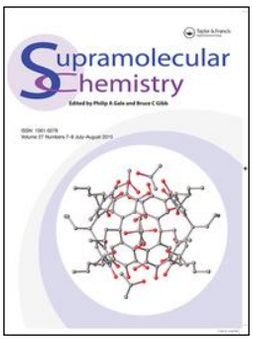

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ARTICLE

Perimedine-linked rhodamine dye in visual sensing of Al^{3+}, Fe^{3+} and Fe^{2+} ions in aqueous organic medium under different experimental conditions

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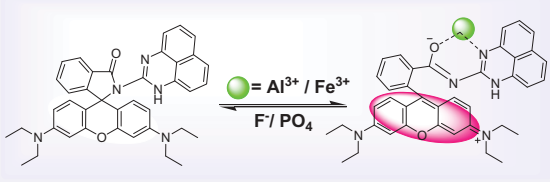
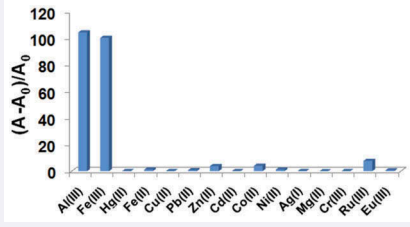
ABSTRACT

Perimedine labelled rhodamine dye **1** has been designed and synthesised. Metal ion binding studies of **1** have been performed in CH_3CN/H_2O (3:1, v/v, 10 mM Tris-HCl buffer, pH = 6.90). Compound **1** senses multiple metal ions such as Al^{3+}, Fe^{3+} and Fe^{2+} by exhibiting *turn on* fluorescence and colour change (colourless to pink) under different experimental conditions. Concentration variation distinguishes Al^{3+} from Fe^{3+} ion. At low concentration (c = 1 x 10^{-4} M), only Al^{3+} ion can exhibit *turn on* fluorescence with sharp colour change. Sensing of Fe^{2+} ion through *turn on* fluorescence and colour change has been possible *via* in situ oxidation by following Fenton's reaction.





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KEYWORDS
Colorimetric sensor; Fenton's reaction; Perimidine labelled rhodamine; Al^{3+}/Fe^{3+}/Fe^{2+} detection; Fluorometric sensor

Introduction

The design and synthesis of efficient chromogenic and fluorogenic chemosensors for desired metal ions is an important research area in supramolecular chemistry (1). In this aspect, metal ions that have harmful effects on living organisms or the environment are taken as targets. In detecting such metal ions, fluorescent sensors have several advantages over other methods to their high sensitivity, specificity, simplicity and real time-monitoring with fast response time (2). In developing such sensors, rhodamine B derivatives and its ring-opening reaction are attracting. In the presence of metal ions, the colourless, non-fluorescent spirocyclic form of the rhodamine B derivative is transformed into the ring-opened amide form which is pink and strongly fluorescent. In addition to this ring-switching behaviour, rhodamine B scaffold is known to exhibit excellent photophysical properties, such as its long absorption and emission wavelengths, high fluorescence quantum yield, and a large absorption coefficient (3). Rational use of Rhodamine B in metal ion recognition is thus noteworthy (4). Although a number of rhodamine-labelled sensors are known in the literature, the exploration of new architectures that are involved in multiple ion recognition under different experimental conditions is still desirable.

Perimidine is an important fluorophore that exhibits strong and stable emission upon irradiation of light of suitable wavelength and thus it has been used to produce fluorescent sensors of various designs for cations and anions (5). Perimidine derivatives can easily be synthesised through various methods. The first synthesis of this scaffold was achieved by Sach (6) in 1909. Since then, a large number of substituted perimidines have been synthesised (7). A number of synthetic compounds consisting of functionalised perimidine motif have been introduced in the last few years to recognise analytes in solution states (5). In this perspective, we have tried to focus the progress made on perimidine-based derivatives that act as supramolecular sensors for analytes (Table S1).

The promising use of perimidine in different designs tempted us to work in new type of structure. During our

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Supplemental data for this article can be accessed here.

ongoing research in ion sensing (8), we wish to report here a perimidine–rhodamine conjugate **1** (Figure 1) which acts as probe for sensing of Al^{3+}, Fe^{3+} and Fe^{2+} ions under different experimental conditions by exhibiting colour change (from colourless to pink) and *turn on* fluorescence in CH_3CN/water (3:1, v/v; 10 mM HEPES buffer; pH = 6.85). At low concentration of metal ions ($c = 1 \times 10^{-4}$ M), Al^{3+} was colorimetrically and fluorometrically distinguished from Fe^{3+}. On the other hand, Fe^{2+} detection has been successful through Fenton's reaction. To the best of our knowledge, this is a first time report on a perimidine-based rhodamine sensor for detection of metal ions.

