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Research Article

COLORIMETRIC "OFF-ON" PROBE FOR CU^{2+} NANOMOLAR DETECTION IN AQUEOUS SOLUTION

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ABSTRACT

An imine based colorimetric probe (**3**) was synthesized and explored it recognition properties against various metals. The absorption spectra of (**3**) showed absorbance maxima at 325nm. The addition of Cu^{2+} in the receptor (**3**), changed the absorption spectrum of receptor (**3**) with the appearance of a new band at ~385 nm. The association constant (K_a) of receptor (**3**) with Cu^{2+} ions was found at 2.3×10^5 M^{-1} with the formation of (receptor-Cu^{2+}) complexes in 1:1 stoichiometry. The receptor (**3**) ($C=1\times10^{-5}$ M) is yellow coloured in CH_3OH/H_20 (80:20, v/v) and addition of Cu^{2+} results into green coloured solution. The LOD was found to be 183nM from 10 blank solutions.

Keywords: Colorimetric probe, Association constant, Stoichiometry, LOD.

1. INTRODUCTION

The colorimetric receptors for discriminating recognition of solitary metal ion systems have been rapidly developed in last decade years [1-5]. Such sensors should have special sensitivity over the sensing of besieged metal in the pool of different metal ions under study. Schiff bases are one of the most important and widely explored organic species [6]. Their low-cost, synthetic ease and tremendous application enthused scientists to prepare and explored its application for metal sensing [7-11].

Several analytical methods (There are many techniques for the detection of copper ions such as voltammetry, inductively coupled mass spectroscopy, atomic absorption spectroscopy etc.) have been developed for accurate detection of Cu^{2+}. Colorimetric methods are extremely attractive because they can be easily read with the naked eye [12-15]. The deficiency of Copper below the limit is known to cause disease like Menkes amyotrophic lateral sclerosis, Alzheimer's disease. The important physiological application of Cu^{2+} and its associated biomedical implications created considerable interest in the design copper receptor which can work in mixed solvent (water/organic solvent) [16,17].

Inspired by the previous work [18-25], our research group has successfully synthesized a Schiff base, (receptor **3**) for Cu^{2+} ion sensing investigation; we describe this (**3**) as a colorimetric sensor selective for Cu^{2+} ions, utilizing absorption shifting and naked eye detection. We wish to report the simple economical receptor for the detection of Cu^{2+} response of (3) in the presence of Cu(II) ions is not affected by metal ions under study

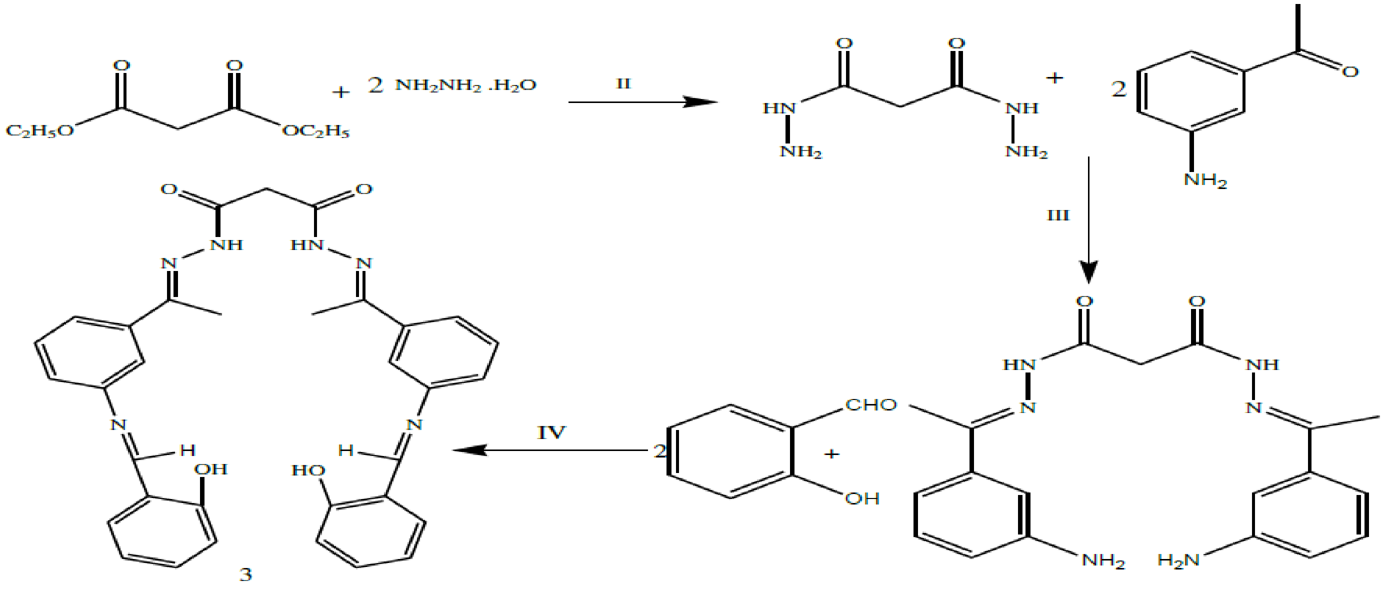
2. SYNTHESIS OF RECEPTOR (3)

