Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 109 (2013) 186–192

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

# A new carbazole-based Schiff-base as fluorescent chemosensor for selective detection of $Fe^{3+}$ and $Cu^{2+}$

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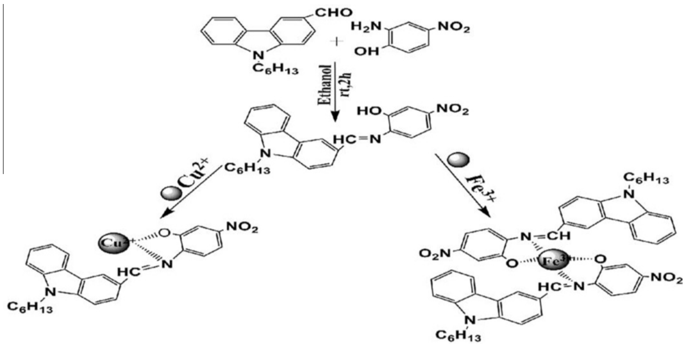
## HIGHLIGHTS

- We designed and synthesized a new carbazole-based Schiff base sensor.
- Compound **1** could be used as a multi-functional sensor for detecting $Fe^{3+}/Cu^{2+}$ by both using UV–Vis and fluorescence methods.
- We found that the bonding mode between compound **1** and $Fe^{3+}/Cu^{2+}$ is different.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

*Article history:*
Received 16 November 2012
Received in revised form 30 January 2013
Accepted 20 February 2013
Available online 1 March 2013

*Keywords:*
Schiff-base
$Fe^{3+}$, $Cu^{2+}$ ion sensor
Fluorescence enhancement
Red shift

## ABSTRACT

A new carbazole-based Schiff-base (**1**) as a multi-functional fluorescent chemosensor was designed, synthesized and characterized, which can selectively recognized $Fe^{3+}$ and $Cu^{2+}$ ions over a number of other metal ions. Compound **1** could detect $Fe^{3+}$ and $Cu^{2+}$ by UV–Vis method and fluorescence method. The stoichiometry ratio of **1**-$Fe^{3+}$ and **1**-$Cu^{2+}$ are 2:1 and 1:1, respectively, by the method of Job's plot. Moreover, the detection limits were calculated to be $4.23 \times 10^{-6}$ mol/L for $Fe^{3+}$ ion and $5.67 \times 10^{-6}$ mol/L for $Cu^{2+}$ ion. In the presence of $Fe^{3+}/Cu^{2+}$ ions, the fluorescence enhancement was attributed to the inhibited C=N isomerization and the obstructed excited state intramolecular proton transfer (ESIPT) of compound **1**. At the same time, the interactions of compounds **1** with other ions were also investigated and unobvious UV–Vis absorption and fluorescence spectral changes were observed. Thus a new kind of chemosensor for $Fe^{3+}/Cu^{2+}$with high sensitivity and selectivity was introduced.

## Introduction

The design and synthesis of fluorescent chemosensors are active and fascinating research areas in supramolecular chemistry, organic chemistry, drug delivery, biological chemistry and environmental chemistry [1–3]. Fluorescent chemosensors have high selectivity and sensitivity for detecting metal ions in aqueous and nonaqueous media [4–7]. Iron and copper are the first and the third abundant transition metal elements respectively. Iron is one of the most essential elements for normal physiological function in human body, because it plays an important role in many cellular processes including DNA and RNA synthesis, energy generation and oxygen transport [8–10]. The deficiency of $Fe^{3+}$ causes intelligence decline, liver damage, hemochromatosis, Parkinson's, anemia, diabetes and cancer [11–13]. However, iron overload can cause deleterious conditions such as β-thalassaemia and Friedreich's ataxia where the presence of excess iron leads to the generation of reactive oxygen species via the Fenton reaction [14]. On the other side, copper is known as an essential element in both biological and industry systems [15]. It is one of the most essential trace mental nutrients to sustain normal human health and sever as an essential cofactor for a wide variety of enzymes in all living

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http://dx.doi.org/10.1016/j.saa.2013.02.043

organisms [13,16]. However, high concentration of copper with redox property could turn into a biologically hazard because of its ability to generate reactive oxygen species, which causes irritation of nose and throat, nausea, vomiting, and diarrhea [17]. Therefore, how to effectively detect iron and copper is of great significance in biology, chemistry, environmental science and medicine. There is a pressing need for analytical methods with speed, accurateness and low-cost. Fluorescent chemosensor could better meet the above requirements. In recent years, it is gradually becoming a new hotspot that analysis and detection for metal ions in environmental systems by taking advantage of fluorescent chemical sensor [18–20].

Different kinds of mechanisms such as photoinduced electron transfer (PET), metal-to-ligand charge transfer (MLCT), internal charge transfer (ICT), photoinduced proton transfer (PPT), excited-state intramolecular proton transfer (ESIPT), chelation-enhanced fluorescence (CHEF) effect and $C{=}N$ isomerization have been utilized for designing fluorescent chemosensors [21–26]. Schiff bases, condensation of amines and reactive aldehydes, are important compound with various potential applications [27]. Schiff bases with a bridged $C{=}N$ structure easily isomerize in the excited state and tend to exhibit very weak fluorescence due to the $C{=}N$ isomerization [28,29]. But when they form complexes with some special metal ions, the $C{=}N$ isomerization is inhibited, and then Schiff bases show strong fluorescence. At present, the most carbazole derivatives are used for photoelectric functional materials. There are few reports on fluorescent chemosensor of the carbazole derivatives for selective detection of metal ions. Moreover, $Fe^{3+}$ and $Cu^{2+}$ ions are well known fluorescent quenchers due to their paramagnetism, which could influence the information of 'turn-on' fluorescent sensors for their detection [25,28].

