Journal of Luminescence 194 (2018) 279–283

Contents lists available at ScienceDirect

Journal of Luminescence

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

A selective colorimetric fluorescent chemosensor for Hg^{2+} in aqueous medium and in the solid state

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ARTICLE INFO

Keywords:
Colorimetric
Fluorescence
Turn-on
Rhodamine

ABSTRACT

A simple colorimetric and turn-on fluorescence receptor **RN** (Rhodamine-based derivative) was prepared and its cation-sensing properties were investigated. Receptor **RN** displayed a selective sensing of Hg^{2+} and showed an obvious colorimetric changing in aqueous solution (from colorless to pink color) and in the solid state (from red to pink color), respectively. The association constant of **RN**-Hg^{2+} complex was calculated to be 8.25×10^{9} M^{-2}, and the detection limit for Hg^{2+} was found to be 27 ppb.

1. Introduction

The design and synthesis of new chemosensors for the efficient detection of trace metal ions are among the most important research topics in environmental chemistry and biology [1–32]. In particular, mercury is recognized as a significant environmental pollutant having ability to accumulate in plants, soil, and water. Ionic mercury is converted to a highly potent neurotoxin methyl mercury by certain bacteria in the marine environment. Methyl mercury toxins are further passed on to the food chain and bioaccumulate in human [33–35]. Accordingly, it is imperative to develop analytical methods for sensitive and selective detection of trace amounts of mercury ion [36,37]. Although a number of chemosensors specific for Hg^{2+} ion have been developed [38–44]; however, most of them required complicated synthesis, slow response, fluorescence quenching upon Hg^{2+} coordination and are aqueous unsolvable. In addition, only few fluorescent sensors could serve as 'naked-eye' indicators and were capable of detecting Hg^{2+} in aqueous solution. Therefore, for practical applications it is a great challenge to design aqueous soluble fluorescent sensors that provide a naked-eye detection and turn-on response of Hg^{2+}. These properties are great advantages for the applications in the analysis of environmental sources and biological systems.

The rhodamine family have emerged as the most effective functional groups for fluorescence signaling due to their excellent spectroscopic properties, high fluorescence quantum yield, large extinction coefficient and high stability to light [45–49]. Therefore, several rhodamine-based sensor for metal ions, such as Cu^{2+} [50–54], Hg^{2+} [55–61] have been studied. Generally, most of the sensors are suitable for detecting metal ions in solution samples but are rarely applicable to solid samples. Herein, we synthesized a rhodamine-hydrazone derivative (receptor **RN**), receptor **RN** demonstrates highly selective colorimetric and fluorescent recognition toward Hg^{2+}. Specially, it shows obvious color change in the presence of Hg^{2+} both in the solution and solid state.

2. Experimental

2.1. Apparatus and reagents

All reagents were obtained from commercial suppliers and were used without further purification. Analytical thin-layer chromatography was performed using silica gel 60 F254 plates (Merck). The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AM 300 spectrometer. Chemical shifts were given in ppm with residual THF as reference. Mass spectra were recorded under electron impact (EI) or electron spray interface (ESI) conditions. UV–Vis spectra were recorded by using Jasco V630 spectrophotometer with a diode array detector, and the resolution was set at 1 nm. Fluorescence spectra were recorded on a Jasco FP-8300 Fluorescene spectrophotometer.

3. Results and discussion

3.1. Synthesis and characterization

Receptor **RN** was synthesized as shown in Scheme 1. The structure of receptor **RN** was confirmed by NMR spectra, Mass data (Figs. S1–S3).

