{2+}$ ions (Figure 5A; pink bars). A similar optical response was also observed in case of $R•Zn^{2+}$ (1:5) complex solution upon addition of $Cu^{2+}$ ions (Figure 5A; red bars). This indicates a higher affinity of $R$ towards $Cu^{2+}$ ions in comparison to $Hg^{2+}$ and $Zn^{2+}$ ions. In order to support this, in a similar set of experiment, 5.0 equiv. of various metal ions were added to $R•Cu^{2+}$ (1:5) complex solution. It was observed that the absorbance intensity at 536 nm and the corresponding colorimetric response of the $R•Cu^{2+}$ complex solution did not alter even in the presence of excess of other metal ions (Figure 5A; orange bars). In the fluorescence study, when 5 equivalents of various metal ions were added to a $R•Cu^{2+}$ (1:2) complex solution, the emission intensity at 468 nm remain unchanged (Figure 5B). The corresponding visual colour change and fluorescence change of the competitive experiments are presented in Figure S8-S13. The competitive assay experiments clearly indicate that $Cu^{2+}$ ion is capable of displacing $Hg^{2+}$ and $Zn^{2+}$ ions from the $R•M^{2+}$ ($Hg^{2+}/Zn^{2+}$) complex solution [Figure S14]. However, the reverse experiment for displacement of $Cu^{2+}$ ion by $Hg^{2+}$ and $Zn^{2+}$ ions was not promising in a similar experimental condition. This strongly evidenced the highest affinity of receptor $R$ toward $Cu^{2+}$ ions.

**Optimisation of solvent for optical discrimination of $Hg^{2+}$, $Zn^{2+}$ and $Cu^{2+}$ via water induced solvent modulation**

In the AcN medium, the receptor $R$ gives a cyan colour fluorescence response only with $Cu^{2+}$ ion while it gives prominent colorimetric response with $Hg^{2+}$, $Zn^{2+}$ and $Cu^{2+}$ ions through a visual colour change in the receptor solution. However, the colorimetric discrimination of $Hg^{2+}$, $Zn^{2+}$ and $Cu^{2+}$ ions by $R$ in presence of each other was often blurred due to the overlapping of absorption bands in the range of 500-600 nm in the UV-visible spectra. This observation prompted us to think for an alternate solvent system which could discriminate the above ions in presence of each other. In this context, we have envisaged to include the presence of water in the solvent media as it plays an important role for tuning the photophysical behaviours of metal complexes in the solution state.$^{16,56}$ Further, it is known that the metal ions behave differently even in the presence of a small aliquot of water as compared to those present in pure organic medium because of their differences in hydration energy.$^{57,58}$

