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Selective colorimetric sensing of Cu^{2+} using triazolyl monoazo derivative

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ABSTRACT

Although the high sensitivity, high selectivity and fast response make emission (fluorescence) based technique as one of the most promising tool for developing the chemosensors for metal ions, the past few years have witnessed a demand for the absorption based chemosensors for paramagnetic heavy metal ions, especially Cu^{2+}. Being paramagnetic, Cu^{2+} leads to the low signal outputs ("turn-off") caused by decreased emission which may sometimes give false positive response, rendering the emission based technique less reliable for analytical purposes. Herein, we report synthesis and characterization of a hetarylazo derivative, characterized by a strong charge-transfer band which gets attenuated convincingly in the presence of Cu^{2+} leading to distinct naked-eye color change (yellow to purple), and to a lesser extent in the presence of Cd^{2+}, Zn^{2+}, Co^{2+}, Pb^{2+}, Fe^{2+}, Ni^{2+}, Fe^{3+} and Hg^{2+} for which the naked eye sensitivity was comparatively (w.r.t. Cu^{2+}) much less. No response was observed for the other metal ions including Li^{+}, Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Mn^{2+}, Ag^{+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, and lanthanides Ce^{3+}, La^{3+}, Pr^{3+}, Eu^{3+}, Nd^{3+}, Lu^{3+}, Yb^{3+}, Tb^{3+}, Sm^{3+}, Gd^{3+}. The proposed sensing mechanism has been ascribed to the stabilization of LUMO after complexation with Cu^{2+} and a 1:1 stoichiometry has been deduced.

1. Introduction

The transition metal cations play an important role in biological and environmental processes. Nowadays, the development of chemosensors for the detection of transition metal cations is a vibrant area of investigation due to the potential applications of these chemosensors as diagnostic tools in medical, physiological and environmental applications [1]. Among transition elements, after Fe^{2+} and Zn^{2+}, Cu^{2+} is third in abundance in human body and plays important roles in various physiological processes [2] such as hemoglobin biosynthesis, bone development and nerve function regulation [3]. On the other hand, presence of excess Cu^{2+}, due to its ability to cycle between multiple oxidation states, can pose serious threats to living organisms especially when it displaces other metal ions acting as cofactor in various enzyme catalyzed reactions [4]. It is also implicated in Alzheimer's disease, Prion diseases, Menkes and Wilson diseases, lipid metabolism and inflammatory disorders [5]. Copper, due to its properties like high electrical conductivity, chemical stability, germicidal efficacy and ability to form alloys with other metal ions [6], has been extensively used for the industrial, pharmaceutical and agricultural purposes. But at the same time, its widespread use is accompanied by a serious threat to environment which is attributed to its ionic form Cu^{2+} [7]. The diversity of its function, both beneficial and otherwise, has led to a strong interest in the development of selective Cu^{2+} probes for biological and environmental applications. Several techniques like electrochemical, atomic absorption, inductively coupled plasma atomic emission and piezoelectric quartz crystals [8], have been employed for sensing of metal ions but their use is limited owing to the requirement of expensive equipment, laboratories and time consuming procedures. However, spectrophotometric techniques such as emission and absorption have become popular for sensing cations owing to their ability to allow the 'naked-eye' detection, offering qualitative and quantitative information without above limitations. Although the fluorescent sensors are qualified with high sensitivity, high selectivity and fast response but for many heavy metal ions including Cu^{2+}, absorption spectrometry has shown edge over the fluorescence spectrometry because these ions, typically paramagnetic Cu^{2+}, often act as fluorescence quenchers [9,10], rendering low signal outputs ("turn-off") less advantageous for analytical purposes as sometimes they may give false-positive results. However, some "turn-on" chemosensors for Cu^{2+} have also been reported [11]. Consequently, the development of colorimetric chemosensors based on absorption changes accompanied by perceptible color changes, for heavy metal ions has emerged as an active area of significant importance. For these reasons and keeping in view the importance of heavy metal ions in day to day life, especially Cu^{2+}, Hg^{2+} and Fe^{3+}, the past few years have witnessed a large number of reports addressing their detection using chemosensors/chemodosimeters [12]. Most of the reported sensors for these metal cations are often structurally complicated and

