Exploring the Role of Anthraquinone-based Colorimetric Dye for the Detection of Copper Ions in Two Different Solvents

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Abstract: *(E)-1-amino-2-((3-hydroxy-4-methoxybenzylidene)amino) anthracene-9,10-dione (L) was synthesized upon condensation of a mixture of 1,2 diamino anthraquinone and ortho-vaniline in 1:1 stoichiometric ratio under reflux in anhydrous ethanol. The spectroscopic studies such as FTIR, ^1H NMR, and ^{13}C NMR of compound* ***L*** *confirmed its formation. Naked-eye sensing studies of compound* ***L*** *was performed in the presence of appreciable numbers of metal ions considering alkali & alkaline metals, transition metals, etc. In the presence of Cu^{2+}or Ni^{2+} or Co^{2+} ions there was a prominent color change of DMF solution of* ***L*** *from yellow to brown, but in methanol, the color changes were only observed solely in Cu^{2+} ions. The UV-Vis spectra of compound* ***L*** *in methanol showed a bathochromic shift of absorption maxima of 150 nm in the presence of Cu^{+2} ions in association with other metal ions concluding no interference of other metal ions. Qualitative and quantitative analysis of* ***L*** *affirmed selectivity towards Cu^{2+} ions in methanol. Job's plot determined the stochiometric complex between L and Cu^{2+} ions. The binding constant of the complex* ***L****-Cu^{2+} was calculated using a linear regression method. Moreover, this probe L can be used as an infield naked-eye detection for contamination of Cu^{2+} ions in water.*

1. Introduction

The existence of metal ions like Na^+, K^+ Ca^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Pb^{2+}, Hg^{2+}, Cd^{2+}, Al^{+3}, Fe^{2+}, Co^{2+}, Ag^{2+}, $Ni^{2+,}$ Mg^{2+} which are naturally distributed in both biological and geological system some of them play a vital role in our biological system (permissible limit). Still, some metals like Pb^+, Cd^{2+}, Hg^{2+} are known for their toxicity. The factors influencing the toxicity of metals depend upon the interaction of toxic metals with essential metals, formation of metal-protein complexes, age, and stage of development, lifestyle factors, chemical form of speciation, and immune status of the host[1].

Cu^{2+} ions being a third most abundant metal almost around 100mg is present in the human body. The daily intake of copper (II) ion in a human body is about few milligrams. It plays an important role in various biological systems, being involved in multiple physiological processes, enzyme functioning, and antioxidants. A tiny amount of cobalt (II) ions is found in human body as a source of vitamin B12. The amount of its intake per day for the human body is about µg. About 2mg of cobalt is said to be present in the human body [1], [2]. Nickel plays a vital role in enzymes, metabolism, bone strength, iron absorption, hormones, etc, [2]. Naturally occurring phenomena like volcanic activity, weathering of rocks, etc causes transportation of metals to our various ecosystems like lithosphere, hydrosphere, and atmosphere but above all, manmade creation plays a major role in this disposition of pollutants in our ecosystem[3]. The excessive ingestion of Cu^{2+} leads to Menkes (copper deficiency) vomiting, nausea, prion disorder, and cancer. Co^{2+} and Ni^{2+} are also known for their toxicity, which can interfere with DNA repair and cellular metabolism, abdominal pain, and lung infection. The presence of these metals in our environment is hard to detect with our naked eyes. Several methods like absorption spectroscopy, electrochemical sensing, etc are used to detect these metals[4]. Still, all these methods are expensive, time-consuming, or need sophisticated instruments.

Chemosensors, abiotic origin plays a vital role in physiology, biology, pharmacology, and environmental science including detecting these pollutant metals. A chemosensor transduce a binding process into a signalling event which can easily be read out by naked eye with color change of probe **L** or fluorescence or electrochemical change. The chemosensor consists of both signalling unit and binding sites which may be chromophores or fluorophores which act as hosts and analytes get bound to it called guest[5]. Guest may be a cationic species like Na^+, K^+ Ca^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Hg^{2+}, Cd^{2+}, Al^{2+} etc anionic species like CN^-, F^-, Cl^-, Br^-, $I^-$and neutral molecules like benzene, urea, methanol, toluene. The binding of this guest molecules depends upon the design of the host molecules. Chemosensor may be specific to the guest molecules. A fluorophore is a compound that incorporates the binding sites through which the chemical signal is generated, which may be due to photophysical change, redox reaction, acid-base interaction, or charge transfer. The fluorescent chemosensor is achieved by various photophysical mechanisms including intra-molecular charge transfer ICT), aggregation-induced emission (AIE), photoinduced electron transfer (PET), and chelation-induced enhanced fluorescence (CHEF). [6] The positively charged receptors like guanidinium groups, quaternary ammonium, and isothiouronium groups are used for detecting the anions which does not depend on the pH of the medium. Especially on an aqueous medium variety of polyamines in different shapes like open chain, branched chain, cyclic chain, etc are used for anion receptors.[7]

