

# A 2-hydroxy-1-naphthaldehyde-derived chemosensor for recognition of Cu<sup>2+</sup>

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A new Schiff base formed by coupling 2-hydroxy-1-naphthaldehyde and Betti base can selectively recognise Cu<sup>2+</sup> over other metal ions such as Zn<sup>2+</sup>, Cd<sup>2+</sup>, Sn<sup>2+</sup>, Pb<sup>2+</sup>, Hg<sup>2+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup>, Cr<sup>3+</sup>, alkali metals and alkaline earth metals in acetonitrile/water. Cu<sup>2+</sup> binds one mole of the base causing an obvious blue-shift ( $\Delta = 43$  nm) in its absorption spectrum and quenching its fluorescence emission. The stability constant is estimated to be  $1.25 \times 10^4$  M<sup>-1</sup>.

**Keywords:** 2-hydroxy-1-naphthaldehyde, chemosensor, Cu<sup>2+</sup>

The development of fluorescent chemosensors for selective response to particular metal ions is an area of immense importance in recent years. Cu<sup>2+</sup> is the third most important trace metal ion in various biological systems and one of the most important environmental pollutants.<sup>1</sup> Therefore, the design and development of simple but effective fluorescent chemosensors selective for copper ion are of considerable interest. Indeed, some sensors for copper ion have been developed recently.<sup>2–7</sup> They are mainly based on fluorescence quenching or enhancement by a fluorescent moiety (fluorophore) which is covalently linked to the recognition moiety (acceptor or ligand) via a spacer to form a PET system.<sup>8–10</sup> Toward the development of another fluorescent sensor for detection of divalent copper with new fluorophores, we here report a new Cu<sup>2+</sup>-selective fluorescent sensor **1**, in which the fluorescent moiety itself acts as a ligand for metal cations.

The ligand **1** has been formed by coupling 2-hydroxy-1-naphthaldehyde and Betti base. The binding of divalent copper with this intrinsic fluorescent ligand affects the fluorescent properties dramatically. This fluorescent chemosensor also shows a good selectivity and sensitivity for the divalent copper cation over other cations, such as Na<sup>+</sup>, K<sup>+</sup>, Zn<sup>2+</sup>, Sn<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Pb<sup>2+</sup>, Ni<sup>2+</sup>, Ba<sup>2+</sup>, Hg<sup>2+</sup>, Cd<sup>2+</sup>, Mn<sup>2+</sup> and Cr<sup>3+</sup>.

## Experimental

### Apparatus

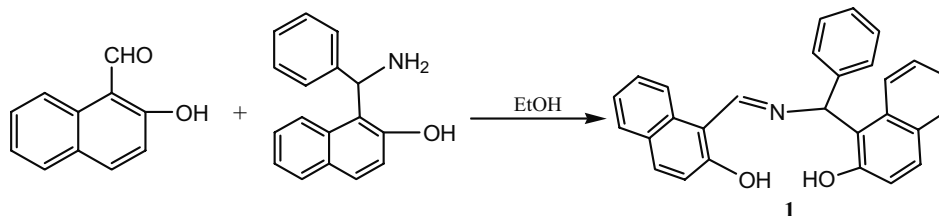
Absorption spectra were determined on a Tu-1901 UV–vis spectrophotometer. Fluorescence spectral measurements were performed on an F-4500 (Hitachi) spectrometer. IR spectra were recorded on a Thermo Nicolet 670 spectrometer (KBr disk). <sup>1</sup>H NMR spectra were recorded using a 400 MHz Varian Gemini instrument. Mass spectra were recorded with Finnigan 4021C MS-spectrometer and Biflex III MALDI-TOF MS-spectrometers. All measurements were at room temperature at about 298K.

### Reagents

Betti base (Scheme 1) was obtained from an authentic sample. All cationic chlorides used were analytical grade. Other solvents and reagents were of commercial quality from freshly opened containers.

### Synthesis of **1**

Ligand **1** was synthesised by the condensation reaction of 2-hydroxy-1-naphthaldehyde and Betti base<sup>11–12</sup> as shown in Scheme 1.



