

A Facile Colorimetric Method For Ultra-Rapid And Sensitive Detection of Copper Ions In Water

Lei Chen

Chengdu University of Information Technology <https://orcid.org/0000-0002-3564-7918>

Yan Li

Chengdu University of Information Technology

Ping Sun

Chengdu University of Information Technology

Hualin Chen

Southwest Minzu University

He Li (✉ lihecd@gmail.com)

Chengdu University of Information Technology

Jun Liu

Southwest Minzu University

Ziyue Chen

Tongji University

Bin Wang

Yibin University

Research Article

Keywords: Colorimetric detection, Copper ions detection, Anions enhanced, ultra-rapid detection

Posted Date: December 6th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-1133764/v1>

License:  This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

A facile colorimetric method for ultra-rapid and sensitive detection of copper ions in water

Lei Chen^a, Yan Li^a, Ping Sun^a, Hualin Chen^{b,*}, He Li^{a,*}, Jun Liu^b, Ziyue Chen^c, Bin Wang^d

^a College of optoelectronic engineering, Chengdu University of Information Technology, Chengdu, 610225, China.

^b Key Laboratory of Basic Chemistry of the State Ethnic Commission, School of Chemistry and Environment, Southwest Minzu University, Chengdu, 610041, China.

^c School of Ocean and Earth Science, Tongji University, Shanghai, 200092, China.

^d Faculty of Quality Management and Inspection & Quarantine, Yibin University, Yibin, 644000, China.

* Corresponding author.

E-mail address: aofly@163.com (Hualin Chen); lihedc@gmail.com (He Li)

Abstract

It is of great meaning to develop a facile, reliable and sensitive method to detect copper ions in water. In the study, a facile method has been developed for rapid and sensitive detection of Cu²⁺. An interesting phenomenon has been observed that 3,3',5,5'-tetramethylbenzidine (TMB) ethanol solution can be extremely fast passed from colorless to yellow once Cu²⁺ ions are added. It easily occurs to us that Cu²⁺ can be quantitatively determined via the absorbance at 904 nm of the color changed TMB solution. More importantly, some specific anions (Cl⁻, Br⁻) can significantly enhance the absorption intensity. Under the optimized experimental conditions, this method exhibits a good linear response range for Cu²⁺ from 0.5 to 100 μM, with the detection limit of 93 nM. Moreover, the possible detection principle has been explored. It is worth mentioning that the color change can be clearly observed by naked eyes for the detection of 1 μM Cu²⁺, which is far below the threshold limit of Cu²⁺ in drinking water suggested by World Health Organization. It means that this method possess great promise for on-site Cu²⁺ detection.

Keywords: Colorimetric detection; Copper ions detection; Anions enhanced; ultra-rapid detection

1. Introduction

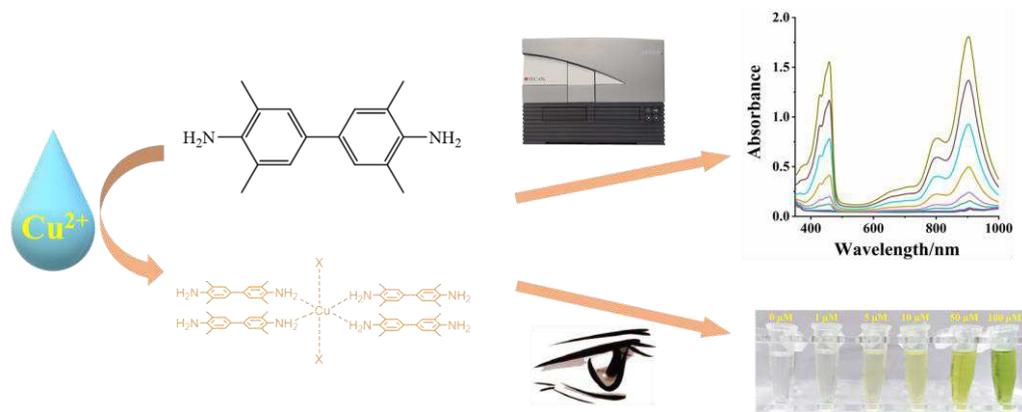
As an essential trace element of human body, Cu²⁺ possess some positive effects, such as participating in the formation of various enzymes, cell metabolism and various biochemical processes [1,2]. But, excessive Cu²⁺ cause negative effects on human health and environment, especially the amplification effect of the biological chain, which can be enriched multiple times and eventually enter the human body [3,4], and caused irreversible gene mutations, oxidative stress and serious damage to the central nervous system [5-7], such as notorious Alzheimer's disease, Parkinson's disease and Prion disease.^[8-10] Thus, the detection of Cu²⁺ is of great significance not only for healthcare issue but also for environment monitoring [11,12]. The World Health Organization (WHO) suggested that the Cu²⁺ content of drinking water should be less than 31.5 μM [13].

