

# Selective Detection of Cu (II) ions in Neat Aqueous Solution – An Innovative Fluorescent Chemosensor

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**Abstract:-** Ion sensors particularly organic fluorescent chemo sensors are very much researched in recent times for detection of metal ions in food and especially water more so in the third world countries. Their significance lies in the ease of use, solubility in aqueous medium, and comparatively cheaper alternative to sophisticated techniques such as AAS, ICP-AES or ICP-MS. Cu (II) ions play a vital role in the physiological system of living organisms and is required to be present within a specified range so as to avoid complications by either being deficient or abundant than the specified limit by WHO. This paper reports the synthesis of a novel water-soluble fluorescent Schiff base as a chemoselective metal ion detector for Cu (II) ions. It displays favorable quenching of fluorescence for Cu (II) ions from amongst a wide range of other metal ions which are commonly present in food and drinking water. The sensor has a detection limit of 1.44  $\mu$ M which is much less than the permissible limit of 31.4  $\mu$ M for Cu (II) ions as specified by WHO. The novel chemo sensor thus synthesized provides rapid, selective and a highly sensitive response to Cu (II) ions which provides the scope of this chemo sensor in being developed further into becoming the sensor of choice for the determination of Cu (II) ions in water samples.

**Keyword:-** Schiff base; Fluorescence; Copper (II) ions; Chemo sensor.

## I. INTRODUCTION

Ion sensors are widely employed in many diverse fields such as chemical toxicology, environmental chemistry, bioinorganic chemistry, bioremediation and waste management and many more. For all such studies, innovative, effective and most importantly selective, organic fluorescence-based sensors have become the need of the hour as real time response system. However, the primary challenge remains the solubility of such sensors in the aqueous phase. Although sophisticated analytical techniques [1] such as the AAS, ICP-AES, ICP-MS, Spectrophotometry, Anodic Stripping Voltammetry are available which counter the limitation of poor solubility of chemo-sensors, they do not acquire the status of being the unequivocal choice for such detection studies in that they are quite expensive, necessitating precise and complex SOP instrument design, and having labor-intensive protocols. All of these factors make them economically unviable for conducting assays in the context of scarce resources and onsite detection [2]. These challenges can however be overcome if it is possible to design an effective fluorescence-based hydrophilic organic sensor.

Copper plays an important role in a variety of fundamental physiological processes in living organisms from bacteria to mammals [3]. Deficiency of copper in the human body can cause anaemia [4] while increased levels can lead to gastrointestinal disturbance, and damages to liver or kidney [5]. The permissible amount of copper ions in drinking water as specified by WHO is  $\leq 31.4 \mu$ M [6]. This necessitates the monitoring of the Cu(II) ion in water and food content [7]. Schiff bases (SB) function as ion carriers in polymeric membranes. The structure of Schiff bases provides appropriate geometric cavity [8] for effective control of host-guest complexation, modulation of lipophilicity, thereby ensuring astounding stability, selectivity and sensitivity for a specific ion [9]. Schiff bases with additional N and O as donor atoms are well known to form strong coordination complexes with transition metal ions [10]. Schiff bases are utilized as fluorescent turn-on/turn-off and colorimetric chemo sensors for the detection of various metal cations such as  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Al}^{3+}$ . In recent times, these complexes have drawn immense attention owing to their intrinsic property as organic fluorescence-based sensors for metal ion monitoring [11].

This paper reports a novel fluorescent Schiff base chemo sensor N, N'-bis(5-sulfosalicyliden)-1,2-phenyldiamine which exhibits effective quenching of fluorescence through selective interaction with the Cu (II) ion.

## II. MATERIALS & METHODS

Chemicals and reagents were purchased from S. D. Fine Chem. (Mumbai, India) and Sigma Aldrich (USA). All reactions were monitored with TLC using Merck silica gel 60 F254. Melting points were recorded on an Analab melting point apparatus. UV-visible absorption spectra were recorded with Labman spectrophotometer. Fluorescence spectra were recorded with a Shimadzu RF6000 spectrophotometer, and the excitation wavelength was 330 nm for all measurements. IR spectra were done on Perkin Elmer, Frontier equipment with a diamond tip. Elemental analysis was performed on model EA300, Euro Vector.