Detection and sensing of Al^{3+} and Fe^{3+} ions attract attention because of their relevance in both biology and environment. Al^{3+} ion has a marked effect on human health. It affects the activity of gastrointestinal enzymes and is also associated with several neuro diseases such as Alzheimer's disease, Parkinson's disease, etc. Bone softening, chronic renal failure and smoking-related diseases are also due to toxic effect of Al^{3+} (9).

Similarly, among transition metal ions, iron is the most abundant essential trace element and plays a vital role in human health, such as in cellular metabolism, enzyme catalysis and as an oxygen carrier in haemoglobin and a cofactor in many enzymatic reactions involved in the mitochondrial respiratory chain (10). However, increasing the level of iron within the body is associated with certain organ dysfunction (11). Therefore, the detection of these ions by synthetic probes is important.

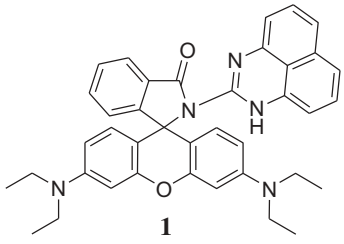


Figure 1. Structure of compound **1.**

Results and discussion

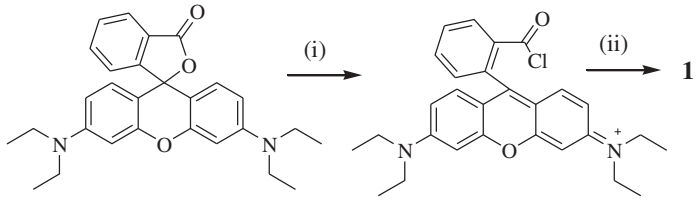
Synthesis

Compound **1** was obtained according to Scheme 1. Reaction of rhodamine acid chloride (*4o*) with aminoperimidine yielded the desired compound in appreciable yield. Compound **1** was fully characterised by ^{1}H NMR, ^{13}C NMR and HRMS.

Metal ion sensing

The metal ion sensing behaviour of compound **1** was ascertained in CH_3CN:H_2O (3:1, v/v, tris-HCl buffer, pH = 6.90). Due to insolubility of **1** in pure water, a compromise with CH_3CN was done to prepare its stock solution. Prior to establishing the metal ion sensing behaviour, the effect of pH on compound **1** was realised. As can be seen from Figure 2a, solution of **1** is colourless on and from pH 6 to 12. Below pH 6, solution is pink in colour due to the opening of spirolactam ring. Recording of UV-vis spectra of **1** at different pHs reveals the strong absorption at 551 nm due to ring-opened xanthenoid form of rhodamine at pH 2–3 (Figure 2b). A similar observation was noticed in fluorescence (Fig. S1). At pH 2 to 3, excitation of **1** at 350 nm gave intense emission at 578 nm for the xanthenoid form. Based on these observations, the metal ion sensing behaviour of **1** was studied at pH 6.90 where the spiro lactam ring is retained.

In the study, effect of different metal ions such as Fe^{3+}, Al^{3+}, Fe^{2+}, Hg^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Ag^{+}, Mg^{2+}, Cd^{2+}, Pb^{2+}, Cr^{3+}, Ru^{3+} and Eu^{3+} (taken as perchlorate salts except Cr^{3+}, Ru^{3+} and Eu^{3+}; Cr^{3+}, Eu^{3+} and Ru^{3+} were taken as $Cr(NO_3)_3$, $Eu(NO_3)_3$, $RuCl_3$) on the absorption and emission of **1** was investigated in CH_3CN:H_2O (3:1, v/v, tris-HCl buffer, pH = 6.90). In UV-vis, compound **1** showed absorption bands at 354, 320 and 270 nm. Upon gradual addition of Al^{3+} or Fe^{3+} ions to the solution of **1** resulted in strong absorption at 551 nm and the solution turnedpink (Figure 3). By contrast, other metal ions brought neither any colour change of the solution of



Scheme 1. (i) $POCl_3$, 1,2-dichloroethane, reflux, 3h; (ii) 1H-Perimidin-2-ylamine Et_3N, dry CH_2Cl_2,stirring, 10h.