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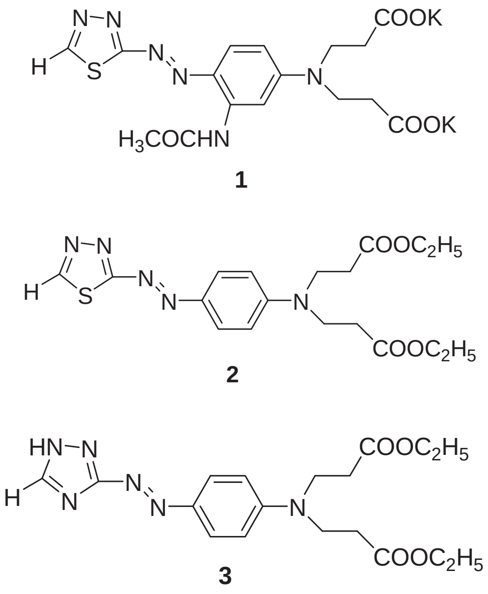


Scheme 1. Molecular structures of **1**, **2** and **3**.

require tedious synthetic procedures. Therefore, the development of simple and easy-to-make chemosensors is strongly demanded. Since our research group is involved in the design and synthesis of colorimetric chemosensors/chemodosimeters [13] based on absorption changes, our particular interest has been the synthesis of easy to make molecules with binding sites appropriate for heavy metal ions [14].

Hetarylazo derivatives are prised for their ease in preparation as well as intense absorptions in the visible region attributed to strong intramolecular charge-transfer (ICT) responsible for their intense colors. In view of the fact that systems exhibiting strong ICT can undergo modulation of their ICT on binding with analytes leading to perceptible color change, hetarylazo derivatives thus can prove to be ideal 'naked-eye' candidates for colorimetric chemosensors. Taking advantage of this, recently we have employed hetarylazo derivative **1** (Scheme 1) for the detection of Zn^{2+} [14a] and more recently, **2** for the simultaneous estimation of Hg^{2+} and Fe^{3+} [14c]. The latter poses one of the rare examples in the literature for multi-analyte detections where optical responses are not fully resolved. In the present investigation, we are reporting the hetarylazo derivative **3**, which detects Cu^{2+} selectively, over other metal cations.

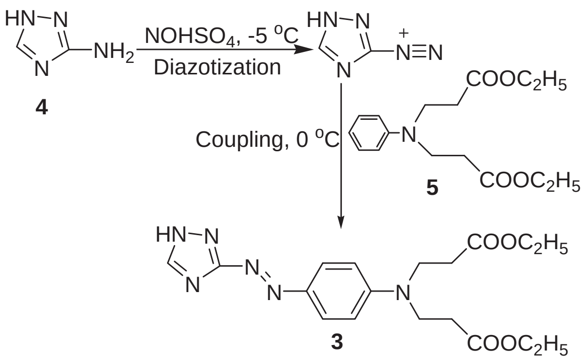
2. Experimental

2.1. Chemicals

3-Amino-1,2,4-triazole (**4**) was purchased from Sigma–Aldrich. Metal salts used in the spectrophotometric studies were of analytical grade and bought from Sigma–Aldrich. For the titrations, Li^+, Na^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Hg^{2+}, Pb^{2+}, Fe^{3+} were added as their perchlorates and K^+, Cu^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, Ce^{3+}, La^{3+}, Pr^{3+}, Eu^{3+}, Nd^{3+}, Lu^{3+}, Yb^{3+}, Tb^{3+}, Sm^{3+}, Gd^{3+} were added as their nitrates. The solvents used were of analytical grade and purchased from Thomas Baker.

