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Journal of Photochemistry and Photobiology A: Chemistry 162 (2004) 591–598
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Detailed studies on complexation behaviour and mechanism of fluorescence quenching of naphthalene linked hydroxamic acid with transition metal ions by UV-visible and fluorescence spectra

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Received 21 July 2003; received in revised form 25 September 2003; accepted 7 October 2003

Abstract

The stoichiometry of the complex formation and mechanism of fluorescence quenching of compounds **1** and **2** with Fe(III), Cu(II) and Zn(II) were carried out in great detail by spectrometric and fluoromertric methods. Complexes of 1:1, 1:2 and 1:3 of metal:ligand were formed and all of them gave charge transfer absorption bands at different wavelengths. The factors effecting the complexation were found as the pH of the medium, ligand and metal ion concentrations. Also, the [metal ion]:[ligand] at a given concentration of ligand is very important in determining the stoichiometry of the complex. The quenching of the fluorescence is found to be static and due to the formation of non-fluorescent complex in the ground state. All the metal ions studied forms a 1:1 complex at 1×10^{-5} M concentration of the ligand **2** at pH 3, 5.6 and 6.4 for Fe(III), Cu(II) and Zn(II), respectively. Linear Stern–Volmer plots were obtained for both compounds and formation constants ($\log K$) for the 1:1 complexes of **2** with Fe(III), Cu(II) and Zn(II) were estimated as 3.63, 3.72 and 2.45, respectively.

Keywords: Hydroxamic acid; Naphthalene; Fluorophore; Fluorescence quenching; Stern–Volmer plots

1. Introduction

Development of fluorescent sensors consisting the fluorophore and ionophore is one of the attractive subject in the studies of chemosensors in the analysis of trace metal ions [1]. The major advantage of this method is higher selectivity and sensitivity compared to other analytical methods such as spectrophotometry. Most of the fluorescent chemosensors are designed as multicomponent systems comprising a signalling unit (fluorophore) and a guest-binding site (receptor): the two are often separated by a spacer unit. Primarily, two different kind of fluorescent sensors have been developed in this regard, namely: (a) chelation enhanced fluorescence (CHEF) sensors [2]; and (b) chelation enhanced fluorescence quenching (CHEQ) sensors [3]. In the first kind, interaction between fluorophore and receptor is most often through photo-induced electron transfer (PET), which leads to quenching of the fluorescence in the free form. In the presence of the guest metal ion to be sensed, the fluorophore–receptor interaction is turned off since the binding of the metal ion to the receptor lowers the PET from the receptor to the fluorophore, and therefore fluorescence intensity is enhanced. These fluorophores are superior in the analysis of metal ions since the intensity of fluorescence is enhanced due to the presence of trace metal ions. The selectivity in the analysis is based on the selectivity of the receptor group that interacts with the metal ion, which is most often by ion–dipole interactions. For example, de Silva et al. successfully developed a fluorescence sensor with anthracene as the fluorophore and crown ether as the receptor [2]. Here, the PET from the crown ether part to the excited anthracene fluorophore quenches the fluorescence. In the presence of sodium ions, which can be fitted in to the crown ether cavity, turned off the PET and enhanced the fluorescence. In the second type of sensors, the fluorophore itself is fluorescent when the receptor site is free. In the presence of the metal ions, the fluorescent intensity is lowered. In most cases, the metal ion is chelated to the receptor unit of the sensor and the complex sensor is non-fluorescent and therefore the net fluorescence is quenched. Basically, these quenching processes can be divided into two kinds of mechanisms: static and dynamic quenching [4]. The static quenching mechanism involves the interaction between the fluorophore molecule and the metal ion, which take place in the ground state of the fluorophore molecule and forms a non-fluorescent complex. The quenching efficiency is governed by the formation constant of the complex as well as the concentration of

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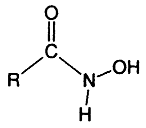
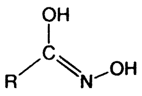
doi:10.1016/S1010-6030(03)00419-2

metal ion. In dynamic quenching, the fluorophore molecule interacts with the metal ion during the lifetime of the excited state of the fluorophore molecule. The quenching efficiencies depend on the viscosity of the solution, lifetime of the excited state of the fluorophore and the concentration of the metal ion quencher. Determination of many kinds of metal ions such as Co(II), Cr(II), Cu(II), Mo(IV) and V(V), inorganic anions, organic and biological materials based on fluorescence quenching technique have been reported [5].

In this study, we used a novel fluoroionophore, with the metal ion receipting site as the hydroxamic acid group and naphthalene as the fluorescent chromophore. Hydroxamic acid and its derivatives have shown chelating properties and have been used as spectrophotometric and gravimetric reagents [6]. Organic hydroxamic acids can be classified as oximes and consist of two tautomeric forms, of which form **I** predominates in acidic solutions. Metal complexes formed, by chelation of the metal ion between two oxygen atoms, give a five-membered ring as given in structure **III**.



