

A Sensitive Colorimetric and Ratiometric Chemosensor for Trivalent Metal Cations

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Abstract A novel hydroxyethyl piperazine functionalized cyanine derivative was designed and synthesized. It presents selective colorimetric as well as ratiometric absorption responses to trivalent metal cations (Cr^{3+} , Fe^{3+} and Al^{3+}) over a variety of divalent and monovalent metal cations in 3:7 ethanol-water solution. Detection limits of this method for Cr^{3+} , Fe^{3+} and Al^{3+} were 3.99 μM , 4.30 μM and 1.85 μM , respectively. The recognition mechanism was attributed to the protonation of the organic probe, which blocked the photoinduced electron transfer (PET) process. In addition, the sensor was also successfully applied to the determination of Cr^{3+} in prepared samples.

Keywords Colorimetric sensor · Ratiometric chemosensor · Trivalent metal cations · Aminocyanine derivative · Hydroxyethyl piperazine

Introduction

Trivalent metal cations (M^{3+}) such as Fe^{3+} , Cr^{3+} and Al^{3+} have been intensively studied due to their own environmental

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importance and biological significance [1–3]. For example, Fe^{3+} , the most abundant transition metal in cellular system, is indispensable for most organisms due to its presence in numerous enzymes and proteins [2]. Its deficiency or excess has been demonstrated to be associated with a various of diseases, such as anemia, low immunity [4, 5] and Alzheimer [6, 7]. As an essential micronutrient for mammals, Cr^{3+} has an impact on the metabolism of carbohydrates, fats, proteins and nucleic acids as it activates certain enzymes and stabilizes proteins and nucleic acid [3, 8]. Both deficiency and high levels of Cr^{3+} can induce various disorders, such as disturbances in glucose levels and lipid metabolism [9]. Meanwhile, the industrial discard of Cr^{3+} causing serious environmental pollution is a matter of great concern in agriculture [3, 10]. As to Al^{3+} , both deficiency and excess of Al^{3+} has also been linked with several serious diseases [11]. And the increase of Al^{3+} caused by acidic rain and human activities is detrimental to plants [10]. Thus, highly sensitive and reliable approaches to the detection of M^{3+} are desired.

Compared with numerous traditional analytical techniques, small-molecule optical sensors display a sight of merits like high sensitivity, selectivity, simplicity, tunability and direct visualization, thus have been developed as a powerful tool for detecting the trace amount of analytes. However the chemosensors for recognition of Al^{3+} , Fe^{3+} and Cr^{3+} is still few, especially simultaneously detecting all of these trivalent cations by single sensor is scarcely reported [3, 12, 13]. More recently, Tang and Das [10] have developed a new method for the detection of these ions, in which the fluorescence responses were attributed to the higher hydrolyzing ability of M^{3+} over M^{2+} and M^{+} . However, the probe with short absorption wavelength is likely to be subject to several problems (such as the interference from other analytes' absorption) and hinders its further application and development. In consequence, designing a novel optical sensor with high

selectivity and excellent sensitivity is of considerable importance and significant interest.

Here we designed and synthesized a near-infrared (NIR) aminocyanine derivative as a colorimetric and ratiometric chemosensor for M^{3+} , which bears a hydroxyethyl piperazine moiety acting as the selective indicator of M^{3+} . The probe presents remarkable color change as well as ratiometric absorption response in the presence of M^{3+} (Cr^{3+} , Fe^{3+} and Al^{3+}) in 3:7 ethanol-water solution. The selective colorimetric and ratiometric responses were attributed to the consequence of protonation of the probe. These features were utilized for quantitative detection of M^{3+} over a variety of divalent and monovalent metal cations in prepared samples and gave ideal recovery percentages, manifesting its high potential for practical application.

Experimental

Reagents and Apparatus

Ethyl-3-bromopropionate and $POCl_3$ were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). *N*-(2-hydroxyethyl) piperazine was obtained from Yantai Peiyang Fine Chemical Co. Ltd. (Shandong, China). Wahaha purified water was purchased from the local supermarket. DMSO and DMF were purified by refluxing with calcium hydride for 4 h and then distilled. The other reagents were of analytical-reagent grade and used without further purification. Distilled water was used throughout this study.

