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Synthesis of Quinoline-based New Organic Chemosensors and its Application in Fluorophoric Detection of Metal-ions in Environmental Samples and Confirmation of Results using Molecular Modelling: A Complete Study

M.S. THAKARE[1], A.K. YADAV[2,*], D. DOMYATI[3], K.K. JOSHI[4], M.S. PATEL[5], V.S. TALISMANOV[6], G.S. SUNDARI[7], V. PRAKASH[8] and S. SEHLANGIA[9,*]

[1]Department of Chemistry, Pratap College Campus (Autonomous), Amalner-425401, India
[2]Department of Civil Engineering, Rajkiya Engineering College, Ambedkar Nagar-224122, India
[3]Department of Chemistry, College of Science, University of Jeddah, P.O. Box 80327, Jeddah 21589, Saudi Arabia
[4]Department of Chemistry, Lovely Professional University, Jalandhar-144001, India
[5]Mohammed Al-Mana College for Medical Sciences, Dammam, Saudi Arabia
[6]Department of Chemistry, Moscow Institute of Physics and Technology, Dolgoprudny, Moscow Region, 141701, Russian Federation
[7]Department of Physics, Koneru Lakshmaiah Education Foundation, Vaddeswaram, Guntur-522502, India
[8]Department of Applied Sciences, Global Group of Institutes, Amritsar-143501, India
[9]School of Basic Sciences, Indian Institute of Technology Mandi, Kamand-175005, India

*Corresponding authors: E-mail: avaneesh@recabn.ac.in; sumanyadav1708@gmail.com

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Quinoline-based two new ligands have been synthesized (**QL1** and **QL2**) by reacting 8-quinoline carboxylic acid with derivatives of L-valine under a condensation reaction. The synthesized ligands were characterized by spectroscopic techniques such as ^{1}H NMR, UV, IR, HRMS and CHNS. The 3D structures of both ligands were optimized for the lowest energy and the HOMO-LUMO orbitals were developed. The photoluminescence analysis of both ligands showed the fluorescence emission wavelengths on 492 and 508 nm, respectively for **QL1** and **QL2**. The substituents on the quinoline ring influence the change in fluorescence emission wavelengths. Synthesized ligands acted as selective fluorescence turn-off chemosensors for Cu^{2+} ions and demonstrated the sensitive detection of Cu^{2+} ions in different water samples at the nanomolar scale. The interaction between metal ion and ligands were also studied by developing DFT structures.

Keywords: Quinoline, L-Valine, Derivatization, Fluorescent probes, Chemosensor, Environmental samples.

INTRODUCTION

In recent years, the growing need for effective and adaptable luminous systems for materials, biological and chemical applications has led to an active research area in developing novel luminescent molecules [1-7]. Among the different chromophores used in creating luminous materials, substituted-quinoline has drawn the most interest because of its distinct coordination and photophysical characteristics [8]. Tris(hydroxyl-8-quinolinato)-aluminium(III), for instance, is one of the most influential metal complexes for OLED applications that have been explored to date. This is due to the exceptional optical and chelating characteristics of quinoline [9].

Quinolines are naturally occurring fused rings aromatic molecules belongs to heterocyclic class. The quinoline and its derivatives have been used vastly in industrial and medicinal applications [2,3,5]. Quinoline derivatives are primarily used in treating bacterial infection, inflammation, cancer, malaria, fungal infection and leishmaniasis. Quinoline derivatives are used to prepare sensors, anti-foaming agents in refineries, dyes, paint, corrosion inhibitors and other petrochemical and chromatographic applications [9-15]. Qulinolines, due to the aromatic system of fused rings, show excellent fluorophores and luminescent properties. Thus, it has gained massive attention in preparing fluorescence and luminescent chemosensors. The chemosensors based on quinolones show great binding capacity with

different analytes due to the presence of the heteroatom (nitrogen atom; act as electro-donor) in the structure and offer highly sensitive detections of analytes in different situations with remarkable sensitivity. Until now, various quinoline-based fluorophoric chemosensors have been developed by derivatizing quinoline at second and eighth positions, for example, styryl substituted 8-hydroxyquinoline derivatives [2,3].

