New imidazole sensors synthesized for copper (II) detection in aqueous solutions

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KEYWORDS

Visual and fluorescent sensor, Imidazole, Copper, dative bond, metal-ligand complex formation.

ABSTRACT

Water security, safety, availability and sustainability of water supply are increasingly problematic and difficult across the planet. Safe and rapid methods have been developed to purify water from cationic pollutants. New imidazole-derived fluorescent sensors, 2-(4,5-diphenyl-1-(p-tolyl)-1H-imidazol-2-yl) phenol (TS) and 2-(1-(4-methoxyphenyl)-4,5-diphenyl-1H-imidazol-2-yl) phenol (AS), have been synthesized and characterized, and their possibility as fluorescence sensors for copper (II) has been examined. In CH3CN/H2O (90 v/v), the TS and AS revealed a noticeable an electronic band at 320.00 nm and fluorescence band at 460.90 nm. The ratio metric alterations in the absorption and fluorescence spectra of TS and AS due to the dative covalent bond between them and the copper (II) were shown by the findings of copper (II) titration. The sensing mechanism was validated by optical investigations and FT-IR spectra. In mixed solvent solutions, the selectivity of TS and AS to copper (II) as fluorescent sensors has been demonstrated, with sensitivity as low as 0.09 and 0.28 µM, significantly less than the limit permitted via the US EPA for drinking water (2.00 µM). The identification limits of TS and AS were assessed to be 0.05 and 0.50 µM, respectively, using the spectrophotometric procedure. Stoichiometry binding between TS and AS with copper (II) was found to be 2:1 (tetrahedral structure) as indicated by Job's method.

1. Introduction

Heavy metal ions have recently received a lot of interest due to their dangerous and harmful impacts on the environment and general health. Heavy metals (HM) are among the most difficult pollutants when present in natural and human environments due to their toxicity and their ability to accumulate in ecosystems biologically due to their inability to biodegrade.Wastewater treatment has become an imperative necessity to protect the environment, ecosystems and public health. Contamination of the world's water resources with copper is on a serious increase, threatening human health and aquatic ecosystems. Concentrations of copper in wastewater have been recorded ranging from about 2.5 mg/L to 10,000 mg/L. [1, 2, 3]. Cu2+ plays an important role in the fields of biological, environmental, and chemical systems as it is ranked third in abundance in the human body among the essential heavy metals, and is an essential trace element for both plants, animals, and humans. [4]. Cu2+ ions have no toxic effect on the human body under normal conditions; However, excess and deficiency can cause different damages. The World Health Organization (WHO) has set the maximum permissible level of Cu2+ in drinking water at approximately 30.00 µM. This means that the permissible limit for copper intake should not exceed 10.00-12.00 mg per day for adults. Therefore, the development of a fluorescent chemical sensor with high sensitivity and selectivity that can be used to efficiently assess Cu2+ levels in environmental and biological systems is of great importance. [5,6] Detection of Cu2+ with simple instruments, such as optical tests, including colorimetric and fluorescent methods, is attractive due to its simplicity of operation and relatively low detection limit, and has the advantage that detection can be accomplished by the naked eye when the fluorescent emission is within the visible light range. [7] It is necessary to establish a reliable, sensitive and effective approach for the detection of copper(II) in environmental and biological samples. Various methods have been used to remove copper from wastewater including ion exchange, reverse osmosis, chemical reduction, precipitation, adsorption and photo catalysis processes. [2] To detect HM, a variety of instrumental approaches were developed, like Inductivity Coupled Plasma-Mass Spectroscopy (ICP-MS), Inductivity Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), Inductivity Coupled Plasma-Optical Emission Spectroscopy (ICP-OES), Atomic Absorption Spectroscopy (AAS), and Flam Atomic Absorption Spectrophotometer (FAAS) [8,9]. These techniques are regarded for heavy metal ions detection due to their sensitivity, selectivity, and capacity to determine several metal ions concurrently. These techniques, on the other hand, necessitate expensive apparatuses, professional procedures, and, in certain cases, additional periods for sample preparation, all of which are able to limit their use [10,11,12]. As a result, alternative techniques for HM detection were developed, taking into account cost, speed, on-site detection, and various principles, such as colorimetric [13,14], fluorescent [15,16], and electrochemical processes [17]. Imidazole is a five-membered heterocyclic compound known for its acidity and basicity, which contributes to its versatility in various chemical reactions. The two nitrogen atoms in the imidazole ring can serve as recognition sites, allowing for the design of fluorescent sensors for various analytes through the integration of other functional groups [18]. Because imidazole has high metal ion coordinative properties, imidazole derivatives are utilized in environmental surveillance, industrial process control, metal loneuro-chemistry, as well as biomedical diagnosis [19]. Some new imidazole derivatives have been created for very sensitive transition metal ion chemosensor. They act as chemosensor, capable of selective and reversible binding with analytes, accompanied by an alteration in some system characteristics, such as color, fluorescence, or redox potential [20]. Imidazole is a flat, compact ligand. Six imidazole ligands fit comfortably around octahedral metal centers, e.g., [Fe(imidazole)6]2+, the M-N(imidazole) bond is freely rotating [21]. In the present research there are new chemosensor of imidazole derivatives TS and AS were synthesized by the Debus-Radziszewski reaction [22] to detect copper (II) in an aqueous solution. They act as fluorescence sensors, nonlinear optical materials, and dye-sensitized solar cells. UV–Vis absorption and fluorescence were utilized to investigate the selectivity and sensitivity of TS and AS. Furthermore, optical spectroscopy and FT-IR were used to confirm the sensing mechanism.

