

# A novel rhodamine-based thiacalix[4]arene fluorescent sensor for Fe<sup>3+</sup> and Cr<sup>3+</sup>

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**Abstract** The novel fluorescent sensor **1**, which is comprised of two rhodamine B lactams as fluorophores that are 1,3-alternately linked to a thiacalix[4]arene, behaves as a highly sensitive ion-induced fluorescent sensor for Fe<sup>3+</sup> and Cr<sup>3+</sup>. This compound was synthesized, and its recognition of metal ions was evaluated by fluorescence and absorption spectroscopy. The possible mechanism of Fe<sup>3+</sup>- and Cr<sup>3+</sup>-induced spirocycle opening of **1** leads to fluorescent and colorimetric enhancement, and these properties were investigated by spectroscopy, <sup>1</sup>H NMR and IR. The stoichiometric ratios and association constants of the complexes between **1** and these ions have been measured and calculated, and showed that the presence of Fe<sup>3+</sup> or Cr<sup>3+</sup> induced sensor **1** to form a stable 1:1 complex.

**Keywords** Fluorescent · Colorimetric · Chemosensor · Rhodamine · Thiacalix[4]arene

## Introduction

The design and synthesis of compounds for sensing environmentally and biologically relevant ionic species [1, 2], particularly for heavy metal and transition metal cations, is currently of great interest [3–6]. Many transition metal ions play important roles in various biological systems [7]. Physiologically relevant metal ions include iron and chromium ions, which play indispensable roles in many biochemical processes [8–12]. The trivalent form of iron is an essential element in the human body, as it provides the oxygen-carrying capacity of heme and acts as a cofactor in many enzymatic reactions [13–15]. The trivalent form of chromium is an essential nutrient for human beings, and its deficiency causes disturbances in glucose levels and lipid metabolism [16]. On the other hand, excessive chromium ion levels in the environment are considered to be toxic for biological activities [17–19]. In this regard, highly selective and sensitive chemosensors that monitor iron and chromium ions are an important area of research.

Rhodamine B is highly effective as a fluorescent labeling reagent owing to its excellent spectral properties [20, 21]. Fluorescent chemosensors based on rhodamine B are particularly attractive because they are simple structures with high sensitivity, and they are capable of recognizing specific ions in the presence of related ones [22–24]. This sensing mechanism is based on a change in structure between the spirocyclic and open-cycle forms, and this change is accompanied by changes in fluorescence [25]. Numerous reports have focused on selective and sensitive fluorescent sensors for the detection of transition metal ions [16, 26–30]. However, due to the paramagnetic nature of iron and chromium ions, their presence is mostly signaled by fluorescence quenching [31–34]. Compared to other fluorescent sensors that “turn-on” in the presence of

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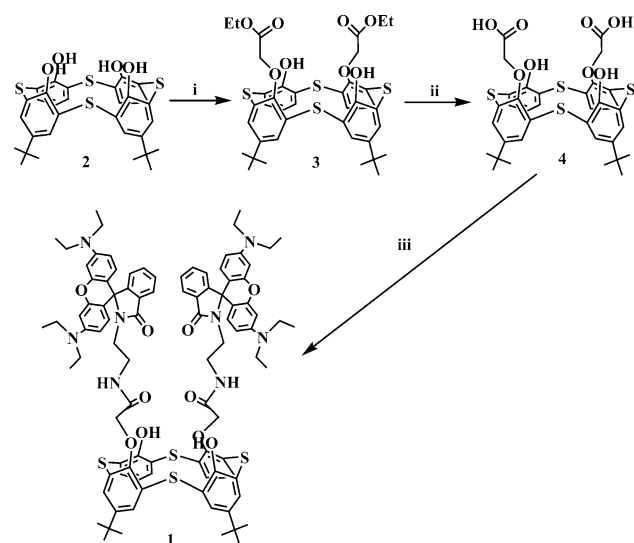
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transition metal ions, few examples employing fluorescent enhancements have been reported for the detection of  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  [35, 36]. Therefore, the development of new fluorescent  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  indicators is still a challenge.