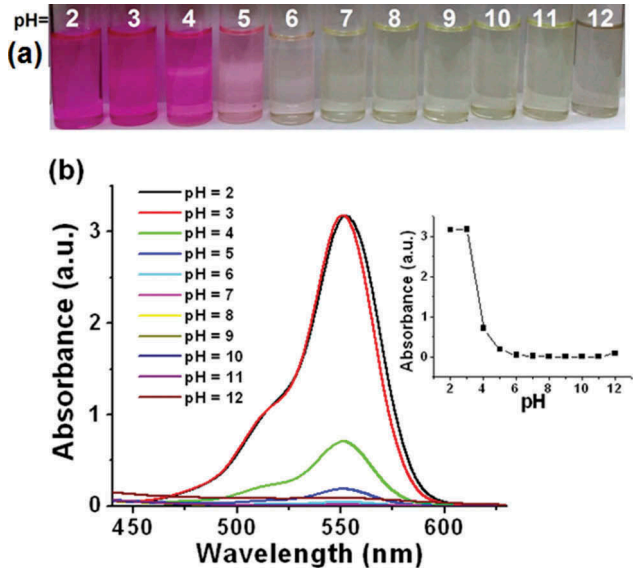


Figure 2. (a) Colour change of the solution of **1** at different pHs in CH_3CN/aqueous Tris-HCl buffer (3:1, v/v); (b) Absorbance at different pHs. The inset interprets the variation of absorbance with pH.

1 nor showed strong absorption at 551 nm for the xanthenoid form (Fig. S2).

A plot of absorbance ratio of **1** with different metal ions in Figure 4 corroborates the sensitivity of **1** towards Fe^{3+} and Al^{3+} ions over the other metal ions.

In fluorescence, excitation of **1** at 510 nm gave almost no emission in the region 520– 650 nm and substantiated the existence of spirolactam ring in **1**. However, gradual addition of Al^{3+} or Fe^{3+} ions brought significant increase in emission at 578 nm with red shift for the xanthenoid form (Figure 5). Other metal ions in the study did not participate in the ring-opening reaction as confirmed by nonappearance of the emission at 578 nm (Fig. S3).

In the event, compound **1** showed 1:1 stoichiometric interaction with both Al^{3+} and Fe^{3+} ions, confirmed by linear nature of Benesi–Hildebrand plots (Fig. S4) (12) and the associated binding constants were determined to be 7.65×10^3 and 6.63×10^3 M^{-1} for Al^{3+} and Fe^{3+} ions, respectively. Detection limits (13) for Al^{3+} and Fe^{3+} ions were found to be 6.24×10^{-8} and 5.30×10^{-8} M, respectively (Fig. S5).

The interaction of **1** with Al^{3+} and Fe^{3+} ions was understood from ^1H NMR and FTIR studies. In ^1H NMR, significant downfield chemical shift of rhodamine ring

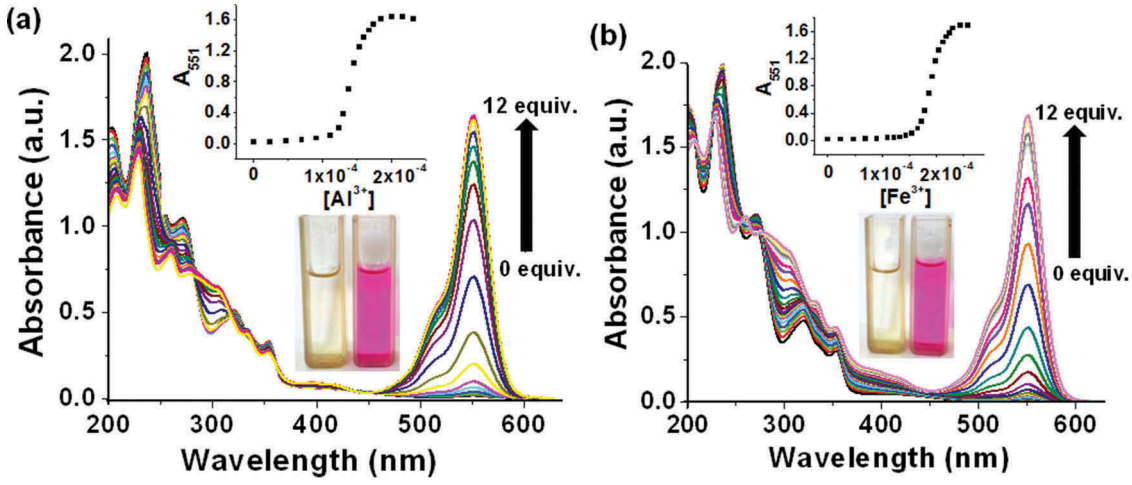


Figure 3. Absorption titration spectra of **1** (c = 2.5 x 10^{-5} M) with addition of 12 equivalent amounts of (a) $Al(ClO_4)_3$ and (b) $Fe(ClO_4)_3$ (c = 1 x 10^{-3} M) in CH_3CN/H_2O (3:1, v/v; 10 mM Tris-HCl buffer; pH = 6.90). Insets show the colour change of solutions under visible light before and after addition of guest and also the variation of absorbance with guest concentration.

