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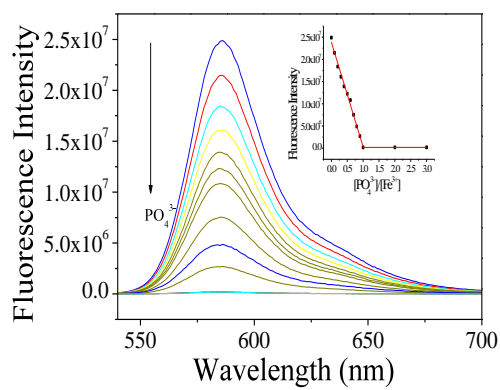
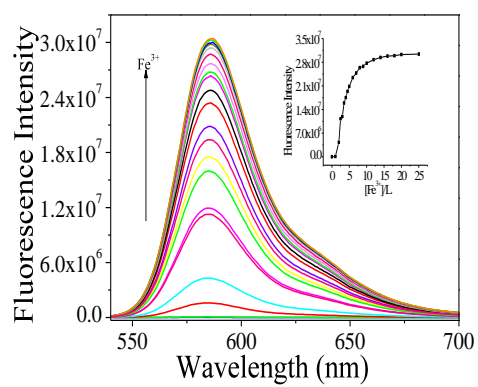
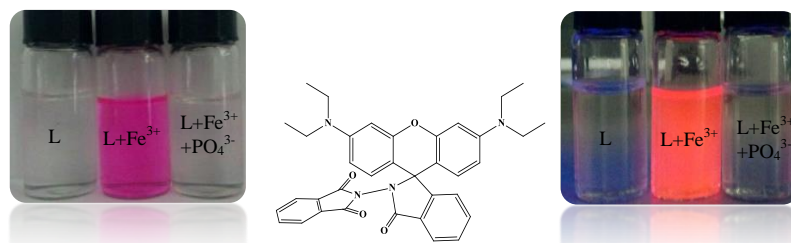


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ARTICLE

Cascade OFF-ON-OFF Fluorescent Probe: Dual Detection of Trivalent Ions and Phosphate Ions†

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A new rhodamine B-based fluorescent probe for the selective cascade signaling of trivalent cations (Fe^{3+} , Al^{3+} , Cr^{3+}) and phosphate anion (PO_4^{3-}) was developed. The non-fluorescent rhodamine derivatives can selectively detect trivalent cations over some other metal ions in $\text{CH}_3\text{CN}/\text{Tris}$ buffer (1/1, v/v, pH 7.0) solutions, leading to prominent fluorescence OFF-ON switching. The obtained probe-cation complex can subsequently serve as a sensitive and selective chemosensor for PO_4^{3-} , exhibiting complete signal quenching (fluorescence ON-OFF switching).

Introduction

Fluorogenic sensing of different metal ions have become particularly attractive because of their simplicity, high sensitivity, and instantaneous response¹⁻⁶. Among them, triple-charged metal cations detection is of significant importance due to its crucial influence in a wide range of environmental and human health⁷⁻¹⁷. For example, Fe^{3+} ion is an essential element in the human body and acts as a cofactor in many enzymatic reactions¹⁸⁻²⁰; widely existed Al^{3+} ion in the environment is considered to be toxic in biological activities, which is responsible for Parkinson's disease^{21, 22}; as for Cr^{3+} , which was also an effective nutrient for human body, a deviation of its concentration from normal level can increase the risk for diabetes and cardiovascular diseases⁴⁰. Simultaneously, detection of anions through fluorescence emission readout has also attracted a lot of attention considering the recognized biological roles played by anions²³. But it was difficult to recognize anions in water or water mixture media comparing with most of the metal cation, as anions usually experience competition from the solvent for sensor binding sites²⁴. Nevertheless, a metal complex may resolve this problem via simple displacement approach causing a signal change in the UV-vis or fluorescence spectrum²⁵⁻²⁸. Phosphate anions (PO_4^{3-}), both inorganic and organic, hold a unique position in nature, as they take part in almost all metabolic processes^{29, 30}. Moreover, phosphorylated bio-molecules play an important role in signal transduction for various biological processes. Human serum contains 0.80-1.45 mM phosphate, and higher phosphate levels are directly connected to cardiovascular disease and acute renal failure³¹.