Calixarenes have been investigated as the framework for many sensors due to their flexible structural properties. The different structure of calixarene fluorescence probe display different selectivity [37, 47]. Calixarene-based ligands provide a wide spectrum of metal ion selectivities and serve as convenient scaffolds for the design of fluorescent chemosensors [38] because they show highly selective and sensitive recognition for transition metal ions [39–41]. Most calixarene-based fluorescent sensors have been designed based on photophysical changes upon metal ion binding. The mechanisms of these photophysical changes include photoinduced electron transfer (PET), photoinduced charge transfer (PCT), formation of monomer/excimer, and energy transfer [42, 43]. Most of them are modified by anthracene [39, 40, 44], pyrene [45, 46] and other fluorescent groups [47]. Compared with classical calixarenes, thiacalixarene has a more flexible cavity and additional binding sites due to sulphur atoms that replace a methylene group in classical calixarenes [48, 49] and rarely modified by rhodamine fluorophore, thus these thiacalix[4]arene fluorescent sensors are better at selectively binding to specific metal cations [50–52].

As a continuation of our work in the design and synthesis of chromogenic and fluorogenic chemosensors [53, 54], we report a novel fluorescent sensor based on thiacalix[4]arene that is modified with rhodamine as an ion-induced type sensor. This sensor can simultaneously exhibit a turn-on response to both  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  ions, and it displays strong



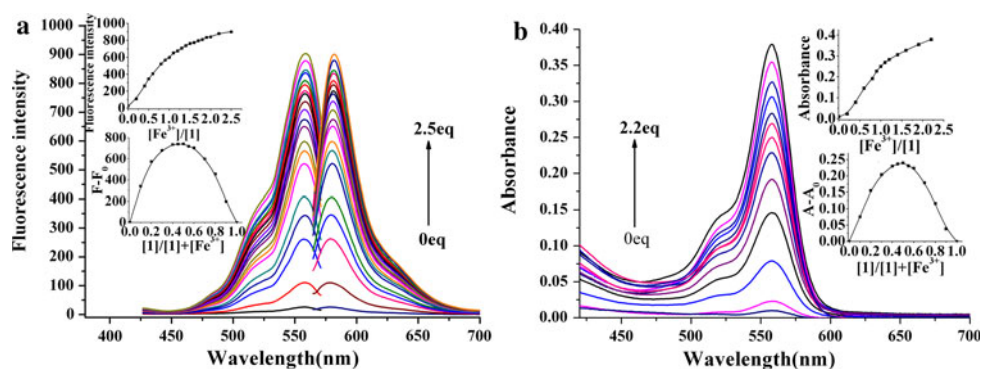
**Scheme 1** **i**  $\text{BrCH}_2\text{COOEt}/\text{Na}_2\text{CO}_3$ , acetone, reflux (46%); **ii** NaOH, EtOH/water, reflux (98%); **iii** rhodamine B-ethylenediamine, HOBt, DCC,  $\text{CH}_2\text{Cl}_2$ , rt (68%)

absorbance and fluorescence intensity enhancement for the two ions. The synthetic route is shown in Scheme 1. Sensor **1** was synthesized by cone 1, 3-bis(hydroxycarbonylmethoxy)thiacalix[4]arene, rhodamine B-ethylenediamine and HOBt in the presence of DCC in  $\text{CH}_2\text{Cl}_2$ .

