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Synthesis of Highly Sensitive and Selective Probe for Fluorescent Detection of Chromium(III)

JUN ZHANG and CHUNWEI YU*

Laboratory of Environmental Monitoring, School of Tropical and Laboratory Medicine, Hainan Medical University, Haikou 571101, P.R. China

*Corresponding author: Fax: +86 898 66989173; Tel: +86 898 66973190; E-mail: yucw_1979@sina.com

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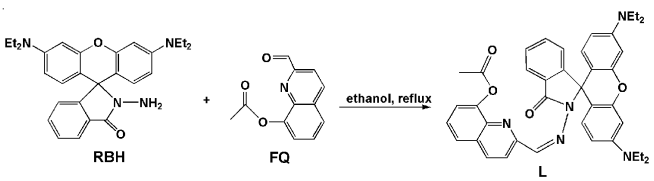
A new fluorescent probe capable of sensing Cr^{3+} has been synthesized. Complexing with Cr^{3+} triggers the formation of a highly fluorescent ring-open form which is pink in colour. The probe shows extremely high fluorescence enhancement upon complexation with Cr^{3+} and it can be used as a 'naked eye' probe.

Keywords: Probe, Chromium(III), Rhodamine B, Fluorescent.

INTRODUCTION

Trivalent chromium, Cr^{3+}, plays an important role in human and animal biology as it is involved in several biochemical processes at the cellular levels[1]. Chromium deciency can increase the risk factors associated with diabetes and cardiovascular diseases. In addition, chromium is a known environmental pollutant that accumulates due to agricultural and industrial activities[2]. Therefore, much attention has been paid to develop selective chemoprobes for chromium. Due to its simplicity, selective fluorimetric detection of Cr^{3+} has advantages over other detection techniques such as electrochemical methods[3-8].

Rhodamine dyes have been employed extensively in the conjugation with biomolecules owing to their excellent fluorescence properties such as long absorption and emission wavelength, large absorption coefcient and high fluorescence quantum yield. Recently, various rhodamine-based turn-on fluorescent probes for metal ions have been reported[9-11]. The sensing mechanism of these probes is based on the change in structure between spirocyclic and open-cycle forms. Inspired by this platform, we have studied a new rhodamine-based probe **L**, which shows a remarkably high sensitivity and selectivity to Cr^{3+}. The probe was synthesized as shown in **Scheme-I**.



Scheme-I: Synthesis route of probe **L**

EXPERIMENTAL

All reagents and solvents are of analytical grade and used without further purification. Metal ions species employed were from NaCl, KCl, $MgCl_2·6H_2O$, $HgCl_2$, $CaCl_2·2H_2O$, $CrCl_3·6H_2O$, $Zn(NO_3)_2·6H_2O$, $AgNO_3$, $CdCl_2$, $CuCl_2·2H_2O$ and $PbCl_2$, respectively.

Nuclear magnetic resonance (NMR) spectra were measured with a Brucker AVIII-500 spectrometer and chemical shifts were given in ppm from tetramethylsilane. Mass spectra (MS) were recorded on a Thermo TSQ Quantum Mass Spectrometer. Fluorescence emission spectra were conducted on a HORIBA Fluoromax-4 spectrofluometer. Absorption spectra were determined on a Beckman DU-800 spectrophotometer. The pH measurements were carried out on a PHS-3C meter.

Synthesis of probe L: Compound **RBH** and **FQ** were synthesized according to the references[9,11].

Synthesis of probe L: RBH (0.5 mmol) and **FQ** (0.5 mmol) was mixed in 50 mL ethanol solution and heated to reflux for 4 h and then the mixture was cooled to room temperature. The solid obtained was filtered and washed by ethanol and used without further purification.Yellow crystals (75 %). MS: m/z 676.12 $[M + Na]^+$. ^1H NMR (δ: ppm, $CDCl_3$): 8.8 (s, 1H, Ar-H), 8.7 (s, 1H, Ar-H), 8.0-8.1 (m, 2H, Ar-H), 7.61 (d, 1H, Ar-H), 7.52-7.60 (m, 1H, Ar-H), 7.47-7.50 (m, 1H, Ar-H), 7.34-7.42 (m, 1H, Ar-H), 7.31 (s, 1H, N=C-H), 7.23 (d, 1H, Ar-H), 7.15-7.17 (m, 1H, Ar-H), 7.08-7.09 (d, 1H, Ar-H), 6.53-6.56 (m, 1H, Ar-H), 6.52 (d, 1H, Ar-H), 6.45-6.46 (d, 1H, Ar-H), 6.24-6.26 (m, 2H, Ar-H), 3.30-3.34 (m, 8H, CH_2), 2.49 (s, 3H, CH_3), 1.14-1.26 (t, 12H, CH_2CH_2-H); ^{13}C NMR (δ: ppm, $CDCl_3$): 166.43, 164.71 (C=O), 153.76, 152.32, 149.21, 148.42, 142.90, 134.31, 133.29, 131.97, 128.72, 128.04, 127.70, 126.58,

