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A chromone based Schiff base: An efficient colorimetric sensor for specific detection of Cu (II) ion in real water samples

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ABSTRACT

A new chromone based Schiff base ligand **L** was synthesized by the condensation of 3-formyl chromone and pyrazine-2-carbohydrazide as a colorimetric probe to detect Cu (II) ions selectively. An instant visual colour change from colourless to yellow was obtained on addition of Cu²⁺ ions to the probe **L** solution, while other metal ions found ineffective. The ligand **L** was characterized by ¹H NMR, FTIR and HRMS spectral techniques. UV-Visible spectroscopic technique was used to study the sensing ability of probe **L** for copper ions above other metal ions. The Job's plot obtained from absorption studies and HRMS data confirmed that the Cu²⁺ ions bind with ligand **L** in 1:1 stoichiometric ratio. DFT computations were also supported the binding framework between **L** and Cu (II) ions. The LOD value and the association constant were obtained 3.9×10^{-7} M and 2.3×10^5 M^{-1} respectively, via Benesi-Hildebrand equation. Selectivity of **L** towards Cu²⁺ ions was also studied and it was found that the probe **L** worked specifically for copper ions without any considerable influence of other intruding metal ions. In addition, in real water samples, the ligand **L** was fully implemented for identification and quantification of Cu²⁺ ions.

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1. Introduction

Copper is an essential transition metal which plays vital roles in various physiological processes [1,2]. It acts as a helper molecule that assists in several biochemical transformations as cuproenzymes [3,4]. Excessive utilization of copper may cause severe side effects to human beings like heptolenticular degeneration, growth retardation, liver damage, melena, Wilson's disease, gastrointestinal disorders etc., in addition less intake of this trace metal can cause diseases like Menkes, connective tissues, low white blood cell count, fatigue, brittle bones etc. in human beings [5-9]. Besides toxicity, neurological disorders and other health problems [10], because of its wide usage in industrial sector, it turns out to be an environment pollutant in combined form [11]. According to a report of the US-EPA (Environmental Protection Agency), maximum acceptable concentration of Cu²⁺ ions in potable water should not exceed 1.3 mg/litre [12]. Consequently, a simple, effectual and facile approach is needed for monitoring Cu²⁺ ions in environmental samples.

Innumerable techniques were developed for the metal ion sensing namely, anodic stripping voltammetry [13], electrochemical

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https://doi.org/10.1016/j.molstruc.2020.129549 0022-2860/© 2020 Elsevier B.V. All rights reserved. sensing [14], atomic absorption spectrometry [15], fluorescence sensing [16], inductively coupled plasma atomic emission spectrometry [17], cold vapour atomic absorption spectroscopy [18], inductively coupled plasma mass spectroscopy [19] mainly include, but their expensive instrument, high maintenance cost and difficult sampling methods constraints their usage. Spectrophotometric technique is usually recommended for metal ion assessments in aqueous phase, due to its simplicity, cost effectiveness and easy availability [20]. Apart from that colorimetric detection is modest, fast and easy method for metal ion sensing; owing to its simplicity it drags researcher's attraction towards itself. There are many colorimetric sensors introduced to detect copper metal ions but their difficult synthetic route, weak LOD values and solvent pH sensitivity put restrictions to their use. Therefore an effective probe is required which is extremely sensitive and selective for metal ion detection.

Schiff bases are well known class of compounds for their large number of applications in various fields. In addition to their several antimicrobial and cytotoxicity evaluation [21-23], Schiff bases act as potent corrosion inhibitors and used as catalysts in various chemical reactions [24]. These Schiff bases act as coordinating ligands and binds with different metal ions through their active -C = N- group which is greatly responsible for their numerous applications [25-26]. Many Schiff bases were introduced as colorimetric probes [27-31] but a few chromone based Schiff

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Scheme 1. Synthetic route for Schiff base L.

bases were familiarised. Chromone derivatives have been widely useful due to their tremendous pharmacological properties and sensing applications [32,33]. Moreover, the term chromone derives from the Greek word Chroma means "colour", and can display a wide range of colours [34]. Considering this, we have synthesized a new chromone based Schiff base Pyrazine-2-carboxylic acid (4-oxo-4H-chromen-3-ylmethylene)-hydrazide from the condensation of pyrazine –2-carbohydrazide and 3-formyl chromone (L) as shown in Scheme 1. The prepared Schiff base was characterized by means of different analytical techniques like ¹H NMR, FT-IR and HRMS. Ligand L worked as an extremely sensitive colorimetric probe for Cu (II) ions detection in methanol and the colour response can be observed through naked eyes. The practical usefulness of sensor L was successfully tested in real water samples at room temperature. Importantly, this probe L can be utilized for the sensing of copper ions at ppm concentration over a wide pH range.

