



Sensing of Fe(III) ion via turn-on fluorescence by fluorescence probes derived from 1-naphthylamine



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ARTICLE INFO

Article history:

Received 3 July 2013

Revised 12 September 2013

Accepted 14 September 2013

Available online 21 September 2013

Keywords:

Fluorescence probes

Naphthylamine

Emission

Turn-on fluorescence

ABSTRACT

Fluorescence probes **NA1** and **NA2** derived from 1-naphthylamine (**NA**) as fluorophore have been synthesized and characterized by different spectroscopic studies. Identification behaviour of these probes towards various metal ions has been investigated. Both the fluorescent probes are selective as well as sensitive towards Fe(III) ion. Novel fluorescence probe **NA2** afforded turn-on fluorescence behaviour for Fe(III) ion over other metal ions such as Ca(II), Mg(II), Mn(II), Fe(II), Co(II), Fe(III), Ni(II), Cu(II), Zn(II) and Hg(II).

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Iron is one of the essential elements present in the biosystem and several metalloenzymes need iron to execute catalytic activities which are responsible for various physiological processes.¹ Several biological functions depend directly or indirectly on the proper concentration and oxidation states of iron to maintain the homeostatic mechanism of biosystem.² Disturbances in such type of balance of iron concentration may create physiological disorders.^{2,3} For that reason detection and localization of Fe(III) are an important area of chemical research. Hence design and synthesis of fluorescence probes which are specific and selective for Fe(III) are highly demanding. For intracellular and extracellular detection of labile iron⁴ many physical and chemical techniques namely atomic absorption spectroscopy (AAS),⁵ colorimetry,⁶ spectrophotometry⁷ and voltammetry⁸ have been utilized. However, there are several limitations of such kind of detection described above.⁹ In this regard fluorimetric methods are highly sensitive and appreciable. Fe(III) is paramagnetic in nature and hence its detection is accompanied by quenching of fluorescence.¹⁰ Enhancement or turn-on fluorescence has tremendously gained importance for the design and synthesis of probes which are specific for Fe(III).¹¹ Various probes such as dansyl-based probes,¹² rhodamine-based probes,¹³ benzimidazole-based probes,¹⁴ imidazole-based probes,¹⁵ naphthyl-based probes,¹⁶ anthracene-appended amino acid probes,¹⁷ 1,8-diquinolynaphthalene probes,¹⁸ quinoline-based polymer,¹⁹ polymer based on 9-aminofluorene²⁰ and N-azacrown carbazole probes²¹ have been used for the detection of

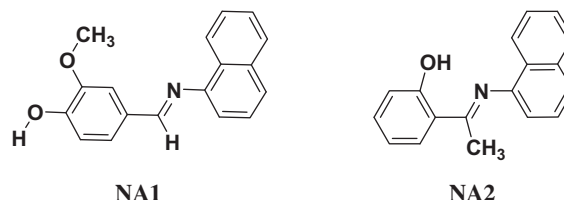


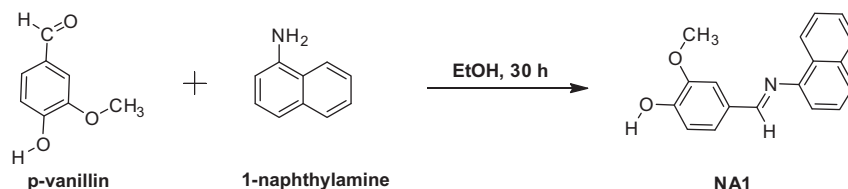
Figure 1. Structure of **NA1** and **NA2**.

Fe(III). Naphthyl-based probes are widely used because of their sensitivity and simplicity.²² Hence naphthyl-based probes are used for the detection of several metal ions such as Ca(II),^{23a} Al(III),^{23b} Zn(II),^{23c} Pb(II)^{23d} and Ni(II)^{23e} but reports on selectivity of Fe(III) are very few and exhibited quenching in fluorescence emission spectra.²⁴ However very few literatures based on enhancement of Fe(III) using naphthyl group are reported.²⁵ To the best of our knowledge naphthyl based probes exhibiting turn-on phenomena are still unexplored.

