A highly selective fluorescent indicator for copper based on a boron complex

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Condensation of 4-(diethylamino)salicylaldehyde with aqueous hydrazine, followed by complexation with $BF_3{\cdot}OEt_2$ gives a fluorescent indicator highly selective for copper. The indicator forms a 2 : 1 complex with Cu^{2+} and displays a highly sensitive and selective fluorescent quenching action with Cu^{2+} upon excitation at 440 nm in water/THF (7 : 3, v/v) solution. This action is pH-independent over the range $4.5 < pH < 9.5$.

Keywords: Cu^{2+}, fluorescent indicator, boron complex, salicylaldehyde, hydrazine, fluorescent quenching

Fluorescent organic dyes have been widely used in metal ion detection as fluorescent probes of high sensitivity and selectivity that allow reduced sample volume.[1–8] Various ions can be successfully detected with a corresponding fluorescent compound, examples being: diketopyrrolopyrrole derivatives as fluorescent probes for Zn^{2+},[9] 4-aminoantipyrine for Al^{3+},[10] and 4-(8-quinolyl)amino-7-nitro-2,1,3-benzoxadiazole for Hg^{2+}.[11] The copper ion ranks third (behind Fe^{3+} and Zn^{2+}) among the essential transition metal ions in the human body and plays a key role in a variety of fundamental physiological processes in organisms that range from bacteria to mammals.[12–15] Lack of Cu^{2+} can cause neurodegenerative diseases such as Menkes disease, Wilson disease, and Alzheimer's disease.[16–19] Therefore, the development of new selective fluorescent probes is necessary to detect the concentration of Cu^{2+}. Several compounds have been used, such as *N,N*-bis(2-pyridylmethyl) amine[20], rhodamine chromene,[21] and rhodamine.[22] Boron complexes are the best-known fluorescent probes and have been widely applied in optical devices,[23–26] biological sensing,[27–29] light harvesting,[30–34] and catalysis[35–38] due to their valuable characteristics, such as: sharp, intense absorption, high molar absorption coefficients and high quantum yield. Boron complexes were also applied to detect different ions such as Zn^{2+},[39–41] Hg^{2+},[42–46] F^{-} [47–48] and CN^{-}.[49]

In the present work, we report a boron complex containing a 4-(diethylamino)-salicylaldehyde hydrazine structure,[50] Boronil (**1**) can effectively detect Cu^{2+} in a water/THF (7 : 3, v/v) solution using UV-Vis absorption and fluorescence techniques; it showed significant fluorescence quenching in the presence of Cu^{2+} with markedly high sensitivity, selectivity and a reduced sample volume.

Results and discussion

Synthesis of boronil (1)

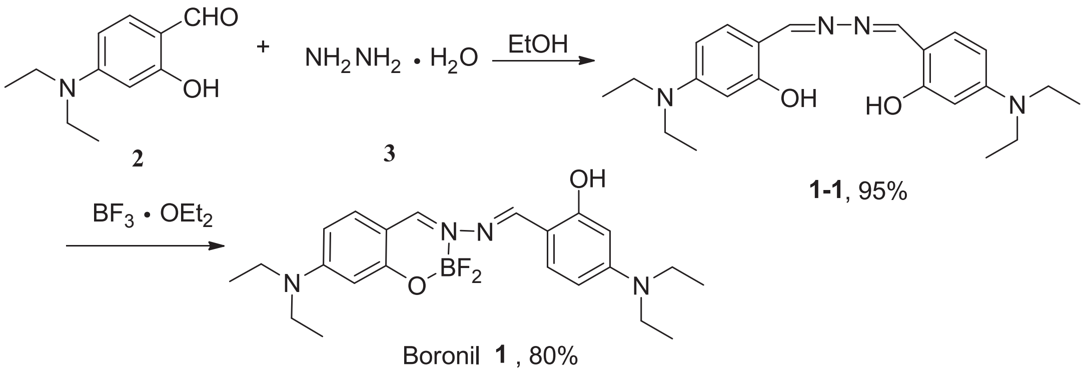
The complex **1** was synthesised in two steps (Scheme 1). First, a condensation reaction of 4-(diethylamino)salicylaldehyde and aqueous hydrazine was performed, the condensation product 4-(diethylamino)-salicylaldehyde hydrazine precursor **1-1** (**2**) was obtained in a 95% yield with EtOH as the solvent. The final boron complex (**1**) was prepared through the complexation of precursor **2** with $BF_3{\cdot}OEt_2$ in DCM with Et_3N as the base: the yield of **1** was 80%.

