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A multifunctional Schiff base fluorescence sensor for Hg²⁺, Cu²⁺ and Co²⁺ ions†

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A multifunctional Schiff base fluorescence sensor (receptor L) was prepared and its metal ion sensing properties were investigated. Receptor L exhibited fluorescence and colorimetric responses toward Hg²⁺, Cu²⁺ and Co²⁺ with different color changes. Moreover, receptor L can be used for selective sensing of Hg²⁺, Cu²⁺ and Co²⁺ based on the distinct color changes in the real sample.

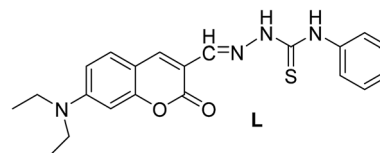
1. Introduction

Development of new receptors for the detection of different analytes simultaneously is emerging as an area of great interest,^{1–4} since such systems would lead to faster analytical processing and potential cost reductions. However most of the reported sensors are effective in selective recognition of only a particular analyte.^{5–11} Since the recognition units of the sensors are distinctive in sensing cation or anion behavior, thus, developing such sensors with multiple analyte recognition capability is a challenging task. In addition, multifunctional sensors that produce different fluorescence or color responses to different metal ions will have more potential in environmental applications. As a result, intense researches have been focused on the development of sensitive and selective receptors for the qualitative and quantitative recognition of multi metal ions. Interestingly, various sensors have been reported are quite specific, either for Cu²⁺ and Hg²⁺,¹² or for Cu²⁺ and Co²⁺,¹³ or for Cu²⁺ and Zn²⁺ (ref. 14) or for Fe³⁺, Co²⁺ and Cu²⁺,¹⁵ but to the best of our knowledge, only a few fluorescent sensors for the simultaneous detection of Hg²⁺, Cu²⁺ and Co²⁺ was reported.¹⁶

Among various important analytes, Hg²⁺, Cu²⁺ and Co²⁺ are all significant environmental pollutants and also play a critical role in various biological processes. The accumulation of excess amounts of copper ions or their misregulation can cause a series of severe diseases such as Alzheimer's and Parkinson's diseases.¹⁷ In the marine environment, Hg²⁺ ion is converted by bacteria into toxic methylmercury, a highly potent neurotoxin, and is passed up the food chain to accumulate in humans.¹⁸ On the other hand, cobalt is another biologically important metal and is required by organisms as a micronutrient. At low content of cobalt is part of vitamin B12, which is one of the necessities of the body healthy. Accumulation of

high levels of cobalt in humans results lung damage and heart disease.^{19,20} Due to the importance of cobalt, sensors are being developed for its detection, but only a few have been reported.

Receptor L has been reported by Wenhui Ma *et al.* recently;²¹ however, its metal ion-sensing properties have not yet been studied. Herein, we reported its application as a colorimetric and fluorescent sensor for selective sensing of Hg²⁺, Cu²⁺ and Co²⁺. Receptor L exhibits high fluorescence sensitivity and selectivity toward Hg²⁺ among a series of ions and show the naked-eyes detection toward Cu²⁺ and Co²⁺.



2. Materials and instrumental methods

2.1. Experimental section

All reagents were obtained from commercial suppliers and were used without further purification. Analytical thin-layer chromatography was performed using silica gel 60 F254 plates (Merck). The ¹H NMR spectra were recorded with a Bruker AM 300 spectrometer. Chemical shifts are given in ppm with residual DMSO as reference. Mass spectra were recorded under electron impact (EI) or electron spray interface (ESI) conditions. UV-vis spectra were recorded by using Jasco V630 spectrophotometer with a diode array detector, and the resolution was set at 1 nm. Fluorescence spectra were recorded on a Jasco FP-8300 fluorescence spectrophotometer.