125.53, 123.82, 123.28, 108.05, 104.27, 98.96 (ArC), 65.91, 44.36, 18.45, 12.68.

General procedure for spectroscopic measurements: A stock solution of **L** (1.0 mM) was prepared in DMSO. To 10 mL glass tubes, 200 μL **L** (1.0 mM) and a proper amount of Cr^{3+} stock solution (1.0 mM) were added subsequently and then diluted with ethanol/HEPES bufferred solution (8:2, v:v, pH 7.4, 20 mM). The resulting solution was mixed thoroughly. For all measurements, excitation and emission slit widths were 5.0 and 2.5 nm, respectively, excitation wavelength was 510 nm.

RESULTS AND DISCUSSION

Effects of pH on L and L with Cr^{3+}: A pH titration experiment was first evaluated as shown in Fig. 1. The fluorescence of the probe-chromium complex displayed a plateau in the pH range from 6.2-8.0. In the view of further use in living body, in our experiment, pH 7.4 was chosen as optimum experimental condition. Therefore, further UV/Visible and fluorescent studies were carried out in ethanol/HEPES mixed buffer solution (ethanol-water = 8:2, v/v, pH 7.4, 20 mM HEPES).

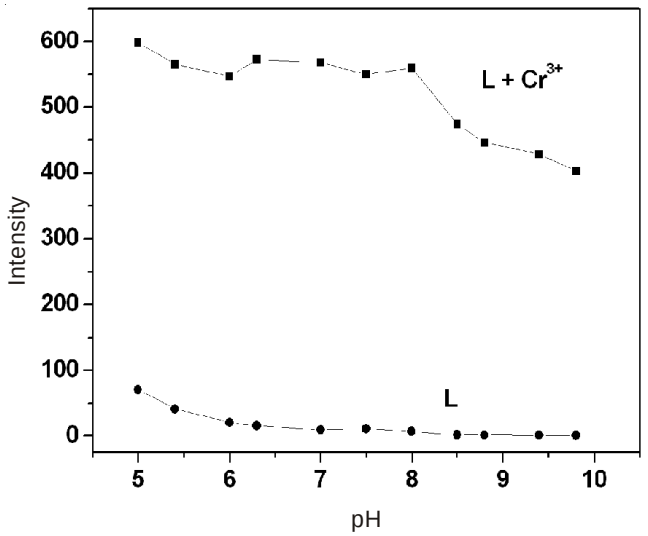


Fig. 1. pH dependent fluorescence response of **L** (20 μM) and probe **L** to Cr^{3+} (200 μM) in the aqueous solution (ethanol/water = 8:2, v/v)

Colorimetric and fluorescent signaling of Cr^{3+}: As expected, compound **L** alone was colourless and scarcely showed absorption in the 500-600 nm region in ethanol-water solution (8:2, v:v, pH7.4, 20 mM HEPES), whereas upon treating with Cr^{3+}, an intense absorption band centered at 560 nm and an enhanced fluorescence produced at 590 nm, presumably because the chelation of Cr^{3+} with nitrogen atom of the amide group of **L** resulted in the formation of the open-ring form (Figs. 2 and 3), respectively. At the same time, related other metal ions did not show any obvious absorption and fluorescent emission under similar conditions.

Furthermore, fluorescence titrations of **L** was conducted in Fig. 4. With increasing [Cr^{3+}], a broad fluorescent band ranging from 540-690 nm increases, a new fluorescent peak at 590 nm appeared mainly *via* the structure transformation from spirolactam to ring-open by the Cr^{3+}-induced reaction. In its emission spectra, the intensity of the fluorescent peak at