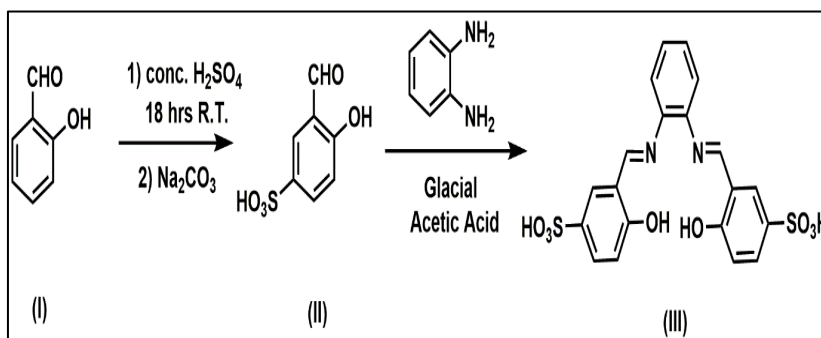
## III. EXPERIMENTAL

The chemo sensor (III) was synthesized as shown in **Scheme 1**. Salicylaldehyde (I) was stirred with concentrated  $\text{H}_2\text{SO}_4$  in an ice bath for 18 hours. The mixture was quenched with water prior to neutralization with  $\text{Na}_2\text{CO}_3$ . The product obtained (II) was purified by recrystallization with water. The protocol for the synthesis of (II) was as reported in literature [12]. The above sulphonated salicylaldehyde (II) was coupled with benzene-

1,2-diamine using glacial acetic acid as catalyst to obtain the chemo sensor (III) as a yellow solid. Recrystallization with

water provided the pure compound as the organic fluorescent chemo sensor.

Colour = Yellow; Yield = 63.58 %; Melting point: >250 °C



Scheme 1: Systematic representation of the synthesis of Chemo sensor (III)

#### IV. RESULTS AND DISCUSSION

**Spectral Analysis of 3,3'-((1E,1'E)-(1,2-phenylenebis(azaneylylidene))bis(methan-eylylidene))bis(4-hydroxybenzenesulfonic acid) (III)**

**IR**( $\nu_{\max}$  / $\text{cm}^{-1}$ ): 3372 (-OH stretch.), 1645(>C=N stretch.), 1470 (>C=C stretch.), 1159 ( $\text{SO}_3^-$ )

**Elemental analysis:**  $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_8\text{S}_2$

Elements	C	H	N
Calculated	50.42	3.38	5.88
Found	50.36	3.42	5.46

##### A. Selectivity studies

The fluorescence spectrum of the sensor (III) in the presence of nine different metal ions with varied atomic weights was observed ( $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Fe}^{2+}$ ), the results being presented in **Figure 1**[13]. The selectivity experiments of (III) with various metal ions have been investigated by fluorescence emission spectrum, **Figure 2**. 100  $\mu\text{M}$  of Sensor (III) in 1 mM Tris-buffer (pH 7) was treated with 1000  $\mu\text{M}$  solution of different

metal ion in 1 mM Tris-buffer (pH7) [14]. The sensor(III) exhibited a high level of selectivity towards  $\text{Cu}^{2+}$  ion and effective quenching of fluorescence at 430 nm was noted [15].

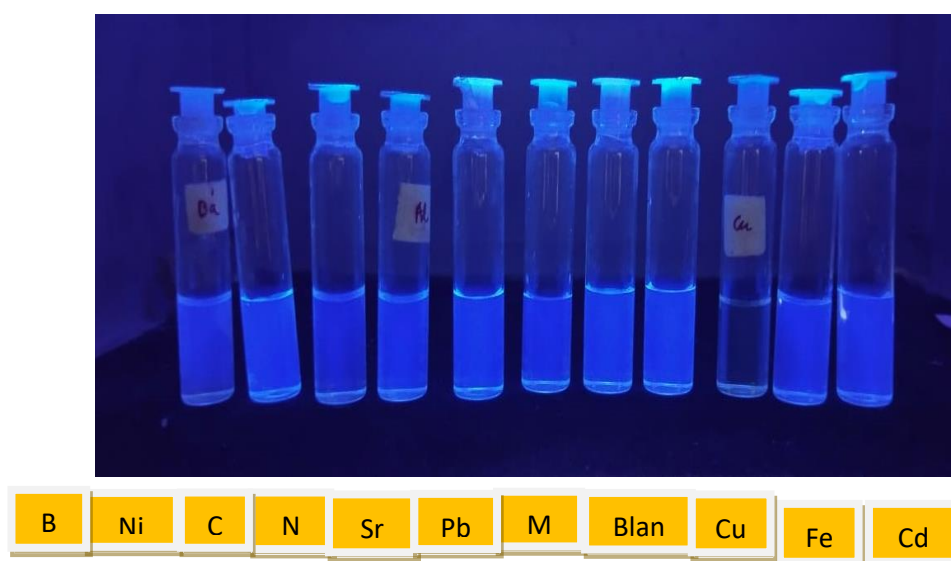


Fig 1: Comparative fluorescence of metals with Sensor (III)

