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A stilbene-based fluoroionophore for copper ion sensing in both reduced and oxidized environments

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ABSTRACT

The high sensitivity and abundance of fluorophores makes fluorescence technique among one of the most promising tools to develop chemo- and biosensors. Fluorescent sensors for ions, also called fluoroionophores, are commonly composed of an ion recognition unit (ionophore) and a fluorogenic unit (fluorophore). Here we report the synthesis and characterization of a new stilbene derivative conjugated with the di-2-picolylamine (dpa) group. It is found that the fluorescence of the stilbene derivative using dpa as ionophore is sensitive to copper ions, including Cu^{2+} (oxidized state) and Cu^{+} (reduced state). The sensitive and selective stilbene-based fluoroionophore for copper ions are based on the internal charge transfer along with the electron donor-π-acceptor stilbene motif and incorporate a dpa-containing aniline-derivatized ligand framework. By modifying the stilbene with di-2-picolylamine (dpa), the significant fluorescence quenching was observed upon binding with copper ions involving both the reduced and oxidized environments, indicating the great sensitivity and specificity for copper ion sensing. The presence of metal ions such as Ag^{+}, Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, K^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, Pb^{2+}, Sn^{2+}, and Zn^{2+} had little influence on the selectivity and sensitivity of Cu^{2+} and Cu^{+}. The optical sensor design undertakes promising for potential application to multiplex sensing of different analytes through distinct ligand conjugation and functionalization of individual fluorophore.

1. Introduction

Copper is third in abundance (after Fe^{3+} and Zn^{2+}) among the essential transition metals in the human body and plays an important role in various physiologic processes. Owing to the possibility of leaking of copper ion into the environment through various routes and causing exposure of human body to high level of copper, recently, much effort have witnessed a large number of reports on exploring fluorescent chemosensors for the detection of copper ions due to their biological and environmental significance [1–3]. Fluorescent sensors for ions, also called fluoroionophores, are commonly composed of an ion recognition unit (ionophore) and a fluorogenic unit (fluorophore). One strategy employed in the design of fluoroionophores for metal cations is to conjugate a fluorophore unit with ionophore [4–7]. There is important significance to understand the multiple roles of copper with availability of fluorescent probe systems permitting quantitative determination and detecting of copper fluxes and levels over a broad concentration range, especially at lower concentration of nM level. The high sensitivity and abundance of fluorophores makes fluorescence technique among one of the most promising tools for chemo- and biosensor development [8–10]. Currently most of the reported Cu^{2+} fluorescent sensors have been underwent a quenching of the fluorescence emission on the binding of the metal ion [11–14], owing to its paramagnetic nature. In addition, although a few sensors in which the binding of a Cu^{2+} ion causes an increase in the fluorescence have also been reported, the fluorescence in most cases has high background with comparatively weak enhancement and usually indicate the sensitivity of μM scale. Therefore, the works related to highly sensitive and selective fluorescent sensor for the determination of Cu^{2+} are of great challenge and increasing interest. Herein, we report a new fluoroionophore (**1**) for both Cu^{2+} and Cu^{+} ions (in oxidized and reduced states, respectively) based on simple stilbene conjugated with a di-2-picolylamine (dpa) group as not only a fluorophore but also a ionophore, which undergoes a remarkable fluorescent quenching resulting from the binding of Cu^{2+} and Cu^{+} down to nM level and a high selectivity toward Cu^{2+} ion over other tested metal ions in aqueous solution.

Electron donor-π-acceptor (D-π-A) conjugated systems generally exhibit characteristic electronic absorption and emission spectra associated with internal charge transfer (ICT). Electronic or structural perturbations on the amine lone pair electrons influ-

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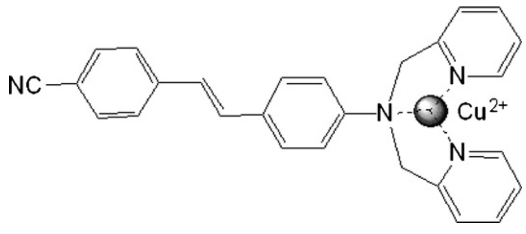


Scheme 1. Binding model of **1** with Cu^{2+}.

