

A Selective Fluorescent Sensor for Hg²⁺

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Received: 25 August 2013 / Accepted: 7 November 2013 / Published online: 19 November 2013
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Abstract A novel rhodamine based fluorescent chemosensor RQP was prepared and characterized by ¹HNMR, ¹³CNMR and HR-MS. The properties of RQP were studied through UV–Vis spectroscopy and fluorescence spectroscopy. RQP showed highly selectivity toward Hg²⁺ over other metal ions, including Ag⁺, Cd²⁺, Cu²⁺, Na⁺, Mg²⁺, Ni²⁺, Pb²⁺, Fe³⁺, and Zn²⁺ in aqueous solutions. The recognition process is reversible and confirmed by EDTA experiment.

Keywords Fluorescence · Chemosensor · Hg²⁺

Introduction

The environmental contaminants, especially transitional heavy metal ions, pose serious problems for human health and the environment in the past decades. Mercury, it is very dangerous to our health and environment. Inorganic mercury or methylmercury, once absorbed by human through food chain, it can accumulate in the human body, resulted in various cognitive and motor disorders, and Minamata disease [1, 2].

Due to fluorescent sensors have advantages such as high selectivity, good sensitivity, quick response and local observation [3, 4], considerable efforts have been made to develop fluorescent sensors for the detection of mercury and mercuric salts with sensitivity and selectivity [5–13]. As a work to search high selective and sensitive fluorescent sensor for monitor Hg²⁺ in aqueous environment, rhodamine derivative, RQP, was synthesized and characterized in this paper.

Experimental Part

All reagents were used as purchased without any purification. NMR experiments were performed with a JEOL AL-300 spectrometer and the chemical shifts were recorded with respect to TMS as an internal reference. HR-MS was recorded on JMS-700 apparatus. UV–Vis and fluorescence experiments were carried out by Shimadzu UV-3100 and Hitachi FL-4500, respectively. The perchlorate salts of Ag⁺, Cd²⁺, Cu²⁺, Hg²⁺, Na⁺, Mg²⁺, Ni²⁺, Pb²⁺, Fe³⁺, and Zn²⁺ ions were used and stock solutions of RQP was prepared in DMSO.

8-Pyridylmethoxy-quinoline-2-carbaldehyde [14] and Rhodamine hydrazide [15] were synthesized by reported methods. RQP was synthesized in one step as shown in Scheme 1. 8-Pyridylmethoxy-quinoline-2-carbaldehyde (0.264 g, 1 mmol) and Rhodamine hydrazide (0.456 g, 1 mmol) was dissolved in 20 ml ethanol solution and the mixture was heated under reflux temperature for 10 h. After completion of the reaction, monitored by TLC, the reaction mixture was cooled and the solvent was removed under reduced pressure, the residue was further purified by chromatography on silica gel (CHCl₃/MeOH=20:1) to give RQP as yellow powder (80 %).

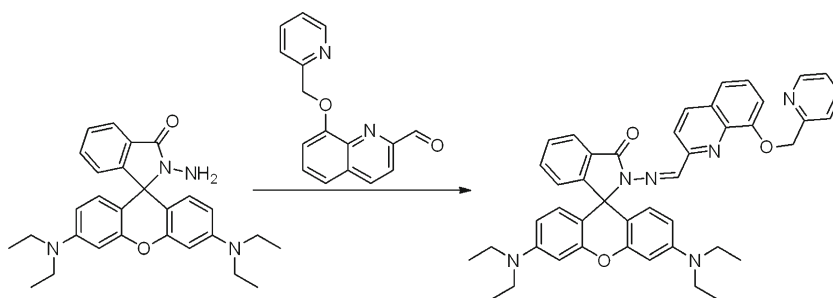
¹HNMR(300 MHz, CDCl₃): δ 9.02 (s, 1H), 8.60 (d, *J*=4.7 Hz, 1H), 8.13 (d, *J*=8.79Hz, 1H), 8.03–8.01(m, 2H), 7.80 (d, *J*=3.48Hz, 2H), 7.49(m, 2H), 7.34–7.32(m, 2H), 7.16(d, *J*=6.42Hz, 2H), 7.03–7.01(m, 1H), 6.58 (d, *J*=8.79Hz, 2H), 6.47(s, 2H), 6.26–6.23(m, 2H), 5.46(s, 2H), 3.31(q, *J*=6.75Hz, 8H), 1.13(t, *J*=7.0Hz, 12H).

¹³CNMR (75 MHz, CDCl₃):165.16, 157.45, 154.26, 154.04, 153.26, 153.22, 152.00, 148.95, 148.27, 139.95, 136.93, 135.70, 133.62, 129.48 128.77, 128.30, 127.81, 126.95, 123.88, 123.60, 122.47, 121.47, 120.20, 118.86, 110.46, 107.94, 106.04, 98.11, 71.48, 66.29, 44.30, 12.06.

