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RESEARCH

Pyridine-2,6-Dicarboxylic Acid As a Facile and Highly Selective "Turn-Off" Fluorimetric Chemosensor for Detection of Cu (II) Ions in Aqueous Media

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Abstract

Copper metal is third most abundant trace element in human body. Determination of Cu (II) ions is a burning topic in field of environment protection and food safety because of its significant impact on ecosystem. In this study, 2,6-pyridine dicarboxylic acid (PDA) has been explored as "turn-off" florescent probe for florescent detection of Cu (II) ions. This sensor showed highly selective complexing ability towards Cu (II) ions. Addition of aqueous solution of Cu (II) ions remarkably quenched the fluorescence intensity of PDA while, on contrary, there was no any prominent fluorescence quenching interference on addition of various metal ions. The binding mode of PDA and Cu (II) ions was determined as stoichiometry of 1:1 and it was further confirmed by single crystal XRD analysis. Mechanisms of static and dynamic quenching were confirmed by stern–volmer plot. Limit of detection (LOD) and limit of quantification (LOQ) for Cu (II) ions was calculated as 3.6 μM and 1.23 μM respectively, which is far below the acceptable value (31.5μM) according to the World Health Organization. The use of the sensor for detection of Cu (II) ions in real samples in aqueous media was also performed.

Keywords Pyridine-2,6-dicarboxylic acid · XRD-structure · Turn off fluorescent probe · Cu (II) ions · Job's plot

Introduction

Water is essential element for existence of life on earth and wellbeing of life worldwide is suffering from problem of absence of clean water that is increasing day by day. The fast growing industrialization, population and urbanization cumulatively contaminating water [1]. Substantial addition poisonous materials like heavy metal, pesticides, pharmaceuticals in water is very harmful for survival of aquatic as well as human beings. Heavy metals impose severe effect on heath even if at very low concentration. Different metal and metalloids are considers as heavy metals for having atomic density greater than 4000 kg/m^3 [2, 3].

There are many metals that come in the category of heavy metals like copper, cadmium, zinc, chromium, arsenic, cobalt, titanium, strontium, tin, nickel, mercury, and lead. The heavy metals characterized as carcinogenic by environment protection agency and international agency [3]. From the range of heavy metal some elements like copper, zinc, nickel and iron are fundamental in the steady growth of different living species but on the other hand their amount above certain levels imposes detrimental effect on their survival [4, 5]. Copper is the third

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most abundant element that plays an important part in maintaining the homeostasis in life activity. Copper is frequently used in batteries, electronic chips, cell phones, paper industry, pesticides and as catalyst.

Copper (II) metal serve an essential part in maintaining different physiological processes like, neurotransmitter, formation of blood cells, metabolism of iron, detoxification of free radicals and as an antioxidant in bacteria and mammals. Apart from physiological importance, copper (II) ions also play critical part as a catalytic/cofactor for enzymes having cytochrome oxidase, tyrosinase and superoxide dismutase [6, 7]. Despite of the diverse beneficial aspects of copper metal in environmental as well as in living systems, a minor imbalance in copper concentration may impose several problems, includes severe neurodegenerative diseases like menke's disorder, stomach cramps, Alzheimer's, Wilson's, Parkinson's diseases, inflammation of pelvic diseases, hashimotos diseases, hematological manifestation, breast diseases and amyotrophic lateral sclerosis [8, 9]. Overuse of copper metal results into the production of combating oxygen species that stop cellular metabolism and liver cirrhosis [10]. Bending of bones, hair, arterial abnormalities [11] and anemia are caused by copper deficiency. Adults may take up copper between 4 to 400 mg/kg of the body weight daily [12]. The normal concentration of copper in human blood should also be in the range of 100–150 g/dl (15.7–23.6 µM) [13, 14] and the World Health Organization (WHO) has recommended 31.5 µM of copper (II) ions in drinking water [15].

The existing approaches for detection of copper (II) ions include the gravimetric and potentiometric method, atomic absorption spectrometry (AAS) [16], X-ray fluorescence spectrometry (XRF), inductively coupled plasma atomic emission spectrometry [17], electro-thermal atomic absorption spectroscopy, inductively coupled plasma mass spectrometry, anodic stripping voltammetry (ASV), cold vapor atomic absorption spectroscopy and ion exchange chromatography [18, 19]. Although these instruments can give result with higher accuracy and precision, but their high cost, intensive sample preparation, sophisticated apparatus and labor intensive behavior limits their applications for actual detection of real sample [20, 21]. As compared to other techniques, fluorescence spectrophotometer quenching method has been recognized as cheapest, easy to operate, selective and practicable for sensing of Cu (II) ions.