Therefore, in this paper we designed and synthesized compound **1** with a bridged $C{=}N$ structure and carbazole ring (fluorophores unit). 4-Nitrophenol linked alkylcarbazole through the $C{=}N$ bond, so the compound **1** formed complexes with some metal ions through the oxygen atom of hydroxyl and the nitrogen atom of $C{=}N$ double bond. It can regulate coordination ability by using the difference of modulation between ligand and the metal ions to achieve the selective recognition for special metal ion. Compound **1** is poorly fluorescent, may due to isomerization of the $C{=}N$ double bond in the excited state, and ESIPT involving the phenolic protons [6]. When compound **1** forms complexes with some special metal ions, the absorbance or the fluorescence intensity maybe changed. In our work, a variety of complexes between compound **1** and the special ions could be detected by UV–Visible absorption method and fluorescence emission spectrum method, so compound **1** could be used as a multi-functional sensor for detecting the special ions by both using UV–Vis and fluorescence methods.

## Experimental

### Materials and instruments

Reagents were purchased as reagent-grade from Sinopharm Chemical Reagent Co. Ltd., (Shanghai, China) and used without further purification unless otherwise state. DMF was freshly distilled from molecular sieve. Double distilled water was used for spectral detection. $CH_3CN$ was HPLC grade without fluorescent impurities. The solutions of metal ions were prepared from nitrate salts except for $FeCl_3$.

The FT-IR spectra were recorded with KBr pellets on a 170 sx spectrometer (Nicolet, USA). Elemental analysis were determined on a Vario EL III spectrometer (Elementar, Germany). $^1$H NMR spectra were obtained on an AV-400 spectrometer (Bruker, Switzerland). Chemical shifts (δ) were given in ppm relative to $CDCl_3$ 7.26 (1H). All spectral characterizations were carried out in HPLC-grade solvents at 20 °C within a 10 mm quartz cell. UV–Visible absorption spectra were recorded on a UV-3600 spectrophotometer (Shimadzu, Japan). Fluorescence emission spectra were recorded on a LS-55 FL spectrophotometer (Perkin Elmer, USA). Stock solutions of metal salts were prepared in distilled water. The stock solutions for compound **1** (1 mM) were prepared in HPLC grade $CH_3CN$ and were used to prepare the $CH_3CN$ solution.

### Synthesis

#### Synthesis of 9H-hexylcarbazole (3)

One gram NaH was added in batches to the stirred solution of carbazole (4.0 g, 24 mmol) in anhydrous DMF (20 mL) and the solution was stirred for another 20 min. Then DMF (10 mL) solution containing 4 mL (28 mmol) 1-bromohexane was added dropwise. After complete addition, the reaction mixture was heated to reflux for 3 h. When the mixture was cooled down to room temperature, it was poured into water and carefully adjusted the pH value to neutral with 1:1 ($HCl/H_2O$, v/v) concentrated hydrochloric acid. Then the product was filtered and recrystallized from ethanol. The yield was 76.58% (4.62 g, 76.58%). FT-IR (Fig. S1, KBr, $cm^{-1}$): 3049 ($=C-H$), 2856-2953 ($-CH_2$, $-CH_3$), 1459 ($-CH_3$), 1323 ($-CH_2-$), 1621-1594 (structure of carbozle). $^1$H NMR (Fig. S2, $CDCl_3$, 400 Hz): $\delta_H$ 8.09 (d, $J$ = 7.60 Hz, 2H), 7.38–7.48 (m, 4H), 7.21 (d, $J$ = 8.00 Hz, 2H), 4.28 (t, 2H), 1.86 (m, 2H), 1.33 (m, 6H), 0.86 (t, 3H).

#### Synthesis of 3-formyl-9H-hexylcarbazole (2)

To a stirred solution of compound **3** (2.51 g, 10 mmol) in anhydrous DMF (30 mL), phosphorus oxychloride ($POCl_3$, 0.2 mol) was added dropwise at 0 °C, and the mixture was stirred for another 30 min at this temperature. Then the reaction mixture was stirred at 70 °C for 2 h. When the mixture was cooled down to room temperature and stirred for 16 h, it was poured into ice water by rapidly stirring and carefully neutralized with potassium bicarbonate. The solution was extracted with ethyl acetate ($3 \times 50$ mL) and dried over anhydrous magnesium sulfate. The crude product was purified by column chromatography (neutral alumina; ethyl acetate/petroleum ether, 1/10, v/v) to give **2** (1.60 g, 57.35%). FT-IR (Fig. S3, KBr, $cm^{-1}$): 1692 ($-C{=}O$), 1375 ($-CH_3$), 1472 ($-CH_2$), 1621-1594 (structure of carbozle). $^1$H NMR (Fig. S4, $CDCl_3$, 400 Hz): $\delta_H$ 10.10 (s, 1H), 8.61 (s, 1H), 8.16 (d, $J$ = 7.60 Hz, 1H), 8.01 (d, $J$ = 8.40 Hz, 1H), 7.45–7.55 (m, 3H), 7.32 (t, 1H), 4.33 (t, 2H), 1.85–1.93 (m, 2H), 1.26–1.42 (m, 6H), 0.86 (t, 3H).