1H and ^{13}C NMR were performed on Bruker Avance 600 MHz spectrometer, using TMS as an internal standard. Mass spectrometry (MS) was obtained from the Thermo Fisher Scientific LCQ Advantage Max. High-resolution mass spectra were acquired on the Bruker Paltonics micro TOF-Q II instrument. All pH measurements were recorded on the Sartorius basic pH-meter PB-10. UV-Vis spectra were measured on the Evolution 300 UV-Visible spectrophotometer. Fluorescence spectra were recorded on the VARINA Eclipse fluorescence spectrophotometer. All measurements were carried out at room temperature under ambient atmosphere.

Preparation of Solutions

A stock solution of probe (1×10^{-3} M) was prepared by dissolving the required amount of TM (0.0075 g) in ethanol and diluting it to the mark in a 10 mL volumetric flask. Further dilution yielded the working solution (1×10^{-5} M) by diluting 2.5 mL of stock solution to 250 mL with ethanol-water (3:7, *V/V*). Stock solutions of cations (1×10^{-3} M) were made from their chloride salts except Al^{3+} (nitrate salt) in distilled water. In experiments, the test samples were prepared by adding the appropriate amount of the stock solutions of cations to

working solution (5 mL). In titration experiments, working solution (9 mL) was added to a 10 mL volumetric flask, to which different equivalents of cation stock solutions were respectively added using a micropipettor, and then it was diluted to the mark with distilled water. For all measurements, the excitation and emission slit widths were both 5 nm and the excitation wavelength was 760 nm.

Calculation of Detection Limit

The detection limits were calculated on the basis of the UV-Vis titrations. The UV-Vis absorption spectrum of the probe was measured 11 times, and the standard deviation of blank measurement was obtained. To gain the slope, the ratio of the absorbance at 760 nm to that at 678 nm (named as $A_{760/678}$) was plotted as a concentration of M^{3+} (Fe^{3+} , Cr^{3+} and Al^{3+}). The detection limits were calculated using the following equation [3, 14, 15]:

$$\text{Detection limit} = \frac{3\sigma}{\kappa}$$

Where σ is the standard deviation of blank measurement, and κ is the slope between the $A_{760/678}$ versus the concentration of M^{3+} ($[M^{3+}]$).

Synthesis

The synthesis of the probe is described in scheme 1.

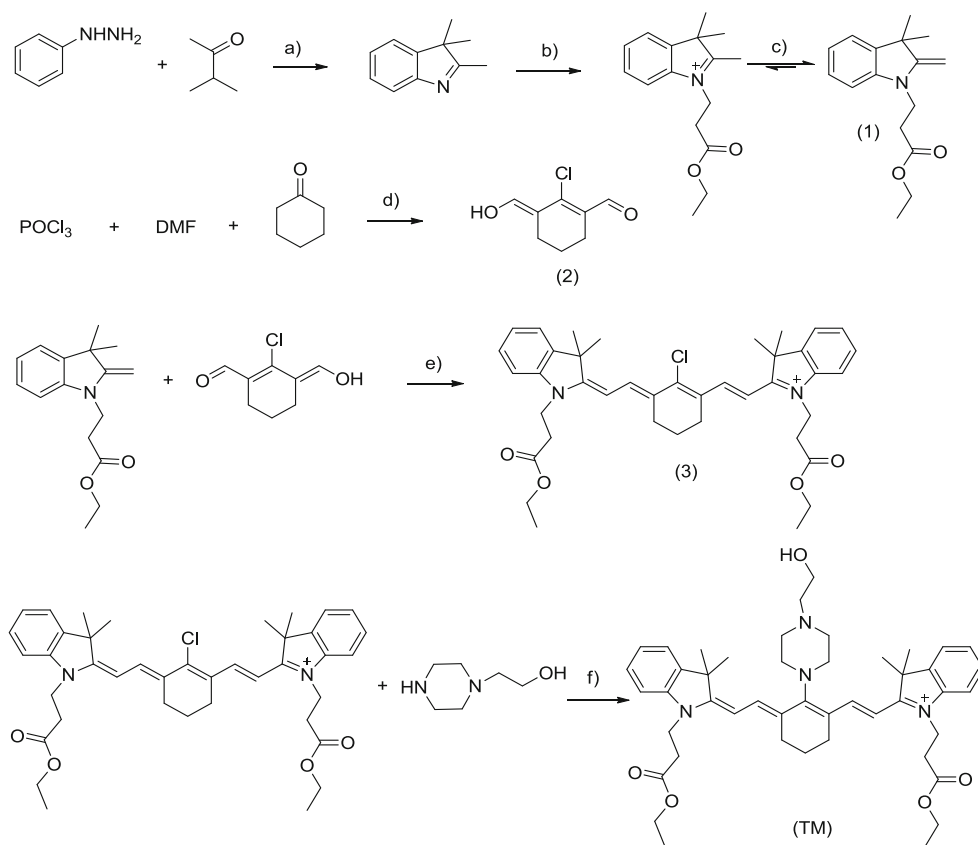
Ethyl-3-(3,3-dimethyl-2-methyleniodolinl-yl)-propionate (compound **1**) and 2-chloro-1-formyl-3-(hydroxymethylene)-cyclohex-1-ene (compound **2**) were prepared according to our previously reported method [16].