In comparison with other detection methods, fluorescent technique has attracted great interest of researchers because of its advantages such as simple operation, onsite analysis, high sensitivity, good selectivity and reproducibility [22, 23]. Various florescent chemosensors base on different fluorophore derivatives have been reported recently. Due to the parental paramagnetic nature, Cu (II) ions show fluorescence quenching on binding with the fluorophore of the sensors as coordination between the binding site of fluorophore and Cu (II) ions changes the electronic distribution of fluorophore.

In this work, PDA has been explored first time for fluorimetric detection of Cu (II) ions in aqueous media. When the emission intensity of the PDA solution in acetone was treated with various metal ions, the florescent intensity was quenched remarkably by Cu (II) ions. Single crystal XRD study of the Cu-PDA complex confirmed 1:1 binding ratio which was also corroborated by job's plot. Stern–Volmer study proposed dynamic as well as static quenching mechanisms. The limit of detection (LOD) and limit of quantification (LOQ) for Cu (II) ions were determined as 3.6 µM and 1.23 µM respectively. The fluorimetric analysis concluded that the probe PDA is an efficient tool for the detection of Cu (II) ions in aqueous medium without maintaining pH of the environment.

Experimental

Materials and Method

Pyridine-2,6-dicarboxylic acid and different salt including $BaCl_2.2H_2O$, $AlCl_3.6H_2O$, $MgSO_4.7H_2O$, $CoCl_2.6H_2O$, $CaCl_2.2H_2O$, $ZnSO_4.7H_2O$, $CuSO_4.5H_2O$, $NiSO_4.6H_2O$, $HgCl_2$, $MnSO_4.H_2O$, $FeSO_4.7H_2O$, Na_2SO_4, $SnCl_2.2H_2O$ and $CdCl_2.2H_2O$ were purchased from Sigma Aldrich. All salts were used without further purification. Pyridine-2,6-dicarboxylic (PDA) was a white crystalline powder with molecular weight of 167.12 g/mol and melting point of about 248 °C. Different solvents of reagent grade include DMSO, methanol, acetonitrile (ACN), dimethyl formamide (DMF), ethanol, acetone and water (H_2O) were obtained from RCI Labscan Limited and Sigma Aldrich. Elma E 30H Elmasonic sonicator was use for preparation of homogeneous solution of sensor and metals. For the fluorescence studies of sensor PDA Cary Eclipse fluorescence spectrophotometer, Agilent Technologies was use to conduct the fluorescence titration at room temperature. Fluorescence quenching of probe PDA was conducted in triplicate without using any buffer solution.

Sample Preparation

All the experiments described in this research paper were performed at room temperature (25°C) with distilled water. In fluorescence titration tests, stock solution of the sensor PDA (1×10^{-4} M) was prepared in acetone that was further diluted to 1×10^{-6} M. Stock solution (1×10^{-4} M) of all metal ions (Mn^{2+}, Fe^{2+}, Ca^{2+}, Ni^{2+}, Sn^{2+}, Cu^{2+}, Al^{3+}, Na^{+}, Ba^{2+}, Mg^{2+}, Co^{2+}, Hg^{2+} and Cd^{2+}) were prepared in distilled water.

Result and Discussion

Spectrometric Study of PDA Sensor

Selection of Solvent

For better observation of fluorescence titration of pyridine-2,4 dicarboxylic acid (PDA) with Cu (II) ions, solubility of the sensor PDA was checked in a range of solvents like DMSO, methanol, acetonitrile (ACN), dimethyl formamide (DMF), ethanol, acetone and water (H_2O). The sensor PDA showed maximum fluorescence intensity of 629 a.u. in acetone solvent, which was selected for further study.

Metal Selectivity of PDA Sensor

To explore the photo-physical properties of the sensor, fluorescence spectroscopy was used to find out the sensitivity of the sensor towards different metal ions. Stock solution (1×10^{-4} M) of the sensor was prepared in acetone that was further diluted to 1×10^{-6} M. The excitation spectra of sensor showed an excitation peak at 370 nm and emission peak at 428 nm with stock's shift of 58 nm and fluorescence intensity of 651 a.u. (Fig. 1).

In order to investigate the fluorescence response of sensor PDA towards different metal ions, fluorescence behavior under Carry-Eclipsed fluorescence spectrophotometer was observed. 1×10^{-4} M solution of different metal ions like Mn^{2+}, Fe^{2+}, Ca^{2+}, Ni^{2+}, Sn^{2+}, Cu^{2+}, Al^{2+}, Na^{+}, Ba^{2+}, Mg^{2+}, Co^{2+}, Hg^{2+} and Cd^{2+} prepared in distilled water was added to 2 mL solution of the sensor taken in cuvette. The emission spectrum was observed before and after the addition of metal ions. The fluorescence titration indicated that only copper (II) quenched the fluorescent intensity of sensor while other interfering metal ions did not show any prominent change (Fig. 2a). The results showed that sensor PDA is selective for detection of copper (II) ions and could be used for qualitative as well as quantitative detection of Cu (II) ions.