#### Synthesis of the Schiff base (**1**)

2-Amino-4-nitro-phenol (0.15 g 1 mmol) was added to the solution of **2** (0.34 g 1.2 mmol) in ethanol (2 mL). The resulting reaction mixture was stirred at room temperature for 2 h during which a pale yellow solid was obtained. The solid compound was filtered, washed, and recrystallized from the mixed solvent of chloroform and ethanol (9:1). The yield was 85.46%. Characterization of compound **1**: FT-IR (Fig. S5, KBr, $cm^{-1}$): 3302 ($-OH$), 3057 ($=C-H$), 2952-2856 ($-CH_2$, $-CH_3$), 1627 ($-CH{=}N$). $^1$H NMR (Fig. S6; 400 MHz; $CDCl_3$; $Me_4Si$): $\delta_H$ 10.10 (s, 1H), 8.93 (s, 1H), 8.71 (s, 1H), 8.29 (d, 1H), 8.12–8.21 (m, 3H), 7.46–7.57 (m, 3H), 7.35 (t, 1H), 7.11 (d, $J$ = 8.80 Hz, 1H), 4.36 (t, 2H), 1.88–1.95 (m, 2H), 1.25–1.46 (m, 6H), 0.88 (t, 3H). Elemental analysis: Anal. Calcd. for $C_{25}H_{25}N_3O_3$: C 72.27, H 6.06, N 10.11, found: C 72.28, H 6.08, N 10.13.

### *Spectrometric procedure*

The stock solution of compound **1** (1 mM) was prepared in HPLC grade $CH_3CN$ solvent, then 0.5 mL sample was diluted in a 50 mL volumetric flask to be used for spectroscopic study. 3 mL diluted solution was transferred to a 10 mm quartz cell, and then metal ions were added for testing. UV–Visible and fluorescent titration and competition experiments were carried out by adding 10.0 mM $Fe^{3+}/Cu^{2+}$ to solution of **1** (10.0 μM) in the presence of miscellaneous cations including $Na^+$, $K^+$, $Ag^+$, $Ca^{2+}$, $Hg^{2+}$, $Zn^{2+}$, $Co^{2+}$, $Mn^{2+}$, $Mg^{2+}$ and $Cr^{3+}$ (10.0 μM, respectively).

The association constant ($K_a$) of compound **1** with metal ions was determined using the Benesi–Hildebrand equation [20] as follows:

$$\frac{1}{F - F_0} = \frac{1}{K_a(F_{max} - F_0)[M]} + \frac{1}{F_{max} - F_0}$$

$F$ and $F_0$ represent the fluorescent intensity of compound **1** in the presence and absence of metal ions, respectively. $F_{max}$ is the saturated fluorescent intensity of compound **1** in the presence of excess amount of metal ions. $[M]$ is the concentration of metal ions added.

Job's plot analyses were used to determine the stoichiometry between compound **1** and $Fe^{3+}/Cu^{2+}$ [6].

## Results and discussion

### *Synthesis and characterization*

The compound **1** was synthesized with a good yield (85.46%) by condensation of 2-amino-4-nitrophenol with 3-formyl-9H-hexylcarbazole (Scheme 1). Then compound **1** was characterized by IR, $^1H$ NMR and elemental analysis. The IR spectrum of the Schiff-base exhibited two characteristic bands in the region 3302 and 1627 $cm^{-1}$ corresponding to —OH and —C=N groups respectively. The carbon skeleton of carbazole showed a characteristic IR band at 1588 and 1517 $cm^{-1}$ (Fig. S5, Supplementary data). The $^1H$ NMR spectrum of compound **1** showed one singlet for imino (—CH=N) proton at 8.71 ppm (Fig. S6, Supplementary data). Compound **1** is poorly fluorescent, may due to isomerization of the C=N double bond in the excited state, and ESIPT involving the phenolic protons [29].

### *UV–Vis absorption spectral studies*

The interaction between compound **1** and cations was investigated by using UV–Vis and fluorescence spectrometries. The binding ability of compound **1** in $CH_3CN$ ($1.0 \times 10^{-5}$ M) with cations, such as $Na^+$, $K^+$, $Ag^+$, $Ca^{2+}$, $Hg^{2+}$, $Zn^{2+}$, $Co^{2+}$, $Mn^{2+}$, $Mg^{2+}$, $Cu^{2+}$, $Fe^{3+}$ and $Cr^{3+}$ showed selective response toward $Fe^{3+}$ and $Cu^{2+}$ ions. As shown in Fig. 1, addition of 1 equiv. $Fe^{3+}$ and $Cu^{2+}$ resulted in an obvious change indicating compound **1** had higher binding affinity toward $Fe^{3+}$ and $Cu^{2+}$ than other surveyed metal ions. The absorption spectrum of compound **1** displayed well-defined bands at 286 and 370 nm (molar extinction coefficient: $2.61 \times 10^4\ M^{-1}\ cm^{-1}$ and $2.98 \times 10^4\ M^{-1}\ cm^{-1}$ respectively). The 286 nm band peak reflected a π–π* transition of the C=N group while the 370 nm band reflected an intermolecular charge transfer (CT) band of the entire conjugated molecule [2]. Addition of 1 equiv of $Fe^{3+}$ to a solution of compound **1**, the observed absorption band of compound **1** at 286 nm (molar extinction coefficient: $3.25 \times 10^4\ M^{-1}\ cm^{-1}$) increased in absorbance and the other band at 370 nm (molar extinction coefficient: $1.93 \times 10^4\ M^{-1}\ cm^{-1}$) showed a decrease in absorbance. Thus, there was a little blue shift of about 6 nm (from 370 nm to 364 nm). While addition of 1 equiv of $Cu^{2+}$ to a solution of compound **1**, the observed absorption band of compound **1** at 286 nm (molar extinction coefficient: $2.83 \times 10^4\ M^{-1}\ cm^{-1}$) increased in absorbance and the other band at 370 nm (molar extinction coefficient: $2.01 \times 10^4\ M^{-1}\ cm^{-1}$) showed a decrease in absorbance. There was a blue shift of about 29 nm (from 370 nm to 341 nm). The phenomenon of a blue shift maybe suggest that the complex of **1**-$Fe^{3+}$ and the **1**-$Cu^{2+}$ were formed in $CH_3CN$ solution.