(I)



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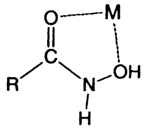
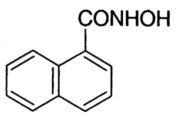


(III)

Hydroxamic acid is a strong chelating group, especially under acidic pH to a number of metal ions and selectivity can be achieved by choosing the correct pH [7]. Even though hydroxamic acid based ligands have a very high selectivity on binding, our literature survey revealed that very little studies have been done on such fluoroionophores [8]. The aim of this research is to synthesise and study fluoroionophores consisting of hydroximic acid as the ion-receipting group linked to the fluorescence chromophore naphthalene. Two different compounds have been prepared: compound **1**, where the two groups are directly attached without any spacer unit between fluorophore and receptor site; and compound **2**, where the two groups are separated by CH_2 groups have been prepared.



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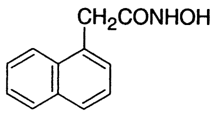

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2. Experimental

Absorption spectra were obtained using a Jasco V-500 UV-visible spectrophotometer. ^{1}H NMR spectra were obtained on a Varian Mercury 300 instrument at 300 MHz with chemical shifts relative to TMS. Fluorescence studies were done using a RF-5000 Shimadzu spectrofluorometer and Thermo Spectronic Aminco–Bowmann Series 2 luminescence spectrometer at 25 °C, and spectra were corrected. Hewlett-Packard 5890 Series II GC coupled with Hewlett-Packard 5989A mass spectrometer was used to obtain the GC/MS spectra. Infrared spectra were recorded on a Jasco FT/IR-5300 and given in wave numbers (cm^{-1}). Melting points were taken on a Stuart melting point apparatus.

All the chemicals except 9-anthracene aldehyde (from Aldrich) were purchased from Fluka. All the solvents used in spectroscopic measurements were either of Analar grade or general-purpose grade (purified by distillation).

2.1. Absorption studies

The absorption spectra of solutions of **1** and **2** in 50% methanol:water were recorded at 25 °C in the UV range 240–320 nm and in the visible range 320–700 nm under different conditions as given in Section 3.

2.2. Fluorescence studies

The emission spectra of **1** and **2** in 50% methanol were recorded under different conditions as given in Section 3.

2.3. Synthesis of 1-naphthoyl hydroximic acid (*1*)

Methyl ester of 1-naphthoic acid was prepared by standard procedure from 1-naphthoic acid. It was used without further purification for the preparation of compound **1** by using standard procedure as given further [9,10]. The ester of 1-naphthoic acid (166.4 mg, 8.946×10^{-4} mol) was dissolved in 95% C_2H_5OH (10 cm^3). A mixture of NH_2OH–HCl (6 cm^3, 0.5 M) in C_2H_5OH (6 cm^3) was added to the above ester solution. The reaction mixture was boiled for 45 min. The solution was then cooled to room temperature. It was acidified with HCl (5 cm^3, 0.5 M). The aqueous solution was then extracted with CH_2Cl_2 (3× 15 cm^3), until the organic layer remained non-fluorescent under UV. The combined extracts were washed with three portions of distilled H_2O (20 cm^3), and dried over anhydrous Na_2SO_4. mp: 176–178 °C. MS, *m/z* (%): 187 (13) [M^+], 186 (68), 156 (14), 155 (100), 127 (81), 126 (16). IR, $\nu_{\max}^{\mathrm{KBr}}$ (cm^{-1}): 3047, 1610, 1313, 1062, 779.

2.4. Synthesis of 1-naphthylacetoxy hydroximic acid (*2*)

Methyl ester of 1-naphthylaceticacid was prepared by standard procedure from 1-naphthylaceticacid acid [9]. The hydroxamic acid **2** was prepared from the ester by using similar procedure as given for **1**. mp: 161–163 °C. ^{1}H NMR (200 MHz, CD_3OD) δ: 3.91 (s, 2H), 8.04–8.10 (m, 1H), 7.84–7.90 (m, 1H), 7.76–7.82 (m, 1H), 7.38–7.56 (m, 4H). IR, $\nu_{\max}^{\mathrm{KBr}}$ (cm^{-1}): 2922, 1620, 1215, 1080, 781.

3. Results and discussion

3.1. Absorption studies of 1 and 2

The absorption spectra of ligands **1** and **2** in 50% methanol:water recorded with and without Fe(III) in the UV range of 240–320 nm (ligand concentration 10^{-5} M) are given in Figs. 1 and 2 for compounds **1** and **2**, respectively.

In order to study, the stoichiometry of the complexes formed by Fe(III) with **1** and **2**, absorption spectra in the range of 380–700 nm were recorded at excess concentrations of **1** or **2**. The pH of the medium was changed as given in Fig. 3 for compound **1**.

In order to determine the effect of the concentration of **2** on the stoichiometry of complexation at pH 3.0, the spectra of **2** at concentrations of 1×10^{-3}, 5×10^{-4}, 1×10^{-4} and 5×10^{-5} M were recorded with increasing concentrations of Fe(III). Fig. 4 gives the spectra of **2**–Fe(III) complex at 5×10^{-4} M concentration of **2** as an example. The plot of minimum Fe(III) concentration of 1:1 complexation versus the concentration of **2** is given in Fig. 5.