## Results and discussion

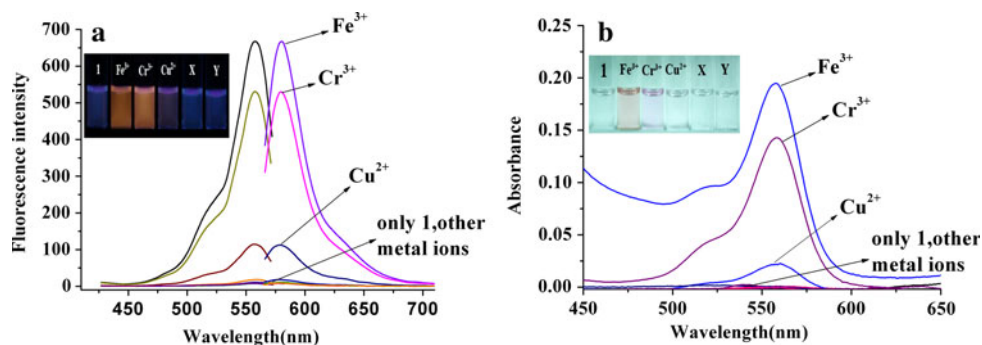
The spectral properties of sensor **1** were studied by fluorescence and UV–vis absorption spectroscopy. Usually, the sensors of rhodamine B derivatives with spiro lactam structures are nonfluorescent, and ring-opening of the spiro lactam gives rise to a strong fluorescence emission. Appropriate pH conditions are necessary for successful operation of the sensor. Acid titration control experiments with a Tris–HCl buffer solution revealed that a solution of **1** in ethanol–water (3:1, v/v) was colorless over a wide pH range (5.0 to 10.0) and did not show obvious fluorescence or absorbance in the visible wavelength range (figure. S1). It is suggested that sensor **1** is suitable for detection in solutions of around pH 6. The solution of free sensor **1** showed very low background fluorescence and absorbance at 557 nm (excitation wavelength) with Tris–HCl buffer (pH 6.0). Addition of  $\text{Fe}^{3+}$  or  $\text{Cr}^{3+}$  to the solution of **1** induced ring-opening of the spiro lactam and gives rise to a significant fluorescence and absorption increase, and a distinct color change ( $\text{Fe}^{3+}$ : from colorless to pink,  $\text{Cr}^{3+}$ : from colorless to light purple. Figure 2, inset) was observed. When a titration of **1** was conducted with  $\text{Fe}^{3+}$  or  $\text{Cr}^{3+}$ , we found that **1** can serve as a “naked-eye” chemosensor that is selective for these two ions in neutral buffer media. Figure 1 depicts the fluorescence spectral change of **1** with increasing amounts of  $\text{Fe}^{3+}$  or  $\text{Cr}^{3+}$ . This result establishes that a 1:1 stoichiometry is reasonable for the binding mode of  $\text{Fe}^{3+}$  or  $\text{Cr}^{3+}$  with **1**, and this model is also supported by the Job’s plot (Fig. 1, inset). The stability constants ( $K_a$ ) based on the 1:1 binding mode were calculated to be  $4.22 \times 10^4$  ( $\text{Fe}^{3+}$ -**1** complex),  $4.22 \times 10^4$  L·mol<sup>-1</sup> ( $\text{Cr}^{3+}$ -**1** complex, fluorescence measured) and  $4.98 \times 10^4$ ,  $1.37 \times 10^4$  L·mol<sup>-1</sup> ( $\text{Cr}^{3+}$ -**1** complex, absorbance measured), showing that **1** has a strong binding ability for  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$ . The fluorescence quantum yields of the  $\text{Fe}^{3+}$ -**1** complex ( $\Phi$ , 0.37) and  $\text{Cr}^{3+}$ -**1** complex ( $\Phi$ , 0.31) were calculated using rhodamine-B ( $\Phi$ , 0.89 in ethanol) as a reference [55].

The fluorescence and UV–visible absorption behavior of the sensor were examined in the presence of various metal ions. It was clear that only the presence of  $\text{Fe}^{3+}$  or  $\text{Cr}^{3+}$  gave enhancement in fluorescence intensity ( $\text{Fe}^{3+}$ : 73-fold,  $\text{Cr}^{3+}$ : 57-fold) and absorption ( $\text{Fe}^{3+}$ : 195-fold,  $\text{Cr}^{3+}$ : 143-fold) with respect to the free solution of sensor **1** (Fig. 2). No changes in the spectral profile or intensity occurred in



**Fig. 1** Changes in **a** fluorescence spectra of **1** ( $6.00 \times 10^{-5}$  mol L $^{-1}$ ) and **b** absorption spectra of **1** ( $6.00 \times 10^{-5}$  mol L $^{-1}$ ) upon addition of Fe $^{3+}$  in ethanol–water (3:1, v/v, Tris–HCl pH 6.0) solution. *Inset a* Change in fluorescence intensity monitored at

580 nm and the Job's plot ( $[1] + [Fe^{3+}] = 2.00 \times 10^{-4}$  mol L $^{-1}$ ), **b** Change in absorbance monitored at 557 nm and under the same conditions



**Fig. 2 a** Fluorescence spectra of **1** ( $2.00 \times 10^{-5}$  mol L $^{-1}$ ) in ethanol–water (3:1, v/v, Tris–HCl pH 6.0) solution in the presence of different metal ions (20 equiv). The solutions of **1** with Fe $^{3+}$  and Cr $^{3+}$  showed obvious fluorescence. The solution of **1** with Cu $^{2+}$  showed a weak fluorescence; Blank **1** and other metal ions (Ni $^{2+}$ ,