Receptor was synthesized by following step:

In the first step, solution of Diethylmalonate (0.158g, 1mmol) was added to the solution of 2 mole of hydrazine hydrate (0.064g, 2mmol) in absence of solvent stirring at room temperature. The compound **1** was formed.

In the second step, compound **1** (0.132g, 1mmol) reacted with 3-amino acetophenone (0.240g, 2mmol) in ethanol (50 mL) and the mixture was stirred and refluxed for 2 hrs. The compound **2** was formed.

In the third step, compound **2** (0.366g, 1mmol) reacted with 2-Hydroxy Benzaldehyde (0.244g, 2mmol) in 50ml methanol and stirred for 3hrs at RT. The receptor (**3**) was obtained with quantitative yield having yellow appearance (Scheme 1). This yellow crystal was filtered, dried (85% yields) and characterized by spectroscopic techniques. The spectral information gave consistent data of structure of receptor 3. H^1 NMR ($CDCl_3$, 400 MHz) δ(ppm): 13.0 (2H, s),12.09(2H,s), 11.9 (2H, s), 8.9 (2H,d), 8.3 (2H,d), 7.6(2H,d), 7.3 (2H,d), 7.2 (2H,d), 6.9(2H,d), 6.8(2H,d),6.7(2H,d), 3.6 (6H,s), 2.3(2H.s), IR (cm^{-1}): 3213cm^{-1} (-NH stretching), 3060cm^{-1} (-O-H stretching), 1673cm^{-1} (-C=O stretching), 1566cm^{-1} (-C=N-N), 1481cm^{-1} (-C=N-stretching), MS (EI+): *m/z* =574.23 ($C_{33}H_{30}O_4N_6$) cald *m/z* = 575.5568 for $C_{33}H_{30}O_4N_6$. CHNO Analysis C, 68.98; H, 5.26; N, 14.63; O, 11.14%.



Scheme 1: Synthesis of receptor (3)

3. ABSORPTION STUDIES OF RECEPTOR (3)

The selectivity of receptor (3) towards various metal cations was studied on UV-Vis absorption spectroscopy in CH_3OH/H_2O (80:20,v/v). The electronic spectrum of 3 (10 μM) showed absorbance maxima at 325 nm, upon addition of 11 equivalents of cations to the solutions of (3) in CH_3OH/H_2O (80:20,v/v) caused a dramatic color change from yellow to green in the presence of Cu^{2+} ions. The addition of Cu^{2+} in the receptor (3), the change absorption spectrum of receptor (3) was observed with the appearance of a new band at ~385 nm (Fig. 1).

