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Selective Cation Recognition by *p*-Tetranitrocalix[4]arene

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Abstract

The present study explores the copper selective complexation character of 5,11,17,23-tetranitro-25,26,27,28-tetrahydroxycalix[4]arene (*p*-TNC4) among a series of different alkali, alkaline earth and transition metal ions, i.e. Li^+, Na^+, K^+,Cs^+ Mg^{2+}, Ba^{2+}, Hg^{2+}, Cd^{2+}, Pb^{2+}, Co^{2+} Ni^{2+} and Zn^{2+} using absorption spectroscopic technique. *p*-TNC4 shows pronounced discriminative specificity towards Cu^{2+} even the interference study of other co-existing ions also proved this selectivity. Furthermore, the solvatochromic effect, effect of acid (acetic acid), alkali (piperidine) on spectra, response time measurement and the stability of *p*-TNC4-Cu^{2+} complex in MeCN has also been investigated. The stoichiometric analysis (i.e. Jobs plot) reveals that *p*-TNC4 forms 1:1 host-guest complex with Cu^{2+}.

Keywords: Macromolecule; Solvatochromic features; Binding affinity; Metal ions; Non-covalent chemistry.

Introduction

The advancement of sensor materials for selective recognition of toxic metal ions is particularly important, since these metal ions retain harmful effects for humans as well as the environment [1]. Among the series of other essential metal ions, Copper is the borderline heavy metal ion and has significant role in human body because; it is the third profuse vital trace element in the human body after Fe^{2+} and Zn^{2+}. However, an excessive ingestion of copper can damage liver or kidney [2] and even in trace amount, it also affects the microorganisms [3]. Moreover, free copper is significantly injurious to aquatic life, both acutely and chronically. It founds mostly as Cu^{2+} in natural or wastewaters [4,5]. A number of analytical methods were explored and optimized for the specific and sensitive detection of Cu^{2+} [6-13]. Absorption spectroscopy still plays an important role because of convenient handling, less expensive, fast response characteristics. Several studies regarding Cu^{2+} detection by synthesized colorimetric/chromogenic sensors have been reported [14-25]. Among the synthetic materials, calixarenes are enthralling group of third generation macromolecular compounds obtained from the condensational product of phenol-HCHO precursors which have been widely employed as the selective trapping agents for ionic species [26, 27]. The calixarene molecules offer an easier way of introducing a variety of specific functionalized chelating groups either at its narrow rim or wide rim and thus possess different shapes and conformational mobility. These macromolecular receptors have proved to be highly selective for the detection of both cations and anions [28-31]. Besides this, for the selective recognition of Cu^{2+} ion researchers have reported different derivatives of calixarene. For example, Liu, *et al* [32] has reported a new Fe^{3+} and Cu^{2+} selective sensor based on calix[4]arene frame work. Park, *et al*

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[23]. has reported Calix azacrown ethers for copper(II) ion-selective electrode. Joseph *et al* [33] has synthesized Benzothiazole appended calix[4]arene with amide functionalized binding sites for Cu^{2+} ion. He has also prepared an amide derived bis(2-picolyl)amine derivative of calix[4]arene which shows fluorescent switch-on sensing properties for Cu^{2+} in CH_3OH(aq.) [34]. Recently, Yilmaz and coworkers [35] has synthesized pyrene appended calix[4]arene based derivatives as fluorescent sensing probe and found a selective sensing response toward Pb^{2+} and Cu^{2+} ions, as a result of conformational variations. Qazi et al [36] has also synthesized fluorescent sensor based on calixarene framework for specific recognition of Cd^{2+} and Cu^{2+}, However, still opportunities exist for the exploration of synthesized fluoroionophores for the selective and sensitive detections of guests.

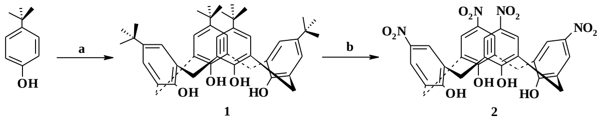
The current work is the modified and extended form of our earlier studies [36-38] for the exploration of the selective behavior of calixarene derivatives for toxic ions. In this study, we describe the analytical application of *p*-tetranitrocalix[4]arene (*p*-TNC4) as an chromoionophore and explored its selective complexation efficiency toward Cu^{2+} ion.