A chemosensor may occur reversibly or irreversibly. Reversibility has a high advantage over irreversibility because of its reusability, dynamic monitoring and quantitative analysis. Although irreversibility has high sensitivity and selectivity but it lacks real time monitoring and single use nature.[8] To achieve high luminescence for chemosensor some photophysical property with high molar absorption coefficient and high luminescensce quantum yield is preferred .[9]

With a variety of metal ions Cu^{2+}, Co^{2+}, and Ni^{2+} play an important role in fulfilling human needs. Among these Cu^{2+} plays a vital role in catalysis, cofactor, cytochrome, tyrosine, etc but it is also known to have toxicity if ingestion or deposition of Cu^{2+} in higher concentrations in our body.[10]

The development of cost effective, ease manipulation and wide applicability of organic molecules plays an important role in the detection of a target molecules such that we have also designed and synthesis Anthraquinone-based chemosensor that can detect trace amounts of Co^{2+}, Co^{2+}, Ni^{2+} in the presence of DMF as a solvent, however in the presence of methanol we can selectively detect the presence of Cu^{2+}.[11]

2. Experimental

2.1 Materials and Instruments

1,2 Diamino anthraquinone (94.34%) and orthovaniline (95%) were purchased from BLD pharm (India) private limited other chemicals like metal salts which were used during sensing studies were locally available. The stock solution of Cu^{2+} was prepared from all the available Copper nitrate, Copper acetate and Copper chloride which was prepared by dissolving the metal salts in distilled water (10^{-2} M). Shimadzu ATR-FTIR was used for obtaining FTIR data, and UV-vis spectra were obtained from Shimadzu UV (UV-1800) having a path length of 10mm of quartz cuvettes. Theoretical analysis was done with the help of Gaussian software. Water samples were collected from Teesta River, which flows through Indian state of Sikkim and West Bengal, Hots Spring water were collected from Ralong Hot Spring situated near Ravangla, South Sikkim.

2.2 Design and synthesis of probe molecules

Firstly, we designed a chemosensor that can bind ions like Cu^{2+}, $Ni^{2+}$and Co^{2+}. In this paper, we have chosen anthraquinone based molecule because of its highly delocalized л -electrons resulting strong absorbance in longer wavelength in UV-vis region. Ortho Vaniline, which acts as a binding site because of its functional group like the hydroxy group in ortho positions which can coordinate with metal ions with the help of hydroxy group in addition in the presence of methoxy group at the meta position which can donate an electron density on the aromatic ring which can enhance the chelating ability. Then we synthesis anthraquinone based chemosensor with a single one-step reaction where 1,2 -diamino anthracene-9,10-dione which was reacted with orthovaniline (1:1) in a refluxed condition where the choice of solvent was Methanol which is less hazardous. The reaction was continuously monitored with the help of the TLC after the confirmation of the complete reaction it was observed it took almost take 6 hours for the completion of the reaction. After the purification of probe molecules, the desired yield was found to be around 80 % and it was characterized by FTIR, and NMR which confirmed the formation of a probe

