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A colorimetric quinoline-based chemosensor for sequential detection of copper ion and cyanide anions

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ABSTRACT

A new quinoline-based chemosensor (**CQ**) for sequential detection of Cu^{2+} and CN^- has been synthesized, where diaminomaleonitrile is introduced as recognition group. After addition of Cu^{2+} , sensor **CQ** in aqueous solution (DMSO/ H_2O) displays remarkable colorimetric change from the light yellow to red, which is attributed to the extended intermolecular charge transfer in **CQ**- Cu^{2+} complex. Sensor **CQ** shows a highly selective and sensitive response to Cu^{2+} , which can be used as Test strips to conveniently monitor Cu^{2+} . In addition, **CQ**- Cu^{2+} complex could be applied to monitor sequentially cyanide anion with dramatic colour change based on copper ion complex displacement mechanism.

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1. Introduction

In recent years, the design and development of specific optical chemosensors for detection of metal ions have received much interest due to the fact that chemosensors can convert molecular recognition into optical signals, which can be easily detect and analyse. Transition metal ions play a critical role in the fundamental physiological process in organisms. For instance, Cu^{2+} is the third most abundant transition metal after Fe^{3+} and Zn^{2+} in human body, which is fundamental in a variety of metabolic processes.^{1,2} However, excess concentration of Cu^{2+} will cause imbalance in cellular processes resulting in Alzheimer or Wilson disease.^{3,4} According to the World Health Organization (WHO), the maximum limit of copper in drinking water is 2 ppm (30 μM).⁵ Hence, the design and synthesis of simple and efficient chemosensor for detection of Cu^{2+} ions is of important concern.

Most of reported fluorescent chemosensors for Cu^{2+} display fluorescence decrease response because Cu^{2+} is a fluorescence quencher for its paramagnetic nature.^{6–11} However, there are a few chemosensors that show “turn-on” fluorescent response for Cu^{2+} based on the $\text{Cu}(\text{II})$ -promoted irreversible chemical reactions.^{12–15}

Compared with the above two types of chemosensors, colorimetric chemosensors are widely attracted to design and use for detection of Cu^{2+} due to its operational simplicity, low cost and lack of equipment required. The most advantage of colorimetric sensors is that the detection process is easily and conveniently implement through the remarkable colour change, without the use of any expensive equipment. Therefore, colorimetric chemosensors for Cu^{2+} have been received considerable attention.^{16–27}

As an extremely toxic anion, cyanide anion can attack human body's red blood cell and cause vomiting, convulsion, loss of consciousness and eventual death.^{28–30} Despite of its lethal toxicity, cyanide anion plays an important role in our industrial process in gold mining, electroplate and so on. The World Health Organization (WHO) has set up the standard for the maximum acceptable level of cyanide in drinking water to be 1.9 μM .³¹ Thus, it is very necessary to develop analysis technique for detection of cyanide anion with high sensitivity and selectivity. Colorimetric chemosensors for monitoring of cyanide have been attracted much attention for more convenient detection in recent years due to the remarkable colour change.^{32–38} To improve the selectivity, the irreversible chemical reaction-based approaches were priority designed for selective recognition for cyanide in these sensors, involving the nucleophilic attack reaction^{33–36} and metal-coordinated activation.^{37,38}

The diaminomaleonitrile Schiff group with function fluorophore, involving coumarin,¹⁶ naphthalimide,²⁰ naphthyl^{39,40} and pyrene,⁴¹ has been explored as colorimetric chemosensors for

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determination of Cu^{2+} . These sensors show good sensing performance and high selectivity. However, some of these display no dramatic colour change or use organic solvent as detection condition, which affect the sensing ability in some content. Hence, the development of chemosensor for Cu^{2+} with dramatic colour change and high selectivity is very necessary. In this paper, we reported a chemosensor **CQ** based on quinoline as a fluorophore, which is colorimetric change and high selectivity to Cu^{2+} . (Scheme 1). Sensor **CQ** was easily obtained via the condensation reaction of 6-methoxyquinoline-2-carbaldehyde and diaminomaleonitrile in EtOH. After treatment of Cu^{2+} , the colour of **CQ** in aqueous solution exhibits remarkable change from pale yellow to red, which can be easily observed by naked-eyes. This significant colour change attracts us to develop sensor for the high toxic cyanide anion. Based on copper ion complex displacement mechanism, the complex Cu^{2+} -**CQ** can be applied to monitor cyanide by releasing the origin **CQ** with also obvious colorimetric change. Hence, sensor **CQ** can be used to detect sequential copper ion and cyanide anions by naked-eyes.

2. Result and discussion

2.1. Synthesis of sensor **CQ**

We have designed a new quinoline-based chemosensor **CQ**, where diaminomaleonitrile is employed as a recognition group. Compound **1** (6-methoxyquinoline-2-carbaldehyde) was synthesized according to the literature.⁴² Then, sensor **CQ** was easily obtained by the condensation reaction of compound **1** with diaminomaleonitrile in EtOH, and characterized by NMR and MS.