In past researches, amount of traditional methods has been developed to determine metal ions, include atomic absorption spectroscopy,[14] inductively coupled plasma spectroscopy,[15] and inductively coupled plasma mass spectrometry,[16] etc. these methods provide satisfactory results for the detection of metal ions, but the significant limitation in practical applications is expensive instruments, complicated operations, time-consuming inspections, etc. However, in practical applications, especially rapid in-site detection of metal ions, there is an urgent need to develop a rapid, reliable, low-cost and simple determination methods, such as electrochemical methods and optical sensing methods. Compared with mature electrochemical methods, optical sensing has attracted much attention due to its inherent advantages and larger research space. [17] It is especially suitable for in-situ analysis of metal ions.[18-20] Among of them, colorimetric sensors are more popular than fluorescent sensors.[21]

Recently, many colorimetric methods have been reported, and most of them exhibited excellent performance for Cu²⁺ detection.

Recently, many colorimetric methods have been reported, and most of them exhibited excellent performance for Cu²⁺ detection. In 2020, Lan Wang et al synthesized a salamo-like chemical probe HL and the sensitive detection of Cu²⁺ ions was successfully realized.[22] At the same year, Willsingh Anbu Durai and Andy Ramu reported a colorimetric method that hydrazone based dual-responsive ratiometric/colorimetric chemosensor for highly selective and sensitive detection of Cu²⁺ ions in dimethyl sulfoxide (DMSO) solvent, the detection limits are found to be 5.8 μM.[23] In a word, colorimetric detection of Cu²⁺ usually leads to the change of probe absorbance directly or indirectly through coordination. Therefore, it is of great significance to develop signal molecules that can strongly coordinate with Cu²⁺ and cause strong changes in absorbance or other properties (such as enzyme activity) of the detection system.

3,3',5,5'-tetramethylbenzidine (TMB) as a chromogenic substrate has been widely used in the colorimetric analysis,[24-28] but it is rarely used for direct detection of metal ions in the absence of H₂O₂. In this study, we found that Cu²⁺ can coordinate with TMB in ethanol within seconds and results stable color and



Scheme 1 The process and mechanism of Cu^{2+} detection.

absorbance change (**Scheme 1**). Especially, it was discovered for the first time that specific anions have an enhanced effect on absorbance, and rigorously studied its mechanism. Which can provide inspiration for the development of other metal ion detection methods and at the same time can also be applied in enzyme linked immunosorbent assay based on TMB to improve its color reaction stability and shorten detection time.[29,30]

2. Experimental sections

2.1. Materials and apparatus

CuCl_2 , CuBr_2 , $\text{Cu}(\text{NO}_3)_2$, CuSO_4 , $\text{Fe}(\text{NO}_3)_3$, FeCl_2 , $\text{Cd}(\text{NO}_3)_2$, $\text{Cr}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, AgNO_3 , CoCl_2 , NaF , NaCl , KBr , NaNO_3 , Na_2SO_4 , ethanol (EtOH), dimethyl sulfoxide (DMSO), 3,3',5,5'-tetramethylbenzidine and acetonitrile (CH_3CN) were analytical grade and were purchased from Aladdin. CuCl , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and hexavalent chromium ion standard solution were purchased from Chengdu Shuoboyanchuang Science and Technology Co., LTD.

The UV-Vis absorbance spectra were recorded using a Spark-Tecan multimode microplate reader, and the FT-IR spectra were obtained by a PerkinElmer Lambda 950 spectrometer. The X-ray photoelectron spectroscopy (XPS) analysis was performed by a ThermoFisher Thermo Scientific K-Alpha+ spectrometer. The ^1H NMR data were collected by an Avance III 400 MHz Digital NMR spectrometer.

2.2 Detection of Cu^{2+}

Some certain of KBr was dissolved in 1 mL of sample solution ($\text{pH} = 7$) amount at room temperature. Thereafter, 20 μL of this aqueous solution was added into 96-well microplate, followed by the addition of 180 μL deoxygenated TMB ethanol solution with mild vibration, and the UV/Vis spectra were recorded by microplate reader immediately. In order to get the best detection performance towards of Cu^{2+} , some specific factors have been optimized, which include solvents, solvent concentration, TMB concentration, pH and detection time.

3. Results and discussion

3.1. Detection conditions optimization

As observed, Cu^{2+} in ethanol solution can be easily coordinated with TMB and then result a yellow solution with three obvious absorption peaks in the range of 350-1000 nm, of which the absorption intensity at 904 nm is the largest. As a result, the absorption intensity at 904 nm was used for the ongoing study (**Figure 1A**).