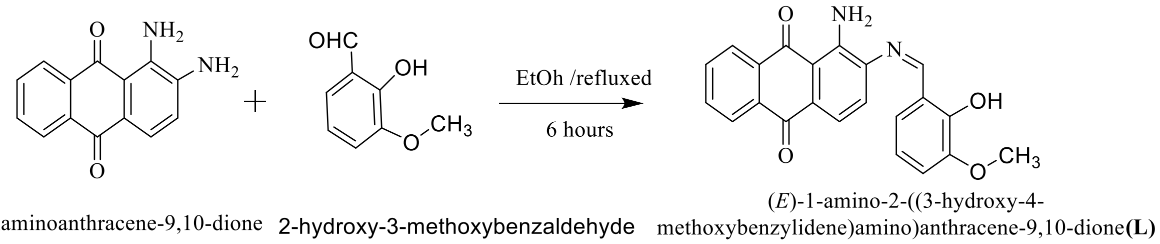


Fig.1. Synthetic scheme of a proposed molecule L

1,2 -diamino anthracene-9,10-dione 100mg taken in a 25ml round bottom flask which was made soluble with the help of anhydrous ethanol (6ml) after that we added 3-hydroxy-4-methoxy benzaldehyde 58 mg. The choice of solvent for the reflux was selected in such a way that it can easily soluble both the reactants. The reaction was continuously monitored with the help of TLC on the completion of the reaction it was cooled. The desired precipitate was obtained by adding pet-ether in the obtained ethanol mixture which was filtered and purified.

3. Results and discussion

3.1 Selection of Organic Solvents

Firstly, we studied the Uv-vis of probe L with the number of different solvents, where it was observed that probe L shows two absorption bands around 300 nm Which is mainly due to spin forbidden transition (n to л*) transitions and around 400 nm is due to the inter-molecular charge transfer.[12]

3.2 Colorimetric studies of metal ions

Colorimetric Studies were observed in the presence of two different solvents DMF and methanol. In DMF in addition of several different metal ions Cu^{2+}, Co^{2+}, and Ni^{2+} showing the colour change from yellow to dark purple for $Co^{2+}$and Cu^{2+} dark blue for Ni^{2+} indicating that probe L shows high affinity toward these three ions, among rest of the other ions tested. In methanol, only Cu^{2+} shows a noticeable change in color indicating high affinity towards the probe. It may be due to a difference in solvent polarity DMF is polar aprotic i.e. it does not have any hydrogen for donation but in case of methanol polar protic solvent in which hydrogen is still competing with other ions like Cu^{2+}, Ni^{2+}, and Co^{2+} for binding with the proposed molecule. Copper is still known to have higher binding affinity gets bound with both DMF and methanol irrespective of competing hydrogen anions.