2.2. Instrumentation

Mass spectra were recorded on Bruker Daltonics esquire 3000 spectrometer and WATERS-Q-Tof Premier-HAB213 spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded on JEOL-FT NMR-AL at 300 and 75 MHz, respectively, with TMS as internal standard using $CDCl_3$ as deuterated solvent. Data are reported as follows: chemical shift in ppm (δ), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet), coupling constant *J* (Hz) and assignment. IR spectra were recorded on Varian 660-IR Fourier-Transform spectrophotometer in the range 400–4000 cm^{-1} using KBr as medium. ESR was recorded on Bruker BioSpin Gn spectrometer. The purity of the solid products was checked by elemental analysis performed on Thermoelectron FLASH EA1112, CHNS analyzer. UV-visible spectral studies were conducted on SHIMADZU 1601 PC spectrophotometer with a quartz cuvette (path length, 1 cm). The cell holder of the spectrophotometer was thermostatted at 25 °C for consistency in the recordings. The absorption spectra were recorded between 1100 and 200 nm. The pH titrations were performed with the Equip-Tronics Digital pH meter model-EQ 610.



Scheme 2. Synthesis of **3**.

2.3. Procedure for synthesis of **3** (Scheme 2)

2.3.1. Synthesis of **5**

Aniline (4.66 g, 4.6 ml, 0.10 mol) and ethyl acrylate (25.03 g, 27.3 ml, 0.50 mol) in acetic acid (9.01 g, 8.6 ml, 0.30 mol) with catalytic amount of cupric chloride were heated at 130–140 °C in a sealed stainless steel container for about 12–14 h to obtain a black tarry mixture which was neutralized with aqueous sodium bicarbonate solution and extracted with ethyl acetate. The extract was washed with water, dried over anhydrous sodium sulphate and the solvent removed under reduced pressure to give the residue which was chromatographed over silica gel G (60–120 mesh) using 80% ethyl acetate/hexane as eluent.

2.3.2. Synthesis of **3**

Diazotization reagent (nitrosyl sulphuric acid) was prepared by adding sodium nitrite (0.83 g, 0.012 mol) to conc. sulphuric acid (14.7 g, 8 ml, 0.12 mol, 98%) at 30 °C and heating the stirred mixture to 60–65 °C to ensure complete dissolution of sodium nitrite. The reaction mixture was cooled to 5 °C followed by the addition of acetic acid (8 ml) and propionic acid (2 ml) with constant stirring. The temperature was then reduced to −5 °C, **4** (0.84 g, 0.01 mol) was added slowly and the whole reaction mixture stirred at the same low temperature for at least 2 h. The completion of diazotization was checked by TLC.

A solution of **5** (2.93 g, 0.015 mol) in acetic anhydride and acetic acid was added to ice/water mixture (200 g) in a beaker equipped with mechanical stirrer and pH meter. A pinch of sulphamic acid was added followed by the addition of diazonium salt liquor at 0–5 °C, over 1 h and the mixture was stirred for 3 h at ambient temperature. The pH was maintained in the range 1.5–2.0 during the addition using aqueous sodium hydroxide solution. The completion of reaction was checked by spotting the reaction mixture on a filter paper close to a spot of an alkaline aqueous solution of H-acid and detecting any color appearance at the interface of the two boundaries. No color indicated the completion of reaction. Finally the pH was raised to 4.0–4.5. **3** was extracted with dichloromethane, dried over anhydrous sodium sulphate, the solvent removed and the residue purified by column chromatography with silica gel G (60–120 mesh) using 60% ethyl acetate/hexane as eluent. Yield: 80%; Mp: 105 °C (Found: C, 55.18; H, 6.86; N, 21.29 $C_{18}H_{24}N_6O_4$ requires C, 55.67; H, 6.18; N, 21.65%); ν_{max}/cm^{-1}: 3451.65 (NH), 2967.08 (aromatic CH), 1729.93 (C=O), 1599.10 (N=N); ^1H NMR (300 MHz; $CDCl_3$; Me_4Si): δ 1.27 (6H, t, J = 7.2, $COOCH_2CH_3$), 2.66 (4H, t, J = 7.2, NCH_2CH_2), 3.80 (4H, t, J = 7.2, NCH_2CH_2), 4.16 (4H, q, J = 7.2, $COOCH_2CH_3$), 6.75 (2H, d, J = 9.3, aromatic *H*), 7.98 (2H, d, J = 9, aromatic *H*), 8.34 (1H, s, NHC*H*N); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si): δ 14.53, 32.78, 47.18, 61.32, 112.06, 127.01, 144.09, 147.14, 151.09, 171.95; m/z (EI): 411 (M^++23).

