



A highly selective chemiluminescent probe for the detection of chromium(VI)



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ABSTRACT

In present work, rhodamine B hydrazide and rhodamine 6G hydrazide were synthesized and the chemiluminescence performance has been investigated. Based on the chemiluminescence of rhodamine 6G hydrazide chromium(VI), a selective and sensitive method for the direct detection of chromium(VI) was developed. The chemiluminescence intensity was linearly related to the concentration of chromium(VI) in the range of 2.60×10^{-8} – 8.00×10^{-6} mol/L with a correlation coefficient of $r = 0.998$ and a detection limit of 1.4×10^{-8} mol/L ($S/N = 3$). The results indicated rhodamine 6G hydrazide was an excellent chemiluminescent probe for chromium(VI) without reduction of chromium(VI) to chromium(III). A possible mechanism of CL emission was also suggested.

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1. Introduction

Since the first application of chemiluminescence (CL) as analytical tool, a large number of papers have been published on new molecules exhibiting CL character. Luminol [1,2], lophine [3], lucigenin [4], peroxyoxalate [5], Tris(2,2'-bipyridine) ruthenium [6], polyphenols [7], permanganate [8], nano-materials [9–12], etc. have been observed to show CL. Compared to other CL molecules, hydrazide compounds such as luminol and its analogues seem to be more attractive. Based on the CL of luminol and its analogues, many analytical applications have been developed for determination of various substances such as catalyzer or inhibitor, etc. [13,14]. However, the quantum yield of these compounds ranged from 0.0017 to 0.1 is not very high [15]. In order to find better chemiluminescent compounds, luminol analogues [16–18], linear hydrazides [19–21], phthalic hydrazide derivatives [22], cinchomeric hydrazide [23], quinolinic hydrazide [24] and 5-(59-Azolociferinyl)-2,3-dihydro-1,4-phthalazinedione [25], etc. have been synthesized and studied respectively. Although the CL efficiency is affected by a variety of factors, some of these results showed that oxidation of hydrazide group may act as an energy source for CL luminophors, and the CL efficiency can be improved by increasing the fluorescence efficiency of CL luminophor.

Rhodamine dyes are fluorophores that belong to the family of xanthenes. An interesting feature of some rhodamine dyes is that they are none or lower fluorescent in the form of spirocyclic, but highly fluorescent in the form of ring-open [26]. Due to their excellent fluorescence efficiency and high absorption coefficient, rhodamines are widely used

as probes or chemosensors to various applications, such as analytical detection [27–30], cells imaging [31], thermometer [32] and molecular ruler [33], etc.

Although rhodamines were also widely used in CL analysis for various analytes [34–36], little attention has been paid to the CL of rhodamine hydrazide. Other than the redox character of hydrazide group, rhodamine hydrazide has a similar nature to corresponding rhodamine, such as none or lower fluorescent in the form of spirocyclic and highly fluorescent in the form of ring-open [37]. Since the first work on ring-opening reaction of rhodamine B hydrazide (RBH) by Czarnik [38] in 1997, many exciting papers on the utilization of this unique ring-opening process of rhodamine hydrazides have been published focused on its fluorescence and spectrophotometric application [39–43], and very few focused on its CL application [44]. From the CL point of view, due to rhodamine hydrazides can be oxidized by suitable oxidants to highly fluorescent rhodamine, hydrazide derivatives of rhodamines may be excellent CL molecule.

In present work, RBH and rhodamine 6G hydrazide (R6GH) were synthesized and their CL performance was investigated systematically. In order to validate the feasibility of rhodamine hydrazide as a CL molecule, a CL analytical model for determination chromium(VI) was developed.

2. Experimental

2.1. Reagents

RB and R6G was purchased from Shanghai Aladdin Reagent Co., Ltd., hydrazine hydrate (80%) was purchased from Chengdu Changzheng Glass Co., Ltd. All the other reagents were of analytical reagent grade

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unless specified otherwise. Deionized and doubly distilled water was used throughout.

Stock solution of R6GH (1.00×10^{-3} mol/L) was prepared by dissolving 0.1066 g of R6GH in 250 mL of water containing 0.04 mol/L H_2SO_4 and kept in the freezer at 4 °C. The diluted solutions of R6GH were prepared, just before use, by accurate dilution with water.

Stock solution of chromium(VI) (2.00×10^{-3} mol/L) was prepared by dissolving 0.1471 g of potassium bichromate in 250 mL of water.

2.2. Synthesis of RBH and R6GH

In this work, two rhodamine hydrazides, RBH and R6GH, were prepared according to the established methods [39–43, Scheme 1]. The details were presented as followings.

Synthesis of RBH: To a 100 mL round-bottom flask, RB (1.2 g, 2.5 mmol) was dissolved in 30 mL absolute ethanol, 4 mL excessive hydrazine hydrate (80%) was then added drop wise with magnetic stirring at ice bath temperature, and then the mixture was heated under reflux for about 3 h. After removal of the solvent under reduced pressure, the residue was dissolved with 50 mL 1 mol/L HCl, and next 1 mol/L NaOH was added slowly under stirring until the pH of the solution reached 9–10. The resulted precipitate was filtered and washed three times with 15 mL water. The product was dried under reduced pressure to give RBH (0.78 g) as pink solid. Further purification of the product was carried out by crystallizing in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$. ^1H NMR (400 MHz, DMSO) δ 7.79–7.73 (m, 1H), 7.5–7.43 (m, 2H), 7.02–6.95 (m, 1H), 6.34 (dt, $J = 10.7, 7.3$ Hz, 6H), 4.25 (d, $J = 8.2$ Hz, 2H), 3.30 (d, $J = 7.1$ Hz, 8H), 1.08 (t, $J = 7.0$ Hz, 12H) (Fig. S1, S2).