In order to achieve the ideal detection performance towards Cu^{2+} , some factors have been optimized. Solvent is an important factor which can affect the coordination of metal ions and ligands.[31,32] The absorption intensity of 100 μM Cu^{2+} detected in various solvents were assayed and shown in **Figure 1B**. It is clear to see that Cu^{2+} have more strong

coordination with TMB in ethanol and acetonitrile. Considering the safety and easy-using, ethanol was chosen as the solvent for Cu^{2+} detection. Also, the influence of solvent concentration on the detection of Cu^{2+} was investigated. **Figure 1C** shows the absorbance at 904 nm for the detection of 100 μM Cu^{2+} in TMB solution with different volume fraction (ϕ) of EtOH. The increase of volume fraction caused a rapid raise of absorbance. The possible reason is that the coordination ability of TMB has been reduced by the conjugated structure of the benzene ring and amino group of TMB. The coordination of TMB and Cu^{2+} will be competed by H_2O molecular and decrease with the increase of water content. Obviously, when water content increase above 10%, the absorbance will decrease sharply. Therefore, ethanol volume fraction was optimized as 90%.

The effect of TMB concentration has been evaluated via measuring the absorbance values at 904 nm which were produced by the coordination of Cu^{2+} and TMB under different TMB concentrations. As shown in **Figure 2A**, the absorbance will raise following the increase of TMB concentration and reach maximum value at 2 mg/mL. Hence, 2 mg/mL TMB ethanol solution was used as the optimized concentration. In addition, as revealed in **Figure 2B**, when the pH is within 4-8, the absorbance remain at high value without obvious change, which demonstrated that the method is applicable over a wide pH range. But when the $\text{pH} < 4$ or $\text{pH} > 8$, the absorbance values decrease rapidly. The reason is that when the solution is under acidic conditions, the complexation of Cu^{2+} with amino groups is subject to H^+ competition, while at higher pH ($\text{pH} > 8$), OH^- will react with copper ions to form $\text{Cu}(\text{OH})_2$. For convenient use, $\text{pH} = 7$ was selected for Cu^{2+} detection. The time-dependent absorption of Cu^{2+} and TMB coordination was studied. As shown in **Figure 2C**, the absorbance can reach a maximum value in an extremely short time just within seconds and remain stable for a relative long time. This result demonstrated that the present method has faster performance than many other reported Cu^{2+} optical chemosensors.[33-35]

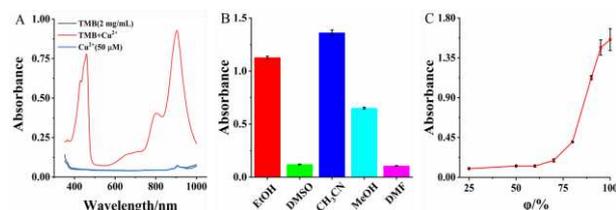


Figure 1 A) UV absorption spectrum of the coordination of Cu^{2+} with TMB; B) Effect of solvents on absorbance intensity [$\text{Cu}^{2+} = 100 \mu\text{M}$]; C) Relationship between volume fraction and absorbance, [Cu^{2+}] = 100 μM .

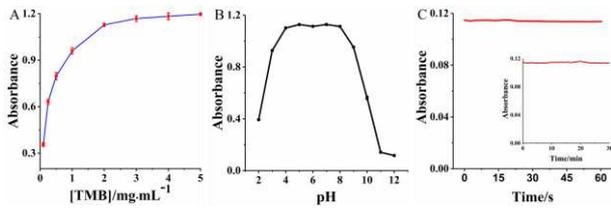


Figure 2 A) Effect of TMB concentration on absorbance values, $[Cu^{2+}] = 100 \mu M$; B) Effect of pH on the detection of Cu^{2+} $[Cu^{2+}] = 100 \mu M$; C) Time-dependent absorbance of Cu^{2+} and TMB ethanol solution $[Cu^{2+}] = 5 \mu M$. All these absorbance were recorded at 904 nm.

3.2 Effect of anions on the detection of Cu^{2+}

In some previous studies, the presence of anions will affect the detection of metal ions.[36,37] In order to assess the effect of anions on Cu^{2+} detection, the absorbance of various Cu^{2+} salts complexation with TMB at the same concentration were measured. As presented in **Figure 3A**, after complexation, the absorbance of detection solutions using $CuBr_2$ or $CuCl_2$ is much higher than that of $CuSO_4$ or $Cu(NO_3)_2$. Then, to further explore the influence of anion concentration on the detection of Cu^{2+} , various anions with different concentration have been added into the detection system and the corresponding absorbance were measured. The effects of different anions on Cu^{2+} detection in ethanol can be revealed by **Figure 3B**. Obviously, only Br^- and Cl^- can greatly increase the absorption intensity of the detection solution. And Br^- has more enhancement effect than Cl^- . In the range of 0-20 mM, the absorbance increases rapidly and reaches the maximum value at 8 mM of Br^- . It is happy to see that Br^- can be applied to detect various Cu^{2+} salts. With the enhancement effect of Br^- , the absorbance of detection system for detecting various copper salts with same concentration can reach almost the same level after adding sufficient bromide ions (**Figure 3C**). In a word, the addition of Br^- has two positive effects: (1) it can improve the detection sensitivity of Cu^{2+} ; (2) it can eliminate the influence of other anions on the detection of Cu^{2+} .