Compound **3**: A mixture of compound **1** (2.59 g, 10 mmol) and compound **2** (0.86 g, 5 mmol) in ethanol (30 mL) was stirred under reflux for 3 h in N_2 atmosphere. After cooling to room temperature, the solvent was removed to afford a violet solid. The residue was purified by flash chromatography with gradient elution (petroleum ether/ethyl acetate=3:1 to dichloromethane/methanol=20:1, *V/V*) affording compound **3** as a green powder (2.26 g, 69.01 %).

1H NMR ($CDCl_3$, 600 MHz) δ : 8.35 (2H, d, $J=13.8$ Hz, -CH=CH-), 7.40 (2H, t, $J=7.8$ Hz, ArH), 7.38 (2H, d, $J=7.2$ Hz, ArH), 7.30 (2H, t, $J=7.8$ Hz, ArH), 7.25 (2H, t, $J=7.2$ Hz, ArH), 6.40 (2H, d, $J=14.4$ Hz, -CH=CH-), 4.62 (4H, t, $J=6.6$ Hz, CH_2), 4.08 (4H, t, $J=7.2$ Hz, CH_2), 2.94 (4H, t, $J=6.6$ Hz, CH_2), 2.77 (4H, t, $J=6$ Hz, CH_2), 2.00~1.91 (2H, m, CH_2), 1.72 (12H, s, CH_3), 1.18 (6H, t, $J=7.2$ Hz, CH_3).

^{13}C NMR ($CDCl_3$, 150 MHz) δ : 172.37, 170.77, 150.64, 144.43, 141.80, 140.87, 128.85, 128.16, 125.45, 122.22, 111.19, 102.00, 61.32, 49.32, 40.58, 32.20, 28.15, 26.52, 20.74, 14.03.

Scheme 1 Synthesis of the probe. Reagents and conditions: a) 100 °C, 2 h, then acetic acid, reflux, 5 h; b) ethyl-3-bromo propionate, 100 °C, 5 h; c) 1 M NaOH, r.t., 2 h; d) CH₂Cl₂, ice bath, then cyclohexanone was added, 80 °C, 3 h; e) ethanol, reflux, 3 h, N₂ atmosphere; f) DMF, 60 °C, 3 h, N₂ atmosphere



HRMS (ESI Positive) calc. for C₄₀H₄₈ClN₂O₄⁺, [M+H]⁺ 655.3303, found 655.3327.

TM: To a DMF (20 mL) solution of intermediate **3** (2.00 g, 3.05 mmol), TEA (485 μL, 3.50 mmol) and *N*-(2-hydroxyethyl) piperazine (0.78 g, 5.99 mmol) were added, and then the resulting mixture was stirred at 60 °C for 3 h in N₂ atmosphere. After cooling to room temperature, the mixture was poured into water (100 mL). The precipitate was collected by filtration and purified by flash chromatography with gradient elution (petroleum ether/ethyl acetate=3:1 to dichloromethane /methanol =20:1) to obtain the title compound (TM) as a blue solid (1.81 g, 79.18 %).

¹H NMR (MeOD, 600 MHz) δ: 7.73 (2H, d, *J*=13.2 Hz, -CH=CH-), 7.44 (2H, t, *J*=7.8 Hz, ArH), 7.36 (2H, d, *J*=7.8 Hz, ArH), 7.16 (4H, t, *J*=7.2 Hz, ArH), 6.04 (2H, d, *J*=14.4 Hz, -CH=CH-), 4.34 (4H, t, *J*=6.6 Hz, CH₂), 4.09 (4H, q, *J*=7.2 Hz, CH₂), 3.92 (4H, s, CH₂), 3.82 (2H, t, *J*=5.4 Hz, CH₂), 2.96 (4H, s, CH₂), 2.82~2.78 (6H, m, CH₂), 2.58 (4H, t, *J*=6.6 Hz, CH₂), 1.90~1.87 (2H, m, CH₂), 1.70 (12H, s, CH₃), 1.18 (6H, t, *J*=7.2 Hz, CH₃).