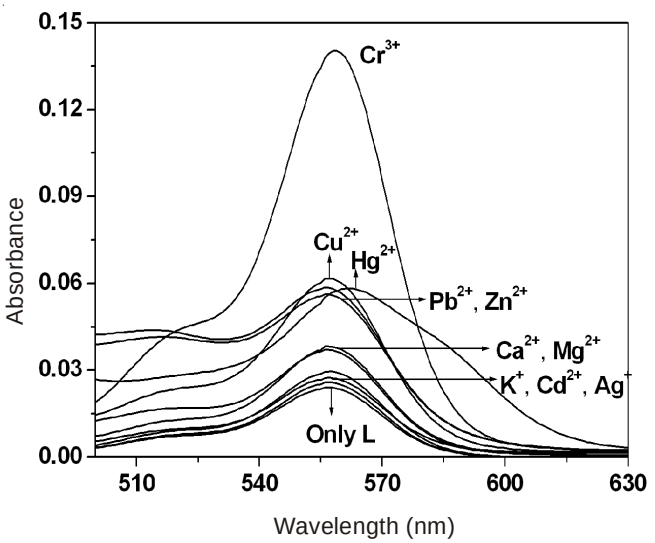


Fig. 2. Absorption spectra of **L** (20 μM) in the absence and presence of different metal ions (200 μM) in aqueous solution (ethanol/water = 8:2, v/v, pH 7.4)

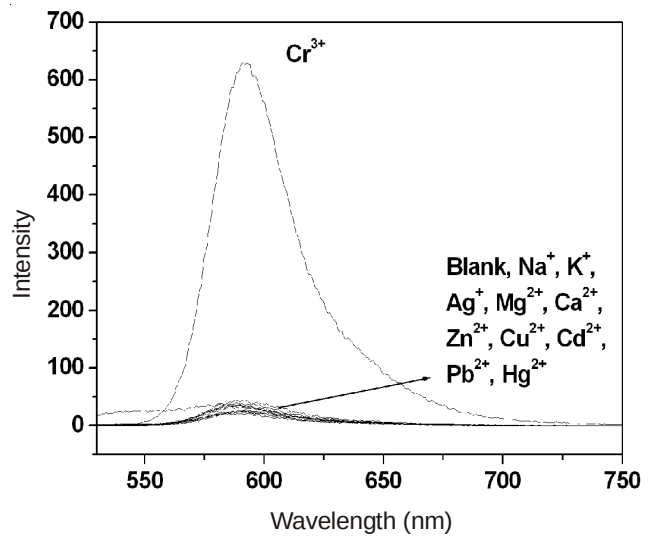


Fig. 3. Fluorescent emission changes of **L** (20 μM) in the presence of different metal ions (200 μM) in 20 % (v/v) water-ethanol solution (20 mM HEPES, pH7.4)

590 nm gradually increased excited by 510 nm light. Upon titration of fluorescence spectra of variable [Cr^{3+}], a good linear relationship was observed between the relative fluorescence intensity of the probe and the concentration of Cr^{3+} in the 3.0 × 10^{-8}-3.0 × 10^{-6} M and the detection limit of **L** for Cr^{3+} was judged to be 1.5 nM in aqueous media. (Based on S/N = 3, inset of Fig. 4).

Reversibility and possible sensing mechanism: The reversibility of this reaction was examined by EDTA-adding experiments. Addition of EDTA to the solution containing **L** and Cr^{3+} diminishes the absorbance signiûcantly, whereas readdition of excess Cr^{3+} could recover the absorbance signal (Fig. 5, **Scheme-II**). The Cr^{3+}-induced colouration and emission of **L** with Cr^{3+} leading to spirocycle opening of **L**, as is the case for related rhodamine-based probes.

To prove the binding stoichiometry of **L** with Cr^{3+}, the Job's plot (Fig. 6) was carried out, which clearly indicated the 1:1 stoichiometry for **L**-Cr^{3+} complex.

