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## Bi-component sensing platform for the detection of Cd<sup>2+</sup>, Fe<sup>2+</sup> and Fe<sup>3+</sup> ions†

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The ability of *N*-(1,3-dioxo-1*H*-benzo[de]isoquinolin-2(3*H*)-yl)isonicotinamide (naphydrazide) or 2,6-pyridinedicarboxylic acid (2,6-H<sub>2</sub>pdc) individually or as a bi-component system in distinguishing and detecting Fe<sup>3+</sup> or Fe<sup>2+</sup> and Cd<sup>2+</sup> ions was investigated. The use of these molecules as single or bi-component analytes in absorption or emission spectroscopy studies showed that under specific conditions each had their own merits for specific purposes. UV-visible spectroscopic studies of 2,6-H<sub>2</sub>pdc for assessing the interactions with ferrous and ferric ions showed characteristic distinctions. The detection limit for Fe<sup>3+</sup> analysed through UV-visible spectroscopy using naphydrazide was 0.46 μM, whereas it was 1.28 μM using 2,6-H<sub>2</sub>pdc. Naphydrazide together with Fe<sup>3+</sup> allowed distinguishing Cd<sup>2+</sup> ions from Zn<sup>2+</sup> and Fe<sup>2+</sup> ions. The bi-component system was useful for the selective detection of Cd<sup>2+</sup> ions using fluorescence spectroscopy, with a detection limit for Cd<sup>2+</sup> ions of 18.31 μM. The presence of Fe<sup>2+</sup> and Cd<sup>2+</sup> ions in a solution of the bi-component had resulted white-light emission. An analogous compound *N,N'*-(1,3,6,8-tetraoxobenzol[*lmn*][3,8]phenanthroline-2,7(1*H*,3*H*,6*H*,8*H*)-diyl) diisonicotinamide (binaphydrazide) was found unsuitable for such detections. Two 2,6-pyridinedicarboxylate Fe<sup>3+</sup> complexes possessing protonated naphydrazide or binaphydrazide were prepared and characterised. These complexes were also found unsuitable for the detection of the said ions in solution. Electrochemical studies with the bi-component system showed that cyclic voltammograms could distinguish Fe<sup>3+</sup> or Fe<sup>2+</sup> from Cd<sup>2+</sup> ions.

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## Introduction

Detection of naturally abundant metal ions present in water at very low concentrations has been well studied.<sup>1–7</sup> Among the metal ions, iron ions are more commonly found in biological systems, soil and water. The activities of iron ions in biological systems are influenced by other essential metal ions. There are many metal ions that interfere in the detection and estimation of iron ions. For example, the presence of about 24 μg g<sup>−1</sup> cadmium ions in biological systems reduces the absorption of iron ions and affect the concentration of iron ions in haemoglobin or in the kidneys.<sup>8</sup> A decrease in the amount of cadmium ions in ferro-proteins present in the duodenum causes anemia.<sup>9</sup> Cadmium ions can enter the human body from food, the surrounding environment or certain therapies used to treat cancer. It has been reported that zinc ions regulate the absorption of cadmium ions during biological activities.<sup>10</sup> In general, Zn<sup>2+</sup> ions interfere in the fluorescence detection of Cd<sup>2+</sup>

ions and *vice versa*. Fe<sup>3+</sup> ions are well known to interfere in the colorimetric detection of Fe<sup>2+</sup> ions.<sup>11</sup> Although large numbers of receptors are used for the detection and quantification of iron and cadmium ions (ESI Tables S3 and S4†), major challenges associated with their performance and specificity persist. The quantitative estimation of cadmium or iron ions in water or soil requires procedures that do not experience interference from other cations. Such detection/quantification processes are important to maintain human and animal health. Semi-conducting quantum dots have been widely explored for the detection of different cations with high sensitivity.<sup>1,2</sup> However, there are some concerns about their practical utility owing to their difficult preparation, leaching and toxicity. Hence, small common organic, less toxic molecules have scope for suitable functionalization and for use in the detection of metal ions present in water. Among the small molecules, naphthalimide derivatives are well known for use as sensors for ions.<sup>3,4,12–15</sup> The optical properties, such as aggregation-induced emission or photochemical electron-transfer processes, of naphthalimide derivatives make them sensitive sensors that can be used to detect ions at the micro-scale to nano-molar-scale concentrations.<sup>16</sup> Beside these, chelate complexes of small organic molecules can be utilized as a masking agent to modulate optical processes for the detection of metal ions.<sup>17,18</sup> A system involving *in situ*-generated protons from a chelator that could

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influence the emission spectra of specific naphthalimide derivatives was recently reported by us.<sup>19</sup> With such a background, the aim of this study was to construct a bi-component detection platform for the detection of iron ions in the presence of cadmium, and *vice versa*. We chose to study the bi-component platform of a pyridine-based naphthalimide fluorophore with a chelating ligand (Fig. 1A and B) for determining its ratiometric responses with different metal ions.<sup>20,21</sup> The proposed solution was based on supramolecular assembly<sup>22</sup> with the following expectations: (a) two ligands competing to bind to a metal ion or mixture of metal ions would provide avenues to study the changes in emission properties stemming from the mixed ligand polynuclear/polymeric self-assemblies (Fig. 1); (b) reversibility in the association and dissociation of a non-covalent assembly would modulate the spectral properties;<sup>23</sup> (c) masking a metal ion by a chelating ligand would prevent a chromophore or fluorophore from having direct contact with the metal ion. This would influence the interference of one or more metal ions in a mixture;<sup>17,18</sup> (d) protons

released during chelation to the solution would influence the photo-electron transfer emission; (e) non-covalent assemblies may be amenable to Foster-resonance electron transfer.<sup>24-26</sup> In the literature, 2,6-pyridinedicarboxylic acid (2,6-H<sub>2</sub>pdc)-based functional nano-materials were used for the selective detections of ions.<sup>27</sup> The use of 2,6-H<sub>2</sub>pdc together with naphthalimide-based ligands allowed the formation of self-assembled coordination polymers.<sup>19</sup> Capitalising on such reports, the detection of and distinction between Cd<sup>2+</sup>, Fe<sup>2+</sup>, and Fe<sup>3+</sup> ions by *N*-(1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl)isonicotinamide (naphydrazide) as a single-component or bi-component system with 2,6-H<sub>2</sub>pdc (Fig. 1) using UV-visible, fluorescence, and electrochemical means are described in this article. The synthesis and characterization of two Fe<sup>3+</sup>-pdc (pdc = 2,6-pyridinedicarboxylate) complexes having organo-cations of naphydrazide or diprotonated *N,N'*-{1,3,6,8-tetraoxobenzo[*lmn*][3,8]phenanthroline 2,7(1*H*,3*H*,6*H*,8*H*)diyl}diisonicotinamide (binaphydrazide) and their roles for distinguishing different ions in solution are also presented.