2.4. Isolation of copper complex of 3

The copper complex of **3** was obtained by mixing **3** (0.500 g, 1.29 mmol) and $Cu(NO_3)_2{\cdot}3H_2O$ (0.311 g, 1.29 mmol), both taken in acetonitrile, and stirring the mixture at room temperature for half an hour. The solvent was removed under reduced pressure and the solid complex was obtained which was recrystallized from dichloromethane-hexane. Yield: 70%; Mp: >300 °C (Found: C, 35.94; H, 4.23; N, 18.81 $C_{18}H_{28}N_8O_{12}Cu$ requires C, 35.31; H, 4.57; N, 18.31%); ν_{max}/cm^{-1}: 3432.72 (OH), 2972.40 (aromatic CH), 1727.76 (C=O), 1604.23 (N=N), 1098.05 (NO); m/z (EI): 634.5 (M^++23); $\mu_{eff.}$: 2.0 B.M.; ESR: two peaks; one at field value of *ca.* 3400 G ($\Delta Ms = \pm 1$) and other at 'half-field' value of *ca.*1700 G ($\Delta Ms = \pm 2$).

For copies of the NMR, EI Mass, IR and ESR, Fig. S1 in Supporting Information.

3. Results and discussion

3.1. Synthesis

The synthesis of hetarylazo derivative **3** (Scheme 2), began from receptor **5**, formed in quantitative yield from aniline and ethyl acrylate using catalytic amount of acetic acid–$CuCl_2{\cdot}2H_2O$ mixture. Finally **3** was obtained by using standard diazotization-coupling protocol between **4** and **5** (Scheme 2).

3.2. Cation-sensing studies

The chemosensor behavior of **3** with group I and II metal ions (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+} and Ba^{2+}), transition and heavy metal ions (Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+} and Fe^{3+}) and lanthanides (Ce^{3+}, La^{3+}, Pr^{3+}, Eu^{3+}, Nd^{3+}, Lu^{3+}, Yb^{3+}, Tb^{3+}, Sm^{3+} and Gd^{3+}) in $CH_3CN:H_2O$ mixture (9:1, v/v), was investigated by UV–vis absorption studies. Our preliminary qualitative experiments revealed that upon addition of one equivalent of the cations in water to the 3×10^{-5} M solution of **3** in acetonitrile, most of the cations did not perturb the absorption spectrum of **3**. Although the cations, Cd^{2+}, Zn^{2+}, Co^{2+}, Pb^{2+}, Fe^{2+} and Ni^{2+}, Fe^{3+}, Hg^{2+} caused a bathochromic shift of 44–74 nm and 84–94 nm, respectively, in the charge-transfer band responsible for the color of **3**, but this perturbation was not appreciated by the 'naked-eye' inspection (Fig. S2 in Supporting Information). Most significant spectroscopic (bathochromic shift of 119 nm) and visual response was observed on the addition of Cu^{2+} (Fig. 1) which is attributed to the high thermodynamic affinity of Cu^{2+} for typical N-donor ligands and fast metal-to-ligand binding kinetics [15]. Therefore we performed the quantitative titrations of **3** with Cu^{2+}.