Up till now, even though a large number of fluorescence chemosensors for divalent metal ions and phosphate anions have been reported in the literature, relative few studies have been devoted to the development of fluorescence sensor which were sensitive to trivalent ions⁴¹⁻⁴³ and phosphate ions³⁹. In view of

achieving rapid qualitative analysis of the pollutants, it is highly desirable to design a probe which is capable for the simultaneous discrimination of trivalent ions and phosphate ions from other ions.

Herein, we report a simple cascade "OFF-ON-OFF" fluorescent chemosensor for trivalent ions and phosphate ions, based on the equilibrium between spiroactam (non-fluorescent) to ring-open amide (fluorescent) form of rhodamine chromophore^{4, 9, 32}. Generally, the chemosensor showed a specific selectivity toward trivalent ions over other common metal ions, leading to prominent fluorescence OFF-ON switching. The resultant sensor-cation complex could selectively recognize PO_4^{3-} over other anions, exhibiting complete ON-OFF signal quenching.

Experimental

Materials and methods

Rhodamine B was obtained from Aladdin. Phthalic anhydride and hydrazine hydrate were purchased from Sinopharm Chemical Reagent. The solution of metal ions was prepared from their chloride salts of analytical grade. The solvents were used as received without further purification. Deionized water was used throughout.

UV-vis spectra were recorded with SCINCO S-4100. A HORIBA Jobin Yvon SPEX spectro fluorimeter was used for fluorescence measurements. The excitation wavelength was 520 nm and the spectra were recorded in the range 540-700 nm. Both ^1H NMR (400 MHz) and ^{13}C NMR spectra (100 MHz) of the compound were recorded on a Burkert Dpx spectrometer in CDCl_3 with tetramethylsilane as the internal standard. The high-resolution mass spectrum was performed on Bruker APEX IV.

Synthetic Methodology

Compound L was synthesized with two steps as shown in Scheme 1. Rhodamine B hydrazide was first synthesized with literature procedures³². Phthalic anhydride (100 mg, 0.67 mmol) was added to a solution of rhodamine B hydrazide (300 mg, 0.66 mmol) which has been dissolved in 40 mL anhydrous toluene. The reaction mixture was heated under microwave irradiation for 30 minutes and allowed to cool to room temperature. After the solvent was removed under reduced pressure, the crude product was purified with a silica gel column using a mixture of petroleum ether and ethyl acetate (2:1,

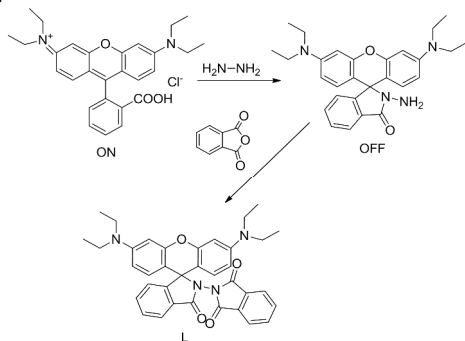
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v/v) as eluent to afford a yellow solid in 30% yield. ^1H NMR (Fig. S1) (400 MHz, CDCl_3) δ 8.02 (d, $J = 7.4$ Hz, 1H), 7.75 – 7.65 (m, 4H), 7.62 (t, $J = 7.2$ Hz, 1H), 7.56 (t, $J = 7.2$ Hz, 1H), 7.25 (d, $J = 7.5$ Hz, 1H), 6.83 (d, $J = 8.9$ Hz, 2H), 6.40 (d, $J = 6.4$ Hz, 2H), 6.26 (d, $J = 2.3$ Hz, 2H), 3.42 – 3.26 (m, 8H), 1.16 (t, $J = 7.0$ Hz, 12H). ^{13}C NMR (Fig. S2) (100 MHz, CDCl_3) δ (ppm) 164.07, 153.68, 153.06, 149.47, 148.82, 133.97, 133.40, 130.88, 130.09, 128.32, 124.45, 123.64, 123.40, 107.52, 104.23, 97.01, 73.37, 44.18, 12.47. HRMS (ESI) (Fig. S3): calcd for $\text{C}_{36}\text{H}_{35}\text{N}_4\text{O}_4$ $[\text{M}+\text{H}]^+$: 587.2658; found: 587.2652.



