Inorganic Chemistry Communications 74 (2016) 62–65

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Sequential detection of copper(II) and cyanide by a simple colorimetric chemosensor

Ji Hye Kang, Seong Youl Lee, Hye Mi Ahn, Cheal Kim *

Department of Fine Chemistry, Bio IT Materials, Seoul National University of Science and Technology, Seoul 139-743, Republic of Korea
Department of Interdisciplinary Bio IT Materials, Seoul National University of Science and Technology, Seoul 139-743, Republic of Korea

ARTICLE INFO

Article history:
Received 30 September 2016
Received in revised form 21 October 2016
Accepted 29 October 2016
Available online 01 November 2016

Keywords:
Colorimetric chemosensor
Sequential detection
Copper
Cyanide
Theoretical calculations

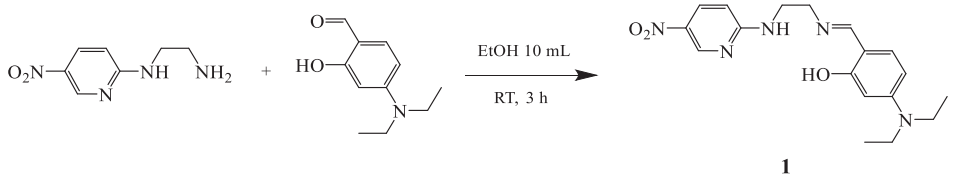
ABSTRACT

A simple colorimetric receptor **1** based on the combination of *N*-(5-nitro-2-pyridyl)-1,2-ethanediamine and 4-(diethylamino)-2-hydroxybenzaldehyde was synthesized for the sequential detection of Cu^{2+} and CN^{-}. The receptor **1** showed a distinct color change toward Cu^{2+} from colorless to yellow. The detection limit of **1** for Cu^{2+} (0.88 μM) was much lower than the World Health Organization guideline (31.5 μM) as the maximum allowable copper concentration in drinking water. In addition, **1**-Cu^{2+} complex could be used to detect cyanide by showing a color change from yellow to colorless, indicating the recovery of **1** from **1**-Cu^{2+}. Furthermore, the sensing mechanism of **1** for Cu^{2+} was supported by theoretical calculations.

Copper ion, as the third most abundant metal ion in human body, plays important roles in variety of fundamental physiological processes [1,2]. As catalyst, copper interacted with enzymes conducts to help a number of body functions such as to transform melanin for pigmentation of the skin and provide energy for biochemical reactions [3]. However, excessive copper accumulation can cause nerve disorder including Alzheimer's, Parkinson's and Wilson's diseases [4–6]. In addition, some copper compounds can cause dermal or eye irritation [7]. Thus, it is absolutely necessary to develop Cu^{2+} sensors with high selectivity and sensitivity. Cyanide is known as one of the most rapidly acting and powerful poisons. The toxicity results from its propensity to bind to the iron in cytochrome *c* oxidase, interfering with electron transport and resulting in hypoxia [8,9]. Nevertheless, cyanide is extensively used in many industrial processes such as synthesis of fibers and polymers, gold mining and electroplating, so cyanide is readily exposed to the environment [10,11]. For these reasons, the recognition and detection of cyanide have also received considerable attention [12].

Herein, we designed and synthesized a novel chemosensor **1** based on the combination of the nitroaniline moiety and diethylaminosalicylaldehyde one, which showed the sequential sensing ability for Cu^{2+} and CN^{-}. Receptor **1** detected Cu^{2+} via obvious color change from colorless to yellow, and in situ formed **1**-Cu^{2+} complex showed a highly selective recognition of CN^{-} through a color change from yellow to colorless in aqueous solution.

Receptor **1** was synthesized by coupling *N*-(5-nitro-2-pyridyl)-1,2-ethanediamine and 4-diethylaminosalicylaldehyde with 44% yield in ethanol (Scheme 1), and analyzed by ^{1}H NMR and ^{13}C NMR, ESI-mass spectrometry, and elemental analysis. To examine the colorimetric sensing ability of **1**, the absorption spectral changes were studied in the presence of 18 different cations such as Na^{+}, K^{+}, Mg^{2+}, Ca^{2+},



1

Scheme 1. Synthetic procedure of **1**.