ence the ICT properties and thus the electronic spectra, providing a useful signal transduction method for the design of chemosensors [3]. The di-2-picolylamine (dpa) group is known to possess a remarkable binding ability to some transition metal ions, which has been applied in the molecular design of fluoroionophores. Currently, most of copper ion sensors based on these dpa-derived D-π-A systems display the "on-off" type fluorescence sensing mode [4]. We describe here the design of a highly sensitive and selective small molecular stilbene-derived fluorescent sensor suitable for the copper ion (Scheme 1). In this system, the dpa ligand in **1** as an ionophore possess an excellent ability to coordinate transition metal ions and have demonstrated particular utility in the formation of metal ion sensors. Highly fluorescent sensory molecules are favourable in performing the "on-off" type of fluorescence signalling. Stilbene **1** displays fluorescence quenching upon the binding of transition metal ions, where the binding-triggered conformational twisting and in turn the inhibition of ICT play an important role. This modular approach allows for the easy variation of the components, which makes the process of system optimisation very simple compared with previously investigated fluorescent probes for copper ions.

2. Experimental section

2.1. Reagents

The following materials were used: α-bromo-*p*-tolunitrile and 2-(bromomethyl)pyridine hydrobromide (Sigma Chemical Co.), 4-nitrobenzaldehyde (Yizheng East Chemical Co.). Other chemicals were purchased from local company as analytical reagents and were distilled prior to use. Column chromatography was performed using EM Silica gel 60 (300–400 mesh).

2.2. Characterization

Melting points were uncorrected. All IR spectra were recorded at room temperature from 4000 to 450 cm^{-1}. UV–vis spectra were recorded with a UV2300 spectrophotometer (Techcomp, China). Fluorescence spectra were recorded with an F2500 spectrophotometer (Hitachi, Japan) with excitation at 360 nm (slit width, 5 mm; 450 W Xe lamp). ^{1}H NMR, and ^{13}C NMR were obtained at 20 °C on either a 400 MHz or a 100 MHz spectrometer, respectively. Chemical shifts were reported in ppm downfield from tetramethylsilane with the solvent resonance as the internal standard. MS spectra were measured on a Shimadzu GC-17A, QP-5000 GC/MS spectrometer.

2.3. Procedure of Wittig reaction for trans-4-(4-nitrostyryl)benzonitrile (3)

In a 50 mL round-bottom flask was placed α-bromo-*p*-tolunitrile (0.980 g, 5 mmol), triphenylphospohonium (1.310 g, 5 mmol), toluene (25.0 mmol) and a magnetic stir bar. The flask was placed in an oil bath to 110 °C and held there for 6 h. After this time, the resulting complex was cooled to room temperature and the filtrate was concentrated under reduced pressure (2.292 g, yield 98.1%). White solid, Mp >300 °C, R_f = 0.4 (ethyl acetate/methanol = 3:1, v/v).

A mixture of phospohonium halide salt (1.146 g, 2.5 mmol), 4-substituted benzaldehyde (0.378 g, 2.5 mmol), tetrabutylammonium iodide (0.923 g, 2.5 mmol) and methylene chloride (20 mL) in a round-bottom flask was slowly added to 15 mL of saturated aqueous solution of potassium carbonate. The solution was then stirred at 57 °C overnight. Then, the organic layer became transparent at the top and the alkaline aqueous layer became turbid at the bottom of the flask. The two layers were separated and the aqueous layer was extracted with methylene chloride three times. The combined organic layer was washed with distilled water or brine and then dried over anhydrous MgSO$_4$. The solid residue after evaporation of the solvent was performed by column chromatography (ethyl acetate:hexane = 1:3). The resulting mixture of *trans* and *cis* isomers was recrystallized in CHCl$_3$/MeOH to afford the *trans* isomer. The filtrate that contains mainly the *cis* isomer was added with a catalytic amount of I$_2$ for *cis* → *trans* isomerization (0.445 g, yield 71.5%). Straw yellow crystalloid, Mp 252–254 °C, R_f = 0.6 (ethyl acetate/hexane = 1:5, v/v). IR(KBr) υ: 2930, 2851, 2221, 1737, 1708, 1606, 1517, 1343, 1257, 1081, 977, 856, 719 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 8.26 (d, J = 8.8 Hz, 1H), 8.12 (d, J = 8.8 Hz, 1H), 7.70 (d, J = 6.0 Hz, 1H), 7.68 (d, J = 6.4 Hz, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.56 (d, J = 8.8 Hz, 1H), 7.35 (d, J = 8.8 Hz, 1H), 7.30 (d, J = 8.8 Hz, 1H), 7.26 (d, J = 3.2 Hz, 1H), 6.79 (d, J = 3.6 Hz, 1H).