¹³C NMR (CDCl₃, 150 MHz) δ: 170.87, 168.52, 145.05, 142.01, 141.14, 140.10, 128.39, 124.24, 123.78, 122.37, 110.65, 109.17, 95.84, 61.34, 64.47, 48.10, 39.31, 31.66, 30.96, 29.68, 29.05, 24.79, 21.66, 14.09.

HRMS (ESI Positive) calc. for C₄₆H₆₁N₄O₅⁺, [M+H]⁺ 749.4642, found 749.4636.

Results and Discussion

Design of the Probe

Considering the stronger hydrolyzing ability of M³⁺ [17] and the better response of aminocyanine bearing a diamine moiety for protons [18] and also the higher affinity of hydroxyethyl piperazine for Cr³⁺ [3], we employed an aminocyanine bearing a hydroxyethyl piperazine moiety to construct the chemosensor for M³⁺ cations. Therefore, hydroxyethyl piperazine-substituted aminocyanine was designed and synthesized via simple synthetic steps. The structures of target compound (TM) and intermediates were confirmed by ¹H NMR, ¹³C NMR and ESI-MS analysis (Figs. S1, S2, S3, S4, S5 and S6 in the Supporting Information). The feasibility and mechanism of the designed probe for naked-eye detection of M³⁺ will be demonstrated in the following sections.

Specificity

A significant feature of a sensor is its high selectivity towards specific analyte over others. Hence, the selectivity of the sensor for trivalent metal cations (such as Al³⁺, Fe³⁺ and Cr³⁺) over a variety of divalent cations (such as Ba²⁺, Ca²⁺, Co²⁺,

Cu^{2+} , Mg^{2+} , Mn^{2+} , Ni^{2+} and Zn^{2+}) and monovalent cations (such as Na^+ , K^+ and Ag^+) was initially examined in ethanol-water solution (3/7, V/V). As shown in Fig. 1, there were no significant changes in the nature of absorption spectra even upon addition of 10 equiv. of divalent cations (M^{2+}) or monovalent cations (M^+) respectively. However, upon interaction of the sensor with trivalent cations, a drastic red shift of the absorption spectrum occurred: a new absorption peak emerged at around 760 nm, while the absorption peak at 678 nm obliterated. Furthermore, this change was also accompanied with a variation of the solution's color from violet-blue to almost colorless. This indicated that this probe could be served as a naked-eye indicator for M^{3+} . The photography of the probe upon addition of the metal ions respectively was shown in Fig. 2. Subsequently, the fluorescence emission spectra of the probe with metal ions were studied. As shown in Fig. 3, the emission maximum and the fluorescence intensity slightly changed after treatment with M^{3+} , while other metal ions (such as Mg^{2+}) caused no significant change. Compared to the variations in absorption spectra, the fluorescent responses were unremarkable. Hence, only the UV-Vis spectrum was chosen for the further discussion.

High selectivity for the analyte over other competitive species coexisting in real sample is another important feature to evaluate the performance of a chemosensor. Hence, the tolerances of the probe towards M^{3+} over other metal ions were investigated and Cr^{3+} was used as a representative. The competitive experiments were carried out in the presence of 5 equiv. of Cr^{3+} mixed with 5 equiv. of miscellaneous metal ions, including Ba^{2+} , Ca^{2+} , Co^{2+} , Cu^{2+} , Mg^{2+} , Mn^{2+} , Ni^{2+} , Zn^{2+} , Na^+ , K^+ and Ag^+ , respectively. Compared with the probe with Cr^{3+} , there were no distinct variations in the absorption spectra of the probe with the mixture of Cr^{3+} and other interfering metal ions. The absorbance of the solution at 760 nm (absorption maxima) is shown in Fig. 4. Similar