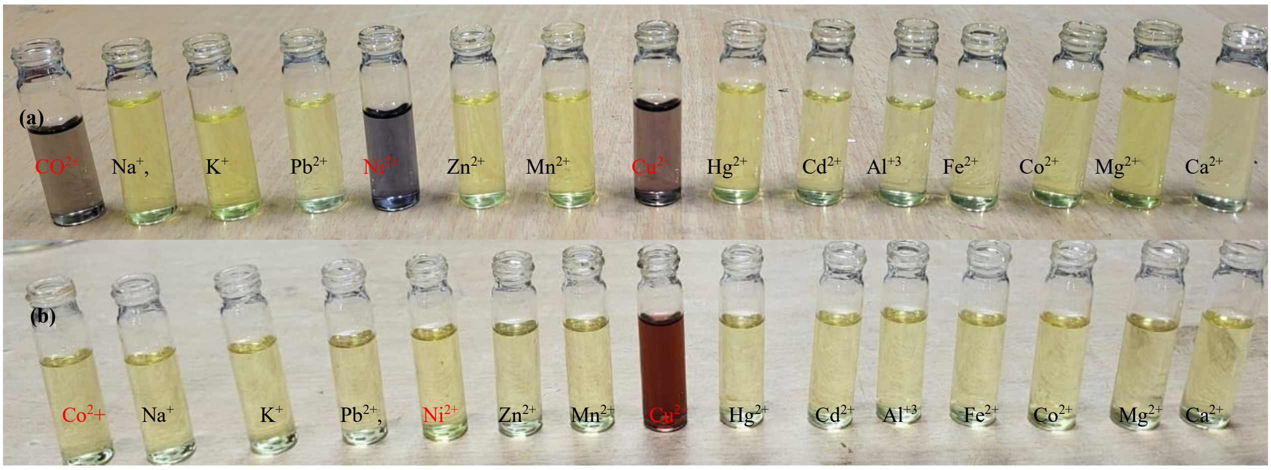
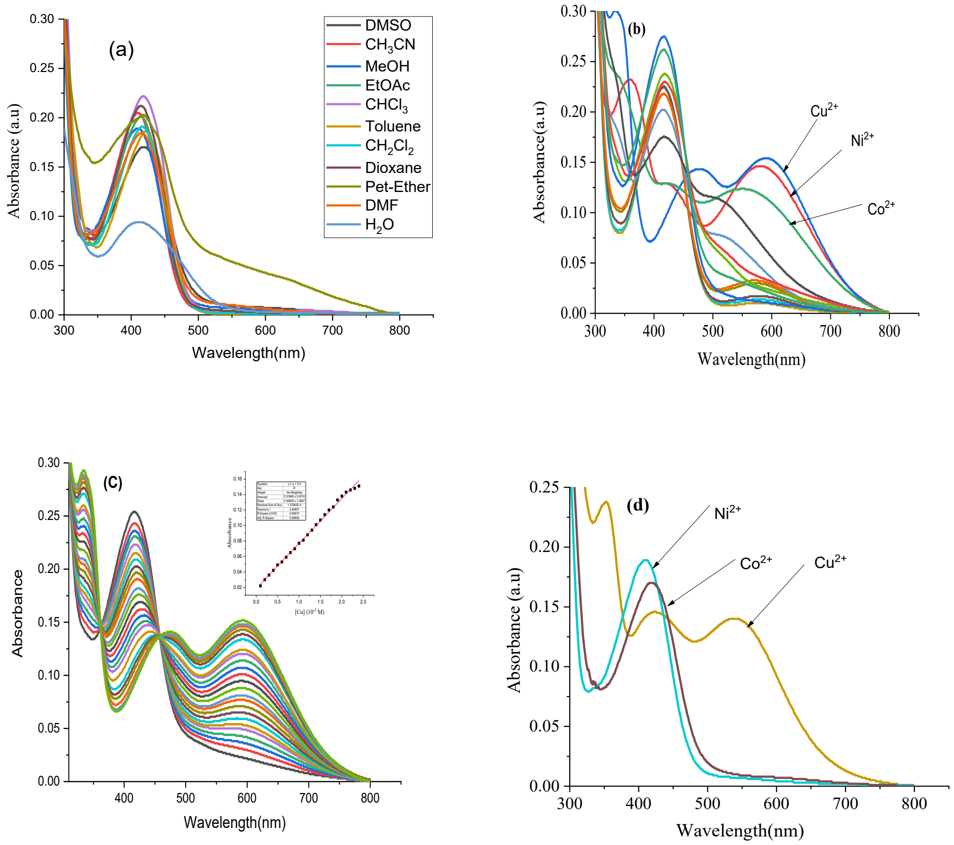


Fig.2. (a) Naked eye detection of metal ions in the presence of DMF as a solvent. (b) Naked eye detection of metal ions in the presence of methanol.

3.3 Electronic Absorption studies of proposed molecules

Molecular interaction was observed in DMF, the studied concentration of a ligand was 10^{-5} M, and the optical response was observed in many metal ions it was found that in Cu^{2+}, Ni^{2+}, Co^{2+} the ligand showed a bathochromic shift from 410 nm to 600 nm. The binding property of Cu^{+2} was studied with linear regression (R^2=0.99) where limit of detection was found to be 1.03 x 10^{-6} mol/L in DMF.

In methanol, Cu^{+2} only showed a bathochromic shift which indicates that solvent plays a crucial role in the field of chemosensors as explained earlier the difference in a polar aprotic and polar protic may have played a crucial role in the detection of metal ions[13]. The binding proportion with the guest molecules was determined by the Jobs Plot 1:1