Rhodamine-hydrazone acetaldehyde (0.5 g, 1.0 mol) was dissolved in dry ethanol (30 mL). 4-Nitrobenzoic hydrazide (0.217 g, 0.0012 mol)

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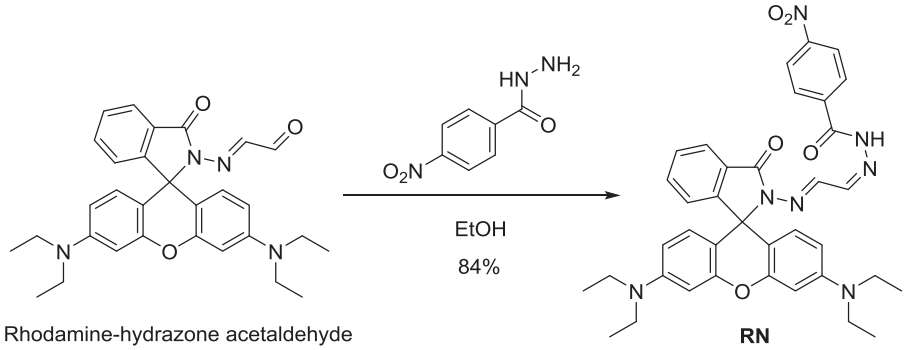
http://dx.doi.org/10.1016/j.jlumin.2017.10.023
Received 16 August 2017; Received in revised form 5 October 2017; Accepted 10 October 2017
Available online 11 October 2017



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

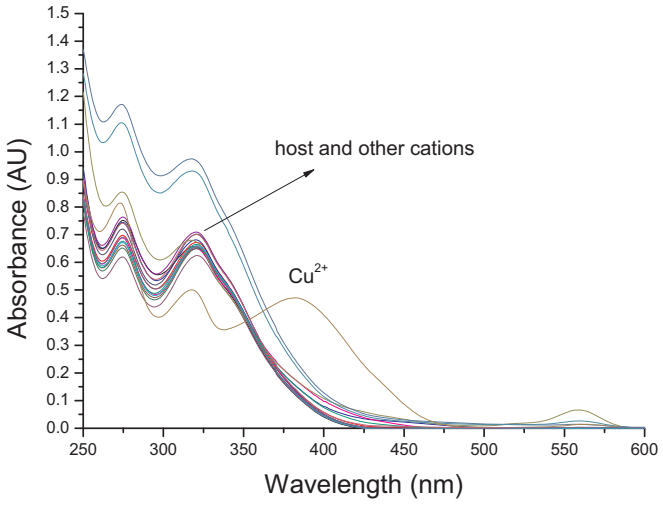


Fig. 1. UV/vis spectra of receptor **RN** (20 μM) recorded in 90% THF/H_2O after addition of 5.0 equiv. of various metal ion.

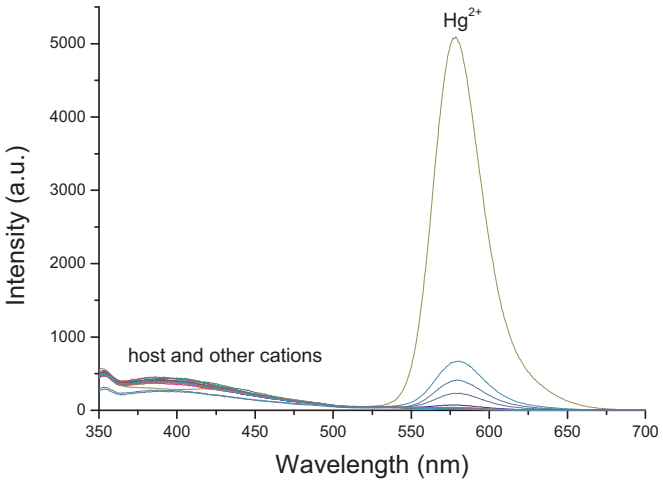


Fig. 3. Fluorescence emission spectra ($\lambda_{ex.}$ = 319 nm) of receptor **RN** (20 μM) in the presence of 5.0 equiv. of various Metal ion in 90% THF/H_2O.