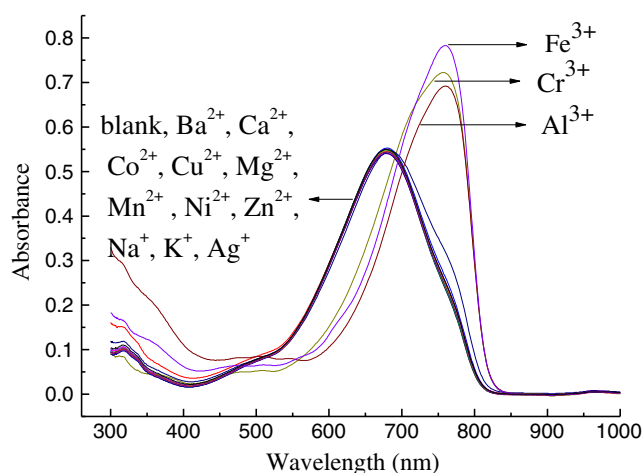


Fig. 1 UV-visible spectra of the probe (10^{-5} M) in the presence of 10 equiv. of different metal ions in 3:7 ethanol-water solutions

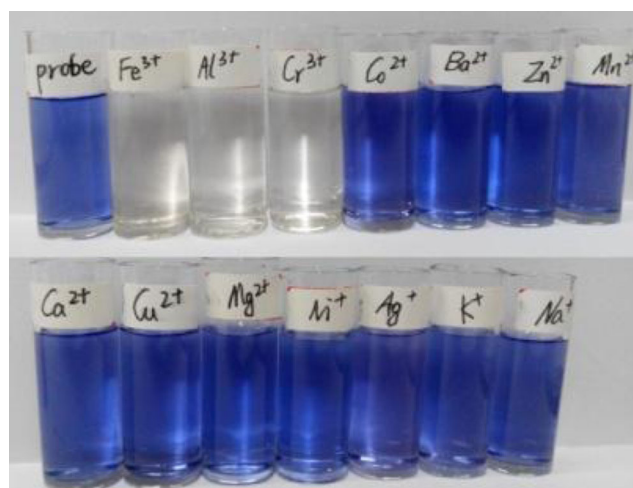


Fig. 2 Visual color change observed in 3:7 ethanol-water solution of the probe (10^{-4} M) after additional of 10 equiv. of different metal ions, respectively

results were obtained in the case of Fe^{3+} and Al^{3+} . The above results further confirmed that the probe had potential application for selective colorimetric detection of M^{3+} .

In order to show this performance more visually, the selectivity of the probe towards Fe^{3+} , Al^{3+} and Cr^{3+} was calculated via a selectivity coefficient ($K_{\text{Fe}^{3+}/\text{Al}^{3+}/\text{Cr}^{3+}} = S_{\text{Fe}^{3+}/\text{Al}^{3+}/\text{Cr}^{3+}} / S_0$, where $S_{\text{Fe}^{3+}/\text{Al}^{3+}/\text{Cr}^{3+}}$ was the response to Fe^{3+} , Al^{3+} and Cr^{3+} , and S_0 was the response to other cations [1, 19]. The selectivity coefficients of Fe^{3+} , Al^{3+} and Cr^{3+} measured against other test cations were listed in Table S1 (Supporting Information). The coefficients clearly indicated that the probe had higher selectivity for M^{3+} than other cations. And the excellent sensitivity of the probe towards M^{3+} lays a foundation for its application as an effective metal ions chemosensor.

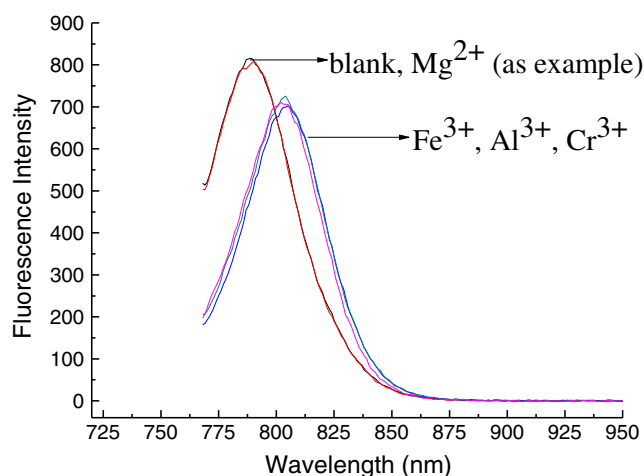


Fig. 3 Fluorescence spectra of the probe (10^{-5} M) in 3:7 ethanol-water solutions upon addition of 10 equiv. of Fe^{3+} , Al^{3+} , Cr^{3+} or Mg^{2+} , respectively