3.3. Analytical Performances for Cu^{2+}

To evaluate the performance of the proposed strategy for the qualitative detection of Cu^{2+} , under the optimized experiment conditions, the absorbance of TMB complexed with various concentrations Cu^{2+} were recorded (**Figure 4A**). Three absorption peaks can be observed at 460nm, 804nm and 904nm, respectively. Moreover, the absorbance at the three observed peaks all have a good linear relationship with the concentration of Cu^{2+} in the range of 0.5-100 μM (**Figure 4B**). Among them, the absorbance values at 904 nm is most sensitive for Cu^{2+} detection, and the

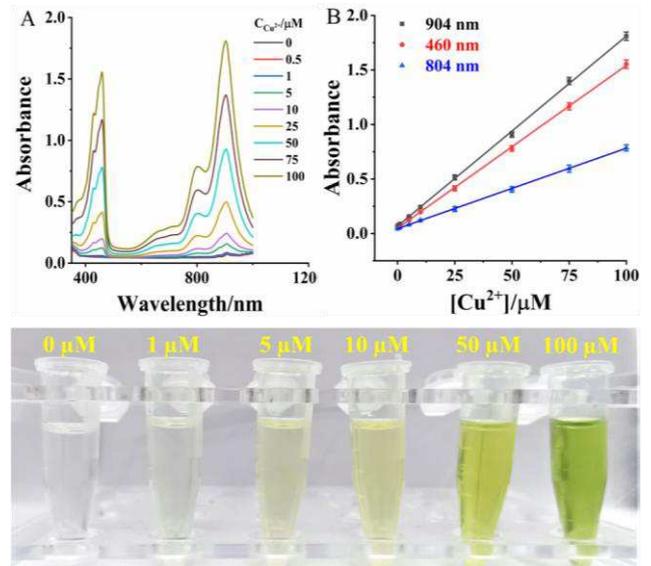


Figure 4 A) Absorbance spectra at various Cu^{2+} concentrations; B) Linear plot of absorbance value towards Cu^{2+} concentrations; C) The color change photographs of various Cu^{2+} concentration solutions. From the left to right: the concentration of Cu^{2+} ions are 0, 1, 5, 10, 50, 100 μM .

corresponding linear calibration curve was determined to be $Y = 0.0174X + 0.0689$ ($R^2 = 0.9992$) with the limit of detection of 93 nM ($S/N = 3$). Besides, the color changes of various Cu^{2+} concentration solutions were recorded by a digital camera. As shown in **Figure 4C**, the color of testing solution were turned from colorless to kelly with the increase of Cu^{2+} concentration from 0 to 100 μM . Surprisingly, an obvious pale-yellow testing solution can also be observed by naked eyes even the Cu^{2+} ions concentration is as low as 1 μM , which is far below WHO issued limit level of Cu^{2+} content of drinking water. It means that our developed method can be used for facile on-site testing of Cu^{2+} .

3.4. Selectivity evaluation of this method

In order to further evaluate the selectivity of this method for Cu^{2+} detection, the absorption intensity of various metal ions with TMB was assayed and shown in **Figure 5**, all this metal ions including Cu^{2+} , Cu^+ , Fe^{3+} , Fe^{2+} , Cd^{2+} , Cr^{3+} , Ag^+ , Ca^{2+} , Co^{2+} , Bi^{3+} , K^+ , Na^+ , Mn^{2+} , W^{4+} , Sn^{4+} , Mg^{2+} , Ni^{2+} and Cr^{6+} , the absorption intensity change was only observed in Cu^{2+} solution, determined that this method possess excellent selectivity for Cu^{2+} detection.

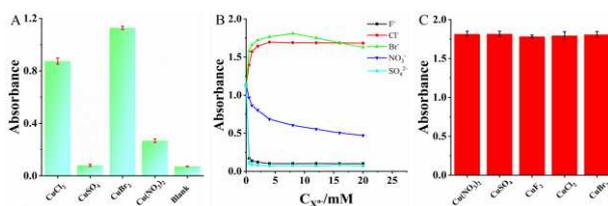


Figure 3 A) Absorbance of Cu^{2+} compounds in EtOH ($[Cu^{2+}] = 100 \mu M$); B) Effect of anions concentrations on the detection of Cu^{2+} in EtOH ($[Cu^{2+}] = 100 \mu M$); C) Absorbance of Cu^{2+} compounds in the presence of Br^- ($[Cu^{2+}] = 100 \mu M$; $[Br^-] = 8 mM$).

