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A selective colorimetric and fluorescence chemosensing sensor for Cr^{3+} based on a rhodamine base derivative

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Abstract A rhodamine-conjugated coumarin (**L**) was used in designing a selective fluorescence chemosensor for the determination of trace amounts of Cr^{3+} ions in acetonitrile–water (MeCN/H_2O (90:10, %v/v) solutions. The intensity of the fluoresce emission of the chemosensor is intensified upon addition of Cr^{3+} ions in MeCN/H_2O (90:10, %v/v) solutions, due to the formation of a selective 1:1 complex between **L** and Cr^{3+} ions. The fluorescence enhancement versus Cr^{3+} concentration has been found to be linear from 1.0×10^{-7} to 1.8×10^{-5} M and a detection limit of 7.5×10^{-8} M. The proposed fluorescent probe proved to be highly selective towards Cr^{3+} ions as compared to other common metal ions and could be successfully applied to the determination of Cr^{3+} concentrations in some water and wastewater samples.

Keywords Fluorescence · Chromium · Enhancement · Sensor

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Introduction

An amount of 50–200 μg of Cr^{3+} is essential for a balanced human or animal diet, especially since the element plays a critical metabolic role on carbohydrates, lipids, proteins, and nucleic acids in the body [1]. Furthermore, Cr^{3+} is considered to be an ecological contaminant emitted by different industrial and agricultural processes [2]. All this attracts much interest toward studies on the development of detection methods for this ion in ecological and biological samples. The known methods to this end include titrimetric determinations, flame atomic absorption, inductively coupled plasma atomic emission, and X-ray fluorescence spectrophotometric techniques as well as electrochemical methods. These techniques mostly require cumbersome sample-preparation stages, as well as expensive and difficult to work instruments, in addition to, in many instances, demanding controlled operating conditions [3–6]. Consequently, the development of fast and facile procedures for the analysis of Cr^{3+} is always demanded and welcomed. The advent and use of colorimetric and/or fluorimetric probes for the analysis of various analytes including Cr^{3+} has become quite popular in recent years, due to the ease, high selectivity, sensitivity, high speed, comparatively negligible costs and direct visual perceptions associated with these sensors. Most of the fluorescent probes reported for Cr^{3+} [7–13] are based on fluorescence quenching, while there are few reports on fluorescent probes functioning based on fluorescence enhancement mechanisms [14].

Cr^{3+} is a paramagnetic species known for its efficient fluorescence quenching properties as compared to other transition metal ions [15–18], and, hence, as described earlier in the case of most Cr^{3+} fluorescent probes, the signal transduction through the so-called chelation-enhanced fluorescence (CHEF) is a challenge.

Rhodamine is a favorite reporter for fluorescent sensors [19, 20] owing to its high absorption coefficient, high fluorescence quantum yield, large extinction coefficient and their spirolactam ring-opening reaction, which can provide a strong fluorescence emission and a distinct color upon selective opening of rhodamine spirolactam ring in the presence of specific metal cations. The structural properties of the rhodamine framework, on the other hand, change it to an ideal choice for the construction of CHEF-based OFF–ON fluorescent probes. This is due to the fact that rhodamine undergoes equilibrium between its two highly fluorescent open-ring and non-fluorescent spirocyclic forms (i.e. the on and off signals, respectively), each of which has its own and completely unlike fluorescent properties [21]. Based on our recent work on the development of a range of highly selective and sensitive fluorescent sensors for various ions [22–28], here we report our research on the application of a rhodamine B hydrazide (**L**) as an ionophore for the construction of a Cr^{3+}-selective fluorescent chemosensor.

Experimental

Reagents

The chemicals were of the reagent grade and were obtained from Fluka and Merck. The solution of metal ions was prepared from their nitrate salts of analytical grade because of their good solubility.