Scheme 1. Schematic illustration for the synthesis of RhB-based fluorescence probe L.

Results and Discussion

The equilibrium between non-fluorescent spirolactam form and fluorescent ring-open amide form of rhodamine derivatives has been proven as an efficient platform for the construction of fluorescent sensors for numerous heavy metal cations (such as Hg^{2+} , Pb^{2+} and Cu^{2+}), ascribing to its large absorption coefficient and high fluorescence quantum yield³³⁻³⁵. In the current research work, this typical ion-recognition mechanism was utilized for the successive detection of trivalent ions and then phosphate ions via fluorescence OFF-ON-OFF switching.

Fluorescence OFF-ON sensing for Fe^{3+} , Al^{3+} and Cr^{3+}

The detection selectivity of probe L (10 μM) toward Fe^{3+} ions was investigated by monitoring fluorescence changes upon addition of 8 equiv. chloride salt of a wide range of cations in $\text{CH}_3\text{CN}/\text{Tris}$ -buffer (1/1, v/v, pH 7.0) media, including Na^+ , K^+ , Mg^{2+} , Cu^{2+} , Hg^{2+} , Cd^{2+} , Fe^{2+} , Pb^{2+} , Zn^{2+} , Mn^{2+} , Ca^{2+} , Fe^{3+} , Al^{3+} and Cr^{3+} . The fluorescence emission spectra of L were measured in 1.0 cm quartz cells, and the excitation and emission slits were set to 2.0 and 2.0 nm, respectively. As shown in Fig. 1, the sensor itself was almost non-fluorescent due to its ring-closed spirolactam structure. After the addition of Fe^{3+} , probe L can exhibit a color change from colorless to pink and a bright red fluorescence. A strong emission band centering at 586 nm was observed with an extreme fluorescence enhancement compared to the metal-free L. This result indicated that the probe L exhibited high selectivity toward Fe^{3+} over the mono-valent and di-valent cations in $\text{CH}_3\text{CN}/\text{Tris}$ -buffer (1/1, v/v, pH 7.0) media.

To further explore the selectivity of the sensor, competitive ions were first added into the detection solution and then Fe^{3+} ion 20 minutes later. As shown in Fig. 2, most of the detection system exhibited minimum interference in the detection of Fe^{3+} , Al^{3+} and Cr^{3+} (80 μM each) also did not induce any obvious interference in the fluorescence sensing of Fe^{3+} , indicating that L has a relative higher binding affinity to Fe^{3+} than Al^{3+} and Cr^{3+} . And the association constants were 6.13×10^4 for $\text{L}-\text{Fe}^{3+}$, 3.14×10^4 for $\text{L}-\text{Al}^{3+}$ and 2.26×10^4 for $\text{L}-\text{Cr}^{3+}$ according to the reported work^{44,45}, respectively. The similar study was carried out with Al^{3+} and Cr^{3+} ,

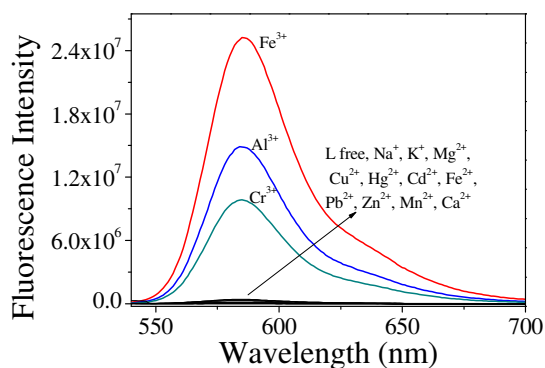


Fig. 1. Fluorescence spectra of L (10 μM) in the presence of various metal ions (80 μM each) in $\text{CH}_3\text{CN}/\text{Tris}$ -buffer (1/1, v/v, pH 7.0), $\lambda_{\text{exc}} = 520$ nm.

and there were also no obvious interferences in the presence of Na^+ , K^+ , Mg^{2+} , Cu^{2+} , Hg^{2+} , Cd^{2+} , Fe^{2+} , Pb^{2+} , Zn^{2+} , Mn^{2+} and Ca^{2+} .