2.4. Synthesis of trans-4-(4-aminostyryl)benzonitrile (4)

A heterogeneous mixture of *trans*-4-(4-nitrostyryl)benzonitrile (**2**, 0.501 g, 2.0 mmol), SnCl$_2$·2H$_2$O (2.256 g, 10.0 mmol) in 20 mL of anhydrous ethanol was heated at 70 °C under nitrogen for 18 h. The solution was allowed to cool and then poured into 15 g of ice. The solution was made slightly basic by addition of 5% NaHCO$_3$ (aq) followed by extraction with ethyl acetate. The organic layer was washed with brine twice and then dried over MgSO$_4$. Evaporation of the solvent provided the crude product of aminostilbene. Further purification was performed by column chromatography (ethyl acetate:petroleum ether = 1:2), and the desired product was afforded (0.273 g, yield 62.2%). Yellow solid, Mp 218–220 °C, R_f = 0.5 (ethyl acetate/petroleum ether = 1:2, v/v). IR(KBr) υ: 3443, 2924, 2853, 2225, 1625, 1595, 1455, 1176, 968, 866, 834, 721 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 7.60 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 16.4 Hz, 1H), 6.90 (d, J = 16.0 Hz, 1H), 6.69 (d, J = 8.4 Hz, 2H).

Ps: *cis*-4-(4-aminostyryl)benzonitrile, yellow solid, Mp 194–196 °C, R_f = 0.7 (ethyl acetate/petroleum ether = 1:2, v/v). ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 7.51 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.4 Hz, 2H), 6.64 (d, J = 12.4 Hz, 1H), 6.57 (d, J = 8.4 Hz, 2H), 6.40 (d, J = 12.0 Hz, 1H), 3.99 (Br, 2H).

2.5. Synthesis of trans-4-(4-(bis(pyridin-2-ylmethyl)amino)styryl)benzonitrile (1)

In a 50 mL round-bottom flask was placed 2-(bromomethyl)pyridine hydrobromide (1.564 g, 7.5 mmol), 1N aqueous solution of sodium hydroxide (10 mL) and isopropyl ether (15 mL). The flask was placed to 0 °C and held there for 3 h. After this time, the two layers were separated and the aqueous layer was extracted with isopropyl ether twice times. The combined organic layer was washed with distilled water or brine and then dried over anhydrous MgSO$_4$. Evaporation of the solvent provided the product of 2-(bromomethyl)pyridine (0.785 g, 73.6%).

A mixture of *trans*-4-(4-aminostyryl)benzonitrile (**3**, 0.184 g, 0.8 mmol), potassium carbonate (0.483 g, 3.5 mmol), potassium iodide (0.5 g, 3.0 mmol) and 2-(bromomethyl)pyridine (0.378 g, 2.2 mmol) in acetonitrile (6 mL) was stirred at room temperature under N_2 for 24 h. The residue obtained after the removal of the solvent was dissolved in ethyl acetate and extracted with water. The organic layer was separated, dried over $MgSO_4$ and the solvent was removed under reduced pressure. Purification was performed by column chromatography, using a mixed solvent ethyl acetate:petroleum ether (1:3) as the eluent to provide the monosubstituted complex (0.108 g, yield 41.5%), and then using ethyl acetate as the eluent to provide the desired product (0.062 g, yield 18.4%).

trans-4-(4-(Pyridin-2-ylmethylamino)styryl)benzonitrile, brown solid, Mp 173–175 °C, $R_f = 0.5$ (ethyl acetate/petroleum ether = 1:3, v/v). IR(KBr) υ: 3373, 3014, 2925, 2854, 2221, 1679, 1608, 1594, 1522, 1455, 1327, 1172, 969, 866, 829, 752 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 8.62 (d, $J = 4.0$ Hz, 1H), 7.80 (t, $J = 7.6$ Hz, 1H), 7.60 (d, $J = 8.4$ Hz, 2H), 7.52 (d, $J = 8.4$ Hz, 2H), 7.46 (t, $J = 9.2$ Hz, 1H), 7.38 (d, $J = 8.0$ Hz, 2H), 7.33 (t, $J = 6.8$ Hz, 1H), 7.14 (d, $J = 16.0$ Hz, 1H), 6.88 (d, $J = 16.0$ Hz, 1H), 6.69 (d, $J = 8.8$ Hz, 2H), 7.05,6.54 (m, 1H), 4.59 (d, $J = 8.0$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: *C* 157.6, 148.3, 142.7, 122.3, 119.3, 112.6; *C*H 149.1, 136.8, 132.5(2), 130.1, 129.3, 128.3(2), 126.2(2), 125.8, 121.6, 113.0(2); *C*H_2 48.8 ppm. MS(EI) *m/z*: 311, 233, 220, 203, 176, 156, 79.

