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# Colorimetric and fluorescence sensing of $Cu^{2+}$ in water using 1,8-dihydroxyanthraquinone-β-cyclodextrin complex with the assistance of ammonia

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ABSTRACT

1,8-Dihydroxyanthraquinone (DHAQ) can form an inclusion complex with β-cyclodextrin(β-CD) in aqueous media, which can be employed to solubilize and stabilize the DHAQ in water. With the assistance of ammonia, the supramolecular DHAQ–β-CD complex showed a selective chromogenic behavior toward $Cu^{2+}$ ions by changing the color of the solution from citrus red to purple red, which could be easily observed with the naked eye. Moreover, fluorescence emission of the system was selectively quenched by $Cu^{2+}$ ions. The fluorescence response was concentration-dependent and can be well described by the typical Stern–Volmer model. An easily applied method for $Cu^{2+}$ determination in an aqueous medium was thus established. Under the optimum conditions, the method exhibits a dynamic response range for $Cu^{2+}$ from $8.0 \times 10^{-7}$ to $2.0 \times 10^{-5}$ M, with a detection limit of $2.7 \times 10^{-7}$ mol $L^{-1}$.

## 1. Introduction

Due to their simplicity, selectivity, sensitivity and short response time, fluorescent chemosensing techniques have been extensively employed for the detection of biologically or environmentally important metal ions. Among various metal ions, recognition and sensing of $Cu^{2+}$ ions has attracted particular attention as it is not only a significant metallic pollutant, but also an essential element for living organisms. A number of synthetic $Cu^{2+}$ fluoroionophores have been continually devised [1–11]. However, these sensor molecules are often structurally complicated and require an elaborate and sophisticated synthetic process. Moreover, the successful examples of water-soluble $Cu^{2+}$ sensors are still limited due to the strong hydration ability of $Cu^{2+}$ in aqueous solution [12–19]. Therefore, there is still a need for development of simple and easy-to-make chemosensing molecules for detection of $Cu^{2+}$ ions in aqueous solution, preferably via dual color as well as luminescence modulations.

Anthraquinone derivatives, an important class of organic compounds that absorb visible light, have a wide range of applications in pharmaceutical, dye as well as paper manufacturing industries. Being capable of forming complexes with cations, the hydroxy-substituted anthraquinones have also been widely used in analytical chemistry as strong chelating agents and chromophores [20–25]. 1, 8-Dihydroxyanthraquinone (DHAQ) is a member of this promising family with two distinct color forms, a yellow one in acidic medium and a red one in alkaline solution. The $pK_a1$ value of the DHAQ in water is 8.30 and the reagent can form fluorescent complexes with the following ions Ca(II), Li(I), Bi(III), Mg(II) and Sb(III) in an alkaline ethanol–water mixture [26]. Due to its high absorption coefficient and possibility of naked eye detection, DHAQ has been chosen as a scaffold to link the ionophores that recognize selectively anions as well as cations in organic solvents [27–30]. With respect to commercial availability and lower cost, DHAQ would be the preferred reagent for developing new high-performance and cost-effective sensors. However, one of the main problems associated with DHAQ as a probe is its poor water solubility. It has to be noted that it is not possible to work in aqueous solution due to solubility problems.

As a class of cyclic oligosaccharides, cyclodextrins (CDs) are water-soluble host molecules, which can include various kinds of guest molecules inside their cavities. For some substances with low water solubility, inclusion in CDs may improve their

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physicochemical proprieties such as solubility, stability and spectroscopic properties [31–35]. In fact, CDs have been shown previously in a number of systems to enhance fluorescence of hydrophobic fluorophores, which can be used to improve the detection limits for the analytes through the signal enhancement [32,34,35]. Herein the absorption and fluorescence emission spectral properties of DHAQ were investigated in aqueous solutions of β-cyclodextrin. We show that with the assistance of ammonia, the DHAQ–β-CD complex exhibits substantial color change and fluorescence quenching upon complexation with $Cu^{2+}$, which could be utilized as a selective colorimetric and fluorescent probe for $Cu^{2+}$ in aqueous solution.

## 2. Experimental

### 2.1. Apparatus

The UV absorption measurements were carried out on a UV-2450 spectrophotometer (Shimadzu, Japan). Fluorescence measurements were performed on a RF-5301 PC spectrofluorometer (Shimadzu, Japan). The samples were excited at 436 nm. The excitation and emission slits were both set at 10 nm. IR spectra were taken as KBr pellets on a SHIMADZU 8400S infrared spectrometer (Nicolet, Waltham, Japan). The pH measurements were carried out on a pHS-3C acidometer (Shanghai Precision & Scientific Instrument Co., Ltd, China).