For both compounds **1** and **2** with the addition of Fe(III), a peak with increasing intensity appeared in the visible wavelength range as given in Fig. 4 for the compound **2** and this can be assign for the charge transfer absorption of the complexes formed between **1** and Fe(III) and between **2** and Fe(III). The peak in the range of 240–320 nm as shown in Figs. 1 and 2 for compounds **1** and **2**, respectively, can be assigned to the π-electron transition of the naphthalene fluorophore. The absorption peak at 282 nm of compound **1** was shifted to longer wavelength with increasing Fe(III) concentration, whereas the peak at 276 nm of compound **2**

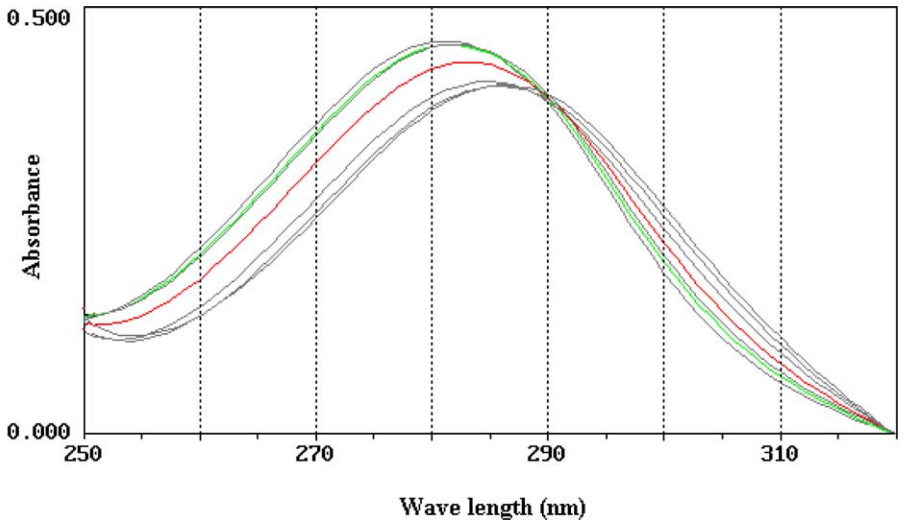

Fig. 1. UV spectra of compound **1** at 1×10^{-5} mol/dm^3 in 50% aqueous methanol with added Fe(III) concentration of 0, 7.5×10^{-6}, 1×10^{-5}, 2.5×10^{-5}, 5×10^{-5}, 7.5×10^{-5} and 1×10^{-4} mol/dm^3 from the smallest to the largest λ_{max} at pH 3.0. Isobestic point is at 290 nm.

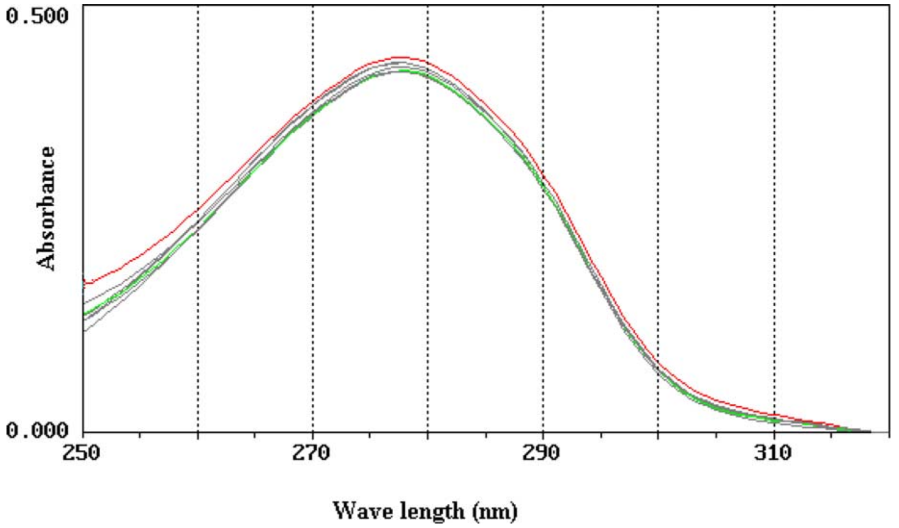

Fig. 2. UV spectra of compound **2** at 1×10^{-5} mol/dm^3 in 50% aqueous methanol with added Fe(III) concentration of 0, 7.5×10^{-6}, 1×10^{-5}, 2.5×10^{-5}, 5×10^{-5}, 7.5×10^{-5} and 1×10^{-4} mol/dm^3 from the smallest to the largest λ_{max} at pH 3.0.