2. Experimental

2.1 Chemical and Instrumentations

Whole solvents and indictors have been of the greatest quality possible, acquired from Sigma-Aldrich Company, and utilized exactly as supplied. A Bruker Avance 600 and 400 MHz spectrometers have been used to record HNMR spectra in CDCl3 solution. A PerkinElmer Spectra 100 FTIR spectrometer has been used to collect IR spectra. Agilent GC7000 mass spectrometers have been used for mass spectroscopy. The Shimadzu UV-1800 Spectrophotometer, an analytical & measuring instrument (Shimadzu Corporation Kyoto Japan) has been used to determine different UV absorption spectra in various solvents. A PerkinElmer LS 55 Fluorescence Spectrometer which is a dual monochromator fluorescence spectrometer, capable of a wide variety of high-sensitivity luminescence measurements (PerkinElmer Ltd, United Kingdom) has been used to record the fluorescence spectra.

2.2 Synthesis and characterization

2.2.1 Synthesis

A solution of diphenylethane-1,2-dione (1) (0.231 g, 1.1×103 µM),2-hydroxybenzaldehyde (2) (0.122g, 1 ×103 µM), 4-methylaniline (3) (0.428 g, 4×103 µM), 4-methoxyaniline (4) (0.492 g, 4×103 µM) or in the existence of ammonium (0.77 g, 10×103 µM) in glacial acetic acid (10 ml) was refluxed under argon for 12 h. After this exposition time, the reaction mixture was cooled, diluted with water (20 ml), and the solid formed was filtered off. The collected precipitate was washed with 10% acetic acid (4×5 ml), water and dried to obtain the pure product [23] TS and AS as shown in Scheme 1.The structure of all compounds was confirmed by IR, 1HNMR and HRMS.

2.2.2 Characterization

2.2.2.1 Characterization of 2-(4,5-diphenyl-1-(p-tolyl)-1*H*-imidazol-2-yl) phenol) TS):

Molecular Formula	$C_{28}H_{22}N_2O$
Melting point	202°C
IR, cm^{-1}	C–H aliphatic 2924, 2855 C=N 1732, C=C stretch 1600,C–O 1292
^{1}HNMR, δ in ppm	(850 MHz, $CDCl_3$) δ 2.37 (3H, s, CH_3), 6.49 (1H, td, J=0.85, 7.65 Hz, CH), 6.6 (1H, d, J=7.65 Hz, CH), 6.86 (2H, s, CH_2), 7.06-7.1 (3H, m Hz, Ar-H), 7.13-7.15(3H,m, Ar-H),7.2 -7.21(1H, m, Ar-H), 7.24-7.28 (5H, m, Ar-H), 7.38 (2H, d, J=8.5, Ar-H), 13.59 (1H, s, O-H)
ESI–MS	m/z $[M+H]^+$calc 403.50 and found 403.17

2.2.2.2 Characterization of 2-(1-(4-methoxyphenyl)-4,5-diphenyl-1H-imidazol-2-yl) phenol (AS):

Molecular Formula	$C_{28}H_{22}N_2O_2$
Melting point	178°C
IR, cm^{-1}	C–H aliphatic 2937, 2841 C=N 1603,C=C stretch 1582,C–O 1295
^{1}HNMR, δ in ppm	(850 MHz, $CDCl_3$) δ 3.81 (3H, s, O-CH_3), 6.49 (1H, td, J=0.85, 7.65 Hz, CH), 6.6 (1H, d, J=7.65 Hz, CH), 6.86 (2H, s, CH_2), 7.06-7.1 (3H, m Hz, Ar-H), 7.13-7.16(3H,m, Ar-H), 7.2 -7.21(1H, m, Ar-H), 7.24 -7.28 (5H, m, Ar-H), 7.38 (2H, d, J=8.5, Ar-H), 13.59 (1H, s, O-H)
ESI–MS	m/z $[M+H]^+$calc 419.50 found 419.17.

Scheme 1. Synthesis of TS and AS

2.2.3 General spectroscopic procedures

The spectrophotometric analysis methods demonstrated that spectrophotometry was sensitive and extremely precise for the determination of metal-chelates, and that the stability constant of metal trivalent chelates was greater than any other metal [24]. Therefore, UV-Vis and fluorescence methods were employed to confirm the binding between the sensors and copper (II).

2.2.4 The standard solutions and the measurement methods

Stock solutions of (1×10^{-3}M) Cu $(NO_3)_2.3H_2O$ salt were prepared in deionized water, and stock solutions of (1×10^{3}µM) of both TS and AS were prepared in acetonitrile. Standard solutions of both TS and AS (1×10 µM) were freshly prepared in an 90% acetonitrile. A standard aqueous solution of copper salt (2×10 µM) was freshly prepared. Sensors were titrated with increments of an aqueous solution of salt and monitored the titration by UV–Vis and fluorescence methods [25]. At room temperature, titration tests have been performed in a 10-mm quartz cell. (λ_{max} = 320.00 nm, λ_{ex} = 460.90 nm).