Quinoline-based chemosensors have been used to detect a variety of metal cations in different samples from chemical, environmental, clinical and biological samples, such as zinc, iron, cobalt, copper, calcium, magnesium, *etc.* [3,5] and have been used in other applications such as chromatographic detections [6,13-15]. Among them, copper is the third-most prevalent transition element in the body; copper is crucial for many physiological processes, including the manufacture of haemoglobin, the formation of bones, the synthesis of dopamine, the regulation of nerve activity, the expression of genes and the improvement of protein structure and function [10-12,16]. However, Cu^{2+} is highly hazardous to living things when overloaded. For instance, excessive accumulation in humans results in several illnesses, such as coronary heart disease, metabolic and genetic problems, obesity, diabetes and Wilson's disease [17,18]. Commonly, human blood typically has an average quantity of Cu^{2+} between 15.7 and 23.6 µM [19]. However, Cu^{2+} pollution has skyrocketed globally due to the extensive use of copper in water pipelines, industry, agriculture and household appliances. As a result, quick, practical and trustworthy analytical techniques must be developed to identify copper both qualitatively and quantitatively, especially in biological samples and drinking water. Thus, developing more advanced technologies and methods is required for copper's qualitative and quantitative detection.

Herein, we report the synthesis of two novel quinoline-based ligands (**QL1** and **QL2**) by introducing L-valine into quinoline. Amino acid as a substituent allows electronic fine-tuning and control the overall properties of the ligands by introducing electron withdrawing or donating substituents on the quinoline. The synthesized ligands used to develop fluorophoric chemsensing method for different metal ions from environmental samples. Additional, the computational calculations were performed to optimize HOMO-LUMO and energy gap, stable structure and metal complex. The sensitivity and selectivity toward the copper ion were calculated.

EXPERIMENTAL

8-Quinoline carboxylic acid, L-valine, oxalyl chloride, ethyl bromide and bromomethyl benzene were purchased from Sigma-Aldrich, USA. The river and industrial water samples were collected from local sites. The solvents (dichloromethane, chloroform, ethyl acetate, acetone, methanol) and other reagents used in current study were purchased from Avra Chemicals (India).

Fluorescence spectrometer (Agilent), UV-2450 spectrophotometer (Shimadzu), FT-IR spectrophotometer (Agilent), NMR instrument (Jeol 500 MHz), HR-MS (Bruker HD) and elemental analyzer were used to characterize the synthesis compounds. The Horiba Pro-850 was used to measure fluorescence lifetimes by the time-correlated single-photon counting (TCSPC) technique.

Synthesis of derivatives of L-valine (V1 and V2): A 30 mL solution of L-valine (5 mmol) was prepared in dry THF and 20 mmol K_2CO_3 was added under heating. In this solution, a solution of ethyl bromide (5 mmol) in 15 mL dry THF was added slowly. Now, the reaction solution was set to stir for 20 h, under refluxing. The reaction was continuously monitored with TLC [20]. Upon completion, the reaction solution was passed through filter paper and the solid residue was removed. The filtrate was then concentrated and dried under reduced pressure. The column chromatography was performed to obtain final purified product (**V1**) [21,22]. Similarly, under the substitution reaction another derivative (**V2**) of L-valine was prepared.

V1: Colour: Off-white solid; yield: 74%; ^{1}H NMR (500 MHz, $CDCl_3$-d_6) δ ppm: 0.92-0.97 (6H, dd), 1.18-121 (3H, t), 2.18-2.26 (1H, m), 2.68-2.85 (2H, dm), 3.40-3.44 (1H, m) and 4.58-4.79 (1H, m). HRMS [$C_7H_{15}NO_2$] 145.11 ($M+H^+$); Anal. calcd. (found) % for $C_7H_{15}NO_2$: C, 57.92 (58.11); H, 10.44 (9.89); N, 9.68 (9.28).

V5: Colour: Off-yellow solid; yield: 58%; ^{1}H NMR (500 MHz, $CDCl_3$-d_6) δ ppm: 0.91-0.97 (6H, dd), 2.08-2.16 (1H, m), 3.79-3.84 (1H, dd), 3.92-3.96 (1H, dd), 4.30-4.35 (1H, m) and 7.20-7.34 (5H, Ar, m). HRMS [$C_{12}H_{17}NO_2$] 207.18 ($M+H^+$); Anal. calcd. (found) % for $C_{12}H_{17}NO_2$: C, 69.55 (67.96); H, 8.28 (9.05); N, 6.77 (6.46).