Absorption and fluorescence spectra of 1 *and precursor* 2

The absorption and fluorescence emission spectra of precursor **2** and **1** are shown in Fig. 1. Compared with the precursor **2**, the maximum absorption band of **1** has a redshift from 415 to 440 nm and 510 to 540 nm in its fluorescence emission spectrum. Thus, the excitation of precursor **2** was taken as being 415 nm and that of **1** was taken as 440 nm. Both precursor **2** and **1** had large Stokes' shifts of approximately 95 nm and 100 nm, respectively.

Sensitivity of 1 *in different solvents*

To achieve the best fluorescence of **1**, the fluorescence emission spectra were measured in different solvents, such as: DMF, MeCN, EtOH and THF, respectively. The maximum emission wavelength of **1** changed slightly in different solvents: *i.e.* DMF (560 nm), MeCN (566 nm), EtOH (568 nm) and THF (536 nm), respectively. The highest intensity of the fluorescence emission spectra of **1** occurred at the lowest wavelength when it was dissolved in THF, thus it was chosen as the solvent for use in subsequent experiments (see S1 in Electronic Supplementary Information, ESI).



Scheme 1 The synthesis of **1**.

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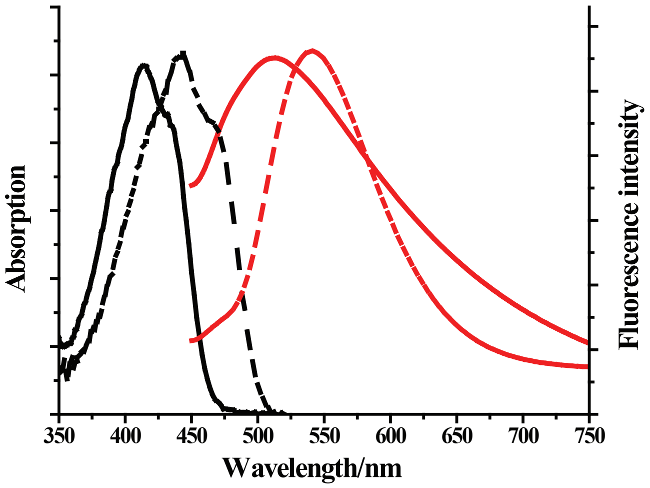


Fig. 1 Absorption (black) and fluorescence emission (red) spectra of 1 (10 μM) (dotted) and precursor **2** (10 μM) (plain) in THF.

Selectivity of **1**

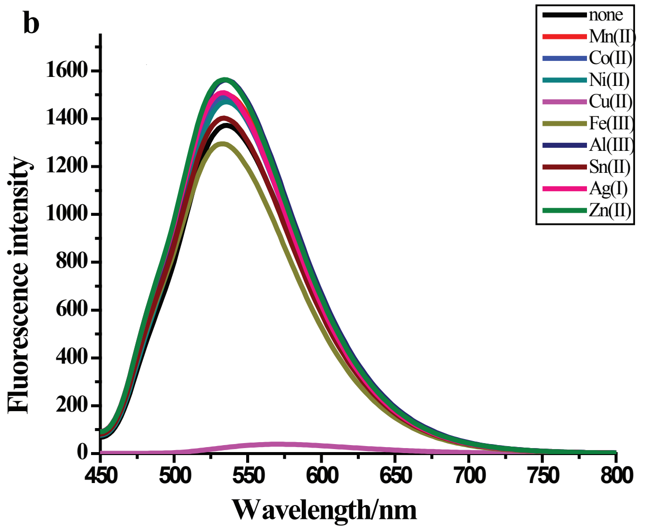
Considering the interest in expanding the potential application of **1**, a preliminary study of the photophysical behaviour of **1** and precursor **2** was undertaken in the presence of various metal ions, such as Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Fe^{3+}, Al^{3+}, Sn^{2+}, Ag^{+}, and Zn^{2+}, using UV-Vis and fluorescence spectroscopy and titration.