Material and Methods

All the solvents and reagents used were of analytical or equivalent grade, purchased from Alfa Aesar (Germany), Merck (Darmstadt, Germany) and were used without further purification. Melting points were determined on a Gallenkamp (UK) apparatus in a sealed capillary tube. Thermo Nicollet AVATAR 5700 FT-IR spectrometer was used for recording IR spectra using KBr pellets in a wide spectral range, *i.e.* 4000-400 cm^{-1}. Elemental analyses were performed using a CHNS instrument model Flash EA 1112 elemental analyzer. UV-visible spectral studies of *p*-TNC4 (Scheme 1) and its metal complexes were performed on a Perkin Elmer Lambda-35 UV-visible double beam spectrophotometer using standard 1.00 cm quartz cells [39, 40]. Analytical TLC was performed on pre-coated silica gel plates (SiO_2, Merck PF_{254}).

Synthesis

The *p*-tetranitrocalix[4]arene (*p*-TNC4) **2** was synthesized [41] from compound **1** as shown in Scheme **1** according to well known published procedure using stoichiometric amount of suitable base [42]. Different techniques such as thin layer chromatography, IR, FT-IR and CHNS analysis were employed for the confirmation of structure and purity of compounds.



Scheme 1. **A schematic representation showing synthesis of calix[4]arene derivatives (a) HCHO/NaOH (b) $CH_2Cl_2/HNO_3/H_2SO_4$.**

Synthesis of p-TNC4-Cu^{2+} complex

For FT-IR experiments, *p*-TNC4 and nitrate salt of Cu^{2+} (1:1) were dissolved in 10 ml of acetonitrile (MeCN) and then mixed followed by continuous stirring up to 24 hrs. The resulting solution was poured in Petri dish to evaporate the solvent; it takes up to 48 hrs. The *p*-TNC4-Cu^{2+} complex was then dried in vacuum oven at ambient temperature.

Analytical procedure

General procedure for UV-visible study

Stock solutions of (1.00 mM) *p*-TNC4 and metal nitrate salts were prepared in MeCN. Test solutions were prepared by placing 100 μL of *p*-TNC4 into a cuvette, adding appropriate aliquot (10 eq.) of each metal stock, and diluting the solution up to 3.5 mL with MeCN. Same equivalents (10 eq.) were taken for the interfacial study of co-existing ions into a solution containing *p*-TNC4-Cu^{2+} complex [39].

Stoichiometric ratio of the metal and ligand in the complex

In order to determine the stoichiometry of *p*-TNC4-Cu^{2+} complex in a MeCN, continual variation method was used. The solutions were prepared by mixing equimolar concentration

(2.8×10^{-5} M) of both components in different ratios varying from 1:9 to 9:1. Then the absorbance was noted [43, 44].

Results and Discussion

Solvatochromic effect

Solvatochromic behavior of particular ligand has intensive importance while exploring analytical parameters. It helps in choosing appropriate solvent or mixture of solvent to achieve maximum chromogenic sensing response. Red shifting "positive solvatochromism" occurs in increasing polarity of a solvent, which may be ascribed to the stabilization of excited state of a particular ligand by a polar solvent in comparison with ground state. A vice versa or "negative solvatochromism" may be attributed to solvent with low polarity [45]. In pursuit of all above mentioned factors, spectral investigations of *p*-TNC4 were evaluated in various solvents (Fig. 1) like CH_3CN (MeCN), $CHCl_3$ (CF), CH_2Cl_2 (DCM), CH_3OH (MeOH), dimethylformamide (DMF) and dimethylsulfoxide (DMSO) at 2.8×10^{-5} M. In MeOH, *p*-TNC4 shows low response may be due to its partial solubility therefore, it has been discarded.