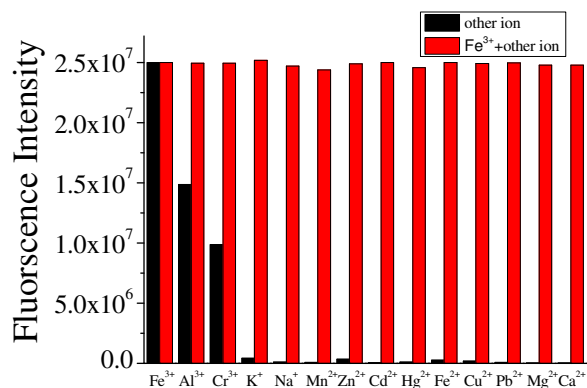


Fig. 2. Change of fluorescence intensity of L (10 μM) in various mixtures of metal ions (the concentration of Fe^{3+} and other metal ion were all 80 μM).

The sensing property of L was investigated in detail utilizing cation Fe^{3+} . Fig. 3 displays the absorption spectrum changes of L upon Fe^{3+} addition. Sensor L exhibited almost no absorption peak in the visible wavelength, ascribing to the spirolactam form of molecule L. However, a new band centered at about 562 nm emerged upon gradual addition of Fe^{3+} , indicating sensor $\text{L}-\text{Fe}^{3+}$ complex formation and Fe^{3+} -induced spirolactam ring-opening processes. Moreover, the titration solution displayed a characteristic color change of rhodamine derivatives, from colorless to pink, indicating that probe L could serve as a “naked-eye” indicator for Fe^{3+} in $\text{CH}_3\text{CN}/\text{Tris}$ -buffer (1/1, v/v) media. With the increasing amount of Fe^{3+} , the absorbance increased proportionally and levelled off when the concentration of Fe^{3+} reached to 250 μM . When UV-Vis titration measurements were carried out with Al^{3+} (Fig. S4) and Cr^{3+} (Fig. S5), similar changes were found as those of Fe^{3+} , that absorbance increased at first and then levelled off.

The appropriate pH conditions for successful operation of the fluorescence sensing were evaluated. Without the addition of Fe^{3+} ion, ring opening of the RhB-based sensor L occurred under acidic conditions ($\text{pH} < 5.0$) as a result of protonation, while no fluorescence change was observed as pH value is over 5 (Fig. 4). The gradual addition of Fe^{3+} , however, led to obvious fluorescence enhancement over a wide pH range from 5.0 to 8.0, which was attributed to the similar opening of spirolactam structure³⁶. Since the

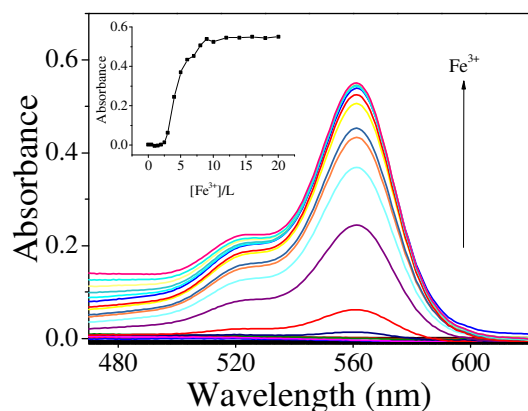


Fig. 3. UV-Vis spectra and (inset) absorbance changes (564 nm) recorded for L (25 μM) in $\text{CH}_3\text{CN}/\text{Tris}$ (1/1, v/v) with various amounts of Fe^{3+} ions.

most remarkable Fe^{3+} -induced OFF-ON fluorescence changes happened under physiological pH window, all the fluorescence measurements were conducted in pH 7.0. Similar phenomenon can also be observed in the fluorescence sensing of Al^{3+} and Cr^{3+} as shown in Fig. S6.