Hg $^{2+}$ , Mn $^{2+}$ , Cd $^{2+}$ , Co $^{2+}$ , Zn $^{2+}$ , Na $^{+}$ , K $^{+}$ , Mg $^{2+}$ , Ca $^{2+}$ , Sr $^{2+}$ ) showed no fluorescence. **b** Absorbance spectra of **1** ( $2.00 \times 10^{-5}$  mol L $^{-1}$ ) under the same conditions. *Inset a* Photograph of **1** with different metal ions (X: Ni $^{2+}$ , Hg $^{2+}$ , Mn $^{2+}$ , Cd $^{2+}$ , Co $^{2+}$ , Zn $^{2+}$ ; Y: Na $^{+}$ , K $^{+}$ , Mg $^{2+}$ , Ca $^{2+}$ , Sr $^{2+}$ ). **b** Photograph under 365 nm UV lights

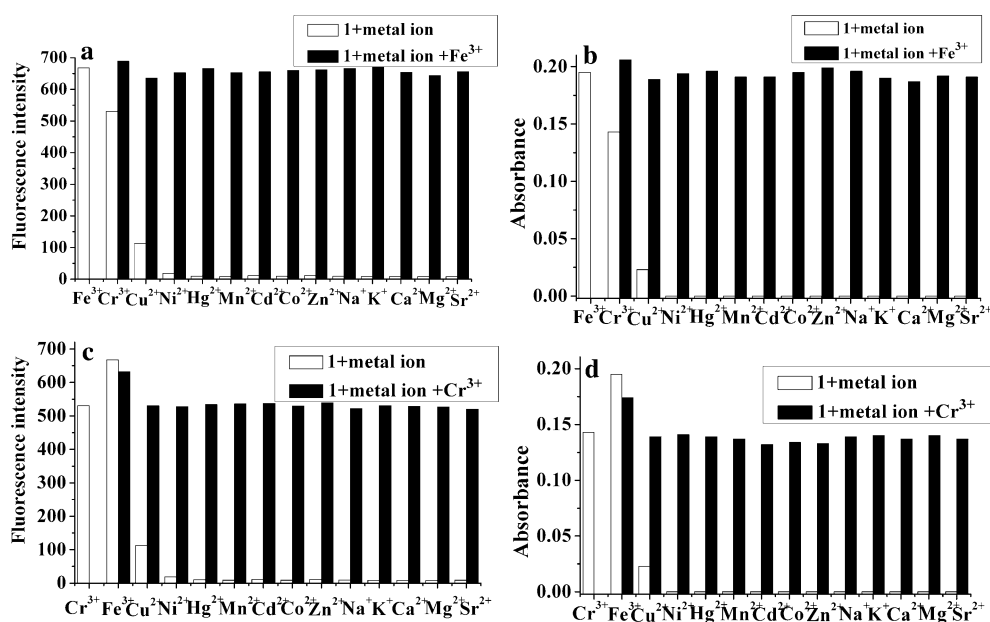
the presence of common metal ions, such as Na $^{+}$ , K $^{+}$ , Ca $^{2+}$ , Mg $^{2+}$ , Sr $^{2+}$ , Co $^{2+}$ , Ni $^{2+}$ , Zn $^{2+}$ , Hg $^{2+}$ , Cd $^{2+}$  and Mn $^{2+}$  under the experimental conditions. However, Cu $^{2+}$  displayed a weak response (Cu $^{2+}$ : 6-fold, 23-fold, fluorescence and absorbance measured values, respectively). These interesting data suggested that the novel rhodamine-thiacalix[4]arene derivative can serve as a “turn on” chemosensor for Fe $^{3+}$  and Cr $^{3+}$ .

Selectivity is a very important parameter for evaluating the performance of a fluorescence sensor. The interference experiments were carried out with excitation fixed at 557 nm and emission at 580 nm. Sensor **1** ( $2.00 \times 10^{-5}$  mol·L $^{-1}$ ) was tested in the presence of 20 equiv of Fe $^{3+}$  mixed with 20 equiv of the aforementioned metal cations (Fig. 3). The increases in fluorescence intensity and absorbance resulting from the addition of Fe $^{3+}$  were not influenced by subsequent addition of miscellaneous cations, with the exception of Cr $^{3+}$ . In this case, the Fe $^{3+}$ -induced **1** spectrum intensity was enhanced; similar results arise from the fluorescence and UV–vis spectra for Cr $^{3+}$ -

induced **1**. The results revealed that the Fe $^{3+}$  (or Cr $^{3+}$ ) induced fluorometric and absorption responses of sensor **1** were unaffected in the presence of test cations.