Synthesis of 2-oxo-2H-chromene-3-carbonyl chloride

First, 5 mmol of salicylaldehyde (compound **1**) dissolved in 10 ml dry ethanol. Next, 5 mmol of diethyl malonate (compound **2**), 0.005 ml of glacial acetic acid and 0.05 ml of piperidine were added to the reaction mixture. This mixture was then refluxed for 6 h (monitored by TLC), and the resulting white precipitate was filtered and washed with cold ethanol several times, before being dried at ambient temperature to obtain compound **3**. Next, this white precipitate was dissolved in 100 ml of 0.5% NaOH and refluxed for 2 h, until a clear solution was achieved. This solution was next acidified with HCl to reach a pH of 2, and cooled to 0 °C. In this way, a white precipitate was obtained, which was filtered and washed with cold ethanol, allowed to dry in ambient conditions and crystalized from ethanol (compound **4**) (6.58 g, 82.2% yield) [29]. At last, to 2.5 mL of thionyl chloride in toluene was added 0.18 g of compound **4** (1 mmol) and the resulting mixture was refluxed at 80 °C for 6 h. Before the reaction was finished, the solvent of the reaction mixture was evaporated to finally collect 2-oxo-2H-chromene-3-carbonyl chloride (compound **5**) without any further treatments.

Synthesis of rhodamine B hydrazide

The synthesis of rhodamine B hydrazide (compound **6**) was carried out, as described elsewhere [30]. According to this procedure, an excess of hydrazine hydrate (0.5 mL) was added to 15 mL of methanol solution containing 0.4 g of rhodamine B hydrochloride, and the resulting mixture was subjected to refluxing in an N_2 atmosphere until its pink color wore off. After 4 h, the mixture was cooled and added to some distilled water, from which it was extracted using ethyl acetate (6 × 25 mL). The organic phases were then mixed and dried with anhydrous sodium sulfate, before being filtered, and concentrated under reduced pressure. This yielded 0.31 g (77.5%) of rhodamine hydrazide **7**.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.94 (bs, 1H, isoindoline ring), 7.46 (bs, 2H, isoindoline ring), 7.12 (bs, 1H, isoindoline ring), 6.46-6.43 (m, 4H, xanthene ring), 6.31 (bs, 2H, xanthene ring), 3.62 (bs, 2H, NH_2), 3.35 (bs, 8H, $N\underline{CH_2}CH_3$), 1.18 (bs, 12H, $NCH_2\underline{CH_3}$).

Synthesis of rhodamine-conjugated coumarin

The obtained crude acid chloride (compound **5**) was dissolved in 10 mL of toluene. To this solution was added dropwise a solution containing 0.2 g of potassium carbonate and 20 mL of rhodamine hydrazide (0.456 g, 1 mmol). The resulting mixture was then refluxed for 6 h under an N_2 atmosphere before being cooled to ambient temperature to obtain an orange precipitate. This product was filtered and washed 3 times with 15 mL of cold toluene.

Yield: 75%; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.95 (bs, 1H, NH), 8.79 (s, 1H, H_8 coumarin), 7.94 (bs, 1H, isoindoline ring), 7.62–6.78 (m, 11 H, 3H isoindoline, 4H xanthene and 4H coumarin ring), 6.36 (bs, 2H, xanthene ring), 3.33 (bs, 8H, $N\underline{CH_2}CH_3$), 1.16 (bs, 12H, $NCH_2\underline{CH_3}$).

Scheme 1 illustrates the sequence of steps for the preparation of rhodamine-conjugated coumarin by hydrazine.

Apparatus

All fluorescence measurements were carried out on a Perkin-Elmer LS50 luminescence spectrometer.