With this aim, we have analyzed the photophysical behavior of receptor-metal ($Cu^{2+}$, $Hg^{2+}$ and $Zn^{2+}$)
complexes (1:5) in AcN medium upon gradual addition of small aliquot of water into the complex solution. Interestingly, it was observed that upon gradual addition of water to 2 mL of R-Cu\textsuperscript{2+} complex (1:5) solution in AcN, the orange colour disappeared by the addition of 40 µL water (Figure S15). However, there was no change in the visual fluorescence response even upon addition of 40 µL of water to the copper complex solutions (Figure S15). On the other hand, addition of 40 µL of water to \textbf{R}-Hg\textsuperscript{2+} and \textbf{R}-Zn\textsuperscript{2+} (1:5) complex solution did not hamper their colorimetric responses at all (Figure S15). In the UV-visible analysis, upon gradual addition of water to 2 mL of R-Cu\textsuperscript{2+} (1:5) complex solution present in pure AcN, the absorption intensity at 518 nm gradually decreases with simultaneous shifting of the absorption band towards 538 nm that eventually disappeared by the addition of 40 µL of water (Figure S16A). On the other hand, the R-Cu\textsuperscript{2+} complex solution at 1:5 ratio has a lower emission intensity as compared to 1:2 ratio in pure AcN but upon addition of only 5 µL of water to 2 mL of 1:5 R-Cu\textsuperscript{2+} complex, the emission band at 468 nm increases significantly by more than 2.5 fold with a bathochromic shift in the emission band towards 476 nm. However, further addition of water show a marginal decrease in emission intensity through subsequent bathochromic shift in the emission band from 476 to 482 nm up to the addition of 200 µL of water (Figure S16B). This overall increase in fluorescence intensity with concomitant bathochromic shift of emission band is probably attributed to the leaching of weakly bonded Cu\textsuperscript{2+} ions from the N,N-diethyl amino binding sites because of the greater hydration enthalpy of Cu\textsuperscript{2+} ions. However, the fluorescence signal even in the presence of 200 µL of water indicated that, the Cu\textsuperscript{2+} ions are still interacting with receptor \textbf{R} in such a way that it promotes chelation enhanced fluorescence (CHEF) enhancement. Thus, we can proposed that in pure AcN medium, initially the azine nitrogen (=N-N=) interact with Cu\textsuperscript{2+} ions below 2.0 equivalents, which enhances the ICT phenomenon responsible for absorption at higher wavelength while the fluorescence enhancement could be due to CHEF. However, beyond 2 equiv. of Cu\textsuperscript{2+} ions, the N,N-diethyl amino group interact with the Cu\textsuperscript{2+} ions that suppress the ICT process (Scheme II). But, upon gradual addition of small aliquots of water, the Cu\textsuperscript{2+} ions bound to N,N-diethyl amino group preferentially leach out showing bathochromic shift in the absorption bands and fluorescence enhancement (Scheme II).

On the other hand, up to the addition of 40 µL of water to \textbf{R}-Hg\textsuperscript{2+} and \textbf{R}-Zn\textsuperscript{2+} (1:5, 2 mL in AcN)
complex solution, did not exhibit any significant change in their UV-visible spectra. However, addition of 200 µL of water to the Hg\(^{2+}\) and Zn\(^{2+}\) complexes exhibited a drastic colorimetric response only in the R-Zn\(^{2+}\) complex solution through a colour change from red to yellow. In the UV-visible spectra, upon addition of 200 µL of water, the absorbance at 534 nm corresponding to R-Zn\(^{2+}\) complex almost disappeared with the reappearance of the receptor absorption band at 416 nm (Figure S16D). In contrast addition of 200 µL of water to the R-Hg\(^{2+}\) (1:5) complex solution in AcN exhibited a marginal decrease in absorbance at 536 nm in its UV-visible spectra (Figure S16C). This observation indicated the preferential leaching of Zn\(^{2+}\) over Hg\(^{2+}\) ions from the receptor core at high percentage of water. Moreover, the percolating effect of water towards Cu\(^{2+}\), Zn\(^{2+}\) and Hg\(^{2+}\) ions in the receptor complexes follows the trend of their enthalpies of hydration. Accordingly the R-Hg\(^{2+}\) complex solution exhibits a higher tolerance level towards water up to the addition of 200 µL of water to the 2 mL of (10 µM) receptor containing 5 equivalents of Hg\(^{2+}\) ions in AcN medium. Based on the above observations, we envisaged to optically discriminate the Cu\(^{2+}\), Zn\(^{2+}\) and Hg\(^{2+}\) ions via solvent modulation using AcN-water (9:1 v/v) solvent medium. Thus, we have investigated a detail binding phenomenon of R with Cu\(^{2+}\), Zn\(^{2+}\) and Hg\(^{2+}\) ions in an aqueous-organic solvent system constituting AcN-H\(_2\)O in 9:1 (v/v) ratio. Addition of various equivalents of the metal ions to the receptor solution (10 µM) did not exhibit any substantial colour change up to the addition of 20 equivalents. However, beyond 20 equivalent addition of Hg\(^{2+}\), Zn\(^{2+}\) and Cu\(^{2+}\) ions, the receptor solution exhibits a prominent colour change from yellow to reddish pink, light orange and light red respectively. However, addition of other metal ions did not exhibit any substantial colour change in the receptor solution even at excess addition (50 equiv.) (Figure 6A).