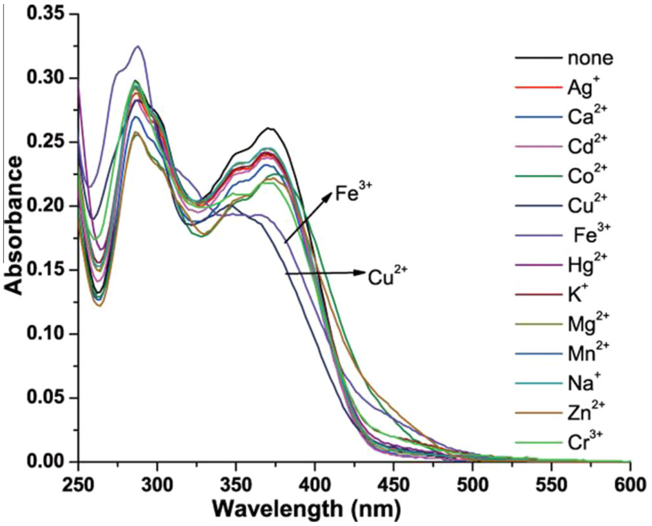
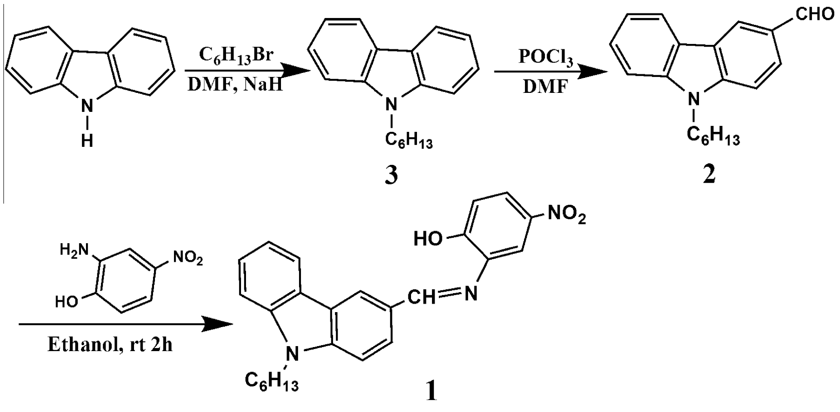


**Fig. 1.** UV–Vis absorption spectrum of **1** (10.0 μM) upon addition of various metal ions (10.0 μM) in $CH_3CN$ solution.



**Scheme 1.** The synthetic route of compound **1**.

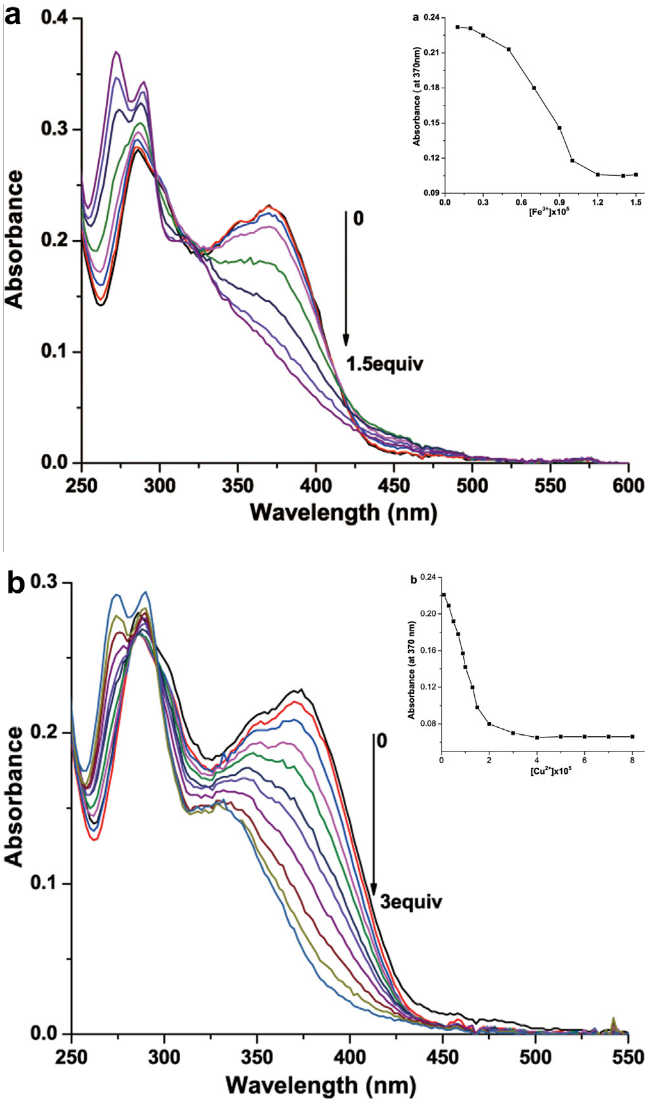


**Fig. 2.** (a) UV–Vis absorption spectrum of **1** (10.0 μM) with gradual addition of $Fe^{3+}$ in $CH_3CN$ solution; inset: changes of absorbance upon addition of $Fe^{3+}$ at 370 nm; (b) the UV–Vis absorption spectrum of **1** (10.0 μM) with gradual addition of $Cu^{2+}$ in $CH_3CN$ solution; inset: changes of absorbance upon addition of $Cu^{2+}$ at 370 nm.

