

A novel colorimetric and fluorescent probe for trivalent cations based on rhodamine B derivative



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ABSTRACT

A novel Schiff-base (**HL**) based on rhodamine B derivative was designed and synthesized as a highly selective and sensitive “turn-on” fluorescent probe for M^{3+} (Cr^{3+} , Fe^{3+} , and Al^{3+}) in methanol. Upon addition of M^{3+} , the spirolactam ring (colorless and nonfluorescent) of **HL** was opened to the ring-open forms (pink and orange-yellow fluorescence). These results indicated that **HL** could be used as a colorimetric and fluorescent probe for the detection of M^{3+} with low detection limit of $0.63 \mu M$ (Cr^{3+}), $0.14 \mu M$ (Fe^{3+}), and $0.22 \mu M$ (Al^{3+}). The binding constant (K_a) of M^{3+} binding to **HL** were calculated to be $0.87 \times 10^4 M^{-1}$ (Cr^{3+}), $1.14 \times 10^4 M^{-1}$ (Fe^{3+}), and $4.48 \times 10^4 M^{-1}$ (Al^{3+}), respectively from a Benesi-Hildebrand plot. The binding stoichiometry between **HL** and M^{3+} was determined from the Job's plot (fluorescent spectrum) and ESI-MS spectrum data to be 1:1. Furthermore, the recognition process of the probe for M^{3+} was chemically reversible on the addition of fluorinon (F^-).

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1. Introduction

The design and synthesis of new chemosensors for trivalent metal ions (M^{3+}) is an important research subject because of their biological significance and environmental importance. For instance, as the third most abundant metal in the Earth's crust, aluminum is widely used in aluminum alloy, aircraft, automobiles, trains, ships and other manufacturing industries [1–8]. However, overdose of Al^{3+} not only disturbs Ca^{2+} metabolism, decreases liver and kidney function, but also causes Alzheimer's disease and osteoporosis [9–12]. Cr^{3+} , an essential trace element in human nutrition, affects the metabolism of carbohydrates, fats, proteins and nucleic acids through activating certain enzymes and stabilizing proteins and nucleic acids. Excessive Cr^{3+} has a negative impact on cellular structure, cellular function, glucose levels, and lipid metabolism, while deficient Cr^{3+} may cause diabetes and cardiovascular disease [13,14]. Moreover, industrial runoff of Cr^{3+} may cause adverse impact on industry and agriculture [15,16]. Fe^{3+} , an essential trace element in biological systems, plays an important role in many chemical and biological processes such as electron transfer reactions and oxygen transport due to its adequate redox potentials and high affinity for oxygen [17,18]. Overdose of Fe^{3+} may cause some dysfunction of heart, pancreas, and liver, while the deficiency of Fe^{3+} may also cause anemia,

hemochromatosis, liver damage, diabetes, and Parkinson's disease [19–22]. Therefore, it's significant to design and synthesize optical chemosensors for detecting the presence of trivalent cation ions (Cr^{3+} , Fe^{3+} , and Al^{3+}) in environmental and biological samples.

Over the past few years, a large number of chemosensors for trivalent metal ions (Cr^{3+} , Fe^{3+} , and Al^{3+}) have been reported [23–28]. Barba-Bon et al. described a highly selective fluorescent probe for trivalent cation ions (Cr^{3+} , Fe^{3+} , and Al^{3+}) based on derivative of fluorescein [11]. Recently, Samanta also reported a new fluorogenic probe for sensing of trivalent cations in live cells [28]. However, the two probes may face some challenges in bioimaging application due to indigo fluorescence (475 nm) [11] and green fluorescence (509 nm) [28]. In vivo fluorescence tracking studies, emission at longer wavelengths is satisfactory because of the improved photon tissue penetration and reduced background autofluorescence, especially emission in the NIR region [29–32]. Tang et al. developed a fluorescent probe emitting red fluorescence for detecting trivalent cations [12]. However, the probe had poor selectivity for trivalent cations because it also responded towards Hg^{2+} in similar condition.

The rhodamine B derivatives are excellent fluorophores due to large molar extinction coefficient, high fluorescence quantum yield, and long absorption, emission wavelengths. On the basis of the equilibrium between spirocyclic (non-fluorescent) and ring-open forms (highly fluorescent) [33–35], we designed and synthesized a new turn-on fluorescent probe for the detection of trivalent cations. The rhodamine B skeleton was used as the

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fluorophore and chromophore and the (4-Hydroxybenzoyl)hydrazine was used as the recognition group. The introduction of a hydroxyl group in the terminal benzene ring could strengthen the electron cloud density of the *para*-position (C=O) to enhance the oxygen coordination ability. The probe, 2-[[3',6'-bis(diethylamino)-3-oxospiro[1-isoindole-1,9'-xanthen]-2-yl]imino]acetaldehyde (HL) exhibited high selectivity towards trivalent cations over commonly monovalent and divalent metal ions in methanol. Significantly, the binding of HL and trivalent cations was chemically reversible by the addition of F⁻ solution.