2.2. Absorption response of sensor **CQ** toward Cu^{2+}

The recognition properties of sensor **CQ** in aqueous solution was carried out in DMSO/HEPES buffer (2:1, 0.02 M, pH 7.0) at room temperature. Fig. 1 displays the UV–Vis absorption titration of **CQ** with various amount of Cu^{2+} . As shown in Fig. 1, **CQ** exhibits the main absorption peak at 390 nm in DMSO/HEPES buffer (2:1, 0.02 M, pH 7.0). As increasing the concentration of Cu^{2+} ion, a new maximum band at 537 nm gradually appeared while the 390 nm peak decreased with an isosbestic point at 442 nm, indicating that sensor **CQ** with Cu^{2+} form the **CQ**- Cu^{2+} complex. Correspondingly, the remarkable absorption red-shift resulted in the solution colour change from the light yellow to red, which can be directly observed by naked eyes. The large absorption red shift of sensor **CQ** toward Cu^{2+} is mainly attributed to the extended intermolecular charge transfer (ICT) in **CQ**- Cu^{2+} complex.¹⁶

The binding mode between **CQ** and Cu^{2+} is investigated through Job's plot analysis. As shown in Fig. 2, the complex of **CQ** and Cu^{2+} exhibits a maximum absorbance in the molecular fraction of Cu^{2+} as 0.5, indicating that sensor **CQ** and Cu^{2+} form complex as 1:1 stoichiometry. To further confirm the binding mode between **CQ**

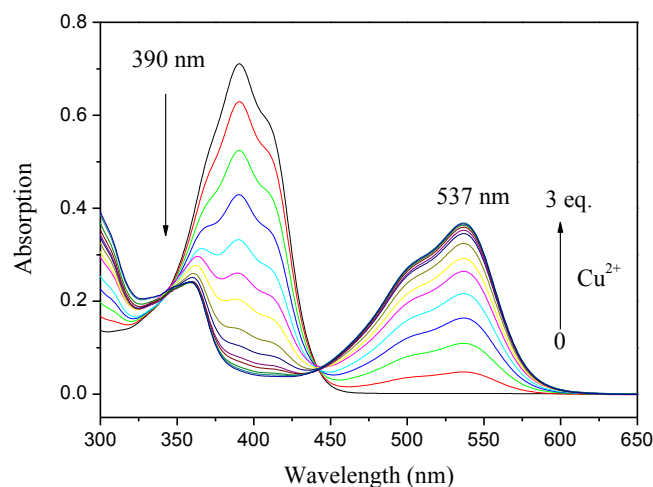


Fig. 1. UV–visible absorption spectral changes of **CQ** (20 μM) with various amounts of Cu^{2+} (0 \rightarrow 3 equiv.) in DMSO/HEPES buffer (2:1, 0.02 M, pH 7.0).

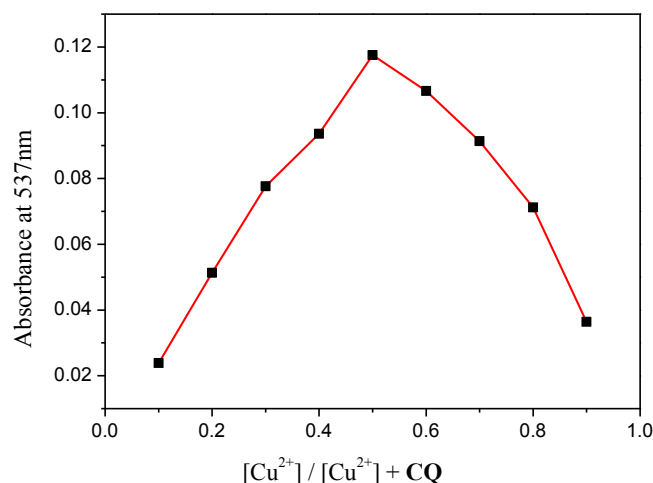
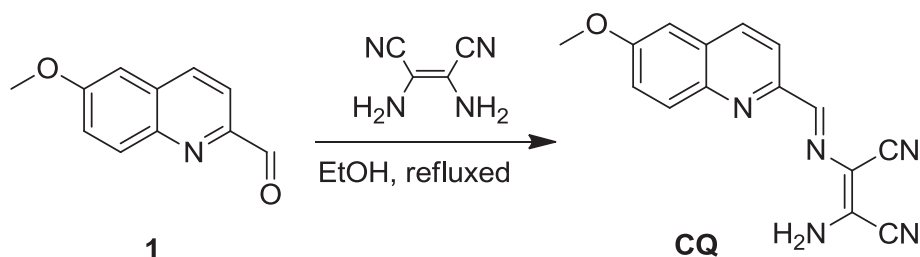


Fig. 2. Job plot of **CQ** in DMSO/HEPES buffer (2:1, 0.02 M, pH 7.0). The total concentration **CQ** and Cu^{2+} ion was 20 μM .

and Cu^{2+} , the MALDI-TOF mass spectroscopy was carried out (Fig. S1). The mass spectrum indicated that a maximum peak at $m/z = 339.8$ was assignable to $[\text{CQ} + \text{Cu}^{2+} - \text{H}^+]^+$ (calcd 339.0). Based on the Job's plot and Mass analysis, the complex of **CQ** and Cu^{2+} is showed as 1:1 stoichiometry. Hence, the stability constant K_s of **CQ**- Cu^{2+} complex is estimated to be $5.8 \times 10^5 \text{ M}^{-1}$ ($R^2 = 0.998$) by using nonlinear curve fitting of the UV–vis titration data (Fig. S2).⁴³

Additionally, To sensor **CQ** solution was added the different copper salts, such as CuSO_4 , $\text{Cu}(\text{NO}_3)_2$ and $\text{Cu}(\text{OAc})_2$, inducing the



Scheme 1. Synthetic route for sensor **CQ**.

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