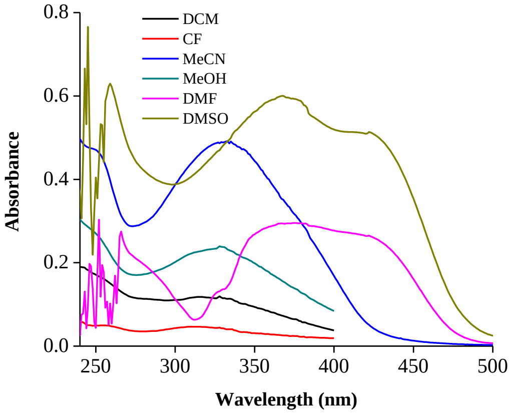


Figure 1. **UV-visible absorption spectra of *p*-TNC4 (2.8×10^{-5} M) in different solvents.**

All of solvatochromic spectral measurement have been summarized as follows: The *p*-TNC4 shows red shifts in DMSO, DMF and MeCN with respect to CF and/or DCM which can be ascribed to the π→π* and n→π* transitions arise as a result of solvents with different polarities. Moreover, since *p*-TNC4 possesses nitro groups that may interact with these polar solvents and gives blue shifting in less polar solvents like CF, DCM.

The order of polarity of solvents used in this study is DMSO>DMF>MeCN> MeOH> CF>DCM. The low polarity solvents (*i.e.* CF, DCM) show hypsochromic shifts in comparison to polar solvents. The UV-visible spectra of *p*-TNC4 in DMSO and DMF were appeared much noisy (>275 nm) due to the absorbance of UV-light by these solvents. Thus in present study, MeCN was selected for complexation on the basis of stability and solubility of *p*-TNC4 as well as nitrate salts of the metals [46].

Since change in the nature of medium in which compound is dissolved may cause significant effect on its spectral behavior because; interactions between solute and solvent molecules are disturbed and thus, the shapes of bands and their positions are changed. In this study, the equilibrium state of *p*-TNC4 was evaluated by the influence of acid and/or alkali (i.e. acetic acid and/or piperidine) in MeCN. As seen from absorption spectra, there is no prominent sign of variations observed on addition of appropriate amount of acid (acetic acid) to the solution of *p*-TNC4 (Fig. 2). While the addition of piperidine in the solution causes hypochromic effect along with red shifting was observed (~10 nm). The red shifting specifies that *p*-TNC4 may exist in a dissociated form in MeCN due to deprotonation of phenolic hydrogen as shown in Fig. 2 [47].

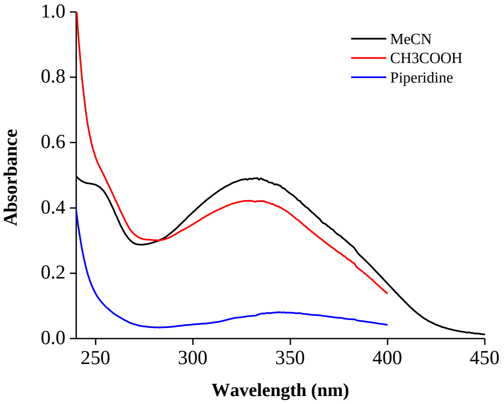
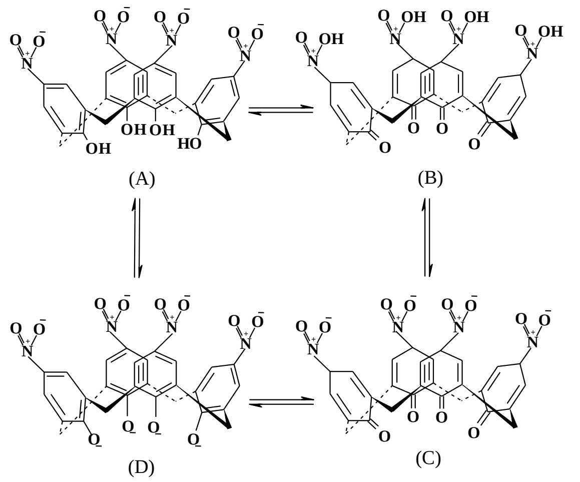


Figure 2. **UV-visible spectra of *p*-TNC4 (2.8×10^{-5} M) before and after the addition of piperidine and acetic acid in MeCN.**



Scheme 2. **The tautomeric and anionic forms of *p*-tetranitrocalix[4]arene (*p*-TNC4).**

Complexation studies

p-TNC4 was chosen for the evaluation of its chromogenic sensing behavior towards toxic metal ions because this macromolecule bears nitro groups as binding sites along with macrocyclic effect. Furthermore, ease of its synthesis may also prove to be a promising candidate for the exploration of selective complexation studies with metal ions. Thus, different experiments were carried out in order to evaluate the selective behavior of *p*-TNC4 for complexation with metals.

