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## NEW APPLICATION OF D- $\pi$ -A MOLECULES AS A SENSOR FOR RECOGNITION OF Cu<sup>2+</sup> IN POLLUTED WATER

Novel chromophore GZP1 with D- $\pi$ -A structure was designed and prepared for its application as a sensor for the recognition of Cu<sup>2+</sup> 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. Cu<sup>2+</sup> ions were recognized via fluorescence spectra. Chromophore GZP1 showed specific detection ability of Cu<sup>2+</sup>. 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 Cu<sup>2+</sup> 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 (Cu<sup>2+</sup>) 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  $1.3 \text{ mg/dm}^3$  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  $\text{Cu}^{2+}$ , most of the fluorescent sensors are fluorescent binding, low selectivity and low sensitivity. Fortunately, large amount of chromophores with D- $\pi$ -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- $\pi$ -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  $^1\text{H}$  NMR (300 MHz) and  $^{13}\text{C}$  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  $50 \text{ cm}^3$  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 ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}} = 476 \text{ nm}$ , MS, m/z: (239  $\text{M}^+$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.40 (s, 1H), 7.82 (s, 2H), 7.32 (d, 2H), 7.01 (d, 2H), 3.98 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 165, 154, 129, 124, 120, 117, 109, 105, 100, 45.

*Procedures of the metal ion sensing.* Nitrate or chlorate salts of  $\text{Ag}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Li}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  and the host probe (1.0 mmol/dm<sup>3</sup>) of chromophore GZP1 were dissolved in water (5.0 mmol/dm<sup>3</sup>) in water. Test solutions were prepared by placing 0.5 cm<sup>3</sup> of the probe solution into a test tube, adding an appropriate aliquot of each ion solution, and diluting the solution with 20 cm<sup>3</sup> 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  $\pi$ -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.

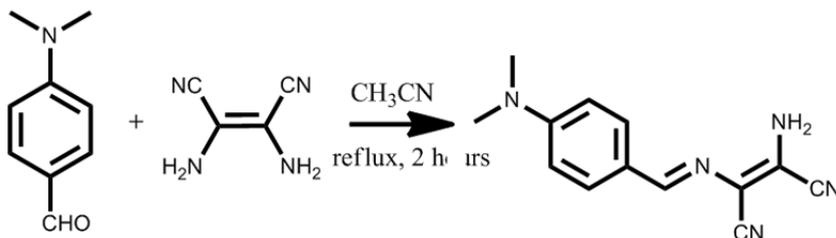


Fig. 1. Scheme of synthesis of chromophore GZP1

#### 3.2. FLUORESCENT SIGNALING OF $\text{Cu}^{2+}$ 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/dm<sup>3</sup> 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  $\text{Ag}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Li}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  (Fig. 2). The fluorescence of GZP1 showed no obvious changes after the addition of metal ions except  $\text{Cu}^{2+}$  ions. However, the addition of  $\text{Cu}^{2+}$  to the solution of GZP1 resulted in a significant decrease (13-fold) in the fluorescence intensity at 587 nm. The quantum yield of GZP1– $\text{Cu}^{2+}$  complex was measured to be 0.0046. Obviously, GZP1 showed excellent selectivity for  $\text{Cu}^{2+}$  over other metal ions.