When 100µL of Cu (II) ions (1×10^{-4} M) was gradually added to the sensor solution, a steady decease in the emission intensity was recorded (Fig. 3a). A linear fitted graph was also obtained by plotting fluorescence intensity against concentration Cu (II) ions, which showed excellent correlation coefficient ($R^2=0.9973$) as shown in in Fig. 3b.

Binding Analysis by Job's Plot and Stern–Volmer Plot

For calculating the binding stoichiometry between the sensor and Cu^{2+} metal ions, continuous variation method was performed for job's plot analysis. 1×10^{-6} M solution of sensor was taken in different vials (4ml, 3.5 ml, 3 ml, 2.3 ml, 2 ml, 1.5 ml, 1v, 0.5 ml and 0 mL). Solution of Cu (II) ions with same concentration was added so that the total volume of the vials was 4 ml. The emission intensity of each solution was determined and a plot between fluorescence intensity and mole fraction showed 1:1 binding ratio (Fig. 5c).

Stern–Volmer analysis was performed to investigate the mechanism of the quenching. The fluorescence quenching can be divided into two patterns i.e. dynamic quenching and static quenching. In dynamic quenching, the excited substances come across quenchers in the course of diffusion. While, in static quenching a non-fluorescent complex is formed between quencher and fluorophore (Fig. 5d). The following equations (Eq. 1–4) can be utilized to determine stern–volmer constants [24].

$$I_o/I = 1 + K_{sv}[Q] \quad (1)$$

Equation for static quenching

$$I_o/I = 1 + K_s[Q] \quad (2)$$

Equation for dynamic quenching

$$I_o/I = 1 + K_D[Q] \quad (3)$$

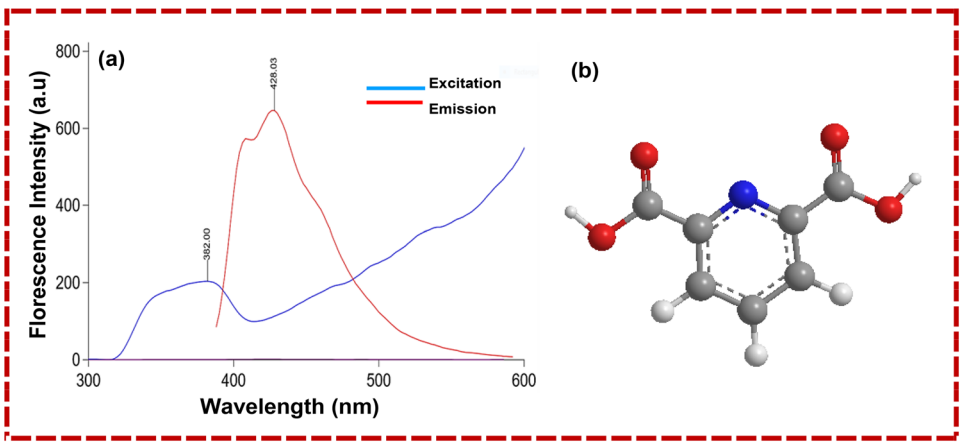

Fig. 1 **a** Excitation and emission spectrum of PDA sensor. **b** Structure of PDA