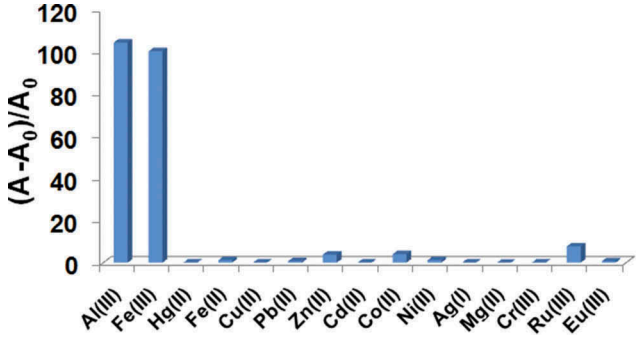


Figure 4. Change in absorbance ratio of **1** (c = 2.5 x 10^{-5} M) at 551 nm upon addition of 12 equivalent amounts of different metal ions (taken as perchlorate salts except Cr^{3+}, Ru^{3+} and Eu^{3+}; Cr^{3+}, Eu^{3+} and Ru^{3+} were used as $Cr(NO_3)_3$, $Eu(NO_3)_3$, $RuCl_3$) in CH_3CN/H_2O (3:1, v/v, tris HCl buffer, pH = 6.90).

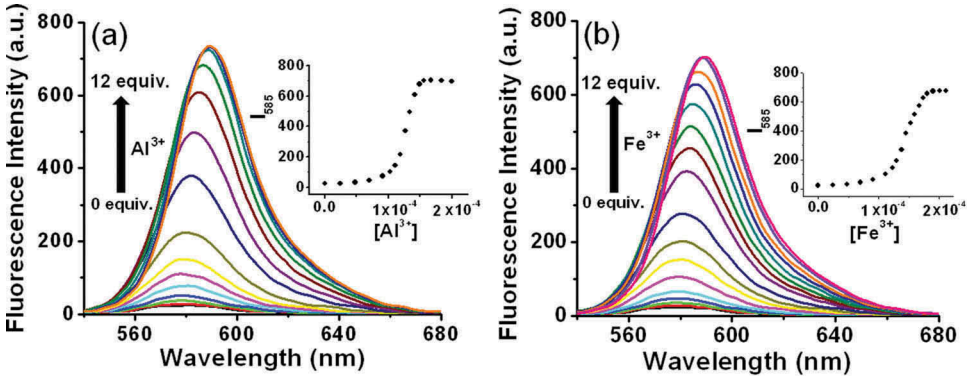


Figure 5. Emission titration spectra of **1** (c = 2.5 x 10^{-5} M) upon addition of 12 equivalent amounts of (a) $Al(ClO_4)_3$ and (b) $Fe(ClO_4)_3$ (c = 1 x 10^{-3} M) in CH_3CN/H_2O (3:1, v/v; 10 mM Tris-HCl buffer; pH = 6.90) (λ_{exc} = 510 nm). Insets show the change in emission at 585 nm with guest concentration.

protons (labelled as 'a', 'b' and 'c') of **1** was noticed in the presence of 1 and 5 equivalent amounts of the metal ions (Figure 6). The signals for protons of other aromatic rings (labelled as 'x', 'y' and 'z') were also shifted to the downfield directions. This was believed to be due to binding of the metal ions in the mode shown in Figure 6a. The signal for –NH– at 10.77 ppm became broad and underwent small downfield chemical shift.

The complexation through spirolactam ring opening was also understood from FTIR study. The amide carbonyl stretching appearing at 1692 cm^{-1} in **1** was reduced to 1646 and 1647 cm^{-1} upon complexation of Al^{3+} and Fe^{3+}, respectively (Figure 7). The C=N stretching at 1615 cm^{-1} was slightly increased to 1620 or 1626 cm^{-1} upon complexation. This indicated the participation of perimidine ring in metal chelation.

