

A highly selective chemosensor for Cu^{2+} and Al^{3+} in two different ways based on Salicylaldehyde Schiff

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ABSTRACT

A novel, easily available colorimetric and fluorescent double-sensor **1** based on Salicylaldehyde bis-Schiff has been investigated in this work. The sensor exhibits highly selective and sensitive recognition toward Cu^{2+} in aqueous solution via a naked eye colour change from colourless to yellow and toward Al^{3+} via a significant fluorescent enhancement in ethanol over a wide range of tested metal ions. This represents the first reported Salicylaldehyde Schiff-based sensor capable of detecting both Cu^{2+} and Al^{3+} using two different modes.

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The design and construction of chemosensors with high selectivity and sensitivity for metal ions such as aluminium and copper have become the focus of numerous studies in supramolecular chemistry due to their significant importance in chemical, biological, and environmental processes [1–4]. Aluminium has been identified as a neurotoxin for over one hundred years [5]. Many scientists have recently found that aluminium can cause health hazard like Alzheimer's disease [6,7], osteomalacia [8] and even to the risk of cancer of the breast [9]. Copper is also widely used and acts as a pollutant that can cause severe risks for the ecosystems. Exposure to a high level of copper even for a short period of time can cause gastrointestinal disturbance, and long-term exposure can cause liver or kidney damage [10]. Consequently, much attention has been drawn to the development of selective Cu^{2+} sensors for biological and environmental applications [11]. Up to now, many colorimetric and fluorescent chemosensors for Cu^{2+} and Al^{3+} have been reported [12–14]. In spite of these works, there are relatively few examples of chemosensors capable of displaying two or more output signals (different signalling ways) upon cation binding [14,15]. Additionally, chemosensors able to display sensing abilities to different cations when using different signalling ways are very rare. However, these systems can be of interest for designing future probes that are able to signal, not just one, but multiple analytes.

Salicylidene Schiff base can be easily synthesised by the condensation reactions of salicylaldehyde and amine derivatives [16–18].

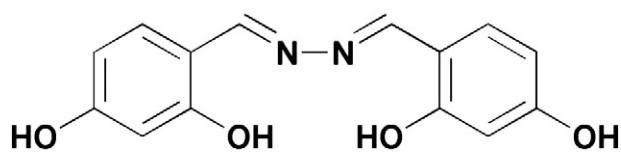
This kind of molecules are known to have strong binding abilities to the metal ions and display different optical properties from the ligands themselves, making them good candidates for cation probes [19]. In this paper, we described the colorimetric and fluorescence variations of a bis-Schiff base derivative **1** (Scheme 1), which displays not only selective colorimetric changes upon the addition of Cu^{2+} but also a remarkable fluorometric enhancement in the case of Al^{3+} . Interestingly, compared to the fluorescent quenching with most fluorescent sensors in the solid state, **1** can emit visible strong green fluorescence under UV light on a paper-made test, fluorescence quenching and colour changing occur along with the addition of the copper ion. The results show that **1** can be presented as a novel cation sensor that can display double signals for recognising both Cu^{2+} and Al^{3+} immediately. This single molecule sensor for multiple analytes by multi-channel optical signals is promising and has been rarely exploited. As far as we are aware, compound **1** is the first chemosensor for Cu^{2+} and Al^{3+} ions utilising two different ways.

Chemosensor **1** was synthesised by a simple and straightforward method with good yield (75%) by condensation of 4-hydroxysalicylaldehyde with hydrazine hydrate in ethanol [20,21]. In compound **1**, two salicylaldehyde moieties are connected by a rotatable N–N single bond which provides two imine-N and two phenolate-O binding sites to interact with metal ions and form salen metal complexes [22]. The chemosensing behaviour of **1** was investigated using UV–Vis and fluorescence measurements.

The metal recognition properties of **1** were initially evaluated by UV–Vis analysis. Fig. 1a illustrates the variation of UV–Vis spectrum of **1** (30 μM) along with the increasing amounts of Cu^{2+} that is available as nitrate, from 0 to 60 μM in EtOH/ H_2O ($v/v = 30/70$). Two absorbance

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Scheme 1. Chemical structure of sensor 1.

bands were observed to be centred at 311 and 363 nm, which could be attributed to $n-\pi^*$ transition of $C=N$ and $\pi-\pi^*$ transitions of benzene rings, respectively [20]. Upon the addition of Cu^{2+} , a new absorption band centred at 415 nm appeared with increasing intensity. Meanwhile, the original absorption band centred at 363 nm decreased gradually and the 311 nm absorption band increased, generating two isosbestic points at 329 and 393 nm, which indicated the formation of a new complex between **1** and Cu^{2+} . As shown in the inset of Fig. 1a, a nearly linear dependence of the ratio of absorbance at 415 and 363 nm as a function of Cu^{2+} concentration from 0 to 30 μM was observed. At the same time, the absorption changes were clearly visible to the naked eye, showing that the colourless solution of **1** became yellow upon titration with Cu^{2+} even at 1 μM concentration (inset photograph in Fig. 1a).

The selectivity of **1** toward other metal ions was investigated by UV-Vis spectroscopy in EtOH/ H_2O buffer solution (30 mM, pH = 7.2, v/v = 30/70). The competitive metal ion includes heavy, transition and alkali earth ions such as Ag^+ , Al^{3+} , Ba^{2+} , Ca^{2+} , Cd^{2+} , Co^{2+} , Cr^{3+} , Hg^{2+} , Mg^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+} . As shown in Fig. 1b, the addition of two equiv of other metal ions resulted in negligible changes in the absorption spectrum of **1** and the colour of the solutions containing these ions remained relatively unchanged, only Cu^{2+} gave an obvious absorption change which was clearly visible to the naked eye, showing that **1** has a good selectivity for Cu^{2+} .