trans-4-(4-(Bis(pyridin-2-ylmethyl)amino)styryl)benzonitrile, yellow solid, Mp 58–61 °C, $R_f = 0.5$ (ethyl acetate). IR(KBr) υ: 3008, 2924, 2856, 2222, 1722, 1666, 1591, 1520, 1435, 1390, 1348, 1174, 964, 879, 825, 754 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 8.62 (d, $J = 4.4$ Hz, 2H), 7.64 (t, $J = 7.6$ Hz, 2H), 7.56 (d, $J = 8.4$ Hz, 2H), 7.49 (dd, $J = 4.8$ Hz, $J = 8.8$ Hz, 2H), 7.36 (t, $J = 9.6$ Hz, 2H), 7.26 (d, $J = 3.6$ Hz, 2H), 7.20 (m, 2H), 7.11 (d, $J = 16.4$ Hz, 1H), 6.86 (d, $J = 16.4$ Hz, 1H), 6.72 (d, $J = 9.2$ Hz, 1H), 6.57 (d, $J = 8.8$ Hz, 1H), 4.87 (d, $J = 21.2$ Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: *C* 158.3(2), 149.7, 137.0, 122.2, 120.9, 112.2; *C*H 143.1, 142.6, 132.9, 132.4(2), 132.2, 132.0(2), 130.2, 129.3, 128.3(2), 126.3(2), 125.1, 122.7, 112.7(2); *C*H_2 57.3(2) ppm. MS(EI) *m/z*: 402, 356, 310, 93, 80, 65.

3. Results and discussion

3.1. Synthesis of stilbene fluorophores

Synthesis of the stilbene derivatives **1** and **2** is depicted in Scheme 2. The stilbene derivatives **3**, *trans*-4-(4-nitrostyryl)benzonitrile was obtained through Wittig reaction of α-bromo-*p*-tolunitrile and 4-nitrobenzaldehyde. Reduction of **3** with $SnCl_2 \cdot 2H_2O$ in EtOH gave *trans*-4-(4-aminostyryl)benzonitrile (**4**), which were then reacted with 2-(bromomethyl)pyridine in acetonitrile to afford the stilbene derivatives **1** and **2** in 18.4% and 41.5% yield, respectively.

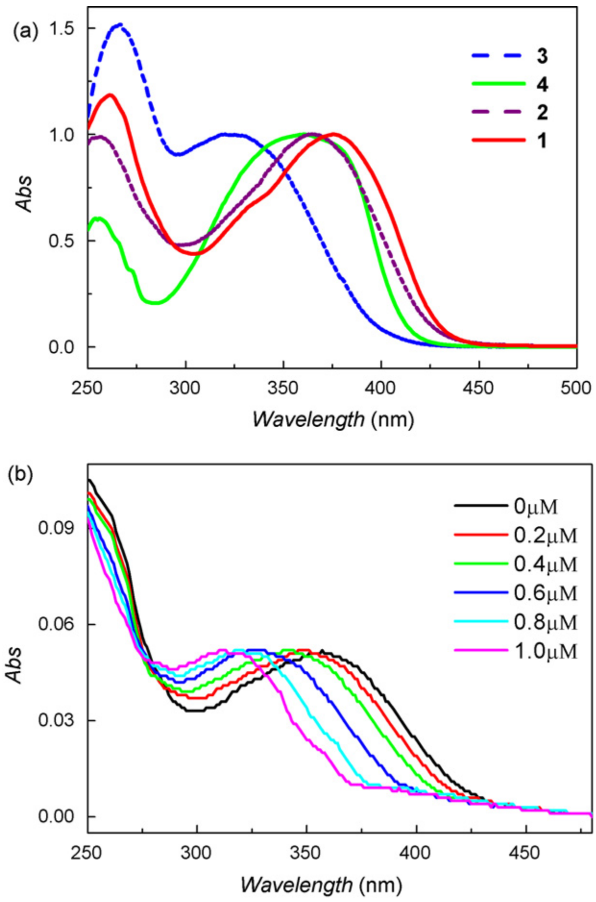
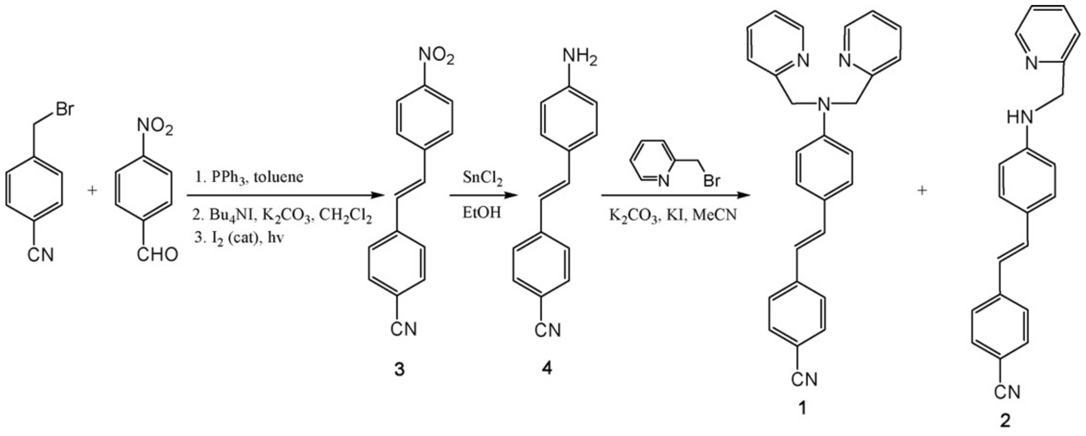