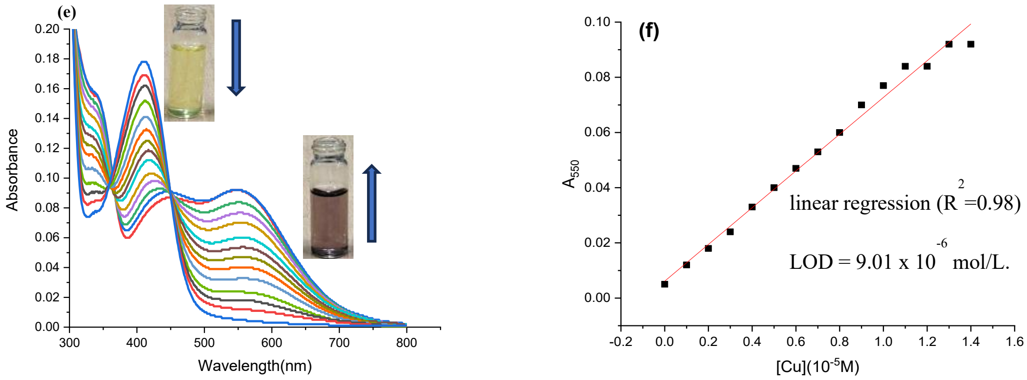


Fig.3. UV-visible spectra of L (10µM) in various organic solvent (a). UV- visible spectra of a probe L in presence of various cations in DMF (b). UV-visible titration of L (10µM) with Cu^{2+} in (0-2.2 equiv) in DMF. UV-visible spectra of probe L in Ni^{2+}, Co^{2+} and Cu^{2+} in Methanol (d). (e) UV-visible titration of probe L (10µM) with Cu^{2+} (0-1.5 equiv) in Methanol. (f)The absorbance at 550 nm as a function of Cu^{+2} ion concentration in Methanol.

3.4. Theoretical rationalization

The arrangement of proposed molecules in three dimensions was determined with the help of DFT (Density functional Theory). The probe L energy was minimized using B3LYP level having a basis set of 6-31G* for C, H and O which helped us to understand molecular stability. The red and green lobes indicate the probability of finding the electrons. HOMO (Highest Occupied Molecular Orbital) shows the localized electrons making the potential sites for electron donation and nucleophilic reaction. The delocalized LOMO (Lowest Occupied molecular orbitals) shows the charge transfer property.

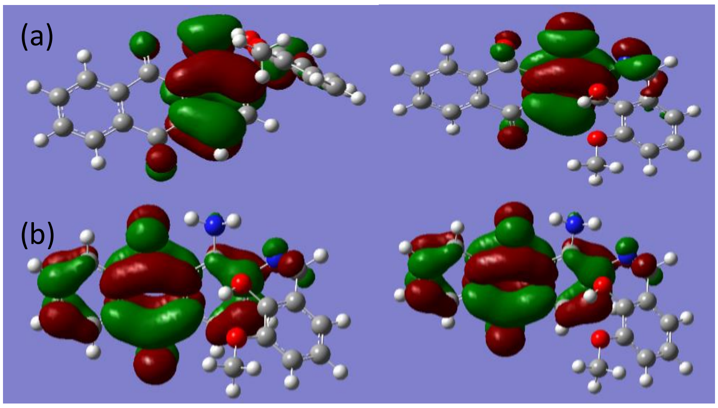


Fig.4. HOMO analysis of a probe L using B3LYP level of theory (a). LUMO analysis of a probe L using B3LYP level of theory (b).

3.5. Real-time analysis of sample water

We prepared a sample containing a methanol mixture for detecting Cu^{2+}in the water sample. Sample water was collected from various sources like tap water, river water, and hot spring water then it was tested with a prepared sample, observing no changes in tap water and river water but we observed a color change in hot spring water, indicating the presence of copper. We also prepared a paper strip simply by dipping it into the sample, which was dried and used for analysis. The result observed was found to be the same.

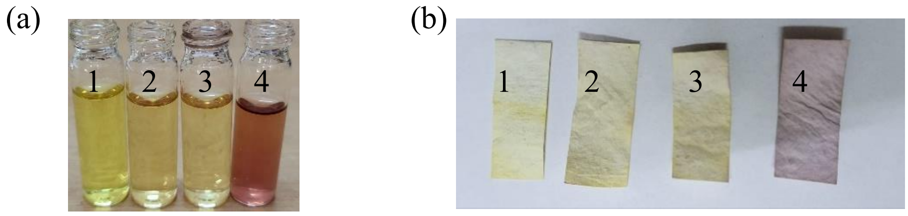


Fig.5. Colorimetric analysis of different source of water in presence of (a) (1) distilled water, (2) Tap water, (3) river water, (4) hots spring water .(b) Paper strip analysis in presence of different source of water in presence of (1) distilled water, (2) Tap water, (3) river water, (4) hots spring water .

4.Conclusion

In summary we have designed and synthesised Anthraquinone based chemosensor with a single one-step reaction with less hazardous solvent and is easily replicable. Photophysical properties are studied in the presence of various cations in DMF and Methanol. In DMF more than one cation can bind with a probe **L** while in the presence of methanol, only one cation Cu^{2+} can bind with the designed probe. Real-time analysis was done in various water samples, and it was able to detect the Cu^{2+} presence in hots spring water, which provides us with the efficiency of the molecules to detect the targeted cation.

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