**Scheme 1** synthesis of compound **1**.

2-Hydroxy-1-naphthaldehyde (10 mg (0.058 mmol)) was dissolved in EtOH (20 mL), Betti base 17 mg (0.069 mmol) in EtOH (2 mL) was added dropwise, then the reaction was kept at room temperature for 4 h. The crude product was collected and washed with EtOH, then purified by flash column chromatography. The solvent were removed under reduced pressure and a yellow solid was obtained in analytically pure form, yield 58%. M.p. 218–220°C (dec). IR (KBr)  $\nu$ : 2972.13, 2512.50, 1626.83, 1544.90 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.11 (s, 1H, CH=N), 8.05 (m, 1H, ArH), 7.82 (m, 1H, ArH), 7.66 (m, 1H, ArH), 7.75 (m, 1H, ArH), 7.54 (m, 2H, ArH), 7.46 (m, 5H, ArH), 7.35 (m, 5H, ArH), 7.21 (m, 1H, ArH), 6.77 (s, 1H, CH-N), 2.89 (br, 2H, ArOH).

### Absorption and fluorescence measurements

The fluorescence spectra of compound **1** were measured in CH<sub>3</sub>CN/H<sub>2</sub>O solution. The concentration of the solution of compound **1** was  $1.0 \times 10^{-4}$  mol L<sup>-1</sup> (CH<sub>3</sub>CN), and the concentration of stock solution of different metal chloride salts used for the fluorescence titration was  $1 \times 10^{-3}$  mol L<sup>-1</sup> (H<sub>2</sub>O). Absorption and fluorescence titrations were performed by addition of 50  $\mu$ L aliquots of **1** in CH<sub>3</sub>CN (2 mL) to a 1 cm quartz cell. Excitation wavelength was 360 nm and the slit widths were 5 and 10 nm, respectively.

## Results and discussion

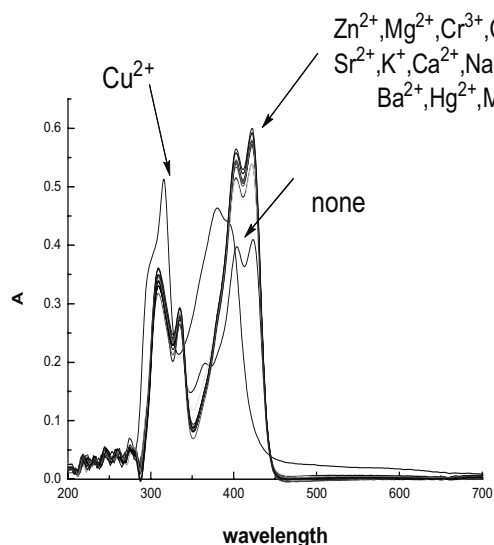
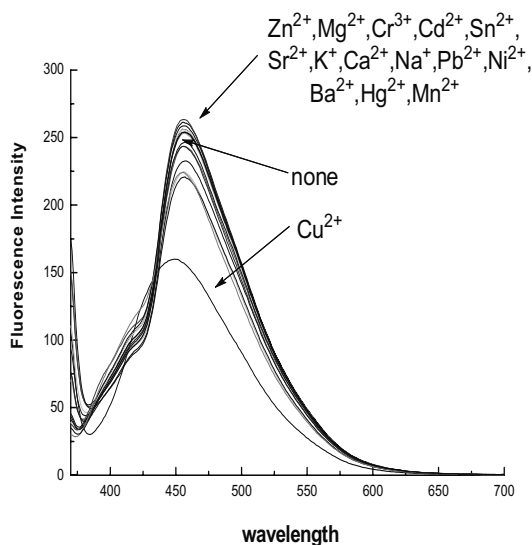
### The interaction of **1** with different metal ions