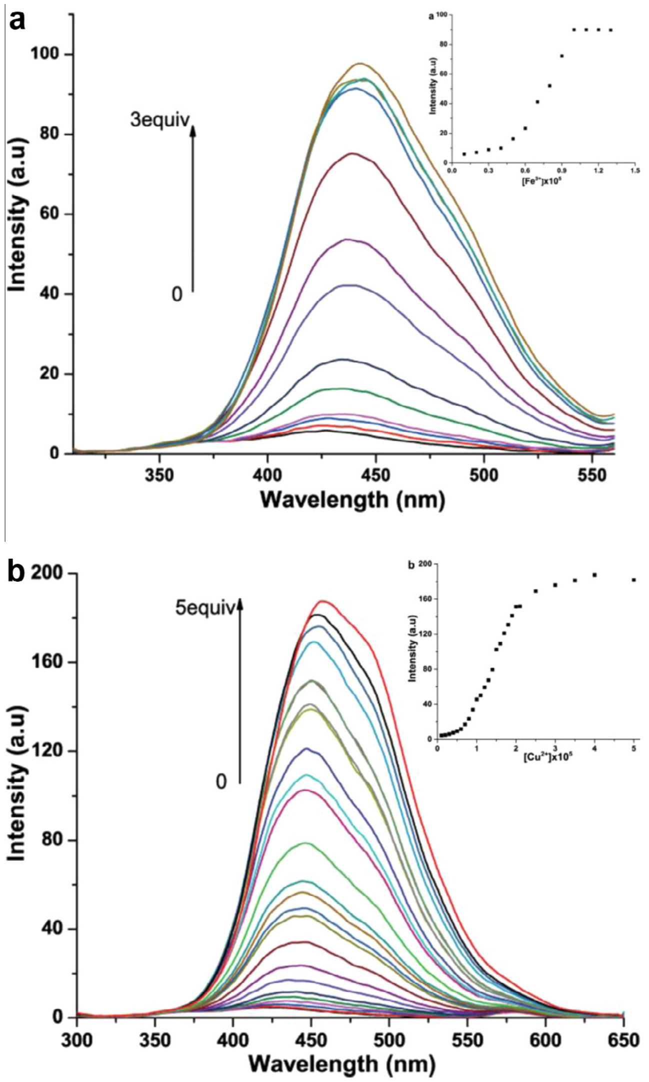


**Fig. 4.** (a) Fluorescence titration of **1** (10.0 μM) with various concentration of $Fe^{3+}$ in $CH_3CN$ solution ($\lambda_{ex}$ = 290 nm); inset: changes of fluorescence upon addition of $Fe^{3+}$ at 423 nm; (b) fluorescence titration of **1** (10.0 μM) with various concentration of $Cu^{2+}$ in $CH_3CN$ solution ($\lambda_{ex}$ = 290 nm); inset: changes of fluorescence upon addition of $Cu^{2+}$ at 423 nm.

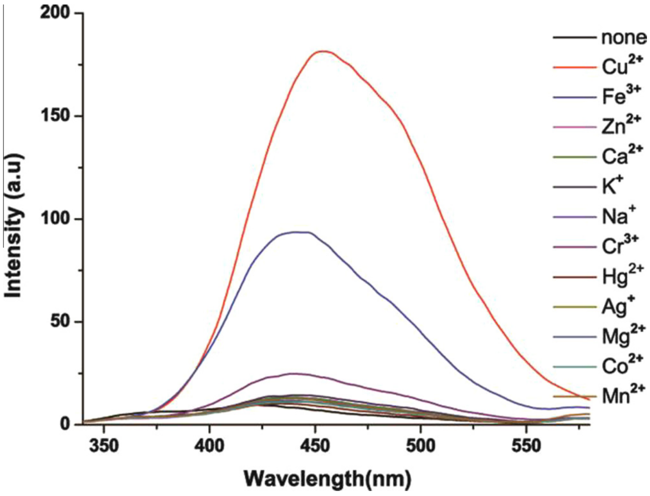


**Fig. 3.** Fluorescence responses of compound **1** (10.0 μM) in $CH_3CN$ solution upon the addition of 5 equiv various metal ions ($\lambda_{ex}$ = 290 nm).

To get more information on binding mechanism of compound **1** toward $Fe^{3+}/Cu^{2+}$, spectrometric titration experiments were performed in the presence of $Fe^{3+}/Cu^{2+}$ (Fig. 2). Addition of $Fe^{3+}$ to a solution of compound **1** in $CH_3CN$ solution ($1.0 \times 10^{-5}$ M) showed decrease close to 100% at 370 nm and about a 127% increase for the 286 nm band with a clear isosbestic point at 296 nm. The absorption peak at 370 nm had completely disappeared when 1.5 equiv $Fe^{3+}$ was added to a solution of compound **1**. And a new absorption peak appeared at 273 nm (Fig. 2a) and its intensity gradually increased when the sequential addition of $Fe^{3+}$ was reached to 1.0 equiv. On the other hand, successive addition of $Cu^{2+}$ to a solution of compound **1** in $CH_3CN$ solution leaded to a stepwise decrease in absorbance at 370 nm and increase in absorbance at 286 nm with a clear isosbestic point at 296 nm. The absorbance at 370 nm had a blue shift (from 370 nm to 328 nm). Moreover, a new absorption peak appeared at 274 nm (Fig. 2b) and its intensity gradually increased when the sequential addition of $Cu^{2+}$ was reached to 1 equiv. So it can be speculated that the stable complex of **1**-$Fe^{3+}$ and the **1**-$Cu^{2+}$ are formed in $CH_3CN$ solution. The association constant of $Fe^{3+}/Cu^{2+}$ ions with compound **1** which deter-