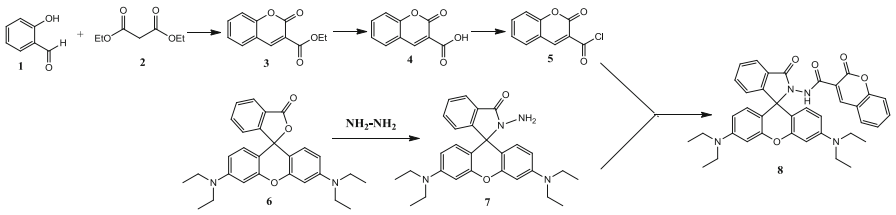
Fluorescence measurements

A fluorimetric cell was filled with 3.0 mL of a solution of the fluorophore L (5×10^{-6} mol/L) in MeCN/H_2O (90:10, %v/v). Then, the emission spectra of the solution were acquired. The solution was simultaneously titrated with a standard Cr^{3+} solution and the fluorescence variations were recorded. The emission intensity at an excitation wavelength of 553 nm was measured. Spectral bandwidths of monochromators for excitation and emission were 5 nm.

Results and discussion

Preliminary studies

To evaluate the reaction between the analytes and **L**, their UV–Vis absorption spectra were monitored. During these studies, the affinity of **L** towards different



Scheme 1 Synthesis of rhodamine-conjugated coumarin (**L**)

metal ions was visually evaluated (see Fig. 1). In the case of adding Cr^{3+}, the color of a 4.0×10^{-5} mol/L solution of **L** was instantaneously changed from colorless to pink. In the case of the rest of the ions tested, however, no detectable color changes was observed except for Ce^{3+} and Co^{2+} which were much lower than that of Cr^{3+}. This was even the case after adding large excesses of the metallic ions. The result indicated that the color changes were most probably due to the formation of a new complex species with different electronic properties from that of the receptor **L**, and therefore a new color (pink) was observed, although Ce^{3+} and Co^{2+} ions were caused to slightly change color.

The spectra obtained for titrating a 5.0×10^{-5} mol/L solution of **L** in acetonitrile–water (MeCN/H_2O) (90:10, v/v) solution with a standard 5.0×10^{-3} mol/L solution of Cr^{3+} is illustrated in Fig. 2. This information indicates that **L** has a broad absorption band centered at 283 nm and 556 nm, most probably due to its $\pi \rightarrow \pi^*$ transition. The intensity of the a bsorption peak at $\lambda_{max} = 283$ nm increased and a new peak appeared at 556 nm with a shoulder at 512 nm. A further three distinct isosbestic points were observed at 255, 293 and 331 nm, which are indicative of the formation of a stable complex between **L** and Cr^{3+} with a certain stoichiometry.