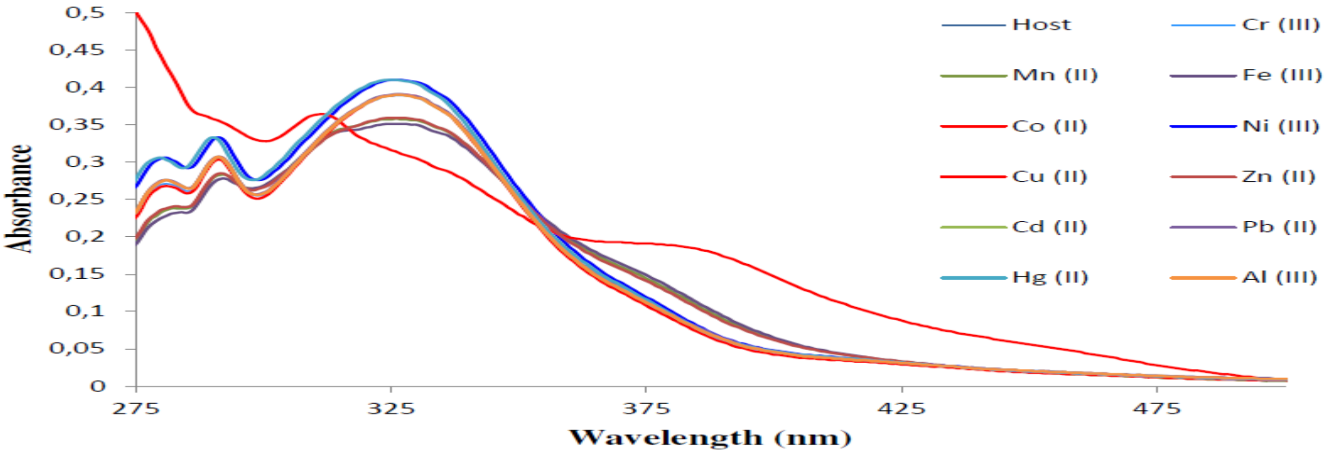


Fig. 1: Absorption spectra of receptor (3) upon addition of 11 equivalents of various metal ion in CH_3OH/H_2O (80:20, v/v) solvent system.

This shift in the wavelength is due to the ligand to metal charge transfer and it appears that the core functionality required for (3) to efficiently bind Cu^{2+}.

On regular addition of Cu^{2+}ions, the peak at 325 nm gradually decreased up to the addition of 100 µM of Cu^{2+} ions and two new peaks appeared at 265 nm and 385 nm due to LMCT. The consecutive accumulation of Cu^{2+} to a solution of receptor 3 illustrated increased and decreased in the absorption maxima at 385nm and 325nm, respectively. This indicates that the existence of one equilibrium in the system. This produces two isobestic points at 360nm and 305nm respectively (Fig. 2). The absorption spectra show the selectivity of Cu^{2+} and ratiometric graph obtained from experimental study. (Fig.3) For competitive studies, receptor (3) was treated with 10 equiv. of Cu^{2+} in the presence of 6 equiv. of other metal ions, as indicated in Fig. 4. There was no interference for detection of Cu^{2+} in the presence of Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+} and Al^{3+}. Thus, receptor (3) could be used as a selective colorimetric sensor for Cu^{2+} in the presence of most competing metal ions.

The linear relationship confirm between absorption with addition of Cu^{2+}; graph plotted A385vs [Cu^{2+}] (Fig.5).