### 2.2. Reagents

1,8-Dihydroxyanthraquinone (DHAQ) was purchased from Alfa Aesar (Lancaster, UK). β-CD was obtained from Wacker Co. (Munich, Germany) and used as received. All the other chemical reagents were of analytical grade and used as received without further purification. Britton–Robinson (B–R) buffer solutions of different pH were prepared by mixing appropriate amounts phosphoric, acetic and boric acids of the same concentration ($0.040\,\text{mol}\,L^{-1}$) and then adjusting to desired pH with $0.20\,\text{mol}\,L^{-1}$ sodium hydroxide. All the metallic ions were supplied from their corresponding nitrates. Stock solution of DHAQ was prepared in ethanol at $1.0 \times 10^{-3}\,\text{mol}\,L^{-1}$ and kept in the dark. All metal ion stock solutions were prepared by dissolving the appropriate amounts of metal salts with water. Doubly distilled water was used throughout.

### 2.3. General procedure

For the pH titration of DHAQ, the absorption and fluorescence spectra were monitored in β-CD solutions of various pH. Into a comparison tube were added 0.1 mL of DHAQ stock solution, 2.5 mL of $1.0 \times 10^{-2}\,\text{mol}\,L^{-1}$ β-CD stock solution and 2 mL of B-R buffer solution sequentially. The mixed solution was diluted to the final 5 mL and then shaken thoroughly before absorption and fluorescence spectra were collected. In the solution obtained, the concentrations of DHAQ and β-CD were $2.0 \times 10^{-5}$ and $5 \times 10^{-3}\,\text{mol}\,L^{-1}$, respectively.

The titrations of DHAQ with $Cu^{2+}$ ions were performed as follows: into a comparison tube were added 0.1 mL of DAAQ stock solution, 2.5 mL of $1.0 \times 10^{-2}\,\text{mol}\,L^{-1}$ β-CD stock solution, 0.4 mL of $1.0 \times 10^{-2}\,\text{mol}\,L^{-1}$ ammonia stock solution and different volumes of $Cu^{2+}$ ions stock solution. The final volume was adjusted to 5 mL with water and was shaken thoroughly. The mixed solution was allowed to stand for 5 min to allow complete formation of metal–ligand complex, then the absorption and fluorescence spectra were measured.

The effect of various metal ions on the determination of $Cu^{2+}$ was investigated by analyzing the sample solutions containing $2 \times 10^{-5}$ M DHAQ, $8 \times 10^{-4}$ M ammonia and $2 \times 10^{-5}$ M interfering metal ions. $Cu^{2+}$ ions were added at a concentration of $2 \times 10^{-5}$ M into above sample solutions. Before fluorimetric detection, the mixed solution was allowed to stand for 5 min to allow complete formation of stable solution.

### 2.4. Analysis of real samples

Tap water and polluted river water samples were used without any treatment. All the water samples were spiked with $Cu^{2+}$ at different concentration levels and then analyzed by following the general procedure described above. The confidence intervals were estimated to results of determination based on $p = 95\%$ and $n = 5$. $p$ and $n$ were the confidence level and times of replicating determination, respectively.

For the assay of copper in tea, 1.000 g of the sample was weighed and transferred into a crucible. The sample was heated to dryness on an electric furnace and then incinerated in a muffle furnace at 600 °C for about 4 h until the sample turned into white color. After cooled to room temperature, the residue was dissolved with $5\,\text{mol}\,L^{-1}$ $HNO_3$. The solution was then transferred into a 10 mL calibrated flask, adjusted to pH 7.0 with NaOH solution of $1\,\text{mol}\,L^{-1}$ and diluted to the mark with double-distilled water. The concentration of $Cu^{2+}$ in the sample solutions was then determined as described in Section 2.3.

## 3. Results and discussion

### 3.1. Photophysical properties of DHAQ and the effect of pH

Anthraquinone derivatives have four $\pi\pi^*$ absorption bands in the region of the wavelength between 220 and 350 nm and an $n\pi^*$ band at longer wavelength near 400 nm [36]. The UV/vis spectrum of DHAQ shows a broad band centered at ca. 416 nm, which can be attributed to $n \rightarrow \pi^*$ transition (Fig. 1a). Absorption spectra of DHAQ at various pH values were recorded. It was found that after pH 8.0 the intensity of the absorption at 416 nm decreased and a new peak at 500 nm appeared whose intensity increased with an increase in pH (Fig. 1a). Change in absorbance at 500 nm indicates release of the first phenolic proton in the pH range 8–10 while the second phenolic proton is released at pH values higher than 11 [22]. Similar studies have been reported in solutions of buffers and organic solvents where the shifting of the absorption maxima towards higher wavelengths and increasing intensity of the long-wavelength absorption bands take place as a result of the transformation from the protonated species to the deprotonated species [22,37,38].

Depending on the pH of the solution, DHAQ exists in aqueous solution in three distinct forms. At acidic and neutral pH, the solution is yellow, it is pink in dilute alkali and deep blue in strongly alkaline solution representing neutral (DHAQ), anionic ($DHAQ^{-H}$) and dianionic ($DHAQ^{-2H}$) states, respectively.