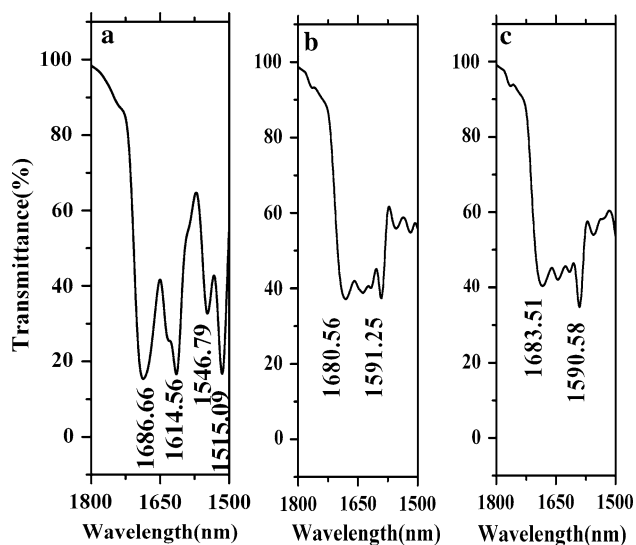
To further investigate the binding mechanism, IR spectra of **1** and the complexes **1**-Fe $^{3+}$  and **1**-Cr $^{3+}$  were measured (Fig. 4). The amide carbonyl absorption of **1** at 1686 cm $^{-1}$  drastically decreases and shifts to lower frequency upon addition of 20 equiv of Fe $^{3+}$  (1591 cm $^{-1}$ ) and Cr $^{3+}$  (1590 cm $^{-1}$ ); these data indicate that the amide carbonyl oxygens of **1** are involved in the coordination of metal cations [27, 30, 56].

For further clarification of the coordination behavior,  $^1\text{H}$  NMR titration of **1** was carried out with Fe $^{3+}$  and Cr $^{3+}$  as shown in Fig. 5. Protons (H $_b$ , H $_c$ , H $_d$ , H $_e$ , H $_j$ ) on sensor **1** shifted downfield upon the addition of the metal cations ( $\Delta\delta = 0.1, 0.42, 0.46, 0.37, 0.1$  ppm upon addition of Fe $^{3+}$ , respectively;  $\Delta\delta = 0.01, 0.06, 0.04, 0.06, 0.01$  ppm upon addition of Cr $^{3+}$ , respectively) and the peaks became broader due to the decrease in electron density of **1**. Protons H $_m$  on **1** displayed upfield shifts ( $\Delta\delta = 0.06$  ppm



**Fig. 3** a Change in the fluorescence intensity at 580 nm of **1** ( $2.00 \times 10^{-5}$  mol L $^{-1}$ ) in ethanol–water (3/1, v/v, Tris–HCl pH = 6.0) solution in presence of Fe $^{3+}$  ( $4.00 \times 10^{-4}$  mol L $^{-1}$ ) upon the addition of  $4.00 \times 10^{-4}$  mol L $^{-1}$  of different metal ions. The white bars represent the emission of **1** in the presence of 20 equiv of the cation of interest. The black bars represents that occurs upon the

subsequent addition of 20 equiv of Fe $^{3+}$  to a solution containing **1** and 20 equiv of the other cation of interest, except the 5 equiv of Cr $^{3+}$ . **b** Change in the absorbance at 557 nm of **1**. Under the same conditions. **c** Change in the fluorescence intensity at 580 nm of **1**–Fe $^{3+}$ . **d** Change in the absorbance at 557 nm of **1**–Cr $^{3+}$



