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Sequential colorimetric recognition of Cu^{2+} and CN^- by asymmetric coumarin-conjugated naphthol groups in aqueous solution

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ABSTRACT

A new chemo-sensor (*E*)-4-((2-((2-hydroxynaphthalen-1-yl)methylene)amino)phenyl-amino)-3-nitro-2H-chromen-2-one (**1**) based on the combination of 2-hydroxy-1-naphthaldehyde and precursor 4-((2-aminophenyl)amino)-3-nitro-2H-chromen-2-one was designed and synthesized as a selective colorimetric sensor for Cu^{2+}. **1** exhibited a color change from yellow to orange in the presence of Cu^{2+} in aqueous solution and the resulting **1**-Cu^{2+} complex sensed cyanide through naked eye. Moreover, **1** could be used as a practical, visible colorimetric test strip for Cu^{2+} in aqueous environment. These results demonstrate a new type of the sequential recognition of Cu^{2+} and CN^- by a convenient, easy and colorimetric method.

1. Introduction

The development of selective and sensitive chemosensors for the detection of metal ions and anions has received considerable attention because of their important roles in medicine, living systems and the environment [1–3]. Among the different types of chemosensors, the sensors based on colorimetric determination of anions and cations have many advantages due to the simplicity, low cost, and rapid tracking of analytes [4,5]. Therefore, colorimetric sensors are recently getting popular due to their capability to detect analyte by the naked eye without resorting to any expensive instruments [6].

Copper (II) ion, as the third most abundant transition metal in human bodies, plays vital roles in many fundamental physiological processes in organisms. Copper dependent enzymes act as catalysts to help a number of body functions to provide energy for biochemical reactions, transform melanin for pigmentation of the skin, assist the formation of crosslinks in collagen and elastin, and thereby maintain and repair connective tissues [7,8]. However, unregulated overloading of copper can induce severe neurodegenerative diseases including Alzheimer's, Parkinson's and prion diseases [9–12]. Moreover, copper can also be a significant environmental pollutant because of its widespread use in industry and agriculture [13]. For these reasons, considerable efforts have been devoted to the development of colorimetric or fluorescent Cu^{2+}-selective chemosensors [14–33].

Cyanide is well known as one of the most rapidly acting and fatal poisons, and its toxicity results from its propensity to bind to the iron in cytochrome *c* oxidase, interfering with electron transport and resulting in hypoxia [30,34]. Several researchers reported that cyanide occasionally plays a significant role in many fire related deaths [35]. Cyanide could be absorbed through lungs, gastrointestinal track and skin, leading to vomiting, convulsion, loss of consciousness, and eventual death [36–38]. Nevertheless, cyanide is widely used in many chemical processes, such as electroplating, plastics manufacturing, gold and silver extraction, tanning, and metallurgy [39–41]. Therefore, it is absolutely necessary to develop selective and sensitive methods for CN^- detection.

Coumarin has been frequently used in recent years as the chromophores and fluorophores to prepare sensors for metal cations [42–48]. In addition, a naphthol group is also an excellent chromogenic and fluorogenic dye that is widely utilized as reporters in chemosensors [49–51]. Therefore, we were interested in the combination of coumarin and naphthol groups to develop a novel chemosensor for detecting metal ions.

Herein we report on the synthesis, characterization and sensing properties of a new colorimetric receptor **1**, based on the

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combination of coumarin and naphthol groups. The receptor **1** displayed highly selective and sensitive colorimetric recognition toward Cu^{2+} by color change from yellow to orange, and the in situ formed **1**-Cu^{2+} complex exhibited highly selective recognition to CN^- through color change from orange to yellow in aqueous solution.

2. Results and discussion

2.1. Synthesis

The receptor **1** was synthesized by coupling of 4-((2-aminophenyl)amino)-3-nitro-2H-chromen-2-one and 2-hydroxy-1-naphthaldehyde with a 58% yield in absolute methanol (Scheme 1). The precursor 4-((2-aminophenyl)amino)-3-nitro-2H-chromen-2-one was obtained by substitution reaction of *o*-phenylenediamine and 4-chloro-3-nitrocoumarin in absolute methanol. Receptor **1** and the precursor 4-((2-aminophenyl)amino)-3-nitro-2H-chromen-2-one were characterized by ^1H NMR, ^{13}C NMR, ESI-mass spectrometry and elemental analysis.

2.2. Absorption spectroscopic studies of 1 toward Cu^{2+}

The colorimetric sensing abilities of **1** were primarily investigated in bis-tris buffer (10 mM, pH 7.0) containing 40% acetonitrile upon addition of various metal ions such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} [52]. Upon the addition of 4 equiv of each cation, only Cu^{2+} induced a distinct spectrum change while other metal ions showed either no or slight change in the absorption spectra relative to the free receptor **1** and Fe^{2+} reduced the band at 480 nm to some extent (Fig. 1(a)). Consistently with the changes of UV–vis spectra, the solution color of **1** in the presence of Cu^{2+} ion changed from yellow to orange (Fig. 1(b)), indicating that receptor **1** can serve as a potential candidate of "naked-eye" chemosensor for Cu^{2+} in aqueous solution. The exclusive selectivity of **1** to Cu^{2+} ion might be due to a particularly high thermodynamic affinity for typical *N,O*-chelate ligands and fast metal-to-ligand binding kinetics [53–55].