Fig. 1. (a) The UV–vis absorption spectra of stilbene derivatives (1.0 μM, 298 K, in MeCN); (b) the UV–vis spectra change of 1 MeCN/H_2O (1:9, v/v) after adding different Cu^{2+} ions (0–1.0 μM) for 2 min.

In the absorption spectrum of stilbene, maximum bands were observed at 260 and 374 nm in CH_3CN. Here the UV–vis absorption spectra of stilbene derivatives possess the similar curves to stilbene while there is a little wavelength shift (Fig. 1a). The UV–vis spectrum of **1**, **2**, **3** and **4** in CH_3CN exhibits the typical absorption band in the region of 340–380 nm. Titration experiments carried out in MeCN/water (1/9, v/v) by using the above-mentioned set of metal cations demonstrate that only Cu^{2+} promotes remarkable responses (Fig. 1b). Thus, the band at $\lambda_{max} = 359$ nm progressively blue-shifted, and at the same time, the point at $\lambda_{max} = 315$ nm from



Scheme 2. Synthesis of stilbene derivatives **1** and **2**.

the blue shift of absorption band of stilbene were found, which also supports the complex formation.

3.2. Ion selectivities of stilbene fluorophores

Selectivity is the most important characteristic of fluoroionophores as it determines the utilizing efficiency of the fluoroionophores in real sample measurement. The fluorescent detection of Cu^{2+} in CH_3CN/H_2O (1/9) was generally complicated by the interference from some metal ions. The influence of pH on the fluorescence of the stillbene **1** was first determined by fluorescence titration in $MeCN/H_2O$ (1:9, v/v) solutions. The fluorescence of free stillbene 1 at 519 nm remained unaffected between pH 11.0 and 5.0 and then gradually decreased from pH 5.0–1.8 with a p*K*a value of 4.0 due to an internal charge transfer (ICT) from the fluorophore to the protonated 2-picolyl group. Therefore, further fluorescence studies were carried out at pH = 5.8. To address the competence of stilbene derivative 1 in detecting all kinds of metal ion, Fig. 2 illustrated the spectroscopic response of the stilbene sensor following addition of a variety of miscellaneous metal ions (including Ag^+, Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^+, Cu^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, K^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+}, Sn^{2+}, Zn^{2+}) [15], which indicated that, when metal ion concentration was lower than 300 nM, the fluorescence of stilbene chemosensor was essentially unaffected by the presence of these common ions except for the Cu^{2+}, Cu^+. Notably, under the concentration of Cu^{2+} and Cu^+ ions lower than 300 nM, stilbene **1** exhibits an excellent selectivity toward Cu^+, Cu^{2+} above other metal ions. Interestingly, it is demonstrated that the fluoroionophore **1** could be simultaneously utilized in the detection of both Cu^{2+} and Cu^+ involving oxidized and reduced environment, on which few reports have been focused. Further investigation on various metal ions with different concentrations indicated that **1** showed better selectivity when the metal ion concentration was lower than 1.0 μM, which possess great *sub*-micromolar scale sensitivity (Fig. 3a). To further characterize the performance of the sensor for Cu^{2+}, a comparison experiment was carried out with stilbene **1** in the presence of metal ions other than copper ions. As shown in Fig. 3b, the addition of 1.0 μM Cu^{2+} to stilbene **1** solution containing any one of 1.0 μM the above-mentioned metal ions results in similar amount of quenching of 80–90% on fluorescence intensity. It is thus concluded that the presence of these metal ions with Cu^{2+} does not affect the sensitivity of stilbene **1** for Cu^{2+} detection.