2. Experiment

2.1. Materials and apparatus

3-formylchromone, pyrazine-2-carboxylic acid and hydrazine hydrate were obtained from Sigma Aldrich. Concentrated sulphuric acid, glacial acetic acid, absolute ethanol, dimethyl sulfoxide (DMSO), ethyl acetate, hexane, methanol, hydrated nitrate salts of Cd²⁺, Hg²⁺, Cr³⁺, Mn²⁺, Ca²⁺, Mg²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Al³⁺ and anhydrous nitrate salts of Ag⁺, Zr²⁺, Na⁺, K^+ and Pb²⁺were purchased from CDH and used as procured without further refinement. ¹H NMR (TMS as internal standard) was recorded from Avance III 400 MHz Bruker instrument using DMSOd₆ as solvent. FTIR spectrum was obtained using Perkin Elmer Spectrum, BX II FT-IR Spectrophotometer over a range from 4000 to 400 cm⁻¹ with KBR pellets. The UV-VIS studies were performed in 200 to 800 nm region by using Varian Cary-5000 UV-VIS-NIR Spectrophotometer with slit width 2.0 nm. The HRMS data of ligand was obtained from SCIX-QTOF Mass Spectrometer in methanol solvent. Systronics Digital pH Meter 335 was employed to check pH sensitivity of the compound synthesized. Throughout all the experiments distilled water was used wherever needed.

2.2. Synthesis

The formation of Schiff Base ligand L involved two steps; first step was the synthesis of pyrazine-2-carbohydrazide while second step was the condensation of prepared hydrazide with 3formylchromone as given below;

2.2.1. Preparation of pyrazine-2-carbohydrazide

Pyrazine-2-carboxylic acid (0.1 g) was dissolved in 20 ml ethanol in a round bottom flask followed by the addition of few drops of conc. sulphuric acid and refluxed for 22 hrs. Then hydrazine hydrate 100% (3 ml) was added to the solution and again refluxed for a period of 7 hr. The product was obtained by filtration and washed with cold water, further recrystallized with ethanol. Yield: 84%.

2.2.2. Preparation of ligand [L]

3-formylchromone (0.25 g) and pyrazine-2-carbohydrazide (0.2 g) were dissolved in 30 ml ethanol in separate beakers and mixed with constant stirring in a round bottom flask. The solution mixture was stirred for 30 min at room temperature. TLC plates were used to monitor progress of reaction. The reaction mixture was then filtered, crude precipitates were obtained and recrystallization of precipitates was done using ethanol. The recrystallized product was then washed with distilled water and ethanol (Scheme 1). Yield: 83.4%. m.p:205 °C. ¹H NMR (400 MHz, DMSO-d₆), δ =12.51 ppm (s,1H), δ =9.27 ppm (s,1H), δ =8.94 ppm (d,1H), δ = 8.87 ppm (s,1H), δ =8.81 ppm (d,1H), δ =8.80 ppm (s,1H), δ =8.15 ppm (dd,1H), δ =7.88 ppm (t,1H), δ =7.75 ppm (dd,1H), δ =7.58 ppm (t,1H). FT-IR (KBr pellet, cm¹): $v_{N=H} = 3282 \text{cm}^{-1}, v_{C=0} = 1681 \text{cm}^{-1}, v_{C=N} = 1644 \text{cm}^{-1}. \text{ HRMS}$ peak at m/z = 295.08 corresponds to $[L + 1]^+$ [calculated mass, 294.28].

2.3. Titration measurements

Primarily, the stock solutions of ligand **L** (10 mM) and metal salts (10 mM) were prepared taking methanol as a solvent and then desired concentration for further titrations was obtained by the dilution. All the solutions were kept at room temperature. The solutions of varying pH to check the pH sensitivity was prepared employing acid (HCl) and base (NaOH) solutions.

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Scheme 2. The expected binding framework between Cu²⁺ ions and receptor L.



Fig. 1. Colorimetric response of ligand L (17 μ M) after the addition of various metal ions (10⁻⁵ M).



Fig. 2. (a) The UV-Visible absorption spectra of prepared ligand L. (b) Absorption changes when ligand L (17 µM) solution was titrated with different metal ions solution.