The changes in the UV-Vis absorption spectra which were induced by the addition of the aforementioned metal cations (1 equiv.) to **1** (10 μM) in THF upon excitation at 440 nm are shown in Fig. 2a; a metal-dependent behaviour was observed. With Mn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Al^{3+}, Sn^{2+}, Ag^{+} and Zn^{2+}, no significant changes in the UV-Vis absorption spectra were observed. However, the peak values of the UV-Vis absorption spectra were broadened and redshifted from 420 nm to 455 nm, with their intensity decreased, when aqueous Cu^{2+} was added to the THF solution of **1**. Also immediately, a change of the colour of the solution was observed from green to colourless under UV irradiation at 365 nm (see ESI, S2).

More interestingly, similar changes were found in the fluorescence emission spectra. The fluorescence emission spectra of **1** were little altered in the presence of the metal ions Mn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Al^{3+}, Sn^{2+}, Ag^{+} and Zn^{2+}, but pronounced changes were observed upon addition of Cu^{2+}. In the presence of Cu^{2+}, the maximum value of the fluorescence emission band shifted from 535 nm in the ion-free solution (water : THF = 7: 3, v/v) to 570 nm, and was accompanied by complete fluorescence quenching (Fig. 3b).

The effects induced by the aforementioned metal cations on the fluorescence emission spectra of precursor **2** (10 μM) upon excitation at 415 nm were also investigated, as shown in Fig. 3c. Upon treating a THF solution of **2** with the aforementioned metal cations, the maxima of the fluorescence emission bands were not significantly changed at 565 nm, but the intensity changed, depending upon which ions were present. The intensity of fluorescence decreased with the addition of Co^{2+}, Cu^{2+}, Al^{3+} and Ag^{+} and increased in the presence of Fe^{3+}, Mn^{2+}, Ni^{2+}, Sn^{2+} and Zn^{2+}.

Therefore, the above results showed that **1** was both sensitive and effective as a fluorescent indicator for Cu^{2+}. The development of sensors for the facile detection of Cu^{2+} is important in environmental monitoring and biological assays.[3,21,22] As shown, **1** has a unique fluorescence quenching effect for Cu^{2+}. To investigate further its use as a probe for Cu^{2+},