The fluorescence emission spectrum of DHAQ in β-CD aqueous solution shows two peaks, with intensity maxima at 514 and 552 nm, respectively. As shown in Fig. 1b, the fluorescence intensity of DHAQ shows small changes in the pH range 2–7. When pH is more than 8, the emission peaked at 552 nm decreases dramatically with increasing pH value, and disappears ultimately at pH 11 due to the deprotonation of DHAQ.

### 3.2. Sensing of Cu(II) by DHAQ–β-CD inclusion complex

#### 3.2.1. Effect of β-CD

DHAQ is practically insoluble in water; however, when it formed a supramolecular complex with β-CD in water, the whole system

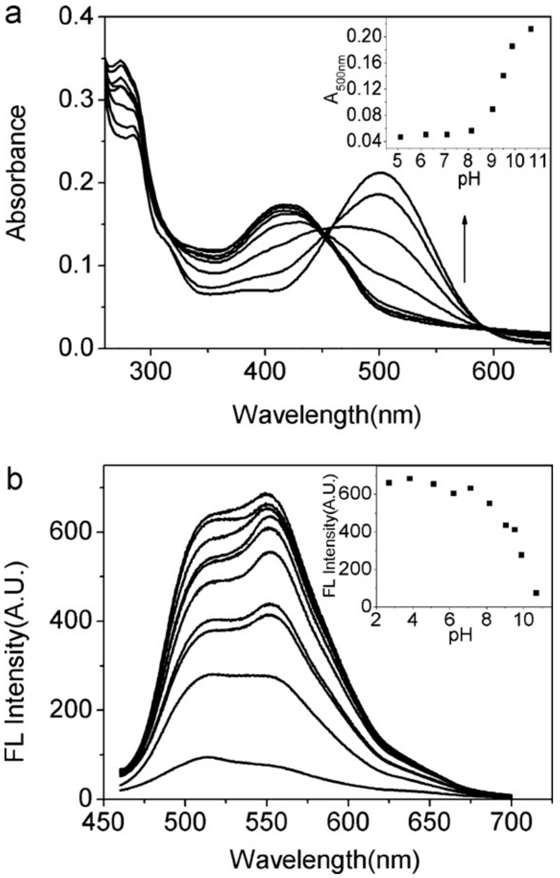


**Fig. 1.** pH effect on the (a) absorption and (b) emission spectra of DHAQ. [DHAQ] = $2 \times 10^{-5}$ mol $L^{-1}$; [β-CD] = $5 \times 10^{-3}$ mol $L^{-1}$.

was soluble and stable. Both absorption and fluorescence intensities of DHAQ were enhanced by β-CD, e.g., the fluorescence intensity of DHAQ was at least 2-fold higher in presence of β-CD (data not shown). Namely, β-CD has the sensitizing effect on the determination of $Cu^{2+}$. Moreover, β-CD has the stabilizing effect on the whole system. Aqueous solution of the DHAQ–β-CD complex remains clear and transparent upon addition of $Cu^{2+}$. Thus, experiments for $Cu^{2+}$ sensing were performed in aqueous solution of β-CD. The use of β-CD at a concentration of $5 \times 10^{-3}$ M gave satisfactory results.

### 3.2.2. *Colorimetric signaling of $Cu^{2+}$ ions*

When $8 \times 10^{-4}$ M ammonia was added to an β-CD aqueous solution of DHAQ, the solution turned from yellow to citrus red, and the absorbance at 416 nm decreased while a longer absorption band with the peak at around 500 nm occurred (No. 2 in Fig. 2). The observed bathochromic shift indicated release of the first phenolic proton of DHAQ and the formation of the monoanion $DHAQ^{-H}$. When unceasingly adding another 1 equiv. of Cu(II), the absorbance at 500 nm deceased gradually, and a new absorption band at 546 nm developed, which induced a color change from citrus red to purple red (For interpretation of the references to color in this text, the reader is referred to the web version of the article.) (No. 4 in Fig. 2). Our experiment shows that a dilute aqueous solution of the $Cu^{2+}$ ions is colorless (No. 5 in Fig. 2), indicating that the new absorption band at around 546 nm is not caused by the absorption of $Cu^{2+}$ ions. Thus the decrease in absorbance at 500 nm due to the $DHAQ^{-H}$ unit and the simultaneous increase in absorbance at 546 nm could be attributed to metal–ligand complex formation. The distinctive color change with the addition of $Cu^{2+}$ indicated the potential of the probe to function as a visible chemosensor for this ion. It is noteworthy that the absorption of the system was enhanced by β-CD (from No. 3 to 4 in Fig. 2), reflecting the sensitizing effect of β-CD on the determination of $Cu^{2+}$. More importantly, β-CD shows the stabilizing effect on the whole system. For the system without β-CD (No. 3 in Fig. 2), more precipitation appeared with the standing time and the solution became cloudy. By contrast, the β-CD system (No. 4 in Fig. 2) remained clear and transparent for a long time.