The reversibility in complexation was checked by adding different anions such as F^-, Cl^- I^-, OAc^-, PO_4^{3-} to the pink coloured solutions of Al^{3+}-**1** and Fe^{3+}-**1** ensemble. Of the different anions used, only F^-, OAc^- and PO_4^{3-} were able to restore the spirolactam ring of **1** and made the solutions colourless. The original absorption spectrum of **1** was rescued (Figure 5). Phosphate ion (PO_4^{3-}) in the series exhibited strong propensity to regenerate the spirolactam ring. Importantly, it was difficult to distinguish Al^{3+} from Fe^{3+} ion.

To check the interference in the sensing of Al^{3+} and Fe^{3+} ions, a competitive experiment was done upon addition of Al^{3+} and Fe^{3+} ions to the solution of **1** containing other metal ions. In the study, only Cu^{2+} ion interfered in sensing of Al^{3+} and Fe^{3+} ions (Figure 8). Addition of either ion (Al^{3+} and Fe^{3+} ions) to the solution of **1** containing Cu^{2+} ions did not induce any change in emission at 578 nm. It is thus presumed that Cu^{2+} ion forms a stable complex with perimidine ring nitrogen for which Al^{3+} or Fe^{3+} is refused form the binding site to open the lactam ring. The interaction of Cu^{2+} with perimidine ring is a well-established fact (*5d-g*) based on which a suggestive mode of interaction of **1** with Cu^{2+} is shown in Fig. S7. Importantly, in the reverse process, addition of Cu^{2+} ions to the solution of **1** containing either Al^{3+} or Fe^{3+} ions did not make the solution colourless. This

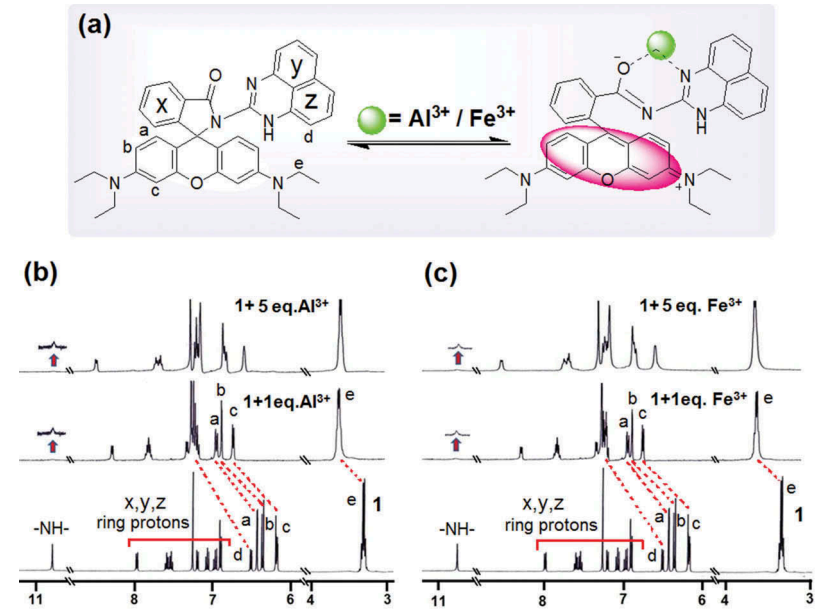


Figure 6. (a) Suggested mode of interaction of **1** with Al^{3+}/Fe^{3+} ions in solution; (b) Partial ^1H NMR (400 MHz) of **1** ($c = 6.5 \times 10^{-3}$) in the absence and presence of 1 and 5 equivalent amounts of (b) Al^{3+} and (c) Fe^{3+} in $CDCl_3$.

