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NEW APPLICATION OF D- π -A MOLECULES AS A SENSOR FOR RECOGNITION OF Cu²⁺ IN POLLUTED WATER

Novel chromophore GZP1 with D- π -A structure was designed and prepared for its application as a sensor for the recognition of Cu²⁺ ions in polluted water. Reaction of aldimine condensation was used to synthesize chromophore GZP1. Its chemical structure was characterized by mass spectrum, nuclear magnetic resonance spectroscopy and ultraviolet-visible absorption spectrum. Cu²⁺ ions were recognized via fluorescence spectra. Chromophore GZP1 showed specific detection ability of Cu²⁺. 14 other metal ions were used as reference. The detection limit was estimated to be 0.06 $\mu\text{mol}/\text{dm}^3$ in aqueous solution, which was significantly lower than the typical concentration of blood Cu²⁺ in normal individuals and the limit of copper(II) in drinking water.

1. INTRODUCTION

Due to rapidly developing societies in recent decades, especially the extensive production and application of chemicals, environmental pollution has seriously affected the quality of our life [1–3]. Water pollution as one of the most important field of environmental pollution has attracted great attentions of the researchers in the recent years. Heavy metal ion contamination is an important part of water pollution [4–6]. In this paper, the research focused on highly selective fluorescent sensors of copper cation. Copper ions (Cu²⁺) play a critical role in environmental, biological and chemical systems [7, 8]. High level of copper in our body even for a short period of time can cause gastrointestinal disturbances. As the time increasing, liver or kidney can be damaged.

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The content of copper in drinking water has been limited in 1.3 mg/dm³ by the USA Environmental Protection Agency (EPA).

Recently, lots of methods have been proposed and utilized for the detection of metal ions, such as photo induced electron transfer method, intramolecular charge transfer, excimer formation [9–11]. According to the method used in the detecting process, various chromophores have been designed and synthesized. But there are still many drawbacks for these novel chromophores such as in using conditions, thermal stability, photochemical stability and reproducibility [12]. Most importantly, according to the special characters of Cu²⁺, most of the fluorescent sensors are fluorescent binding, low selectivity and low sensitivity. Fortunately, large amount of chromophores with D- π -A structure was designed and prepared for their application in nonlinear optical materials, and some of the chromophores are suitable for their application as cationic probes [13–16]. In this paper, we designed a novel chromophore with D- π -A structure, according to the coordination feature of copper(II) cation. The copper(II) cation could be detected just by the change of fluorescence spectra of the chromophore.

2. EXPERIMENTAL

Reagents. Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. 4-(dimethylamino)benzaldehyde was obtained from TCI Chemical Reagent Co., Ltd. Diaminomaleonitrile was obtained from Beijing Inno Chem Science & Technology Co., Ltd. Other chemicals were provided by Qinghai Sany Chemical Reagent.

General method. The ¹H NMR (300 MHz) and ¹³C NMR (125 MHz) spectra were recorded on a VARIAN, Unity Plus 300M spectrometer using tetramethylsilane (TMS, $\delta = 0$ ppm) as the internal standard. The MS spectra were obtained on MALDI-TOF (Matrix Assisted Laser Desorption/Ionization of Flight) on BIFLEXIII (Broker, Inc.) spectrometer. The UV-Vis spectra were recorded on Cary 5000 photo spectrometer. Fluorescence spectra were recorded on Edinburgh FLS-920 spectrophotometer.

Synthesis. 4-(dimethylamino)benzaldehyde (1.49 g, 10 mmol) and diaminomaleonitrile (1.08 g, 10 mmol) were dissolved in 50 cm³ of acetonitrile. The mixture was refluxed for 2 h under magnetic stirring. After removal of the solvent, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 5:1), a light yellow solid was obtained (2.19 g, 92%). UV-Vis (CHCl₃): $\lambda_{\max} = 476$ nm, MS, m/z: (239 M⁺); ¹H NMR (300 MHz, CDCl₃): δ 9.40 (s, 1H), 7.82 (s, 2H), 7.32 (d, 2H), 7.01 (d, 2H), 3.98 (s, 6H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 165, 154, 129, 124, 120, 117, 109, 105, 100, 45.

Procedures of the metal ion sensing. Nitrate or chlorate salts of Ag^+ , Ca^{2+} , Cd^{2+} , Co^{2+} , Fe^{2+} , Fe^{3+} , Hg^{2+} , Li^+ , Mg^{2+} , Na^+ , Ni^{2+} , Pb^{2+} , Zn^{2+} , Cu^{2+} and the host probe (1.0 mmol/dm³) of chromophore GZP1 were dissolved in water (5.0 mmol/dm³) in water. Test solutions were prepared by placing 0.5 cm³ of the probe solution into a test tube, adding an appropriate aliquot of each ion solution, and diluting the solution with 20 cm³ of water. For all measurements, excitation and emission slit widths were 5 and 10 nm, respectively.