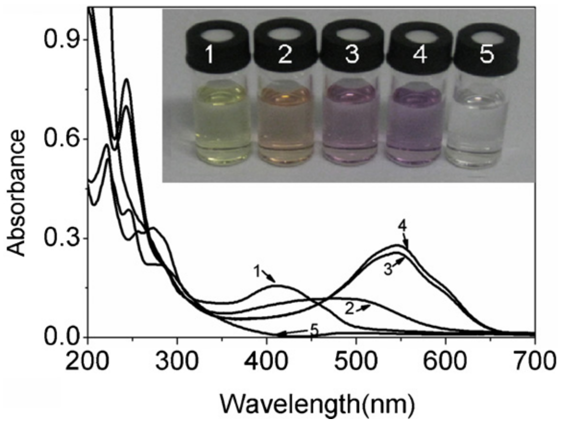


**Fig. 2.** Absorption spectra of aqueous solutions of (1) DHAQ + β-CD, (2) DHAQ + β-CD + ammonia, (3) DHAQ + ammonia + $Cu^{2+}$, (4) DHAQ + β-CD + ammonia + $Cu^{2+}$ and (5) ammonia + $Cu^{2+}$. [DHAQ] = $2 \times 10^{-5}$ mol $L^{-1}$; [β-CD] = $5 \times 10^{-3}$ mol $L^{-1}$; [ammonia] = $8 \times 10^{-4}$ mol $L^{-1}$; [$Cu^{2+}$] = $2 \times 10^{-5}$ mol $L^{-1}$.

Similar measurements for other metal ions were examined. The addition of other metal ions such as $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Hg^{2+}$, $Pb^{2+}$, $Cd^{2+}$, $Co^{2+}$, $Mn^{2+}$, $Cr^{3+}$, $Ag^+$, $Al^{3+}$, $Fe^{2+}$ and $Fe^{3+}$ did not cause noticeable color change (Fig. 3), manifesting a good chromogenic selectivity of the system toward $Cu^{2+}$ ions in aqueous media.

The spectrophotometric titration of DHAQ with $Cu^{2+}$ is depicted in Fig. 4 and the inset shows a linear dependence of the ratio of absorbance at 546 nm and absorbance at 498 nm as a function of $Cu^{2+}$ concentration. Good linearity was observed in the range of 3–20 μM. The plot of the increase in absorbance at 546 nm reached the saturation point when the ratio of $Cu^{2+}$ got to the equivalent concentration, indicating a 1:1 stoichiometry between DHAQ and $Cu^{2+}$ ions

### 3.2.3. *Fluorescence signaling of the $Cu^{2+}$ ions*

The effect of Cu (II) ions on the fluorescence emission of DHAQ in β-CD aqueous solution in the presence of ammonia is shown

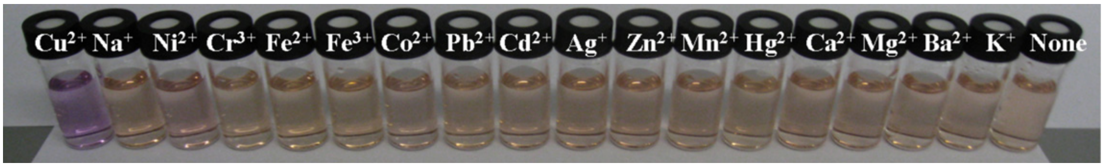


**Fig. 3.** Color changes of DHAQ ($2.0 \times 10^{-5}$ M) upon addition of various metal ions ($2.0 \times 10^{-5}$ M) in β-CD aqueous solutions. [β-CD] = $5 \times 10^{-3}$ mol $L^{-1}$; [ammonia] = $8 \times 10^{-4}$ mol $L^{-1}$.

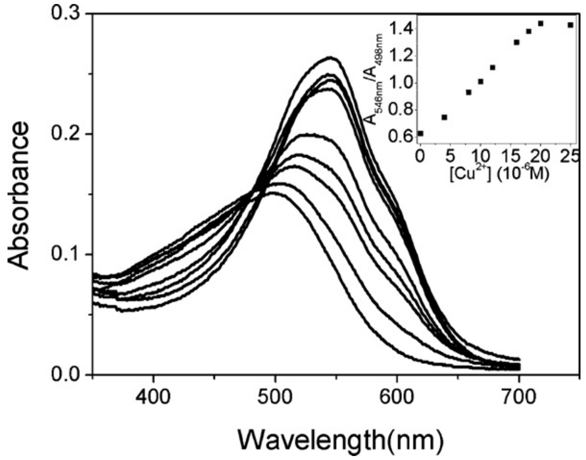


**Fig. 4.** $Cu^{2+}$-titration induced the absorption changes of DHAQ in β-CD aqueous solution. [DHAQ] = $2 \times 10^{-5}$ mol $L^{-1}$; [β-CD] = $5 \times 10^{-3}$ mol $L^{-1}$; [ammonia] = $8 \times 10^{-4}$ mol $L^{-1}$. Inset: Plot of the ratio of absorbance at 546 nm and absorbance at 498 nm as a function of $Cu^{2+}$ concentration.

in Fig. 5. The fluorescent intensity of DHAQ can be significantly quenched by $Cu^{2+}$ ions with no significant change in the position of the emission maxima. The fluorescence intensity was reduced down to less than 13% of the original value in the presence of 1 equiv of $Cu^{2+}$ ions. Quenching effect of $Cu^{2+}$ ion on the fluorescence emission of DHAQ was found to be concentration dependent. Therefore, this supramolecular complex system could be used for the fluorescence determination of $Cu^{2+}$ in water.