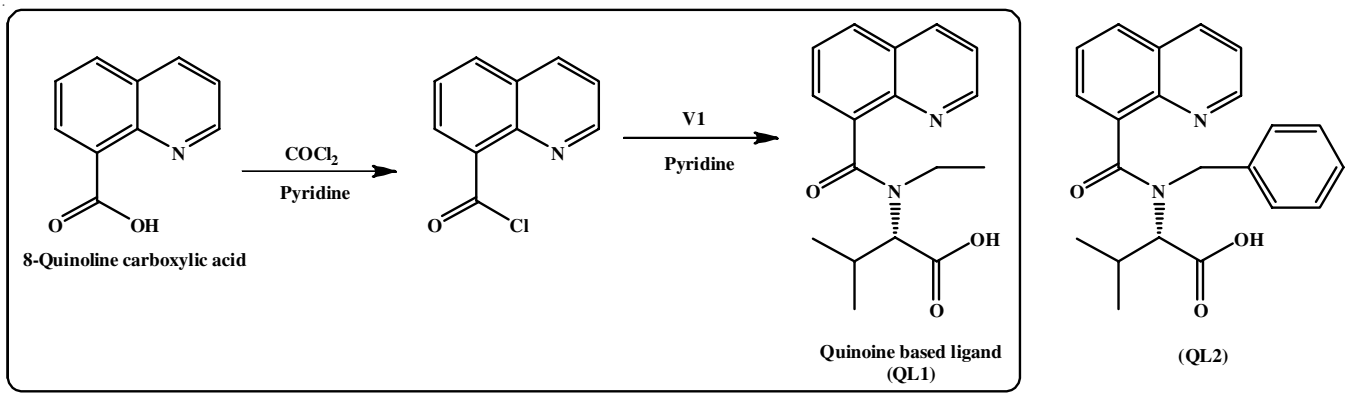
Synthesis of 8-quinolinecarboxylic acid based ligands (QL1 and QL2): The oxalyl chloride was used to activate the 8-quinoline carboxylic acid's (8-QC's) carboxylic group in the presence of a catalytic amount of pyridine [20-25]. The acid chloride group, under the substitution reaction with synthesized derivatives of L-valine (**V1** and **V2**), was then converted to amide (**Scheme-I**) [22,26].

QL1: Colour: pale-yellow solid; yield: 99%; ^{1}H NMR (500 MHz, $CDCl_3$-d_6) δ ppm: 0.92-0.97 (6H, dd), 1.19-1.22 (3H, t), 2.16-2.25 (1H, m), 2.67-2.83 (2H, dm), 3.38-3.41 (1H, m), 4.57-4.78 (1H, m), 7.47-7.50 (1H, t), 7.56-7.59 (1H, m), 8.07-8.10 (1H, dt), 8.22-8.25 (1H, dt) and 8.85-8.87 (1H, dd). HRMS [$C_{17}H_{20}N_2O_3$] 300.22 ($M+H^+$); Anal. calcd. (found) % for $C_{17}H_{20}N_2O_3$: C, 67.97 (67.11); H, 6.72 (5.88); N, 9.34 (9.79).

QL2: Colour: yellow-solid; yield: 98%; ^{1}H NMR (500 MHz, $CDCl_3$-d_6) δ ppm: 0.92-0.97 (6H, dd), 2.09-2.17 (1H, m), 3.78-3.85 (1H, dd), 3.91-3.94 (1H, dd), 4.29-4.33 (1H, m), 7.21-7.34 (5H, Ar, m), 7.44-7.48 (1H, t), 7.56-7.59 (1H, m), 8.10-8.11 (1H, dt), 8.24-8.26 (1H, dt) and 8.86-8.87 (1H, dd). HRMS [$C_{22}H_{22}N_2O_3$] 362.19 ($M+H^+$); Anal. calcd. (found) % for $C_{22}H_{22}N_2O_3$: C, 72.90 (72.15); H, 6.13 (6.37); N, 13.25 (12.79).