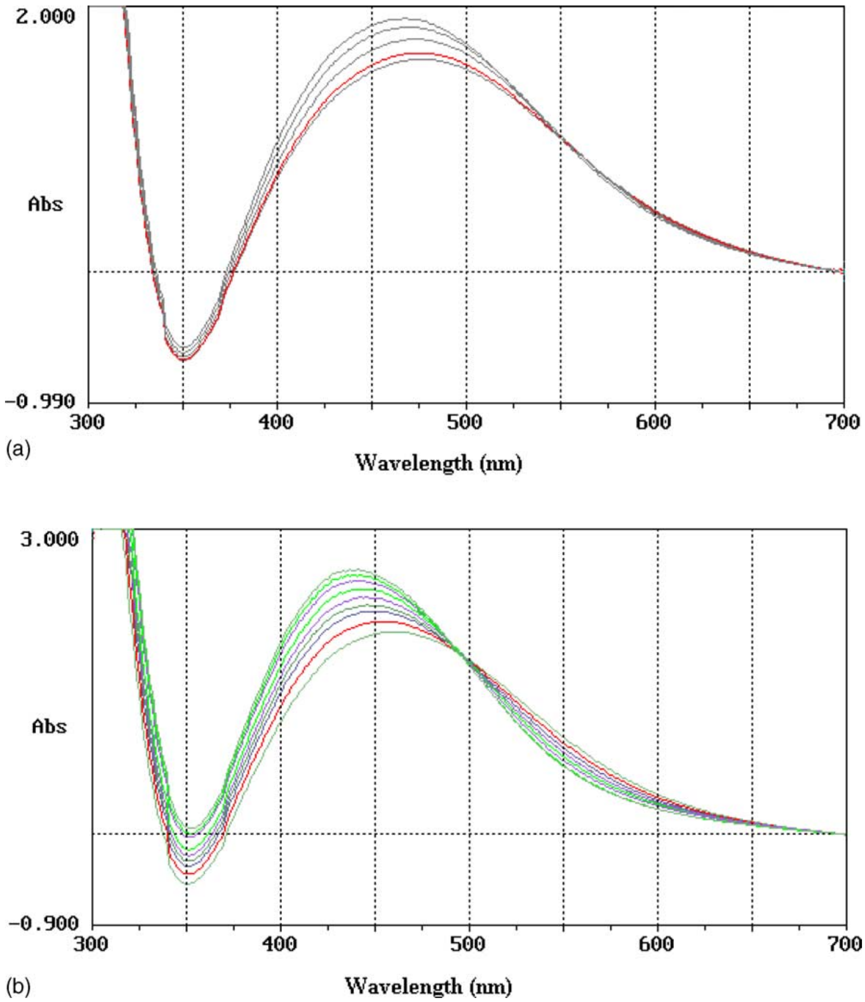

Fig. 3. (a) UV-visible spectra recorded for **1**–Fe(III) samples at pH 3.94, 4.25, 4.54, 4.87 and 5.19 from the smallest to the largest absorbance at 470 nm. $C_{\mathrm{Fe(III)}} = 5.6 \times 10^{-4}\,\mathrm{mol/dm^3}$, $C_{\mathrm{compound}\,\mathbf{1}} = 3 \times 10^{-3}\,\mathrm{mol/dm^3}$, isobestic point at 568 nm. (b) UV-visible spectra recorded for **1**–Fe(III) samples at pH 5.53, 5.82, 6.09, 6.24, 6.36, 6.56, 6.94 and 7.4 from the smallest to the largest absorbance at 420 nm. $C_{\mathrm{Fe(III)}} = 5.6 \times 10^{-4}\,\mathrm{mol/dm^3}$, $C_{\mathrm{compound}\,\mathbf{1}} = 3 \times 10^{-3}\,\mathrm{mol/dm^3}$, isobestic point at 495 nm.

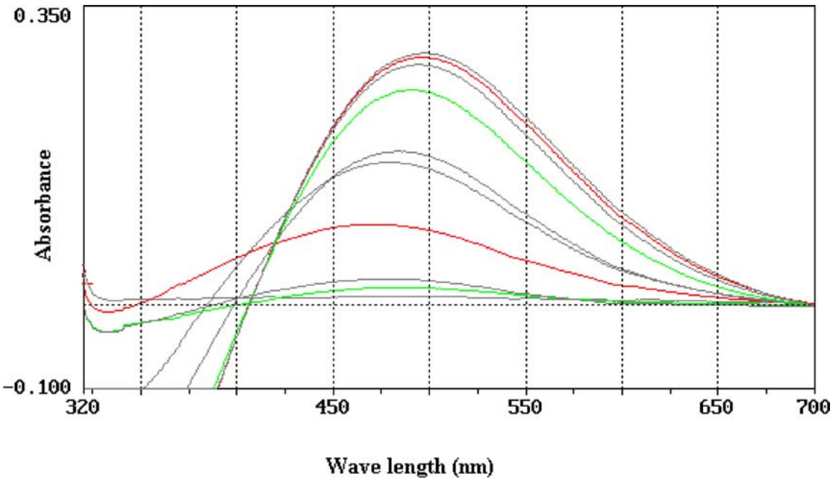

Fig. 4. UV-visible spectra of compound **2** in CH_3OH:H_2O (1:1) with added Fe(III) concentration of 0, 7.5×10^{-6}, 1×10^{-5}, 2.5×10^{-5}, 5×10^{-5}, 7.5×10^{-5}, 1×10^{-4}, 2.5×10^{-4}, 5×10^{-4}, 7.5×10^{-4} and $1 \times 10^{-4}\,\mathrm{mol/dm^3}$ from the smallest to the largest $\lambda_{\max}$ at pH 3.0. Concentration of **2** is $5 \times 10^{-4}\,\mathrm{mol/dm^3}$.