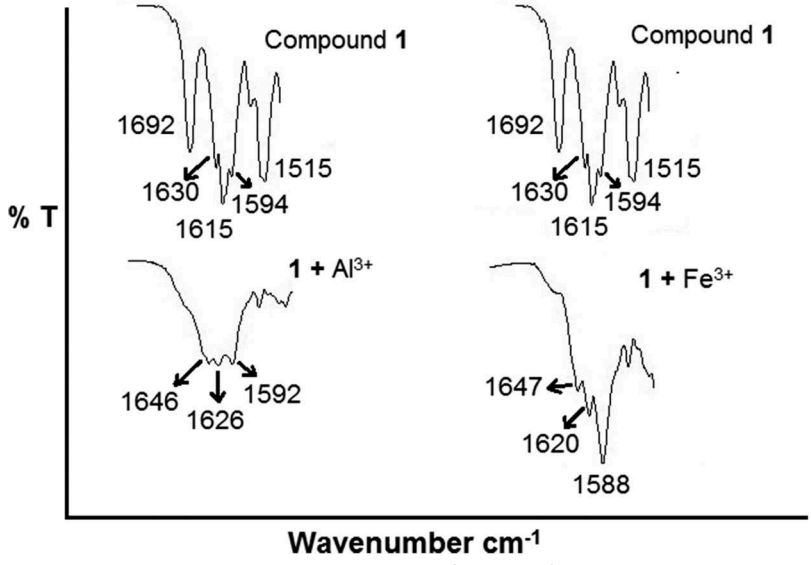


Figure 7. Partial FTIR spectra of **1** in the absence and presence of Al^{3+} and Fe^{3+}.

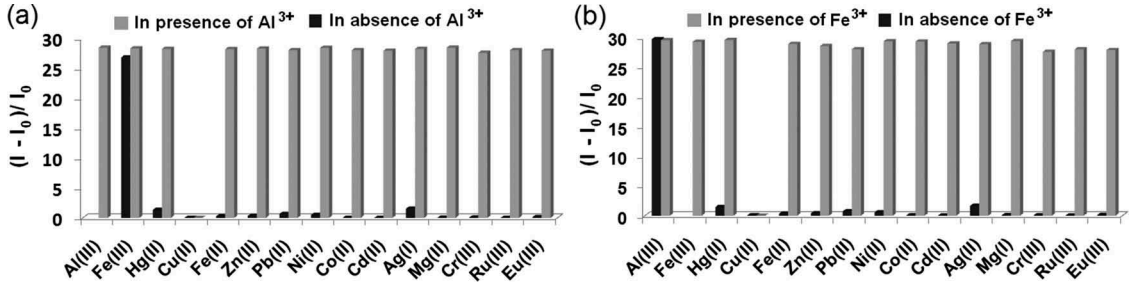


Figure 8. Change in fluorescence ratios of **1** ($c = 2.5 \times 10^{-5}$ M) with (a) Al^{3+} and (b) Fe^{3+} ions in the absence and presence of 12 equivalent amounts of other metal ions in CH_3CN/H_2O (3:1, v/v, tris-HCl buffer, pH = 6.90) (λ_{exc} = 510 nm).

signifies that once the complex is formed through lactam ring opening as shown in Figure 6a, the displacement of either Al^{3+} or Fe^{3+} by Cu^{2+} ion is difficult.

As we became unsuccessful to distinguish between Al^{3+} and Fe^{3+} by any chelating agent, we attempted to check their complexation behaviours with variation of their concentrations. Importantly, the distinction was possible at low concentrations of Al^{3+} and Fe^{3+} ions. At concentration of 1 x 10^{-4} M of metal ions, compound **1** successfully distinguished Al^{3+} from Fe^{3+} by exhibiting different changes in UV-vis and emission spectra as well as in colour of the solution of **1**. Figure 9 clearly depicts the fact.

Fenton's reaction and Fe^{2+} ion sensing

We also examined the applicability of compound **1** to sense Fe^{2+} ion *via* Fenton's reaction. For this, the change in absorbance of compound **1** in CH_3CN/H_2O (3:1, v/v; 10 mM Tris-HCl buffer; pH = 6.86) in the presence of Fe^{2+} ion was noticed upon gradual addition of H_2O_2. During addition of H_2O_2, the absorbance at 551 nm was increased and the solution turned pink. The observation is similar to the case of interaction of **1** with Fe^{3+} ions. H_2O_2 initiates the Fenton's reaction by oxidising Fe^{2+} to Fe^{3+} ions. Importantly, no significant change was observed in absorbance of compound **1** upon addition of Fe^{2+} ion, but with increasing addition of H_2O_2, an increase in absorbance at 551 nm was observed (Figure 10). This study reveals the practical applicability of compound **1** to detect *in situ* generated Fe^{3+} ion *via* Fenton's reaction.