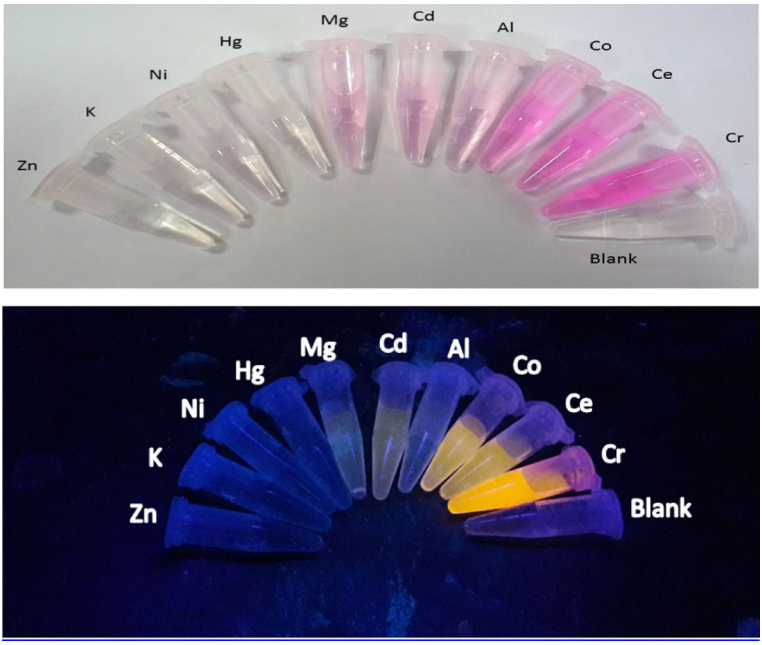


Fig. 1 Color response of the receptor **L** in MeCN (4.0×10^{-5} mol/L) to the addition of cations (4.0×10^{-4} mol/L in MeCN) under visible and UV light. *From left to right*: **L** + Zn^{2+}, **L** + K^+, **L** + Ni^{2+}, **L** + Hg^{2+}, **L** + Mg^{2+}, **L** + Cd^{2+}, **L** + Al^{3+}, **L**+ Co^{2+}, **L**+ Ce^{3+}, **L** + Cr^{3+}, **L** only

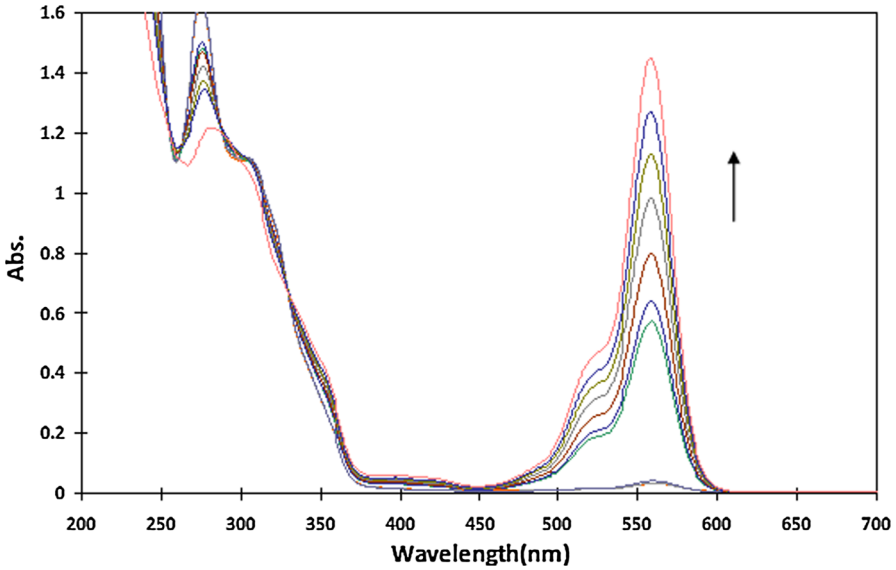


Fig. 2 Changes in the UV–vis spectra of **L** (5×10^{-5} M) upon addition of Cr^{3+} (5×10^{-3} mol/L) in MeCN/H_2O (90:10,% v/v)

Fluorescence titration

To assess the selectivity of **L** as a fluorescent chemosensor for Cr^{3+}, the initial studies included the evaluation of the complexation reactions between **L** and a series of metal ions. These spectrofluorometric studies were conducted by titrating 90:10 (%v/v) MeCN–H_2O solutions of **L** (5.0×10^{-6} mol/L) at 25.0 ± 0.1 °C with microliter volumes of of 1.0×10^{-4} mol/L solutions of metal ions (i.e. K^+, Mg^{2+}, Hg^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Zn^{2+}, Al^{3+} and Ce^{3+}), while the absorption of the **L** solution was spectrofluorometrically monitored at λ_{ex} = 553 nm with the ionic strength of the solution fixed using a 0.01 M ammonium nitrate solution in 25.0 ± 0.1 °C.

The results for the tested ions are illustrated in Fig. 3, based on which it can be clearly concluded that only in the case of Cr^{3+} is a significant increase in the fluorescence intensity of **L** observed, while other rather abundant metal ions like Cd^{2+}, Hg^{2+} etc. did not lead to considerable intensity increases. Actually, in the case of most of the other metal ions tested, the emission intensity remained constant or was quenched. Al^{3+}, Co^{2+} and Ce^{3+}, as exceptions to this rule, led to slight increases in the intensity. In the case of Cr^{3+}, the considerable elevation in the intensity of the fluorescence signal of **L** was attributed to the strong interactions between the cation and **L**.