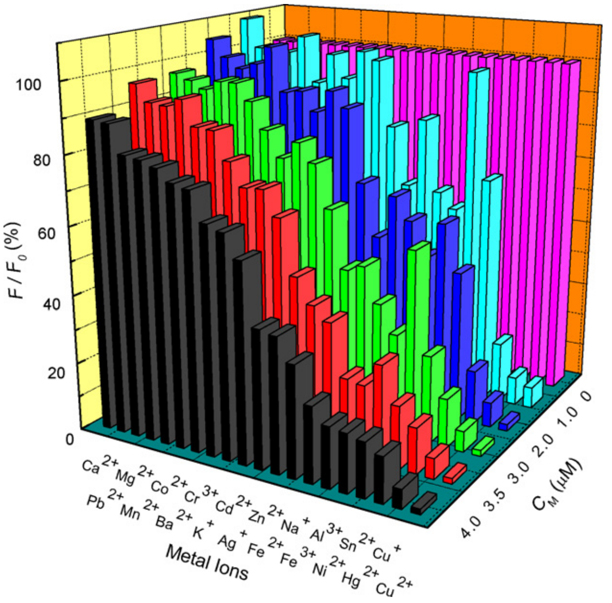


Fig. 2. The relative fluorescence intensity at 519 nm for stilbene (1.0 μM, 298 K, $MeCN/H_2O$ = 1:9, v/v) at 359 nm excitation (blank sample), and after adding different metal ions (0–4.0 μM) for 2 min.

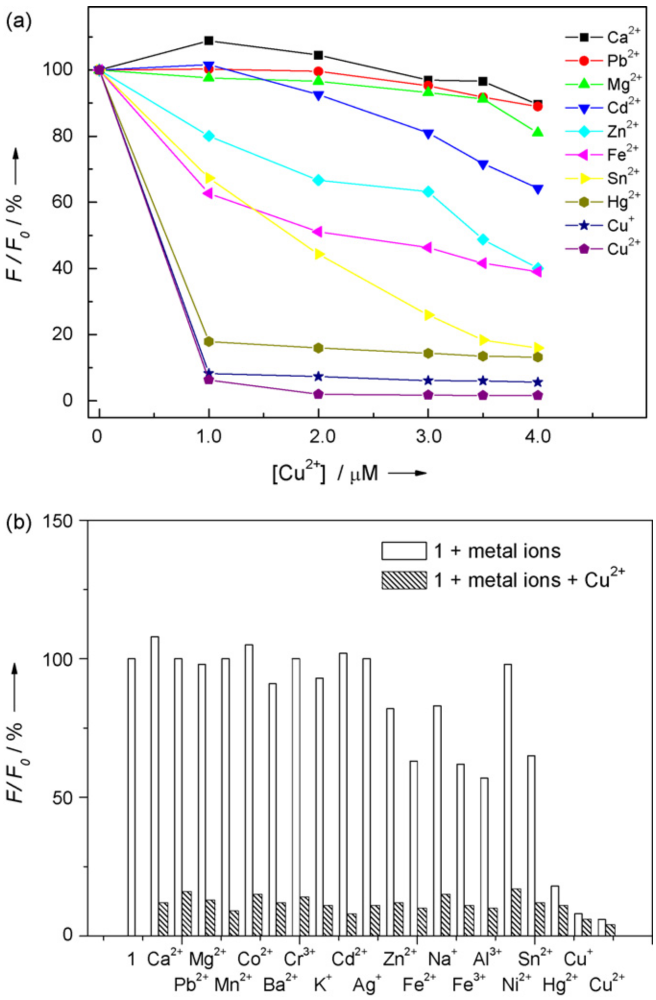


Fig. 3. (a) The relative fluorescence intensity of stilbene (1.0 μM, 298 K, $MeCN/H_2O$ = 1:9, v/v) at 359 nm excitation with titration of Ca^{2+}, Pb^{2+}, Mg^{2+}, Cd^{2+}, Zn^{2+}, Fe^{2+}, Sn^{2+}, Cu^+, and Cu^{2+} at different concentrations (pH = 5.8); (b) Relative fluorescence intensity of 1 (1.0 μM, 298 K, $MeCN/H_2O$ = 1:9, v/v) in the presence of various metal ions alone (1.0 μM) and interfering ions with Cu^{2+} (1.0 μM), respectively. λ_{ex} = 359 nm, λ_{em} = 519 nm.