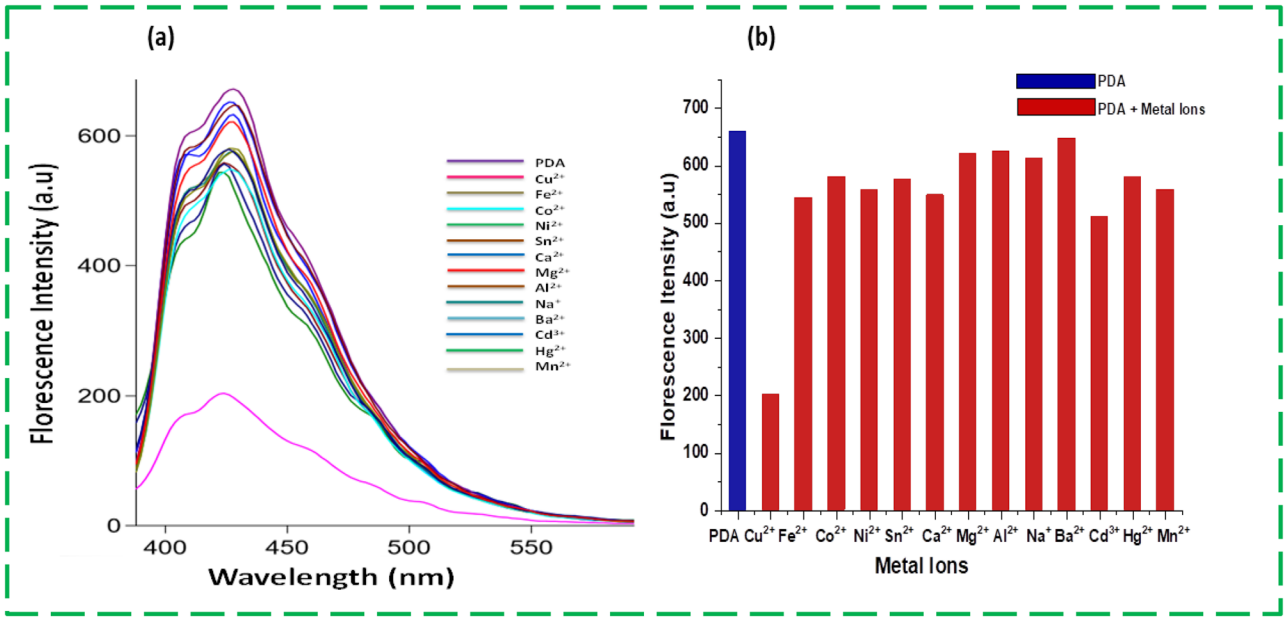

Fig. 2 **a** Fluorescent emission spectra of PDA SENSOR (acetone, 1×10^{-6} M) in presence of different metals ions. **b** Graphical representation of Fluorescence spectra of PDA in the presence of metal ions

For sum of static and dynamic quenching

$$I_o/I = (1 + K_s[Q])(1 + K_D[Q]) \quad (4)$$

where, I_o and I represent the fluorescence intensities in the absence and presence of Cu (II) ions respectively whereas [Q] represents the concentration of the Cu (II) ions. K_S and K_D are static and dynamic stern–volmer constants respectively. The experiment was performed by gradually increasing the concentration of Cu (II) ions into the sensor solution and a polynomial curve was obtained with a correlation's coefficient R^2 close to 0.96. The results illustrated both dynamic and static quenching mechanisms (Fig. 5b). From the equation-1 the stern–volmer constant was calculated as 1×10^5 mol^{-1} L.