UV-visible study

From the solvatochromic spectral measurements of *p*-TNC4 and on the basis of stability, solubility of nitrate salts of selected metals and to ascertain effective complexation without the formation of aggregates; MeCN was selected as the best and preferable solvent for complexation study [48].

To explore the binding efficiency of *p*-TNC4 towards various metal ions, in first instance, UV-visible spectroscopic technique was applied. The complexation ability of *p*-TNC4 was examined in acetonitrile (2.8×10^{-5} M) with the addition of selected metal ions such as Li^+, Na^+, K^+, Cs^+ Mg^{2+}, Ba^{2+}, Ag^+, Hg^+, Hg^{2+}, Cd^{2+}, Pb^{2+}, Co^{2+} Ni^{2+}, Zn^{2+} (2.8×10^{-4} M) and Cu^{2+} (8.4×10^{-5} M). A UV-visible spectrum of *p*-TNC4 after the addition of metal ions is shown in Fig 3. The UV-visible spectral analysis of free ligand (*p*-TNC4) show a strong band at 335 nm as a result of n → π* transition (Fig. 3). Usually, in complexation phenomena the bands are shifted to shorter or longer wavelengths (blue or red shift) after the addition of metal ion in to the ligand solution, however, the high intensity (hyperchromic shift) of the bands after complexation also confers complexation formation. After complexation, pronounced changes in the absorption spectra of *p*-TNC4 have been observed, which show that *p*-TNC4 has remarkable affinity toward the metal ions and in particular with Cu^{2+} ions. Since, Cu^{2+} forms stronger complex with *p*-TNC4 by showing significant differences in the absorption spectra through the disruption at 311 nm could be assigned to oxygen-metal charge transfer absorption [49]. Finally, all these spectral results obtained from titration experiments suggest that further investigations may be carried out only with Cu^{2+} ions.

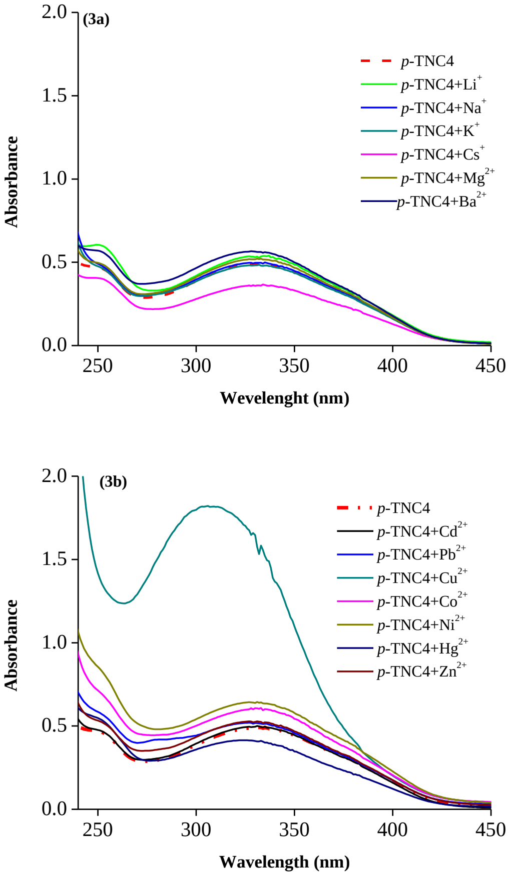


Figure 3. **UV-visible absorption spectra of *p*-TNC4 in MeCN (2.8×10^{-4} M) upon addition of 10 mol equiv. of different (i.e. (a) alkali and alkaline (b) transition) metal ions except Cu^{2+} (i.e.3 mol eq.).**

In an attempt to observe the Cu^{2+} selective chromogenic sensing response of *p*-TNC4; various equivalents of Cu^{2+} salt were added in to the solution of *p*-TNC4 and absorption spectral profile versus Cu^{2+} ion concentration was obtained, which inferred that linear response of absorption intensity increment with respect to Cu^{2+} ion concentration (Fig. 4).

