Tetrahedron 70 (2014) 2822–2828

Contents lists available at ScienceDirect

Tetrahedron

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

A colorimetric and fluorescent sensor for sequential detection of copper ion and cyanide

Gyeong Jin Park [a,b], In Hong Hwang [a,b], Eun Joo Song [a,b], Hyun Kim [a,b], Cheal Kim [a,b,*]

[a] Department of Fine Chemistry, Seoul National University of Science and Technology, 172 Kongnung 2-Dong, Nowon Gu, Seoul 139-743, Republic of Korea

[b] Department of Interdisciplinary Bio IT Materials, Seoul National University of Science and Technology, 172 Kongnung 2-Dong, Nowon Gu, Seoul 139-743, Republic of Korea

ARTICLE INFO

Article history:
Received 1 August 2013
Received in revised form 19 February 2014
Accepted 21 February 2014
Available online 28 February 2014

Keywords:
Colorimetric
Fluorescent sensor
Copper
Cyanide
Julolidine
Naphthol

ABSTRACT

A simple cation sensor **1** ((*E*)-9-((2-hydroxynaphthalen-1-ylimino)methyl)-1,2,3,5,6,7-hexahydropyrido[3,2,1-*ij*]quinolin-8-ol) bearing both a julolidine moiety and a naphthol moiety was designed and synthesized as a colorimetric sensor for Cu^{2+}. In methanol solution of **1**, the presence of Cu^{2+} led to a distinct naked-eye color change from yellow to purple. The proposed sensing mechanism might be attributed to the decrease in internal charge transfer band. Moreover, the resulting **1**–Cu^{2+} complex sensed cyanide in a fluorometric way via fluorescent changes. These results demonstrate a novel type of the sequential recognition of Cu^{2+} and CN^- using two different sensing methods, color change, and fluorescence.

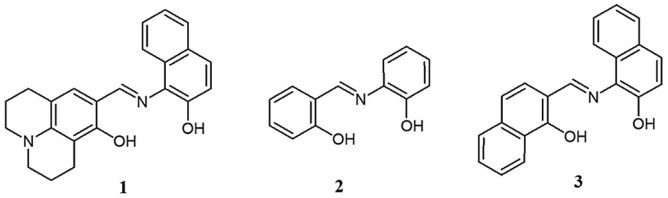
1. Introduction

Until recently, there has been a great emergence of interests in the development of fluorescent or colorimetric probes for various metal cations and anions.[1–7] Among them, transition metal ions have especially received an increasing concern due to their importance in many biological and environmental processes.[8–10] In particular, Cu^{2+} is a pivotal divalent cation, that is, utilized as a catalytic cofactor for various metalloenzymes, including superoxide dismutase, cytochrome *c* oxidase, tyrosinase, and nuclease.[11] However, with excessive loading, copper ion can cause extremely negative health effects such as gastrointestinal disturbance and liver or kidney damage.[12–15] Accordingly, considerable efforts have been devoted to the development of fluorescent or colorimetric Cu^{2+}-selective chemosensors.[16–35]

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.[36] In addition, various industrial processes such as gold mining, electroplating, and metallurgy require the presence of cyanide, and thus, serious problems are often caused because of accidental release of cyanide into the environment.[37] Therefore, the recognition and detection of cyanide have also received considerable attention.[36,38–50]

During recent years, a number of researches on the sequential recognition of Cu^{2+} ion and CN^- ion have been documented.[37,51,52] The observed optical signals for the sequential Cu^{2+} and CN^- recognition were either "fluorescent on–off–on" or "off–on–off" types. To the best of our knowledge, the sequential recognition of Cu^{2+} and CN^- using two different sensing methods, color change, and fluorescence has not been reported.

On the other hand, we have recently reported two new receptors **2** and **3** (Scheme 1). Receptor **2** exhibited fluorescence enhancement upon binding only to Al^{3+} ion[7] and **3** served as a colorimetric and fluorescent sensor for the detection of Al^{3+} and



Scheme 1. Structures of receptors **1**, **2**, and **3**.

* Corresponding author. Tel.: +82 2 970 6693; fax: +82 2 973 9149; e-mail addresses: chealkim20@daum.net, chealkim@seoultech.ac.kr (C. Kim).

0040-4020/$ – see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2014.02.055

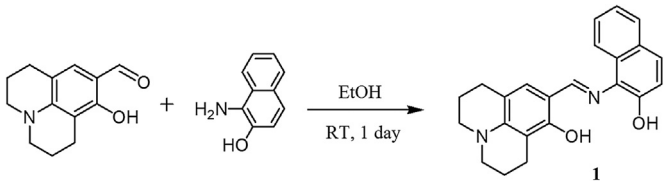
Cu^{2+} ions.[53] These results led us to conclude that the small change of the substituents on a receptor may result in a significant change of the sensing properties of the receptor. In this work, therefore, we planned to displace the naphthol group of **3** with a julolidine moiety in order to examine the change of the sensing properties of the new receptor **1**. Much to our surprise, the receptor **1** showed a very different sensing property, the sequential recognition of Cu^{2+} by the naked eye, and CN^- by emission spectra, from that of the receptor **3**.