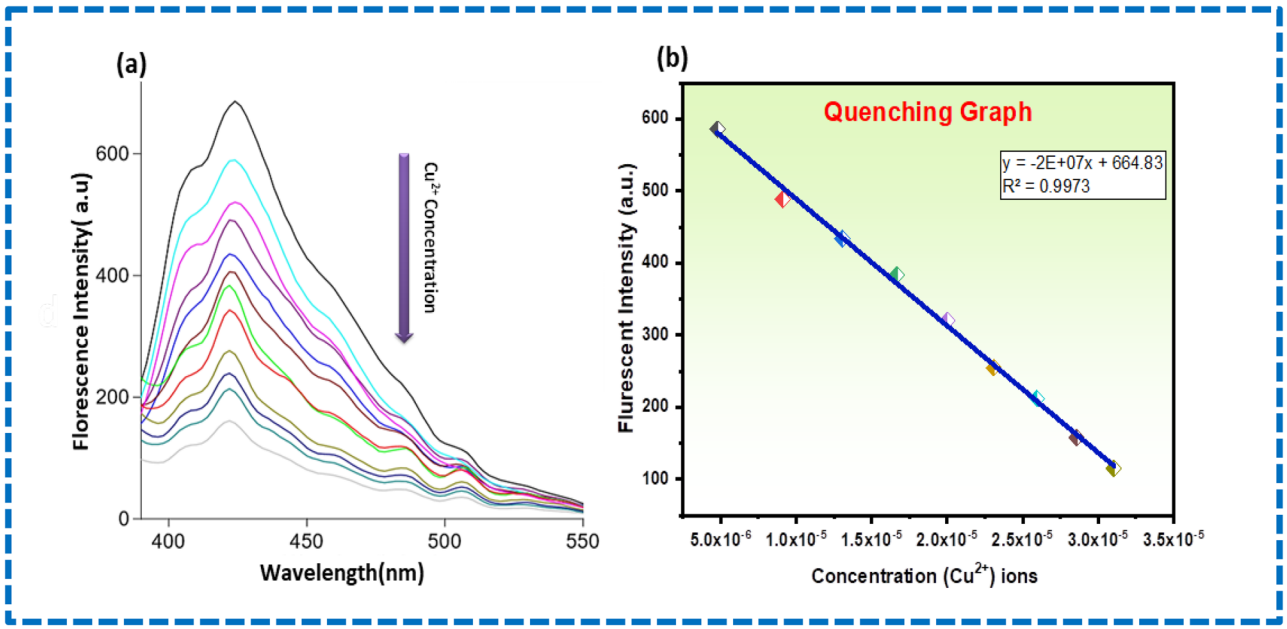

Fig. 3 **a** Quenching graph plotted of Fluorescence intensity of PDA against concentration of Cu (II) ions. **b** Graphical representation showing quenching of Fluorescence intensity of PDA against concentration of Cu (II) ions

Competitive Experiment with Other Metals

Competitive metals in the presence of Cu(II) were added in sensor PDA solution. The emission intensity pattern changes before and after addition of Cu(II) solution is displayed in Fig. 4. The competitive experiment justified that other metal ions had no considerable effects on emission intensity of PDA, which showed that PDA is an excellent fluorescent probe for sensing of Cu(II) ions in the presence of other common metal ions.

Limit of Detection and Limit of Quantification

For the determination of LOD and LOQ of sensor the sensor, a graph was plotted between I_{max}-I/I_{max}-I_{min} and concentration of Cu (II) ions (where I_{max} is emission intensity of the sensor in absence of Cu (II) ions, I_{min} is the minimum fluorescence intensity that was observed after adding Cu (II) ions into the solution and I is the fluorescence intensity at different copper (II) concentration). Following equations (Eqs. 5 & 6) were used to calculate limit of detection (LOD) and limit of quantification (LOQ).

$$\text{LOD} = 3.3 \times \text{SD of intercept/Slope} \quad (5)$$

$$\text{LOD} = 10 \times \text{SD of intercept/Slope} \quad (6)$$

A linear graph was obtained with correlation coefficient (R^2) of 0.9973. Limit of detection and limit of quantification were calculated as 3.6 µM and 1.23 µM respectively (Fig. 5a). According to the WHO guidelines, admissible value for the Cu^{2+} ion is drinking water is 31.5 µM which is much higher than that is reported in this work. Table 1 shows comparison of limit of detection of various reported fluorescent chemosensors.

Synthesis of Cu-PDA Complex

Copper chloride dihydrate (26.9 mg, 0.2mmol) was dissolved in 3 ml water while 2,6-pyridinedicarboxylic acid (31.44 mg, 0.11mmol) was dissolved in 3 ml acetone. Both metal salt and ligand solution were mixed and refluxed at 120 C^o for 1 h. The resultant solution was filtered to evaporate, after 5 days light blue crystals were found near the bottom of vial.

Single Crystal XRD of Cu-PDA Complex

Suitable crystal of complex was selected for data collection which was performed on a D8-QUEST diffractometer equipped with a graphite-monochromatic Mo-Kα radiation at 296 K. The structure was solved by direct methods using SHELXS-2013 [44] and refined by full-matrix least-squares methods on F^2 using SHELXL-2013 [45]. The H atoms of aqua ligands were located in a difference map and refined freely. The other H atoms were located from different maps and then treated as riding atoms with C-H distances of 0.93 Å. The following procedures were implemented in our analysis: data collection: Bruker APEX3 [46]; program used for molecular graphics were as follow: MERCURY programs [47]; GUI for other software related to structure solution: WinGX [48]. Molecular structure and infinite 1D layer of complex is shown in Fig. 6a and b respectively. Details of data collection and crystal structure determinations are given in Tables S1 to S3.