The corresponding UV-visible spectra of colour complex solutions shows a strong absorption band at 536 nm in presence of Hg\(^{2+}\) ion while it shows very weak absorption bands at 534 and 538 nm in presence of Zn\(^{2+}\) and Cu\(^{2+}\) ions respectively at 20 equivalents (Figure 6B). A plot of absorbance at 536 nm versus various metal ions in the receptor solution indicates the highest colorimetric response of R towards Hg\(^{2+}\) ions in AcN-water (9:1 v/v) medium (inset Figure 6B).

In the fluorescence study, addition of 30 equivalents of various metal ions to receptor R exhibited a bright bluish green colour only in presence of Cu\(^{2+}\) ions under a UV-lamp of 365 nm (Figure 7A). The emission spectrum of the corresponding R-Cu\(^{2+}\) complex shows a strong emission band at 482 nm, where as other metal ions did not exhibit any change in the fluorescence spectrum of the receptor solution in AcN-H\(_2\)O (9:1 v/v) medium (Figure 7B). A plot of fluorescence intensity at 482 nm versus various metal ions in the receptor solution depicts the highest fluorogenic

![Figure 6](image-url)

Figure 6 — (A) Colorimetric response of R (10 µM) in AcN-water (9:1 v/v) upon addition of 20 equiv. of various metal ions. (B) UV-Visible spectra of corresponding solutions and inset show the change in absorption intensities of corresponding solutions at 536 nm.
response of receptor $\mathbf{R}$ towards $\text{Cu}^{2+}$ ions in the aqueous-organic medium (inset Figure 7B). Further, earlier studies have revealed a possibility of metal ion induced hydrolysis of receptors in aqueous or aqueous-organic medium. This possibility in our case has been evaluated by UV-visible and fluorescence experiments of the coumarin precursor $\mathbf{3}$ in presence of excess of $\text{Hg}^{2+}$, $\text{Zn}^{2+}$ and $\text{Cu}^{2+}$ ions in $\text{AcN}$ and $\text{AcN}$-water (9:1, v/v) medium. It was observed that, no change in the absorption and emission wavelengths or intensities occurred in precursor $\mathbf{3}$ by addition excess of metal ions (Figure S17). This clearly signified that the receptor interacts with the metal ions even in aqueous-organic medium without undergoing hydrolysis resulting in various optical changes as depicted earlier.

The UV-visible titration profile of $\mathbf{R}$ with various amounts of $\text{Hg}^{2+}$ ions in $\text{AcN}$-$\text{H}_2\text{O}$ (9:1 v/v) medium shows a marginal change in the absorption intensity at 536 nm up to 10 equivalents. Beyond that, a sudden rise in the peak intensity at 536 nm was observed which get saturated after 20 equivalents of $\text{Hg}^{2+}$ addition (Figure 8A). In a similar experiment, addition of $\text{Zn}^{2+}$ ions to $\mathbf{R}$ showed a steady increase in absorption peak at 534 nm in the $\text{AcN}$-$\text{H}_2\text{O}$ medium. However, the rate of increment of absorption intensity

Figure 7 — (A) Fluorescence response of $\mathbf{R}$ (10 µM) in AcN-Water (9:1) upon addition of 30 equiv. of various metal ions under a UV-lamp of 365 nm. (B) Fluorescence spectra of corresponding solutions, inset show the change in emission intensities of corresponding solutions at 482 nm ($\lambda_{ex}$ = 416 nm).