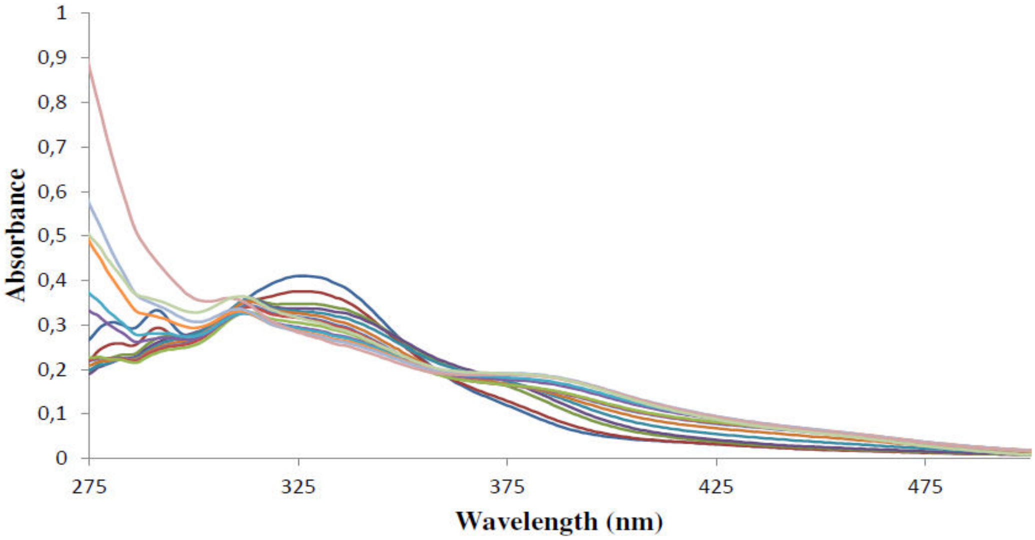


Fig. 2: Change in absorption of (3) upon gradually addition of Cu^{2+}.

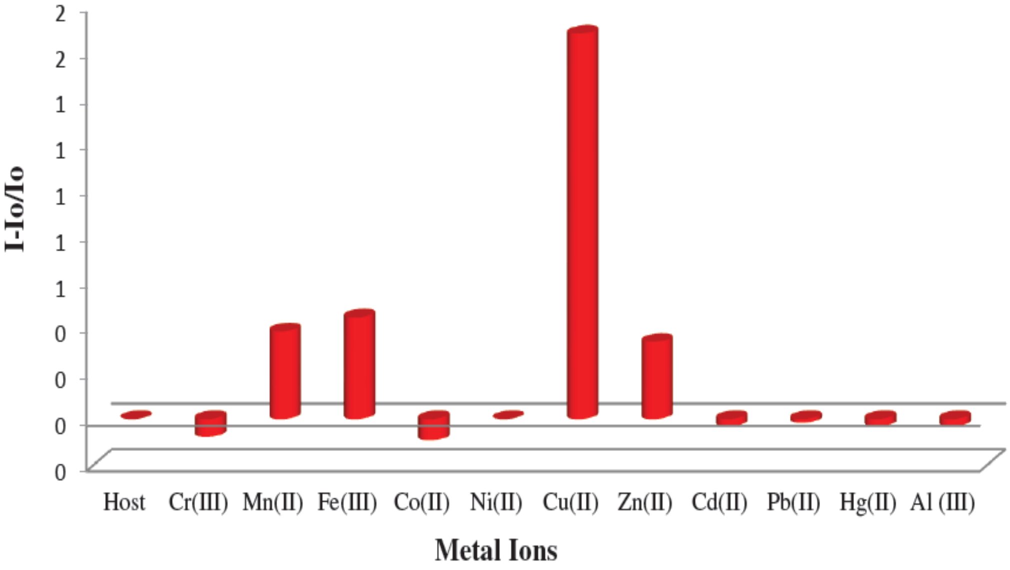


Fig. 3: Absorption ratiometric of (3) on addition of different metals CH_3OH/H_2O (80:20, v/v).