**Fig. 4** Infrared spectra of compound **a** **1**; **b** **1** + Fe $^{3+}$ ; **c** **1** + Cr $^{3+}$

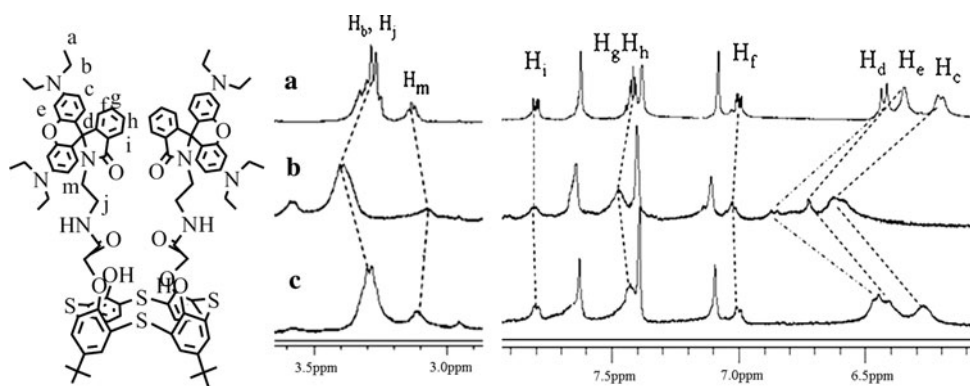
upon addition of Fe $^{3+}$ ;  $\Delta\delta = 0.01$  ppm upon addition of Cr $^{3+}$ ) due to the increase in electron density of **1**. These data suggested that Fe $^{3+}$  and Cr $^{3+}$  induced the formation of the xantheno moiety of the rhodamine. In summary, the IR and  $^1\text{H}$  NMR spectra indicate that the amide carbonyl oxygens in **1** form a chelate ring with Fe $^{3+}$  or Cr $^{3+}$ , and also explain the mechanism by which the Fe $^{3+}$  or Cr $^{3+}$  ion induces ring-opening of the spirolactam in **1**.

In addition, the diethylenetriamine-adding experiments were conducted to examine the reversibility of this reaction (Scheme 2). It was observed that addition of 30 equiv of diethylenetriamine to a solution of **1** with 20 equiv of Fe $^{3+}$  (or Cr $^{3+}$ ) caused an immediate disappearance of both the pink color and the orange fluorescence; followed 30 equiv of Fe $^{3+}$  (or Cr $^{3+}$ ) was added to the solution, the color and the fluorescence appeared again. These results indicated that **1** was a reversible chemosensor for Fe $^{3+}$  and Cr $^{3+}$  [27, 57, 58].

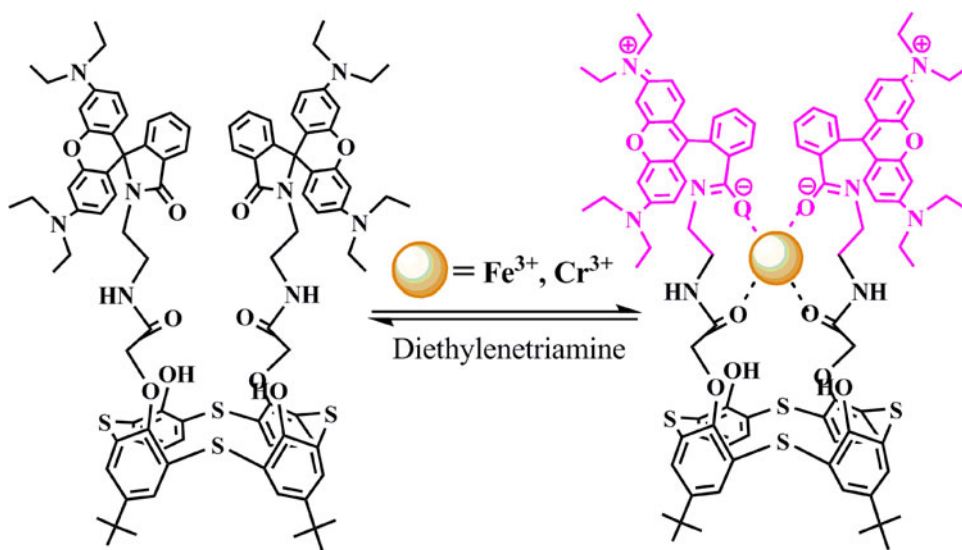
The possible mechanism for these fluorescent changes is shown in Scheme 2. Linking with two rhodamine functional groups, thiacalix[4]arene as an perfect construction platform, provided a three-dimensional structures to facilitate the coordination of metal ions by side-chain and rhodamine regiment. The two binding sites (the rhodamine amide carbonyl oxygen and the thiacalix[4]arene amide carbonyl oxygen) in **1** form a chelate ring with cation [30]. At the same time, the moiety of thiacalix[4]arene also played a role in shielding other metal ions. This appropriate structure enhanced the recognition ability and selectivity for Fe $^{3+}$  or Cr $^{3+}$ . Modification of calixarenes with different functional groups can obtain different properties, and have been confirmed by other scholars and our preliminary job [54].