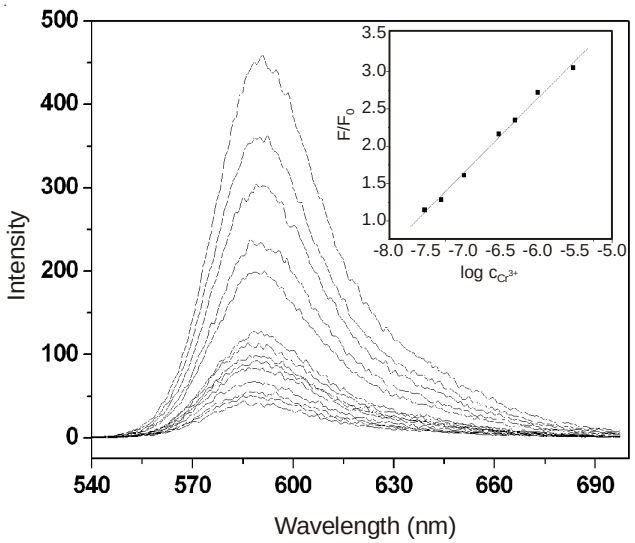


Fig. 4. Emission spectra of **L** (20 μM) with increasing concentrations of Cr^{3+} (0-100 μM) in aqueous solution (ethanol/water = 8:2, v/v, pH 7.4). Inset: Linear fluorescence intensity (F/F_0) of **L** (20 μM) upon addition of Cr^{3+} (0.03-3 μM). The response (F) is normalized to the emission of the free probe **L** (F_0)

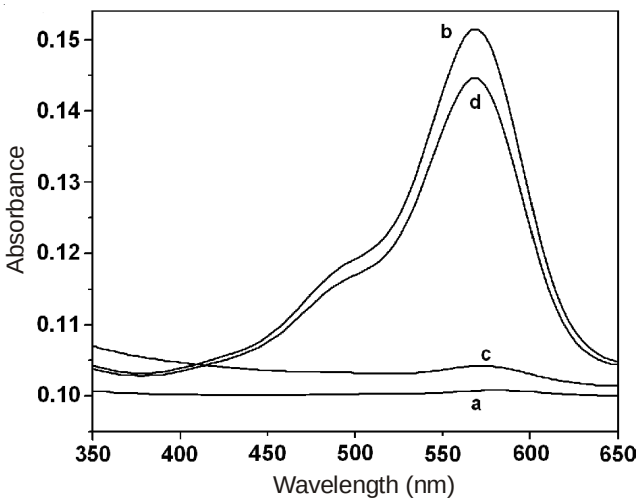
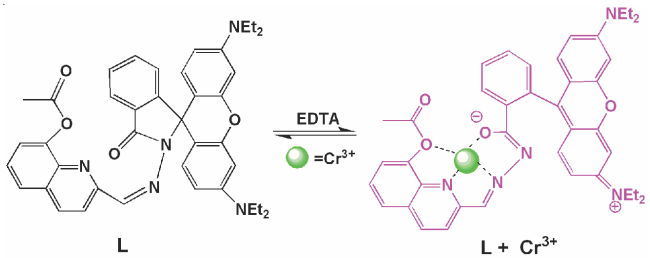


Fig. 5. Reversible titration response of **L** to Cr^{3+} in ethanol-HEPES buffer (20 mM, pH 7.4) (8:2, v/v): (a) **L** (20 μM); (b) **L** (20 μM) with Cr^{3+} (200 μM); (c) **L** (20 μM) with Cr^{3+} (200 μM) and then addition of EDTA (300 μM); (d) **L** (20 μM) with Cr^{3+} (200 μM) and EDTA (300 μM) and then addition of 300 μM Cr^{3+}



Scheme-II: Proposed reaction mechanism of probe **L** with Cr^{3+} and the investigation of coordination reversibility

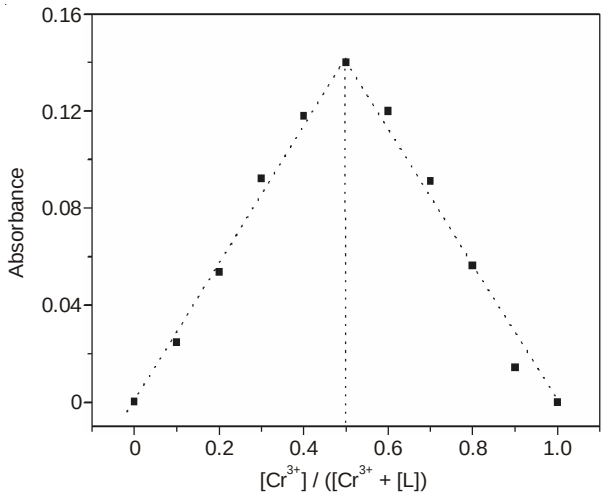


Fig. 6. Job's-plot of **L** for Cr^{3+} in the aqueous solution (ethanol/water = 8:2, v/v, pH 7.4)

Conclusion

In summary, a new rhodamine derivative used as selective and sensitive probe was developed, which could specically recognize Cr^{3+} in the aqueous buffer solution by the 'naked eye', UV/visible and fluorescent responses. It also showed a "turn-on" type of absorption and fluorescence response.

ACKNOWLEDGEMENTS

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