3. Results and discussion

3.1. The absorption and fluorescence studies of receptor L toward various metal ions

UV-vis and fluorescence spectra of receptor L were investigated in DMSO–H₂O (9 : 1; v/v) by the presence of various metal ions

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(as perchlorate salts): Li^+ , Na^+ , K^+ , Ca^{2+} , Mn^{2+} , Hg^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+} , Zn^{2+} and Al^{3+} . Upon addition of Hg^{2+} , Cu^{2+} and Co^{2+} ions to the solution of receptor L, a prominent change was observed in UV-vis absorption spectra and fluorescence spectra, as shown in Fig. 1 and 2, respectively. In the presence of Hg^{2+} , the absorption spectra of receptor L showed a major band at 445 nm with a blue shift. In the presence of Cu^{2+} and Co^{2+} , the absorption spectra of receptor L showed a major band at 481 nm and 499 nm with a red shift, respectively (Fig. 1). As shown in Fig. 2, upon addition of Cu^{2+} and Co^{2+} to the solution of receptor L, the fluorescence intensity of receptor L was strongly quenched. The solution of receptor L with Cu^{2+} showed a dramatic color change from yellow to orange. On the other hand, the solution of receptor L with Co^{2+} showed a dramatic color change from yellow to red which could easily be detected by the naked-eye, as shown in Fig. 3 and 4.



Fig. 3 The color changes observed by naked eye of receptor (20 μM) upon addition of 5 equiv. of Hg^{2+} , Co^{2+} , Cu^{2+} in $\text{H}_2\text{O}/\text{DMSO} = 1/9$ (v/v).

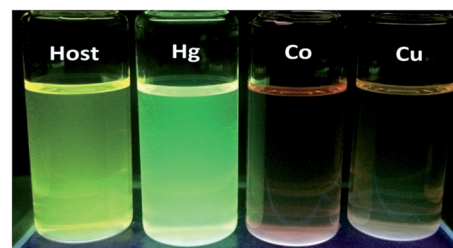


Fig. 4 The color changes observed by UV light of receptor (20 μM) upon addition of 5 equiv. of Hg^{2+} , Co^{2+} and Cu^{2+} in $\text{H}_2\text{O}/\text{DMSO} = 1/9$ (v/v), respectively.

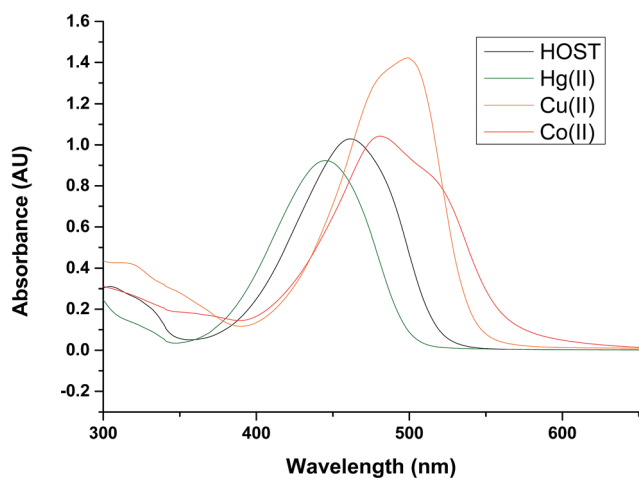


Fig. 1 UV-vis spectra of receptor L (20 μM) recorded in $\text{H}_2\text{O}/\text{DMSO} = 1/9$ (v/v) after addition of 5 equiv. of Hg, Co, Cu Metal ion.

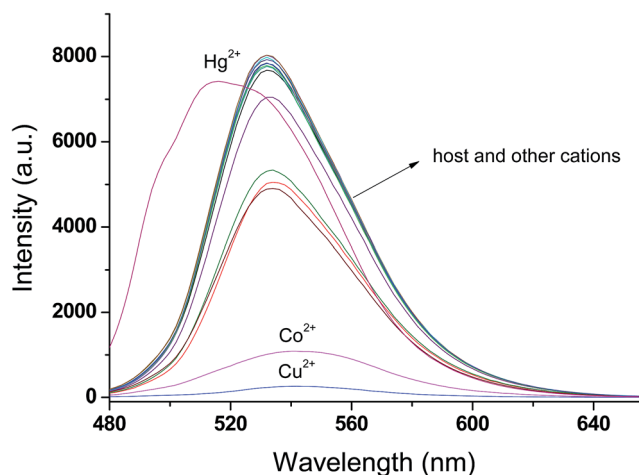


Fig. 2 Fluorescence emission spectra ($\lambda_{\text{ex}} = 460$ nm) of receptor L (20 μM) in the presence of 5 equiv. of various cation in $\text{H}_2\text{O}/\text{DMSO} = 1/9$ (v/v).