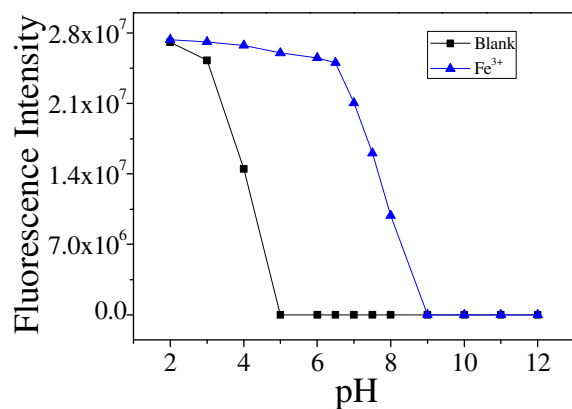


Fig. 4. Fluorescence intensity recorded for L (10 μM , $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ 1:1, v/v) at various pH values in the (a) absence and (b) presence of 8 equiv. Fe^{3+} ($\lambda_{\text{ex}} = 520 \text{ nm}$, $\lambda_{\text{em}} = 586 \text{ nm}$).

The relative affinities of Fe^{3+} toward sensor L were evaluated from fluorescence spectroscopic titration experiments in $\text{CH}_3\text{CN}/\text{Tris}$ -buffer (1/1, v/v) medium as shown in Fig. 5. The concentration of L was maintained at 10 μM while the concentration of Fe^{3+} was varied between 0 and 250 μM . The fluorescence spectra recorded at an excitation wavelength of 520 nm and emission wavelength of 540-700 nm. For free L, no obvious characteristic emission of rhodamine derivatives was observed. With the increasing concentration of Fe^{3+} , the fluorometric titration reaction curve showed a steady and smooth enhance, which has been used as the basis of the Fe^{3+} -sensing. The recognition interaction was completed immediately after the addition of Fe^{3+} within 1 min. When the concentration of Fe^{3+} was greater than 200 μM , the fluorescence intensity increased no further and a plateau was reached. The inset in Fig. 5 shows the dependence of the fluorescence intensity at 586 nm on the Fe^{3+} concentration. Plotting of the fluorescence intensity versus Fe^{3+} concentration (1-4 equiv.) afforded a good linear relationship ($R = 0.9844$) (Fig. S7). Detection limit of Fe^{3+} was calculated from the equation $\text{DL} = (3\text{Sb}_1 - I)/S$ instead of $\text{DL} = 3\text{Sb}_1/S$ ^{37, 38} as the intercept is not negligible, where Sb_1 is the standard deviation of the blank solution, I was the intercept and S was the slope of the calibration curve. The detection

limit of L for Fe^{3+} was $1.10 \times 10^{-5} \text{ M}$. And the detection limits of L were $3.20 \times 10^{-7} \text{ M}$ (Fig. S8-S9) for Al^{3+} and $2.55 \times 10^{-5} \text{ M}$ for Cr^{3+} (Fig S10-S11).

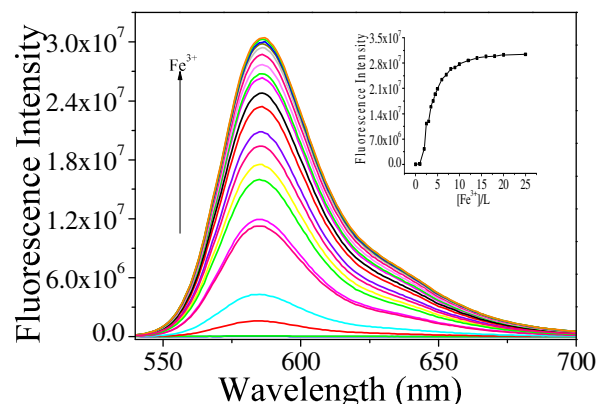


Fig. 5. Fluorescence titrations of L (10 μM) with Fe^{3+} ions in $\text{CH}_3\text{CN}/\text{Tris}$ (1/1, v/v, pH 7.0). Inset: fluorescence emission intensity changes with increasing Fe^{3+} ions ($\lambda_{\text{ex}} = 520 \text{ nm}$, $\lambda_{\text{em}} = 586 \text{ nm}$).