Conclusions

In conclusion, we have thus designed and synthesised perimidine-labelled rhodamine dye **1** which efficiently acts as chromogenic and fluorogenic probe for Al^{3+}, Fe^{3}

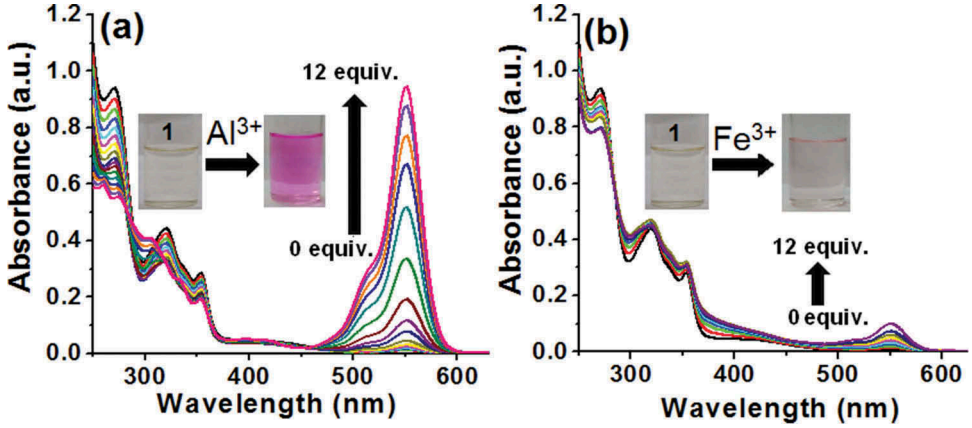


Figure 9. Absorption titration spectra of **1** (c = 2.5 x 10^{-5} M) upon addition of 12 equivalent amounts of (a) Al^{3+} and (b) Fe^{3+} (c = 1 x 10^{-4} M) in CH_3CN/H_2O (3:1, v/v; 10 mM Tris-HCl buffer; pH = 6.90). Insets represent the colour change of the solution of **1.**

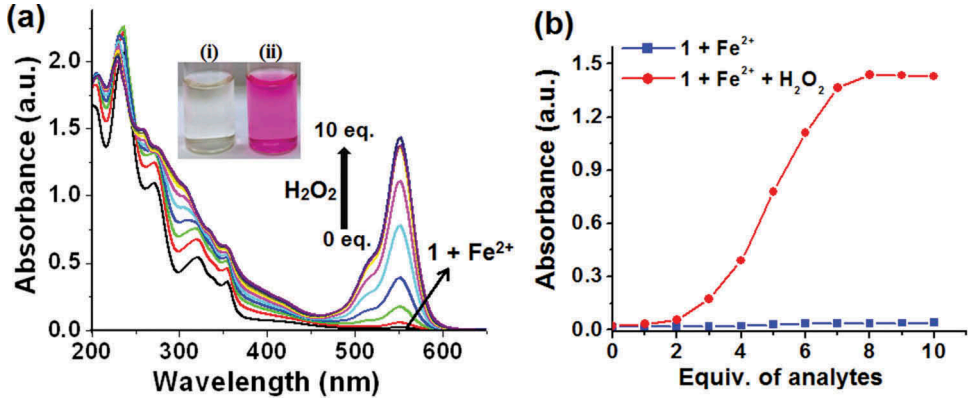


Figure 10. (a) Absorption titration spectra of the ensemble of **1** + Fe^{2+} (12 equivalent amount) upon gradual addition of H_2O_2 solution in CH_3CN/H_2O (3:1, v/v; 10 mM Tris-HCl buffer; pH = 6.90); Insert represents colour change of solutions of (i) ensemble (**1** + Fe^{2+}) and (ii) ensemble after addition of H_2O_2; (b) Change in absorbance upon addition of Fe^{2+} to the solution of **1** itself and H_2O_2 to the solution of **1** containing Fe^{2+}.

$^{+}$ and Fe^{2+} ions in CH_3CN:H_2O (3:1, v/v) at pH 6.85 under different experimental conditions. Compound **1** senses these metal ions with excellent detection limits (Al^{3+}: 6.24×10^{-8} M and Fe^{3+}: 5.30×10^{-8} M) by exhibiting *turn on* fluorescence and colour change (colourless to pink). Importantly, the detection limits for both Al^{3+} and Fe^{3+} are comparable with the reported systems (Table S2). It is further to note that the probe **1** shows strong affinity to both Al^{3+} and Fe^{3+} ions and thus they were difficult to distinguish. Only they were differentiated at low concentration. While at low concentration of metal ions ($c = 1 \times 10^{-4}$ M) Al^{3+} ion exhibits *turn on* fluorescence with colour change, Fe^{3+} remains almost non-interacting to the probe. Furthermore, detection and sensing of Fe^{2+} ion has been possible through *turn on* fluorescence and colour change by its *in situ* oxidation through Fenton's reaction. Therefore, the present study, for the first time, intimates that perimidine can be used as a good metal ion binder in conjunction with rhodamine for successful colorimetric and fluorometric detection of metal ions. Further study along this direction is underway in the laboratory.