Figure 4 illustrates that, upon addition of **L**, the quantity of metal ions increased, and then they begin to level off and go up again at a metal/ligand ion molar ratio of 1. The experimental data illustrated in this figure also supports the significant increase in fluorescence intensity of **L** as the result of the addition of Cr^{3+} and based

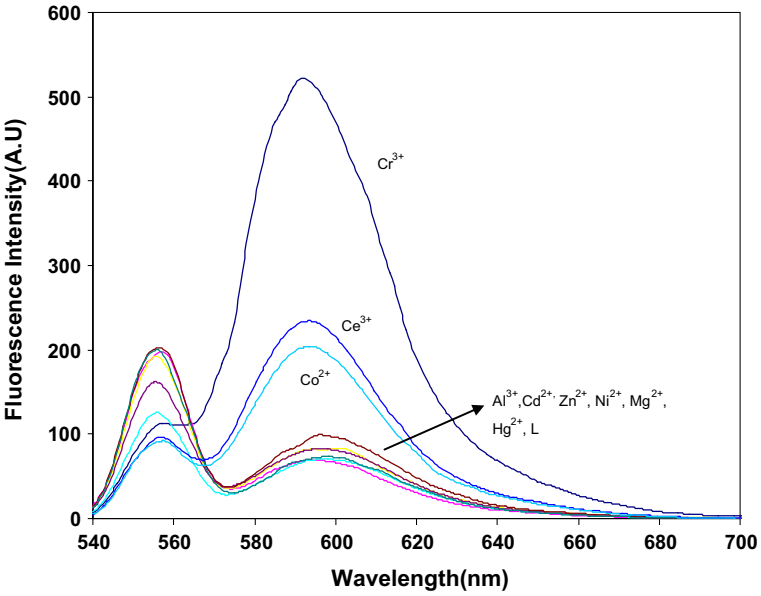


Fig. 3 Changes in the emisson spectra of **L** (5×10^{-5} M) upon addition of metal ions (5×10^{-3} mol/L) in MeCN/H_2O (90:10,% v/v)

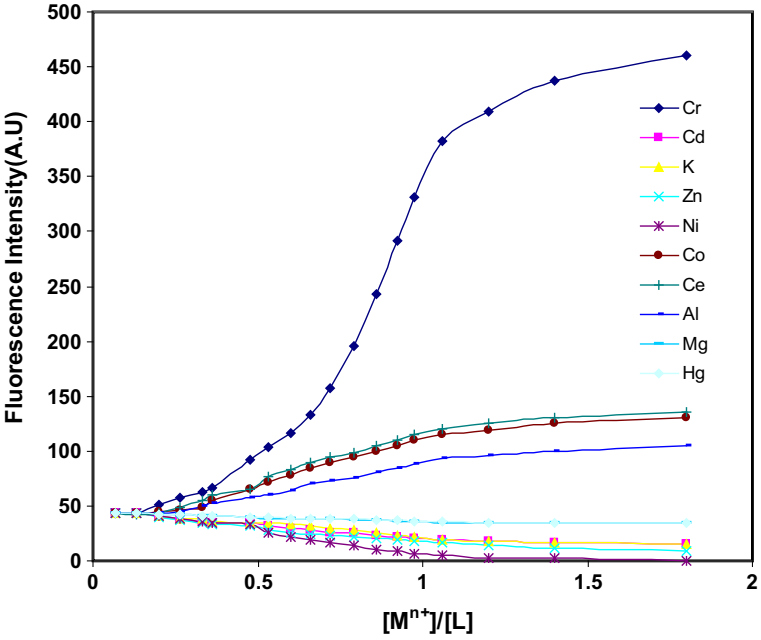


Fig. 4 Fluorescence intensity versus $[M^{n+}]/[L]$ mole ratio plots in AN solution for different transition metal ions

on the unanticipated appearance of an emission band for the complexed **L**, as compared to the free **L** (Fig. 4).