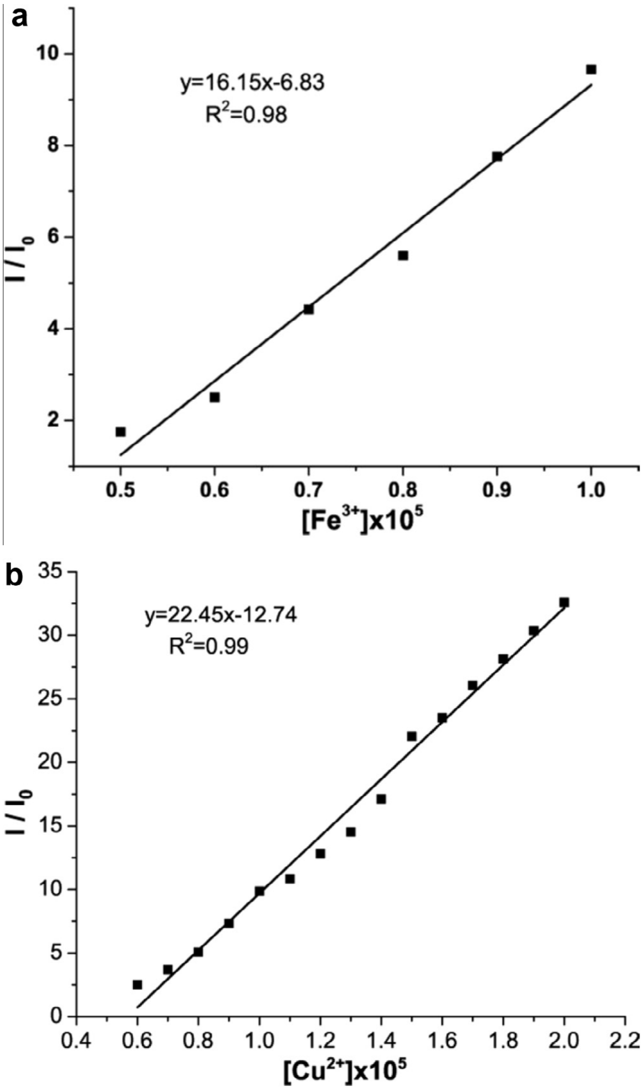


**Fig. 5.** (a) Stern–Volmer plots for **1** for estimation of enhancement constants in presence of $Fe^{3+}$ ($\lambda_{ex}$ = 290 nm); (b) Stern–Volmer plots for **1** for estimation of enhancement constants in presence of $Cu^{2+}$ ($\lambda_{ex}$ = 290 nm).

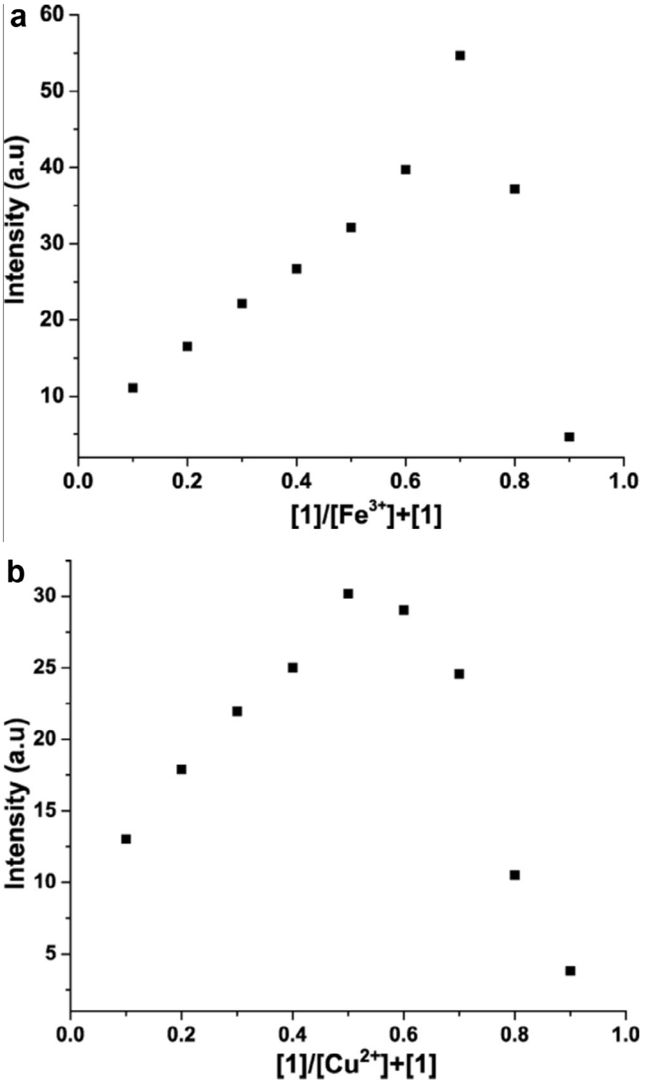


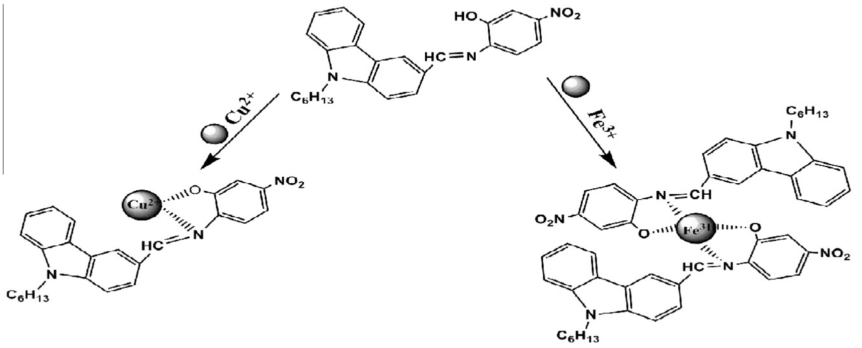
**Fig. 6.** (a) The Job's plot for **1** and $Fe^{3+}$ ($\lambda_{ex}$ = 290 nm); (b) the Job's plot for **1** and $Cu^{2+}$ ($\lambda_{ex}$ = 290 nm).