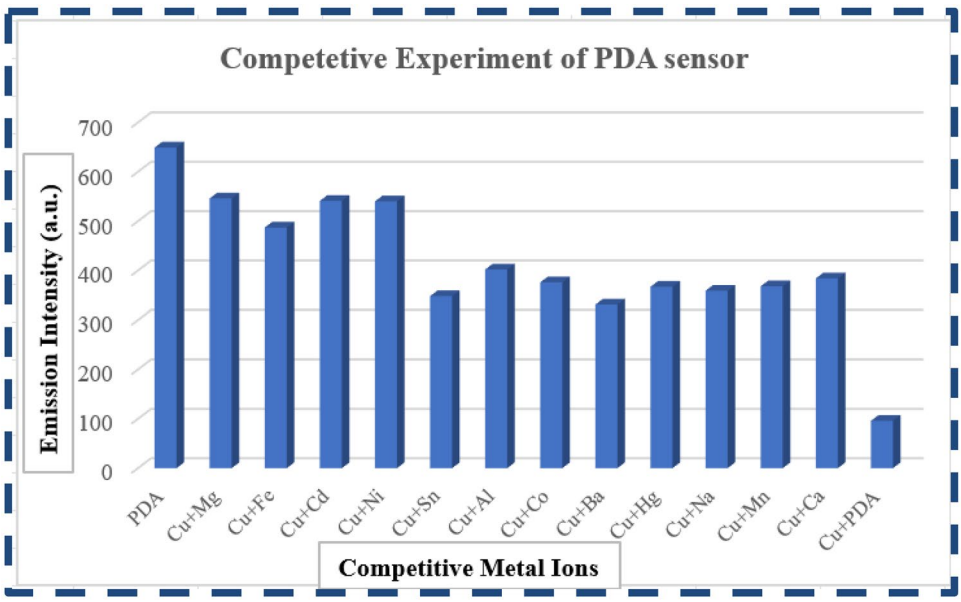

Fig. 4 Competitive experiment with other metals

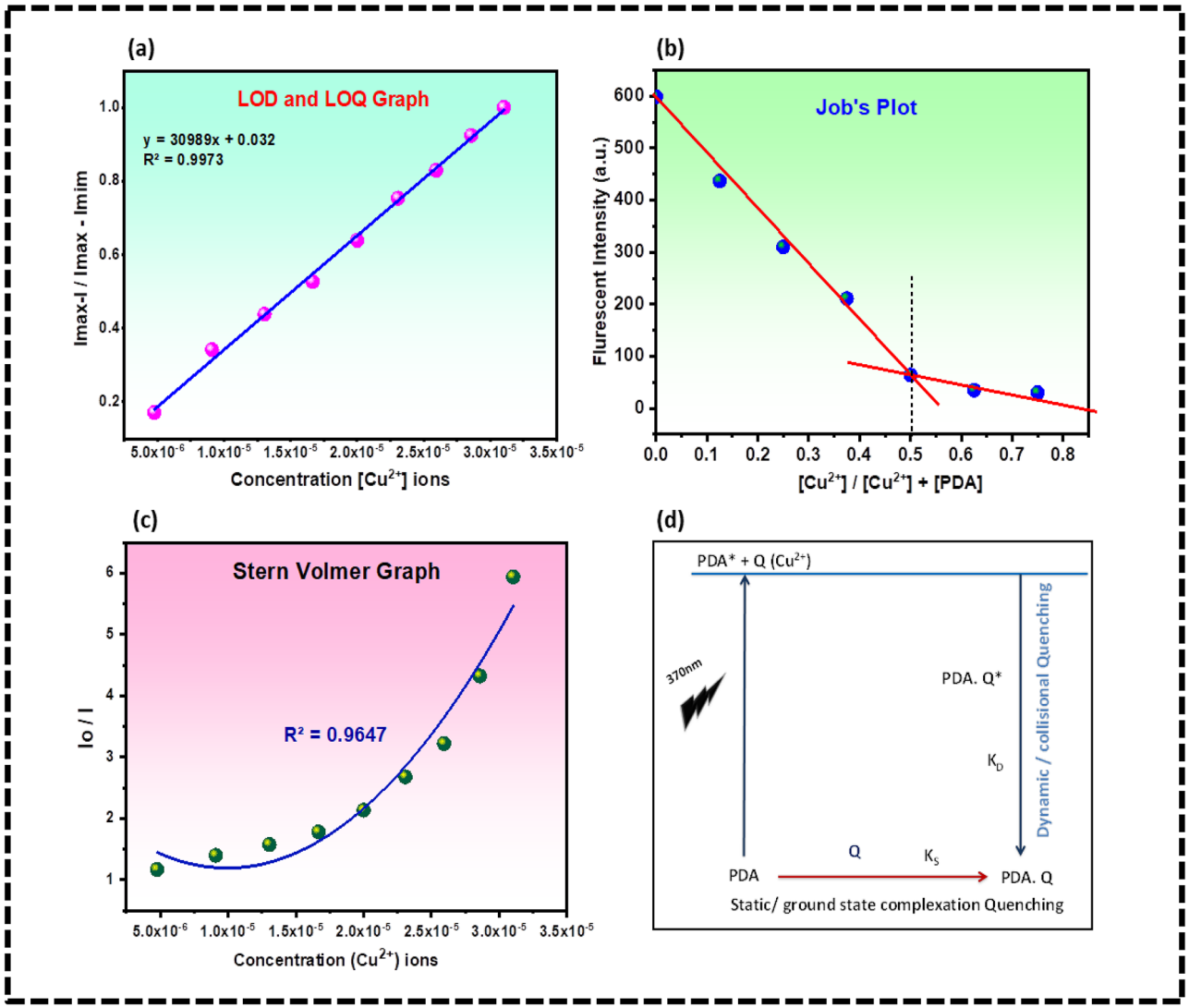

Fig. 5 **a** Graph plotted of I_{max}-I/I_{max}-I_{min} against concentration of Cu^{2+} for determination of LOD and LOQ for the Cu (II) ions using PDA **b** stern–volmer graph for quenching of ligand PDA in the presence of different concentrations of Cu (II) ions (λex = 370nm, λem = 429nm) **c** job's plot experiment of PDA with Cu (II) ions by plotting graph between intensity and $[Cu^{2+}]/[Cu^{2+}]+[PDA]$ **d** Illustration of quenching mechanism of fluorescence of PDA sensor by Cu (II) ions

Reversibility of PDA Sensor

Reversibility of PDA was revealed by measuring the emission intensities after addition of 100 µL (100 µM) of EDTA. After binding of Cu with EDTA, emission intensity of sensor was recovered. While for same experiment without EDTA emission was not recovered [49]. These outcomes clearly depicted the regeneration and reversibility of PDA sensor against copper.

Real Samples Application

PDA sensor was applied on real samples to check the practical suitability. Samples from four sources were collected. Tap water was collected from research laboratory 1, (RL1) Chemistry Department, drinking water from filtered water near Material Chemistry Laboratory, river water from Ravi River Lahore and waste water was collected from electrical wire manufacturing factory located in Lahore. PDA sensor containing 100 uL of known concentration was mixed in every collected real