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Tetrahedron Letters 48 (2007) 5525–5529

Tetrahedron Letters

A novel colorimetric and fluorescent chemosensor: synthesis and selective detection for Cu^{2+} and Hg^{2+}

Honglei Mu, Rui Gong, Qiao Ma, Yimin Sun and Enqin Fu*

Hubei Key Laboratory on Organic and Polymeric Optoelectronic Materials, Department of Chemistry,
Wuhan University, Wuhan 430072, PR China

Received 4 April 2007; revised 23 May 2007; accepted 29 May 2007
Available online 2 June 2007

Abstract—A novel two-channel metal ion sensor has been synthesized from macrocyclic dioxotetraamine and 1,8-naphthalimide derivative. The metal ion-selective signaling behaviors of the sensor were investigated. The sensor presented the selective coloration for Cu^{2+} and Hg^{2+} that can be detected by the naked-eye, respectively. Besides, the addition of Cu^{2+} and Hg^{2+} quenched the fluorescence of **1** obviously and the detection limit was found to be 3×10^{-7} M for Cu^{2+} and 7×10^{-7} M for Hg^{2+}. This sensor can be utilized for the visual and spectroscopic detection of Cu^{2+} or Hg^{2+} in the presence of the other competing metal ions.

The recognition of ions and molecules is an essential part of supramolecular chemistry. The design and synthesis of chemosensors for heavy and transition metal ions (HTM) are currently a task of prime importance for medical, environmental, and biological applications.[1] Presently, one of the most attractive approaches focuses on the research of novel colorimetric and fluorescent metal ion sensors, which allow naked eyes a real time and space detection of the change of color and fluorescent emission upon metal ion binding without any use of a spectroscopic instrument.[2] It is still a challenge to design a chemosensor, which can be used for detecting different metal ions by both the selective coloration and the change in the fluorescence spectra.

Macrocyclic dioxotetraamines have attracted increasing attention because of some interesting coordination behaviors[3] and they are well known for their ability to complex with some metal ions, such as Cu^{2+}, Co^{2+}, and Ni^{2+}.[4] On the other hand, the 4-amino-1,8-naphthalimide group is a well-known chromophore and fluorophore.[5] It contains an electron-donating group and an electron-withdrawing group conjugated to the π-system. When its electron donating or withdrawing character is affected, some optical changes will be expected. Keeping this in mind, we have designed a chemosensor **1**, which links 4-amino-1,8-naphthalimide as an appended group to the macrocyclic dioxotetraamine, and expected that the 4-amino-1,8-naphthalimide could chelate to different metal ions together with the macrocyclic dioxotetraamine in different coordinating modes and transmit the signal of recognition.

This Letter reports the synthesis of the novel chemosensor **1** and its optical properties for the selective detection of Cu^{2+} and Hg^{2+}. Chemosensor **1** was synthesized as shown in Scheme 1. First, 4-bromo-*N*-butyl-1,8-naphthalimide was prepared as described in the procedure.[6] Second it reacted with ethanolamine catalyzed by copper sulfate (0.1 equiv) to yield compound **3**. Then phosphorus tribromide was added dropwise to **3** in dry chloroform at 0–5 °C and the mixture was allowed to reflux for 3 h to afford **2**. Finally, compound **1** was obtained by the reaction of **2** with **L**, which was prepared according to the literature.[7] The structures of the product were identified by using ^{1}H NMR, ^{13}C NMR, and MS.[8]

The absorption spectrum of **1** showed a typical naphthalimide absorption band at 440 nm in the methanol solution, which was responsible for its yellow-green color.[9] In the presence of Cu^{2+} or Hg^{2+}, the color of the solution changed from yellow green to almost colorless or orange, respectively. When the other control metal ions (Fe^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Mg^{2+}, Mn^{2+}, Cd^{2+}, and Ag^{+}) were added into the solution of **1**, no

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Keywords: Macrocyclic dioxotetraamine; 1,8-Naphthalimide; Selective coloration; Recognition; Cu^{2+}; Hg^{2+}.

* Corresponding author. Tel.: +86 27 87219044; fax: +86 27 68756757; e-mail: fueq@whu.edu.cn

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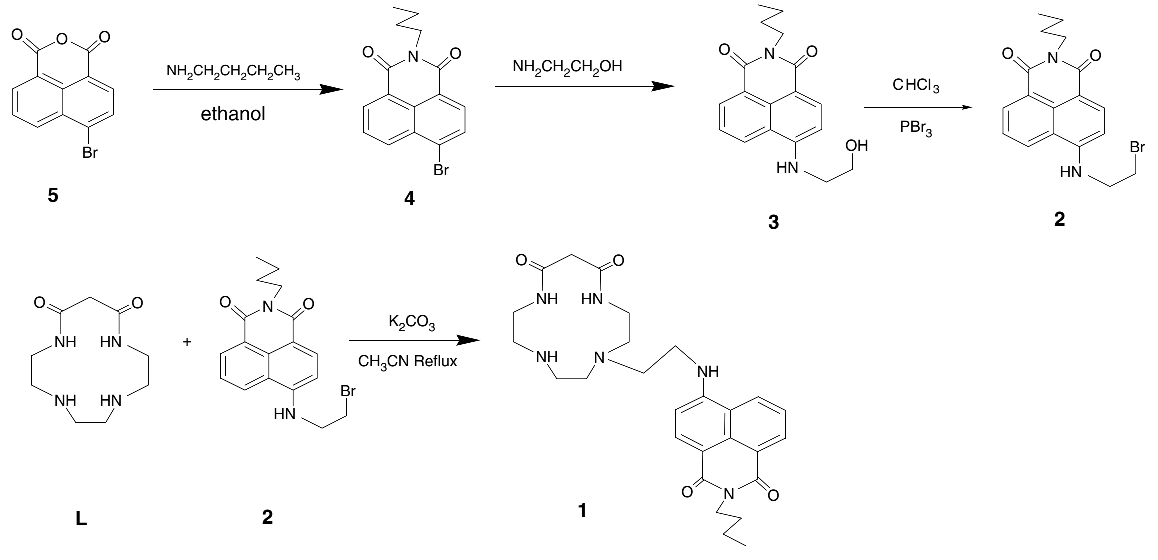
doi:10.1016/j.tetlet.2007.05.155