3.3. Sensitivity of stilbene fluorophores

The sensitivity of fluorescence quenching from 1 by Cu^{2+} was further investigated, and the results are presented in Fig. 4. In the fluorescence spectra of **1**, maximum excitation and emission wavelengths were observed at 359 and 519 nm, respectively (Fig. 4a). The fluorescence intensity of 40% has been quenched when 0.1 μM of Cu^{2+} is added (Fig. 4a inset). The emission intensity of **1** decreases abruptly with increasing Cu^{2+} concentration and finally reached at a plateau at about 1.0 μM, which indicated a hyperbolic curve (Fig. 4b). Thus, a turning point was observed when one equivalent of Cu^{2+} was added indicating a 1:1 binding ratio. The experimental curve of fluorescence quenching was shown in Fig. 4b inset. Fluorescence quenching is described by the Stern–Volmer equation:

$$\frac{F_0}{F} = 1 + k_q\tau_0[Q] = 1 + K_{SV}[Q] \tag{1}$$

where F_0 and F are the fluorescence intensities before and after the addition of the quencher, respectively, k_q is the bimolecular quenching constant, τ_0 is the lifetime of the fluorophore in the absence of quencher, $[Q]$ is the concentration of the quencher, and K_{SV} is the Stern–Volmer quenching constant. Accordingly, the relationship between F_0/F and Cu^{2+} concentration was: $F_0/F = 5.88 \times 10^6[Cu^{2+}] + 1$. The linear range of the method was found to be $[Cu^{2+}] = 0.01–0.50$ μM with a correlation coefficient of $r/R = 1.00116$. The Stern–Volmer quenching constant was estimated as 5.88×10^6 M^{-1}. The detection limit, based on the definition by IUPAC ($C_{DL} = 3S_b/m$) [16], was found to be 25 nM from 10 blank solutions. Thus, the formation constant of 1 with Cu^{2+} was calculated as 2.88×10^6 M^{-1} using the method reported by Connors [17].

For the sake of comparison with **1**, mono-substituted stilbene derivative **2** was also synthesized (Scheme 2). Similar to **1**, the partially fluorescence quenching of **2** in the presence of Cu^{2+} could also be observed, but it is much less than that of **1** induced by Cu^{2+} under the same conditions (Supporting Information), which indicates the specificity of binding between **2** and Cu^{2+} less than that of **1**. A typical assay of this chemsensor with various concentration divalent copper ions was shown in Fig. 5. The fluorescence of stilbene **1** became faint even disappeared in naked eyes with increasing $[Cu^{2+}]$ above 1.0 μM. Comparably, the effects of other metal ions at the nM scale on the fluorescence of stilbene **1** are not so abrupt as copper ions. We consider this as good information in terms of sensor design with Cu^{2+} sensitivity at μM scale because the various binding affinity between **1** and metal ions will help differentiate the binding of the ligand with its target ion from other metal ions.