The fluorescent properties of **1** were also studied and a weak fluorescence emission band centred at around 425 nm and 505 nm was observed in the spectrum of **1** (15 μM) in ethanol when excited at 360 nm. As has been reported by Yu, [14] compound **1** contains an intramolecular hydrogen bond between the phenolic O–H and the nitrogen of the imine group that undergoes excited-state intramolecular proton transfer (ESIPT) and yields a normal emission at 425 nm and a tautomer emission at 505 nm from the proton transfer tautomer (Scheme 2) [23]. The low fluorescence of **1** is assigned to the

existence of a very effective non-radiative intramolecular rotation decay of the excited state most likely due to the structure of **1** with two salicylaldehyde moieties connected by a rotatable N–N single bond [20]. However, the addition of Al^{3+} significantly enhanced the fluorescence intensity. As shown in Fig. 2a, the emission peak of **1** increased with increasing Al^{3+} concentration. With the concentration of Al^{3+} up to three equiv of compound **1**, an 18-fold increase in fluorescence intensity was observed. As a bonus, the development of the strong blue-green emission and the efficient fluorescence turn-on may be detected by the naked eye, as can be seen in the inset photograph of Fig. 2a. As shown in the inset pictures of Fig. 2a, a good linearity of the fluorescence intensity as the function of the concentration of Al^{3+} between 0 and 1×10^{-8} M is established, and the detective limit of aluminium determination is calculated at around 1.0×10^{-9} M. These results mean that **1** could be used as a highly sensitive off-on fluorescent chemosensor for Al^{3+} .

The fluorimetric response of **1** to other metal ions was also studied in the same condition. The addition of Zn^{2+} induced a 4-fold emission enhancement which is much smaller than the 15-fold enhancement induced by Al^{3+} . In addition, a 29 nm blue shift of emission wavelength from 505 nm to 476 nm was also observed, making it easy to distinguish from that of Al^{3+} , which is only 7 nm blue shift. However, fluorescence quenching was observed upon the addition of Cu^{2+} . The quenching by Cu^{2+} is most likely due to an energy transfer having occurred from **1** to the open-shell d-orbitals of Cu^{2+} exhibiting a faster and more efficient nonradiative decay of the excited states of **1**. A similar quenching effect by Cu^{2+} was shown to be the result of the complexation of Cu^{2+} to a bisthiazole derivative with phenolic substituents [23]. In contrast, Zn^{2+} and Al^{3+} have closed-shell d-orbitals so the energy transfer processes cannot take place. In addition, coordination of Zn^{2+} and Al^{3+} removes the phenolic proton of **1** and disrupts the ESIPT causing emission with a normal Stokes' shift (Scheme 2) [21].

All of these observations showed that common coexisting metal ions did not interfere with the measurement of Al^{3+} , thus, compound **1** shows high selectivity toward Al^{3+} over other metal ions tested (Fig. 2b). Thus the selectivity shown by **1** toward metal cations is easily selected by an appropriate choice of the output channel, which is the detection of Cu^{2+} via the colour channel (from colourless to yellow) and signalling of Al^{3+} via a remarkable enhancement of the emission intensity.

To explore the binding mechanism, the Job's plot of the UV-Vis titrations of Cu^{2+} and the fluorescence titrations of Al^{3+} were revealed in Fig. S5. A maximum absorption was observed when the molar fraction

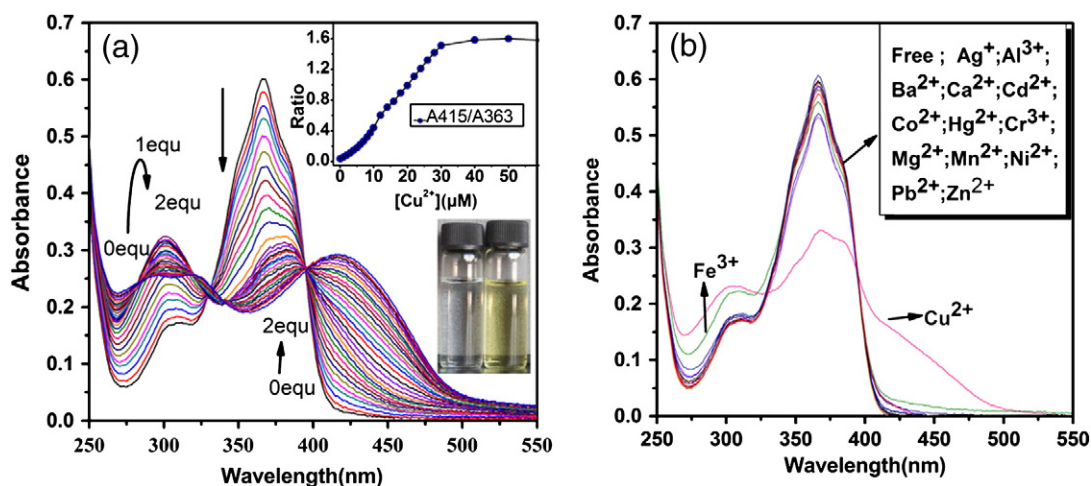


Fig. 1. (a) Absorbance spectra of **1** (30 μM) with increasing concentrations of Cu^{2+} in the form of nitrate salt in EtOH/ H_2O (v/v = 30/70). Inset: the ratio of absorbance at 415 nm and 363 nm as a function of Cu^{2+} concentration. Inset photograph: free **1** solution (left) and solution after addition of 1 μM Cu^{2+} (right) under natural light. (b) UV-Vis spectral changes of **1** in EtOH/ H_2O (v/v = 30/70) (30 μM) upon addition of two equiv of different nitrate salts (60 μM).

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