## Experimental section

Naphydrazide<sup>28</sup> and binaphydrazide<sup>29</sup> were synthesized according to reported procedures. UV-visible spectra were recorded on a PerkinElmer Lambda 350 UV/VIS/NIR instrument (USA). Fluorescence emission spectra were recorded at room temperature using the Horiba Jobin Yvon Fluoromax-4 spectrofluorometer (USA). Lifetime decay profiles were measured on Lifespec II and FSP 920 luminescence spectrometers (Edinburgh Instruments, UK). Powder X-ray diffraction patterns were recorded on a 9 kW powder X-ray diffraction system (Rigaku Technologies, Smartlab, Japan). Thermogravimetric analysis was performed on a Netzsch, STA 449F3 instrument (Germany) at a heating rate of 10 °C min<sup>-1</sup> under an argon atmosphere. Optical microscopic images were captured by a Zeiss optical microscope (Germany) from crystals on a glass slide. Infra-red spectra of the solid samples in the region of 400–4000 cm<sup>-1</sup> were recorded with a PerkinElmer Spectrum-Two FT-IR spectrometer (USA) using the ATR method. Cyclic voltammetry studies were performed on a Potentiostat Model CHI6044E (USA) with a three-electrode set-up dipped in a cylindrical cell with a solution of the respective compound (1 mM, 10 mL solution in DMF). A glassy carbon electrode was used as the working electrode, platinum as the counter electrode, Ag/AgNO<sub>3</sub> as the reference electrode, and tetrabutylammonium perchlorate (0.1 mM) as the supporting electrolyte. For measuring the UV-visible spectra, stock solutions of the naphthalimide derivative (2.0 mM in DMF), 2,6-pyridinedicarboxylic acid (20.0 mM in DMF), and different metal acetates or ferric chloride (1 mM in water) were prepared. The UV-visible studies of the solution of the single-component or bi-component system were performed in a quartz cuvette. The UV-visible titrations were performed by adding the desired amounts of the solution of the metal salt dissolved in water (1.0 mM) to such solution. After each aliquot added by a micro-pipette, each solution was stirred prior to obtaining a homogeneous solution after each addition. The fluorescence spectroscopic titrations were carried out in similar

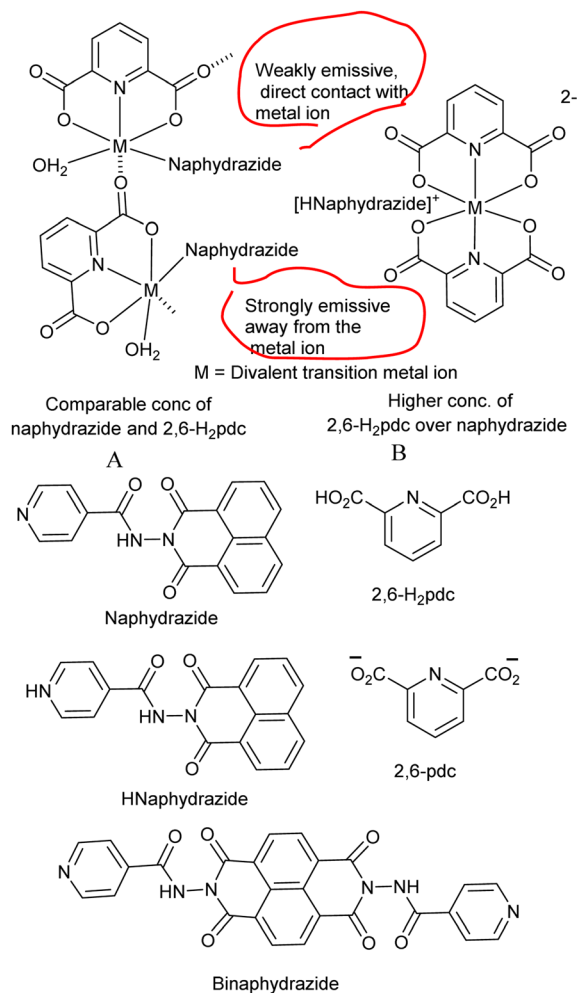


Fig. 1 (A and B) are the two proposed bi-component platforms formed by H<sub>2</sub>26pdc and naphydrazide with a metal ion to detect another ion among various other possible assemblies, and the others are the structures of the analytes.



Table 1 Crystallographic and refinement parameters of the iron complexes

Parameters	[(Hnaphydrazide)[Fe(2,6-pdc) <sub>2</sub> ]]·H <sub>2</sub> O	[(H <sub>2</sub> binaphydrazide)[Fe(2,6-pdc) <sub>2</sub> ]]·4.5H <sub>2</sub> O
Empirical formula	C <sub>32</sub> H <sub>20</sub> FeN <sub>5</sub> O <sub>12</sub>	C <sub>54</sub> H <sub>46</sub> Fe <sub>2</sub> N <sub>10</sub> O <sub>31</sub>
Formula weight	722.38	1442.71
Crystal system	Triclinic	Monoclinic
<i>a</i> /Å	7.808(6)	16.017(3)
<i>b</i> /Å	14.712(11)	14.142(3)
<i>c</i> /Å	14.844(12)	26.803(6)
$\alpha$ /°	117.038(16)	90
$\beta$ /°	92.27(2)	90.347(9)
$\gamma$ /°	98.607(15)	90
<i>V</i> /Å <sup>3</sup>	1490(2)	6071(2)
<i>Z</i>	2	4
$\rho_{\text{cal}}$ (g cm <sup>-3</sup> )	1.610	1.578
$\mu$ (mm <sup>-1</sup> )	0.585	0.582
<i>F</i> (000)	738.0	2960.0
Refl. collected	35 011	71 609
Independent refl.	5296	5567
Ranges ( <i>h</i> , <i>k</i> , <i>l</i> )	-9 ≤ <i>h</i> ≤ 9 -17 ≤ <i>k</i> ≤ 17 -17 ≤ <i>l</i> ≤ 17	-19 ≤ <i>h</i> ≤ 19 -16 ≤ <i>k</i> ≤ 17 -32 ≤ <i>l</i> ≤ 32
Max $\theta$ (degree)	25.204	25.409
Data/restraints/parameter	5296/0/462	5567/0/397
Goof ( <i>F</i> <sup>2</sup> )	1.067	1.045
<i>R</i> Indexes	0.0415	0.0532
[ <i>I</i> > 2 $\sigma$ ]	0.0375	0.0404
WR <sub>2</sub>	0.1062	0.1258

manners. The excitation for obtaining the emission spectra was done for the naphydrazide- and binaphydrazide-containing solutions at 335 nm and 375 nm, respectively.