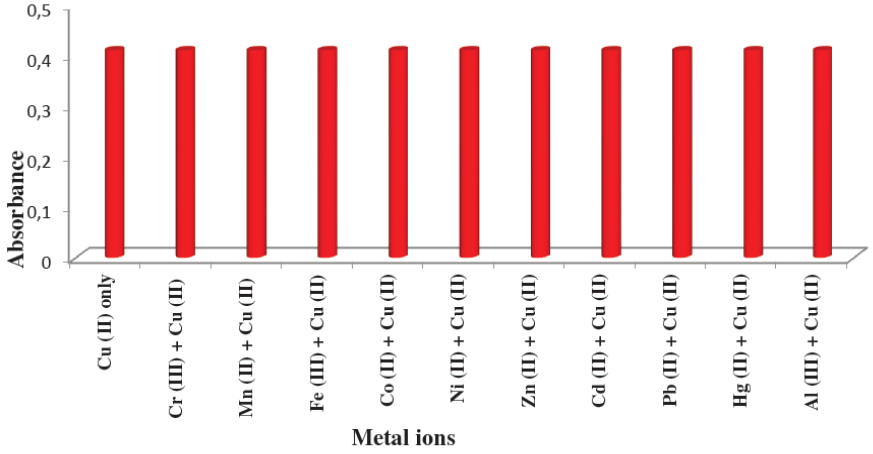


Fig. 4: Interference study graph

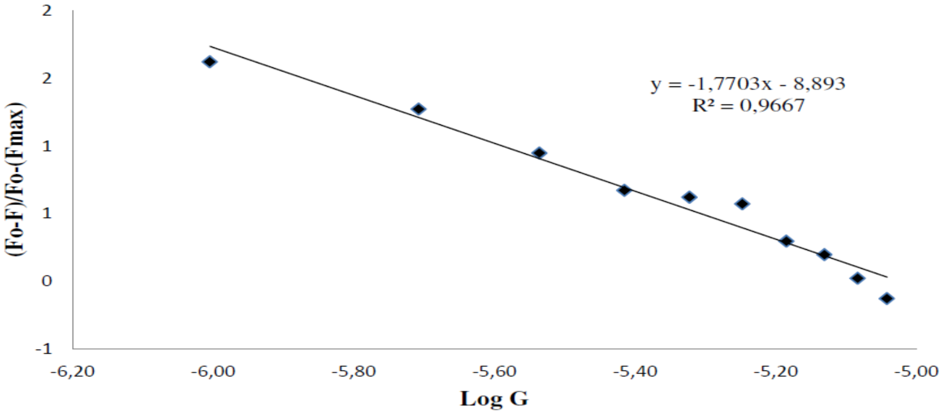


Fig. 5: The linear relationship dependence shown by graph between A385 and [Cu^{2+}] with regression 0.9667.

3.1. Binding constant and Stoichiometry of receptor (3) with Cu^{2+}

On the basis of Benesi-Hildebrand plot [26] (Eq.1) methodology, association constant (Ka) was calculated by following equation.

$$1/(F-F0) = 1/(F\infty - F0)\, Ka[G] + 1/(F\infty - F0) \qquad \text{(Eq.1)}$$

Based on UV-Vis titration, the association constant (Ka) of (**3**) with the Cu^{2+} ion was calculated using the Benesi–Hildebrand equation. The Ka value turned out to be $2.3 \times 10^5\ M^{-1}$, which is within the values (10^4–10^5) previously reported for Cu^{2+}-binding chemosensors (Fig. 6).