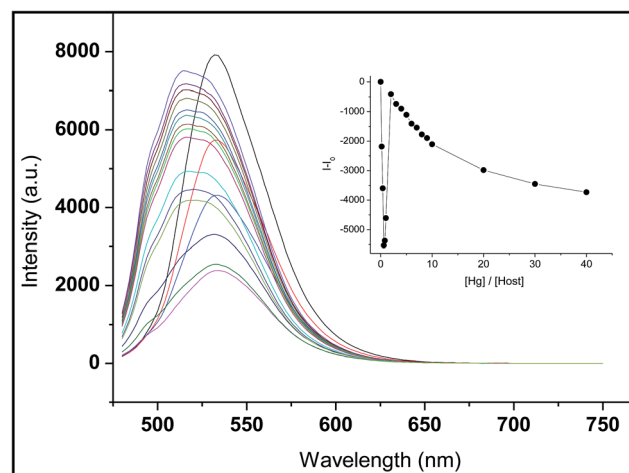


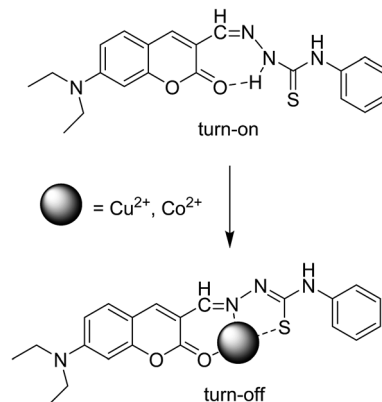
Fig. 5 Fluorescence spectra of receptor L (20 μM) in $\text{H}_2\text{O}/\text{DMSO} = 1/9$ (v/v) upon addition of increasing concentrations Hg^{2+} (0–800 μM).



band was gradually decreased. Meanwhile, the solution of receptor **L** showed a dramatic color change from yellow to light green which could easily be detected by the naked-eye (Fig. 3). The inconsistent fluorescence spectra with Hg^{2+} have suggested about the possibility of Hg^{2+} -induced irreversible desulphurization chemical reaction leading to formation of urea derivative (**X**) by a complexation reaction with sulfur atom of thiourea subunit in the early stages. The structure of urea derivative (**X**) is similar with receptor **L**, therefore, the urea derivative (**X**) can also recognize Hg^{2+} leading to fluorescence quenching. Every mercury ion could generate the effective coordination with excessive receptor **L** at the low concentration of Hg^{2+} . Along with the addition of a concentration, Hg^{2+} displays two functions; one is coordination role and the other is desulphurization. Therefore, we proposed a possible mechanism that the coordination and desulphurization of Hg^{2+} , as shown in Scheme 1.

On the other hand, with the addition of increasing amounts of Cu^{2+} or Co^{2+} to a solution of receptor **L**, the maximum peak at 540 nm decreased gradually, as shown in Fig. S1 and S2,[†] respectively. There is obviously an intramolecular hydrogen bond present between carbonyl group and amine in the receptor **L**. The presence of Cu^{2+} or Co^{2+} might destroy the intramolecular hydrogen bond and led to fluorescence quenching. The possible mechanism is shown in Scheme 2. These results indicated that receptor **L** can be used for selective sensing of Hg^{2+} , Cu^{2+} and Co^{2+} based on the distinct color changes in environmental analysis.

From the fluorescence titration profiles, the association constants for receptor **L**- Hg^{2+} , **L**- Cu^{2+} and **L**- Co^{2+} were determined as $1.85 \times 10^4 \text{ M}^{-1}$, $5.69 \times 10^5 \text{ M}^{-1}$ and $3.52 \times 10^6 \text{ M}^{-1}$, respectively, by the Stern-Volmer plot (Fig. S3 and S4[†]). A Job plot indicated a 1 : 1 stoichiometric complexation of receptor **L** with Hg^{2+} , Cu^{2+} and Co^{2+} ions (Fig. S5–S7[†]). In addition, the formation of 1 : 1 complex between receptor **L** and Hg^{2+} was further confirmed by the appearance of a peak at m/z 596, assignable to [receptor **L** + Hg^{2+}] (Fig. S8[†]). Similarly, the peak at m/z 458 and m/z 453 were assignable to [receptor **L** + Cu^{2+}] (Fig. S9[†]) and [receptor **L** + Co^{2+}] (Fig. S10[†]), respectively. The detection limit of receptor **L** for the analysis of Hg^{2+} ion was determined as 0.20 ppb, for Cu^{2+} ion as 0.29 ppb and for Co^{2+} it was determined as 0.007 ppb.