2.4. Copper ion detection in water samples

Spectrophotometric titrations for the detection of Cu²⁺ions were performed using ligand L (17 μ M) solution in various water samples (tap water, ground water and canal water). Initially, using whatman filter paper, the collected water samples were filtered to remove insoluble impurities; afterwards samples were spiked with different Cu^{2+} ions concentration (5 ppm & 10 ppm). The absorbance spectra of the spiked samples were obtained and the calculations were made by using Beer–Lambert's Law.

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Fig. 3. (a) Absorption spectra of L with incremental addition of Cu^{2+} ions from 0.0 to 1.0 equivalent. (b) Absorbance versus mole fraction plot for L- Cu^{2+} at wavelengths 428 nm and 311 nm.



Fig. 4. (a) Job's plot corresponding to wavelength 428 nm of L-Cu²⁺ complex with varying concentration of copper ions from 0.0 to 1.0 equivalents, using the UV–Vis absorption spectra. (b) The Benesi-Hildebrand plot to find out association constant (K_a) among L and Cu²⁺ ions.



Fig. 5. (a) The HRMS analysis for Schiff base L (b) Mass spectrum of L in the presence of Cu^{2+} ions in methanol solvent.

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■ L+competetive ions

L+Cu+ competetive ions



Fig. 6. Bar graph showing the selectivity of ligand L (17 μ M) for Cu²⁺ions over other competing ions.



Fig. 7. The influence of pH changes on the absorbance of L-Cu (II) solution at wavelength 428 nm.

2.5. DFT- Calculations

Quantum mechanical calculations were performed using the B3LYP density functional theory (DFT) employed in Gaussian 09 program package [35]. Geometry optimizations of the probe L and metal attached to L were characterized to the minima without imposing any constrains on the potential energy surfaces. The computations were carried out with 6–311 G (d, p) basis set for ligands L, and LANL2DZ basis set for its Cu (II) complex.

3. Results and discussions

3.1. Design and synthesis of L

Schiff bases are well known chelating ligands. The azo methine (-C = N) group of Schiff bases act as an active binding site for transition and post transition metal ions and therefore selected as chromophores for the metal ions detection. Taking this under consideration, a chromone based Schiff base **L** has been synthesized. Pyrazine-2-carbohydrazide was prepared by refluxing pyrazine-2-carboxylic acid with conc. sulphuric acid in ethanol followed by

the addition of hydrazine hydrate solution. The prepared hydrazide was then allowed to condensed with 3-formylchromone to give the desired Schiff base Pyrazine-2-carboxylic acid (4-oxo-4H-chromen-3-ylmethylene)-hydrazide (Scheme 1). The prepared ligand **L** was characterized by spectral techniques such as; ¹H NMR, FTIR and HRMS spectrometer. The FT-IR data [Figure S1] confirms the structure of ligand by showing the characteristic band of functional groups like C = N at 1644 cm⁻¹, C = O at1681 cm⁻¹ and N-H at 3282 cm⁻¹. Also, the structure is supported by ¹H NMR spectrum that shows peaks at δ =12.51 ppm corresponds to N-H proton and δ =8.87 ppm for imine proton [Figure S2]. The HRMS data shows molecular ion peak [M + 1]⁺ at 295.08 also in close agreement with the calculated mass 294.28 of the ligand **L** [Fig. 5(a)].

3.2. Colorimetric analysis

Naked eye or colorimetric detection of ions using a chemosensor is the modest and benign method. When methanolic solution of prepared ligand **L** (17 μ M) was added individually with different metal ions i.e. Na⁺, Mg²⁺, Ca²⁺, K⁺, Pb²⁺, Al³⁺, Cr³⁺, Mn²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Ag⁺, Zn²⁺, Cd²⁺, Hg²⁺ and Zr²⁺, an instant colour response was observed for Cu²⁺ ions above various other metal ions. Upon addition of Cu²⁺ ions, the colourless liquid **L** turned into yellow which was visible through naked eyes, while no noticeable change was observed for other metal ions as shown in Fig. 1. The results indicated that ligand **L** might serve as a colorimetric probe for selective recognition of Cu²⁺ ions through naked eyes.

3.3. Absorption studies

The UV-Visible absorption studies are well recognized for understanding the interaction of metal ions with the Schiff base ligands [36]. Taking the colorimetric results under consideration, further metal ions interaction with L was examined through UV-Visible titrations using methanol as a solvent. Absorption spectra of ligand L showed two strong absorption bands one at 258 nm and the other one at 311 nm.