2.3 Selectivity

The selectivity test has been carried out by measuring UV-Vis absorbance and fluorescence intensity changes of TS and AS solutions (1×10µM) in 90% acetonitrile at λ_{max} = 320.00 nm and λ_{ex} = 460.90 nm, respectively, upon reaction with various cations Cr(III), Ag(I), Co(II), Cu(II), Hg(II), Ni(II), Pb(II), and Zn(II) at the concentration (1×10^{2} µM). Also, measurements of absorbance and the fluorescence of the reaction mixture, which consists of sensors (1×10µM) and copper (II) (5×10µM) with different cations (5×10µM) [26]. Each experiment was repeated three times to take the average value. Then, the response of the sensors to copper (II) was compered in available and unavailable of the other ions.

2.4 Validation of the method

The absorption and emission of zero cation solution were measured ten times on UV-Vis and fluorescence instruments to examine the reliability of the new approach. Standard deviation (SD) was calculated to estimate method's precision. A series of different concentrations of copper (II) solutions were tittered with a fixed concentration of sensors to acquire calibration curves. In the concentration range of 4–100 µM for salt, the linear correlation coefficients of the calibration curves between counts (peak area) and concentrations have been higher than 0.96 for copper (II) with TS and AS. The limit of detection [LOD] for an instrument is calculated using the equation $LOD = 3SD/\rho$, where SD is of 10 blank measurements and ρ is the slope of intensity against the concentration of sample. The limit of quantification (LOQ) is also calculated using the equation: $LOQ = 10SD/ \rho$ [27].

2.5 The continuous variations method (Job's method)

The stoichiometry ratio of the complexes TS with copper (II) [$Cu_{:}$ $(C_{28}H_{21}N_2O_2)$] and AS with copper (II)[Cu: $(C_{28}H_{21}N_2O)$] in 90% acetonitrile solution is determined by Job's method. The mole fractions of TS and AS are changed, while their sum of the molar concentrations was be left constant. The mole fractions of such two components have been displayed versus an observable (absorbance and fluorescence), which is proportional to complex creation. If sufficient high levels have been utilized, the plot's maximum (or minimum) matches the two species' stoichiometry [28,29].

3. Results and Discussion

3.1 Manufacturing of TS and AS

As seen in Scheme 1, the sensors were manufactured via the Debus-Radziszewski compression of salicylaldehyde with 1,2-diphenylethane-1,2-dione and 4-methylaniline (for AS sensor) or with 1,2-diphenylethane-1,2-dione with 4-methoxyaniline (for TS sensor) in the existence of ammonium acetate. The molecular structures of the TS and AS were emphasized using FTIR, 1H NMR, and mass spectra as mentioned earlier in the characterization section.

3.2 The electronic absorption and fluorescence spectra properties.

Fig 1 show the electronic absorption spectra of TS and AS sensors have been measured in 90% acetonitrile. All spectra of sensors were measured versus 90% acetonitrile as a blank. Fluorescence spectra of TS and AS sensors in 90% acetonitrile are also measured versus 90% acetonitrile as a blank. Fig 2 and 3 show the UV-Vis spectra and fluorescence spectra for the formed complexes between TS and AS sensors with copper (II) were the λ*max for absorption band was observed at 320* nm for absorption and for fluorescence at λex 460.9 nm.

3.3 Validation method

As shown in Fig 4 and 5, a calibration curves were plotted between TS and AS sensors' absorption versus copper (II) concentration in µM. The calibration curves were constructed in a range of the concentrations (4, 8, 20, 40, 60, 80, 100 µM). The linear regression equations for the calibration curve were derived by Appling the least-squares method. Calibration curves plots were found to be linear, with small slope and slope values and a good correlation coefficient, reflecting excellent linearity plots for both TS and AS sensors' absorption versus copper (II) concentration. The precision of the method was determined by repeating the measurement of the absorption and the fluorescence for ten times of zero cation solutions of sensors, then the *SD* and the *RSD* have been computed. The sensitivity of the used spectroscopic method is tested by calculating *LOD* and *LOQ*.by spectrophotometric and spectrofluorophotometric approaches, the LOD for TS was determined to be 0.0578 and 0.0944 µM, respectively. While for AS, LOD was 0.5556 and 0.2850 µM by spectrophotometric and spectrofluorophotometric approaches, respectively. The value of LOQ for TS was determined to be 0.1928 and 0.9448µM using spectrophotometric and spectrofluorophotometric approaches, respectively. While for AS, LOQ was 1.8519 and 0.9501 µM using spectrophotometric and spectrofluorophotometric procedures, respectively. The LOD and LOQ were found to have modest values, demonstrating the high sensitivity of the proposed applied spectroscopic method.