Scheme 2 The proposed mechanism for receptor **L** with Cu^{2+} and Co^{2+} .

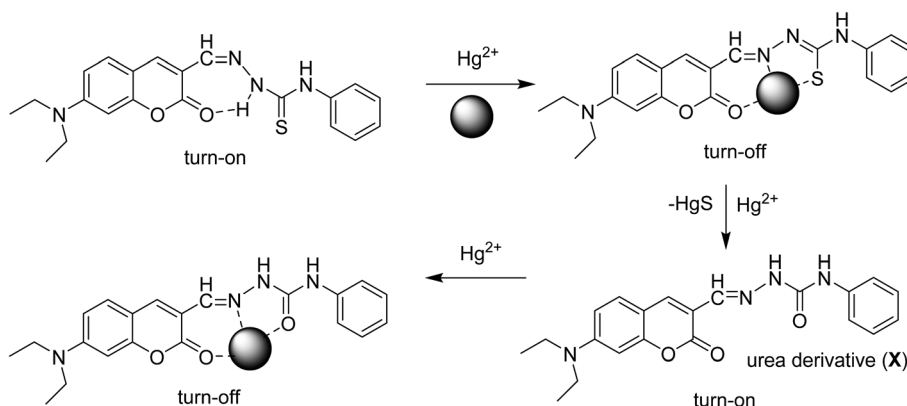
3.3. Application in real samples

The practical application of receptor **L** for selective sensing of Hg^{2+} in different source of water such as DI, tap, drink, ditch, lake and ground water has also been demonstrated. Hg^{2+} , Cu^{2+} and Co^{2+} were dissolved in different source of water, respectively.

Addition of receptor **L** into each sample water with Hg^{2+} clearly showed changing color from bright yellow to bright green under UV light (Fig. 6). Addition of receptor **L** into each sample water with Cu^{2+} or Co^{2+} clearly showed changing color from bright yellow to orange and red by the naked-eye



Fig. 6 The color changes observed by UV light of receptor **L** upon addition of 5 equiv. of Hg^{2+} in different source of water.



Scheme 1 The proposed reaction for receptor **L** with Hg^{2+} , Cu^{2+} and Co^{2+} .



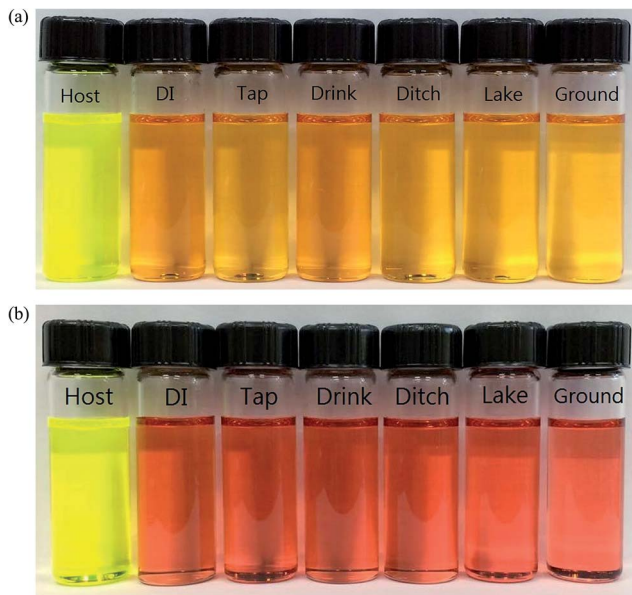


Fig. 7 The color changes observed by naked eye in different source of water containing (a) Cu^{2+} (top) (b) Co^{2+} (bottom) respectively.

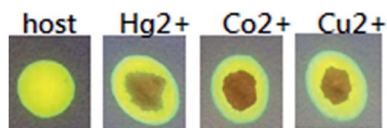


Fig. 8 Photographs of test paper for detecting Hg^{2+} , Cu^{2+} and Co^{2+} in water.

detection, respectively (Fig. 7). These results indicated that receptor **L** can be used for selective sensing of Hg^{2+} , Cu^{2+} and Co^{2+} based on the distinct color changes in the real sample.

On the other hand, the indicator paper experiments were done using filter paper coated with the solution of receptor **L**.