3. RESULTS AND DISCUSSION

3.1. SYNTHESIS OF CHROMOPHORE GZP1

The structure of chromophore GZP1 is shown in Fig. 1. Due to a strong electron donating ability, N,N-dimethylaniline was used as the electron donor. Carbon–nitrogen double bond with good electron mobility was used as π -electronic bridge. 2,3-diaminosuccinonitrile was used as an electron acceptor. As shown in Fig. 1, chromophore GZP1 could be synthesized by one step reaction. The reflux of 4-(dimethylamino)benzaldehyde and 2,3-diaminosuccinonitrile in the solvent of acetonitrile yield chromophore GZP1 directly.

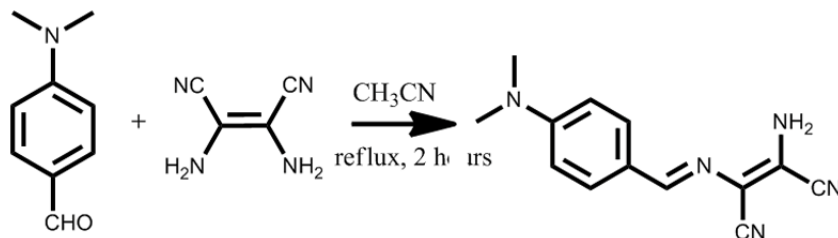


Fig. 1. Scheme of synthesis of chromophore GZP1

3.2. FLUORESCENT SIGNALING OF Cu^{2+} IONS

Chromophore GZP1 displays strong fluorescence with a maximum intensity at 587 nm and the quantum yield of 0.041 in aqueous solution (10 mmol/dm³ tris-HCl, pH 7.4, 25 °C). The quantum yield of chromophore GZP1 was calculated using acriflavine as a reference from the equation:

$$\Phi = \frac{F_1 \varepsilon_1}{F_2 \varepsilon_2}$$

where F_1 and F_2 are the fluorescence intensities of chromophore GZP1 and acriflavine respectively, $\varepsilon_1, \varepsilon_2$ – the absorption coefficient for chromophore GZP1 and acriflavine

respectively. The fluorescence spectra of GZP1 were investigated in the presence of fourteen metal ions such as Ag^+ , Ca^{2+} , Cd^{2+} , Co^{2+} , Fe^{2+} , Fe^{3+} , Hg^{2+} , Li^+ , Mg^{2+} , Na^+ , Ni^{2+} , Pb^{2+} , Zn^{2+} , Cu^{2+} (Fig. 2). The fluorescence of GZP1 showed no obvious changes after the addition of metal ions except Cu^{2+} ions. However, the addition of Cu^{2+} to the solution of GZP1 resulted in a significant decrease (13-fold) in the fluorescence intensity at 587 nm. The quantum yield of GZP1– Cu^{2+} complex was measured to be 0.0046. Obviously, GZP1 showed excellent selectivity for Cu^{2+} over other metal ions.

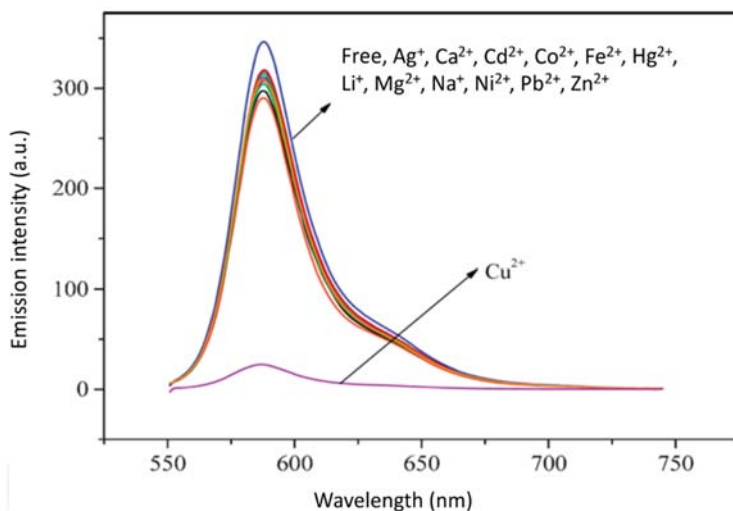


Fig. 2. Emission spectra of GZP1 (10 mmol/dm^3) in the presence of various metal ions (5 mmol/dm^3 of Ag^+ , Ca^{2+} , Cd^{2+} , Co^{2+} , Fe^{2+} , Fe^{3+} , Hg^{2+} , Li^+ , Mg^{2+} , Na^+ , Ni^{2+} , Pb^{2+} , Zn^{2+} , Cu^{2+}) in tris HCl buffer (1 mmol/dm^3 , pH 7.4, 25°C , $\lambda_{\text{ex}} = 538 \text{ nm}$)