Under the optimized conditions, the fluorescent responses of sensor **1** were calculated to cover a linear range from  $5.00 \times 10^{-6}$ – $6.00 \times 10^{-5}$  mol•L $^{-1}$  and  $4.00 \times 10^{-6}$ – $1.00 \times 10^{-5}$  mol•L $^{-1}$  for Fe $^{3+}$  and Cr $^{3+}$ ,

**Fig. 5** Partial  $^1\text{H}$  NMR (400 MHz) spectra of **1** measured in  $\text{CDCl}_3:\text{CD}_3\text{CN}$  (4/1, v/v) (a) signified without metal cations and (b) signified with 1 equiv  $\text{Fe}^{3+}$ , (c) signified with 1 equiv  $\text{Cr}^{3+}$



**Scheme 2** Proposed binding structure of **1** to metal cation



respectively. The detection limits were  $3.50 \times 10^{-8}$  and  $1.60 \times 10^{-7} \text{ mol}\cdot\text{L}^{-1}$  (based on  $S/N = 3$ ), and the relative standard deviation (RSD) for five repeated measurements were 2.4% and 2.4%, respectively. The linear ranges for the absorption responses of sensor **1** were  $5.00 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ – $1.00 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$  and  $1.00 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ – $1.50 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$  for  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$ , respectively. The detection limits were  $1.60 \times 10^{-7}$  and  $5.00 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ , and the RSDs for five repeated measurements were 2.1 and 2.5%, respectively.

To study the practical applicability, sample of  $\text{Fe}^{3+}$ - or  $\text{Cr}^{3+}$ -polluted water (synthetic samples) were analyzed by the proposed fluorescence and absorption method (Table 1). The results show satisfactory recovery and RSD values for the sample. Prepared sample: tap water,  $2.00 \times 10^{-5} \text{ mol L}^{-1} \text{ Fe}^{3+}$  or  $\text{Cr}^{3+}$ ,  $2.00 \times 10^{-4} \text{ mol L}^{-1}$  **1**,  $[\text{Tris-HCl}] = 4.5 \times 10^{-3} \text{ mol L}^{-1}$  (pH = 6.0), ethanol–water (3/1, v/v) solution. a, b: The data were obtained from fluorometric and absorbance measurement method, respectively,  $n = 3$ .

## Experimental section

### Apparatus and reagents

Absorbance spectra measurements were performed on an Ultrospec 5300 pro UV–visible spectrophotometer (Amersham Biosciences). Fluorescence spectra measurements were acquired on a Cary Eclipse fluorescence spectrophotometer (Varian). NMR spectra were recorded on a Nova-400 spectrometer (Varian) at 293 K. IR spectra were recorded on a Vertex 70 FT-IR spectrometer (Bruker). ESI-MS spectra were obtained on an Agilent LC/MSD spectrometer (Agilent) without using the LC part. Melting points were determined on an electrothermal melting point apparatus (X-5, Gongyi Yuhua Co., Ltd.) and are uncorrected. All reagents were supplied by Aldrich, Alfa Aesar Chemical Co., Ltd., and Chengdu Chemical Reagent Co. Analytical grade chemicals are commercially available and were used without further purification. Doubly distilled water was used in all experiments.

**Table 1** Analytical results of synthetic water samples

Sample	Fe <sup>3+</sup> /Cr <sup>3+</sup> added (10 <sup>-6</sup> mol•L <sup>-1</sup> )	Fe <sup>3+</sup> /Cr <sup>3+</sup> found (10 <sup>-7</sup> mol•L <sup>-1</sup> )	Recovery (%)		RSD (% , n = 3)	
Prepared sample Fe <sup>3+</sup>	0.00	18.96 <sup>a</sup> 18.77 <sup>b</sup>	95 <sup>a</sup>	94 <sup>b</sup>	5.3 <sup>a</sup>	5.2 <sup>b</sup>
	10.00	30.05 <sup>a</sup> 28.57 <sup>b</sup>	100 <sup>a</sup>	95 <sup>b</sup>	4.1 <sup>a</sup>	4.9 <sup>b</sup>
	20.00	41.69 <sup>a</sup> 41.83 <sup>b</sup>	104 <sup>a</sup>	105 <sup>b</sup>	3.8 <sup>a</sup>	4.3 <sup>b</sup>
	30.00	49.87 <sup>a</sup> 54.22 <sup>b</sup>	100 <sup>a</sup>	108 <sup>b</sup>	4.4 <sup>a</sup>	5.1 <sup>b</sup>
Prepared sample Cr <sup>3+</sup>	0.00	20.11 <sup>a</sup> 20.96 <sup>b</sup>	101 <sup>a</sup>	105 <sup>b</sup>	3.7 <sup>a</sup>	4.4 <sup>b</sup>
	25.00	46.33 <sup>a</sup> 43.05 <sup>b</sup>	103 <sup>a</sup>	96 <sup>b</sup>	3.3 <sup>a</sup>	3.9 <sup>b</sup>
	50.00	69.06 <sup>a</sup> 68.85 <sup>b</sup>	99 <sup>a</sup>	98 <sup>b</sup>	3.7 <sup>a</sup>	3.8 <sup>b</sup>
	70.00	87.98 <sup>a</sup> 93.41 <sup>b</sup>	98 <sup>a</sup>	104 <sup>b</sup>	3.2 <sup>a</sup>	3.1 <sup>b</sup>