Scheme 1. The synthetic route of **1**.

observable color changes of the solution (Fig. 1) could be detected. These results indicated that **1** could be used as a potential candidate of colorimetric chemosensor for Cu^{2+} and Hg^{2+} with very high selectivity.

Then, the influence of water on the absorption of **1** in the presence of Cu^{2+} or Hg^{2+} was investigated. With the addition of water, the absorption at 483 nm of **1**–Hg^{2+} system disappeared gradually and transformed into the original absorption at 438 nm of free **1** (Fig. S1, Supplementary data). This is probably due to the small stability constant of **1**–Hg^{2+}. In the presence of water, the Hg^{2+} ion tended to form the hydrate ion instead of forming a complex with compound **1**. As for the absorption of **1**–Cu^{2+} system, it had little change with the increasing water content. This means that the chemosensor can be used for the detection of the Cu^{2+} in aqueous solution, which is very important for the application of **1** in biological systems.

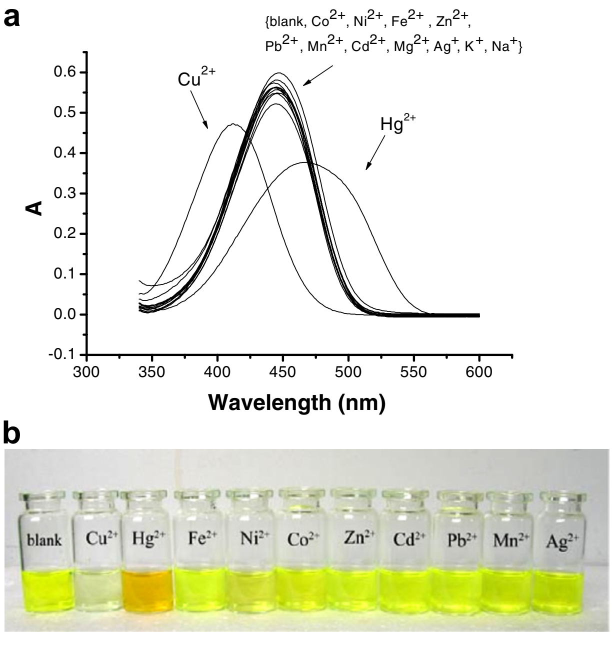


Figure 1. (a) UV–vis spectra of **1** in methanol solution in the presence of different metal ions (1 equiv of Cu^{2+}, 1 equiv of Hg^{2+}, 5 equiv of other metal ions). (b) The color response of **1** to different transition metal ions.

In order to have the optimum condition for the realization of peak selectivity and practicability for the target metal ions, the further UV–vis titration of **1** with Cu^{2+} was carried out in aqueous methanol solution and UV–vis titration of **1** with Hg^{2+} was carried out in methanol solution. The changes in the absorption spectra of **1** upon the addition of Cu^{2+} are shown in Figure 2a. The absorption at 437 nm ($\varepsilon = 16{,}000\ M^{-1}\ cm^{-1}$) decreased sharply with the gradual addition of Cu^{2+} to the solution of **1**. At the same time the high-energy bond at 403 nm increased prominently ($\varepsilon = 12{,}500\ M^{-1}\ cm^{-1}$) with two isosbestic points at 417 nm and 305 nm. This was attributed to the formation of a **1**–Cu^{2+} complex.[10] The presence of Cu^{2+} induced a color change from yellow green to almost colorless. From the absorption spectra of **1**–Cu^{2+}, we can see that not only was the absorption band at 438 nm blue shifted but also the developed new band at 403 nm had a smaller molar absorption coefficient than the original one. The possible reason is that the lone pair electron of the 4-amino group in the chromophore may perpendicularly coordinate to the Cu^{2+}, which was located in the cavity of macrocyclic dioxotetraamine. The coordination has raised the energy of the charge transfer from the amino group to the carbonyl fragment in the 1,8-naphthalimide group. This five-coordinated complex had been confirmed in some similar macrocyclic derivatives.[11]

However, with the gradual addition of Hg^{2+} to the methanol solution of **1**, the absorption at 438 nm ($\varepsilon = 12{,}600\ M^{-1}\ cm^{-1}$) was reduced in intensity and a new absorption band at ca. 483 nm ($\varepsilon = 13{,}400\ M^{-1}\ cm^{-1}$) was developed (Fig. 2b). The color of solution changed from yellow green to orange. The appear-