HR-MS: C₄₄H₄₂N₆O₃, Calcd.702.3318, Found: 702.3318

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Scheme 1 Synthesis route for RQP



Result and Discussion

Like other rhodamine derivatives, free RQP was colorless and has weak absorption in aqueous solution. Upon addition of Hg²⁺ (10equiv) to the solution of RQP (10 μM), as shown in Fig. 1, a new strong absorption band centered at 559 nm appeared and the color change from colorless to pink was observed. This indicated that the opened-ring form of RQP became the main species in the examined solution. The insert figure showed the time dependent curves after addition of 1 equiv. of Hg²⁺, it is very clearly to figure out the reaction was completed in 400 s.

To get into the further insight of the binding properties of RQP, the fluorescence responses of RQP towards Hg²⁺ and other metal ions were investigated. As shown in Fig. 2, without metal ions, RQP displayed a band centered at 600 nm in the emission spectra, however, when 10 equiv. of Hg²⁺ ion was added to the aqueous solutions of RQP, a significant enhancement of fluorescence at 580 nm was observed, which meaning Hg²⁺ ion induced the formation of open-cycle with strong fluorescence. From the fluorescent spectra of RQP, as

depicted in Fig. 2, Hg²⁺ resulted in an obviously enhanced fluorescence at 580 nm, while Cd²⁺ induced a relative higher fluorescence increase. Other metal ions, such as Ag⁺, Cu²⁺, Na⁺, Mg²⁺, Ni²⁺, Pb²⁺, Fe³⁺ and Zn²⁺, has a little fluorescence intensity change. The fluorescence response of RQP (5 μM) toward Hg²⁺ was explored by performing titration experiments at various concentrations of Hg²⁺ (0, 1, 2.5, 5, 15, 30, 50, 75, 100 and 150 μM), as shown in Fig. 3, upon addition of Hg²⁺, the fluorescence signal at 580 nm significantly enhanced and after addition of about 20 equiv. of Hg²⁺, the fluorescent intensity gets saturated as observed in the insert figure.

Furthermore, to validate the high selectivity of RQP for Hg²⁺, the competitive experiments of Hg²⁺ with other metal ions were also studied. Ni²⁺ and Zn²⁺ showed a relative fluorescence quenching properties as shown in Fig. 4, other metal ions almost no interference to Hg²⁺, these results indicated that RQP is a Hg²⁺ selective fluorescent sensor. In addition, the EDTA experiments were conducted to examine the reversibility of this reaction as shown in Fig. 5, the solution changed from pink to colorless when EDTA was added to the solution of equimolar RQP/Hg²⁺, the fluorescence was

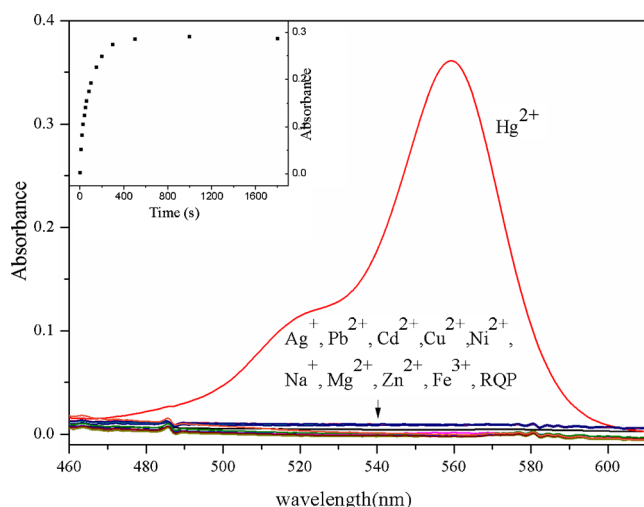


Fig. 1 Absorption spectra of RQP (5 μM) upon addition of various metal ions (10equiv) in aqueous solution. Insert: Time-dependent of absorbance change upon addition of Hg²⁺