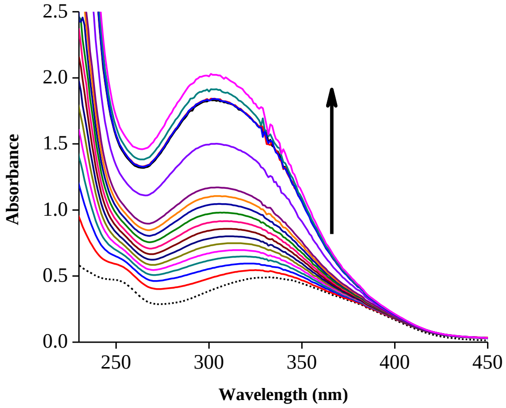


Figure 4. **UV-visible absorption spectra of *p*-TNC4 (2.8×10^{-4} M) upon addition of Cu^{2+} (0-12 eq.) in MeCN. Inset showing the ratiometric calibration curve as a function of Cu^{2+} concentration in equiv.**

Method of continuous variation was also applied to determine the stoichiometry of *p*-TNC4-Cu^{2+} complex. For this purpose, titrations experiment were carried out by taken a solution of *p*-TNC4 and Cu^{2+} of same concentrations with different volumes. Fig. 5 represents a graph of absorbance versus mole fractions. All spectral measurements were examined at 311 nm with 0.5 as maximum point of the mole fraction which can be attributed to 1:1 stoichiometry of *p*-TNC4-Cu^{2+} complex.

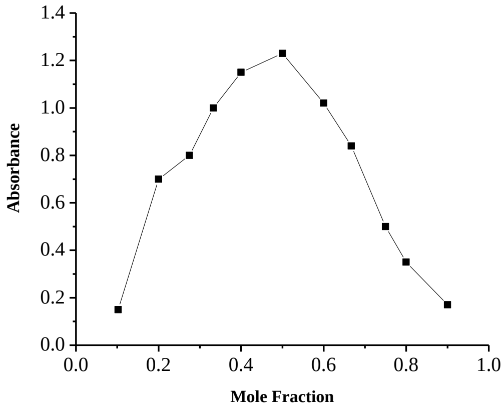


***Figure 5*. Job's plot of *p*-TNC4-Cu^{2+} complexation.**

Response time and the stability of p-TNC4-Cu^{2+} complex in MeCN

It has also been aimed to examine the stabilities of *p*-TNC4 and *p*-TNC4-Cu^{2+} complex with respect to time. Therefore, the UV-visible spectra of *p*-TNC4-complex in MeCN were instantly taken after continuous UV irradiation with the passage of 0-75 min with the interval of 5 min [50]. The results confirm the stability of *p*-TNC4 in MeCN as there were no spectral variations observed with the passage of time (Fig. 6). Furthermore, *p*-TNC4 responds very fast on addition of Cu(NO$_3$)$_2$·3H$_2$O, it shows enhancement in absorption of a band followed by significant blue shifting in the region of 311-335 nm that occurs very fast and remains stable (Fig. 6).

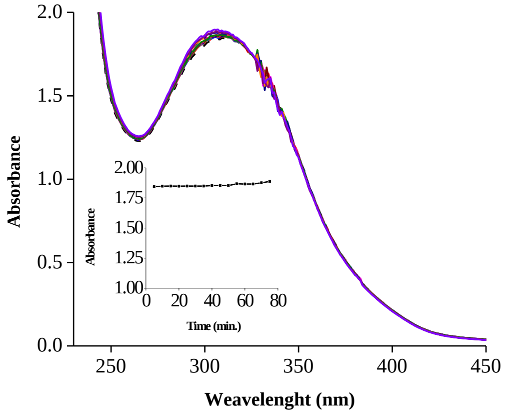


Figure 6. **UV-visible absorption spectra of in MeCN (2.8×10^{-5} M) upon continuous irradiation of UV light.**