The absorption spectrum of 3×10^{-5} M solution of **3** in CH_3CN is characterized by a very weak band at 270 nm (π–π^*) (ε_{max} = 8946.67 $m^2\,mol^{-1}$) and a strong band at 416 nm (n–π^*) (ε_{max} = 27,530 $m^2\,mol^{-1}$) (Fig. 1). The latter results in the yellow color of **3** and is attributed to internal charge-transfer (ICT) of the chromophore push–pull effect of the electron donating N,N-di(β-ethoxycarbonylethyl)aniline group and electron-withdrawing triazole moiety. Before investigating the chemosensing properties of **3**, the effect of pH variation on **3** was noted during titration of a 3×10^{-5} M solution of **3** with $NaHCO_3$ as well as HCl in the concentration range 0.1–1 M and 0.01–0.1 M, respectively. No significant change (Fig. 2) was observed in the wavelength position of the charge-transfer absorption band at 416 nm as well as in the color of **3** over the covered pH range (2.0–12.0). Thus, **3** demonstrated considerable stability to pH variation which is often considered an advantage for rapid monitoring of aqueous analytes in environmental or biological settings without resorting to buffered media.

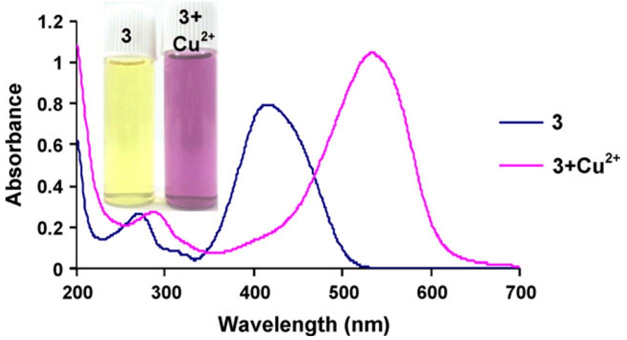


Fig. 1. UV–vis spectra of **3** (3×10^{-5} M, in CH_3CN) upon addition of Cu^{2+} solution (3×10^{-5} M, in H_2O). The $CH_3CN:H_2O$ ratio in the resulting solution is 9:1 (v/v).

In order to understand the binding characteristics of **3** with Cu^{2+}, the aqueous solutions of increasing concentration of Cu^{2+} (1×10^{-6} M to 5×10^{-5} M) were added to the 3×10^{-5} M solution of **3** in CH_3CN. Notably, stepwise addition of Cu^{2+} ions leads to the bathochromic shifting of the bands at 270 and 416 nm to 288 and 535 nm, respectively, which attained maximum intensity on the addition of 3×10^{-5} M (1 equiv.) solution of Cu^{2+} ions, after which no significant change was observed (Fig. 3). Well defined isosbestic points were observed at λ = 277, 343 and 472 nm during titrations, indicating the presence of only one spectrally distinct complex. The detection limit (DL) for Cu^{2+} ion with **3** was determined from the calibration curve of absorbance versus composition (Fig. 3(b)) and was found to be 1.36×10^{-5} M under the present conditions [16].

Since the ICT band in **3** originates from the electron-donation from HOMO, localized on the N,N-di(β-ethoxycarbonylethyl)aniline group to LUMO, localized on the triazole group, the considerable perturbation in this band on addition of Cu^{2+} can be ascribed to the stabilization of LUMO and a consequent decrease in energy gap between HOMO and LUMO (Fig. S3 in Supporting Information) caused by binding of Cu^{2+} to nitrogen atom of triazole and nitrogen atom of the –N=N– link

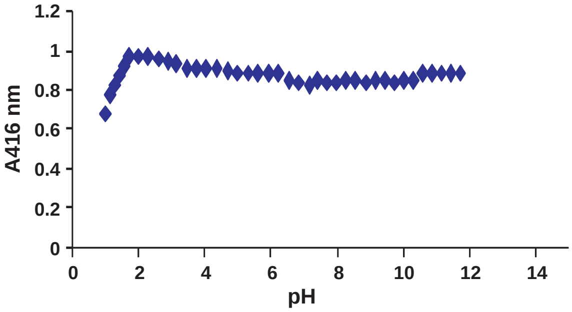


Fig. 2. Changes in the absorbance of **3** at 416 nm upon pH titrations with HCl (0.01 and 0.1 M) and $NaHCO_3$ (0.1 and 1 M).