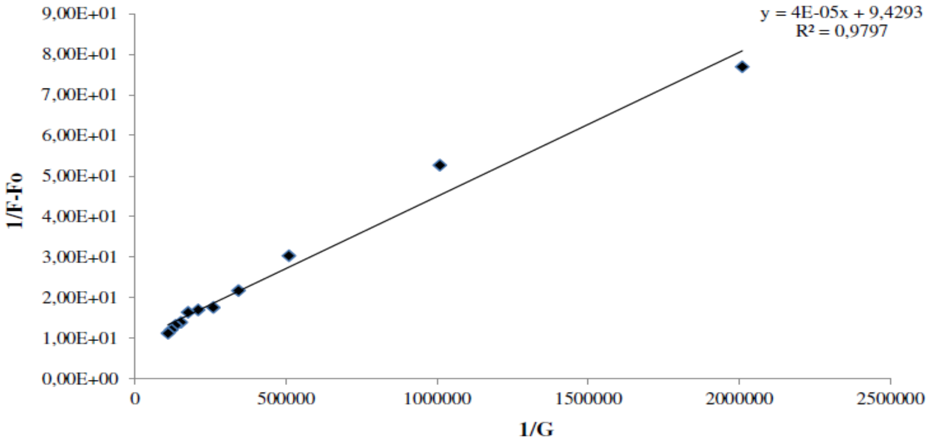


Fig.6:- Benesi-Hildebrand Plot receptor (3) where R^2=0.9797 and the Ka value at $235725 M^{-1}$

The Job's continuous variation method was used to determine the binding stoichiometry between (3) and Cu^{2+} [27]. The results indicate the formation of Host-Guest (receptor - Cu^{2+}) complexes in 1:1 binding stoichiometry (Fig. 7).

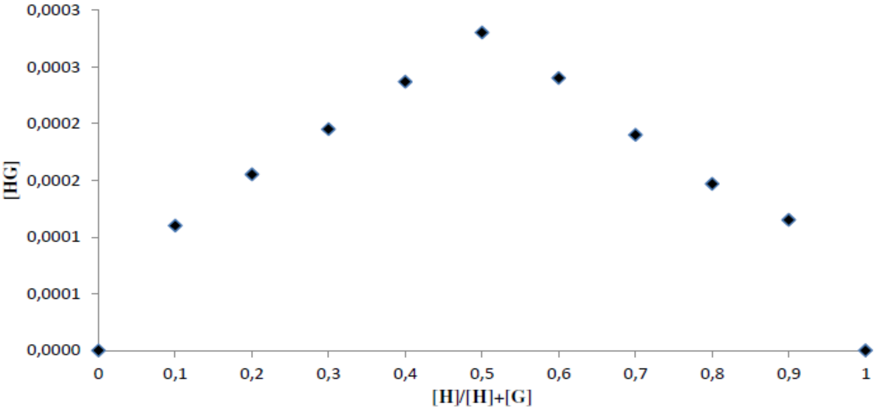


Fig. 7: Continuous Variation Plot (Job plot) for the 1:1 Stoichiometry of the host guest relationship.

3.2. Colorimetrically naked eye detection and Detection limit

The significant aspect of this study is naked eye detection upon addition of Cu^{2+} it gives ON-SITE detection of Cu^{2+} in real environment **(Fig. 8)**. The receptor (3) ($C=1\times10^{-5}$ M) is yellow colour in CH_3OH/H_20 (80:20,v/v) and addition of eq. of Cu^{2+} result into green coloured solution. The **Fig. 9** shows the sensitivity of visuals colour changes on the addition of small amount of Cu^{2+} such as 5, 10, 20 and 40 ppm respectively. When the Cu^{2+} ion concentration was increased, the color of the receptor (3) solution changed from yellow to orange and then wine red and it easily differentiable by naked eyes. The LOD found to be 183nM from 10 blank solutions. The discovery furthest reaches of receptor (**3)** as a colorimetric sensor for the examination of Cu^{2+} particles was observed to be 183nM. The U.S. Natural Protection Agency (EPA) has set the sheltered furthest reaches of copper in drinking water at 2.0×10^{-5} M. Henceforth with its much lower identification confine for Cu^{2+} particles, receptor (**3)** could be an effective for the recognition of copper ions in drinking water.

Fig. 8: The colorimetric colour change of ligand and ligand+Cu^{2+} ion.