Experimental setup

Materials and methods

All the chemicals and reagents were purchased from Spectrochem and Sigma. Perchlorate salts of the metal ions as purchased from Sigma-Aldrich were carefully handled. All solvents used in the reaction were purified, dried and distilled as required. Thin-layer chromatography was done on Merck precoated silica gel 60-F_{254} plates. ^{1}H and ^{13}C NMR spectra were accumulated using Bruker 400 MHz instrument using TMS as internal standard. FTIR spectra of the compounds were obtained from Perkin-Elmer L120-00A spectrometer (n_{max} in cm^{-1}) using KBr pellet. UV-vis studies were performed using Shimadzu UV-2450 spectrophotometer.

Synthesis

3′,6′-bis(Diethylamino)-2-(1H-perimidin-2-yl)spiro[isoindoline-1,9′-xanthen]-3-one 1

To a solution of rhodamine B (0.5 g, 1.04 mmol) in dry 1,2-dichloroethane (20 mL), $POCl_3$ (0.23 mL, 2.52 mmol) was added and the resulting solution was refluxed for 3 h. Then, the solvent was removed under vacuum to have a crude mass which was dissolved in dry CH_2Cl_2 (30 mL) for reaction in the next step. To this solution, 1H-perimidin-2-amine (0.18 g, 0.98 mmol) dissolved in dry CH_2Cl_2 (25 mL) containing Et_3N (0.37 mL, 2.52 mmol) was added dropwise. The reaction mixture was stirred for 10 h and the progression of the reaction was checked by thin-layer chromatography. After completion of the reaction, CH_2Cl_2 was removed and water was added to it. The aqueous layer was extracted with ethyl acetate (20 mL x3). The ethyl acetate layer was dried over anhydrous Na_2SO_4 and then evaporated to have the crude product which was purified by silica gel column chromatography using petroleum ether: ethyl acetate (7:3 v/v) as eluent to afford pure compound **1** (0.37 g, yield: 58%) as solid, mp 142 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.77 (1H, s); 7.97 (1H, d, J = 8 Hz); 7.57 (1H, t J = 8 Hz), 7.53 (1H, t, J = 8 Hz), 7.19 (1H, d, J = 8 Hz); 7.06 (1H, t, J = 8 Hz); 6.96 (1H, t, J = 8 Hz); 6.89 (2H, d, J = 8 Hz); 6.50 (1H, d, J = 8 Hz); 6.42 (2H, d, J = 2.4 Hz); 6.35 (2H, d, J = 8 Hz); 6.18–6.15 (3H, m); 3.30 (8H, q, J = 8 Hz); 1.13 (12H, t, J = 8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.2, 154.2, 153.4, 148.7, 144.5, 144.1, 137.2, 135.2, 134.6, 129.5, 128.7, 128.5, 127.5, 127.2, 124.9, 123.2, 121.4, 118.1, 118.0, 114.2, 107.2, 106.7, 102.4, 97.4, 67.6, 44.3, 12.6; FTIR (KBr) ν cm^{-1}: 3424, 3249, 2966, 2924, 1692, 1630, 1615, 1594, 1515, 1477, 1466, 1341; HRMS (EI): Calcd. 608.3020 $(M + H)^{+}$ and found 608.3021 $(M + H)^{+}$.

General procedures for fluorescence and UV-vis titrations

To conduct fluorescence and UV-vis titrations, stock solution of compound **1** was prepared in CH_3CN:H_2O (3:1, v/v, tris-HCl buffer, pH = 6.86) in the concentration range of ~10^{-5} M. Then, an amount of 2 ml of the compound was taken in the cuvette and to this solution, metal ion – prepared in the concentration range of ~10^{-3} M in the same solvent – was added in different amounts. Upon adding metal ions, the change in emission as well as absorbance of compound **1** was noted. Both fluorescence and UV-vis titrations were carried out at 25 °C.

Calculation of detection limit

Fluorescence titration data were used to determine the detection limit. In this process, the standard deviation of blank measurement was obtained after recording the emission of compound **1** six times. Then emission intensities were plotted against concentrations of metal ions to determine the slope. The values of standard deviation and slope were fitted into the equation: detection limit = $3s/k$ (where s is the standard deviation of the blank measurement and k is the slope) to have the detection limit (13).

Acknowledgments

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Disclosure statement

No potential conflict of interest was reported by the authors.

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