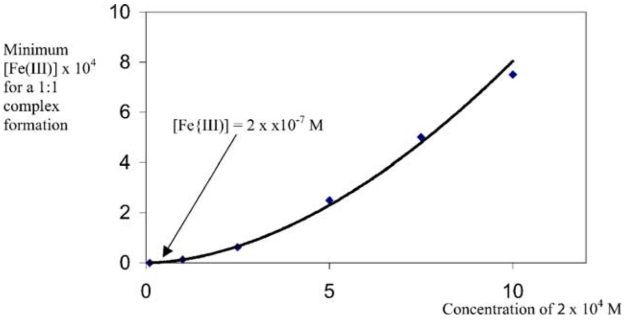

Fig. 5. Plot between minimum Fe(III) concentration for 1:1 complex formation vs. concentration of **2**.

was unaffected by addition of Fe(III). This can be explained by considering the structure of compounds **1** and **2**.

The naphthalene fluorophore of **1** is conjugated to the metal ion receptor site, hydroxamic acid group, and therefore increases the conjugation of π-electrons giving an absorbance at longer wavelength at 282 nm compared to that of **2** at 276 nm. Also binding of the Fe(III) to the receptor site in **1** further increases the conjugation and shifts the peak to longer wavelength. The fluorophore of **2** is separated from the metal ion receptor hydroxamic acid group by a $–CH_2–$ group. Therefore, chelation of the metal ion does not effect the π-electron distribution of the naphthalene chromophore and insignificant change in the peak is expected.

3.1.1. *Stoichiometry of the hydroximate complex of **1** and **2** with Fe(III)*

The peak that developed at longer wavelength due to the charge transfer transition was shifted to shorter wavelength with the increase of pH and two isobestic points could be identified for both **1** and **2** as shown in Fig. 3 for the compound **1**. For the compound **1**, the isobestic points are at 495 and 568 nm, whereas for **2** at 485 and 558 nm. These observations are in accordance with Ferkes et al. and can be assigned as 1:1, 1:2 and 1:3 complexes between hydroxamic acid and Fe(III) [11]. The maxima of these charge transfer absorptions of complexes for **1** and **2** can be estimated and are given in Table 1. The higher wavelength of absorbance for all the complexes of **1** compared to that of **2** can be accounted for the structures of **1** and **2** as mentioned before. It is clear that both compounds **1** and **2** show similar behavior in complexation. The most stable complexes for both, at excess concentration of **1** or **2** with Fe(III) at pH 3.0 is 1:3.

Table 1
The charge transfer band maxima of the complexes of Fe(III) with **1** and **2**

Ligand	Maximum wavelength (nm) of absorbance for different complexes		
	1:1	1:2	1:3
1	510	470	420
2	496	465	410

Table 2
The minimum ratio of [Fe(III)]:[**2**] for 1:1 complexation

[**2**] ($\times 10^4$ M)	Minimum [Fe(III)] for 1:1 complexation ($\times 10^4$ M)	Minimum ratio of [Fe(III)]:[**2**]for 1:1 complexation
10.00	7.50	1:1.3
7.50	5.00	1:1.5
5.00	2.50	1:2
2.50	0.63	1:4
1.00	0.13	1:8
0.10	[a]	1:50 (Estimated)

[a] Cannot measure due to weakness of the charge transfer emission.

In addition to the pH, the concentration of ligand and [metal]:[ligand] ratio is also important for the stoichiometry of complexation. For example, at a constant ligand concentration of **2**, 5×10^{-4} M, as the concentrations of Fe(III) was gradually increased from 0 to 2.5×10^{-4} M, the charge transfer absorption band was shifted to a constant value of 496 nm which corresponds to 1:1 complexation. The shifting can be explained due to the presence of other complexes, 1:2 and/or 1:3 at lower concentrations of Fe(III). Therefore, the lowest limit of the Fe(III) concentration required to form only a 1:1 complex is 2.5×10^{-4} M. The [metal]:[ligand] ratio under these conditions is 1:2. From column 3 of Table 2, it is clear that the [metal]:[ligand] ratio for 1:1 complexation is highly dependent on the ligand concentration. This can be simply explained qualitatively by the Le Chatleyer principle. The fluorescence quenching studies of **1** and **2** with Fe(III) were carried out at pH 3 with a concentration of 1×10^{-5} M concentration of ligand. Unfortunately, at this concentration of **2**, the minimum concentration of Fe(III) required for 1:1 complexation cannot be determined due to the weakness of the charge transfer band. However, by extrapolating the plot between minimum Fe(III) ion concentration versus concentration of **2** as given in Fig. 5, the [metal]:[ligand] of 1:50 can be estimated as the lowest limit for 1:1 complexation (Table 2). Therefore, it is reasonable to assume that as low as 2×10^{-7} M of Fe(III) concentration forms only a 1:1 complex with **2** at pH 3.