The band at 258 nm may be due to Π - Π * transition and at 311 nm could be due to *n*- Π * transition as shown in Fig. 2(a). On addition of distinct metal ions no considerable changes in the



Fig. 8. Geometrical optimization of ligand L (a) and L-Cu (II) complex (b) at B3LYP/ LAN L 2DZ level of theory. Selective bond lengths (in Å) are shown.

absorption bands were obtained apart from Cu (II) ions as shown in Fig. 2(b). In case of Cu^{2+} ions, a new band was appeared at 428 nm with the complete disappearance of 311 nm absorption band which indicated a bathochromic shift in the absorption spectrum. This new band must be due to the complexation amongst the Cu²⁺ions and ligand L [37]. The intramolecular charge transfer (ICT) process was evident during the complex formation [38, 39]. Upon incremental addition of Cu²⁺ ions from 0.0 to 1.0 equivalent in terms of molar ratio to the ligand L solution, band at 311 nm decreased gradually and a new band at 428 nm appeared progressively. This gave a clear isosbestic point at 363 nm and proposed that a stable metal complex between Cu (II) ions and ligand L is formed as shown in Fig. 3(a). The Fig. 3(b) shows graph between the absorbance changes in bands at 428 nm and 311 nm versus the mole fraction of L-Cu²⁺, indicating that with the hike in concentration of copper ions in the solution, the band at 428 nm increases and at 311 nm decreases gradually.

3.4. Job's plot measurements

To understand the mechanism of binding among Schiff base ligand **L** and the Cu²⁺ ions, the job's plot measurement was implemented. In order to obtain the plot, solutions of ligand **L** and copper metal salt of equal concentration (17 μ M) were prepared in methanol. UV-Visible titrations of **L** were carried out with increasing extents of Cu²⁺ions from 0.1 to 1.0 equivalents and overall concentration of solution was maintained constant at 17 μ M. The Fig. 4(a) shows a Job's plot of absorbance at wavelength 428 nm with increase in mole fraction of Cu²⁺ ions. It was observed that absorbance of ligand **L** reached its maximum value at ~0.5 mole fraction suggesting that the stoichiometric binding ratio among Cu (II) ions and **L** is 1:1. The High Resolution Mass Spectrometry (HRMS) data also validate the 1:1 stoichiometry between **L** and Cu²⁺ ion as shown in Fig. 5(b) and the peak at m / z 355.9 in the mass spectrum corresponding to $[L+Cu^{2+}]^+$ clarified the metal coordination with ligand in 1:1 molar ratio. With the help of Benesi-Hildebrand equation, association constant (K_a) for **L** was computed 2.3 × 10⁵ M^{-1} using:

$$\frac{1}{A-Ao} = \frac{1}{Ka[Amax - Ao][Cu2+]} + \frac{1}{Amax - Ao}$$
(1)

where A_0 is absorbance value of ligand **L** in absence of copper ions, *A* is absorbance recorded in the presence of copper ions at particular concentration, A_{max} is maximum absorbance recorded in the presence of copper ions and K_a stands for association constant. The limit of detection (LOD) of **L** for Cu²⁺ ions was computed 3.9 × 10⁻⁷ M using expression;

$$LOD = 3\sigma/K \tag{2}$$

where σ stands for the standard deviation and K_a stands for the association constant obtained from equation-1 with the help calibration curve shown in Fig. 4(b).

3.5. Selectivity of l for Cu^{2+} ions

To check the selectivity of **L** for Cu (II) ions over Na⁺, Mg²⁺, Ca²⁺, K⁺, Pb²⁺, Al³⁺, Cr³⁺, Mn²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Ag⁺, Zn²⁺, Cd²⁺, Hg²⁺, and Zr²⁺ ions, competitive titrations were performed using 17 μ M solution of **L**. When 1:1 equivalent solutions of **L** and various other metal ions were treated with copper ions individually, no considerable changes were observed in the absorption spectra, even after using 2.0 equivalents of the other metal

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| Table | 1 | | | |
|-------|---|------------|---|---------------------------------------|
| C | | C -1-166 1 | 1 | · · · · · · · · · · · · · · · · · · · |

Some reported Schiff base colorimetric probe with their properties.