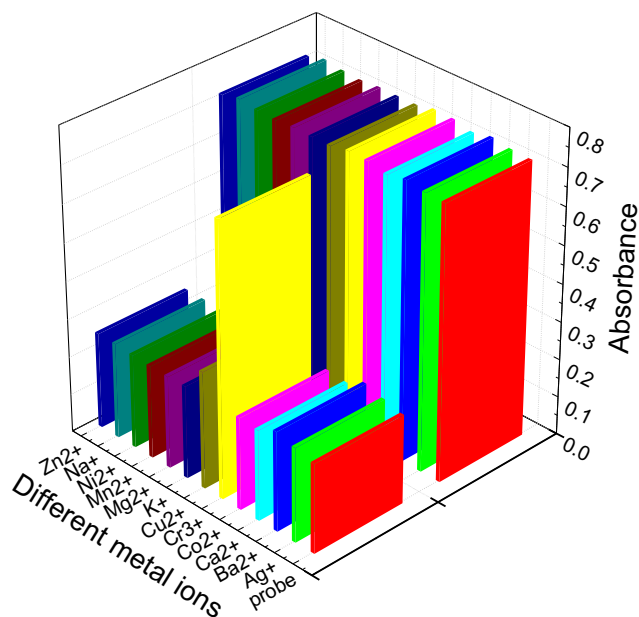


Fig. 4 The relative absorbance at 760 nm of probe (10⁻⁵ M) in the presence of 5 equiv. of different metal ions (front row), and upon addition of 5 equiv. of Cr³⁺ (back row)

Detection Limit and Sensitivity

To obtain a quantitative appraisal of the probe’s selectivity to trivalent metal ions, UV-Vis titration in ethanol-water (3/7, V/V) solution with 10⁻⁵-10⁻⁴ M of Cr³⁺ (10⁻⁶-10⁻⁴ M of Fe³⁺ and 10⁻⁵-10⁻⁴ M of Al³⁺) were investigated. As an evidence from a representative results obtained with Cr³⁺, incremental addition of Cr³⁺ resulted in a gradual reduction in absorbance of the absorption peak at 678 nm, meanwhile, a new absorption peak appeared at 760 nm, and its absorbance gradually increased along with the observation of an isobestic point at 686 nm. The absorption peak at 760 nm approached the saturation when 5 equiv. of Cr³⁺ was added (As shown in Fig. 5). Similar trends

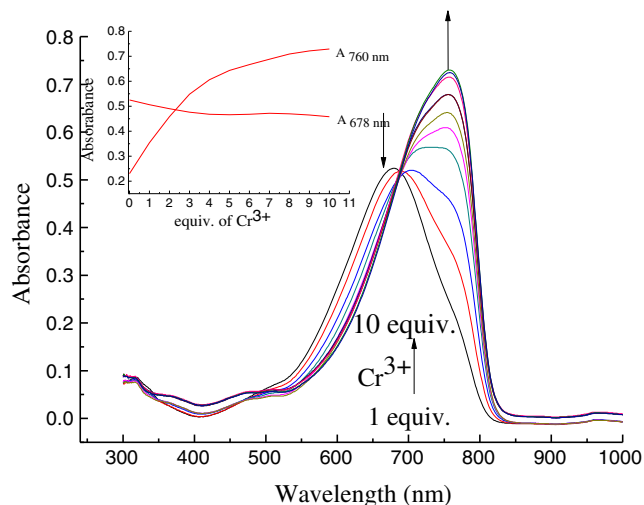


Fig. 5 UV-visible spectra of the probe (10⁻⁵ M) upon addition of Cr³⁺ in 3:7 ethanol-water solutions

were also observed in Fe³⁺ and Al³⁺ (As shown in Figs. S7 and S8, Supporting Information).

It known that changes at two wavelengths provide an interesting opportunity for the ratiometric determination of analytes, which could eliminate the interference from instrumental efficiency and environmental conditions through the self-calibration of two absorption peaks [20]. Hence, to improve the sensitivity of the developed method for M³⁺, we used the ratio of the absorbance at 760 nm to that at 678 nm (named as A_{760/678}) as the foundation for quantitative analysis. The ratio of absorbance at 760 nm and 678 nm (A_{760/A678}) was enhanced from 0.45 to 1.58 for Cr³⁺, and it varied from 0.44 to 2.02 for Fe³⁺, 0.78 to 1.9 for Al³⁺. As shown in Fig. 6, A_{760/A678} increased linearly with the concentration of Cr³⁺ in the range of 0–30 μM by a calibration function of A_{760/A678}= 0.238 [Cr³⁺]+0.448 ([Cr³⁺] is the equiv. of Cr³⁺, R²= 0.9996). The limit of detection for Cr³⁺ was 3.99×10⁻⁶ M. A similar trend was also observed in Fe³⁺ and Al³⁺ (Fig. S9, Supporting Information). The detection limit emerged to be 1.85×10⁻⁶ M for Fe³⁺ and 4.30×10⁻⁶ M for Al³⁺. These results strongly indicated that this probe could be served as a trace level determination method for M³⁺.