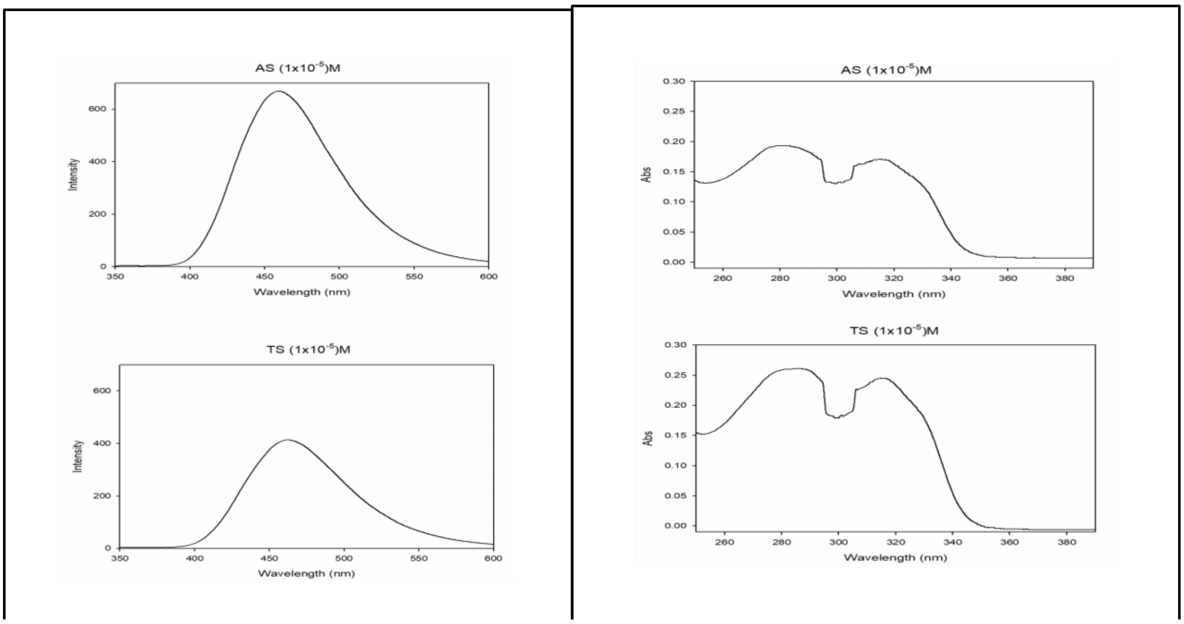

Fig 1. Absorption and fluorescence spectra of AS and TS (1×10 µM) in 90% acetonitrile.

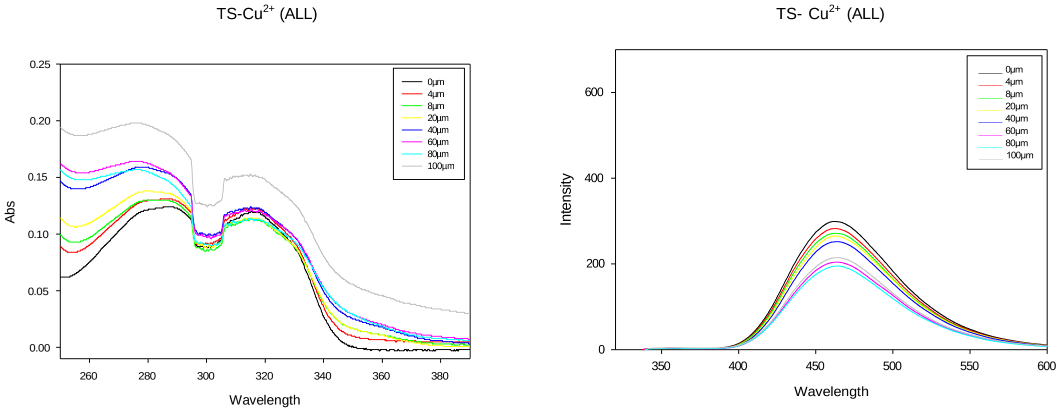

Fig 2. Absorption spectra and fluorescence spectra of TS (1 × 10^{-5}M) across the inurement of copper (II) at various concentration in 90% acetonitrile. The intensity of fluorescence was recorded at 25°C (λ_{max}=320.00 nm, λ_{ex}=460.90 nm).

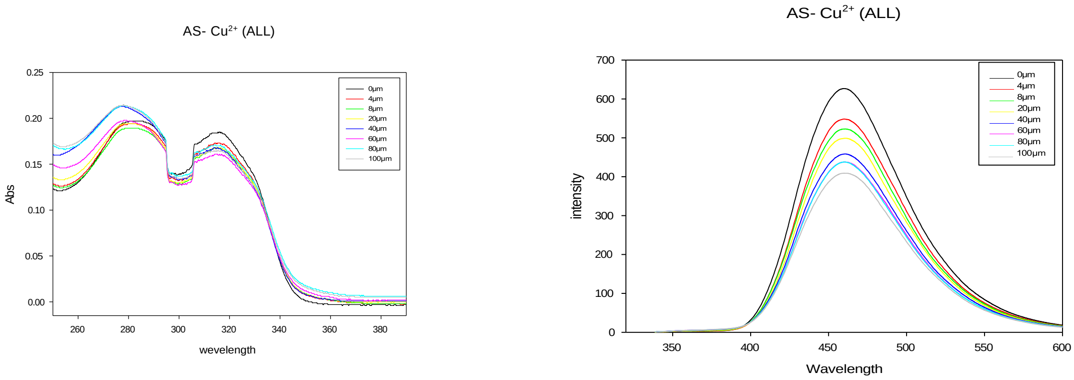

Fig 3. An electronic absorption and fluorescence spectra of AS (1 × 10^{-5}M) upon the addition of copper (II) at different concentrations in 90%. The intensity of fluorescence was recorded at 25°C (λ_{max}= 320nm, λ_{ex}= 460.