RESULTS AND DISCUSSION

The L-valine was converted to its substituted derivatives under the substitution reaction, where the bromo group (leaving group) of ethyl-bromide or bromomethyl benzene was substituted with an amino group of L-valine [23] and yields around 70-75% yield. The carboxylic group of 8-QC, in the presence of chlorinating reagent (oxalyl chloride and pyridine), was converted to acyl chloride under S_N^2 substitution. The chlori-



Scheme-I: Synthesis of quinoline based chemosensor (**QL1** and **QL2**)

nating reagent, oxalyl chloride and catalyst (pyridine), is considered an excellent reagent for the acylation of carboxylic groups [22,23,27] and yields nearly 100% of the desired product. Acyl chloride is very potent toward the nucleophile attack. It gives the easy formation of an ester of amide bond in the presence of suitable nucleophiles under the substitution reaction and yields a remarkable amount of products [28-30]. Following this, acyl chloride of 8-QC and amino group of L-valines (**V1** or **V2**) were allowed to react in the presence of catalytic amount of pyridine. The reactants were quickly reacted and yielded nearly 100% of desired ligand (**QL1** and **QL2**).

It is well-known that compounds based on quinole have fascinating photoluminescence characteristics [5,31-33]. Thus, in a mixture of methanol and buffer (HEPES) (9.5:0.5%, v/v), the fluorescence characteristics of **QL1** and **QL2** (5×10^{-5} M) were examined. The maximum fluorescence emissions were observed at 492 and 508 nm for ligands **QL1** and **QL2**, respectively. The fluorescence emission that **QL1** and **QL2** exhibited in the following order: **QL2** > **QL1**. Since the main difference between the two ligands is in the amino acids, it is plausible to conclude that the animo acid's electronic effect substantially influences the ligands' fluorescence properties.

Since ligands **QL1** and **QL2** have suitable binding sites, we wished to examine their chemosensing capacities for several metal ions, including Ag^{+}, Al^{3+}, Na^{+}, Cr^{3+}, Ni^{2+}, Pb^{2+}, Fe^{3+}, Cd^{2+}, Hg^{2+}, Zn^{2+} and Cu^{2+}. When present in excess, many of these metal ions are recognized as harmful environmental contaminants and can harm health. Except for Cu^{2+}, there were no discernible changes in the fluorescence intensities of **QL1** and **QL2** solutions following the addition of these metal ions. The addition of Cu^{2+} to the **QL1** and **QL2** solutions resulted in a considerable quenching of the fluorescence peaks at 492 and 508 nm, respectively (Fig. 1i) shows the fluorescence spectra of **QL2**.

Moreover, using the Stern-Volmer plots, the quenching constants for **QL1** and **QL2** towards Cu^{2+} were determined to be 1.43×10^{5} M^{-1} and 1.76×10^{5} M^{-1}, respectively. The non-linear characteristics and upward bend of the Stern-Volmer plots in each of these examples (Fig. 1ii), Stern-Volmer plot of **QL1)** indicate that a combination of dynamic and static quenching is responsible for the quenching of the fluorescence [34]. Using the Benesi-Hildebrand method, the binding constants of **QL1** and **QL2** towards Cu^{2+} were determined to be 1.13×10^{5} M^{-1} and 1.32×10^{5} M^{-1}, respectively (Fig. 1iii). **QL1** and **QL2** were shown to have detection limits of 54.30 nM and 47.40 nM, respectively, towards Cu^{2+} [35], (Fig. 2i). **QL2** had the lowest detection limit towards Cu^{2+} than **QL1**.

The competing studies with other cations (Ag^{+}, Al^{3+}, Na^{+}, Cr^{3+}, Ni^{2+}, Pb^{2+}, Fe^{3+}, Cd^{2+}, Hg^{2+} and Zn^{2+}) were performed present under comparable experimental conditions to evaluate the great selectivity of **QL1** and **QL2** towards Cu^{2+} ions. These investigations showed that other metal cations did not significantly interfere with **QL1** and **QL2**'s ability to detect Cu^{2+} (Fig. 2ii). Consequently, **QL1** and **QL2** are extremely selective fluorescence chemosensors to identify Cu^{2+}.