Figure 8 — UV-visible titration spectra of receptor $\mathbf{R}$ (10 µM) in $\text{AcN}$-water (9:1 v/v) medium with $\text{Hg}^{2+}$ ions (A) and fluorescence titration spectra with $\text{Cu}^{2+}$ ions (B) (from respective perchlorate salts). Inset of A and B show the change in absorbance at 536 nm and fluorescence at 482 nm upon addition of various equiv. of $\text{Hg}^{2+}$ and $\text{Cu}^{2+}$ ions respectively.
with Zn\textsuperscript{2+} ions is smaller than that observed with Hg\textsuperscript{2+} ions (Figure S1B). On the other hand, the gradual addition of Cu\textsuperscript{2+} ion to the receptor solution show a steady increase of a weak absorption band at 538 nm after the addition of 15 equivalents of Cu\textsuperscript{2+} ions which subsequently decreases beyond 22 equivalents (Figure S1A). However, the fluorescence titration data of R with Cu\textsuperscript{2+} showed a rapid increase in fluorescence intensity at 482 nm (Figure 8B). This observed differences in optical properties of receptor-metal ion complexes in AcN-water (9:1 v/v) medium could be attributed to their different degree of hydration in the aqueous-organic medium. Further on comparison of the absorption intensities of the R-M\textsuperscript{2+} complexes at their respective wavelengths with various equivalents of metal ions, it is found that receptor R showed an exceptionally high chromogenic response for Hg\textsuperscript{2+} ions than Zn\textsuperscript{2+} and Cu\textsuperscript{2+} ions. (Figure 9).

To sum up the results obtained from the above experiments, it is evident that the receptor R showed a diagnostic fluorogenic response only for Cu\textsuperscript{2+} ions both in organic(AcN) and aqueous-organic (AcN-H\textsubscript{2}O;9:1 v/v) medium via a fluorescence colour change from colourless to cyan and bluish green respectively. On the other hand, receptor R exhibited a prominent colorimetric response for Hg\textsuperscript{2+} and Zn\textsuperscript{2+} ions in organic medium. However, the distinction between Hg\textsuperscript{2+} and Zn\textsuperscript{2+} ions colorimetrically by receptor R in organic medium is often blurred due to their overlapping absorption bands. Thus the solvent modulation using an aqueous-organic mixture (AcN-H\textsubscript{2}O;9:1 v/v) is came out as a successful model to discriminate the two competitive ions (Hg\textsuperscript{2+} and Zn\textsuperscript{2+}). The receptor R showed a distinct colorimetric response for Hg\textsuperscript{2+} ions in comparison to Zn\textsuperscript{2+} in AcN-H\textsubscript{2}O (9:1 v/v) medium.

**Evaluation of the binding stoichiometry, association constant and detection limits of R in AcN and AcN-Water (9:1 v/v) medium**

The binding characteristics of receptor R with Hg\textsuperscript{2+}, Zn\textsuperscript{2+} and Cu\textsuperscript{2+} ions were quantitatively analysed by UV-visible and fluorescence techniques in AcN medium. Job’s plot analysis of receptor R with Cu\textsuperscript{2+} ion exhibited a maximum absorbance (λ\textsubscript{abs} = 538 nm) and maximum emission (λ\textsubscript{em} = 468 nm) at 0.33 mole fraction of R that indicates a 1:2 binding stoichiometry between the receptor and Cu\textsuperscript{2+} ion (Figure S19). On the other hand the binding interaction of receptor R with Hg\textsuperscript{2+} and Zn\textsuperscript{2+} ions exhibited a maximum absorbance at 0.5 (λ\textsubscript{abs} = 536 nm) and 0.66 (λ\textsubscript{abs} = 534 nm) mole fraction of R indicating a 1:1 and 2:1 stoichiometry between R with Hg\textsuperscript{2+} and Zn\textsuperscript{2+} ions, respectively (Figure S20).