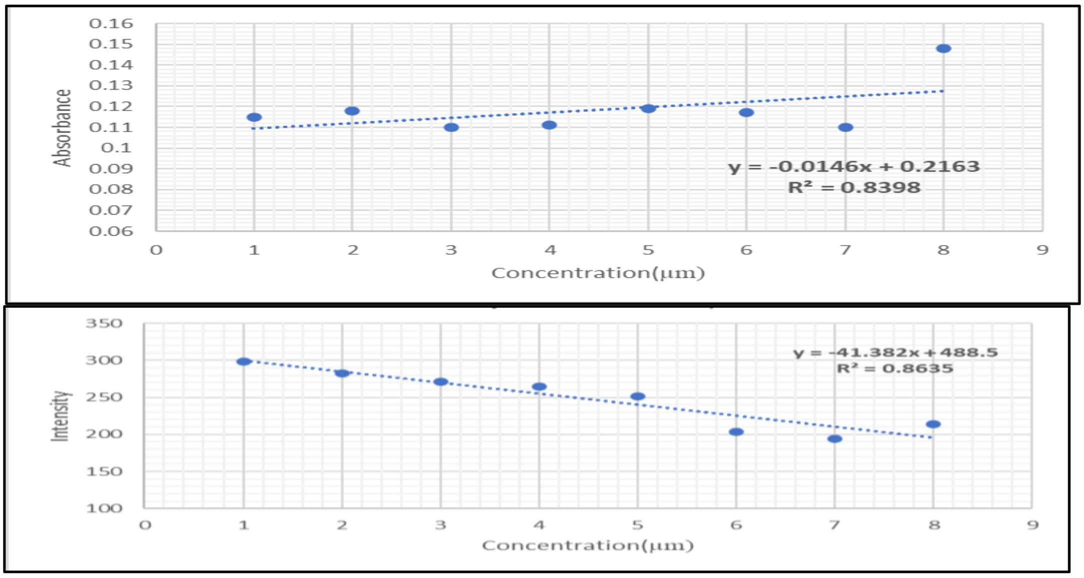

Fig 4. a- Absorption intensity and fluorescence intensity calibration curves of TS (1×10^{-5}M) as a function of copper (II) concentration in 90% acetonitrile.

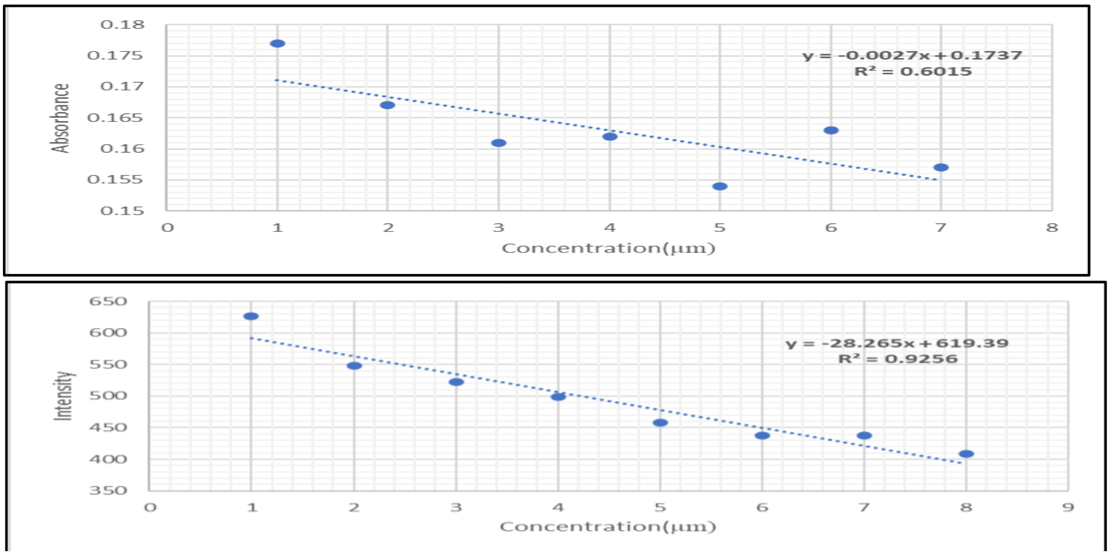

Fig 5. Calibration curves of AS (1×10^{-5}M) absorption intensity and fluorescence intensity as a function of copper (II) concentration in 90% acetonitrile.

3.4 Selectivity study

A chemo sensor's selectivity is a critical trait for its potential applications. As a result, the selectivity of TS and AS for detecting copper (II) in the presence of other cations was investigated. The fluorescence of free dye solution alone, after being combined with various cations of 10 equivalent, and after being combined with various cations in the presence of copper (II) in 5 + 5 equivalent. in 90% acetonitrile solutions, was measured. Interestingly, TS and AS was detected a greater selectivity toward copper (II) than other cations as presented in Fig 6. Despite the fact that the other cations were employed in far greater quantities (10 equivalent.) than the copper (II) (5 equiv.) [30]. TS and AS fluorescence, on the other hand, were only slightly altered compared to the massive alteration caused by the copper (II). Furthermore, the interference cation test verified that the massive change noticed has been owing to the selectiveness of TS and AS toward copper (II). Fig 6. show the selectivity of TS and AS.