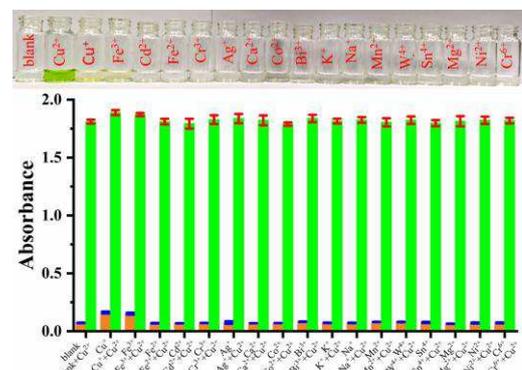


Figure 5 Color and absorbance changes of testing solution with equivalent various metal ions mixed with TMB. $[M^{n+}] = 100 \mu M$; $[Br^-] = 8 mM$, All these absorption intensities were recorded at 904 nm.

Table 1 Detection results of Cu²⁺ in the tap water samples

Samples	Added (μM)	Found (μM)	Recovery (%)	Relative standard deviation (%), n=6)
1	1	1.28	128	2.4
2	5	5.17	103.4	1.7
3	10	9.91	99.1	2.8
4	50	48.52	97.04	1.9
5	100	104.94	104.94	3.1

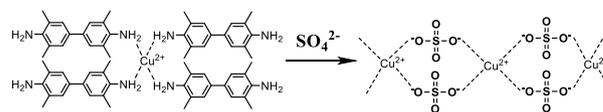
3.5. Real samples detection

A standard addition method was adopted to detect the concentration of Cu²⁺ in the tap water samples, which was used to evaluate the feasibility of this method for practical application.[38] As presented in **Table 1**, the recovery range from 97.04 to 128 %, and the relative standard deviations range from 1.7 to 3.1 %. Beyond that, the Cu²⁺ concentration of the lake water in our campus has been detected as 0.96 μM by this developed method, which is comparable with the result of 1.04 μM determined by the standard ICP-MS method. These results validate the feasibility of this method for Cu²⁺ detection in real water samples.

4. Exploration of Cu²⁺ detection Mechanism

As reports, the oxidation potential of TMB is 1.13 V,[39] which is higher than standard reduction potential of Cu²⁺ (0.34 V).[40] Regarding on the mechanism of this method, we hypothesized that it may come from the coordination of copper ions with TMB, while not from the oxidation of copper ions with TMB. Inspired by the theory of coordination and the experimental results, we propose the following mechanism (**Scheme 2**). According to the ligand-field splitting parameter and Jahn-Teller effects,[41,42], in ethanol solution, The coordination ability of amino group of TMB with Cu²⁺ is higher than that of hydroxyl group of ethanol. Therefore, Cu²⁺ is preferentially coordinated with TMB. Moreover, two halide ions and four amino groups form a “elongated” octahedron. Among them, the two halide ions are used to simultaneously satisfy the main valence and the vice valence of Cu²⁺.

According to the ionic polarization theory, there is no absolute ionic bonds and it always contains a covalent bond component.[43] The total polarization of Cu²⁺ compounds depends on the mutual polarization of Cu²⁺ and anions. F⁻ has the strongest electronegativity and smallest ionic radius. Then it is easy to polarize Cu²⁺ but not easy to be polarized. When extra F⁻ were added, Cu²⁺ will be further polarized under the influence of additional F⁻, increased the covalent components of ionic bond. Thus, it is difficult to ionize Cu²⁺ to participate in coordination. Compared with F⁻, Cl⁻ and Br⁻ have a larger radius and lower electronegativity, which make Cu²⁺ difficult to be polarized. But when supernumerary Cl⁻ or Br⁻ were added, the average polarization of Cu²⁺ to every anion was reduced, and the total polarization was decreased. It causes the ionic bond component increases, and more Cu²⁺ was ionized to coordinate with TMB. It is worth mentioning that the excessive anions ([Cl⁻], [Br⁻] > 8 mM) will decrease the absorbance instead (**Figure 3B**). The reason is that the space around Cu²⁺ is limited, and then too much Cl⁻ or Br⁻ will hinder the coordination of TMB with Cu²⁺ (Br⁻ have a larger ion radius, so the absorbance will decrease more obviously). In ethanol, nitrate and sulfuric acid are not suitable for forming the Jahn-Teller distortion due to their electron-deficient structure and steric hindrance, especially the sulfate ion. The sulfate ion not only

**Scheme 3** Mechanism of the SO₄²⁻ bridge bonds.

has a large steric hindrance, but also can be used as a bridge to bridge two Cu²⁺(**Scheme 3**).