The apparent association constants (K\textsubscript{a}) for R in presence of Hg\textsuperscript{2+}, Zn\textsuperscript{2+} and Cu\textsuperscript{2+} ions were determined from their UV-Visible titration data using nonlinear regression analysis (inset Figure 3A-C) at λ\textsubscript{max} 536, 534 and 538 nm and found out to be 2.44x10\textsuperscript{6}, 1.75x10\textsuperscript{5} and 4.89x10\textsuperscript{4} M\textsuperscript{-1} respectively (Table I). This indicates a highest binding affinity of R toward Cu\textsuperscript{2+} ion in comparison to Hg\textsuperscript{2+} and Zn\textsuperscript{2+} ion in AcN medium. The binding affinity of R with Hg\textsuperscript{2+}, Cu\textsuperscript{2+} and Zn\textsuperscript{2+} ion was also evaluated in AcN-H\textsubscript{2}O (9:1 v/v)

![Figure 9 — Comparative changes in absorbance for R-M\textsuperscript{2+} (M\textsuperscript{2+} = Hg\textsuperscript{2+}/Cu\textsuperscript{2+}/Zn\textsuperscript{2+}) in acetonitrile-water (9:1 v/v) solvent medium by the gradual addition 10.0-22.0 equiv. of metal ions. Pink, Brown and gray ball indicated the absorbance at 536, 538 and 534 nm for Hg\textsuperscript{2+}, Cu\textsuperscript{2+} and Zn\textsuperscript{2+} ions respectively.](image-url)
medium using non-linear and linear fitting curves (inset Figure 8A and Figure S21A-B). These findings indicated a higher binding constant for Hg$^{2+}$ ion ($3.22 \times 10^6$ M$^{-1}$) than that of Cu$^{2+}$ ($1.11 \times 10^5$ M$^{-1}$) and Zn$^{2+}$ ions ($1.27 \times 10^5$ M$^{-1}$) in aqueous-organic medium (Table I).

The knowledge of detection limit (DL) of a receptor towards various ions is an important parameter for practical applications. The receptor R is found to exhibit both colorimetric and fluorometric response towards Cu$^{2+}$ ions whereas it shows only colorimetric response towards Hg$^{2+}$ and Zn$^{2+}$ ions in AcN medium. Thus, DL of the receptor for Cu$^{2+}$ ion was determined by measuring the change in emission signal at 468 nm as a function of increasing concentration of Cu$^{2+}$ ion and was found to be 12.5 nM (Figure S22A). In the UV-visible studies the DL of R for Cu$^{2+}$, Hg$^{2+}$ and Zn$^{2+}$ was determined by measuring the change in absorbance at 538, 536 and 534 nm respectively as a function of increasing concentration of Cu$^{2+}$, Hg$^{2+}$ and Zn$^{2+}$ ions and was found to be 2.37, 5.3 and 1.06 µM respectively (Figure S22B). In AcN-water (9:1 v/v) medium the detection limits calculated from the absorbance values were found to be 43.23 and 18.10 µM for Hg$^{2+}$ and Zn$^{2+}$ ions respectively (Figure S23). On the other hand, the DL for Cu$^{2+}$ ion was calculated from the emission value at 482 nm in 9:1 (AcN-water, v/v) medium and was found to be 23.81 µM. Such a very low values of DL clearly signify the ability of receptor R to sense Cu$^{2+}$ ion fluoro-genically at nanomolar concentration while it detects Hg$^{2+}$ and Zn$^{2+}$ ions chromogenically at micromolar concentrations. Further, the detection limit of R is within the permissible level of Cu$^{2+}$, Hg$^{2+}$ and Zn$^{2+}$ in drinking water set by the World Health Organization (WHO).

Table I — For non-linear fit adjusted R$^2$, apparent binding constant $K_a$ and limit of detection