The sharp inflection point at a 1:1 molar ratio can be held as valid evidence that, in all cases, a 1:1 $[\mathbf{ML}]^{n+}$ complex is formed between the metallic cations and the **L** in the (90:10, %v/v) MeCN–H_2O solutions. Furthermore, the formation constants (Kf) values for each complex were evaluated through fitting the fluorescence intensity–metal ion molar ratio data to a 1:1 model. To do this, a nonlinear least-squares curve-fitting program was used [31], and the acquired results are given in Table 1. Although at such different experimental conditions a different trend was observed for fluorescence changes, it could be concluded that $[\mathrm{Cr}\mathbf{L}]^{3+}$ is the most stable complex which formed.

Many rohodamine derivatives have been reported to be colorless and non-fluorescent substances, owing to their stable spirolactam conformations [32, 33], which was the case with **L** in this study. However, it is also known that the disentanglement of this form leads to noticeably altered spectral characteristics. Based on our speculations, the addition of Cr^{3+} to the solution led to the same disentanglement phenomenon and the formation of a highly delocalized Π–conjugated **L** structure, enhancing the fluorescence at 556 nm. [21, 32].

The results in Figs. 4 and 5 also revealed a linear correlation between the fluorescence emission intensity of **L** and the concentration of Cr^{3+} in the range of 1.0×10^{-7} to 1.8×10^{-5} mol/L, with a detection limit of 7.5×10^{-8} mol/L based on 3δ of the blank according to the definition by IUPAC.

Selectivity

Since the selectivity behavior can be regarded as the most critical characteristics of a chemosensor, this was also studied. Selectivity, defined as the relative response toward the primary ion over other ions present in solution, was evaluated based on the affinity of **L** towards other metal cations through the study of the effect of different metal cations on the fluorescence behavior of **L** (Fig. 6). The results showed no observable changes in the fluorescence intensity ratio even when twice the equivalent amounts of the other metal ions were used.

Table 1 The formation constants of $L - M^{n+}$ complexes

Cation	Log Kf
Ce^{3+}	4.25 ± 0.11
Cd^{2+}	2.35 ± 0.11
Hg^{2+}	< 2.0
Co^{2+}	3.95 ± 0.11
Ni^{2+}	3.00 ± 0.11
Zn^{2+}	3.25 ± 0.12
Cr^{3+}	6.86 ± 0.13
Mg^{2+}	< 2.0
K^{+}	< 2.0
Al^{3+}	3.58 ± 0.17