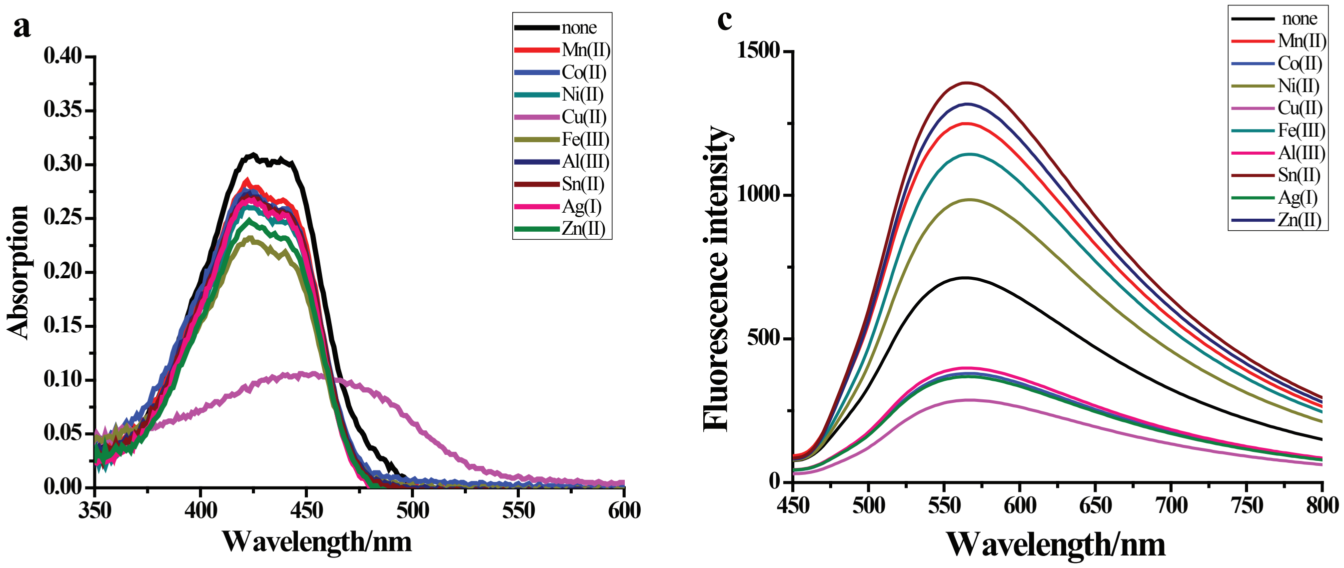


Fig. 2 Absorption and fluorescence response of **1** (10 μM) (a, b) (λ_{ex} = 440 nm) and fluorescence response of precursor **2** (c) (λ_{ex} = 415 nm) with 1.0×10^{-5} M of Cu^{2+} and other metal ions in THF solution.

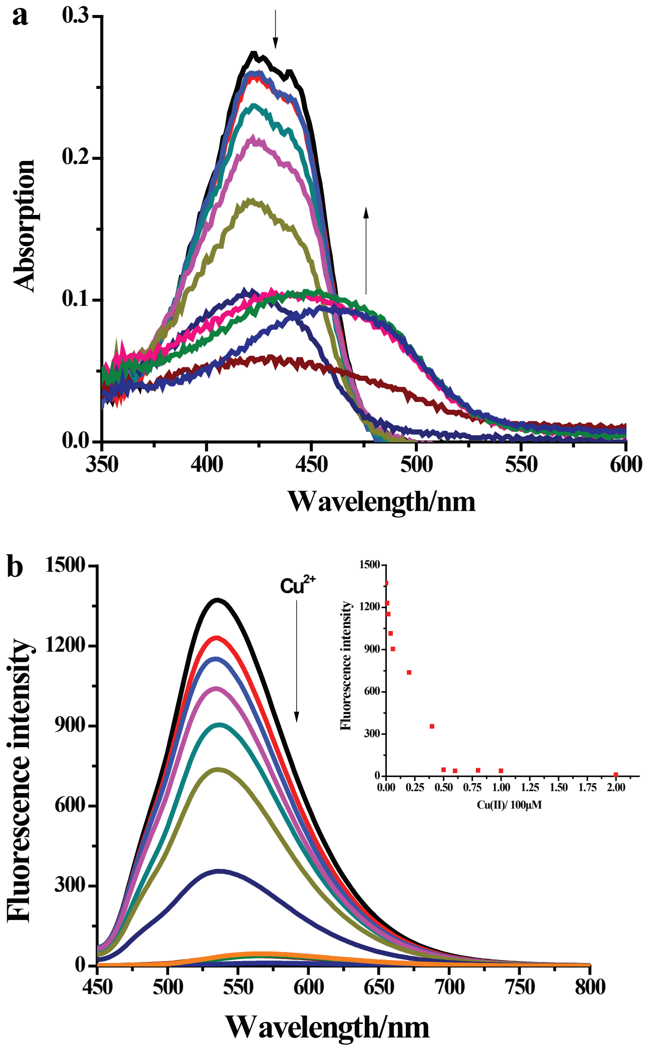


Fig. 3 Absorption (a) and fluorescence response ($\lambda_{ex}=440$ nm) (b) of **1** (10 μM) exposed to Cu^{2+} of various concentrations: 0, 1.0×10^{-7}, 2.0×10^{-7}, 6.0×10^{-7}, 1.0×10^{-6}, 2.0×10^{-6}, 4.0×10^{-6}, 5.0×10^{-6}, 6.0×10^{-6}, 8.0×10^{-6}, 1.0×10^{-5}, 2.0×10^{-5} M (from top to bottom). Inset shows fluorescence titration curve of **1** with Cu^{2+}. These spectra were measured in water/THF (7 : 3, v/v) solution.

the fluorescence and absorption titration of **1** in the presence of different Cu^{2+} concentrations was performed. As shown in Fig. 4a, upon increasing the metal ion concentration, the main energy absorption band at 425 nm decreased in intensity and redshifted progressively to 455 nm. The immediate change, from green to colourless, in the solution could also be observed under the UV lamp (365 nm) and from green and yellow to colourless by the naked eye (see ESI, S3). As shown in Fig. 4b, the fluorescence titration curve of **1** with Cu^{2+} showed a reduced fluorescence intensity under excitation at 440 nm with an increase in Cu^{2+} content and the fluorescence emission was quenched fully upon increasing the concentration of Cu^{2+} to 5 μM (0.5 equiv.).