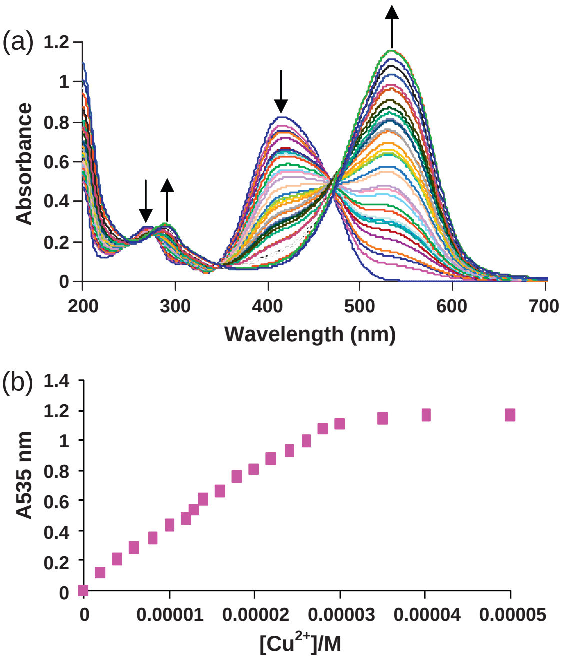
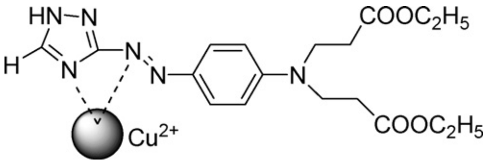


Fig. 3. (a) Changes in the absorption spectrum of **3** (3×10^{-5} M, in CH_3CN) upon addition of increasing concentration of Cu^{2+} solution (1×10^{-6} M to 5×10^{-5} M, in H_2O). (b) Changes in the absorbance of **3** at 535 nm as a function of Cu^{2+} added.



Scheme 3. Binding mode of **3** with Cu^{2+}.

(Scheme 3) causing the observed bathochromic shift in the ICT band. Bathochromically shifted ICT band is responsible for the perceptible change in color from yellow to purple.

Titration data of **3** with Cu^{2+} was fitted using HypSpec – a non-linear least-squares fitting programme [17]. It allowed the establishment of the stoichiometry (1:1) of the most stable species (**3**:Cu^{2+}) present in the solution with a binding constant $\log\beta_{1,1}=6.26$. The 1:1 stoichiometry was further confirmed by using the method of continuous variations (Job's plot) where the absorbance at 535 nm got to maximum when molar fraction of Cu^{2+} was 0.5 (Fig. 4). The formation of 1:1 (**3**:Cu^{2+}) complex is also supported by the isolation and characterization of the complex (*cf.* Section 2.4). Interestingly the ESR spectrum of the isolated complex is spread over a magnetic field of 0–6000 G suggestive of the polycrystalline nature of the sample. The appearance of two peaks, one at field value of *ca.* 3400 G (due to transition associated with ΔMs = ±1) and other at 'half-field' value of *ca.* 1700 G (due to transition associated with ΔMs = ±2) (Fig. S1 in Supporting Information), indicates that in addition to mononuclear 1:1 complex, some dinuclear 1:1 complex is formed [18].

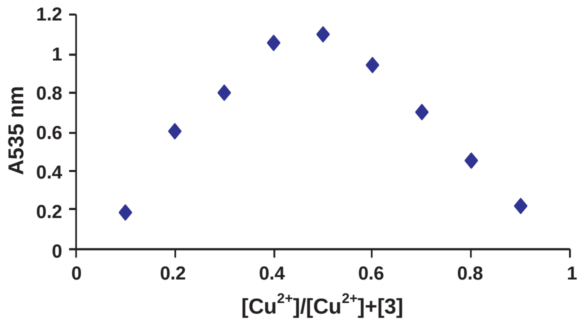


Fig. 4. Job's plot of Cu^{2+} complex formation. {$[Cu^{2+}]/[Cu^{2+}]+[\mathbf{3}]$} is the mole fraction of copper ion.