<table>
<thead>
<tr>
<th>Medium of Solvent</th>
<th>Metal ions</th>
<th>R$^2$</th>
<th>$K_a$ (M$^{-1}$)</th>
<th>Detection limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>Cu$^{2+}$</td>
<td>0.999</td>
<td>4.89x10$^5$</td>
<td>2.37 µM (12.5 nM$^*$)</td>
</tr>
<tr>
<td></td>
<td>Hg$^{2+}$</td>
<td>0.998</td>
<td>2.44x10$^6$</td>
<td>5.3 µM</td>
</tr>
<tr>
<td></td>
<td>Zn$^{2+}$</td>
<td>0.995</td>
<td>1.75x10$^5$</td>
<td>1.06 µM</td>
</tr>
<tr>
<td></td>
<td>Cu$^{2+}$</td>
<td>0.997</td>
<td>1.11x10$^5$</td>
<td>65.00 µM (23.81 µM$^*$)</td>
</tr>
<tr>
<td>Acetonitrile-Water (9:1 v/v)</td>
<td>Hg$^{2+}$</td>
<td>0.999</td>
<td>3.22x10$^6$</td>
<td>43.23 µM</td>
</tr>
<tr>
<td></td>
<td>Zn$^{2+}$</td>
<td>0.995</td>
<td>1.27x10$^7$</td>
<td>18.10 µM</td>
</tr>
</tbody>
</table>

$^*$Detection limit were determined as result of change in emission intensity.
*Other detection limits were determined as result of change in absorbance intensities.

In order to get a detailed binding mechanism of receptor R in presence of Hg$^{2+}$, Zn$^{2+}$ and Cu$^{2+}$ ions, $^1$H NMR titration experiments were carried out in DMSO-$d_6$ for a 5 mM receptor solution by the addition of 0.5, 1.0, 2.0, 4.0 equivalents of metal ions (Figure 10). The $^1$H NMR spectra of the receptor in DMSO-$d_6$ shows a triplet at 1.14 ppm integrating to twelve protons for -CH$_3$(a) groups of diethylamino unit, a singlet at 2.21 ppm for six protons of acetyl-CH$_3$(g) group, a quartet at 3.46 ppm for eight protons of -CH$_2$-(b) of diethylamino group. The aromatic proton signals appeared as a singlet at 6.58 ppm for Ar-H(c), a doublet at 6.74-6.77 ppm for two protons for Ar-H(d), another doublet at 7.59-7.61 ppm for two protons for Ar-H(e) and a singlet at 8.23 ppm for protons for Ar-H(f) of the coumarin ring (Figure S4). Figure 10A represents the $^1$H NMR titration spectra of receptor R upon addition of 0.5, 1.0, 2.0 and 4.0 equiv. of Hg$^{2+}$ ions. On addition of 0.5 equivalents of Hg$^{2+}$ ions to the receptor solution, only a negligible change in the NMR signals were observed but on subsequent addition of Hg$^{2+}$ ions (1.0, 2.0 and 4.0 equiv.), the proton signal at 2.21 ppm corresponding to acetyl-CH$_3$(g) group exhibited a gradual downfield shift which get saturated at 2.33 ppm ($\Delta$δ = 0.12 ppm) up to 4.0 equivalents of Hg$^{2+}$ ions. Similarly, the proton signal at 8.23 ppm corresponding to coumarin ring-H(f) also exhibited a downfield shift ($\Delta$δ = 0.12 ppm) which get saturated at 8.35 ppm beyond the addition of 4.0 equivalents of Hg$^{2+}$ ions. Other protons did not exhibit any significant change even after the addition of excess of Hg$^{2+}$ ions (data not shown). In contrast, the $^1$H NMR titration of Cu$^{2+}$ ion with R exhibited a completely different pattern (Figure 10B). The proton signal at 2.21 ppm
corresponding to acetyl-\(\text{CH}_3\) group exhibited a gradual up field shift \((\Delta\delta = 0.05 \text{ ppm})\) which get saturated at 2.16 ppm after the addition of 4.0 equivalent of \(\text{Cu}^{2+}\) ions. The proton signal at 8.23 ppm corresponding to coumarin ring-H(f) also exhibited similar up field shift of \(\Delta\delta = 0.05 \text{ ppm}\) while a minor change was observed in the other protons signals. However, in the case of \(\text{Zn}^{2+}\) titration no significant shifting in the proton signals was observed. These observations suggested that the mode of binding of \(\text{Hg}^{2+}\) ion is quite different than that of \(\text{Cu}^{2+}\) ions with the receptor molecule. As shown in Scheme II, the binding of \(\text{Hg}^{2+}\) ion with \(\text{R}\) is away from the \(\text{–CH}_3\) and coumarin-H(f) protons. Further the \(\text{Hg}^{2+}\) binding enhances the electron/charge transfer from the \(\text{–CH}_3\) and C-H(f) carbon centres toward the N and O sites of the azine and coumarin units respectively. This mechanism perhaps causes a deshielding effect on the \(\text{–CH}_3\) and C-H(f) proton signals resulting in a downfielded shift. In contrast, the two \(\text{Cu}^{2+}\) ions bind with the receptor on two opposite sides (Scheme II). As a result, \(\text{–CH}_3\) (g) and C-H(f) protons lie on very close proximity with the \(\text{Cu}^{2+}\) ion which is paramagnetic in nature. Thus in addition to the usual deshielding effect of metal ion binding on \(\text{–CH}_3\) (g) and C-H(f) signals, the nearby \(\text{Cu}^{2+}\) ion perhaps causes a shielding effect. Hence these two effects counterbalance with each other resulting in an overall upfield shift in \(\text{–CH}_3\) (g) and C-H(f) signals. This might be possibly attributed to the selective fluorescence response of \(\text{R}\) for \(\text{Cu}^{2+}\) ions in comparison to \(\text{Hg}^{2+}\) and \(\text{Zn}^{2+}\) ions.