The binding properties of **1** with Cu^{2+} were further studied by UV–vis titration experiments (Fig. 2). The peak at 480 nm in the UV–vis spectrum decreased gradually upon the addition Cu^{2+}, while new bands developed at 430 nm and 550 nm. Then, the bands reached maxima at 4 equiv of Cu^{2+}. Meanwhile, two clear isosbestic points were observed at 460 nm and 510 nm, indicating that only one product was generated from **1** upon binding to Cu^{2+}. The color change could be explained by ligand-to-metal charge-transfer (LMCT) mechanism. The two bands with molar extinction coefficients in the thousands, 1.1×10^3 M^{-1} cm^{-1} at 430 nm and 2.2×10 M^{-1} cm^{-1} at 550 nm are too large to be Cu-based d–d transitions and thus must be ligand-based transitions [56].

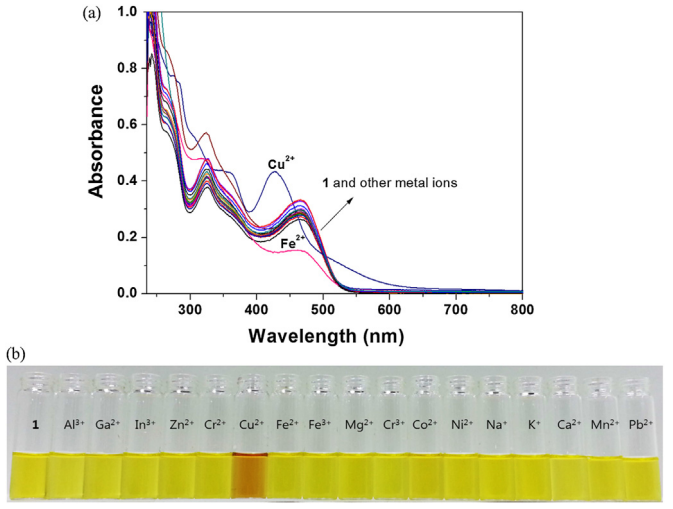


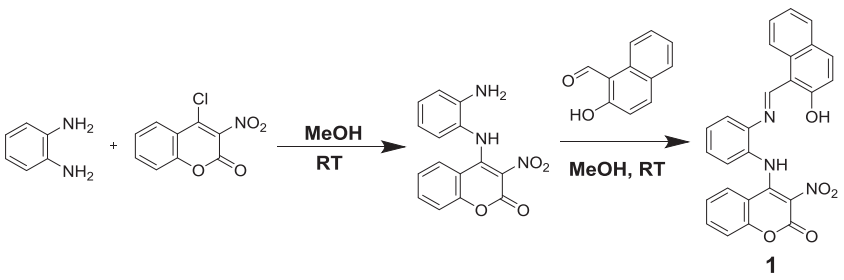
Fig. 1. (a) Absorption changes of receptor **1** (20 μM) upon the addition of various metal ions (4 equiv) in MeCN/bis-tris buffer solution (v/v, 4:6). (b) The color changes of **1** (50 μM) upon addition of various metal ions (4 equiv) in MeCN/bis-tris buffer solution (v/v, 4:6). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The Job plot analysis [57] revealed a 1:1 stoichiometric ratio between the Cu^{2+} ion and **1** (Fig. 3), which was further confirmed by ESI-mass spectrometry analysis. The positive ion mass spectrum indicated the 1:1 binding mode between **1** and Cu^{2+} [*m/z* 567.47; calcd, 567.07] as shown in Fig. 4. Based on the Job plot, and ESI-mass spectrometry analysis, and the similar type of crystal structures reported in the literatures [58], we propose the structure of a 1:1 complex of **1** and Cu^{2+} as shown in Scheme 2.

Based on UV–vis titration, the association constant (K) of **1** with Cu^{2+} ion was calculated by using Benesi–Hildebrand equation [59] (Fig. S1). The K value was found to be 5.0×10^3 M^{-1}, which indicates a weak binding between **1** and Cu^{2+}. The detection limit [60] of receptor **1** as a colorimetric sensor for the analysis of Cu^{2+} ions was found to be 2.95×10^{-5} M (Fig. S2). The WHO has recommended the maximum limit of copper in drinking water to be 2 ppm (31.5 μM) [61]. Therefore, receptor **1** could be used as a good indicator for monitoring Cu^{2+} ion in drinking water.

The preferential selectivity of **1** as a colorimetric sensor for Cu^{2+} was studied in the presence of different cations such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+}. Upon the addition of 4 equiv of each metal ion into the mixed solution of **1** and Cu^{2+}, there was no interference in the detection of Cu^{2+} from all metal ions tested, as indicated in Fig. 5. This result strongly indicates that receptor **1** could be an excellent chemosensor for the biologically important detection of Cu^{2+}.

To examine the reversibility of receptor **1** toward Cu^{2+} in MeCN/bis-tris buffer (v/v, 4:6) solution, ethylenediaminetetraacetic acid (EDTA, 4 equiv) was added to the mixed solution of receptor **1** and



Scheme 1. Synthesis of receptor **1**.