Achieving high selectivity for the analyte of interest over a complex background of potentially competing species is a challenging task in sensor development. To explore the use of **1** as an ion-selective fluorescent probe for Cu^{2+}, competition experiments were carried out. The fluorescence response of **1** (10 μM) in the presence of copper (1 equiv.) or other metal ions (1 equiv.) and a metal/copper (1 : 1) combined system, showed that the competing metal ions exhibited only little, or no, interference with the detection of Cu^{2+} (ESI, S4).

*Coordination modes between **1** and Cu^{2+}*

To determine the binding stoichiometry of **1** and Cu^{2+}, Job's method for its emissions was used (Fig. 5). The concentration ratio of **1** and Cu^{2+} were varied, while the sum of the two concentrations was kept constant at 1.0×10^{-5} M. When the molecular fraction of Cu^{2+} was close to 33%, the complex of **1** and Cu^{2+} exhibited full fluorescence emission quenching. This indicated that a 2 : 1 stoichiometry pertained for the binding mode of **1** and Cu^{2+}. An illustration of a structure for the coordination of the copper complex is given in Scheme 2.

Effect of the pH on spectroscopic properties

To investigate the dependence of the fluorescence properties of **1** on the pH value, the UV-Vis absorption and fluorescence spectra of **1** (10 μM) in a water/THF (7 : 3, v/v) solution were measured in a buffer solution at different pH values. The absorption spectra (Fig. 4a) show that the maximum absorption peak changed with different pH values. The maximum absorption peak was approximately at 420 nm at $4.5\leq pH\leq9.5$, however, it decreased and a new absorption peak appeared at

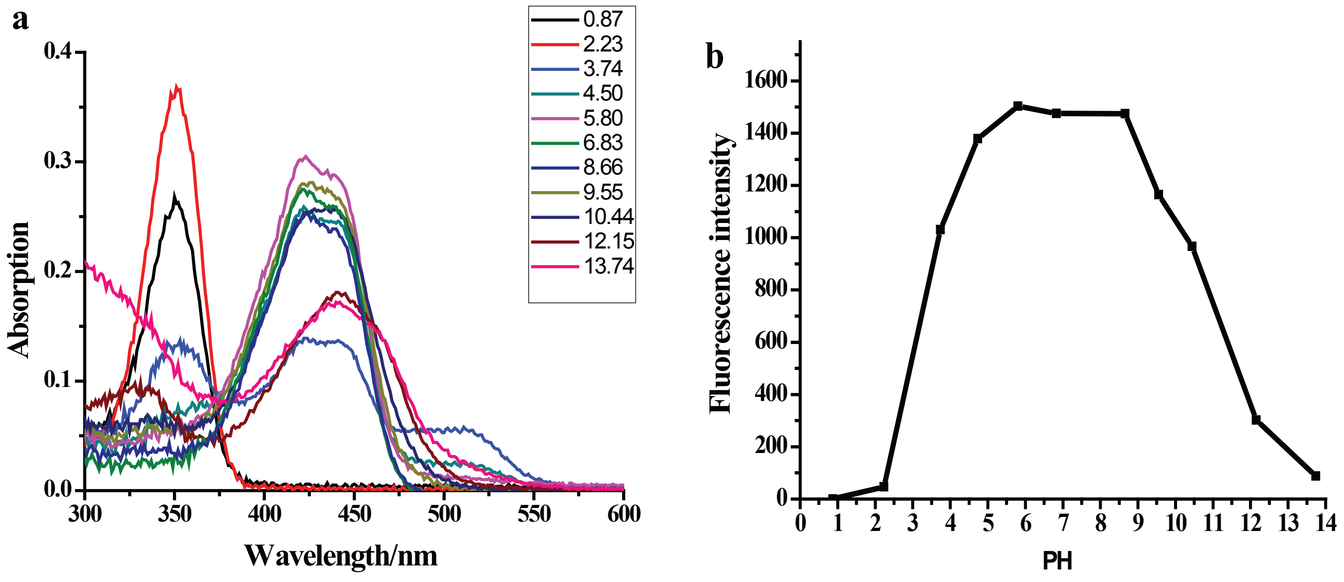
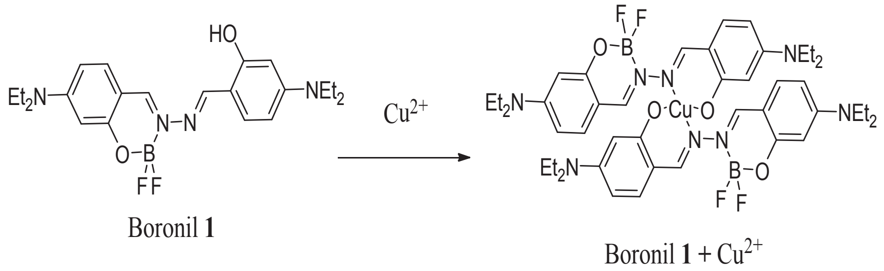