**Practical applications of receptor R toward optical discrimination of Cu\(^{2+}\), Hg\(^{2+}\) and Zn\(^{2+}\) ions**

Considering the importance of copper, mercury and zinc ions in environmental and biological system\(^{22-24}\), the detection of these ions by receptor \(\text{R}\) via fluorescence and colorimetric method in AcN and AcN-Water medium have been investigated. Moreover to verify the possible interference of other components and ions present in real samples during the detection of above ions, we have taken the town supply tap water as the medium of analysis. For this, a 10 \(\mu\text{M}\) receptor solution in AcN:tap water (9:1 v/v) was prepared and different amounts of ions present in tap water were added to 2 mL of the receptor solution in order to make the final concentrations of metal ions within 100 to 200 \(\mu\text{M}\). The observed fluorescence and visual colour changes were depicted in Figure 11 which indicated that the probe could be applied for the detection of \(\text{Cu}^{2+}\), \(\text{Hg}^{2+}\) and \(\text{Zn}^{2+}\) ion at micro-molar concentration in environmental samples through naked eye.

Ultimately the crucial challenge was to discriminate the above metal ions in presence of each other. \(\text{Cu}^{2+}\) ion showed the highest binding affinity towards the receptor \(\text{R}\) via a strong fluorescence response in AcN-Water (9:1 v/v) medium while \(\text{Hg}^{2+}\) and \(\text{Zn}^{2+}\) ions exhibit different colorimetric responses in the absence of \(\text{Cu}^{2+}\) ion in the same solvent medium. This made their discrimination feasible. The observed fluorescence and visual colour changes as a result of solvent modulation were depicted in Figure 12 which indicated that the probe
Conclusions

could be applied for the discrimination of Cu$^{2+}$, Hg$^{2+}$ and Zn$^{2+}$ ion in environmental samples through a visual colour change.