Synthesis R6GH: R6GH was synthesized through a similar route as above for RBH synthesis. Excess hydrazine monohydrate (8 mL, 80%) was added drop wise (20 min) to a vigorously stirred R6G solution (2.40 g, 5 mmol) in 60 mL ethanol at ice bath temperature. Then, the reaction mixture was refluxed for about 3 h. The resulting precipitate was filtered and washed five times with 150 mL EtOH/ H_2O (1:1 v/v). The pure product was isolated and vacuum-dried to yield R6GH (1.95 g) as a light pink solid. ^1H NMR (400 MHz, DMSO) δ 7.78–7.73 (m, 1H), 7.49–7.43 (m, 2H), 6.93 (dd, $J = 6.5, 1.8$ Hz, 1H), 6.27 (s, 2H), 6.10 (s, 2H), 5.00 (t, $J = 5.4$ Hz, 2H), 4.22 (s, 2H), 3.19–3.08 (m, 4H), 1.87 (s, 6H), 1.21 (t, $J = 7.1$ Hz, 6H) (Figs. S3, S4).

2.3. Analytical Procedure

The experiments were carried out by using a flow injection analyzer (Beijing Titan Instruments Co., Ltd) coupled with a CL detector (Xi'an Remax Electronic Science-Tech Co. Ltd., Xi'an, China).

R6GH solution, H_2O_2 solution and Tween 80 solution were piped through Teflon tube (connected with silicone tube) to a the quartz flow cell placed in front of the photomultiplier tube window as shown in Fig. S5. Water was used as the carrier and delivered the injected sample solution to flow cell and reacted with other CL reagents.

The fluorescence and CL spectra were recorded on a fluorophotometer (F-280, Tianjing Gangdong Sci. & Tech. Development Co., Ltd., China). The adsorption spectra were recorded using an UV-Vis spectrophotometer (UV-5200PC, Shanghai Metash Instruments Co., Ltd., China).

Water samples were collected from Yan Lake in our university, filtered through a filter membrane (0.45 μm) before being used.

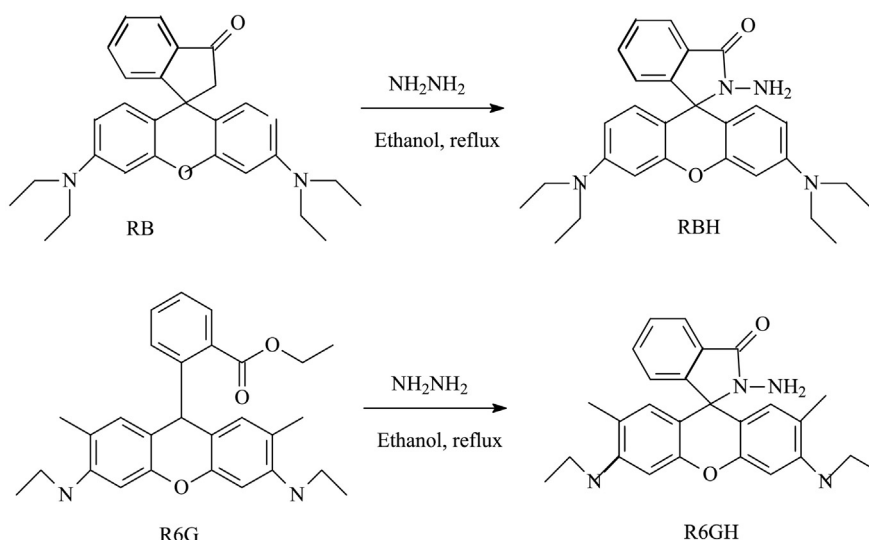
The quantitative determination was based on the net CL intensity $I = I_s - I_0$, where I_s is the CL intensity in the presence of chromium(VI) and I_0 is the intensity of blank signal.

3. Results and Discussion

3.1. Enhancement Effect of Chromium(VI) on R6GH CL Reaction

Preliminary investigation indicated that RBH and R6GH are chemiluminescent when reacted with potassium bichromate, sodium hypochlorite, *N*-bromosuccinimide, sodium nitrite, potassium bromate, and with H_2O_2 in the presence of mercuric nitrate. As a model for analysis application, CL of RBH and R6GH with chromium(VI) was investigated. It was found that CL of RBH chromium(VI), R6GH chromium(VI) increased by H_2O_2 and Tween. Fig. 1a showed the CL intensity of chromium(VI)- H^+ -Tween 80- H_2O_2 in present of RB, R6G, RBH and R6GH. As can be seen, strong CL intensity could be observed with RBH, and stronger with R6GH, while almost no signal could be observed with RB and R6G.

The CL performance of chromium(VI)- H^+ -Tween 80- H_2O_2 in present of R6GH was further investigated. Only very weak background light could be recorded when added chromium(VI) into acidic R6GH solution, and slightly higher in present of hydrogen peroxide. However, very strong CL signal could be recorded if added chromium(VI) solution into an acidic mixture solution of R6GH, hydrogen peroxide and Tween 80. The CL intensity with respect to time was also investigated by static-



Scheme 1. Synthesis of RBH and R6GH.

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