Under optimum conditions, a quantitative analysis of the fluorescence data was made as a function of the $Cu^{2+}$ ion concentration. The data were plotted according to the Stern–Volmer equation: $F_0/F = 1 + K_{SV}[Cu^{2+}]$, where $F_0$ and $F$ are fluorescence intensities in the absence and in the presence of $Cu^{2+}$, respectively. The calibration plot of $F_0/F$ versus $[Cu^{2+}]$ shows a good linear relationship (correlation coefficient, $R^2 = 0.9944$) for copper (II) ion concentration in the range from 0 to $2.0 \times 10^{-5}$M (Fig. 5 inset). The Stern–Volmer quenching constant was estimated as $3.359 \times 10^5$ $M^{-1}$. The detection limit is $2.7 \times 10^{-7}$ mol $L^{-1}$, which is satisfactory to the $Cu^{2+}$ detection in drinking water within U.S. Environmental Protection Agency limit (20 μM) [16].

The fluorescence sensing selectivity of this system for $Cu^{2+}$ was examined. Under the same conditions as used above for $Cu^{2+}$, we tested the fluorescence responses of DHAQ towards other metal ions such as $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Hg^{2+}$, $Pb^{2+}$, $Co^{2+}$, $Cr^{3+}$, $Ag^+$, $Fe^{2+}$ and $Fe^{3+}$. As depicted in Fig. 6, the addition of other tested metal ions produced insignificant changes in fluorescent spectra of the system. Compared with other transition metal ions, copper(II) has a particularly high thermodynamic affinity for typical N,O-chelate ligands and fast metal-to-ligand binding kinetics [39], which could account for the selectivity of the system to $Cu^{2+}$. The chelation-induced fluorescence quenching is probably induced by redox active $Cu^{2+}$ ions via either ligand-to-metal electron or energy transfer mechanisms [40]. Although the other transition metal ions also have the complex ability as well, which is not as strong as copper ions, they only lead to the decrease in fluorescence to a certain degree [41].

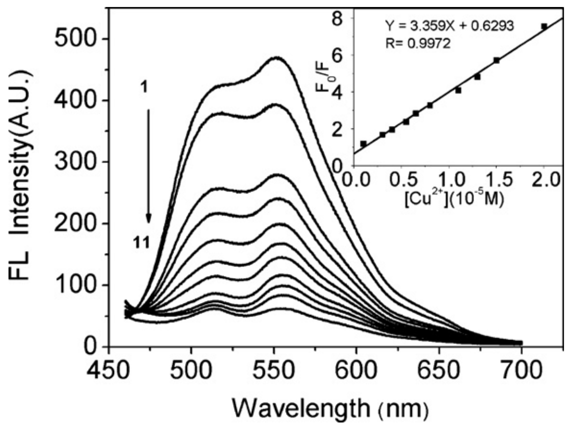


**Fig. 5.** Fluorescence spectra of DHAQ in β-CD aqueous solution with various concentrations of $Cu^{2+}$. [DHAQ] = $2 \times 10^{-5}$ mol $L^{-1}$; [β-CD] = $5 \times 10^{-3}$ mol $L^{-1}$; [ammonia] = $8 \times 10^{-4}$ mol $L^{-1}$; $[Cu^{2+}]$($10^{-5}$ mol $L^{-1}$) = (1–11) 0, 0.1, 0.3, 0.4, 0.55, 0.65, 0.8, 1.1, 1.3, 1.5, 2.0. Inset: Stern–Volmer quenching plot of DHAQ/β-CD complex with increasing concentration of $Cu^{2+}$.