When this coated test paper was dropped in Hg^{2+} , Cu^{2+} and Co^{2+} water solution, the color of the paper was changed from yellow to brown instantly under UV light, as shown in Fig. 8. This indicated that the change in color on the test paper was caused by the interaction of receptor **L** and Hg^{2+} , Cu^{2+} and Co^{2+} , implying that the visually test paper showed specific recognition to Hg^{2+} , Cu^{2+} and Co^{2+} .

3.4. Reversible and competition experiments

Reversibility is a prerequisite in developing novel sensor for practical application. To examine the reversibility of receptor **L** toward Hg^{2+} in DMSO– H_2O (9 : 1; v/v) solution of EDTA (20 μM), was added to the complex solution of receptor **L** and Hg^{2+} . As expected, Hg^{2+} -induced irreversible desulphurization chemical reaction leading to formation of urea/amide derivative (2), therefore fluorescence signal at 420 nm was not quenched (Fig. S11[†]). On the other hand, when solution of EDTA (40 μM) was added to the complex solution of receptor **L** and Cu^{2+} , as expected, a fluorescence signal at 442 nm was completely quenched, which indicated the regeneration of the free receptor **L** (Fig. S12[†]). However, when the same experiment was performed for receptor **L** and Co^{2+} , it showed irreversible character (Fig. S13[†]). This result indicates due to high binding constant of complex **L**– Co^{2+} , cobalt ions are less likely to be replaced by EDTA.

The selectivity toward Hg^{2+} , Cu^{2+} and Co^{2+} was further ascertained by the competition experiment. As shown in Fig. S14–S16,[†] receptor **L** was treated with Hg^{2+} or Cu^{2+} or Co^{2+} in the presence of other metal ions of the same concentration. Relatively low interference was observed for the detection of Hg^{2+} and Co^{2+} in the presence of other ions. For the detection of Cu^{2+} , receptor **L** shows good selectivity in the presence of most metal ions, whereas quenching the fluorescence was observed in presence of Hg^{2+} . The quenching is due to the displacement of Cu^{2+} by Hg^{2+} from receptor **L**– Cu^{2+} . Although the Hg^{2+} replacement part of Cu^{2+} but still does not affect the detection

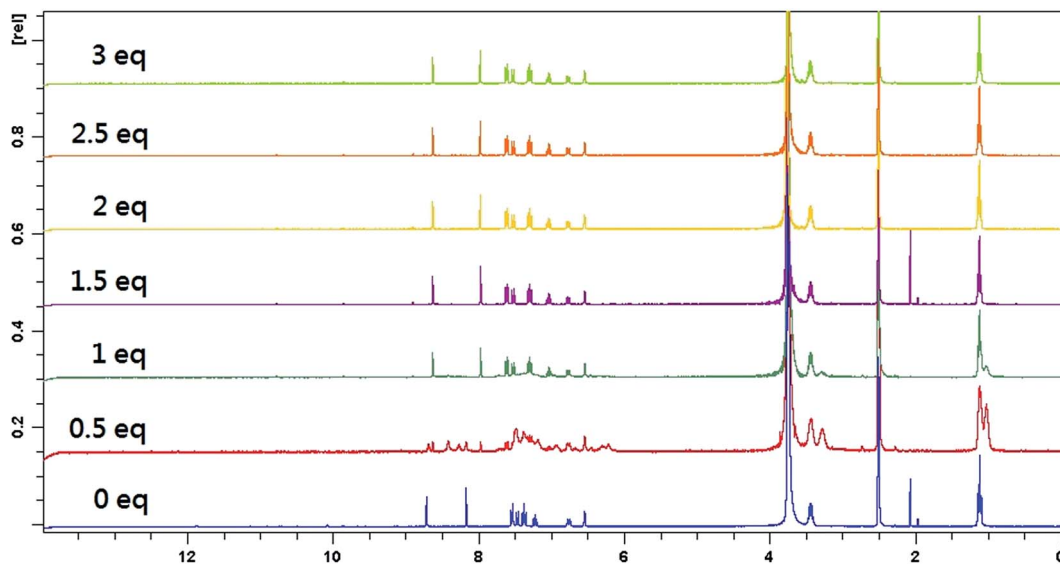


Fig. 9 ^1H NMR titration plots of receptor **L** with Hg^{2+} in DMSO/ D_2O (9 : 1, v/v).