In order to prove the mechanism, we characterized the coordination product. **Figure S1 A** shows the Cu XPS spectra. The Binding Energy of Cu 2p_{3/2} and Cu 2p_{1/2} states were noticed at 934.65 eV and 955.3 eV, respectively, indicate +2 oxidation state for copper.[44-46] The XPS of Copper was proved that the change in absorbance value is not due to the oxidation of metal ions to TMB. Furthermore, the C1s HR-XPS spectrum exhibits three peaks at 284.5, 285.7 and 287.37 eV, which are attributed to C-C/C=C, C-N (sp²) and C-N (sp³) of TMB, respectively (**Figure S1 B**). The binding energy for N1s can be deconvoluted to three components: 399.45, 400.70.8, and 402.05 eV, which are assigned to: -NH₂, -N-Cu²⁺ and N-benzene, respectively in **Figure S1 C**. [47-49]

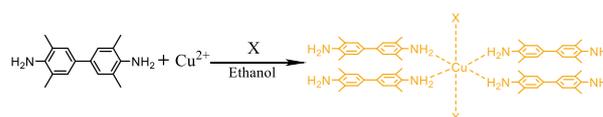
As shown in **Figure S1 D**, the red line is the infrared spectrum of TMB, the black lines is the infrared spectra of Cu²⁺ and TMB complex. The two absorption peaks of TMB 3200-3400 cm⁻¹ are attributed to the stretching vibration of NH. 3000-3100 cm⁻¹ is the stretching vibration of hydrocarbon on benzene ring, 2900-3000 cm⁻¹ is the stretching vibration of C-H of methyl group. Broadening of N-H absorption peak due to coordination of metal ion with TMB amino group.

¹H-NMR analysis confirmed the structure of the complex. As shown in **Figure S2 A**, TMB shows a sharp singlet at 6.98 ppm due to four hydrogen atoms on the benzene ring, a single broad peak at 4.42 ppm is designated as a hydrogen atom at -NH₂, and a single peak at 2.09 ppm is designated as -CH₃ on the benzene ring. Compared with TMB, there are several multiple peaks between 7-7.5 and 2-3, which are assigned to H that on the benzene ring and methyl group. The reason for the peak splitting may be the different coordination states of TMB and Cu ions; The broad peak at 3.40 may be formed by the coincidence of the solvent water peak with the hydrogen spectrum of -NH₂, the reason for the shift of the -NH₂ chemical shift to a low field is due to the disappearance of the p-π conjugate (**Figure S2 B**). In addition, the lone pair of electrons of the TMB amino group forms a p-π conjugate with the benzene ring, but when the amino group is coordinated with Cu²⁺, this conjugate is broken and the electron cloud density on the benzene ring is reduced, resulting in the chemical shift δ of H on the benzene ring and methyl group increases.

In addition, pure oxTMB is difficult to obtain. The ¹H-NMR data of oxidation state TMB obtained by Chemdraw fitting shows that the chemical shift of the hydrogen atom of =NH is located at 9.36, indirectly indicated that there is no oxidation state TMB in the complex (**Figure S2 C**).

5. Conclusions

In summary, a simple, ultra-fast, sensitive and selective colorimetric method has been developed for the detection of Cu²⁺

**Scheme 2** The proposed mechanism of Cu²⁺ coordinated with TMB. (X=Br⁻, Cl⁻).

only based on the simple coordination of TMB and Cu²⁺. After added Cu²⁺ to the ethanol solution of TMB, the color changes from colorless to yellow within extremely short time, which can be used to accurately and quantitatively detect Cu²⁺. In addition, added anions (Br⁻ or Cl⁻) can greatly improve the absorbance help to improve the detection sensitivity. Even trace amount of Cu²⁺ ions as low as 1 μM can result obvious color change observed by naked eyes. It means that our developed method has great potential for facile on-site testing of Cu²⁺.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author contributions

Lei Chen: Methodology, Writing - Original Draft

Yan Li: Writing - Original Draft

Hualin Chen: Guidance of Theoretical analysis

He Li: Designed the experiment and wrote the revised the paper

Jun Liu: Writing - Review & Editing

Ziyue Chen: Writing - Review & Editing

Bin Wang: Writing - Review & Editing

Acknowledgements

The authors would like to thank the financial support from Sichuan Province Science and Technology Support Program (No. 2020YFN0029), the One-Thousand-Talents Scheme in Sichuan Province, Scientific Start-up Research Fund of Chengdu University of Information Technology (No. KYTZ201714), and the Central University Basic Research Fund of Southwest Minzu University (2018NZD08).