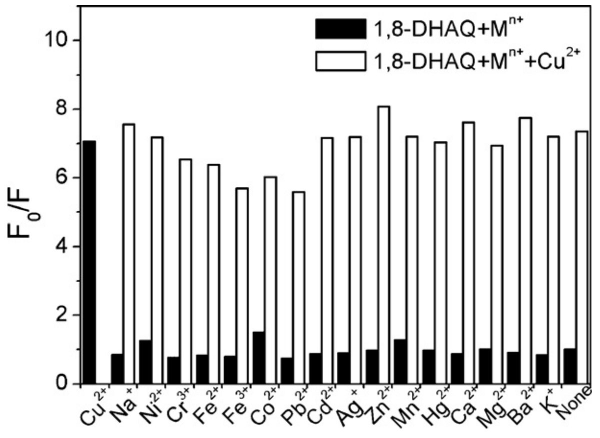


**Fig. 6.** metal-ion responses for DHAQ (20 μM) in the absence ($F_0$) and presence ($F$) of metal ions in aqueous solution of β-CD. [β-CD] = $5 \times 10^{-3}$ mol $L^{-1}$; [ammonia] = $8 \times 10^{-4}$ mol $L^{-1}$; $[Cu^{2+}]$ = $2 \times 10^{-5}$ mol $L^{-1}$; $[M^{n+}]$ = $2 \times 10^{-5}$ mol $L^{-1}$.

The competition experiments were further conducted. Fig. 6 shows the fluorescence response of DHAQ to $Cu^{2+}$ in the presence of other coexisting related metal ions. The emission intensity of the DHAQ–$Cu^{2+}$ complex was not remarkably affected by other metal ions, suggesting the high selectivity of the system for $Cu^{2+}$ over other metal ions. The potential interference of concomitant anions were also investigated. The tolerance concentrations of each species was taken as the largest amount yielding an error less than ±5% of the analytical signal of an aqueous solution containing $2 \times 10^{-5}$ M DHAQ, $8 \times 10^{-4}$ M ammonia and $5 \times 10^{-6}$ M $Cu^{2+}$ ions. The following maximal quantities of ions can be tolerated: 400 μM of $F^-$, $C1^-$, ${SO_3}^{2-}$; 400 μM of $Br^-$; 1000 μM of $S^{2-}$; 2000 μM of $I^-$, ${SO_4}^{2-}$, ${NO_3}^-$, ${NO_2}^-$. And thus the system witnesses a highly selective detection method potential to future use. In addition, due to the low cost of β-CD and DHAQ, the method is much less expensive than some other more sensitive $Cu^{2+}$ fluorescent or electrochemical assays currently in use.

### 3.3. *The possible binding mechanism*

The observed UV spectral variation, in particular the red shift of the DHAQ absorption by $Cu^{2+}$, indicated that the complexes were formed between DHAQ and $Cu^{2+}$. The stoichiometry between DHAQ and Cu(II) in the complexed system was determined by the changes in the fluorescence response of DHAQ with varying concentrations of $Cu^{2+}$. In Fig. 7, the emission intensity change at 552 nm is plotted against molar fraction of DHAQ under a constant total concentration. Maximum change in emission intensity was reached when the molar fraction was 0.5, indicating a 1:1 stoichiometry of the $Cu^{2+}$ to DHAQ in the complex. The association constant $K$ of $Cu^{2+}$ binding in the system was evaluated graphically by plotting $1/\Delta F$ against $1/[Cu^{2+}]$ and was found to be $1.51 \times 10^5$ $M^{-1}$.

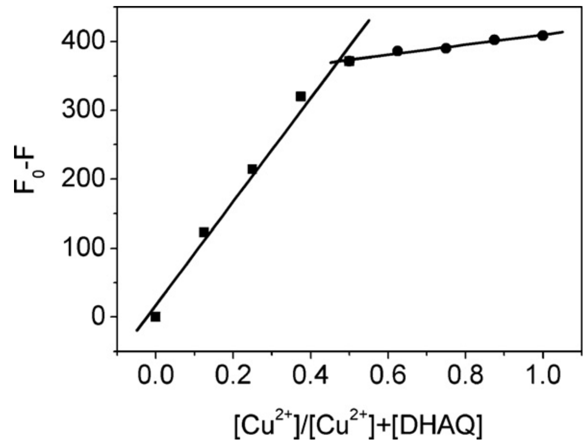


**Fig. 7.** Job's plot for DHAQ and $Cu^{2+}$ complexation in aqueous solution of β-CD. [β-CD] = $5 \times 10^{-3}$ mol L$^{-1}$; [ammonia] = $8 \times 10^{-4}$ mol L$^{-1}$; The total concentration of DHAQ and $Cu^{2+}$ is $2 \times 10^{-5}$ mol L$^{-1}$.