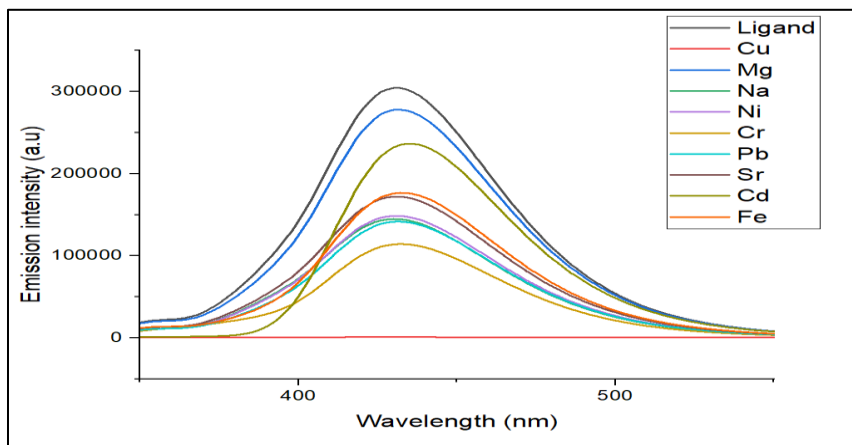


Fig. 2: Selectivity in fluorescence response of III towards Metal ions

### B. Sensitivity studies

Sensitivity investigation of Sensor(III) was done using varying concentrations of  $\text{Cu}^{2+}$  ions. An increase in the concentration of  $\text{Cu}^{2+}$  ions showed a steady decrease in the fluorescence intensity. An aqueous solution of sensor(III) at a concentration of  $25 \mu\text{M}$  in a  $1 \text{ mM}$  Tris-buffer ( $\text{pH } 7$ ) exhibits a linear reduction in intensity over a concentration

range of  $10 \mu\text{L}$  to  $140 \mu\text{L}$  of  $\text{Cu}^{2+}$  ions, **Figure 3**. The fluorescence emission intensity was sensitive and proportionately decreased with increasing concentration of  $\text{Cu}^{2+}$  [16].

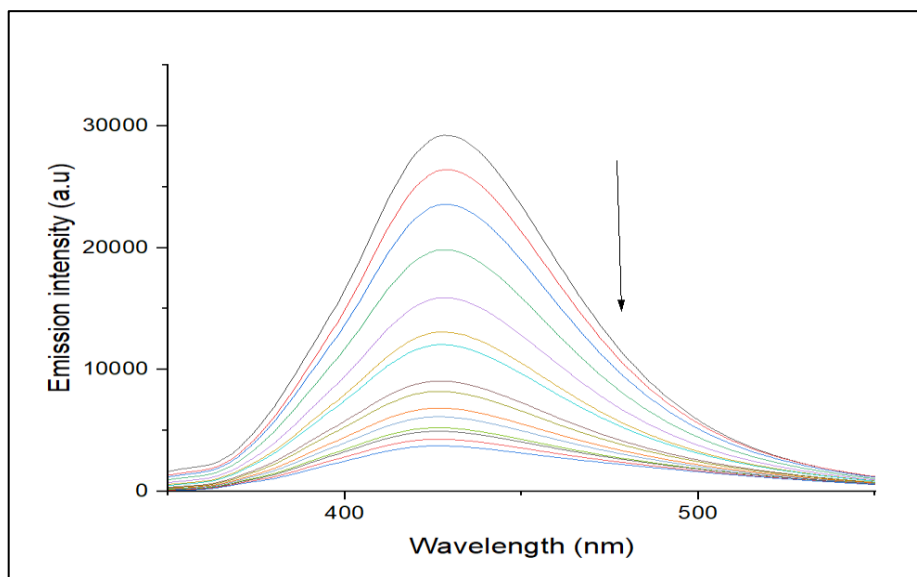


Fig 3: Fluorescence emission spectra of sensor (III) in increasing concentrations of  $\text{Cu}^{2+}$  ions