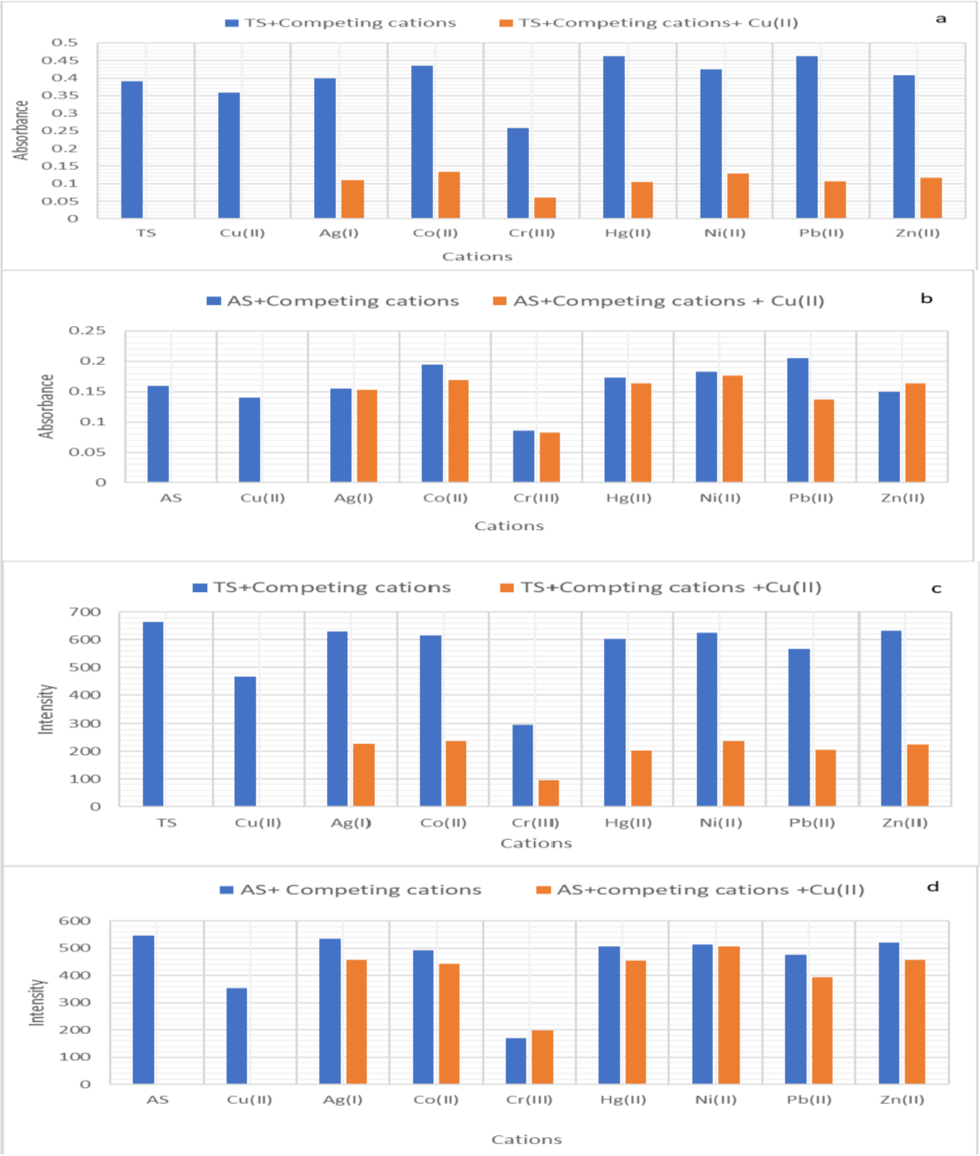

Fig 6. a,b-The absorbance change of both TS (1 × 10^{-5}M) and AS (1 × 10^{-5}M) in 90% acetonitrile in the presence of competing cations. c,d- The fluorescence intensity change of TS (1 × 10^{-5}M) and AS (1 × 10^{-5}M) in 90% acetonitrile in the presence of competing cations.

3.5 The stoichiometry of the formed complexes

Job's method was utilized to determine the stoichiometric ratio for the formed complexes between the two sensors and copper (II). Job's plots indicated the formation of a 2:1 ratio (sensor: Cu (II)) complex (Fig 7.) were the two molecules of sensors were bonded to one copper (II) by four dative covalent bonds, so the tetrahedral structure represented tertiary metal-ligand complexes. The expected structures of TS-Cu (II) and AS-Cu (II) complexes are shown in Fig 8.