### Determination of the detection limit

The fluorescence intensity at 400 nm of a solution of naphydrazide (2.5 mL, 2.0 mM) and 2,6-H<sub>2</sub>pdc (400  $\mu$ L, 20.0 mM) in DMF upon the addition of different aliquots of solutions of Cd<sup>2+</sup> ions (different aliquots taken from a 20 mM stock solution of water) was plotted. The detection limit was calculated by using this plot. Detection limit =  $3\sigma/K$ ; where  $\sigma$  is the standard deviation of blank measurements (taken from six blank experiments) and *K* is the slope. Standard deviation of each emission reading was estimated from two independent sets of experiments by observing three sets of readings after three min intervals for each measurement (Table S5<sup>†</sup>).

**Synthesis of [(Hnaphydrazide)[Fe(2,6-pdc)<sub>2</sub>]]·H<sub>2</sub>O.** Ferric chloride (16.2 mg, 0.1 mmol) was added to a well-stirred solution of naphydrazide (31.7 mg, 0.1 mmol) and 2,6-H<sub>2</sub>pdc (33.4 mg, 0.2 mmol, in 20 mL) in warm methanol. The reaction mixture was stirred for 3 h. A brown precipitate was formed, which was re-dissolved by adding Millipore water (10 mL). The solution was then filtered and kept undisturbed for 2–3 days for crystallization to obtain yellow crystals. Isolated yield: 70%. IR (neat, cm<sup>-1</sup>): 3461 (s,  $\nu_{\text{O-H}}$ ), 3324 (s,  $\nu_{\text{amide N-H}}$ ), 1721 (s,  $\nu_{\text{imide C=O}}$ ), 1635 (s,  $\nu_{\text{amide C=O}}$ ).

**Synthesis of [(H<sub>2</sub>binaphydrazide)[Fe(2,6-pdc)<sub>2</sub>]]·4.5H<sub>2</sub>O.** This complex was prepared by a similar procedure as for the previous compound using binaphydrazide (50.6 mg, 0.1 mmol) and 2,6-H<sub>2</sub>pdc (66.8 mg, 0.4 mmol) and ferric chloride

(0.2 mmol, 32.4 mg). In this case, brown crystals were obtained in a 60% yield. IR (neat, cm<sup>-1</sup>): 3423 (s,  $\nu_{\text{amide N-H}}$ ), 1738 (s,  $\nu_{\text{imide C=O}}$ ), 1640 (s,  $\nu_{\text{amide C=O}}$ ). The complex was further characterized by XPS, thermogravimetry analysis, powder XRD, and single-crystal structure determination.

### Structure determination

Single-crystal X-ray diffraction data for the complexes were collected at 297 K using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) on a Bruker Nonius SMART APEX CCD diffractometer (Germany) equipped with a graphite monochromator and an Apex CCD camera. Data reductions and cell refinement were carried using SAINT and XPREP software. The structures were solved by a direct method and were refined by full-matrix least squares on *F*<sup>2</sup> using SHELXL-2018 software. All non-hydrogen atoms were refined in an anisotropic approximation against *F*<sup>2</sup> for all the reflections. Hydrogen atoms were placed at their geometrical positions according to the riding model and were refined by isotropic approximation. The crystal and structural refinement parameters are listed in Table 1.

## Results and discussion

### UV-visible spectroscopic study

The solution of naphydrazide in dimethylformamide (DMF) displayed a UV-absorption peak at 335 nm ( $\epsilon = 4.51 \times 10^{-3}$  mol<sup>-1</sup> m<sup>2</sup>) (Fig. S1<sup>†</sup>). Upon the addition of an aqueous solution of Fe<sup>2+</sup> ions to the naphydrazide solution, the intensity of the absorption at 335 nm was increased (Fig. S2<sup>†</sup>). Whereas, in a similar experiment performed by adding an aqueous solution



of  $\text{Fe}^{3+}$  ions (Fig. 2a), the absorption peak was red-shifted by 20 nm to 315 nm, and there was an increase in the intensity at this wavelength. Both showed a linear increase in the intensities with the increasing concentration of iron ions; the ratio of the two slopes from their respective plot showed the 7.90 times higher sensitivity of naphydrizide for  $\text{Fe}^{3+}$  ions over  $\text{Fe}^{2+}$  ions (Fig. 2c). A similar titration of a solution of 2,6- $\text{H}_2\text{pdc}$  (which had an absorption peak at 270 nm and  $\epsilon = 3.67 \times 10^{-3} \text{ mol}^{-1} \text{ m}^2$ ) upon interaction with  $\text{Fe}^{2+}$  ions displayed an increase in the absorption intensity at 270 nm. Whereas,  $\text{Fe}^{3+}$  ions with 2,6- $\text{H}_2\text{pdc}$  displayed two new absorption peaks at 315 nm and 360 nm. The intensities of these two absorption peaks were increased with the increasing amount of  $\text{Fe}^{3+}$  ions (Fig. S4†) added to the solution. The relative increase caused by  $\text{Fe}^{3+}$  at 315 nm with respect to that at 270 nm by  $\text{Fe}^{2+}$  was compared from the respective slopes through a linear plot of the intensity vs. concentration. The slope obtained from titration with  $\text{Fe}^{3+}$  was 100.46 times higher than the one from such a plot with  $\text{Fe}^{2+}$  ions. Hence, based on the relative positions as well as from the intensities of the absorptions, these two ions could be distinguished. Among the commonly used reagents, 1,10-phenanthroline<sup>30</sup> is a popular choice for the colorimetric estimation of  $\text{Fe}^{2+}$ , but in such a detection  $\text{Fe}^{3+}$  ions interfere. However, a large improvement in the detection of  $\text{Fe}^{2+}$  by 1,10-phenanthroline could be achieved by using it together with carbon dots.<sup>31</sup> As there is an overlapping region for the absorption peak of the  $\text{Fe}^{2+}$ -1,10-phenanthroline complex with the emission

spectra of carbon dots, fluorescence at a longer wavelength through resonance energy transfer was observed. Selective disassembly of the bio-composites with gold nanoparticles was caused by  $\text{Fe}^{2+}$ ; which provided an avenue to detect  $\text{Fe}^{2+}$  ions without interference from  $\text{Fe}^{3+}$  ions.<sup>32</sup> In the present case, the absorptions shown by 2,6- $\text{H}_2\text{pdc}$  with  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  were distinguishable from each other.