References

- [1] J. Wang, C. Luo, C. Shan, Q. You, J. Lu, *Nat Chem.* (2015) <https://doi.org/10.1038/nchem.2381>
- [2] W. J. Lu, Y. F. Gao, Y. Jiao, S. M. Shuang, C. Z. Li, et al. *Nanoscale.* (2017) <https://doi.org/10.1039/C7NR02336G>
- [3] G. Ondrasek, P. L. Clode, M. R. Kilburn, P. Guagliardo, D. Romic, et al. *Int J Environ Res Public Health.* (2019) <https://doi.org/10.3390/ijerph16030373>
- [4] C. M. Rico, S. Majumdar, M. Duarte-Gardea, J. R. J. Agric Food Chem. 2011; 59: 3485-3498. <https://doi.org/10.1021/jf104517j>
- [5] M. Lan, J. Zhang, Y. S. Chui, P. Wang, X. Chen, et al. *ACS Appl Mater Interfaces.* (2014) <https://doi.org/10.1021/am5062568>
- [6] R. Singh, N. Gautam, A. Mishra, R. Gupta. *Indian J. Pharmacol.*, (2011) <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3113373/>
- [7] S. Tiwari, C. Lata. *Heavy Metal Stress, Front Plant Sci.* (2018) <https://doi.org/10.3389/fpls.2018.00452>
- [8] F. Yu, P. Gong, Z. Hu, Y. Qiu, Y. Cui, et al. *J Neuroinflammation.* (2015) <https://doi.org/10.1186/s12974-015-0343-3>
- [9] J. H. Viles. *Coordination Chemistry Reviews.* (2012) <https://doi.org/10.1016/j.ccr.2012.05.003>
- [10] M. J. Pushie, I. J. Pickering, G. R. Martin, S. Tsutsui, F. R. Jirik, et al. *Metallomics.* (2011) <https://doi.org/10.1039/c0mt00037j>
- [11] H. Elmizadeh, M. Soleimani, F. Faridbod, G. R. Bardajee. *J Fluoresc.* (2017) <https://doi.org/10.1007/s10895-017-2174-3>
- [12] S. R. Patil, J. P. Nandre, P. A. Patil, S. K. Sahoo, M. Devi, et al. *RSC Advances.* (2015) <https://doi.org/10.1039/C4RA10419F>
- [13] X. Ma, Z. Tan, G. Wei, D. Wei, Y. Du. *Analyst.* (2012) <https://doi.org/10.1039/C2AN16155A>
- [14] G. Yang, W. Fen, C. Lei, W. Xiao, H. Sun. *J Hazard Mater.* (2009) <https://doi.org/10.1016/j.jhazmat.2008.05.007>
- [15] C. Ianni, E. Magi, F. Soggia, P. Rivaro and R. Frache. *Microchemical Journal.* (2010) <https://doi.org/10.1016/j.microc.2009.07.016>
- [16] P. Leonhard, R. Pepelnik, A. Prange, N. Yamada and T. Yamada. *J. Anal. At. Spectrom.* (2002) <https://pubs.rsc.org/en/content/articlehtml/2002/ja/b110180n>
- [17] H. Li, X. He, Z. Kang, H. Huang, Y. Liu, et al. *Angew Chem Int Ed Engl.* (2010) <https://doi.org/10.1002/anie.200906154>
- [18] V. K. Gupta, A. K. Singh, M. R. Ganjali, P. Norouzi, F. Faridbod, et al. *Sensors and Actuators B: Chemical.* (2013) <https://doi.org/10.1016/j.snb.2013.03.062>
- [19] W. Chen, X. Tu, X. Guo. *Chem Commun (Camb).* (2009) <https://doi.org/10.1039/B820145E>
- [20] Y. Zhou, S. Wang, K. Zhang, X. Jiang. *Angew Chem Int Ed Engl.* (2008) <https://doi.org/10.1002/anie.200802317>
- [21] W. Zhao, W. Jia, M. Sun, X. Liu, Q. Zhang, et al. *Sensors and Actuators B: Chemical.* (2016) <https://doi.org/10.1016/j.snb.2015.09.119>
- [22] L. Wang, Z.-L. Wei, Z.-Z. Chen, C. Liu, W.-K. Dong, et al. *Microchemical Journal.* (2020) <https://doi.org/10.1016/j.microc.2020.104801>
- [23] W. Anbu Durai, A. Ramu. *J Fluoresc.* (2020) <https://doi.org/10.1007/s10895-020-02488-0>
- [24] Z. Zhang, X. Zhang, B. Liu, J. Liu. *J Am Chem Soc.* (2017) <https://doi.org/10.1021/jacs.7b00601>