2. Experimental section

2.1. Materials and instruments

Rhodamine B and cationic salts such as Al(NO₃)₃, Ba(OAc)₂, Ca(NO₃)₂, Cd(OAc)₂, Co(OAc)₂, Cr(NO₃)₃, Cu(NO₃)₂, Fe(NO₃)₂, Fe(NO₃)₃, K(OAc), Mg(NO₃)₂, Mn(NO₃)₂, NaClO₄, Ni(NO₃)₂, Pb(OAc)₂, Zn(NO₃)₂, Li(NO₃), Ag(NO₃), and HgCl₂ were obtained from commercial suppliers and used without further purification. ¹H NMR spectrum were measured on the JNM-ECS 400 MHz spectrometer. Chemical shifts are reported in ppm using TMS as an internal standard. ESI-MS were determined on a Bruker esquire 6000 spectrometer. UV-vis absorption spectrum were measured with a Shimadzu UV-240 spectrophotometer. Fluorescence spectrum were determined on a Hitachi RF-4500 spectrophotometer equipped with quartz cuvettes of 1 cm path length. The melting point was determined on a Beijing XT4-100 x microscopic melting point apparatus.

2.2. Synthesis

(4-Hydroxybenzoyl)hydrazine was synthesized according to the method reported [36]. The HL was synthesized according to the route as shown in Scheme 1.

2.2.1. Synthesis of rhodamine B hydrazine (1)

To a 0.8 g of rhodamine B dissolved in 30 mL of methanol, an excessive hydrazine hydrate (1 mL) was added and then the reaction solution was refluxed till the pink color disappeared. After cooling to room temperature, the solvent was removed under reduced pressure. The precipitate was washed with deionized

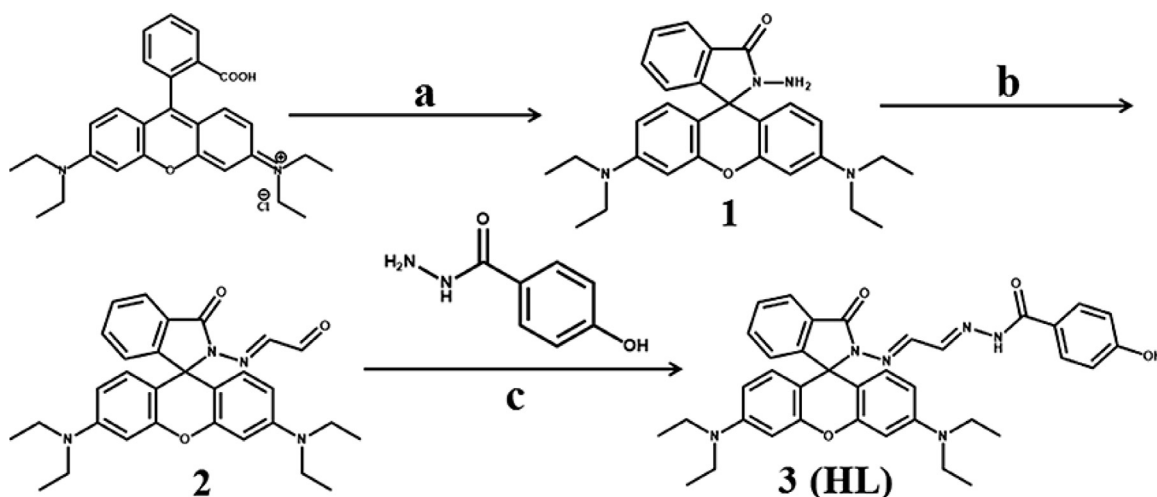
water and dried under reduced pressure to give the final product in the field of 64%. Melting point: 192–195 °C. ¹H NMR (400 MHz, CDCl₃, TMS) (Fig. S1): δ_H ppm 1.16 (t, 12H, NCH₂CH₃, *J* = 6.8 Hz), 3.33 (q, 8H, NCH₂CH₃, *J* = 6.8 Hz), 3.60 (s, 2H, N—NH₂), 6.28 (m, 2H), 6.41–6.46 (m, 4H), 7.09–7.11 (m, 1H), 7.44 (m, 2H), 7.92 (m, 1H). ¹³C NMR (400 MHz, CDCl₃, TMS) (Fig. S2): δ_C ppm 12.63 (CH₃), 44.88 (CH₂), 66.33, 98.08, 104.67, 108.12, 122.95, 124.24, 128.17, 130.35, 133.00, 149.12, 151.65, 154.33, 166.53 (C=O).