The 2,6- $\text{H}_2\text{pdc}$  was able to distinguish between  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  in solution in the presence of  $\text{Cd}^{2+}$  ions. The UV spectrum of a solution of 2,6- $\text{H}_2\text{pdc}$  and  $\text{Cd}^{2+}$  ions upon the addition of  $\text{Fe}^{2+}$  ions showed multiple overlapping UV peaks (Fig. S3†), whereas, 2,6- $\text{H}_2\text{pdc}$  with  $\text{Fe}^{3+}$  ions had a peak at 360 nm, and the intensity of this peak increased with increasing the concentration of  $\text{Fe}^{3+}$  ions, but was not affected by  $\text{Cd}^{2+}$  ions (Fig. S6b†). The solution of naphydrizide containing  $\text{Cd}^{2+}$  ions upon the addition of  $\text{Fe}^{3+}$  ions (Fig. 2c) showed large difference in the UV-visible spectra of the solution with  $\text{Fe}^{2+}$  ions. This was not the case with the UV spectral changes of the solution of naphydrizide containing  $\text{Zn}^{2+}$  ions upon the addition of  $\text{Fe}^{3+}$  ions. Thus, the UV-visible spectroscopic titrations of the solution of naphydrizide allowed distinguishing  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in the presence of  $\text{Cd}^{2+}$  ions. The distinctions among these ions were possible due to the relative binding of 2,6- $\text{H}_2\text{pdc}$  and naphydrizide to the corresponding metal ion, which were reflected in the individual intensity vs. concentration plots. Once the  $\text{Zn}^{2+}$  ions formed a complex with 2,6- $\text{H}_2\text{pdc}$ , the  $\text{Fe}^{3+}$  ions as well as  $\text{Fe}^{2+}$  ions could not replace the zinc ion from the coordination sphere. The  $\text{Fe}^{3+}$  ions had a better binding ability to form a complex with naphydrizide than the  $\text{Cd}^{2+}$  ions. So, the enhancement of the absorption intensity at 315 nm was specifically caused by  $\text{Fe}^{3+}$  ions. There was an insignificant change in the experiments with the UV titration of naphydrizide with  $\text{Cd}^{2+}$  ions, while the similar titration with 2,6- $\text{H}_2\text{pdc}$  showed an increase in the intensity at 335 nm (Fig. S7b†). Alternatively,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  ions could be distinguished by naphydrizide in the presence of  $\text{Fe}^{3+}$  ions. An equimolar solution of naphydrizide and 2,6- $\text{H}_2\text{pdc}$  could also distinguish between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions. The UV-visible titration of such a solution with  $\text{Fe}^{2+}$  showed an increase in the absorption at 270 nm as well as at 335 nm. However, in the titration with  $\text{Fe}^{3+}$  ions, there were two new absorptions at 315 nm and 360 nm. These two absorption peaks were from the respective complexes of the  $\text{Fe}^{3+}$  ions with the individual components. The intensities of these peaks increased with the increasing concentration of  $\text{Fe}^{3+}$  ions. Hence, there was a distinction upon the addition of  $\text{Fe}^{3+}$  ions to the bi-component solution with respect to the individual components. The bi-component solution showed UV changes at 270 nm in the presence of different metal ions. The ratio of the slopes of the plots for the changes in intensities of the bi-component solution caused at 270 nm by  $\text{Fe}^{3+}$  with respect to that for  $\text{Fe}^{2+}$  ions was 1.70 (Fig. S5c†). So, the distinctions between the two ions by naphydrizide or the bi-component solution were similar, but it was inferior in the latter case. In the bi-component solution, there was a smoother increase at the common wavelength of 270 nm. This provided a common absorption wavelength to monitor the cations by the bi-component system. The limit of detection (LOD) for  $\text{Fe}^{3+}$  ions

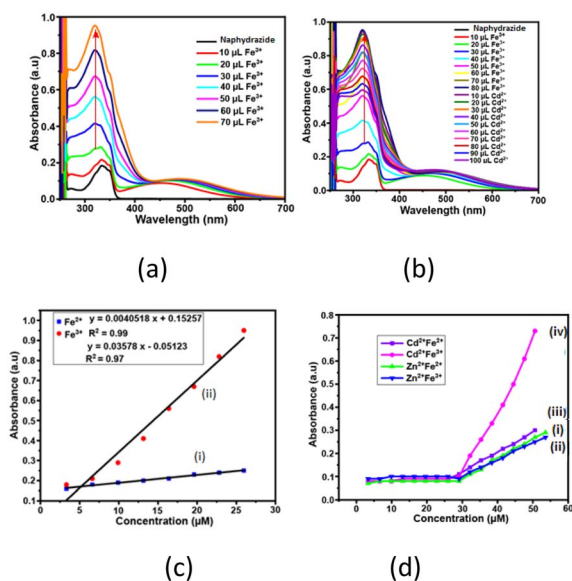


Fig. 2 UV-visible titration of naphydrizide (3.32  $\mu\text{M}$  in DMF, 3 mL) with each aliquot addition of (a)  $\text{Fe}^{3+}$  ions, and (b) with different aliquots of a solution of  $\text{Fe}^{3+}$  ions, followed by the addition of  $\text{Cd}^{2+}$  ions. (c) Plots of the absorbance of solutions of naphydrizide (3 mL) with different aliquots of (i)  $\text{Fe}^{2+}$  ions at 335 nm and (ii)  $\text{Fe}^{3+}$  ions at 315 nm. (d) Plots of the intensity absorbance of solutions of naphydrizide (each 3.32  $\mu\text{M}$  in DMF) at 315 nm upon addition of a solution of  $\text{Zn}^{2+}$  ions, followed by (i)  $\text{Fe}^{2+}$  or (ii)  $\text{Fe}^{3+}$  ions;  $\text{Cd}^{2+}$  ions, followed by (iii)  $\text{Fe}^{2+}$  or (iv)  $\text{Fe}^{3+}$  solution (in each titration, 10  $\mu\text{L}$  stock solution from 1 mM in water of the specific metal ion was used).



by naphydrizide (determined by the changes at 315 nm) was 0.45  $\mu\text{M}$  (at 315 nm), while by 2,6- $\text{H}_2\text{pdc}$  it was 1.28  $\mu\text{M}$ , and for the bi-component it was 0.09  $\mu\text{M}$ . These LOD values of  $\text{Fe}^{3+}$  were within the permissible limit 0.3–0.5  $\text{mg L}^{-1}$  of  $\text{Fe}^{3+}$  ions in drinking water recommended by the WHO.<sup>33</sup> Hence, the key advantage of this single-component naphydrizide or bi-component system was the ability distinguish among the three ions  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Cd}^{2+}$  ions and the detection of  $\text{Fe}^{3+}$  ions with a reasonable LOD, while the main limitation was that the absorptions were measured in the UV region, which is less attractive for practical applications.