We report on the new julolidine-containing naphthol-based probe **1** as a selective colorimetric receptor of Cu^{2+} using the decrease in the internal charge transfer (ICT) band. Subsequently, chemosensing ensemble **1**–Cu^{2+} exhibited highly selective detection to CN^- via fluorescence enhancement by utilizing the copper–cyanide affinity.

2. Results and discussion

2.1. Synthesis

The receptor **1** was obtained by the condensation reaction of 8-hydroxyjulolidine-9-carboxaldehyde and 1-aminonaphthalen-2-ol with an 80.6% yield in absolute ethanol (Scheme 2). Receptor **1** was characterized by ^1H NMR, ESI-mass spectrometry, and elemental analysis. The photophysical properties of **1** with several metal ions using their nitrate salts and of **1**–Cu^{2+} complex with nine anions in methanol were investigated by UV–vis, fluorescence measurements, and titration studies.



Scheme 2. Synthesis of receptor **1**.

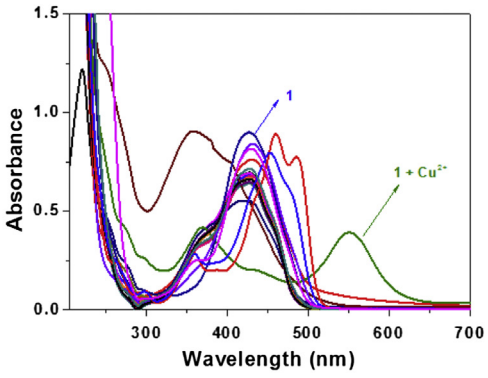
2.2. Absorption spectroscopic studies of 1 toward Cu^{2+} ion

The chromogenic sensing ability of **1** was studied in the presence of 18 different cations such as Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Na^+, K^+, Mg^{2+}, Ca^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Ag^+, Pb^{2+}, and Cr^{3+}. Upon the addition of 10 equiv of each metal ion, only Cu^{2+} induced a distinct spectra change while other metal ions showed either no or slight change in the absorption spectra relative to the free receptor **1** (Fig. 1a). In consistency with the absorption spectra, the solution color of **1** changed from yellow to purple with copper ion (Fig. 1b), indicating that the receptor **1** could serve as a potential candidate of colorimetric chemosensor for Cu^{2+}. In addition, these results demonstrated our expectation that the small change of the substituents on a receptor may result in a significant change of the sensing properties of the receptor (e.g., colorimetric and fluorescent detections of Al^{3+} and Cu^{2+} ions by **3** and a colorimetric detection of Cu^{2+} by **1**).

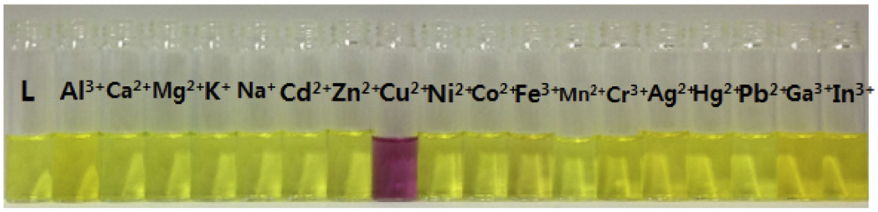
The binding properties of **1** with Cu^{2+} were further studied by UV–vis titration experiments. On the treatment with Cu^{2+} ion to the solution of **1**, the absorption band at 425 nm significantly decreased, and a new band at 550 nm gradually reached a maximum at 10 equiv of Cu^{2+} (Fig. 2).

The Job plot revealed a 1:1 stoichiometric ratio between the Cu^{2+} ion and **1** (Fig. 3). In addition, the 1:1 stoichiometry of the **1**–Cu^{2+} complex was confirmed by ESI-mass spectrometry analysis. The positive ion mass spectrum indicated the 1:1 binding model between **1** and Cu^{2+} [*m*/*z* 420.1; calcd, 420.1] as shown in Fig. 4.

Based on Job plot and ESI-mass data analysis, we propose that the two oxygen atoms and the imine nitrogen of **1** might bind to Cu^{2+} and the remaining site of the **1**–Cu^{2+} complex may be occupied by a nitrate anion (Scheme 3). The coordination of nitrate ions was previously proposed when chemosensors were bound to Cu^{2+} with a 1:1 stoichiometry in organic solvents.[51,54–58]



(a)



(b)

Fig. 1. (a) Absorption changes of receptor **1** (3.0×10^{-5} M) upon addition of 10 equiv of different metal nitrate salts in MeOH. (b) Color changes observed for **1** (3.0×10^{-5} M) upon the addition of Al^{3+}, Ca^{2+}, Mg^{2+}, K^+, Na^+, Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Mn^{2+}, Cr^{3+}, Ag^{2+}, Hg^{2+}, Pb^{2+}, Ga^{3+}, and In^{3+} (10 equiv).