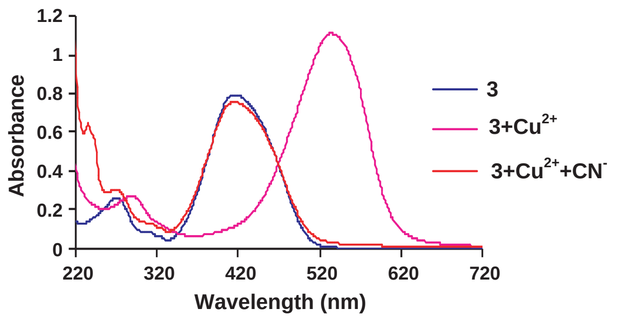


Fig. 5. Absorption spectra of **3** (3×10^{-5} M, in CH_3CN) before and after addition of Cu^{2+} solution (3×10^{-5} M, in H_2O) and reversal of change upon addition of cyanide solution.

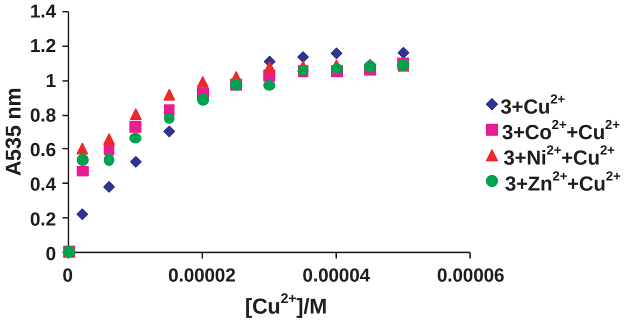


Fig. 6. Changes in the absorption spectrum of **3** (3×10^{-5} M, in CH_3CN) upon titration with increasing concentration of Cu^{2+} solution (1×10^{-6} M to 5×10^{-5} M, in H_2O) in the presence of other metal ions (3×10^{-5} M, in H_2O).

To check the reversibility of the sensing system, the solution of **3**:Cu^{2+} was decomplexed by adding the solution of NaCN (CN^- is known to form strong complex with Cu^{2+} [19]) which caused the absorption spectrum to revert to the original spectrum of **3** (Fig. 5), thus demonstrating the reversibility of the sensing process.

To further enhance the scope of the above sensing event, any possible interference by the immediate neighboring transition metal ions such as Co^{2+}, Ni^{2+} and Zn^{2+} was also ruled out by performing the titrations of **3** (3×10^{-5} M, in CH_3CN) with Cu^{2+} in the presence of 3×10^{-4} M aqueous solutions of these cations. The titrations were monitored at 535 nm and the results are depicted in Fig. 6. It can be seen that the absorption band at 535 nm remains

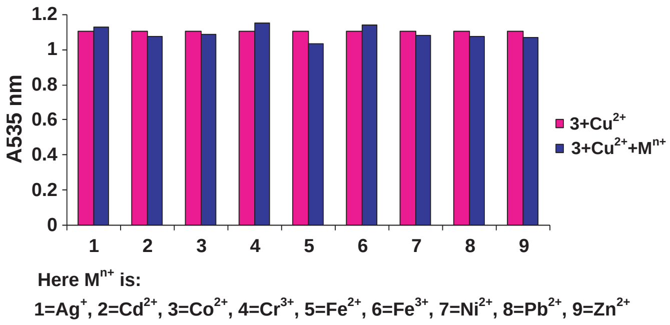
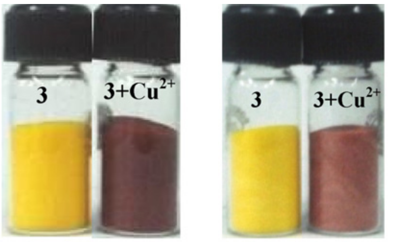


Fig. 7. Comparative absorbance of **3** (3×10^{-5} M, in CH_3CN) at 535 nm in the presence of Cu^{2+} ion (3×10^{-5} M, in H_2O) and Cu^{2+} plus other metal ions (3×10^{-4} M, in H_2O).