Time Response

As a sensor, stability and real-time detection are necessary. Thus, the time evolution of the probe’s responses in the presence of 5.0 equiv. of M³⁺ in ethanol-water (3/7, V/V) solution and the kinetic characteristic of the reaction systems were investigated. The results showed that, upon the reaction of the probe with M³⁺, the color of all the tested solutions remarkably changed and dramatic red shifts of the absorbance maxima appeared within the first 2 min. Furthermore, no obvious absorbance variations of the tested solutions were observed over a period of 2 h.

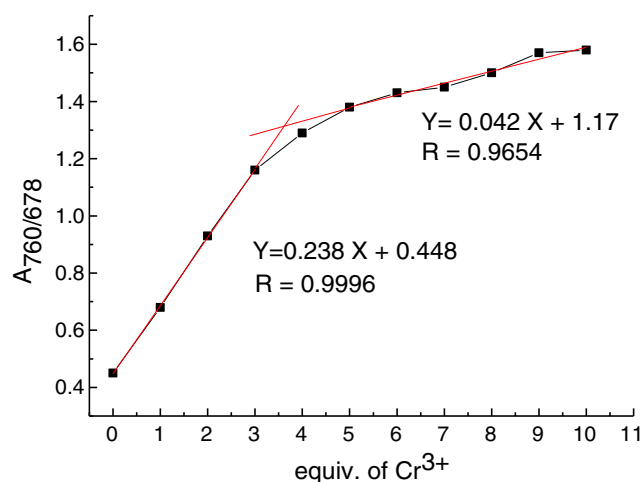


Fig. 6 Plot of A_{760/678} against the ratio of Cr³⁺ to probe (10⁻⁵ M) in 3:7 ethanol-water solution

Table 1 Application of the probe to the detection of Cr³⁺ in prepared samples

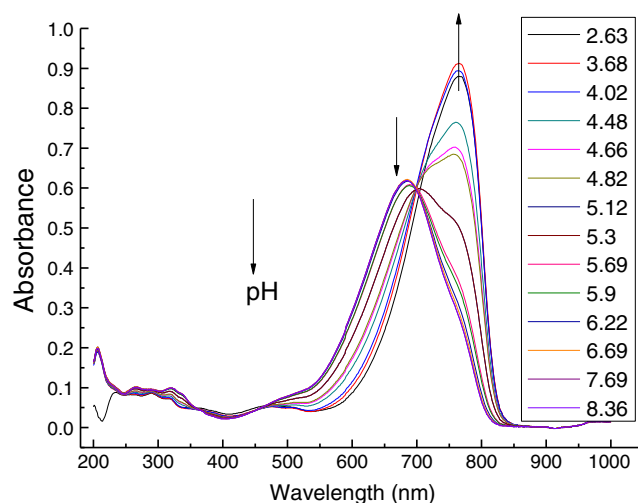
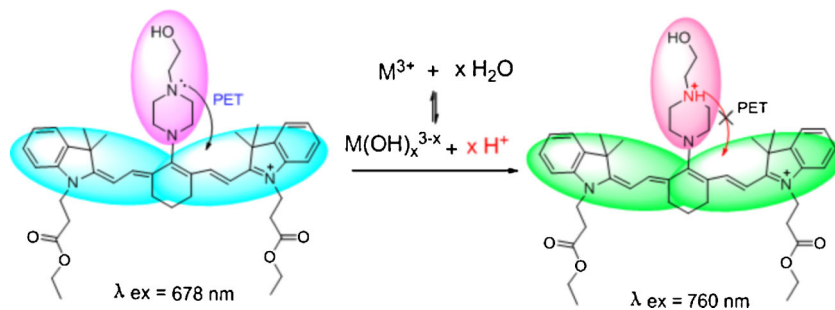
Sample	Cr ³⁺ added (μM)	Cr ³⁺ found (μM)	Recovery (%)	RSD
Wahaha purified water	0.00	0.00		
	10.00	10.07	100.7	2.13 %
Prepared samples	0.00	10.1	101	2.23 %
	10.00	20.08	100.4	0.9 %

Prepared sample: Cr³⁺, Zn²⁺, Mg²⁺, Ca²⁺, K⁺ and Na⁺ added in wahaha purified water (10 μM); Conditions: 10 μM probe in 3:7 ethanol-water solution

These assays strongly exhibited that the probe was of great potential for real-time determination of M³⁺.