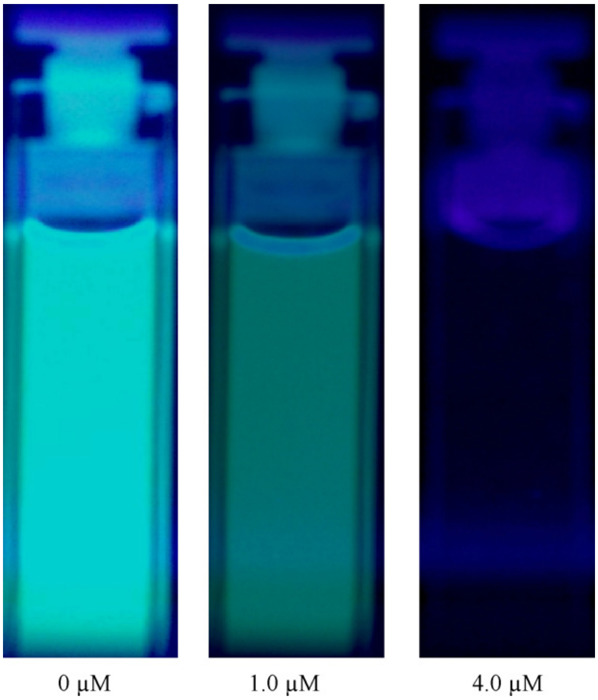


Fig. 5. Typical liquid-phase quenching assay of 1. Fluorescence emission spectra of 1 (1.0 μM, 298 K, $MeCN/H_2O = 1:9$, v/v) in the presence of various concentration of Cu^{2+} in 0, 1.0 and 4.0 μM. Fluorescence excitation was provided with a handheld low-wattage mineral lamp at set on "long wavelength" (365 nm). The image was acquired after 2 min of incubation.

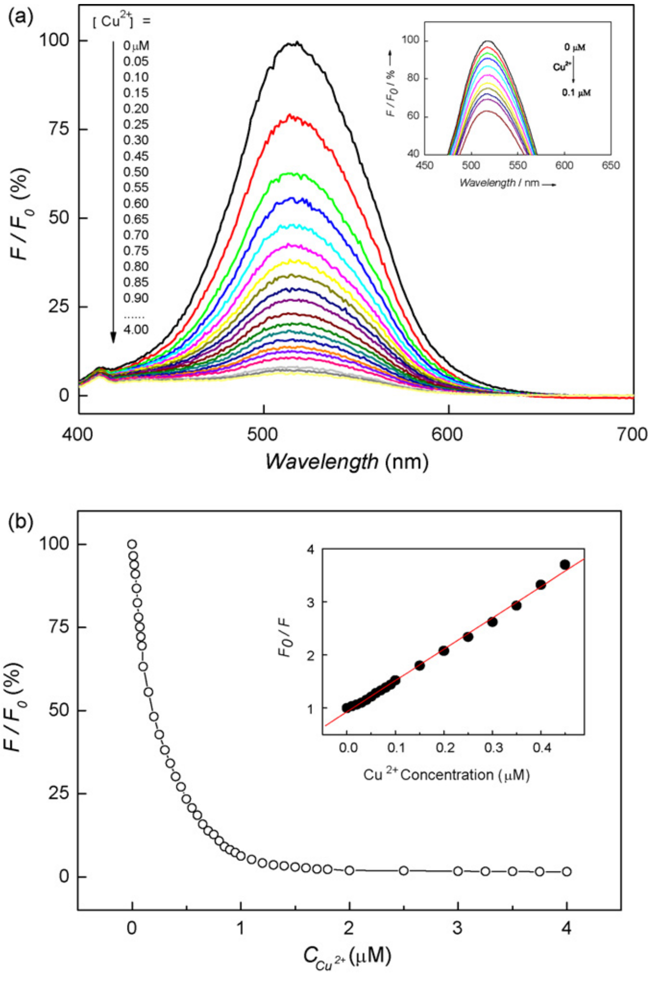


Fig. 4. (a) Fluorescence emission spectra of 1 (1.0 μM, 298 K, $MeCN/H_2O = 1:9$, v/v) in the presence of increasing concentration of Cu^{2+}. The concentrations of Cu^{2+} for curves bottom to top are 0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50 ...... 4.00 μM). Inset: fluorescence emission spectra of 1.0 μM 1 in the presence of 0–0.1 μM Cu^{2+}; (b) the relative fluorescence intensity of stilbene 1 with increasing Cu^{2+} concentration. Fluorescence intensity at $\lambda_{em} = 519$ nm as a function of copper concentration. Inset: F_0/F at 519 nm as a function of Cu^{2+} concentration within 0–0.50 μM range. Excitation wavelength: 359 nm.

4. Conclusion

In conclusion, a copper-sensitive fluorescent fluoroionophores was synthesized by modifying the stilbene with di-2-picolylamine (dpa), in which significant fluorescence quenching was observed upon binding with copper ions, indicating a high sensitivity and specificity of this chemosensor for copper ions. The presence of metal ions such as Ag^+, Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, K^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+}, Sn^{2+}, and Zn^{2+} had little influence on the selectivity and sensitivity of Cu^{2+} and Cu^+. This type of optical sensor design is promising for potential application to multiplex sensing of different analytes through distinct ligand conjugation and functionalization of individual fluorophore, as well as intracellular biochemical detection by a fluorophore sensing.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2010.01.002.

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