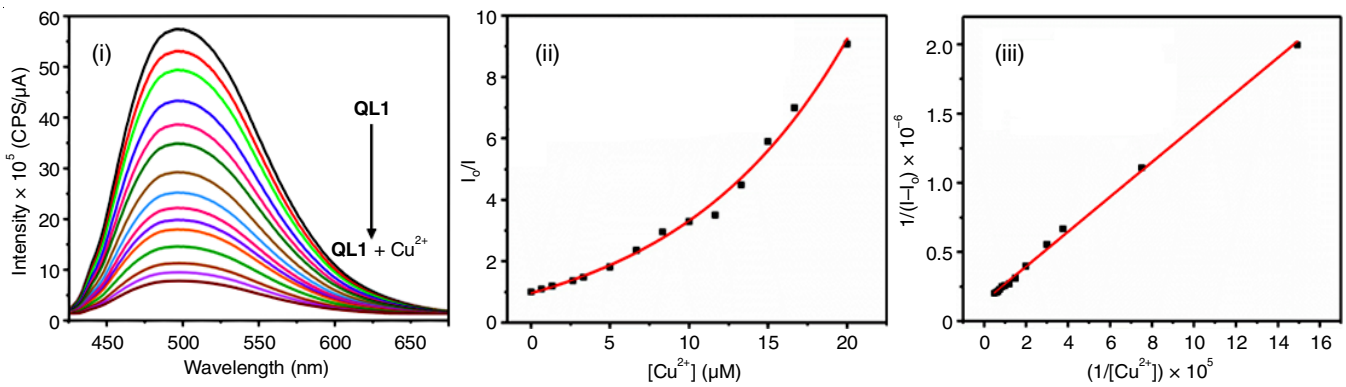


Fig. 1. (i) Fluorescence spectra of **QL1** (5×10^{-5} M) in MeOH:H_2O (9.5: 0.5%, v/v) upon incremental addition of Cu^{2+} concentration, (ii) Stern-Volmer plot of **QL1** with Cu^{2+}, (iii) Binding constant of **QL1** with Cu^{2+}

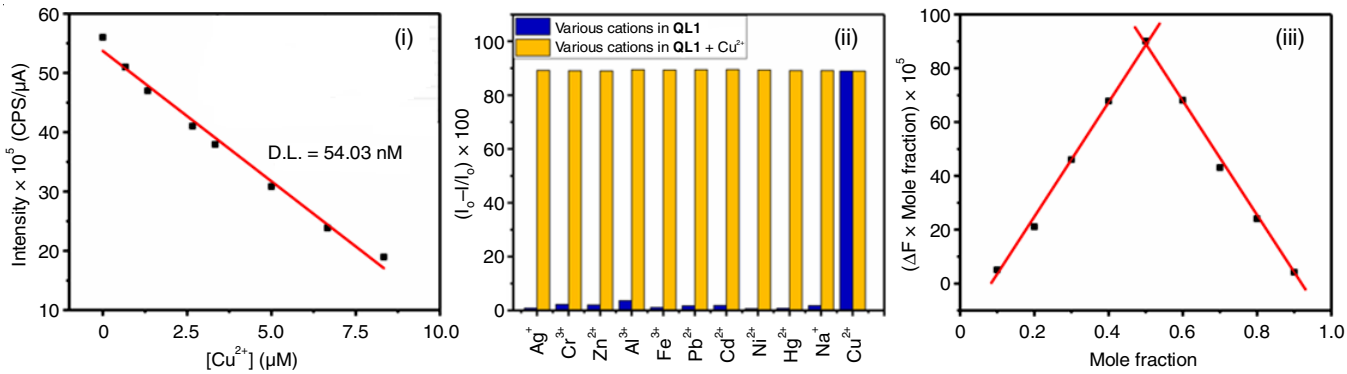


Fig. 2. (i) Detection limit of **QL1** with Cu^{2+}, (ii) Fluorescence response of **QL1** (a) and **QL2** (b) (5×10^{-5} M) in MeOH:H_2O (9.5:0.5%, v/v) upon addition of various metal ions (blue bars), followed by addition of 20×10^{-6} M of Cu^{2+} (yellow bars), (iii) Job's plot of **QL1** (5×10^{-5} M) towards Cu^{2+}

The Job's plot analysis was performed to verify the stoichiometry and the mechanism of **QL1** and **QL2** interaction with Cu^{2+} ions. The highest fluorescence intensity at 0.5 mol fraction was observed for **QL1** and **QL2**, indicating a stoichiometry ratio of 1:1, according to the Job's plot [36] of the fluorescence intensity fluctuation at λ_{em} of **QL1** and **QL2** against the mole fraction of Cu^{2+} (Fig. 2iii).