<sup>a</sup>(Fe<sup>3+</sup>), <sup>b</sup>(Cr<sup>3+</sup>): The data were obtained from fluorometric and absorbance measurement method, respectively, n = 3

Intermediate products **3** and **4** were synthesized according the reported method [16].

### Synthesis of **1**

A mixture of **4** (500 mg, 0.6 mmol), Rhodamine B-ethylenediamine (1.6 g, 3 mmol) and HOBt (0.8 g, 3 mmol) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (30 mL) under a N<sub>2</sub> atmosphere. Then DCC (0.64 g, 3 mmol) was added as a solution in 15 mL CH<sub>2</sub>Cl<sub>2</sub> at 0–5 °C, and the mixture was stirred for 48 h at room temperature. The reaction solution was filtered, the filtrate was concentrated, and the crude product was purified by column chromatography (silica gel, CHCl<sub>3</sub>/acetone, v/v, 10:1) to afford **1** as a light red solid (0.72 g, 68%). m.p. 201–203.5 °C. IR (KBr, cm<sup>-1</sup>) ν: 3395(OH), 2968 (CH), 1684 (C=O); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), δ (ppm): 0.82 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.11 (t, 12H, J = 6.8 MHz, NCH<sub>2</sub>CH<sub>3</sub>), 1.30 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 3.12 (q, 2H, J = 6.4 MHz, NCH<sub>2</sub>CH<sub>2</sub>NH), 3.28 (q, 10H, J = 6.4 MHz, NCH<sub>2</sub>CH<sub>3</sub>), 4.78 (s, 1H, OCH<sub>2</sub>CO), 6.18 (d, 2H, J = 8.8 MHz, Xanthene-H), 6.34 (s, 2H, Xanthene-H), 6.41 (t, 2H, J = 8.4 MHz, Xanthene-H), 6.96 (s, 1H, Ar-H), 7.03 (d, 1H, J = 6.0 MHz, Ar-H), 7.38 (s, 2H, Ar-H), 7.59 (s, 1H, Ar-H), 7.82 (d, 1H, J = 4.0 MHz, Ar-H); <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>), δ (ppm): 169.2, 168.5, 156.2, 155.9, 153.9, 153.3, 148.8, 148.2, 142.7, 134.7, 133.1, 128.8, 128.6, 123.8, 123.1, 122.1, 108.3, 105.2, 97.9, 73.9, 65.3, 44.4, 39.6, 34.2, 34.1, 31.6, 30.8, 12.7; ESI-MS m/z: 1791.81 (M + Na)<sup>+</sup>; Anal. calcd for C<sub>104</sub>H<sub>120</sub>N<sub>8</sub>O<sub>10</sub>S<sub>4</sub>: C 70.56, H 6.83; N 6.33, O 9.04; found C 70.42, H 6.88; N 6.30, O 9.14.

### Conclusions

We reported a rhodamine-based thiocalix[4]arene derivative. This ion-induced sensor exhibits fluorescence and colorimetric responses toward Fe<sup>3+</sup> and Cr<sup>3+</sup> in aqueous ethanol solution with high sensitivity. Similar to many reported rhodamine-spirolactam-based fluorescent sensors,

the fluorescence and colorimetric responses of sensor **1** toward the two ions are most likely the result of the reversible spiro ring-opening mechanism. The sensor shows almost unchanged responses to Fe<sup>3+</sup> and Cr<sup>3+</sup> before and after addition of other interfering metal ions. This result illustrates that the response of the sensor is unaffected by the presence of the other metal ions and that the fluorescence of sensor **1** is sensitive (detection limit about 10<sup>-8</sup>–10<sup>-7</sup> mol•L<sup>-1</sup>) and selective for the presence of Fe<sup>3+</sup> and Cr<sup>3+</sup>. In addition, this sensor can be used in colorimetric assays and meet the sensitive requirements for biomedical and environmental monitoring application.

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