Application in Prepared Samples

The above results proved that the probe can selectively and sensitively monitor the fluctuation of free M³⁺ in ethanol-water solution. Encouraged by the results, we sought to utilize the probe for the detection of M³⁺ ions in real samples. Thus, the detection of Cr³⁺ in prepared sample made of Cr³⁺ (10 μM) and other metal ions (Zn²⁺, Mg²⁺, Ca²⁺, K⁺ and Na⁺, 10 μM, respectively) in Wahaha purified water was investigated, and Wahaha purified water was used as reference. Recovery studies were carried out by adding a known concentration of Cr³⁺ (10 μM) in the test samples, and then analyzed by the established analytical method. Each measurement was done in quintuplicate, and the average was presented with relative standard deviation (RSD). The results summarized in Table 1 showed good agreement between experimental and actual values for the concentration of Cr³⁺ in the systems. The recovery studies of Cr³⁺ based on the probe were satisfactory with RSD values ranging from 0.9 to 2.23 %. The satisfying and reasonable results clearly demonstrated that the developed probe for Cr³⁺ detection was reliable and possessed the potential in practical applications.

Scheme 2 The proposed mechanism for the interaction between the probe and M³⁺**Fig. 7** The influence of protonation on the absorption spectra of the probe

Hypothesis of the Spectral Responses Mechanism

The above results demonstrated that the probe could be served as a naked-eye and real-time indicator for M³⁺ with excellent selectivity and high sensitivity. To acquire better understanding of the interaction between the probe and M³⁺, the mechanism was explored. Cr³⁺ was used as a representative (named as probe-Cr³⁺ system) and ESI-MS of this system was carried out firstly to determine the stoichiometry between the probe and Cr³⁺. But out of our expectation, there was no complex formation between the probe and Cr³⁺, as no change in ESI-MS before and after the addition of Cr³⁺ into the solution of the probe, and no precipitate was observed in the system. Similar results were also observed for the systems of probe-Fe³⁺ and probe-Al³⁺. However, in the present study, a similar pattern of red shift observed in the absorption spectra of probe-M³⁺ systems strongly suggested the formation of new species. And it is necessary to mention here that, some researchers demonstrated that M³⁺ has a higher hydrolyzing ability than M²⁺ and M⁺ ions [17], which releases more protons in the ethanol-water mixed solvent. It means that the addition of M³⁺ into the ethanol-water solution of probe is

equivalent to the addition of acid [3, 10]. Besides, Nagano [18] has reported that aminocyanine bearing a amine or diamine moiety has a strong response of pH values. Hence, We anticipated that the changes of the sensor's optical properties were based on the high hydrolyzing ability of the M^{3+} , which released protons and then induced the protonation of the sensor resulting in the inhibition of photoinduced electron transfer (PET) effect (illustrated in Scheme 2). Following this consideration, the influence of protonation on the absorption spectra of the probe was investigated. As shown in Fig. 7, upon addition of H^+ (HCl solution, 4 %), a new absorption peak at around 760 nm progressively increased and that at 678 nm gradually decreased with an isobestic point appearing at 686 nm, much like that described in the UV-Vis titration of M^{3+} . The analogous absorption trend of the probe- H^+ and probe- M^{3+} strongly suggested that the colorimetric and ratiometric responses of the probe towards M^{3+} could be attributed to a proton-binding-induced absorption change.

Conclusion

In the present study, a novel hydroxyethyl piperazine substituted aminocyanine derivative was designed and synthesized as an efficient probe for the naked-eye recognition and quantification of M^{3+} . The obtained sensor rendered selective colorimetric as well as ratiometric absorption responses to M^{3+} based on the protonation of the probe. Besides, the probe exhibited excellent selectivity over the competition of other metal ions and possessing low limit detection (sub-ppm level), which could meet the requirements for practical applications. Moreover, the chemosensor has been successfully applied for the detection of Cr^{3+} in prepared samples with no interference by others, further demonstrating its potential in the field of bio-analytical chemistry.

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