| F F F | | | | | | | | |
|-------------------|----------------------|---------------------------------|--------------|-------------------------------------|--|--|--|--|
| Building Block | Colour Change | Detection limit | Reference | Solvent | | | | |
| Bisthiophene | Yellow to colourless | $6.21~\times~10^{-6}~M$ | [40] | CH ₃ OH-H ₂ O | | | | |
| Napthaldehyde | Yellow to claybank | $4.65 \times 10^{-7} \text{ M}$ | [41] | DMF-H ₂ O | | | | |
| Cinnamaldehyde | Yellow to pink | $2.85~\times~10^{-6}~M$ | [42] | CH ₃ CN-H ₂ O | | | | |
| Thiosemicarbazide | Colourless to yellow | $1.7~	imes~10^{-6}~M$ | [43] | CH ₃ OH-H ₂ O | | | | |
| Amide | Colourless to yellow | $1.8~	imes~10^{-6}~M$ | [44] | CH ₃ OH-tris buffer | | | | |
| Triazole | Colourless to yellow | $12 \times 10^{-7} M$ | [45] | CH ₃ OH-tris buffer | | | | |
| Chromone | Colourless to yellow | $3.9~	imes~10^{-7}~M$ | Present work | CH ₃ OH | | | | |
| | | | | | | | | |

ions no significant interference was observed. The Fig. 6 displaying the bar graph of absorbance changes at wavelength 428 nm for L + Cu and L + Cu + competitive ions, which gave clear indication that the Schiff base **L** might work as a selective colorimetric sensor in the presence and in absence of various other analytes.

3.6. pH effects

Many of the chemosensors involves the detection of metal ions through the proton transfer phenomenon and this process is affected by pH of the solution. To check the acceptable pH range for metal ion detection in biological and environmental samples, effect of pH changes on the liability and selectivity of ligand L towards $\text{Cu}^{\bar{2}+}$ ions was too tested. For this intent, 17 μM ligand L solution was prepared using methanol and the pH of solution was sustained from 2 to 11 in separate vessels using pH meter with the help of acid (HCl) and base (NaOH) solutions. Solutions of ligand L of different pH were then treated with Cu²⁺ ions solution and further these solutions were subjected for UV-Visible absorbance studies. The Fig. 7 shows the changes in absorbance at 428 nm with respect to the change in pH from 2 to 11. It was observed that ligand L work effectively in neutral and basic medium (pH 6–11) while no satisfactory results were obtained at very low pH values (2–3). The results justified the working pH which is 7.9; also it was revealed that the sensor can work over a broad pH range. Apart from that, it was noted that as the basicity increases the colorimetric changes were observed more effectively.

To compare the efficiency of the ensuing probe, comparison of probe **L** in terms of selectivity and detection limit for Cu^{2+} ions with other formerly reported colorimetric probes is given below in Table 1 with their visual colour change and detection limit, confirming that the developed chromone based Schiff base **L** is comparable and has even better performance in terms of detection limit.

3.7. Sensor's stability and reproducibility

The stability of the prepared compound **L** was tested after 15 days and no specific change was observed in characteristic absorbance band at 428 nm for Cu^{2+} ions. The ligand **L** showed the identical results as were obtained earlier. Moreover, **L** showed an immediate colour response as soon as the Cu^{2+} ions solution was added to the **L** solution and a fast response time ~40 s for the ligand **L** was recorded. In order to find the reproducibility of probe **L** for the detection of Cu (II) ions, the recommended procedure was repeated three times under optimal conditions. The reliability of

Table 2

ligand **L** was tested for different water samples using spectrophotometric method and the relative standard deviation (RSD) values of all the taken samples are shown in Table 2, RSD values were not found more than 2.8% in case of entire sample range, which was quite reliable for analysis at ppm level. These studies revealed the potency of the synthesized ligand **L** as an effective chemosensor for Cu²⁺ ions detection in environment samples.

3.8. DFT-Calculations

Full geometrical optimization of ligand **L** and its Cu (II) complex was carried out at the B3LYP level in their ground state shown in Figs. 8(a) and 8(b). The bond distances of coordination bonds formed among Cu (II) and donor atoms of ligand **L** are Cu-N: 2.1258 Å; Cu-O: 1.9411 Å and Cu-O: 1.9763 Å. The frontier orbitals of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of ligand **L** and L-Cu²⁺ complex are also given in Figs. 9(a) and 9(b). It was indicated that electron density of HOMO in ligand **L** is mainly located on 3-(iminomethyl)–4H-1-benzopyran-4-one site and anticipated as a possible binding site for the Cu²⁺ions, while LUMO for **L** was localized on pyrazine-2-carboxamide site. Similar fashion of MOs localization was observed in Cu (II) complex of ligand **L**.