The DFT calculations were performed to develop the lowest energy structures of the ligands (**QL1** and **QL2**) and the metal complexes of the ligands with Cu^{2+} ions (Fig. 3a-b) [37,38]. The difference in the energy-gap between the homo and lumo orbitals was found 4.45 eV and 4.21 eV, respectively, for **QL1** and **QL2**. Ligand **QL2** with a lower energy gap in HOMO-LUMO orbitals show better reactivity with Cu^{2+} ions [2,3,31]. The complex structure of ligands with Cu^{2+} (Fig. 3b) shows the formation of two chealating ring that form a tetrahedral structure with metal ions and in this structure, the fourth valancy was stabilized with used solvent.

Analytical applications: It has been observed that even in the presence of competing metal ions, compounds **QL1** and **QL2** demonstrated the preferential chemosensing capabilities towards Cu^{2+} ions. This observation is significant and we were interested in investigating **QL1** and **QL2** potential as chemosensors for analytical uses. However, copper is crucial for many physiological processes and a vital co-factor for many metalloenzymes in living organisms [10-12,39,40]. However, Cu^{2+} is highly hazardous to living things when overloaded. For instance, excessive accumulation in humans results in several illnesses, such as coronary heart disease, metabolic and genetic problems, obesity, diabetes and Wilson's disease [17,18]. The human body can be exposed to Cu^{2+} by heavy metals from soil caused by acid rain or contaminated water from consumer or

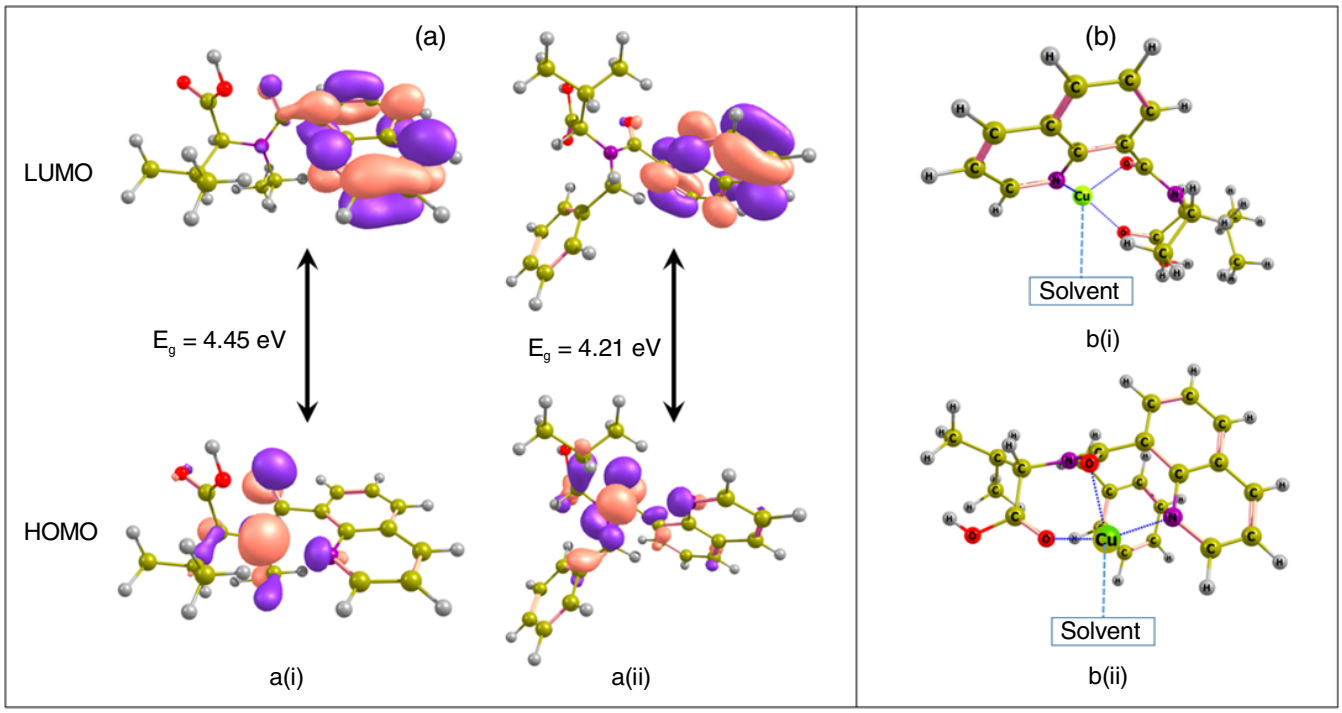


Fig. 3. (a) HOMO-LUMO diagrams of geometrically optimized (i) **QL1** and (ii) **QL2** and (b) geometrically optimized DFT structures of the metal complexes of (i) **QL1** and (ii) **QL2**