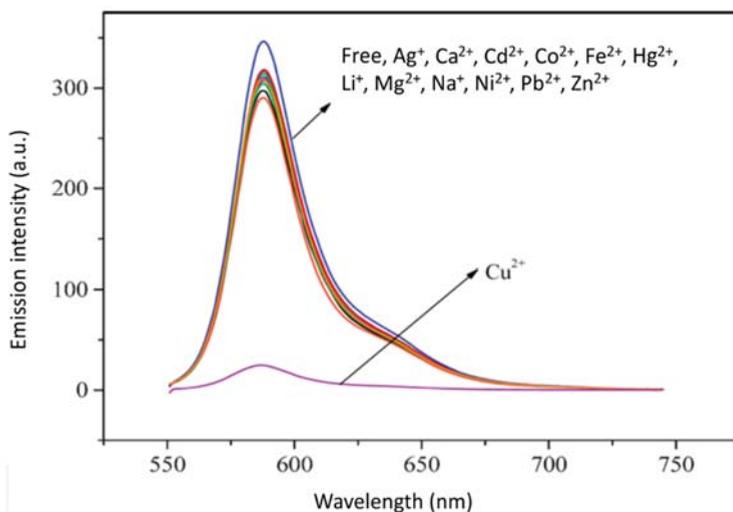


Fig. 2. Emission spectra of GZP1 ( $10 \text{ mmol/dm}^3$ ) in the presence of various metal ions ( $5 \text{ mmol/dm}^3$  of  $\text{Ag}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Li}^+$ ,  $\text{Mg}^{2+}$ , 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

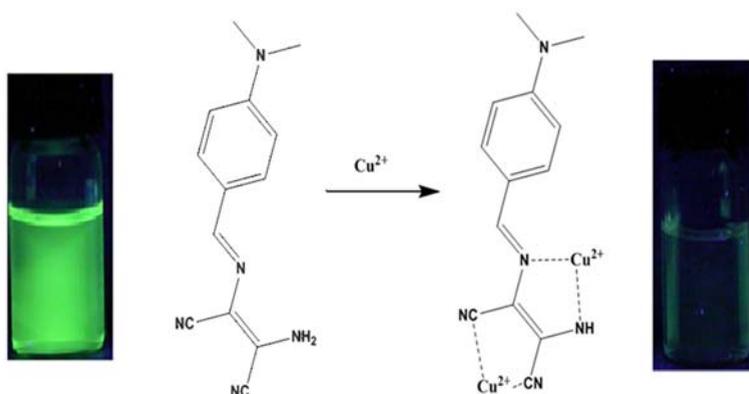


Fig. 3. Proposed sensing mechanism of GZP1 with  $\text{Cu}^{2+}$  in water

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.

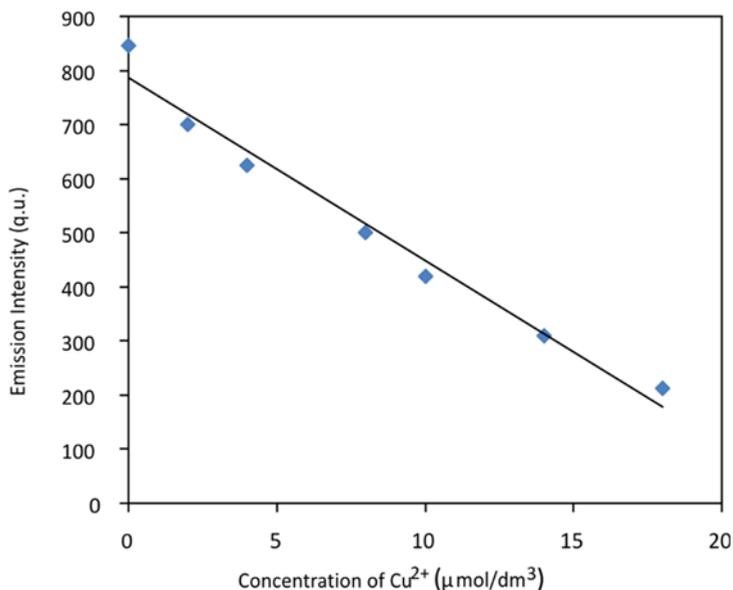


Fig. 4. The calibration curve for 0–20  $\mu\text{mol}/\text{dm}^3$  of  $\text{Cu}^{2+}$   
 $\lambda_{\text{ex}} = 540 \text{ nm}$ ,  $\lambda_{\text{em}} = 587 \text{ nm}$ ,  $1 \mu\text{mol}/\text{dm}^3$  tris-HCl buffer, pH 7.0

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  $\text{Cu}^{2+}$  to GZP1, which was further confirmed by a Job's plot analysis from Fig. 4. The binding constant for the GZP1– $\text{Cu}^{2+}$  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  $\text{Cu}^{2+}$ . At 10  $\text{mmol}/\text{dm}^3$  concentration of GZP1, a good linear relationship between the fluorescence response and the concentration of  $\text{Cu}^{2+}$  (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  $\text{mmol}/\text{dm}^3$ ) 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- $\pi$ -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.

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