Besides DHAQ, ammonia could also bind $Cu^{2+}$ cooperatively through the lone-pair electrons on the nitrogen atom. In fact, the color change of the DHAQ solution caused by $Cu^{2+}$ only occurred in the presence of ammonia. To understand the crucial role of ammonia, which possibly behaves as an assistant copper ligand, the effect of ammonia concentration on the UV spectra of the system was investigated. As shown in Fig. 8, little UV change was observed for the DHAQ/$Cu^{2+}$ system at lower concentration of ammonia. When the concentration of ammonia is greater than $2 \times 10^{-4}$ M, the absorbance at 416 nm due to the neutral DHAQ deceases gradually, and a new peak at 546 nm appears whose intensity increases with an increase of ammonia concentration. Considering the adding of ammonia will change the pH of the solution, the effect of pH on the DHAQ/$Cu^{2+}$ system was investigated in the absence of ammonia for comparison. Britton–Robinson (B–R) buffer solutions were used to adjust the acidity of solution. At the same pH of 9.4, the DHAQ/$Cu^{2+}$/ammonia system shows a maximum absorption band at 546 nm while the DHAQ/$Cu^{2+}$ buffer solution shows an absorption maximum at 502 nm (Fig. 8). This strongly supports that ammonia molecules play an important role in the perceived color change of the system. Therefore, we can conclude that both the anthraquinone moiety and ammonia molecule may participate in the binding and jointly form a stable complex with the $Cu^{2+}$ ion. Here ammonia acts as a base as well as a ligand for $Cu^{2+}$.

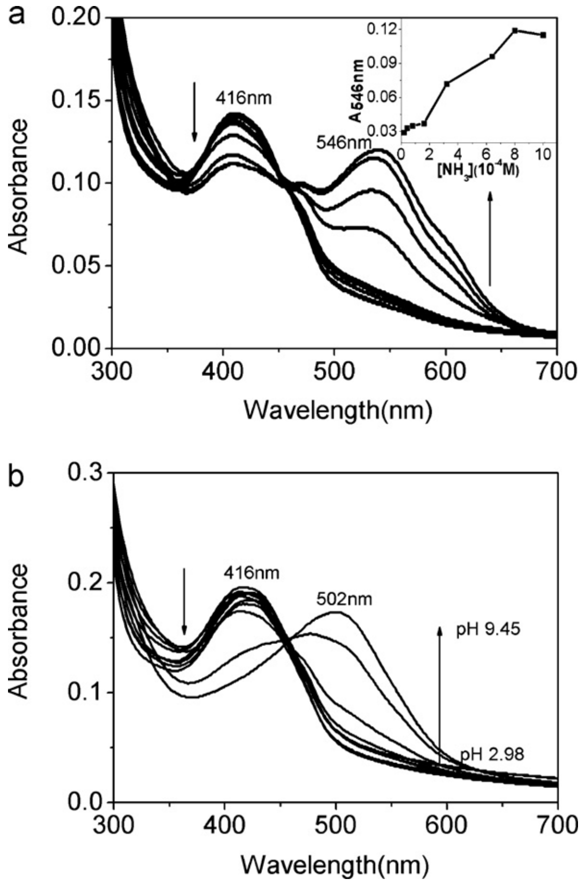


**Fig. 8.** Effect of ammonia concentration (a) and BR buffer at different pH values (b) on the absorption spectra of the DHAQ/$Cu^{2+}$ system in β-CD aqueous solution. [DHAQ] = $2 \times 10^{-5}$ mol L$^{-1}$; [β-CD] = $5 \times 10^{-3}$ mol L$^{-1}$; [$Cu^{2+}$] = $2 \times 10^{-5}$ mol L$^{-1}$.

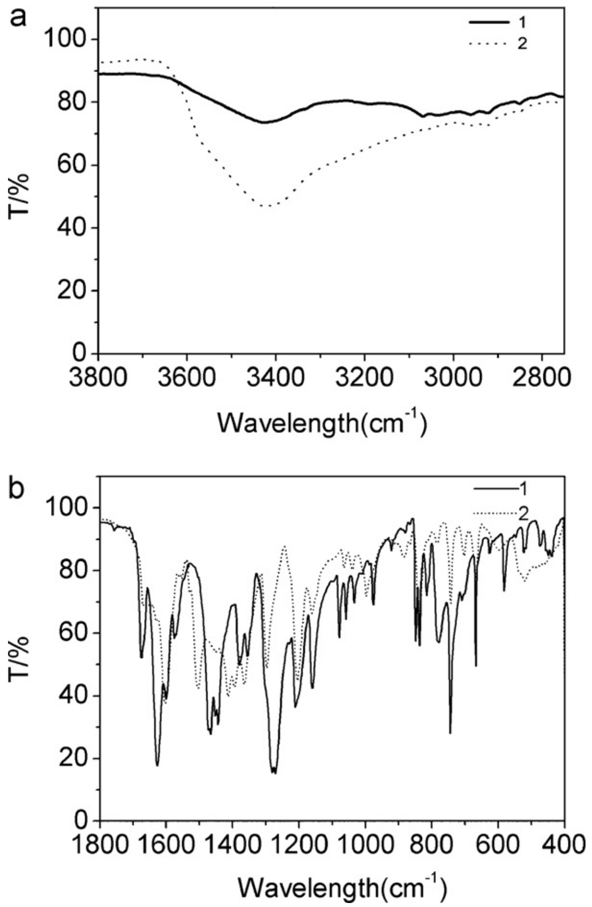
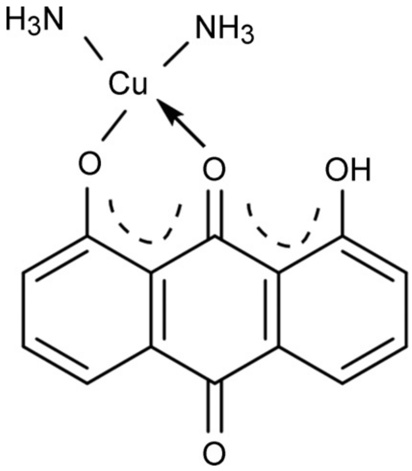