Fig. 4 Absorption (a) and fluorescence spectra (b) of l **1** (10 μM) in water/THF (7 : 3, v/v) solution with different pH ($\lambda_{ex}=440$ nm).



Scheme 2 Schematic illustration of the coordination between **1** and Cu^{2+}.

350 nm when the pH of the buffer solution decreased below 4.5 nm and again at 445 nm when the pH of the buffer increased from 9.5. Moreover, **1** displayed a significant fluorescence enhancement at approximately 535 nm at 4.5≤pH≤9.5 and did not vary with pH over that range (Fig. 4b), which was convenient for practical application of **1** to the determination of Cu^{2+} in actual samples.

Experimental

All of the chemicals used in the current study were purchased from commercial vendors and used as-received without further purification, unless otherwise noted. All solvents were purified and dried using standard methods prior to use. FTIR spectra were performed using a Thermo Nicolet 6700 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 500 spectrometer with chemical shifts reported as ppm at 500 and 125 MHz, respectively, in $CDCl_3$, TMS as internal standard. Fluorescence spectra were obtained with an F-7000 fluorescence spectrophotometer in a solution of 10 μM with PMT voltage at 500V. UV-Vis absorption spectra were measured on a UV-2550 instrument.

Synthesis of boronil (**1**)

4-(Diethylamino)-salicylaldehyde hydrazine (precursor **2***)*: Aqueous hydrazine (85%) (0.2950 g, 5 mmol) in ethanol (10 mL), was added to a solution of 4-(diethylamino)salicylaldehyde (1.9365 g, 10 mmol) in ethanol (50 mL) over a period of 1 h at 0 °C. Then the mixture was stirred for more 4 h until the reaction was complete as detected by TLC. The solution was concentrated to give crude solid which was recrystallised from ethanol and dried *in vacuo* to give the pure product 4-(diethylamino)-salicylaldehyde hydrazine (**2**). Yield 1.8066 g, yellow solid (95%);[51] m.p. 234–235 °C. FTIR (KBr, cm^{-1}) 2971.8, 1629.9, 1593.1, 1514.3, 1412.8, 1351.4, 1230.5, 1131.5, 1080.0, 964.2, 827.3, 788.8, 709.7. ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.84 (s, 2H), 8.46 (s, 2H), 7.11 (d, J=8.7 Hz, 2H), 6.27 (dd, J_1=8.7 Hz, J_2=2.5 Hz, 2H), 6.23 (d, J=2.5 Hz, 2H), 3.40 (q, J=7.1 Hz, 8H), 1.22 (t, J=7.1 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.43 (2C), 160.90 (2C), 151.20 (2C), 133.26 (2C), 106.94 (2C), 103.95 (2C), 97.87 (2C), 44.55 (4C), 12.69 (4C).