To determine the interaction stoichiometry between sensor L and Fe^{3+} , Job's method was employed using absorbance intensity at 562 nm as a function of molar fraction of L, as the total concentration of L and Fe^{3+} ion was located at 50 μM . A maximum absorbance was observed when the molar fraction of L reached 0.50 (Fig. 6), which was indicative of 1:1 stoichiometry complexation between L and Fe^{3+} . This result was further confirmed by high-resolution mass spectrum (HR-MS Fig. S12), in which the peak at m/z 786.0831 ($\text{calcd} = 786.0811$) corresponding to $[\text{L} + \text{Fe}^{3+} + 2\text{H}^+ + 4\text{Cl}]^+$ was clearly observed when 5 equiv of FeCl_3 was added to probe L. Similarly, the stoichiometric ratios were 1:1 for Al^{3+} (Fig. S13) and Cr^{3+} (Fig. S14). Inferred by the FTIR (Fig S15), the structure of the L-M^{3+} complex was proposed as shown in Fig.S16. When treated probe L with Fe^{3+} , The characteristic amide carbonyl absorption peak at 1631 cm^{-1} shifted to 1608 cm^{-1} , indicating that the amide carbonyl O of rhodamine B unit was actually involved in the recognition of Fe^{3+} , which was also agreed with reported work^{46, 47}.

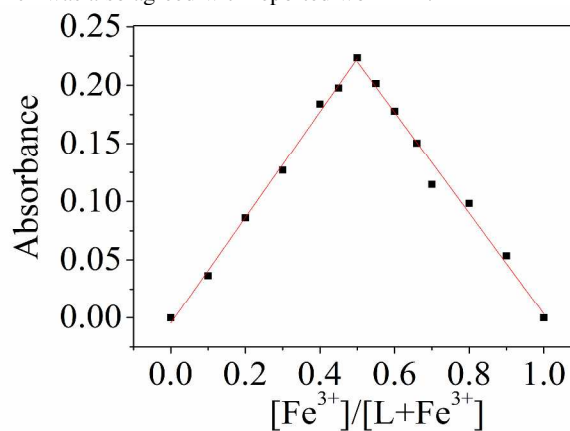


Fig. 6. Job's plot obtained for the determination of binding stoichiometry between L and Fe^{3+} in $\text{CH}_3\text{CN}/\text{Tris}$ (1/1, v/v). The total concentration of L and Fe^{3+} was fixed at 50 μM . The absorbance was measured at 564 nm.

Fluorescence ON-OFF sensing for PO_4^{3-}

Interestingly, when the L-Fe^{3+} complex was treated with a sodium salt of PO_4^{3-} , the color of the solution changed from pink to colorless and the emission was completely quenched within 1 min (Fig. 7a), while other anions such as Cl^- , Br^- , I^- , SO_4^{2-} , SO_3^{2-} , HPO_4^{2-} , H_2PO_4^- , NO_3^- did not show any interference to the detection. This observation suggested that the probe L could not only act as a sensor

for Fe^{3+} but also for PO_4^{3-} in a successive way. Once the Fe^{3+} ion interacted with sensor L, the spirolactam ring was opened, giving high fluorescence emission. But when treated it with PO_4^{3-} anion, the metal ion was abstracted and the spirolactam ring closed, leading to the absence of fluorescence. PO_4^{3-} anion-sensing capability of the obtained complex was further investigated in detail with fluorescence titration analysis (Fig. 7b). A titration curve showed an excellent linear decrease, and about 1.0 equiv of PO_4^{3-} (compared with Fe^{3+}) was required to absolute fluorescence quenching. The detection limit was calculated to be $0.20 \mu\text{M}$ (Fig. S17) according to the fluorescence titration curve, which reveals a high sensitivity for the analysis of phosphate ion by using the L- Fe^{3+} complex. The Al^{3+} complex can also serve as a sensor for PO_4^{3-} via simple displacement approach due to a strong affinity of PO_4^{3-} to Al^{3+} . Moreover, cascade fluorescence OFF-ON-OFF response can be observed with alternate addition of Fe^{3+} cation and PO_4^{3-} anion into the detection solution (Fig. S18), suggesting that the obtained fluorescence probe L can respond to the cation and anion in the co-existence of them. EDTA was further utilized to check the reversibility of the Fe^{3+} sensing process (Fig. S19). The results indicate that EDTA could also cause "ON-OFF" response of the L- Fe^{3+} complex via chelation. After the addition of excess Fe^{3+} to the detection solution, recovered fluorescence emission can clearly observed, suggesting that the probe exhibit good detection reversibility.