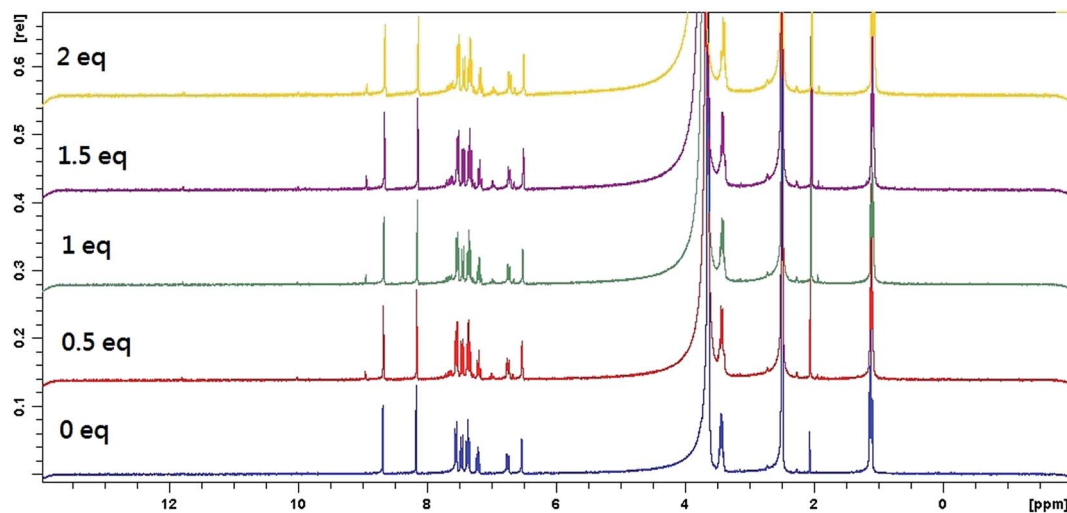


Fig. 10 ^1H NMR titration plots of receptor **L** with Co^{2+} in $\text{DMSO}/\text{D}_2\text{O}$ (9 : 1, v/v).

of Cu^{2+} . Thus receptor **L** can be used as a selective fluorescent sensor toward Hg^{2+} , Cu^{2+} or Co^{2+} in the presence of most competing ions.

3.5. ^1H -NMR titration experiments

To better understand the complexation behavior of receptor **L** with Hg^{2+} and Co^{2+} , ^1H NMR experiments were carried out in DMSO. The spectral differences for Co^{2+} and Hg^{2+} are depicted in Fig. 9 and 10, respectively. Upon addition of Co^{2+} , no significant change was observed. Upon addition of 0.5 eq. Hg^{2+} , dual peaks of quinoline ring and ethyl amines were appeared. These observations obviously indicated the presence of two isomers of receptor **L**. Upon the addition of 1.0 equiv. of Hg^{2+} , the imine proton at 8.2 ppm was shifted upfield toward 8.0 ppm. The proton of quinoline ring at 8.7 ppm was shifted upfield toward 8.6 ppm. Meanwhile, most of the aromatic protons displayed downfield shift compared to those of receptor **L** alone. The result indicated that Hg^{2+} -induced irreversible desulphurization chemical reaction leading to formation of urea/amide derivative (2).

In order to elucidate the formation of the L-Hg^{2+} , we also performed the IR experiments of receptor **L** and receptor L-Hg^{2+} complex. The typical IR spectra are shown in Fig. S17.† The IR spectrum of the receptor **L** indicated a sharp peak at 1251 cm^{-1} , which was assigned to $\text{C}=\text{S}$ stretching. In addition, receptor **L** displayed a $\text{C}=\text{O}$ stretching band in the 1715 cm^{-1} region. Interaction of **L** with Hg^{2+} , the $\text{C}=\text{S}$ stretching band was disappear, along with a shift in the N-H stretching vibration from 3475 cm^{-1} to 3500 cm^{-1} can be assigned to the formation of amide derivative as a consequence of Hg^{2+} ion induced irreversible desulphurization chemical reaction.

4. Conclusion

In summary, we have successfully designed and synthesized a simple, fluorescent and colorimetric receptor **L**, capable of recognizing Hg^{2+} , Cu^{2+} and Co^{2+} . Receptor **L** exhibited an

excellent selectivity and sensitivity towards Hg^{2+} fluorescent intensity enhancement with blue shift. In addition, receptor **L** also showed a good selectivity towards Cu^{2+} and Co^{2+} by inducing a rapid color change from yellow to orange and red, respectively.

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