The interactions of **1** with different metal ions were investigated by the UV–vis absorption and fluorescence spectra. As shown in Fig. 1, **1** displayed two obvious absorption bands at 404 nm ( $\epsilon = 1.59 \times 10^5$  L mol<sup>-1</sup> cm<sup>-1</sup>) and 423 nm ( $\epsilon = 1.64 \times 10^5$  L mol<sup>-1</sup> cm<sup>-1</sup>), respectively. When 10 equiv of Cu<sup>2+</sup> was added to a solution (CH<sub>3</sub>CN: H<sub>2</sub>O; v/v = 99:1) of **1**, the maximum absorption of **1** shifted from 423 to 380 nm ( $\Delta = 43$  nm) (Fig. 1), the fluorescence intensity was substantially quenched and the maximum emission peak shifted from 455 to 448 nm (Fig. 2). These changes in absorption and fluorescent spectra of **1** are probably due to the binding of Cu<sup>2+</sup> with the hydroxyl of the 2-hydroxy-1-naphthal group, the donor of the intramolecular charge transfer (ICT) system. The resulting reduced ICT effect causes the blueshift in UV-vis spectra, and energy transfer between Cu<sup>2+</sup> and the fluorophore quenches the emission. These effects also have been reported in related references<sup>5–7,13–16</sup>. However, when other metal ions such as Na<sup>+</sup>, K<sup>+</sup>, Zn<sup>2+</sup>, Sn<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Pb<sup>2+</sup>, Ni<sup>2+</sup>, Ba<sup>2+</sup>, Hg<sup>2+</sup>, Cd<sup>2+</sup>, Mn<sup>2+</sup> and Cr<sup>3+</sup> were added respectively, there was only slight enhancement and shift in absorption and fluorescence spectra of **1**. The relative fluorescence intensities of **1** binding with these metal ions at 455 nm are shown in Table 1, which shows that **1** has good selectivity for Cu<sup>2+</sup> over other metal cations.

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**Table 1** Relative fluorescence intensities of compound **1** upon addition of different metal ions

	None	Na <sup>+</sup>	K <sup>+</sup>	Zn <sup>2+</sup>	Sn <sup>2+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Sr <sup>2+</sup>
R <sub>if</sub> (455nm)	<b>1</b> Pb <sup>2+</sup>	1.131 Ni <sup>2+</sup>	1.140 Ba <sup>2+</sup>	1.132 Hg <sup>2+</sup>	1.176 Cd <sup>2+</sup>	1.086 Mn <sup>2+</sup>	1.166 Cr <sup>3+</sup>	1.153 Cu <sup>2+</sup>
R <sub>if</sub> (455nm)	1.087	1.005	1.001	1.035	1.142	1.096	1.127	0.702

**Fig. 1** Absorption spectra of compound **1** ( $1.0 \times 10^{-4}$  M) upon addition of different metal ions ( $1 \times 10^{-3}$  M) in CH<sub>3</sub>CN:H<sub>2</sub>O (v/v = 99:1).**Fig. 2** Absorption spectra of compound **1** ( $1.0 \times 10^{-4}$  M) upon addition of different metal ions Fluorescence spectra of compound **1** ( $1.0 \times 10^{-4}$  M) upon addition of different metal ions ( $1 \times 10^{-3}$  M) in CH<sub>3</sub>CN: H<sub>2</sub>O (v/v = 99:1) (Ex = 360 nm).

#### Binding of **1** with Cu<sup>2+</sup>

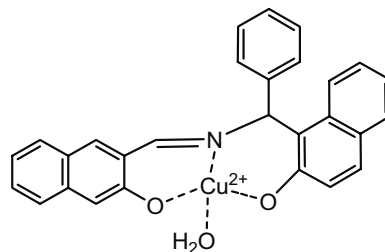
To illustrate the interaction between **1** and Cu<sup>2+</sup>, the UV-vis and fluorescent spectra with varying concentrations of Cu<sup>2+</sup> were recorded in CH<sub>3</sub>CN:H<sub>2</sub>O (v/v = 99:1). The absorbance at 423 nm decreases and the absorbance at 380 nm increases gradually upon the addition of Cu<sup>2+</sup> to a solution of **1**. Two isosbestic points at A (399 nm) and B (446 nm) are clearly observed, indicating a stable complex formation. To look into the nature of the recognition process, <sup>1</sup>H NMR experiments were performed in CD<sub>3</sub>Cl. <sup>1</sup>H NMR spectra of **1** showed dramatic changes upon addition of 10 equivalents of