was added, and the mixture was stirred for 5 h at 80 °C. Ethanol was evaporated completely under reduced pressure, the crude product was column chromatographed on silica-gel (elution with hexanes/EtOAc = 2:1, v/v) to give **RN** as light yellow solid (0.6 g, 84%). M.p.: 206 °C; ^{1}H NMR (*d*-THF, 300 MHz) *δ*:8.28-8.24 (m, 3 H), 8.02-7.99 (m, 3 H), 7.88 (d, *J* = 6.6 Hz, 1 H), 7.51-7.46 (m, 2 H), 7.08-7.05 (m, 1 H), 6.46-6.42 (m, 4 H), 6.31-6.27 (m, 2 H), 3.37 (d, *J* = 7.2 Hz, 8 H), 1.16 (t, *J* = 6.6 Hz, 12 H); ^{13}C NMR (*d*-DMSO, 75 MHz) *δ*:164.3, 158.4, 152.1, 148.7, 147.0, 143.1, 134.6, 133.8, 128.9, 127.3, 126.9, 123.7, 123.3, 119.0, 117.1, 116.6, 108.2, 104.2, 97.5, 65.0, 43.7, 12.4; HRMS (EI): *m/z* cald for $C_{37}H_{37}N_7O_5$ [M+], 659.2856, found: 659.2851.

3.2. Absorption studies of receptor *RN* toward various metal ions

The UV–vis spectra of receptor **RN** were studied in the presence of various metal ions (as perchlorate salts): Li^+, Na^+, K^+, Ca^{2+}, Mn^{2+}, Hg^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+} and Al^{3+}. As shown in Fig. 1, receptor **RN** showed two major absorption bands at 275 and 325 nm, respectively. In the presence of Cu^{2+}, the absorption spectra of receptor **RN** in THF/H_2O (9:1, v/v) solution showed a red shift. However, in the presence of Hg^{2+}, the solution of receptor **RN** changed from colorless to pink which could easily be detected with naked eye (Fig. 2).

3.3. Fluorescence studies of receptor *RN* toward various metal ions

The effect of Hg^{2+} on the fluorescence properties of receptor **RN** was also investigated in THF/H_2O (9:1, v/v) solution. As shown in Fig. 3, the free receptor **RN** displayed very weak single fluorescence emission band at 400 nm. Upon addition of Hg^{2+}, receptor **RN** exhibited a prominent fluorescence enhancement with a red shift relative to the band of 400 nm (Fig. 4). The fluorescent enhancement efficiency observed at 570 nm was 16 fold greater than that of the control in the absence of Hg^{2+} (Fig. 5). In the absence of Hg^{2+}, receptor **RN** exists in the spirocyclic form which is colorless and non-fluorescent. Addition of Hg^{2+} leads the spirocycle unit open via coordination, resulting in color change and generation of strong fluorescence. The result showed that

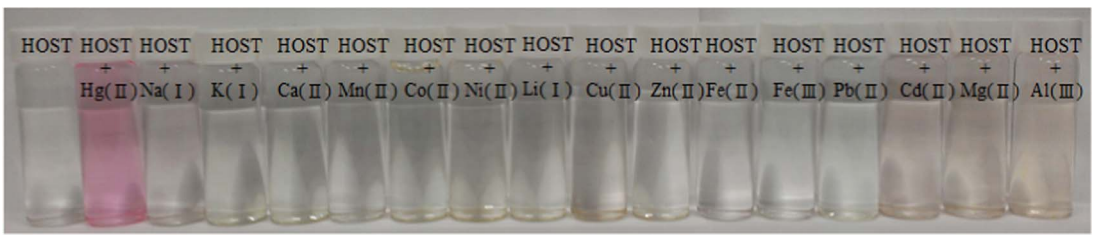


Fig. 2. The color changes observed by naked eye of receptor **RN** (20 μM) upon addition of 5.0 equiv. of various Metal ion in 90% THF/H_2O. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)