### Fluorescence study

Naphydrizide belongs to the family of naphthalimide, which has potential for fluorescence sensing.<sup>34</sup> It had very weak emission at 400 nm in DMF solution upon excitation at 335 nm. The emission was due to the photo-electron transfer OFF-state of the  $\pi^*$  to  $\pi$  transition.<sup>28</sup> The emission spectrum of a solution of naphydrizide at 400 nm did not change upon the addition of  $\text{Cd}^{2+}$  ions; whereas the solution of a mixture of naphydrizide and 2,6- $\text{H}_2\text{pdc}$  in DMF showed selectively for  $\text{Cd}^{2+}$  ions, as it caused a sharp increase in the emission intensity maximum at 383 nm that appeared at a shifted peak position of 400 nm ( $\lambda_{\text{ex}} = 335$  nm, Fig. 3a) for naphydrizide. Further, there was no change in the emission of the respective solution of naphydrizide and 2,6- $\text{H}_2\text{pdc}$  in DMF upon the addition of other ions, such as  $\text{NH}_4^+$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{Al}^{3+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ , or  $\text{Ag}^+$  ions. A feeble increase in the emission intensity was caused by the addition of  $\text{Ag}^+$  or  $\text{Zn}^{2+}$  ions to the bi-component solution. A comparison of the differences in the relative emission intensities is shown in the bar diagram in Fig. 3b. This showed that the change caused by  $\text{Cd}^{2+}$  was approximately eight times higher than the emission increase caused by  $\text{Zn}^{2+}$  ions and 3.2 times that caused by  $\text{Ag}^+$  ions; whereas  $\text{Cd}^{2+}$  ions did not affect the emission spectrum of naphydrizide in the absence of 2,6- $\text{H}_2\text{pdc}$ . The interferences of different ions on the emission of the bi-component solution caused by  $\text{Cd}^{2+}$  ions were also studied (Fig. 3c). From this study, it was clear that the emission of the bi-component solution was significantly affected only by  $\text{Cd}^{2+}$  ions among all the ions tested. The change in intensity was due to chelation of the cadmium ions and their subsequent protonation to cause photo-electron transfer to be turned ON.

Mixed ligand complexes of 2,6- $\text{H}_2\text{pdc}$  with  $\text{Cd}^{2+}$  ions<sup>35</sup> with a coordination number higher than six have been reported in literature. It was reported that when forming a 2,6-pdc-complex with a metal ion by 2,6- $\text{H}_2\text{pdc}$ , protons liberated in the solution protonated the pyridine atom of the naphydrizide to generate a PET-ON state.<sup>19</sup> It may be mentioned that the acid–base properties of naphthalimide derivatives can help in anion detection.<sup>36</sup> On the other hand, a silver complex with naphydrizide in the solid state showed dual emission at 445 nm and 553 nm, whereas in solution it showed an aggregation-induced emission enhancement at 394 nm.<sup>28</sup> Optimization of the best ratio for obtaining the best performance by the bi-component mixture of naphydrizide with 2,6- $\text{H}_2\text{pdc}$  in a solution containing  $\text{Cd}^{2+}$  ions (Fig. S15†) showed that a 1 : 3.2 molar ratio was

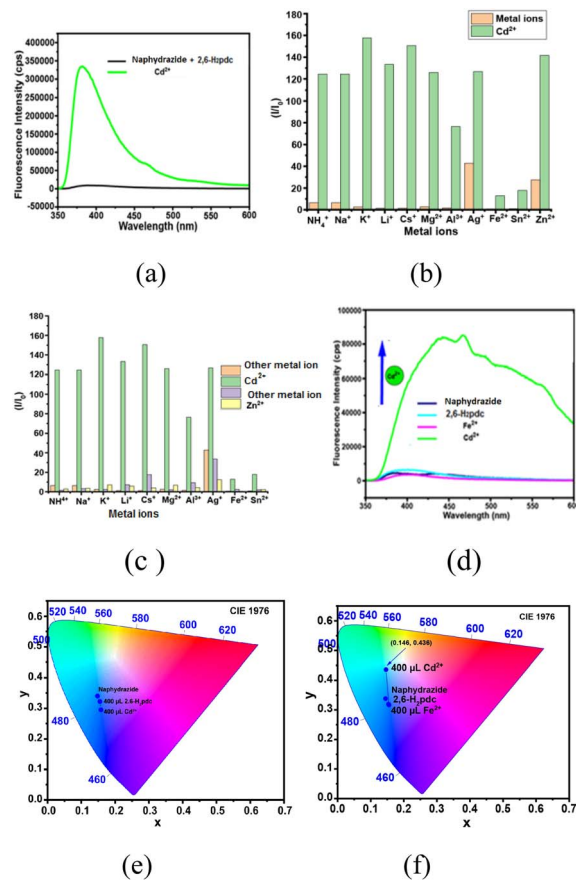


Fig. 3 (a) Fluorescence spectra ( $\lambda_{\text{ex}} = 335$  nm) of a solution of naphydrizide (2 mM in DMF) together with 2,6- $\text{H}_2\text{pdc}$  (20 mM in DMF) (i) with  $\text{Cd}^{2+}$  ions (400  $\mu\text{L}$  of 20 mM in water); (ii) without  $\text{Cd}^{2+}$  ions; (b) Bar graph showing the relative changes in emission at 400 nm caused by different metal ions compared to the one caused by  $\text{Cd}^{2+}$  ions; (c) Bar graph showing the relative changes in emission intensity at 400 nm caused by different metal ions in the presence of a particular ion shown in the x-axis; (d) emission spectra showing the effect of  $\text{Fe}^{2+}$  ions on the emission spectra of a solution containing naphydrizide (2.5 mL taken from 2 mM solution in DMF) + 2,6- $\text{H}_2\text{pdc}$  (0.4 mL taken from 20 mM in DMF) after the addition of  $\text{Cd}^{2+}$  (400  $\mu\text{L}$  of 20 mM) together with  $\text{Fe}^{2+}$  (400  $\mu\text{L}$  of 20 mM). (e and f) Chromaticity CIE (1976) diagram of a solution of naphydrizide and 2,6- $\text{H}_2\text{pdc}$  with cadmium ions (2.5 mL of 2 mM, 400  $\mu\text{L}$  of 20 mM 2,6- $\text{H}_2\text{pdc}$  and 400  $\mu\text{L}$  of 1 mM of  $\text{Cd}^{2+}$ ) and the same solution but with  $\text{Fe}^{2+}$  ions (400  $\mu\text{L}$  of 1 mM), respectively.