3.2. *Emission spectra*

The effect of Fe(III) on fluorescence was studied by recording the spectra of **1** and **2** at the concentration of 1×10^{-5} M with increasing concentration of Fe(III). The results are given in Fig. 6 for compound **2**. All the measurements were done at pH 3.

The effect of Cu(II) and Zn(II) on the fluorescence of **2** was studied at different pH values. The maximum quenching was at pH 5.6 for Cu(II) and at pH 6.4 for Zn(II).

3.2.1. *Determination of quantum yields*

The relative fluorescence quantum yields were calculated from the area under the emission spectra. The quantum yield of free ligand in 50% methanol in the absence of Fe(III) was taken as 1.00 as comparing the area under the emission spectra for each of the Fe(III) concentrations with that of

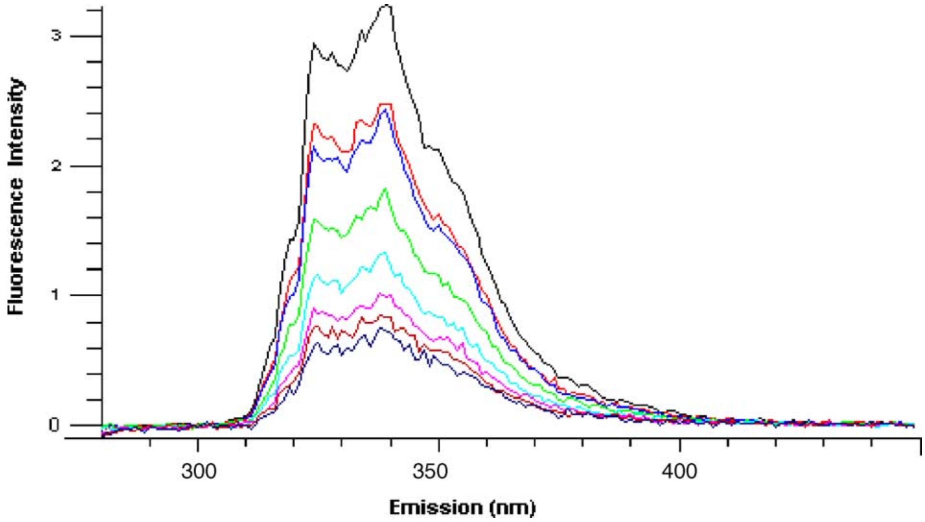

Fig. 6. Emission spectra of compound **2** at 1×10^{-5} mol/dm^3 in 50% aqueous methanol with added Fe(III) concentrations of 0, 7.5×10^{-6}, 1×10^{-5}, 2.5×10^{-5}, 5×10^{-5}, 7.5×10^{-5} and 1×10^{-4} mol/dm^3 from the largest to the smallest emission at pH 3.

free ligand, the relative fluorescence quantum yields of the ligand in the presence of Fe(III) were estimated. The results obtained for the quantum yields of compounds **1** and **2** are given in Table 3. The fluorescence quantum yields of **1** and **2** were found as 0.051 and 0.500 with respect to quinine sulphate in 1 M H_2SO_4.

The emission spectra of **2** with added Cu(II) and Zn(II) were recorded at different pH values and the relative fluorescent quantum yields are given in Table 4.

3.2.2. *Emission studies of **1** and **2***

The fluorescence quantum yield of **1** (0.051) is about 10 times less compare to that of **2** (0.500). The lower fluorescence quantum yield of **1** can be explained by the increased intersystem crossing in **1** due to the conjugated carbonyl group to the naphthalene fluorophore. The fluorescence of compound **2** is quenched upon the addition of Fe(III). The quenching of fluorescence is very efficient for compound **2** compared to that of **1** as shown in Table 3. This may be due to the inherent lower fluorescence quantum yield of **1**. The fluorescence measurements were done using a 1×10^{-5} M concentration of **2**, and at this concentration, at least up to a minimum concentration of 2×10^{-7} M of Fe(III) 1:1 complex formation is expected. The lowest concentration of metal ion used in our studies is 1×10^{-6} M and therefore confirms the formation of a 1:1 complex in the whole working range of the metal ion concentration. Also in the absorption measurements of compound **1** in the range of 240–320 nm with the concentration of 1×10^{-5} M in the addition of Fe(III) gives only one isobestic point at 290 nm as given in Fig. 1. The insignificant effect of the metal ions on the fluorescence band position reveals that the complex between **2** and metal ions is non-fluorescent. All this evidence confirms the formation of a 1:1 non-fluorescent complex in the ground state, which leads to a static quenching of fluorescence of the ligand by the bound metal ion. It is well known that a static quenching mechanism due to the formation of non-fluorescent complex abides by the Stern–Volmer equation:

$$\frac{\phi_f^0}{\phi_f} = 1 + K[M]$$

Table 3
Relative fluorescence quantum yields of compounds **1** and **2** with Fe(III) at pH 3.0