Conclusions

To summarize our work, a chromoluminescent azine receptor R functionalized with coumarin units has been synthesized through simple condensation reactions in quantitative yields. The receptor R fluorogenically discriminates Cu$^{2+}$ ions among the other metal ions through a diagnostic cyan colour fluorescence “turn-on” response with the appearance of an emission band at 468 nm in AcN medium. Colorimetrically, lower concentrations of Cu$^{2+}$ ion show a purple coloration in the receptor solution that corresponds to 538 nm but at higher concentration it exhibited a orange coloration corresponding to 518 nm in AcN medium. However, Hg$^{2+}$ and Zn$^{2+}$ ions show purple and red colouration respectively in the AcN solution of $R$ at lower as well as higher concentrations exhibiting a strong absorption peak at 536 and 534 nm in their UV-visible spectra. Competitive binding assay revealed that the receptor R could optically discriminate the presence of Cu$^{2+}$ ion in AcN medium with significant fluorescence “turn-on” behaviour. On the other hand Hg$^{2+}$ and Zn$^{2+}$ can be optically distinguished by receptor R via solvent modulation in AcN:water (9:1 v/v) medium producing deep pink and light red coloration respectively in the absence of Cu$^{2+}$ ion. Job’s plot analysis revealed a 1:2, 1:1 and 2:1 binding stoichiometry between the R with Cu$^{2+}$, Hg$^{2+}$ and Zn$^{2+}$.

Figure 11 — Visual colour change of $R$ (10 $\mu$M in AcN:tap water (9:1 v/v) at various concentration of Hg$^{2+}$ (A) and Zn$^{2+}$ (B) ion taken in tap water as their respective perchlorate salts. Visual (C) and fluorescence colour change (D) (under UV light 365 nm) of $R$ (10 $\mu$M) at various concentration of Cu$^{2+}$ ion in tap water.

Figure 12 — Visual colorimetric and fluorescence response of receptor $R$ (10 $\mu$M) in AcN as result of solvent modulation in presence of 20 eq. of Cu$^{2+}$, Hg$^{2+}$ and Zn$^{2+}$ ions present in tap water.
ion respectively. $^1$H NMR titration experiments of R with Cu$^{2+}$, Hg$^{2+}$ and Zn$^{2+}$ ions further revealed different binding process for the above metal ions in DMSO-d$_6$. The results obtained from the $^1$H NMR titration experiments were well consistent with the fluorogenic and colorimetric changes in case of Cu$^{2+}$ and Hg$^{2+}$ respectively. The detection limit of R was found to be in nanomolar range for Cu$^{2+}$ in AcN medium and in micromolar range for Hg$^{2+}$ and Zn$^{2+}$ ions in AcN as well as AcN:water (9:1 v/v) medium that indicated a high level of sensitivity. Further, the analytical applications of the synthesized receptor R were found to be excellent for optical discrimination of Cu$^{2+}$, Hg$^{2+}$ and Zn$^{2+}$ via solvent modulation in real samples. Taken together, the receptor exhibits highly selective chromoluminescent responses in presence of Cu$^{2+}$ and Hg$^{2+}$ ions by altering the working solvent from organic to aqueous-organic system. This study would pave the way toward the development of solvent dependent multianalyte optical sensors.

**Supplementary Information**

Supplementary information is available in the website http://nopr.niscair.res.in/handle/123456789/60.

**Acknowledgments**

SNS gratefully acknowledges the financial assistance received from DST, New Delhi, Govt. of India, for the Fast-Track project grant (SR/FT/CS-46/2011) and S&T Department, Govt. of Odisha for the research grant. The research grant received from GNM Foundation for Prof. G. N. Mahapatra Endowment Chair award is gratefully acknowledged. SKP is thankful to DST and UGC New Delhi for a project assistantship and BSF fellowship respectively. NM is thankful to S&T Department, Govt. of Odisha for project fellowship. Authors are thankful to Central Instruments Facility, NIT Rourkela and IIT Guwahati for recording the NMR spectra. A special thanks to Dr. H. Sahoo, NIT Rourkela for providing the mass spectral data reported in this paper. Authors are also thankful to Prof. Pravin K. Kar and Mr. Aditya Purohit, VSSUT, Burla for providing the FT-IR data received in this paper. The financial assistance received from UGC and DST New Delhi under the DRS and FIST grant respectively to School of Chemistry is gratefully acknowledged. The authors are thankful to Dr. H. Chakraborty for his useful suggestions toward the improvement of this manuscript.

**References**