- [25] L. Jin, Z. Meng, Y. Zhang, S. Cai, Z. Zhang, et al. *ACS Applied Materials & Interfaces.* (2017) <https://doi.org/10.1021/acsami.7b01616>
- [26] H. Huang, L. Liu, L. Zhang, Q. Zhao, Y. Zhou, et al. *Anal Chem.* (2017) <https://doi.org/10.1021/acs.analchem.6b02966>
- [27] X. Wang, Y. Yang, L. Li, M. Sun, H. Yin, et al. *Anal Chem.* (2014) <https://doi.org/10.1021/ac500281r>
- [28] M. Moreno-Guzman, A. Jodra, M. A. Lopez, A. Escarpa. *Anal Chem.* (2015) <https://doi.org/10.1021/acs.analchem.5b03928>
- [29] P. M. Kanerva, T. S. Sontag-Strohm, P. H. Ryöppy, P. Alho-Lehto, H. O. Salovaara. *Journal of Cereal Science.* (2006) <https://doi.org/10.1016/j.jcs.2006.08.005>
- [30] B. Singh, E. Flampouri, E. Dempsey. *The Analyst.* (2019) <https://doi.org/10.1039/C9AN00982E>
- [31] T. Puangsamlee, Y. Tachapermporn, P. Kammalun, K. Sukrat, C. Wainiphithapong, et al. *Journal of Luminescence.* (2018) <https://doi.org/10.1016/j.jlumin.2017.11.048>
- [32] M. S. Kim, T. G. Jo, H. M. Ahn, C. Kim. *J Fluoresc.* (2017) <https://doi.org/10.1007/s10895-016-1964-3>
- [33] Z. Guo, Q. Niu, T. Li, T. Sun, H. Chi. *Spectrochim Acta A Mol Biomol Spectrosc.* (2019) <https://doi.org/10.1016/j.saa.2019.01.044>
- [34] J. M. Liu, H. F. Wang, X. P. Yan. *Analyst.* (2011) <https://doi.org/10.1039/C1AN15460E>
- [35] H. Shao, Y. Ding, X. Hong, Y. Liu. *Analyst.* (2018) <https://doi.org/10.1039/C7AN01619K>
- [36] G. J. Park, G. R. You, Y. W. Choi, C. Kim, *Sens. Actu. B Chem.* (2016) <https://doi.org/10.1016/j.snb.2016.01.133>
- [37] Y. J. Na, Y. W. Choi, J. Yeong Y, n, K. M. Park, P. S. Chang, *Spectrochim. Acta. A Mol. Biomol. Spectrosc.* (2015) <https://doi.org/10.1016/j.saa.2014.10.060>
- [38] T. G. Jo, Y. J. Na, J. J. Lee, M. M. Lee, S. Y. Lee, et al. *New Journal of Chemistry.* (2015) <https://doi.org/10.1039/C5NJ00125K>
- [39] J. Chen, Q. Ma, M. Li, D. Chao, L. Huang, et al. *Nat Commun.* (2021) <https://doi.org/10.1038/s41467-021-23737-1>
- [40] D. Karabelli, S. Ünal, T. Shahwan and A. E. Eroğlu. *Chemical Engineering Journal.* (2011) <https://doi.org/10.1016/j.cej.2011.01.015>
- [41] K. I. Kugel', D. I. Khomskii. *Physics-Uspeski.* (1982) <https://doi.org/10.1070/PU1982v025n04ABEH004537>
- [42] G. A. Gehring, K. A. Gehring. *Physics-Uspeski.* (1975) <https://doi.org/10.1088/0034-4885/38/1/001>
- [43] K. Fajans, N. J. Kreidl, J. Am. Ceram. Soc. (1948) <https://doi.org/10.1111/j.1151-2916.1948.tb14273.x>
- [44] Q. Hao, D. Zhao, H. Duan, C. Xu. *ChemSusChem.* (2015) <https://doi.org/10.1002/cssc.201403420>
- [45] Ç. Oruç, A. Altındal. *Ceramics International.* (2017) <https://doi.org/10.1016/j.ceramint.2017.05.006>
- [46] W. Zheng, Y. Li, M. Liu, C.-S. Tsang, L. Y. S. Lee, et al. *Electroanalysis.* (2018) <https://doi.org/10.1002/elan.201800076>
- [47] J.-R. M. R. N. Francisco Yarur. *Environmental Science: Nano.* (2019) <https://doi.org/10.1039/C8EN01418C>
- [48] S. Liu, J. Tian, L. Wang, Y. Luo, X. Sun. *RSC Adv.* (2012) <https://pubs.rsc.org/en/content/articlehtml/2012/ra/c1ra00709b>
- [49] P. Li, Z. Feng, Z. Yu, Y. Chen, P. Li, et al. *Int J Biol Macromol.* (2019) <https://doi.org/10.1016/j.ijbiomac.2019.03.011>

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [SupplementaryMaterial.pdf](#)