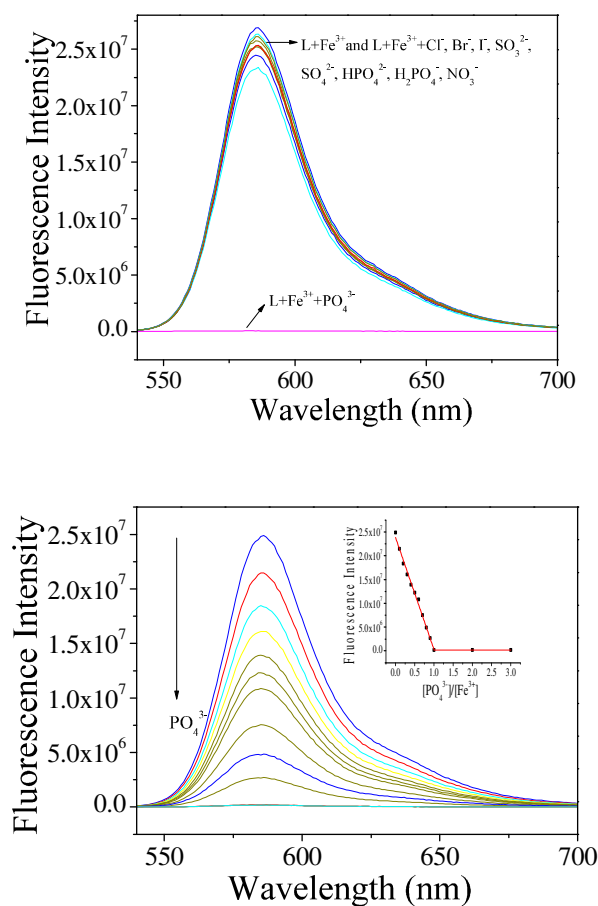


Fig. 8. (a) Fluorescence spectra obtained for L ($10 \mu\text{M}$) in the presence of Fe^{3+} ($80 \mu\text{M}$) in $\text{CH}_3\text{CN}/\text{Tris}$ (1/1, v/v) 10 min after the addition of various anions ($80 \mu\text{M}$ each), $\lambda_{\text{exc}} = 520 \text{ nm}$. (b) Fluorescence emission spectra and (inset) variation of fluorescence intensity recorded for L ($10 \mu\text{M}$) with 8 equiv. Fe^{3+} ions upon gradual addition of PO_4^{3-} (0-30 equiv. for Fe^{3+}) in $\text{CH}_3\text{CN}/\text{Tris}$ (1/1, v/v). The spectra were obtained 10 min after PO_4^{3-} addition ($\lambda_{\text{exc}} = 520 \text{ nm}$, $\lambda_{\text{em}} = 586 \text{ nm}$).

Conclusions

In summary, we report the synthesis and characterization of a new probe for the cascade fluorogenic detection of trivalent ions and phosphate ions. The probe L showed excellent "OFF-ON" fluorescence signals with high sensitivity and selectivity in the presence of trivalent ions, whereas remained silent in the presence of mono-valent and di-valent cations such as Na^+ , K^+ , Mg^{2+} , Cu^{2+} , Hg^{2+} , Cd^{2+} , Fe^{2+} , Pb^{2+} , Zn^{2+} , Mn^{2+} , Ca^{2+} . A successive "ON-OFF" fluorescence switching was then observed in the presence of PO_4^{3-} in $\text{CH}_3\text{CN}/\text{Tris}$ -buffer (1/1, v/v) media.

Acknowledgment

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