sample after filtration. Variation in fluorescence emission intensity was observed before and after spiking of 10 µM Cu(II) solution. The emission intensity at wavelength of 428 nm was recorded (Fig. 7) and % recoveries was calculated by evaluating emission intensity before and after quenching (Table S4).

Table 1 Comparison of present work with some reported fluorescent chemosensors

Fluorescent Chemosensor	Limit of Detection (μM)	Reference
1,2,4-aminonaphthol sulfonic acid	3.7	[24]
Spiropyran derivative fluorescent sensor	10	[25]
TPE-TSC	15.7	[26]
Triphenylamine and fluorobenzene groups (MZ-F)	3.9	[27]
ICT-basedfluorescentON	6.4	[28]
Benzothiazole-based chemosensor BTN	3.3	[29]
Asymmetric chemosensor	18	[30]
Tris (2-chloroethyl)amine/Salicyladehyde based receptor	4.6	[31]
A binol derivative in buffered solution	4.0	[32]
Isatin-Shiff base sensor	10	[33]
Rhodamine-Shiff base probe	3	[34]
Sugar and Rhodamine based probe	10	[35]
Rhodamine and Coumarin based sensor	2.3	[36]
Benzoxadiazole modified sensor	3	[37]
2-methylquinoline based derivate	8.7	[38]
Coumarin and Quinoline based sensor	0.1	[39]
Calix [12] arene and oxalylamido based derivatives	6	[40]
Thiazolothiazole based sensor	6.1	[41]
Trisphaeridine based derivatives	12.9	[42]
Shiff base containing ferrocenyl-1,3,4- thiadiazole	4.5	[43]
pyridine-2,6-dicarboxylic acid (PDA)	3.6	**Present Work**

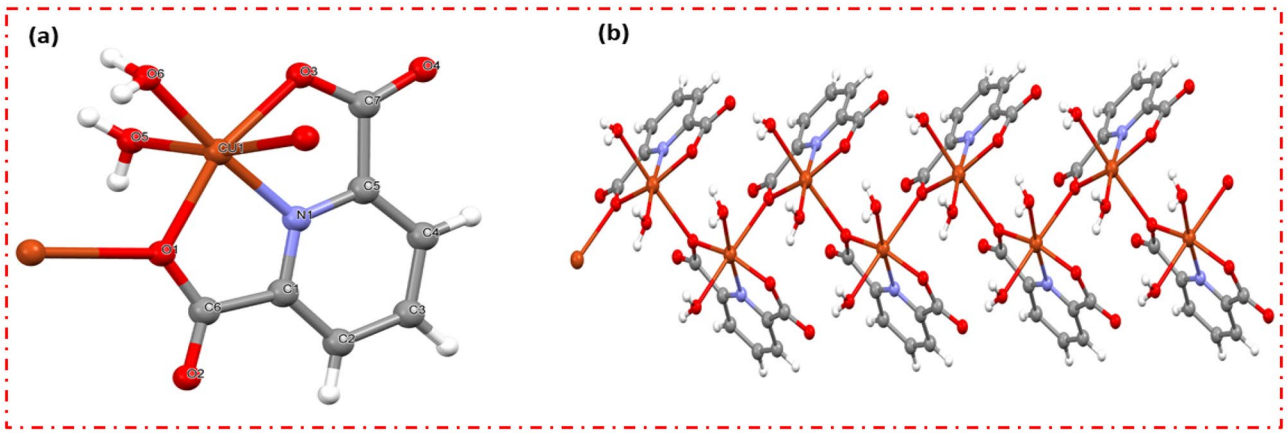

Fig. 6 **a** The molecular structure of complex showing the atom numbering scheme. **b** An infinite 1D layer in complex