* Corresponding author.
E-mail address: chealkim@seoultech.ac.kr (C. Kim).

http://dx.doi.org/10.1016/j.inoche.2016.10.039
1387-7003/

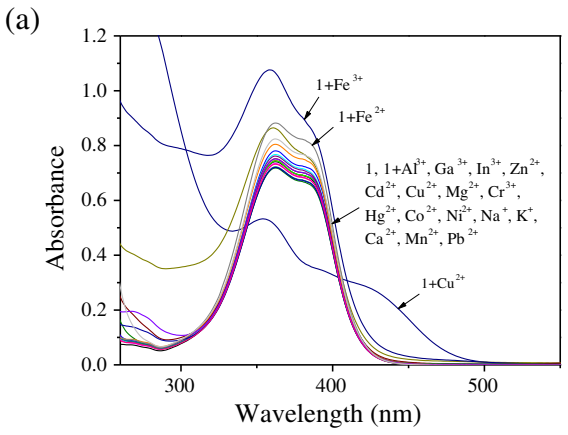


Fig. 1. (a) Absorption spectral changes of 1 (20 μM) in the presence of 24 equiv. of various metal ions in bis-tris buffer/DMF (1/1, v/v, 10 mM bis-tris, pH = 7.0). (b) The color changes of **1** (20 μM) in the presence of 24 equiv. of various metal ions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Al^{3+}, Ga^{3+}, In^{3+} and Pb^{2+} in bis-tris buffer/DMF (1/1, v/v, 10 mM bis-tris, pH = 7.0). As shown in Fig. 1a, **1** showed a particular spectral change to Cu^{2+} in the visible region, while other metal ions caused either little or no spectral changes in absorption peaks. Consistent with the absorption spectral change, the addition of Cu^{2+} to **1** showed promptly a color change from colorless to yellow (Fig. 1b), demonstrating that receptor **1** can serve as a potential candidate of "naked-eye" chemosensor for Cu^{2+} in aqueous solution. The binding property of **1** with Cu^{2+} was studied by UV–vis titration experiments (Fig. 2). The absorption peak at 385 nm decreased gradually upon the addition of Cu^{2+} to a solution of **1**, while a new absorption peak appeared at 436 nm and reached a maxima at 24 equiv. of Cu^{2+}. Meanwhile, an isosbestic point was clearly observed at 401 nm, demonstrating that only one product was formed

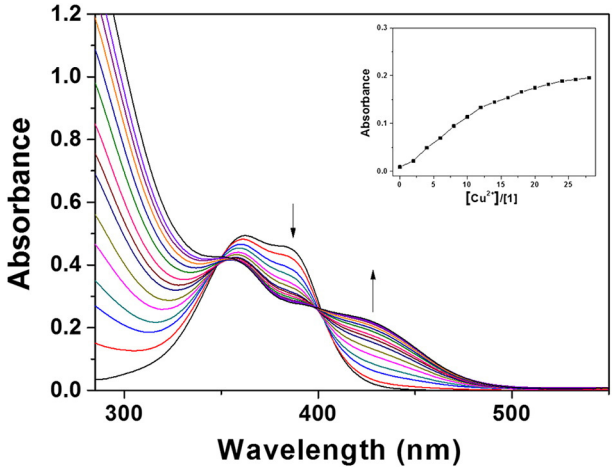


Fig. 2. Absorption spectral changes of 1 (20 μM) after addition of incremental amounts of Cu^{2+} in bis-tris buffer/DMF (1/1, v/v, pH = 7.0) at room temperature. Inset: Absorption at 436 nm versus the number of equiv. of Cu^{2+} added.