mined by the Benesi–Hildebrand plot (Fig. S7, Supplementary data) came as $8.33 \times 10^4\ M^{-1}$ and $2.57 \times 10^4\ M^{-1}$, the result was indicated a strong and stable complexation of compound **1** and $Fe^{3+}$/$Cu^{2+}$ ions. Their detection limits were calculated to be $3.02 \times 10^{-6}$ mol/L for $Fe^{3+}$ ion and $3.62 \times 10^{-6}$ mol/L for $Cu^{2+}$ ion (Fig. S8, Supplementary data) [30,31].

### *The fluorescence spectral studies*

In $CH_3CN$ solution, the fluorescence emission intensity of **1** was recorded at 423 nm, but it was weak, which was probably due to the fact that C═N isomerization was the predominant decay process of the excited states of **1** with an unbridged C═N structure and also due to excited-state intramolecular proton transfer (ESIPT). Surprisedly a dramatic enhancement of the fluorescent intensity was observed in the presence of $Cu^{2+}$/$Fe^{3+}$. While the addition of other metal ions, such as $Na^+$, $K^+$, $Ag^+$, $Ca^{2+}$, $Hg^{2+}$, $Zn^{2+}$, $Co^{2+}$, $Mn^{2+}$, $Mg^{2+}$ and $Cr^{3+}$, had no distinct influence on fluorescent intensity (Fig. 3). As shown in Fig. 3, the addition of 5 equiv of $Cu^{2+}$ caused the great enhancement of fluorescence intensity and the fluorescence intensity increased 20.5-fold. At the same time, there was a red shift from 423 nm to 452 nm. On the other hand, the addition of 5 equiv of $Fe^{3+}$ caused a 10.7-fold increase of fluorescence intensity and a red shift from 423 nm to 441 nm. The fluorescence intensity of adding $Cr^{3+}$ was slightly enhanced about 2.8-fold. This mean that the compound **1** exhibited high fluorescent selectivity to $Cu^{2+}$/$Fe^{3+}$ over other metal ions. It indicated that binding of $Cu^{2+}$ or $Fe^{3+}$ to compound **1** prevented C═N isomerization and excited-state intramolecular proton transfer (ESIPT) between the enol-imine and the keto-imine forms and led to enhancement.

In addition, the effect of $Fe^{3+}$/$Cu^{2+}$ on the fluorescence properties of compound **1** in the $CH_3CN$ solution was investigated (Fig. 4). Fig. 4 showed that upon the continuous addition of $Fe^{3+}$/$Cu^{2+}$ ions, the intensity at 423 nm ($\lambda_{max}$) was gradually enhanced with a small red-shift. The results indicated that compound **1** can serve as a good fluorescence probe for $Fe^{3+}$/$Cu^{2+}$ in $CH_3CN$ solution. This enhancement of fluorescence intensity can be explained as follows: The fluorescence intensity of compound **1** is weak in $CH_3CN$ solution, which may be due to ESIPT involving the phenolic protons and C═N isomerization. The C═N isomerization is the predominant decay process of the excited state for compound **1**. Upon addition of $Fe^{3+}$ or $Cu^{2+}$, the coordination of compound **1** with the metal ion inhibits the C═N isomerization and prevents



**Scheme 2.** The binding mode of compound **1** and $Fe^{3+}/Cu^{2+}$.

ESIPT. Additionally, the reaction of a chelating agent with a metal ion induces rigidity of the resulting molecule and tends to produce a large chelation-enhanced fluorescence (CHEF) effect. However, other ions fail to form such framework, probably because of several combined influences leading to selective recognition for $Fe^{3+}$ and $Cu^{2+}$, such as the suitable coordination geometry conformation of the Schiff base sensor, the appropriate ion radius and sufficient binding energy of the $Fe^{3+}$ and $Cu^{2+}$.