[Fe(III)] (M)	Relative fluorescence quantum yield	
	1	**2**
0	1.00	1.00
7.5×10^{-6}	0.99	0.78
1.0×10^{-5}	0.97	0.73
2.5×10^{-5}	0.89	0.55
5.0×10^{-5}	0.79	0.40
7.5×10^{-5}	0.71	0.35
1.0×10^{-4}	0.65	0.30

Table 4
Relative fluorescence quantum yields of **2** with Fe(III), Cu(II) and Zn(II) at pH 3.0, pH 5.7 and 6.4, respectively

[Metal ion] (M)	Fe(III)	Cu(II)	Zn(II)
0	1.00	1.0	1.0
1.0×10^{-6}	0.96	0.95	–
2.5×10^{-6}	0.89	0.89	–
5.0×10^{-6}	0.84	0.85	–
7.5×10^{-6}	0.78	0.74	–
1.0×10^{-5}	0.73	0.69	0.97
2.5×10^{-5}	0.55	0.53	0.94
5.0×10^{-5}	0.40	0.38	0.92
7.5×10^{-5}	0.35	0.31	0.90
1.0×10^{-4}	0.30	0.26	0.87
2.5×10^{-4}	–	0.22	0.83
5.0×10^{-4}	–	–	0.74

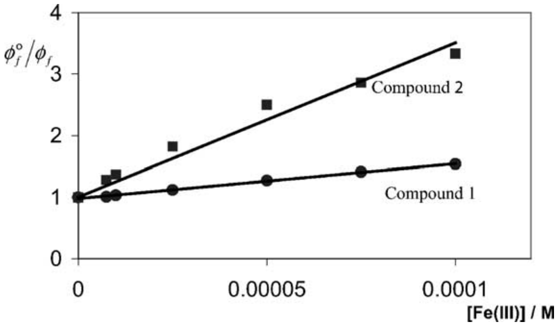

Fig. 7. The Stern–Volmer plot for quenching processes of compounds **1** and **2** by Fe(III).

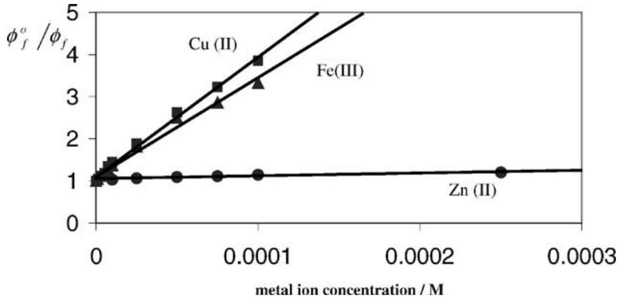

Fig. 8. The Stern–Volmer plot for quenching processes of compound **2** by Fe(III), Cu(II) and Zn(II).

where ϕ_f^0 and ϕ_f are fluorescence quantum yields of fluorophore in the absence and presence of the quencher metal ion, M. K is a constant and depends on the formation constant of the complex between the free fluorophore and Fe(III). The plot of ϕ_f^0/ϕ_f versus the concentration of the metal ion gives a straight line for compounds **1** and **2** as shown in Fig. 7. The linearity of the Stern–Volmer plot further confirms the formation of only one type of complex for the whole range of Fe(III) concentrations and according to the above discussion this should be a 1:1 non-fluorescent complex. The slopes give the quenching constants for **1** and **2** as 5.3×10^3 and $2.5 \times 10^4\ \mathrm{M}^{-1}$, respectively. As it mentioned before, the fluorescence quenching of **2** is very sensitive to the metal ion concentration and hence it was selected for the further studies with different metal ions.

The quenching of **2** was studied at pH 2 and 5.6 with Cu(II), the relative quantum yields indicates that there is hardly any quenching at pH 2. However, at pH 5.6 the fluorescence of **2** was efficiently quenched (Fig. 8). This result confirms that formation of a complex with metal ion is required for the quenching of fluorescence of the ligand. Furthermore, the Stern–Volmer plot for the quenching of **2** by Cu(II) at pH 5.6 is linear, confirming that the quenching is due to the formation of a 1:1 complex. As it mentioned earlier, the formation of the metal–hydroximate complex is highly dependent on the pH of the medium. Studies by Ferkes et al. have shown that Cu(II) forms a complex with hydroxamic acid and that stable complex formation occurs when the medium is at pH 5.6. Our observation of fluorescence quenching of **2** with Cu(II) is in accordance with the observation of Ferkes et al. The high quenching of fluorescence of **2** with Cu(II) at pH 5.6 is due to the higher efficiency of the formation of the complex. It is also known that Zn(II) forms a complex with hydroxamic acid at pH 6.4 [11]. The fluorescence quenching of **2** was measured with Zn(II) at pH 6.4 and the results are given in Table 4. The Stern–Volmer plot is given in Fig. 9. The quenching of fluorescence of **2** is very low with Zn(II) even though a complex is formed between **2** and Zn(II).