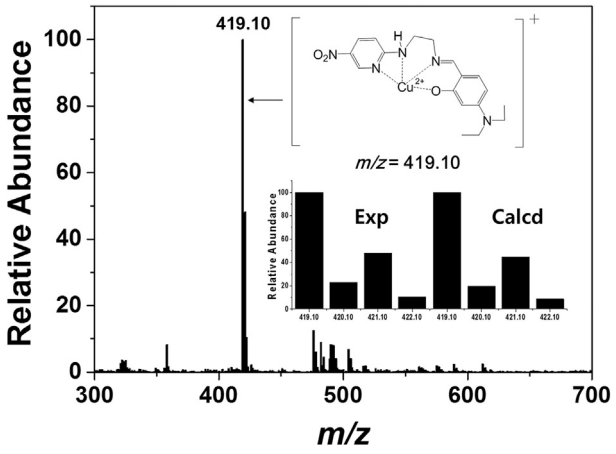


Fig. 3. Positive-ion electrospray ionization mass spectrum of **1** (100 μM) upon addition of Cu^{2+} (24 equiv.).

between the receptor **1** and Cu^{2+}. In addition, **1** showed a fast reaction with copper ion, as shown in Fig. S1.

The 1:1 stoichiometric ratio of the **1**-Cu^{2+} complex was determined by Job plot (Fig. S2) [13]. Moreover, a 1:1 binding mode between **1** and Cu^{2+} was further confirmed by ESI-mass spectrometry analysis (Fig. 3). The positive-ion mass spectrum demonstrated that a peak at m/z = 419.10 was assignable to **1**-H^+ + Cu^{2+} [calcd, 419.10]. Based on UV–vis titration, the binding constant of **1**-Cu^{2+} complex was calculated as $2.4 \times 10^3\ M^{-1}$ by using non-linear fitting analysis (Fig. S3), which indicates a weak binding between **1** and Cu^{2+}. The detection limit of receptor **1** as a colorimetric sensor for the analysis of Cu^{2+} ion was found to be 0.88 μM (Fig. S4) by using 3σ/K [14]. This value was much lower than the World Health Organization (WHO) guideline (31.5 μM) in drinking water [15].

To further examine the practical applicability of **1**, the affinity of **1** toward other coexistent metal ions such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Al^{3+}, Ga^{3+}, In^{3+} and Pb^{2+} was studied. As shown in Fig. S4, there was no interference except Al^{3+}, Ga^{3+}, In^{3+} and Cr^{3+}. Although they showed some interference in UV–vis (Fig. S5a), it was still discernable in the color change (Fig. S5b). This result indicates that **1** could be a good colorimetric sensor for Cu^{2+} over different metal ions in aqueous solution.

To investigate the practical applicability, we studied the pH effect on the absorption response of receptor **1** to Cu^{2+} ions in pH values ranging from 2 to 12 (Fig. S6). **1** showed no color change between pH 2 and 12, while an apparent color change of **1**-Cu^{2+} complex was observed at the pH range of 7–12. These results indicate that Cu^{2+} could be detected by the naked eye or UV–vis absorption measurements using **1** over the various pH range of 7.0–12.0.

In order to check the application validity of the chemosensor **1** to detect Cu^{2+} in real samples, we constructed a calibration curve (Fig. S7), which exhibited a good linear relationship between the absorbance of

Table 1
Determination of Cu^{2+} in water samples.

Sample	Cu(II) added (μmol L^{-1})	Cu(II) found (μmol L^{-1})	Recovery (%)	R.S.D. (n = 3) (%)
Tap water	0.00	0.0		
	6.00[a]	6.35	105	0.58
Drinking water	0.00	0.0		
	6.00[a]	6.07	101	0.45
Pond water[b]	0.00	0.60		
	6.00[a]	6.34	96.1	0.14

Conditions: [**1**] = 20 μmol L^{-1} in 10 mM bis-tris buffer-DMF solution (1:1, v/v, pH 7.0).
[a] 6.00 μmol L^{-1} of Cu^{2+} ions was artificially added.
[b] Pond water samples were collected from a pond in Seoul National University of Science & Technology.