Cu(ClO<sub>4</sub>)<sub>2</sub> in CD<sub>3</sub>Cl. CH=N and CH-N proton signals show significant downfield shifts (from 9.047 to 9.325,  $\Delta\delta = 0.28$  and from 6.746 to 6.854,  $\Delta\delta = 0.1$ , respectively); while all aromatic protons show obvious shift changes because of the interaction between **1** and Cu<sup>2+</sup>. The interesting ratiometric fluorescence response of **1** upon the addition of Cu<sup>2+</sup> might be utilised for Cu<sup>2+</sup> analysis.

To further investigate the binding model of **1** and Cu<sup>2+</sup>, experiments of absorption spectra titration, (Job's method) and MALDI-TOF spectra were carried out. The absorbance of **1** decreased linearly upon the addition of Cu<sup>2+</sup> ( $1.0 \times 10^{-4}$  mol L<sup>-1</sup>, from 5 to 80  $\mu$ L), and varied very slightly when more than 1.0 equiv Cu<sup>2+</sup> was added. The nonlinear fit of the data revealed the binding of **1** and Cu<sup>2+</sup> was most probably a 1:1 stoichiometry<sup>17</sup>. The data of a Job's plot, using a total concentration of  $1.0 \times 10^{-5}$  mol L<sup>-1</sup> for **1** and Cu<sup>2+</sup>, exhibited a maximum absorbance at 380 nm when the molecular fraction of **1** was close to 50%, which also suggested 1:1 stoichiometry for the **1**-Cu<sup>2+</sup> complex. Based on these results, the binding constant of **1** to Cu<sup>2+</sup> was determined to be  $1.25 \times 10^4$  M<sup>-1</sup> by the nonlinear fitting of the spectra data.<sup>18</sup>

Furthermore, the MALDI-TOF mass spectra of **1** in the presence of 10 equiv Cu<sup>2+</sup> exhibited a clear peak at  $m/z$  487.506 [ $M + Cu^{2+} \cdot 2H^+ + 1.25H_2O$ ], corresponding well with the calculated value 487.072, suggesting 1:1 stoichiometry of **1**-Cu<sup>2+</sup> complex formation.

The selectivity for Cu<sup>2+</sup> might be attributed to the geometrical difference between the Cu<sup>2+</sup>-complex and other metal complexes as observed in other metal-ligand systems.<sup>19</sup> In acetonitrile-water, these ions generally form octahedral complexes. Due to the Jahn-Teller effect for Cu<sup>2+</sup>, the coordination interaction of the four equatorial sites is stronger than that of the remaining axial positions.<sup>20</sup> Consequently, four-coordinated Cu<sup>2+</sup> complexes are generally characterised by a square planar geometry if there are no special geometrical constraints

**Scheme 2** proposed binding mode between compound **1** and Cu<sup>2+</sup>

in the ligands, just as in the present ligand **1**. In contrast, there is usually no intrinsic preference for axial over equatorial coordination in other metal ions in aqueous solution. Therefore, compound **1** can be superior binding Cu<sup>2+</sup> over other metal ions. In this case, the Cu<sup>2+</sup> ion may locate at the centre of the pseudocavity of compound **1** and coordinate with oxygen atoms in naphthol and the nitrogen atom of imine. Moreover, a molecule of H<sub>2</sub>O may also participate in the coordination as the fourth chelating group. The proposed binding model between compound **1** and Cu<sup>2+</sup> is shown in Scheme 2.

#### Conclusion

In summary, a new chemosensor, **1**, was synthesised and characterised. It shows selective and sensitive absorption and fluorescent response to Cu<sup>2+</sup> over other metal cations in acetonitrile/water. Furthermore, the linear fluorescence response of **1** upon the addition of Cu<sup>2+</sup> might be utilised for quantitative Cu<sup>2+</sup> analysis.

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