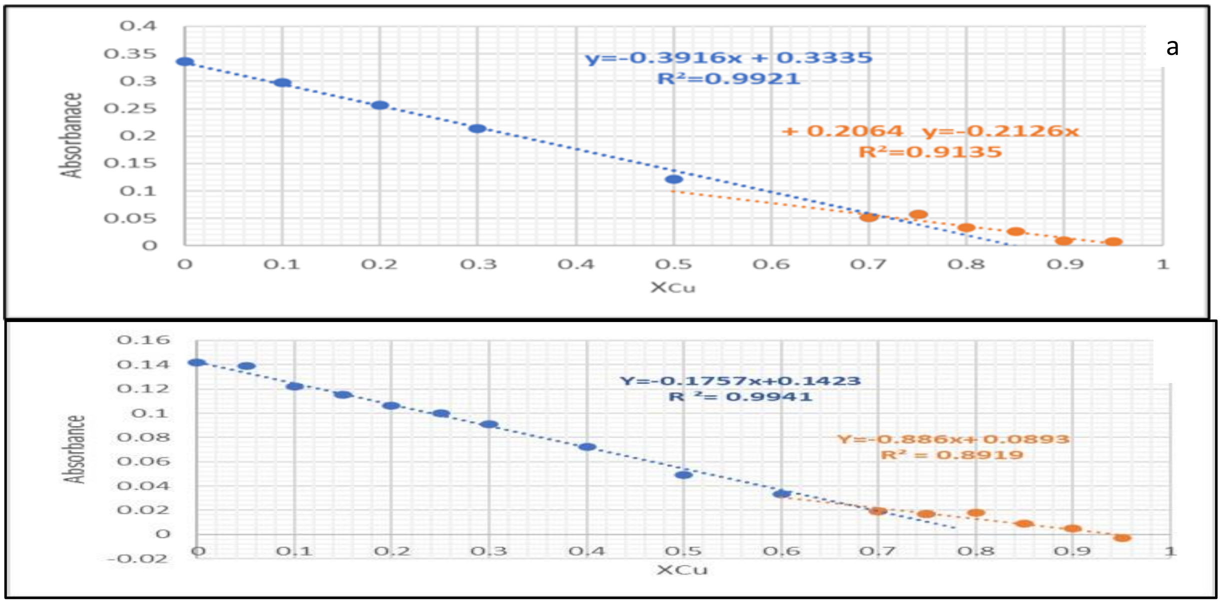

Fig 7. a- Job's plot of TS-Cu (II) complex formation using UV spectroscopy, b- Job's plot of AS-Cu (II) complex formation using UV spectroscopy.

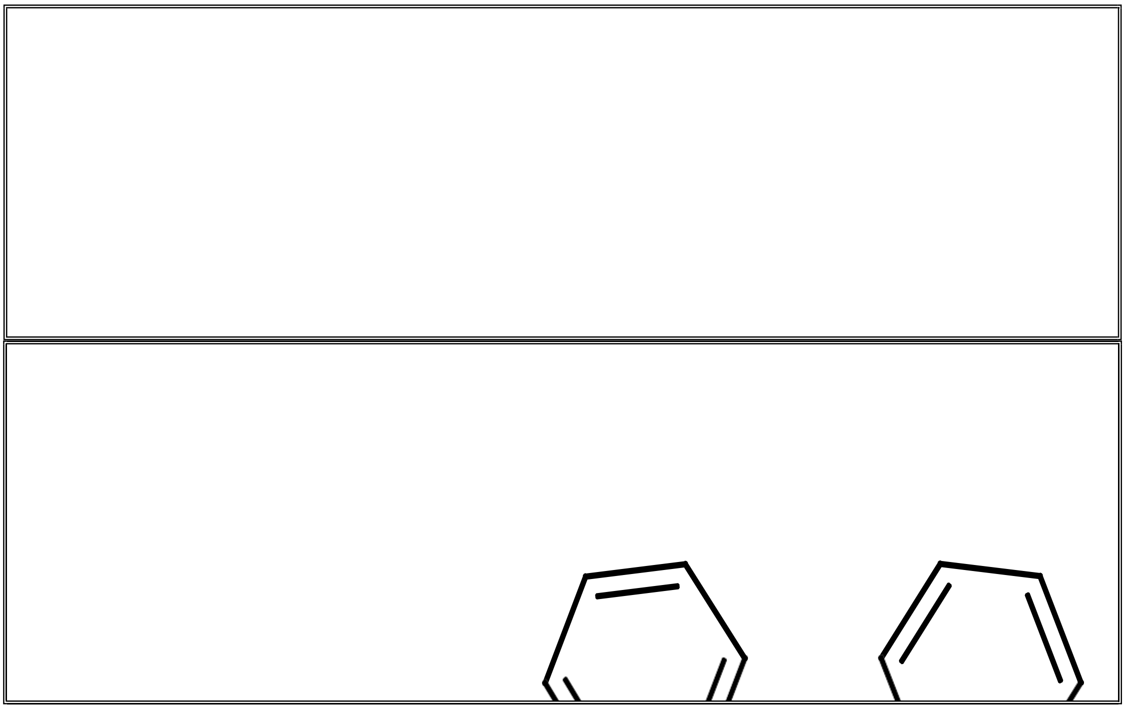

Fig 8. a- The expected structure of TS-Cu (II) tetrahedral complex. b- The expected structure of AS-Cu (II) tetrahedral complex

3.6 Sensing mechanism

In general, photon emission determines fluorescence that occurs quickly following absorption. Fluorescence chemosensor for HM detection ought to have two critical parameters: a metal-binding site as well as at least one fluorophore, which could absorb and emit light. The metal-binding site, which serves as a possible sensor, must alter the sensor's electronic or molecular shape. The electronic form is concerned with the wavelength or intensity of light, while the molecular form is concerned with the distance between a set of fluorophores known as a donor–acceptor molecule [31]. In this sensing process, the fluorophore and the ionophore are linked directly. In fact, the donor–acceptor dipole strength is affected by the metal ion's attachment to each of the acceptor or donor group, which changes the system's photophysical properties. The reaction between the donor group and the metal, for example, conduct to diminish the donor group's electron-donating activity, causing the system to blue shift [32]. The sensing mechanism was achieved through a dative covalent bond between copper (II) and the imidazole derivative sensors TS and AS. The FT-IR tool was used to confirm the structure of two complexes Fig 9. On the AS-Cu (II) complex spectrum, the aromatic C=N bond, which appeared at 1603 cm^{-1} before binding, had a blue shift to 1640 cm^{-1} after complexation, and the aromatic C-O bond, which appeared at 1295 cm^{-1} before binding, had a blue shift to 1374 cm^{-1} after complexation. On the TS-Cu (II) complex, the aromatic C=N bond which appeared on 1600 cm^{-1} before binding had a blue shift to 1636 cm^{-1} after complexation, and the aromatic C-O bond which appeared on 1292 cm^{-1} before binding had a blue shift to 1375 cm^{-1} after complexation. In the two cases, the shift in wavenumber indicates the enhancement in the vibrational energy of these bonds between aromatic carbon and nitrogen or oxygen atoms [33]. That confirms the formation of new TS-Cu (II) and AS-Cu (II) complexes via dative covalent bonds.