In addition to electron donating nature of oxygen containing nitro functionality and the electron with drawing characteristics of cations, the ionic interaction could be favorably considered and it has been expected that *p*-TNC4 can easily trapped the metal ion with soft or borderline metal ions. Thus, in order to recognize the complexation process, different analytical investigation were performed and it has been found that *p*-TNC4 forms complex with Cu^{2+} ion selectively. From the observations it can be deduced that the nitro groups containing binding sites are neither so hard as in oxides, which prefer hard metal ions, i.e. alkali or alkaline earth metal ions nor so soft to prefer soft transition metal ions such as Ag^{+} or Hg^{2+}. But here in this case, the nature of oxygens in the nitro groups present at the upper (wide) rim of calixarene moiety may be intermediate, i.e. it matches with the nature of Cu^{2+} ion that is a borderline metal ion. Thus, the observations from obtained results confer to follow the Pearson's 'hard and soft acids and bases' concept [51] since the presence of borderline nature containing binding sites where nitro groups shows high binding tendency towards more polarizable/borderline transition metal ions especially Cu^{2+}. Moreover, the literature review shows that the Cu^{2+} forms stable square planner complexes with macrocyclic compounds especially calix[4]arene with four ligating sites most probably arranged in square planer geometry [37,38,45]. The proposed interaction of *p*-TNC4 with Cu^{2+} is shown in Fig. 7.

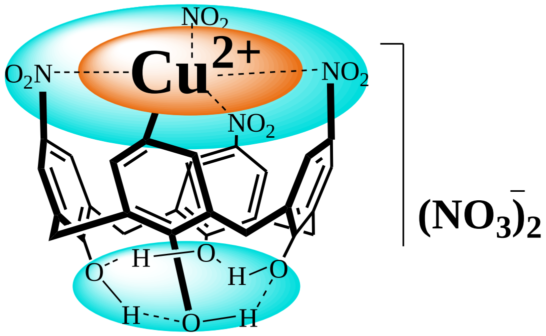


***Figure 7.* Representation of proposed interaction between *p*-TNC4 and Cu^{2+} ion.**

Interference study of competing ions

The studies regarding foreign cations (Li^+, Na^+, K^+, Cs^+ Mg^{2+}, Ba^{2+}, Hg^{2+}, Cd^{2+}, Pb^{2+}, Co^{2+} Ni^{2+} and Zn^{2+}) for the binding affinity of *p*-TNC4 (1:3:5 ratio of *p*-TNC4:Cu^{2+}:interfering metal ions) show that there is no prominent interference of other co-existing ions. However, a negligible effect on the copper selective complexation ability of *p*-TNC4 has been noticed when Ni^{2+}, Cd^{2+}, or Zn^{2+} (Fig. 8) have been added. Finally, all aforementioned observations deduced that the *p*-TNC4 is selective for Cu^{2+} due to well-matched ionic radii of Cu^{2+} with cavity size of *p*-TNC4, as well as nature and geometry of both the host and guest already discussed in the previous section.

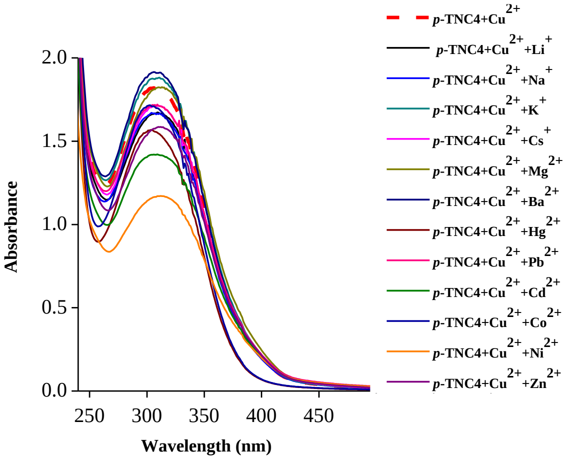


***Figure 8.* Interference study of *p*-TNC4-Cu^{2+} complex with selected metal ions (5 eq) in MeCN.**

Conclusion

In the present study, the complexation potential of *p*-TNC4 was found to be highly specific towards Cu^{2+} among a wider series of metal ions owing to greater spectral variations in terms of both intensities as well as wavelength in absorption spectra of *p*-TNC4 (free) and *p*-TNC4-Cu^{2+} complex. Cu^{2+} selective complexation has also been confirmed by FT-IR analysis. Furthermore, structural features of *p*-TNC4 that encompass four $-NO_2$ containing trapping functionalities seem to be perfect according to geometry of molecule in terms of size, arrangement for the adjustment of Cu^{2+}. It also surmises the significance of pre-organization in designing receptor. From the careful examination of results, it has been deduced that this research work may be considered as an assessment for the sensing of Cu^{2+}.

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