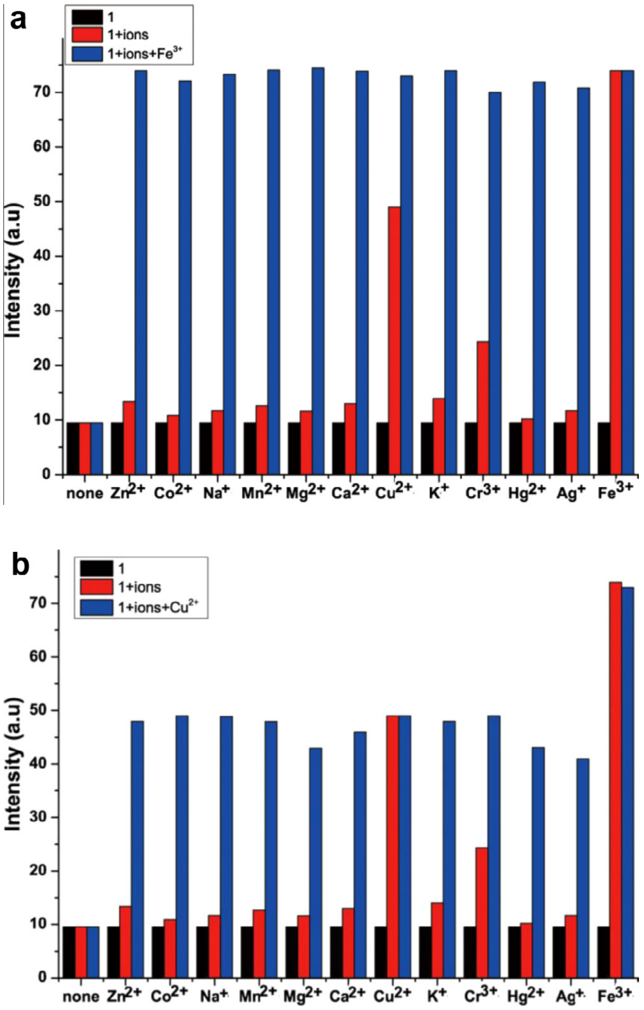


**Fig. 7.** Metal ions selectivity of **1** (10.0 μM) in $CH_3CN$ solution. (a) The black bars represent the fluorescent intensity of **1**. The red bars represent the fluorescent intensity of **1** and various ions. The blue bars represent the fluorescent intensity of **1** and $Fe^{3+}$ ($\lambda_{ex}$ = 290 nm). (b) The black bars represent the fluorescent intensity of **1**. The red bars represent the fluorescent intensity of **1** and various ions. The blue bars represent the fluorescent intensity of **1** and $Cu^{2+}$ ($\lambda_{ex}$ = 290 nm). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The sensitivity was assessed by a Stern–Volmer plot (Fig. 5). A Stern–Volmer plot between fluorescence intensity vs. concentration of $Fe^{3+}$ and $Cu^{2+}$ exhibited linear relationship ($R^2 = 0.98$ and $R^2 = 0.99$, respectively), suggesting limit of detection of $4.23 \times 10^{-6}$ M and $5.67 \times 10^{-6}$ M, and indicating that compound **1** is potentially useful for detection of $Fe^{3+}$ and $Cu^{2+}$. To further determination of stoichiometry between compound **1** and $Fe^{3+}/Cu^{2+}$, Job's plot (Fig. 6) analyses were used. A maximum fluorescence was observed when the molar fraction of $Fe^{3+}$ reached 0.33, which is indicative of a 2:1 stoichiometry complexation between **1** and $Fe^{3+}$. When molar fraction of $Cu^{2+}$ was 0.5, the fluorescence at 423 nm got to maximum, indicating that forming a 1:1 complex between **1** and $Cu^{2+}$ (Scheme 2). The association constant ($K_a$) of **1**-$Fe^{3+}$ was determined by nonlinear curve fitting and **1**-$Cu^{2+}$ was determined using the Benesi–Hildebrand equation which came as $9.27 \times 10^4\ M^{-1}$ and $9.15 \times 10^4\ M^{-1}$, respectively (Fig. S9, Supplementary data). These further confirmed the extent of coordination between **1** and $Fe^{3+}/Cu^{2+}$. And compound **1** could use as a sensor for $Fe^{3+}/Cu^{2+}$ by both using UV–Vis and fluorescence methods. In other words, compound **1** showed good selectivity toward $Fe^{3+}/Cu^{2+}$ in ground state as well as in excited.

### *The competitive binding studies*

The results of UV–Visible competitive binding studies are depicted in Fig. S10 (Supplementary data). These miscellaneous competition cations did not induce significant absorption changes of **1** in the absence of $Cu^{2+}$ and $Fe^{3+}$, which indicate that the compound **1** can be used as the high selective chemosensor for $Cu^{2+}$ and $Fe^{3+}$ by using familiar UV–Vis method. With the same method, fluorescent competition experiment was shown and depicted in Fig. 7. These miscellaneous competition cations did not induce significant fluorescence intensity changes of compound **1** in the absence of $Fe^{3+}/Cu^{2+}$. One could easily understand that the effects on emission intensity of compound **1** upon the addition of higher concentrations of various cations were almost negligible except for $Fe^{3+}/Cu^{2+}$. It was clear that the interference of other ions was negligible small during the detection of $Fe^{3+}/Cu^{2+}$.

## Conclusion

In conclusion, an imine-linked carbazole-based chemosensor was synthesized and characterized for recognition of $Fe^{3+}/Cu^{2+}$. Studies showed that compound **1** showed good selectivity toward $Fe^{3+}/Cu^{2+}$ over other competing ions in ground state as well as in excited state. In addition, the binding stoichiometry was confirmed as 1:1 (1/$Fe^{3+}$) and 2:1 (1/$Cu^{2+}$) by both using UV–Vis and fluorescence methods. The fluorescence enhancement upon binding $Fe^{3+}$/$Cu^{2+}$ was attributed to a cancellation of C=N isomerization that otherwise led to non-radiative decay of the excited state and ESIPT. The carbazole-based Schiff-base can be used to develop fluorescent chemosensor for various other heavy transition metal ions.

## Acknowledgments

This research was financially supported by the Key University Natural Science Research Project of the Natural Science Fund of Anhui Province (No. 11040606M33), the Dr. Research Project Fund of Anhui University (No. 02303319), Youth Scientific Research Fund of Anhui University and the Excellent Youth Fund in University of Anhui Province (No. 2012SQRL025), the Graduate Academic Innovation Research Project Fund of Anhui University (No. yph100080).

## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.02.043.

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