(a) 60-120 Silica **(b) 100-200 Silica**

(i) **1x10^{-5} M Cu^{2+} (0.33 equiv)** (ii) **2x10^{-5} M Cu^{2+} (0.67 equiv)** (iii) **3x10^{-5} M Cu^{2+} (1 equiv)**

Fig. 8. Demonstration of colors of **3** (3×10^{-5} M) with Cu^{2+} (3×10^{-4} M) in (a) 60–120 silica mesh and (b) 100–200 silica mesh. (c) Photographs of **3** in the presence of aqueous solutions of (i) 1×10^{-5} M, (ii) 2×10^{-5} M and (iii) 3×10^{-5} M Cu^{2+} ions.

unperturbed throughout the titration of Cu^{2+} in the presence of these cations. The preference of **3** for Cu^{2+} over Co^{2+}, Ni^{2+} and Zn^{2+} can be attributed to the lower values of their binding constants ($\log \beta_{1,1} = 4.0$, 5.41 and 5.77, respectively for Co^{2+}, Ni^{2+} and Zn^{2+}) as compared to Cu^{2+}. The other commonly occurring cations showed negligible interference during the similar competition experiments (Fig. 7).

Since triazole ring can also function as an anion binding motif [20], therefore we too investigated the anion sensing properties of **3** for the different anions such as $CO_3{}^{2-}$, $HCO_3{}^{-}$, $SO_3{}^{2-}$, $SO_4{}^{2-}$, $HSO_3{}^{-}$, $HSO_4{}^{-}$, I^-, Br^-, Cl^-, F^-, $H_2PO_4{}^{-}$, $HPO_4{}^{2-}$, $PO_4{}^{3-}$, $NO_2{}^{-}$, $NO_3{}^{-}$, CN^-, OH^-, acetate and citrate (added as Na^+ salts). However, no significant changes were observed in the absorption spectrum of **3** upon the addition of above mentioned anions.

Binding of **3** with Cu^{2+} could not be monitored by NMR studies due to the paramagnetic nature of Cu^{2+} which leads to the broadening of the peaks.

4. Practical application

The sensing of Cu^{2+} by **3** worked also when it was supported on silica. Thus, a solution of **3** in CH_3CN (25 mL, 1×10^{-3} M) was added to silica (60–120 and 100–200 mesh, 2.50 g, colorless), stirred for 1 min and the solvent was removed to get dark yellow silica (Fig. 8a and b) which was treated with a solution of Cu^{2+} (2 mL, 3×10^{-4} M) in double distilled water. An instant color change from yellow to pinkish purple was noticed. Solvent was removed under reduced pressure and silica dried in oven to obtain pinkish purple silica. Since the color change was rapid and clearly detected, the sensor **3** can be used for practical applications [21]. The detection limit within visual color changes in 3×10^{-5} M solution of **3** is allowable to 1×10^{-5} M level Cu^{2+} ions (Fig. 8c).

5. Conclusions

In the present investigation, we have developed a simple yet selective colorimetric chemosensor **3** based upon absorption changes which detects Cu^{2+} over other metal ions. The ICT band of the chromophore shows a remarkable red shift when Cu^{2+} gets bonded to the electron acceptor moiety of the chromophore. Since the absorption spectrum of **3** remains unperturbed in the pH range (2.0–12.0), it can be used for rapid monitoring of aqueous Cu^{2+} without resorting to buffered media. The fact that **3** can be prepared in multi gram quantities using simple laboratory preparative method, the practicability of the method is obvious.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2010.11.072.

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