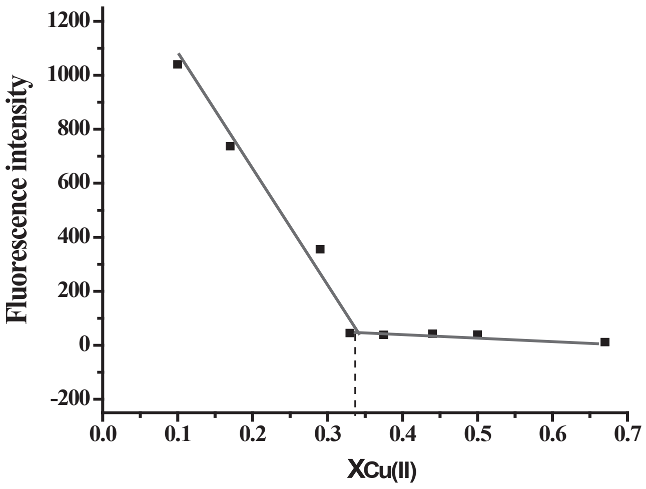


Fig. 5 Job's plot for **1** and Cu^{2+}. Total concentration of **1** and Cu^{2+} kept at 1.0×10^{-5} M (λ_{ex}=440 nm).

Boron complex (**1**)

NEt_3 (1.5 mL, 10 mmol) by syringe was added to a stirred solution of **2** (0.1955 g, 0.5 mmol) in degassed anhydrous dichloromethane (25 mL) at 50 °C under a nitrogen atmosphere. After stirring for 20 min, BF_3•OEt_2 (1.25 mL, 10 mmol) was successively added and the mixture was stirred until the reaction was complete as detected by TLC, then the mixture was cooled to room temperature. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography (silica gel, eluting DCM: PE=4: 1) to afford clean product **1**. Yield 0.1700 g of orange-yellow solid (80%); m.p. 242–243 °C. FTIR (KBr, cm^{-1}) 2971.8, 1621.9, 1600.6, 1510.8, 1455.4, 1341.4, 1305.6, 1245.3, 1132.7, 1077.7, 970.0, 827.3, 788.8. ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.11 (s, 1 H), 8.86 (s, 1H), 8.17 (s, 1H), 7.18 (d, J=9.0 Hz, 1H), 7.15 (d, J=9.0 Hz, 1H), 6.36 (dd, J_1=9.0 Hz, J_2=2.4 Hz, 1H), 6.28 (dd, J_1=9.0 Hz, J_2=2.4 Hz, 1H), 6.24 (d, J=2.4 Hz,1H), 6.18 (d, J=2.4 Hz, 1H), 3.45 (q, J=7.2 Hz, 4H), 3.41 (q, J=7.2 Hz, 4H), 1.25 (t, J=7.2 Hz, 6H), 1.22 (t, J=7.2 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.40 (1C), 160.19 (1C), 159.97 (1C), 155.63 (1C), 155.28 (1C), 151.87 (1C), 134.77 (1C), 133.07 (1C), 106.54 (1C), 106.31 (1C), 104.65 (1C), 104.45 (1C), 98.13 (1C), 97.76 (1C), 45.09 (2C), 44.60 (2C), 12.68 (2C), 12.65 (2C). ESI-MS: 431.3 $(M+H)^+$. HRMS (ESI-TOF) *m/z* calcd for *m/z* $C_{22}H_{29}BF_2N_4O_2$ $(M+H)^+$ (431.2424), found 431.2425.

Conclusions

A new visible light excitable, fluorescent chemosensor (**1**) was synthesised based on a boron complex. This new boron complex showed high selectivity and sensitivity as a fluorescent probe for copper ion, displaying large absorption and fluorescence changes in an analytically-relevant wavelength region. Upon excitation at 440 nm, **1** displayed a significant fluorescence quenching in the presence of Cu^{2+} and a high selectivity towards Cu^{2+} among various metal ions in a water/THF solution (7 : 3, v/v). Complex **1** also formed a 2 : 1 complex with Cu^{2+} and its fluorescent effect was pH-independent over the range 4.5≤pH≤9.5.

Electronic Supplementary Information

The ESI is available through:
stl.publisher.ingentaconnect.com/content/stl/jcr/supp-data.

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