**Fig. 9.** Infrared spectra of DHAQ (1) and DHAQ–$Cu^{2+}$–$NH_3$ complex (2). Note: Solids of the DHAQ–Cu–$NH_3$ complex grown from aqueous solution are used to make pellets with potassium bromide for the infrared spectrum of the complex.

We measured IR spectra of DHAQ and its complex to further examine the binding site. As shown in Fig. 9, a carbonyl group shift (from 1736 to 1729 cm$^{-1}$) was observed in the IR spectrum of DHAQ upon the addition of $Cu^{2+}$, which confirms the participation of carbonyl oxygen in the binding with $Cu^{2+}$. The newly formed band at ~519 cm$^{-1}$ in the spectra of the complex can be tentatively assigned to Cu–O vibration. Thus, in accordance with the 1:1 stoichiometry, DHAQ is the most likely to chelate $Cu^{2+}$ via its carbonyl and phenol O atoms. In the spectra of the complex the broad band at ~3400 cm$^{-1}$, together with a new band at ~702 cm$^{-1}$ indicate the presence of coordinating $NH_3$ [42], supporting the notion that the ammonia molecule is involved in the coordination of $Cu^{2+}$ ions.

Based on the spectroscopic data (UV–vis, Fluorescence and IR), we suppose that the composition of the four-coordinated $Cu^{2+}$



**Scheme 1.** Possible interaction mode between DHAQ, $Cu^{2+}$ and $NH_3$.

complexes is Cu·DHAQ·2$NH_3$. Due to the Jahn–Teller effect, coordinating interaction of the four equatorial sites is stronger than that of the remaining axial positions [43]. Consequently, four-coordinated $Cu^{2+}$ complexes are generally characterized by a square planar geometry if there is no special geometrical constraints in ligands, just like in the present system. In this case, the carbonyl and phenol O atoms of DHAQ may coordinate with $Cu^{2+}$ ions and the remaining coordination sites on each metal are occupied by two ammonia donors. The proposed structure of the complex is shown in Scheme 1.

### *3.4. Preliminary analytical application*

To examine its potential applicability, the proposed method was preliminarily applied in the determination of $Cu^{2+}$ in tap and polluted river water samples as well as in tea. With a given amount of Cu(II) spiked in tea and water samples, recovery yields were determined using the calibration curve and listed in Table 1. As shown in Table 1, the system was able to measure the concentrations of spiked $Cu^{2+}$ with good recovery, suggesting that the method could potentially be used for detecting $Cu^{2+}$ in real samples.

## 4. Conclusions

With the assistance of ammonia, DHAQ functions both as a chromogenic and fluorogenic probe for $Cu^{2+}$ with high selectivity. β-CD has the sensitizing effect on the determination of $Cu^{2+}$. Moreover, β-CD has the stabilizing effect on the whole system. The detection limit for this method was in the order of $10^{-7}$ M. There are several advantages for this 'new' fluorescent system; first, the excitation (436 nm) and emission (552 nm) wavelengths for the detection of $Cu^{2+}$ ions were in the visible range; second, the color change can be distinguished easily by the naked eyes without resorting to any expensive instruments; third, DHAQ can be commercial obtained as a cheap industrial material and no complicated chemical modification was needed.

**Table 1**
Determination of Cu (II) in water and tea samples.

| Samples | $Cu^{2+}$ added (μM) | $Cu^{2+}$ found (μM) | Recovery (%) | R.S.D.[a] (%) |
|---|---|---|---|---|
| Tap water 1 | 0.00 | 0.80 ± 0.07 | | 1.67 |
| Tap water 2 | 0.50 | 1.33 ± 0.13 | 106 | 2.68 |
| Tap water 3 | 1.00 | 1.75 ± 0.10 | 95 | 1.09 |
| River water 1 | 0.00 | 5.41 ± 0.21 | | 1.41 |
| River water 2 | 5.00 | 10.51 ± 0.18 | 102 | 1.55 |
| River water 3 | 10.00 | 15.02 ± 0.34 | 96 | 0.91 |
| Tea 1[b] | 0.00 | 16.26 ± 0.38 | | 2.57 |
| Tea 2[b] | 6.4 | 22.40 ± 0.46 | 96 | 2.13 |
| Tea 3[b] | 12.8 | 28.42 ± 0.34 | 95 | 1.98 |

[a] Relative standard deviation, $n = 5$.
[b] Expressed as $\mu g\,g^{-1}$.

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