3.2.3. *Mechanism of quenching process*

It is clear that all of the metal ions Fe(III), Cu(II) and Zn(II) quench the fluorescence of **1** and **2**. However, both Fe(III) and Cu(II) give higher quenching when they complex with **2**, whereas quenching is lower with Zn(II). This result can be explained by the paramagnetic properties of Fe(III) (d^5) and Cu(II) (d^9) ions, both having unpaired d-electrons which effectively quench both singlets and triplets of **1** and **2** [12]. The quenching of the fluorescence by paramagnetic metal ions is a well-known phenomenon. However, high

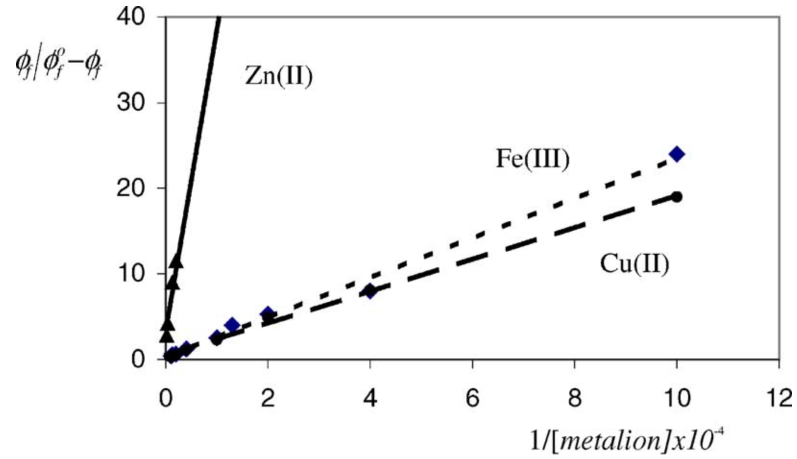

Fig. 9. The plot of $\phi_f/(\phi_f^0 - \phi_f)$ vs. 1/[metal ion] for compound **2**.

concentrations of metal ion (over 10^{-4} M) are necessary for the normal collisional quenching process and such quenching is dynamic in nature. As discussed previously, the quenching of fluorescence of **1** and **2** by metal ions is static and is due to the formation of the non-fluorescent complexes in the ground state. Quenching of electronically excited states of aromatic hydrocarbons by co-ordination complexes has been of much detailed investigation and Fe(III) and Cu(II) complexes have been shown to be particularly active [13]. Electron transfer to the (hydroxamoto)Fe(III) or (hydroxamoto)Cu(II) and/or energy transfer to low-lying metal centred excited states might well account for explaining the efficient quenching of the singlet excited state of naphthalene in our compounds **1** and **2** [14]. The complete quenching of the excited fluorophore takes place by the bound metal ion even at low concentration since it is close to the fluorophore. On the other hand, the fluorescent quenching of the aromatic hydrocarbon by closed-shell heavy metal ions such as Zn(II), Ag(I) and Cd(II) in aqueous solutions have been explained by non-fluorescent complex formation followed by rapid intersystem crossing [13]. However, these quenching rates are much lower compare to those of paramagnetic metal ions such as, Fe(III) and Cu(II). This is evidence to confirm the efficient quenching of **2** by Fe(III) and Cu(II) compared to lower quenching by Zn(II).

*3.2.4. Formation constant for the complexes of **2** with Fe(III), Cu(II) and Zn(II)*

From the fluorescence change with the concentration of Fe(III), the formation constant between **2** and Fe(III) can be calculated. If a 1:1 complexing system is supposed contain Fe(III), **2** and the complex **2**–Fe(III), there can exist the relationship [15]:

$$\frac{\phi}{\phi^0 - \phi} = \frac{1}{K_{\mathbf{2}\text{–Fe(III)}}[\text{Fe(III)}]}$$

where ϕ is fluorescence quantum yield with Fe(III), ϕ^0 fluorescence quantum yield without Fe(III), $K_{\mathbf{2}\text{–Fe(III)}}$ the formation constant between **2** and Fe(III). In Fig. 4, a linear plot of the mixture of **2** and Fe(III) by the use of fluorescence change for the peak between 230 and 320 nm is shown; this serves to confirm that the stoichiometry of complex should be 1:1. The formation constant ($\log K$) was calculated as 3.63. The formation constants ($\log K$) for the Cu(II) at pH 5.3 and Zn(II) at pH 6.3 were obtained in a similar way as 3.72 and 2.45.

4. Conclusion

In conclusion, the stoichiometry of the complex formation between hydroxamic acid and metal ions not only depend on the pH of the medium but also on the concentration of both metal ion and hydroxamic acid. The linear relationships in Stern–Volmer plots confirm the formation of 1:1 complex. Compound **2** gives very high quenching with paramagnetic metal ions and will be a successful probe for the analysis of metal ions at trace levels. Further studies are under way to develop fluorimetric methods for the analysis of trace metal ions.

Acknowledgements

National Science Foundation in Sri Lanka is greatly acknowledged for the financial support under the Grant Number RG/C/2000/03.

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