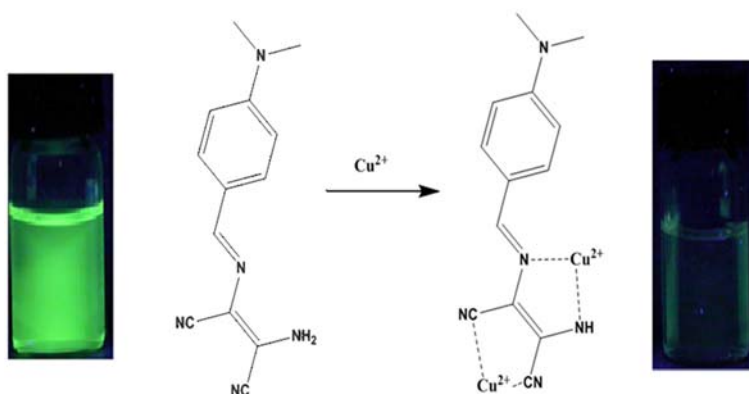


Fig. 3. Proposed sensing mechanism of GZP1 with Cu^{2+} in water

The proposed mechanism of structural changes of GZP1 molecule leading to fluorescence quenching is shown in Fig. 3. Two nitrogen atoms with copper(II) cation constitute a five-membered ring structure. Two cyano groups with another copper(II) cation constitute another five-membered ring. Due to the strong electron withdrawing ability of these structures and the coplanar structure with the N, N-dimethylaniline electron donor, most of the donor electrons would move to a part of the electron acceptor. Electron cloud of such a chromophore molecule would have strong non-centrosymmetric structure, displaying only weak fluorescence, which is consistent with the result of our experimental data.

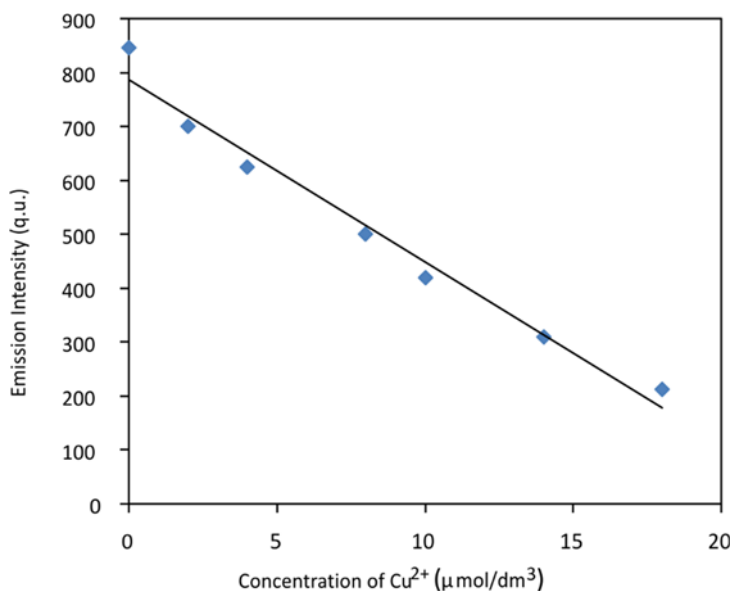


Fig. 4. The calibration curve for 0–20 $\mu\text{mol}/\text{dm}^3$ of Cu^{2+}
 $\lambda_{\text{ex}} = 540 \text{ nm}$, $\lambda_{\text{em}} = 587 \text{ nm}$, $1 \mu\text{mol}/\text{dm}^3$ tris-HCl buffer, pH 7.0

The calibration curve for 0–20 $\mu\text{mol}/\text{dm}^3$ of $\text{Cu}(\text{II})$ solution is shown in Fig. 4. The titration profile based on the emission efficiency suggested a 2:1 binding stoichiometry of Cu^{2+} to GZP1, which was further confirmed by a Job's plot analysis from Fig. 4. The binding constant for the GZP1– Cu^{2+} complex was calculated to be $2.01 \times 10^7 \text{ dm}^3/\text{mol}$ based on the fluorescence titration, indicating a strong binding ability of GZP1 with Cu^{2+} . At 10 mmol/dm^3 concentration of GZP1, a good linear relationship between the fluorescence response and the concentration of Cu^{2+} (0–20 $\mu\text{mol}/\text{dm}^3$) was found. The detection limit was estimated to be $0.06 \mu\text{mol}/\text{dm}^3$ in aqueous solution, which is significantly lower than the typical concentration of blood copper(II) (11.8–23.6 mmol/dm^3) in normal individuals and the limit of copper(II) in drinking water (15.6 $\mu\text{mol}/\text{dm}^3$).