a suitable to study the changes in fluorescence by cadmium ions. This implied that an excess amount of 2,6- $\text{H}_2\text{pdc}$  was required to form a bis-chelated complex (see Fig. 1B) with cadmium ions and to protonate the pyridine of naphydrizide. The addition of  $\text{Fe}^{3+}$  ions to the solution caused a quenching of the weak emission, which was expected as the role of  $\text{Fe}^{3+}$  as a quencher has been well documented.<sup>37</sup> However, when a solution of  $\text{Fe}^{2+}$  ions was added to the same solution, the emission intensity was sharply increased (Fig. 3d). These observations reflected that the  $\text{Fe}^{3+}$  ions were replacing the coordinated cadmium ions from the 2,6- $\text{H}_2\text{pdc}$  complex, which caused a drastic change in the absorption spectrum that was not observed with the  $\text{Fe}^{2+}$  ions. In the fluorescence emission



study, we found that the  $\text{Fe}^{2+}$  ions did not inhibit the enhancement of the emission peak of the bi-component solution containing  $\text{Cd}^{2+}$  ions, but the spectral profile was changed drastically by  $\text{Fe}^{2+}$  ions, which caused a spread of the emission over wavelengths of 350 nm to 600 nm (Fig. 3d). Hence, white-light emission took place when  $\text{Fe}^{2+}$  and  $\text{Cd}^{2+}$  ions were present together in the solution of the bi-components. The effect of  $\text{Fe}^{2+}$  ions on such a solution for two different ratios of the bi-components was studied at two other ratios of 2,6- $\text{H}_2\text{pdc}$ : naphthylidene, namely 1 : 1.25 and 1 : 2.50. At the 1 : 1.25 ratio (Fig. S10<sup>†</sup>), a broad overlapping emission from two peaks at 469 nm and 529 nm was observed, whose intensities were enhanced with the amount of  $\text{Cd}^{2+}$  ions, and finally broadened to spread over the range 390–650 nm.

Whereas with the ratio 1 : 2.50, the intensity of the broad emission peak spread over 390–650 nm increased, but at this concentration of 2,6- $\text{H}_2\text{pdc}$ , the broad emission was skewed (Fig. S15B<sup>†</sup>), showing a maximum at 469 nm. The chromaticity indices of the two samples, one having  $\text{Cd}^{2+}$  ions and other containing both  $\text{Cd}^{2+}$  and  $\text{Fe}^{2+}$  ions together in the bi-component solution, were determined, and these are shown in Fig. 3e and f. From the chromaticity index plots, blue emission was observed from the solution of naphthylidene together with 2,6- $\text{H}_2\text{pdc}$  in the presence of  $\text{Cd}^{2+}$  ions, but in the case of the solution having both  $\text{Fe}^{2+}$  and  $\text{Cd}^{2+}$  ions, white-light emission was observed. Due to the combined effect of f-f transition vs.  $\pi^*-\pi$  transition of naphthalimide,<sup>38</sup> an europium-naphthalimide complex was reported to show white-light emission. On the other hand, certain halo-bridged cadmium coordination polymers also show white-light emission.<sup>39</sup> Here, the white-light emission observed by us upon adding  $\text{Fe}^{2+}$  ions in a bi-component solution containing  $\text{Cd}^{2+}$  ions was possibly due to a combination of PET ON and exciplex formation. The lifetime decay profile of the bi-component solution with  $\text{Cd}^{2+}$  ions displayed a bi-exponential decay profile with very short lifetimes, specifically, 0.050 ns and 0.225 ns (for the following fractions 89.58% and 10.42%), respectively. As the emission of the bi-component was poor, the lifetime without cadmium ions could not be determined. In the present case, it could be from the decay of an excited state generated by the interaction of the existing assembly of the bi-component system with  $\text{Cd}^{2+}$  ions (PET-ON state). Upon the addition of  $\text{Fe}^{2+}$  ions to the solution, the decay profile was bi-exponential and had lifetimes of 0.100 ns (fraction 27.03%) and 0.203 ns (fraction 72.97%), showing that the addition of  $\text{Fe}^{2+}$  led to an enhanced modified short-lifetime path, and a new path with a relatively higher lifetime was generated. Such, very short lifetimes have also been observed for excited state complexes of naphthalimide with organic molecules<sup>40</sup> and also in two photon excitations of naphthalimide, as reported in the literature.<sup>41</sup> So, the multiple emission paths contributed to the white-light emission. A recent report suggested that white-light emission could be generated from naphthalimide derivatives.<sup>42</sup>

The maximum permissible limit for  $\text{Cd}^{2+}$  ions in drinking water set by the World Health Organization is 44  $\mu\text{M}$  (0.005  $\text{mg L}^{-1}$ ).<sup>33</sup> In the present case, the limit of detection was 18.31  $\mu\text{M}$  (0.002  $\text{mg L}^{-1}$ ), which is 2.5 times more sensitive than

the required limit. This value is also comparable to many sensors reported in the literature (Table S4<sup>†</sup>), but less sensitive to several sensing molecules used for the detection of  $\text{Cd}^{2+}$  ions.<sup>43–48</sup> However, those receptors had different binding mechanisms and also involved complex synthetic and pre-treatment requirements.<sup>43–48</sup> In certain examples, stringent requirements for pH maintenance using a buffer were required. In the present example, a buffer was not required, and the detection could be performed in a bi-component system in DMF. Naphthalimide functionalized at the 4-position was identified as suitable for selective fluorescence ON with  $\text{Cd}^{2+}$  ions and OFF with  $\text{Cu}^{2+}$  ions.<sup>49</sup> This sensor had a better sensitivity than the present example towards sensing  $\text{Cd}^{2+}$  ions, but in the present case, the reported synthesis was simple, while the former involving a Schiff base also had a possibility to hydrolyze, which was absent in the present case. There are also examples of chelation-induced emission enhancement by  $\text{Cd}^{2+}$  ions on coumarin-based sensors having a higher response than  $\text{Zn}^{2+}$  ions.<sup>50</sup> A hydroxynaphthalene-based Schiff base showing a preference for  $\text{Zn}^{2+}$  over  $\text{Cd}^{2+}$  was also reported.<sup>51</sup> A terpyridine-based receptor could also reportedly distinguish  $\text{Cd}^{2+}$  from  $\text{Zn}^{2+}$  in solution with a detection limit comparable to the present bi-component sensing platform, but the detection process described here could not only differentiate  $\text{Cd}^{2+}$  from  $\text{Zn}^{2+}$ , but also differentiate  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions in the presence of  $\text{Cd}^{2+}$  ions in colorimetric as well as in fluorescence detections.