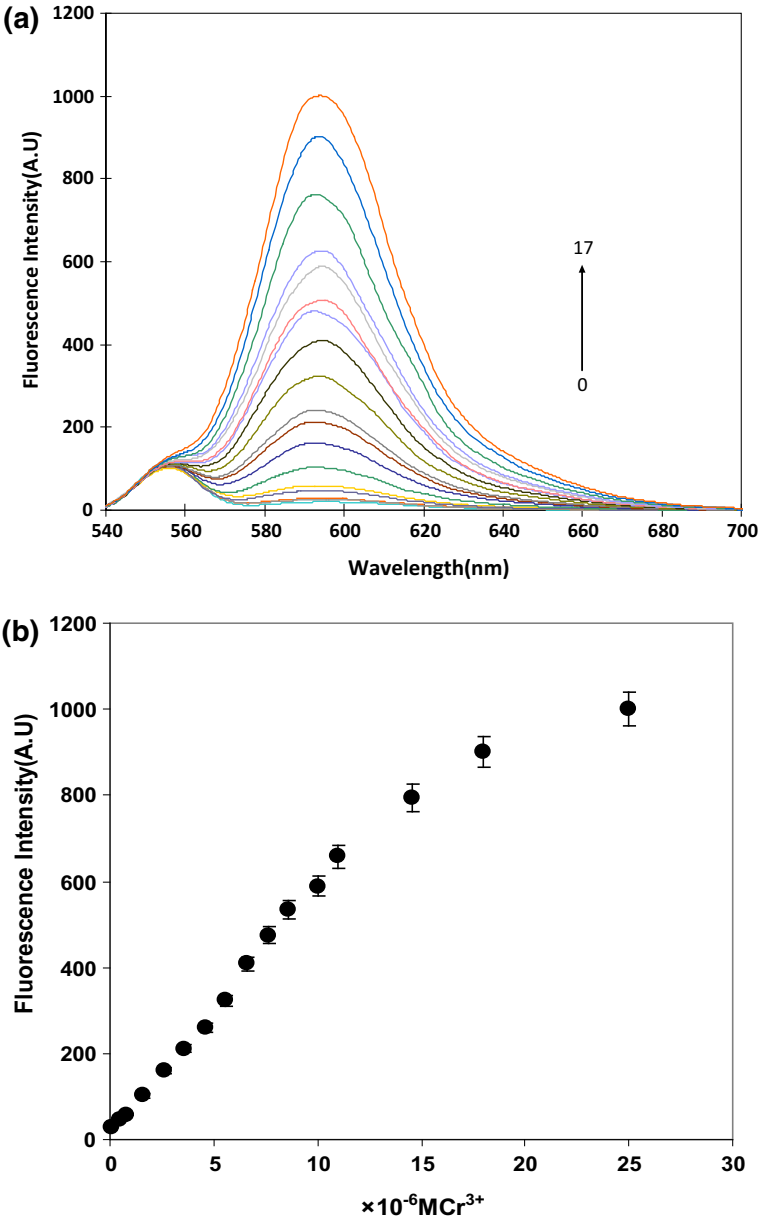


Fig. 5 **a** Fluorescence titration of **L** (1×10^{-5} mol/L) in MeCN/H_2O (90:10, % v/v). Solution in the presence of varying concentrations of Cr^{3+} ion: (1) 0,(2) 1.0×10^{-7} mol/L, (3) 5.0×10^{-7} mol/L, (4) 8.3×10^{-7} mol/L, (5) 1.6×10^{-6} mol/L, (6) 2.6×10^{-6} mol/L, (7) 3.6×10^{-6} mol/L, (8) 4.6×10^{-6} mol/L, (9) 5.6×10^{-6} mol/L, (10) 6.6×10^{-6} mol/L, (11) 7.6×10^{-6} mol/L, (12) 8.6×10^{-6} mol/L, (13) 1.0×10^{-5} mol/L, (14) 1.1×10^{-5} mol/L, (15) 1.4×10^{-5} mol/L, (16) 1.8×10^{-5} mol/L, (17) 2.5×10^{-5} mol/L $\lambda_{ex} = 553$ nm. **b** Plot of fluorescence intensity versus of concentration of Cr^{3+} in MeCN/H_2O (90:10, %v/v) solution