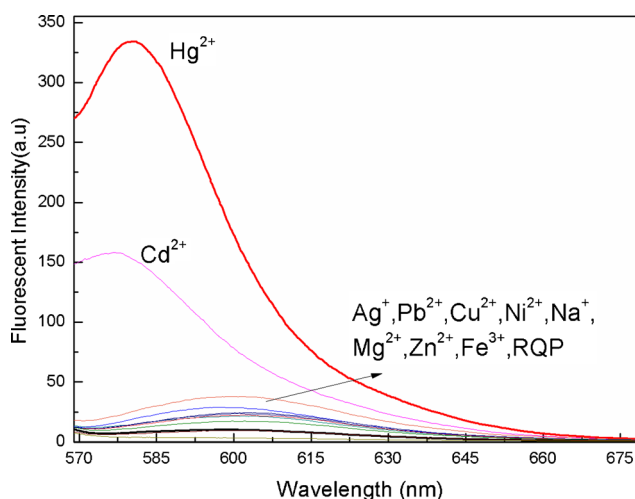


Fig. 2 Fluorescence intensity change of RQP (5 μM) upon addition of various metal ions (10equiv) in aqueous solution. Ex=559 nm

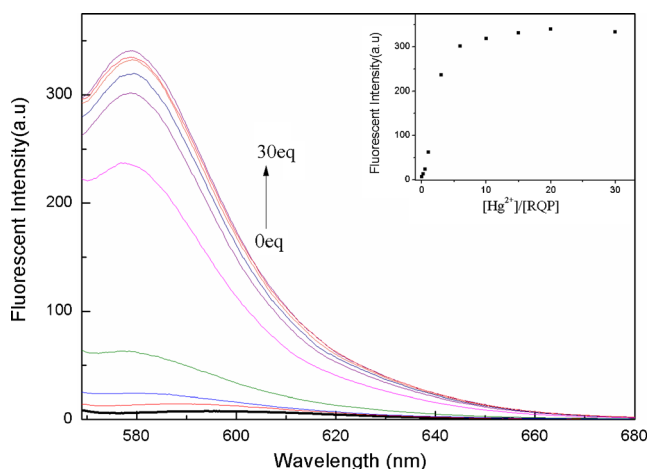


Fig. 3 The emission spectra of RQD (5 μM) upon addition of various of Hg^{2+} (0, 1, 2.5, 5, 15, 30, 50, 75, 100 and 150 μM). $\text{Ex}=559\text{ nm}$. Insert: Fluorescence intensity change via $[\text{Hg}^{2+}]/[\text{RQP}]$

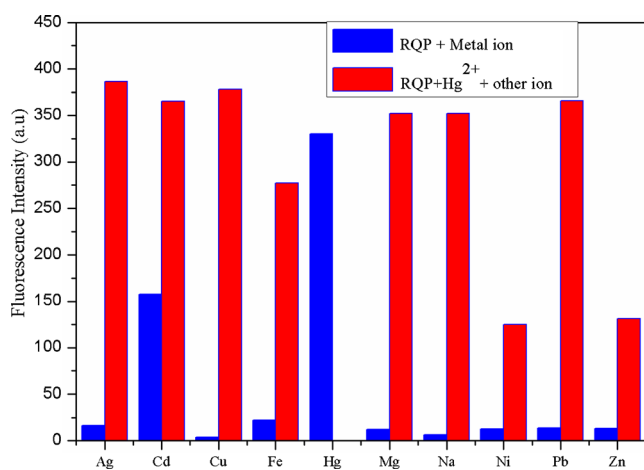


Fig. 4 Fluorescence intensity responses of RQD (5 μM) to various metal ions in aqueous solution

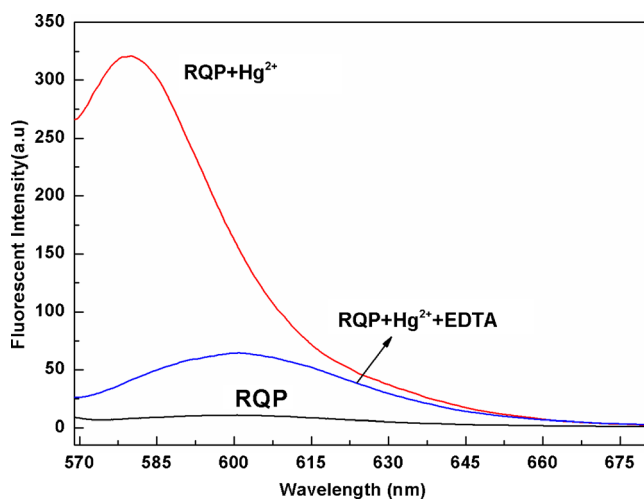


Fig. 5 Reversibility of RQD- Hg^{2+} upon addition of EDTA

turned off in several seconds. These results indicated that RQP was a reversible chemosensor for Hg^{2+} .

In conclusion, a novel rhodamine derivative RQP was synthesized and characterized. RQP showed a good selectivity toward Hg^{2+} ion in aqueous solution over other metal ions and RQP can be used as a selective chemosensor for Hg^{2+} .

Acknowledgment This work was supported by Shaanxi Normal University Science Foundation (2013KJ011).

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