### C. Job's plot measurement

The Job's Plot measurement was undertaken to determine the coordination ratio of the sensor (III) with  $\text{Cu}^{2+}$  ions in tris buffer solution ( $\text{pH } 7$ ). Keeping the total concentration of the sensor (III) and  $\text{Cu}^{2+}$  ions at a constant, the ratio of the individual concentrations of  $\text{Cu}^{2+}$  ions and

the sensor (III) was varied to 0:10, 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1, and 10:0. Fluorescence intensity was measured at  $390 \text{ nm}$  for each of these concentration ratios, and a graph plotted as the ratio of  $[\text{salt}]/\{[\text{salt}] + [\text{ligand}]\}$  as shown in **Figure 4**.

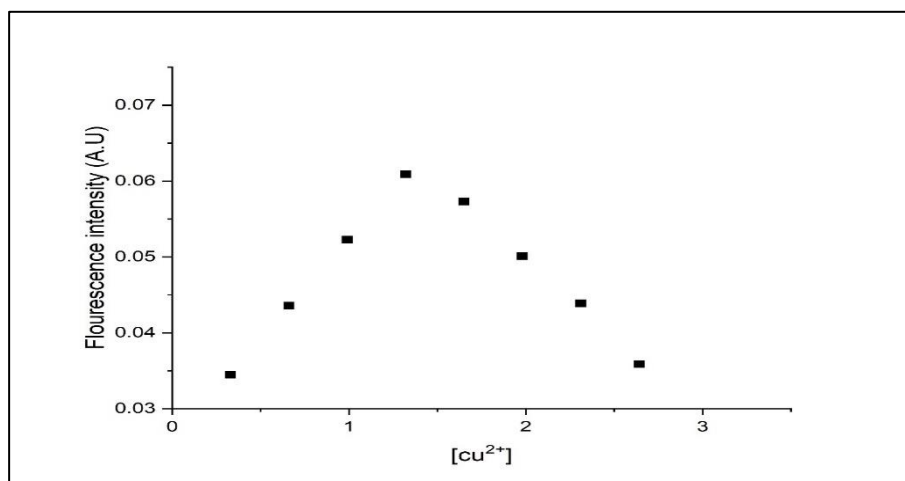
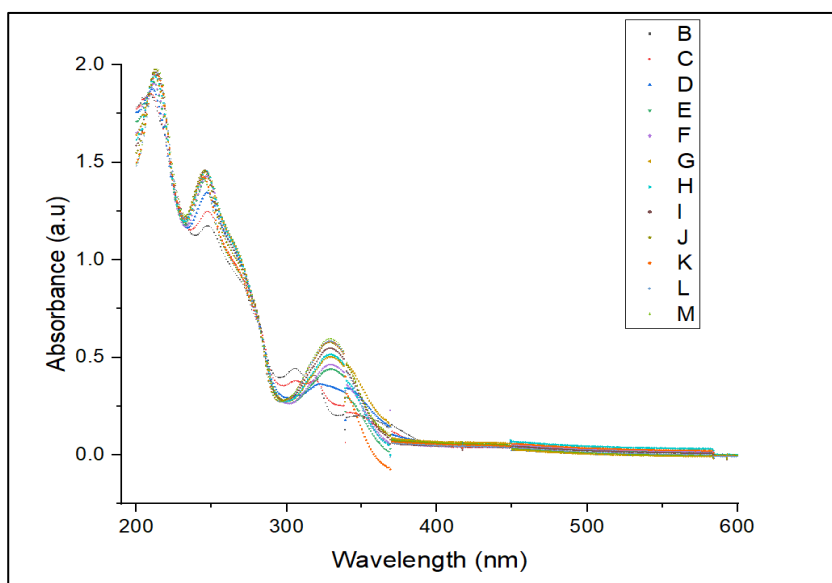


Fig. 4: Job's plot measurement

#### D. UV- vis spectrophotometer study

UV absorption spectra of sensor (III) with different concentrations of Cu<sup>2+</sup> ions were also studied. The UV-visible spectrum had peaks at 330 nm and 235 nm, and an isosbestic point at 320 nm, **Figure 5**. The sensor (III) and the metal ions both equally absorbed light at these specified wavelengths, leading to the isosbestic point. The distinct isosbestic point indicates that the sensor (III) and Cu<sup>2+</sup> ions

coordinate to form a single component. A distinct isosbestic point is observed at 320 nm, indicating that coordination of the sensor (III) with Cu<sup>2+</sup> ions produce a single component.