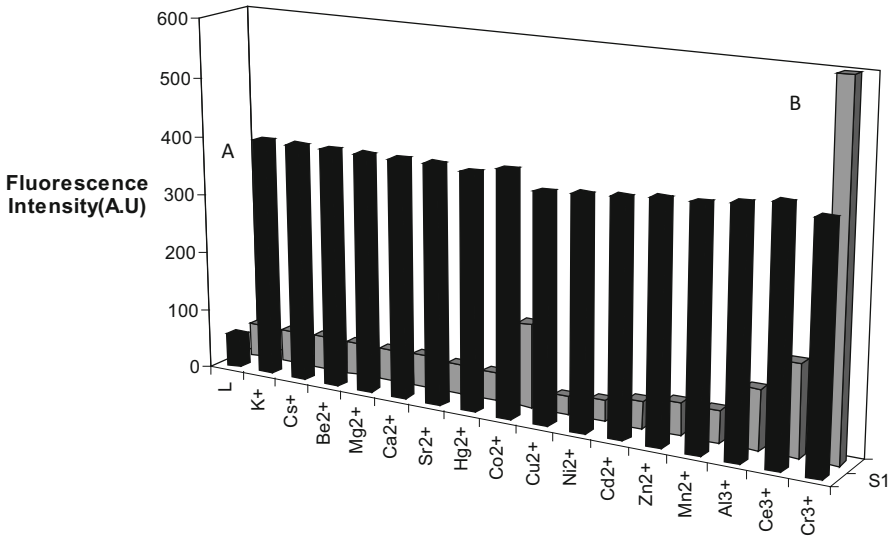


Fig. 6 **a** (*gray*) Fluorescence responses of L (3 ml 5×10^{-6} mol/L) upon addition of cations (50 m mol/L) (λ_{ex}: 553 nm) and **b** (*black*) fluorescence responses of L (3 ml 15×10^{-6} mol/L) containing 30 mmol/L Cr^{3+} and the background cations (30 mmol/L) (λ_{ex}: 553 nm)

Furthermore, the applicability of **L** as a suitable agent for the construction of a Cr^{3+}-selective fluorescent chemosensor was studied through competition experiments through mixing 20 μmol/L of Cr^{3+} with 20 μmol/L of background metal cations (i.e. alkali, alkali earth, transition and heavy metal ions). The results, in terms of the fluorescence intensity of solutions containing both background species, other cations and Cr^{3+}, revealed no noticeable differences compared with solutions merely containing Cr^{3+}, except for Ce^{3+} and Co^{2+}. Since there was a slight fluorescence enhancement before, we can see a synergic effect upon the addition of Cr3+ and additional increase of fluorescence intensity which is in agreement with previous experiments.

Analytical applications

Finally, the proposed fluorescent sensor was used for the determination of traces of Cr^{3+} ions in spiked water samples. According to the procedure, 10.0 mL of each water sample (tap and river water samples, Tehran, Iran) was taken and diluted in a 25.0-mL volumetric flask using distilled water. Then, various quantities of Cr^{3+} (5.0×10^{-7}, 1.0×10^{-6} mol/L) were added to the samples, and the proposed chemosensor was applied to determine the Cr^{3+} content using a calibration method. The results, summarized in Table 2, clearly prove that the chemosensor can be used for the determination of Cr^{3+} in different aqueous samples.

Table 2 Determination of Cr^{3+} ions in water samples and wastewater with the proposed sensor

Sample	Added (ppm)	Found[a] (ppm)	Relative error (%)
Wastewater	5.0×10^{-7}	$(5.4a \pm 0.1) \times 10^{-7}$	8.0
	1.0×10^{-6}	$(0.95 \pm 0.2) \times 10^{-6}$	5.0
River water	5.0×10^{-7}	$(5.30 \pm 0.05) \times 10^{-7}$	6.0
	1.0×10^{-6}	$(1.08 \pm 0.1) \times 10^{-6}$	8.0

[a]Results are based on three measurements

Conclusion

In conclusion, a novel enhancement fluorescent chemosensor, **L**, for Cr^{3+} in (MeCN/H_2O (90:10, %v/v) solution was synthesized and investigated. It showed a selective and sensitive fluorescence response to Cr^{3+}in (MeCN/H_2O (90:10, %v/v) solution. The fluorescence enhancing of **L** is attributed to the 1:1 complex formation between **L** and Cr^{3+} which has been utilized as the basis for the selective detection of Cr^{3+}. Receptor **L** exhibits enhanced fluorescent probe results along a wide concentration range of Cr^{3+} with no interference of background cations.

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