The energy gap between HOMO-LUMO of ligand **L** and L-Cu (II) complex was measured to be 3.77 eV and 0.98 eV, correspondingly. The Cu (II) complex of ligand **L** exhibited decrease in energy gap, which gave clear indication of the easy electron transfer mechanism and intensive colour of the complex. These results supported the colorimetric changes in **L** with Cu (II) ions and the formation of stable L-Cu²⁺ complex.

From the results obtained by Job's plot, HRMS analysis and DFT-calculations, it was concluded that the expected binding framework of Cu^{2+} ions with the receptor **L** would be as depicted in Scheme 2.

4. Practical utility

So as to further examine the feasibility and suitability of chemosensor **L** in environmental samples, a calibration curve was constructed as shown in Fig. 10(a). Probe **L** displayed a straight line graph for varying concentration of Cu²⁺ions from 0 to 10 ppm with a correlation coefficient $R^2 = 0.9865$, which signifies that **L** could be suitable for Cu²⁺ions quantitative measurement. The real sample analysis was accomplished with canal, ground and tap water

Percentage RSD and Recovery values for different water samples.

| Water Samples | Cu Spiked (ppm) | Cu Found (ppm) | % Recovery | % RSD (<i>n</i> = 3) |
|---------------|-----------------|----------------|------------|-----------------------|
| Canal Water | 5 | 5.16 | 103% | ±2.1 |
| | 10 | 9.87 | 98% | ± 1.04 |
| Ground Water | 5 | 5.19 | 104% | ± 2.07 |
| | 10 | 10.15 | 101.5% | ± 1.32 |
| Tap Water | 5 | 5.44 | 108% | ± 2.81 |
| | 10 | 10.40 | 104% | ± 1.14 |



Fig. 9. (a) Calculated frontier molecular orbitals of ligand L and (b) the corresponding L-Cu²⁺binding.



Fig. 10. (a) Calibration curve for absorbance of L-Cu²⁺ against varying concentration of Cu ions from 0 to 10 ppm. (b) Spectrophotometric analysis of Cu (II) ions at varied concentrations in different water samples.

samples and the UV-Visible titration response of **L** against these water samples is as shown in Fig. 10(b).

The standard procedure of addition was followed for the real time analysis. Acquired to the calibration curve, relevant recovery values of the water samples were obtained using Beer-Lambert's Law as depicts in Table 2. Based on the obtained results, we could say that sensor **L** might be applicable for the recognition and quantification of Cu (II) ions in biological and environmental samples at a very low concentration level.

5. Conclusion

In present work, a chromone based Schiff base **L** was being synthesized and characterized by means of different spectral techniques like FTIR, ¹H NMR and HRMS. The ligand **L** showed selective recognition of Cu^{2+} ions over other ions such as, Na⁺, Mg²⁺, Ca²⁺, K^+ , Pb²⁺, Al³⁺, Cr³⁺, Mn²⁺, Fe³⁺, Co²⁺, Ag⁺, Ni²⁺, Zn²⁺, Cd²⁺, Hg²⁺ and Zr²⁺through colorimetric response from colourless to yellow. UV-Visible titrations also assisted the selectivity of **L** towards

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 $\rm Cu^{2+}$ ions. HRMS and the Job's plot data authenticated the 1:1 stoichiometry among L and $\rm Cu^{2+}$ ions. The LOD value for the detection of $\rm Cu^{2+}$ ions was determined to be 3.9×10^{-7} M and association constant (K_a) was computed to be $2.3\times10^5~M^{-1}$ using Benesi-Hildebrand equation. Density functional Theory (DFT) computation data also certify the binding stoichiometry among L and $\rm Cu^{2+}$ ions. The pH tests performed to check the sensitivity of chemosensor L revealed that it can operate over large pH values. Sensor L was effectively implemented for quantified sensing of $\rm Cu^{2+}ions$ in different water samples at different concentrations. From overall results, it has been concluded that L could work as an excellent colorimetric and selective probe to sense $\rm Cu^{2+}$ ions for environmental and biological monitoring.

Author's credit statement

Nisha Tomer and Apurva Goel contributed equally to this work. Rajesh Malhotra contributed as being the supervisor of this research work.

Vikas D. Ghule contributed to DFT calculations.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2020.129549.

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