industrial waste. According to the World Health Organization (WHO), drinking water should contain no more than 2 ppm (30 µg) of copper due to these effects [41,42]. Human blood typically has an average quantity of Cu^{2+} between 15.7 and 23.6 µM [19]. Consequently, developing sensitive and selective fluorescent probes to identify copper in various environment samples is crucial. Hence, synthesized quinoline-based ligands **QL1** and **QL2** were investigated for their chemosensing properties in different environment samples.

Detection of Cu^{2+} in tap water: To achieve this, two sample solutions *viz*. sample A, which comprises tap water with intentionally added Cu^{2+} (20 µM) ions and sample B, which is tap water that has been heated for 5-10 min. Ligand **QL2** exhibited a fluorescence emission at 492 nm in MeOH:H_2O (9.5:0.5%, v/v) solution. The fluorescence intensity of **QL2** did not significantly alter when sample A was added to this solution. But when sample A containing Cu^{2+} ions was introduced, **QL2**'s fluorescence intensity was quenched. Compound **QL1** also demonstrated the same outcomes under the same experimental settings, indicating that both compounds have the ability to detect Cu^{2+} in samples of tap water. The **QL1** and **QL2** detection limits [35] toward Cu^{2+} in tap water were computed as 48.53 nM and 41.30 nM, respectively. As a result, compared to **QL1**, **QL2** showed the lowest detection limit for Cu^{2+} in tap water. In tap water, the binding constants of **QL1** and **QL2** towards Cu^{2+} were calculated as 7.92×10^5 M^{-1} and 0.76×10^4 M^{-1}, respectively. Additionally, the quenching constants towards Cu^{2+} for **QL1** and **QL2** were computed as 1.04×10^5 M^{-1} and 2.17×10^5 M^{-1}, respectively.

Detection of Cu^{2+} in river water and industrial waste samples: A similar study was conducted with environmental samples, such as river water and industrial wastewater. The results were found to be similar to the analysis performed for the tap water samples. The spectral hindrance or disturbance was not observed during the fluorescence detection study (Fig. 4; the fluorescence spectra of **QL1** in industrial wastewater sample). Thus, the developed method is robust and stable even in the presence of unwanted impurities or metal ions.

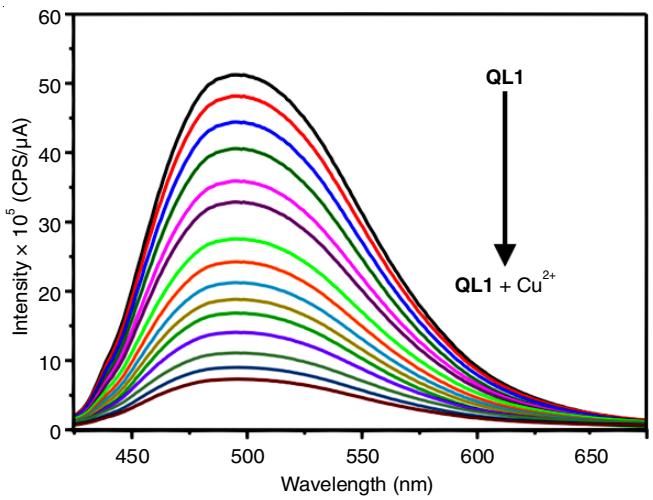


Fig. 4. Fluorescence spectra of **QL1** (5×10^{-5} M) in MeOH:H_2O (Industrial waste) (9.5: 0.5%, v/v) upon incremental addition of Cu^{2+} concentration

Conclusion

In summary, a novel class of well-defined ligands based on quinoline based moieties have been created as tuneable chemosensors for the first time. Two quinoline based ligands (**QL1** and **QL2**) were developed for flourosense analysis. When exposed to nanomolar concentrations of Cu^{2+}, these ligands demonstrated sensitive and specific fluorescence chemosensing capabilities. According to this study, the electronic effects of substituent can regulate the photoluminescence and chemosensing characteristics of this class of compounds. These chemosensors can be used analytically to find traces of Cu^{2+} in industrial waste, river and tap waters.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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