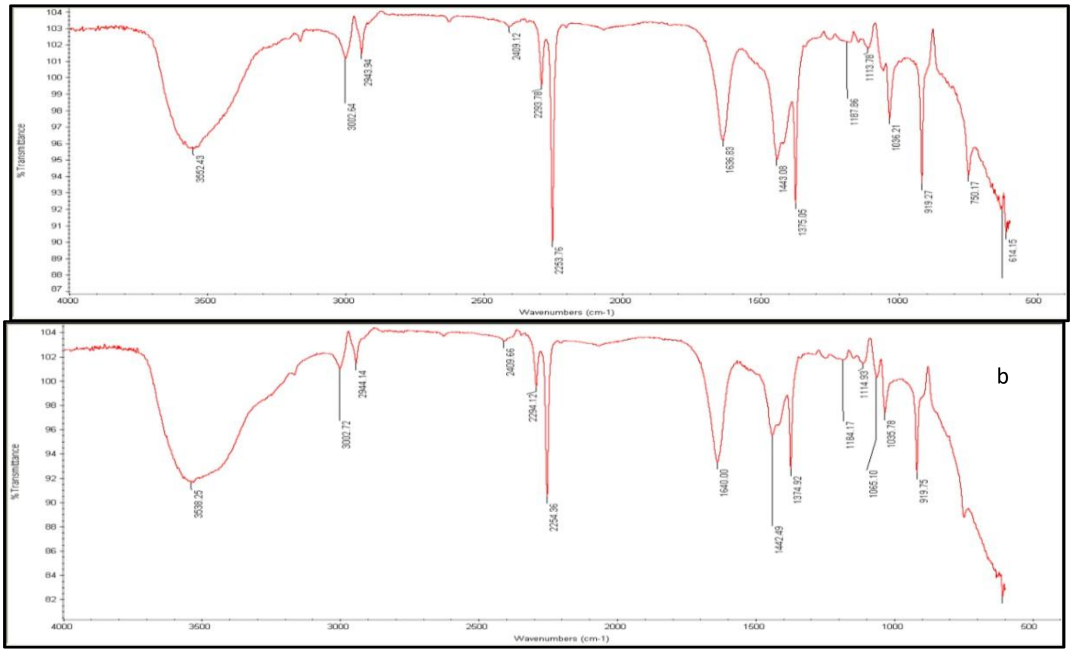

Fig 9. a- FTIR spectrum of TS-Cu (II) complex, b- FT-IR spectrum for AS-Cu (II) complex

Conclusion

Metal ion recognition and detection in biological and environmental specimens has received a lot of interest in recent years. Metal ions are detected using a variety of analytical techniques. Fluorescent chemical sensors have led researchers to increasingly desire anion or cation selective detection due to: high selectivity, high sensitivity (potentially single molecule detection), high spatial and temporal resolution, short response time, low cost and easily implemented instrumentation. The fluorescence approach is one of the developing techniques due to its simplicity, selectivity, and application to bioimaging. Because conventional approaches can only identify but not eliminate metal pollutants, the development of imidazole-based chemosensor. which able to identify and eliminate metal ions is very favorite. A new chemosensor based on- Debus-Radziszewski condensation (TS and AS) for sensing copper (II) were synthesized and characterized. TS and AS were turn-off fluorescent sensors for copper (II). The sensitivity of the detection method was as low as 0.09 and 0.28 μM for TS and AS respectively, that is slighter by far than the WHO's permissible limit (2 μM). Job’s method indicated the formation of a 2:1 ratio for (sensor: Cu (II)) complexes. The optical studies and the FT-IR spectra confirmed the sensing mechanism. As a result, this research donates new, simple, and highly sensitive copper sensors viable for application qualitatively and quantitatively by fluorescence approach. More research is being conducted to develop new chemosensor appropriate for sensing applications. In addition, using our two new chemosensors with real waste may decrease the effort and cost that could be paid for doing such pilot-scale work for the electrochemical treatment of wastewater. In the future, more research must be conducted to develop new chemical sensors suitable for sensing applications with high accuracy and effectiveness.

Data Availability

All data are incorporated in the manuscript.

Competing interests

All the authors declare that they have no competing interest.

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Author Contributions:

Author contribution: Faten M. Ali Zaini, Mashael T. Al-Sulami, Huda Al-Ghamdi interpreted, conceptualized, corrected and completed the final manuscript, while Faten M. Ali Zaini and Mashael T. Al-Salami made technical corrections, suggestions, and critically reviewed the manuscript over time and then submitted it.

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