4. CONCLUSION

Novel application area of organic conjugated small molecules with D- π -A structure in detection of metal ions has been presented. By the precise design of the coordinating atoms in the part of electron acceptor, such kind of molecule showed strong selectivity for copper(II) ion. According to the traditional method, the detection limit of the method used in this article was improved greatly, reaching 0.06 $\mu\text{mol}/\text{dm}^3$ in aqueous solution.

REFERENCES

- [1] ROCHA J., ROEBELING P., RIAL-RIVAS M., *Assessing the impacts of sustainable agricultural practices for water quality improvements in the Vouga catchment (Portugal) using the SWAT model*, *Sci. Total Environ.*, 2015, 536, 48.
- [2] KAPUSTA P., SOBCZYK L., *Effects of heavy metal pollution from mining and smelting on enchytraeid communities under different land management and soil conditions*, *Sci. Total Environ.*, 2015, 536, 517.
- [3] CHU S., WANG J., LEONG G., WOODWARD L., LETCHER R., LI Q., *Perfluoroalkyl sulfonates and carboxylic acids in liver, muscle and adipose tissues of black-footed albatross (Phoebastria nigripes) from Midway Island, North Pacific Ocean*, *Chemosphere*, 2015, 138, 60.
- [4] LU C., YU S., YAO T., ZENG C., WANG C., ZHANG L., *Zeolite X/chitosan hybrid microspheres and their adsorption properties for Cu(II) ions in aqueous solutions*, *J. Por. Mater.*, 2015, 22, 1255.
- [5] MAJUMDER S., GANGADHAR G., RAGHUVANSHI S., GUPTA S., *A comprehensive study on the behavior of a novel bacterial strain Acinetobacter guillouiae for bioremediation of divalent copper*, *Bioproc. Biosyst. Eng.*, 2015, 38, 1749.
- [6] CHEN H., HU W., LI C., *Colorimetric detection of mercury(II) based on 2,2'-bipyridyl induced quasi-linear aggregation of gold nanoparticles*, *Sens. Act. B-Chem.*, 2015, 215, 421.
- [7] HAMMUD H., EI-SHAZYL S., SONJI G., SONJI N., BOUHADIR K., *Thiophene aldehyde-diamino uracil Schiff base. A novel fluorescent probe for detection and quantification of cupric, silver and ferric ions*, *Spectrochim. Acta Part A, Mol. Biomol. Spectry*, 2015, 150, 94.
- [8] PENNINGTON P., WATMOUGH S., *The Biogeochemistry of Metal-Contaminated Peatlands in Sudbury, Ontario, Canada*, *Water Air Soil Poll.*, 2015, 226, 326.
- [9] BALTAKYS K., EISINAS A., BARAUSKAS I., PRICHOCKIENE E., ZALECKAS E., *Removal of Zn(II), Cu(II) and Cd(II) from aqueous solution using gyrolite*, *J. Sci. Ind. Res.*, 2012, 71, 566.
- [10] SIKDER M., ISLAM M., KIKUCHI T., SUZUKI J., SAITO T., KURASAKI M., *Removal of copper ions from water using epichlorohydrin cross-linked beta-cyclodextrin polymer. Characterization, isotherms and kinetics*, *Water Environ. Res.*, 2014, 86, 296.
- [11] DE JONGE M., LOFTS S., BERVOETS L., BLUST R., *Relating metal exposure and chemical speciation to trace metal accumulation in aquatic insects under natural field conditions*, *Sci. Total Environ.*, 2014, 496, 11.
- [12] TANG L., ZHOU P., HUANG Z., ZHAO J., CAI M., *A new quinoline-based acylhydrazone for highly selective fluorescence recognition of Cu(II) and sulfide in aqueous solution*, *Bull. Korean Chem. Soc.*, 2013, 34, 2905.
- [13] ZHANG C., WANG C., DALTON L., ZHANG H., STEIER W., *Progress toward device-quality second-order nonlinear optical materials. 4. A trilinear high $\mu\beta$ NLO chromophore in thermoset polyurethane: A guest-host approach to larger electrooptic coefficients*, *Macromol.*, 2001, 34, 253.
- [14] LIU J., GAO W., KITYK I., LIU X., ZHEN Z., *Optimization of polycyclic electron-donors based on julolidinyl structure in push-pull chromophores for second order NLO effects*, *Dyes Pigm.*, 2015, 122, 74.
- [15] LIU J., HOU W., FENG S., QIU L., LIU X., ZHEN Z., *Synthesis and nonlinear optical properties of branched pyrrolone chromophores*, *J. Phys. Org. Chem.*, 2010, 24, 439.
- [16] GUO Z., GUO L., CHEN H., *Synthesis of a new chromophore containing a new electron donor*, *Res. Chem. Int.*, 2015, 41, 2277.