Fig 5: U.V. absorption spectra of sensor (III) and Cu<sup>2+</sup> ions in incremental concentrations

#### E. Linearity and Limit of detection

The limit of linearity was determined by 10Q/S. The limit of linearity was calculated (ICH guidelines) to be 4.81 μM. LOD was calculated using the formula 3Q/S, where Q is the standard deviation of the blank and S is the slope of the linear plot. The slope of the linear plot was found to be 1.808 for sensor (III). With the slope of the regression line

and the standard deviation of the blank, the limit of detection was calculated (ICH guidelines) to be 1.44 μM ( $R^2 = 0.978$ ) for (III) which is far less than the detection limit of 31.4 μM of WHO. The linear Stern–Volmer plot, **Figure 6**, is generally indicative of a single class of fluorophores that are all equally accessible to the quencher.

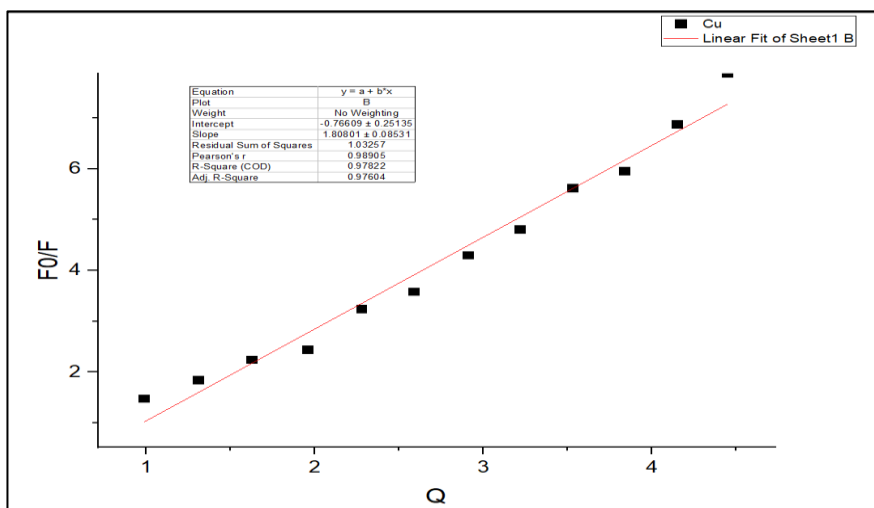


Fig. 6: A Stern– Volmer plot of the fluorescence quenching of Cu<sup>2+</sup> ions

## V. PROPOSED MECHANISM OF ACTION OF SENSOR (III)

The (sensor (III) + Cu<sup>2+</sup>ion) fluorescence quenching response is possibly the result of opening of a nonradiative deactivation channel by the fluorophore thereby facilitating the transport of electron or energy. The fluorescence of Cu (II) ion was completely quenched which can be due to a metal–ligand charge transfer (MLCT) mechanism. The paramagnetism induced by the formation of the complex ((III) + Cu<sup>2+</sup>ion) probably induces a rapid occurrence of the MLCT. The Cu<sup>2+</sup> ion having a substantially stronger paramagnetic quenching ability adequately covers additional possible mechanisms. Similarly, for the lighted new complex ((III) + Cu<sup>2+</sup> ion), the paramagnetic quenching property of Cu<sup>2+</sup>ion played a leading role. This resulted in a completely quenched fluorescence by the ((III) + Cu<sup>2+</sup>), or a switch “OFF” [17].

## VI. CONCLUSION

This paper reports the synthesis of (III) as an innovative and effective highly hydrophilic fluorescence quencher. Studies have found it to be an efficient organic fluorescence-based sensor for Cu<sup>2+</sup> ion. The sensor shows a high selectivity and quick response for Cu<sup>2+</sup>ion over other common metal ions present in drinking water. The developed sensor can be applied successfully for the determination of copper ions in water and tea samples. The value of LOD and LOL obtained, 1.44 μM and 4.81 μM respectively, is far less than the WHO specified detection limit of 31.4 μM. A stoichiometric ratio of 1:1 was obtained by Job's plot using the continuous method of variation. This method developed hence serves as an inexpensive and quick technique for the determination of Copper (II) ions. The simple molecular design of the reported sensor can serve as the lead to contribute towards the further development of other more efficient and useful fluorescent probes for the detection of Cu<sup>2+</sup> ions.

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