2.2.2. Synthesis of 2-[[3',6'-bis(diethylamino)-3-oxospiro[1-isoindole-1,9'-xanthe-n]-2-yl]imino]acetaldehyde (2)

Rhodamine B hydrazine (0.46 g) was dissolved in absolute ethanol (30 mL). An excess of glyoxal (2 mL) was added, and the mixture was stirred overnight at room temperature. Then plenty of saturated potassium chloride solution was added to precipitate the crude product. The crude product was collected, washed with ethanol and water, and dried under reduced pressure. ¹H NMR (400 MHz, CDCl₃, TMS) (Fig. S3): δ_H ppm 1.16 (t, 12H, NCH₂CH₃, *J* = 6.4 Hz), 3.33 (q, 8H, NCH₂CH₃, *J* = 6.4 Hz), 6.25 (d, 2H, Ar-H, *J* = 8.4 Hz), 6.40–6.46 (m, 4H, Ar-H), 7.10 (d, 1H, Ar-H, *J* = 7.6 Hz), 7.38 (d, 1H, CH=N, *J* = 7.2 Hz), 7.46–7.56 (m, 2H, Ar-H), 8.04 (d, 1H, Ar-H, *J* = 7.2 Hz), 9.44 (d, 1H, CH=O, *J* = 7.6 Hz). ¹³C NMR (400 MHz, CDCl₃, TMS) (Fig. S4): δ_C ppm 12.69 (CH₃), 44.45 (CH₂), 66.05, 98.17, 103.79, 108.27, 123.95, 124.14, 126.72, 127.82, 128.82, 134.74, 141.21, 149.32, 152.66, 153.04, 166.04 (C=O), 192.71 (CHO).

2.2.3. Synthesis of 2-[[3',6'-bis(diethylamino)-3-oxospiro[1-isoindole-1,9'-xanthe-n]-2-yl]imino]acetaldehyde-(4-hydroxybenzoyl)hydrazone 3 (HL)

2-[[3',6'-bis(diethylamino)-3-oxospiro[1-isoindole-1,9'-xanthen]-2-yl]imino]acetaldehyde (0.2483 g, 0.5 mmol) and (4-hydroxybenzoyl)hydrazine (0.0761 g, 0.5 mmol) were mixed in 40 mL ethanol and refluxed overnight under N₂. After cooling to room temperature, the precipitate was collected, washed with cold ethanol, and dried in vacuum. Yields: 40%. Melting point: 218 °C. ¹H NMR (400 MHz, DMSO-*d*₆, TMS) (Fig. S5): δ_H ppm 11.68 (s, 1H), 10.17 (s, 1H), 7.98 (s, 1H), 7.92 (d, 1H, *J* = 7.6 Hz), 7.85 (s, 1H), 7.79 (d, 1H, *J* = 8.8 Hz), 7.70 (d, 2H, *J* = 8.8 Hz), 7.60 (t, 1H, *J* = 7.6 Hz), 7.55 (t, 1H, *J* = 7.6 Hz), 7.06 (d, 1H, *J* = 7.6 Hz), 6.85 (dd, 2H, *J* = 8.8 Hz, *J* = 16.8 Hz), 6.45 (d, 1H, *J* = 2 Hz), 6.43 (s, 1H), 6.41 (s, 1H), 6.37 (d, 1H, *J* = 2.4 Hz), 6.35 (d, 1H, *J* = 2.4 Hz), 3.36–3.29 (q, 8H), 1.09 (t, 12H, *J* = 6.8 Hz). ¹³C NMR (400 MHz, DMSO-*d*₆, TMS) (Fig. S6): δ_C ppm 30.36 (CH₃), 55.35 (CH₂), 98.44, 106.99, 112.50, 119.03, 119.35,



Scheme 1. The synthetic route of 2-[[3',6'-bis(diethylamino)-3-oxospiro[1-isoindole-1,9'-xanthen]-2-yl]imino]acetaldehyde-(4-hydroxybenzoyl)hydrazone (HL). Reagents and conditions: (a) methanol, hydrazine hydrate, 65 °C, reflux, 12 h, compound 1 Yields: 64%; (b) absolute ethanol, glyoxal, saturated potassium chloride solution, room temperature, 24 h, compound 2 Yields: 72%; (c) absolute ethanol, 80 °C, reflux, 24 h, compound 3 Yields: 40%.

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