Fig. 9: The colorimetric colour change of ligand on addition of Cu^{2+} ion (first one from left side only ligand and 5, 10, 20 and 40 ppm Cu^{2+} with ligand)

3.3. Proposed binding mechanisms of receptor (3)

The (3) is planer highly conjugated π electron systems **Fig.10**. Addition of Cu^{2+} ion in (3) was distinctly absorbance and shifting due to the paramagnetic nature of Cu^{2+} ion. The planarity of the receptor prevents the co-ordination of Cu^{2+} ions to phenolic oxygen atom of two aromatic moieties in (3). One of the aromatic moiety will move perpendicular to another by rotation around C=N bond facilitating the bonding of Cu^{2+} ion. Thus, the (3) sensed Cu^{2+} ions based on PET mechanism. The Cu^{2+} ion coordinates to 3 through two phenolate oxygen atoms and two nitrogen atoms of imines.

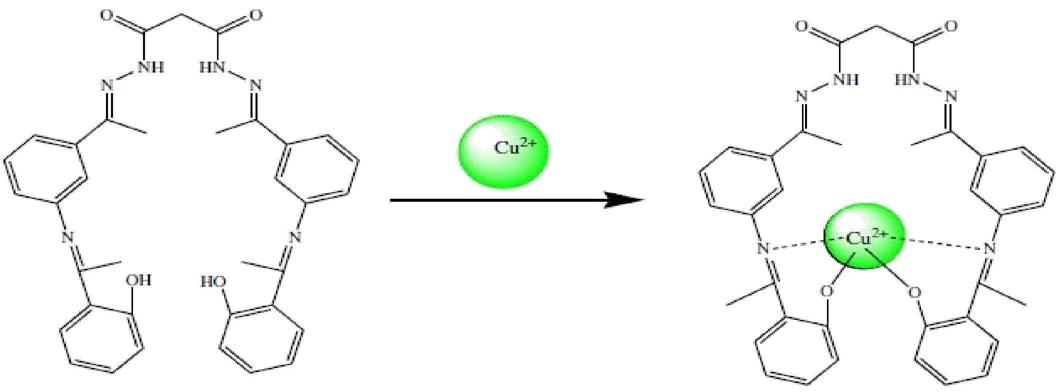


Fig. 10: Proposed mechanism

4. APPLICATION ON REAL LIFE SAMPLE

In order to see its real-life application, we plan the Cu^{2+} recovery experiment. We utilized our recently outlined sensors for the onsite location identification of Cu^{2+} particle in genuine water samples. All the samples are spiked with Cu^{2+} at 10 to 25 μg/L were analyzed by (**3**) (**Table 1**). The results show that the (**3**) is able to detect Cu^{2+} with high recovery with no impedance from other ecologically pertinent aggressive metal particles [32].

Table 1 Recovery of Cu^{2+} with receptor (3)

Source	Cu^{2+} added (μg/L)	Cu^{2+} found (μg/L)
Mineral water	10	9.65 ± 0.059
	15	14.71 ± 0.078
	25	24.83 ± 0.062
Well water	10	9.89 ± 0.082
	15	14.74 ± 0.058
	25	24.62 ± 0.052

5. CONCLUSIONS

In conclusion, receptor (3) has been designed and it behaves as a Cu^{+2} ion selective chemosensor through LMCT processes in CH_3OH/H_2O (80:20, v/v) solvent system. The processes have been supported by the spectrophotometrically, Stoichiometry and proposed mechanism. This probe is also useful in detecting Cui^{2+} ions in presence of other survey metals ions. The K_a of (**3**) with Cu^{2+} ions was found at 2.3×10^5 M^{-1} and 1:1 complexation is determined by the jobs continuous variation method. The Cu^{2+} ion-selective colorimetric probe is superior to the previously reported colorimetric probes in terms of detection limit, with LOD (183 nM).

6. REFERENCES

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