### Synthesis and characterization of the complexes

Naphthalimide-based complexes in general provide avenues for different  $\pi$ -stacking arrangements,<sup>52,53</sup> and various naphthalimide-linked imidazole-based ligands forming metal complexes have been reported in the literature.<sup>54</sup> Also, independent reactions of naphthylidene with ferric chloride in the presence of 2,6-pyridinedicarboxylic acid could provide the complex  $[(\text{Hnaphthylidene})[\text{Fe}(2,6\text{-pdc})_2]] \cdot \text{H}_2\text{O}$ . This complex has an Hnaphthylidene cation and  $[\text{Fe}(2,6\text{-pdc})_2]^-$  (Fig. 4a). The ferric ion in the complex is in a distorted octahedral environment and the  $[\text{Fe}(2,6\text{-pdc})_2]^-$  portion of the complex displayed similar structural features to others reported in the literature<sup>55</sup> with different organo-cations. The metal ligand bonds are listed in Table S2.<sup>†</sup> The bulk purity of the complex was determined by comparing the experimental powder X-ray diffraction (PXRD) patterns and crystallographic information file (CIF) generated pattern (Fig. S17a<sup>†</sup>), and it was found to be a single form of the complex in the solid state. The complex was thermally unstable above 263 °C (Fig. S20a<sup>†</sup>). A similar complex  $[(\text{H}_2\text{-binaphthylidene})[\text{Fe}(2,6\text{-pdc})_2] \cdot 4.5\text{H}_2\text{O}]$  was obtained by using binaphthylidene instead of naphthylidene. It had a di-protonated binaphthylidene with two  $[\text{Fe}(2,6\text{-pdc})_2]^-$  anions, as shown in Fig. 4b. The asymmetric unit of the complex had half portions of the cation and one anion. In the self-assembly, the organocation  $\text{H}_2\text{binaphthylidene}$  is sandwiched between the planes of 2,6- $\text{H}_2\text{pdc}$  rings from two anions located below and above. The bond parameters of the anionic portion of the complex are listed in Table S2<sup>†</sup> and are typical of six-coordinated bis-chelated complexes. The water molecules of crystallization were highly



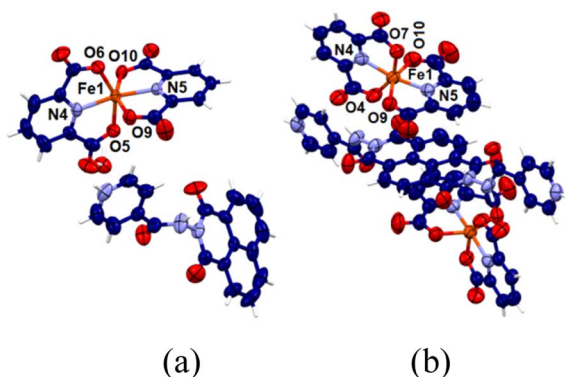


Fig. 4 Crystal structures of (a) [(Hnaphydrizide)[Fe(2,6-pdc)<sub>2</sub>] $\cdot$ H<sub>2</sub>O and (b) [(H<sub>2</sub>binaphydrizide)[Fe(2,6,0pdc)<sub>2</sub>]<sub>2</sub> $\cdot$ 4.5H<sub>2</sub>O (water molecules were squeezed).

disordered. As the disorder could not be resolved by X-ray diffraction data refinement, the squeeze command was applied to omit them from the structure. The purity and integrity of the composition of the complex were further confirmed by recording the PXRD pattern and matching it with one generated from the CIF file (Fig. S17b<sup>†</sup>). The thermogram of the compound showed weight losses due to evaporation of the four and half water molecules at 93 °C (Fig. S20b<sup>†</sup>). To confirm this was due to the loss of water molecules. The IR of the pristine sample of the complex was compared with a sample that was heated to 100 °C and cooled to room temperature. It was found that the O–H stretch of water molecules in the pristine sample at 3461 cm<sup>-1</sup> disappeared in the sample heated prior to recording the spectrum. The complex was thermally unstable above 325 °C. A solution of [(Hnaphydrizide)[Fe(2,6-pdc)<sub>2</sub>] $\cdot$ H<sub>2</sub>O in DMF displayed UV-absorption maxima at 270 nm and 332 nm. Plots of the absorption intensity at 270 nm in different concentrations vs. concentrations of the complex in the range of 3.33–29.12 μM showed a linear increase in absorption (Fig. S21a<sup>†</sup>), indicating there was no aggregation of the complexes in the respective dilute solutions. This was also the same in the case of the other complex (Fig. S21b<sup>†</sup>). Both the complexes were non-fluorescent; hence, they were not suitable for the detection study in solution. The formation of the complexes at ambient conditions showed that the complex formation was a key step for the detection, but at a low concentration the results showed such species remained in solution.

### Cyclic voltammetry study

In general, naphthalimide derivatives show two reversible redox couples<sup>56</sup> on the -ve side of the cyclic voltammogram (CV) due to the formation of anion radicals followed by dianions. We found that the solution of naphydrizide in DMF showed such two quasi-reversible couples at  $E_{1/2}$  at -0.807 and -1.321 V (Fig. S22<sup>†</sup>). The two redox couples for naphydrizide are depicted in Fig. 5a. The complex (Hnaphydrizide)[Fe(pdc)<sub>2</sub>] $\cdot$ H<sub>2</sub>O showed quasi-reversible redox peaks at -0.418 and -0.697 V, but there was another peak at -1.02 V (Fig. S23<sup>†</sup>). The quasi-reversible peak at -0.418 V was attributed to the Fe<sup>2+</sup>/Fe<sup>3+</sup>

couple, whereas the  $E_{1/2}$  at -0.697 V was related to anion radical formation on the protonated naphydrizide. The protonated form of the Hnaphydrizide in the complex had a reduction peak at a more -ve emf (volt) than the free naphydrizide. The dianion formation was irreversible, so only a reduction peak at -1.02 V was observed. Cyclic voltammetric titrations performed with naphydrizide by adding Fe<sup>2+</sup> and Cd<sup>2+</sup> ions did not show any noticeable change (Fig. S24<sup>†</sup>), other than a small change in the  $I_{pc}$  value. The CV bi-component solution of naphydrizide with 2,6-H<sub>2</sub>pdc showed a significant difference in the couple of the anion radical from the parent naphydrizide. In this case, the radical anion generated was irreversible; whereas the couple for the dianion (Fig. 5a) remained unchanged (Fig. 5b).