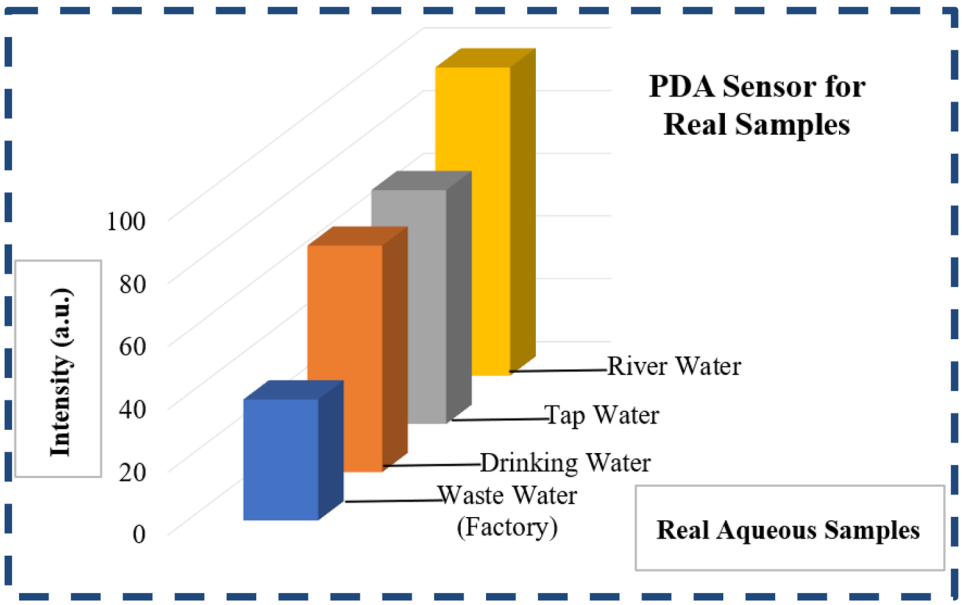

Fig. 7 Emission intensity quenching behavior of PDA sensor in real samples

Conclusions and Future Prospects

In summary, for the time we have reported pyridine-2,6-dicarboxylic acid (PDA) as a facile and efficient florescent sensor for detection of Cu (II) ions in aqueous environment. During fluorescence study, it was observed that emission intensity of the sensor solution was remarkably quenched (71%) by Cu (II) ions only in presence of various metal ions such as Mn^{2+}, Fe^{2+}, Ca^{2+}, Ni^{2+}, Sn^{2+}, Cu^{2+}, Al^{3+}, Na^{+}, Ba^{2+}, Mg^{2+}, Co^{2+}, Hg^{2+} and Cd^{2+}. job's plot and XRD analysis revealed that the sensor and Cu^{2+} ion has stoichiometry ratio of 1:1. Nature of fluorescence quenching was studied by Stern–Volmer plot which confirmed static as well as dynamic in nature. The sensor showed limit of detection (LOD) and limit of quantification (LOQ) as 3.6 µM and 1.23 µM respectively. It is concluded that PDA sensor may be used for detection of Cu (II) ions in real samples in aqueous media.

PDA as a sensor may not only contemplate as fluorophoric system for Cu(II) ions but might also serve as an electrochemical sensor for Cu(II) ions in electrochemical devices. It is also imperative to mention here one of the main area of future developments is the sensing of multiple metal ions at the same time. To fulfill such requirements new multifunctional sensors may be developed in future by synthesizing derivatives of the ligands to be selectively coordinated with more than one metal ions.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10895-024-03764-z.

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Author Contributions Javed wrote and revised the manuscript. Shahzad designed the study and proofed the manuscript. Shahbaz designed and synthesized the material. Bilal performed luminescence study. Sundas prepared samples and graphs. Onur performed a single XRD analysis. Khurram performed an experiment and prepared graphs. Hijaz Ahmad helped in characterization and analysis of data. Essam A. Al-Ammar critically proofed the manuscript.

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Availability of Data and Materials Data will be made available on request.

Declarations

Ethical Approval Not applicable.

Competing Interests The authors declare no competing interests.

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