Upon the addition of Fe<sup>3+</sup> or Fe<sup>2+</sup> ions to the solution, the reversibility for obtaining the anion radical was regained. The irreversibility conferred by 2,6-H<sub>2</sub>pdc to the anion radical (Fig. 5c) of naphydrizide was not recovered by adding Cd<sup>2+</sup> ions. According to the UV-vis study, the bi-component system could clearly distinguish cadmium ions over ferric ions, so the competitive binding ability of cadmium over Fe<sup>3+</sup> ions towards 2,6-H<sub>2</sub>pdc was not the prime factor in the electrochemical process. It was the redox active ferrous or ferric ions that affected the anion radical reconversion to the neutral species. A solution of binaphydrizide in DMF had two couples at  $E_{1/2}$  = -0.815 V (for anion radicals) and -1.247 V (dianions). The [(H<sub>2</sub>binaphydrizide) [Fe(pdc)<sub>2</sub>]<sub>2</sub>] $\cdot$ 4.5H<sub>2</sub>O had three redox couples with  $E_{1/2}$  at -0.367, -0.766, and -1.744 V. In this case,

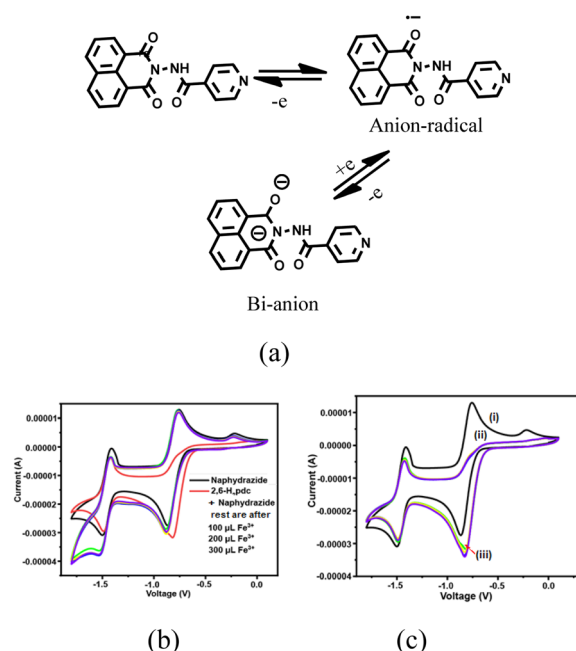


Fig. 5 (a) Redox couples of naphydrizide. Cyclic voltammetric titrations: (b) (i) naphydrizide and (ii) naphydrizide and 2,6-H<sub>2</sub>pdc (1 mM, 10 mL of each) in DMF to which a solution of Fe<sup>3+</sup> ions was added and (c) (i) naphydrizide, (ii) naphydrizide and 2,6-H<sub>2</sub>pdc, and (iii) naphydrizide + 2,6-H<sub>2</sub>pdc + Cd<sup>2+</sup> ions (100 μL solution in different aliquots from a 1.0 mM solution of the corresponding stock solution of the metal ion).



the other quasi-reversible peak at  $-0.376$  V was assigned to the ferric/ferrous couple.

## Summary and conclusions

UV-visible spectroscopic studies revealed that a bi-component platform could provide a common wavelength to monitor the concentrations of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions, while single-component systems had distinct advantages in UV studies in terms of distinguishing the ions. For example, 2,6- $\text{H}_2\text{pdc}$  could effectively distinguish  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . Naphydrazide could distinguish  $\text{Fe}^{3+}$  from  $\text{Fe}^{2+}$  in the presence of  $\text{Cd}^{2+}$  ions. In the fluorescence detection, the bi-component system was suitable for the specific detection of  $\text{Cd}^{2+}$  ions. This platform had the least interferences from many commonly abundant cations, and hence could provide a means for the useful and efficient sensing of specific ions. A comparison through UV studies on the use of naphydrazide alone or in a bi-component platform was performed and illustrated within the portions shown within the square bracket of Scheme 1. UV studies on the bi-component platform could distinguish the specific metal ions, but were not efficient enough in comparison with the specific single-component systems. The major disadvantage in the UV study was the use of shorter wavelengths.

The emission spectral changes observed with the bi-component platform were sensitive enough for the detection of  $\text{Cd}^{2+}$  ions. Chelation and the act of the photo-electron transfer ON process, followed by exciplex with different metal ions to cause or not to cause a further ON-state, were key for the

selective detection. The reversibility of the redox couple involving the anion of naphydrazide was affected by 2,6- $\text{H}_2\text{pdc}$ , but could be regained specifically by adding  $\text{Cd}^{2+}$  ions. This strategy of ion-selective electrochemical changes has scope for the further development of electrochemical signal transduction using a particular ion with a bi-component system. The use of a bi-component platform of organic compounds with multiple metal ions to cause white-light emission has scope to modulate the intensity of UV radiation. This study provides a picture on the utility of a multi-component system from easily available compounds for influencing signal transductions through the choice of a suitable combination of components.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Author contributions

The JS has contributed as a PhD student under the supervision of JBB and both the authors have contributed equally.

## Conflicts of interest

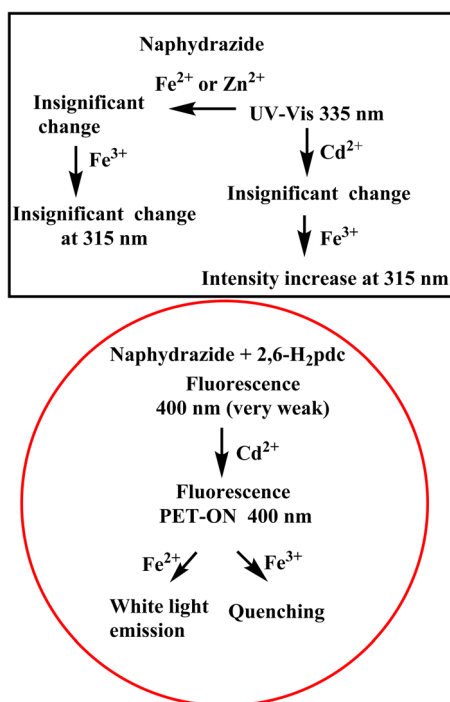
There are no conflicts of interest to declare.

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**Scheme 1** Schematic representation of the UV-visible spectral study with naphydrazide and of the emission spectroscopy from the bi-component solution with cations.





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