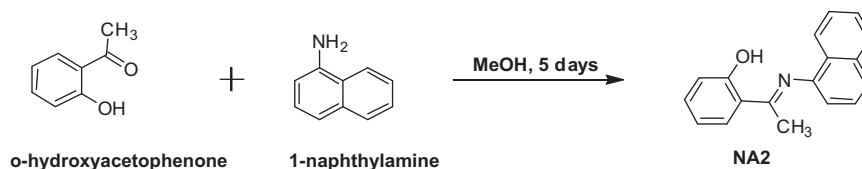
In this Letter we have synthesized two Schiff's bases namely **NA1** and **NA2** (Fig. 1) derived from 1-naphthylamine. **NA1** was synthesized in one step by the condensation of *p*-vanillin with 1-naphthylamine in ethanol at 25 °C for 30 h as reported earlier (Scheme 1).²⁶ On the other hand, a new Schiff's base **NA2** was synthesized by the reaction of *o*-hydroxyacetophenone with 1-naphthylamine in methanol (Scheme 2). Both **NA1** and **NA2** are characterized by various spectroscopic techniques like IR, UV-vis, ¹H NMR, ¹³C NMR spectral studies and ESI-MS (data are deposited in the Supporting information Figs. S1–S5).

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Scheme 1. Synthesis of NA1.



Scheme 2. Synthesis of NA2.

The photophysical properties of **NA1** and **NA2** were examined in methanolic solution. **NA1** exhibits fluorescence intensity enhancement without any shift in emission wavelength upon addition of Fe(III) ions and hence this fluorescence probe is probably based on photo electron transfer (PET).^{27,28} The UV–vis spectra of **NA1** and **NA2** in methanol exhibited typical naphthalene absorption band at 280 nm.^{24b} An emission band around 425 nm in methanol was found when excitation of **NA1** was done at 279 nm. **NA1** was found to be selective and sensitive for Fe(III) only among the served metal ions like Ca(II), Mg(II), Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) (Fig. 2a). A bar diagram is also shown for **NA1** with different metal ions (Fig. 2b). The emission band at around 425 nm showed about eightfold emission intensity only for Fe(III).²⁹

Fluorescence emission spectra were recorded for **NA1** with increasing concentration of Fe(III) (shown in Fig. S6 in supporting information). Weak fluorescence near 425 nm was observed in the absence of Fe(III) ions at $\lambda_{\text{ex}} = 279$ nm.³⁰ We found a gradual increase in fluorescence intensity upon addition of Fe(III) ions into the solution. Figure S6 clearly indicated that the maximum intensity of fluorescence was obtained when concentration of Fe(III) ions was 50 μM . The sensitivity curve indicated that the probe **NA1** maintained at a concentration of 50 μM , can be used for the analysis of micromolar concentrations of Fe(III) ions. Job's plot according to the method of continuous variation afforded 1:1

binding stoichiometry between **NA1** and Fe(III) ion as proposed (Fig. 3b). As shown in Figure S7, fluorescence intensity was maximum at around 5 min after mixing and showed a negligible change in fluorescence intensity after that.³¹

Fluorescence spectral studies on **NA2** were performed in methanol. **NA2** alone displayed a very weak, single fluorescence emission band at 355 nm when it was excited at 290 nm. In addition to that, only weak changes of fluorescence intensity of **NA2** were observed on addition of the other metal ions such as Ca(II), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Hg(II). However, unlike the previous observation, we did not get any enhancement of fluorescence (shown in Fig. 4a). Interestingly, addition of Fe(III) gave rise to the generation of a new band near 435 nm which indicates selective on-off signalling behaviour of Fe(III) (shown in Fig. 4b). **NA2** exhibited fluorescence intensity enhancement in the new fluorescence band as well as new emission band upon addition of Fe(III) ions. In the presence of Fe(III) the fluorescent enhancement efficiency was ~ 40 -fold greater compared to free **NA2**. Such type of change in fluorescence spectra was observed in the literature and the mechanism was probably due to internal charge transfer (ICT).^{27,28} The observed fluorescence enhancement may be due to the formation of rigid system after binding with Fe(III) ion (Fig. 4b).³² Considering the structures of **NA1** and **NA2** we could easily figure out that the metal binding sites for the

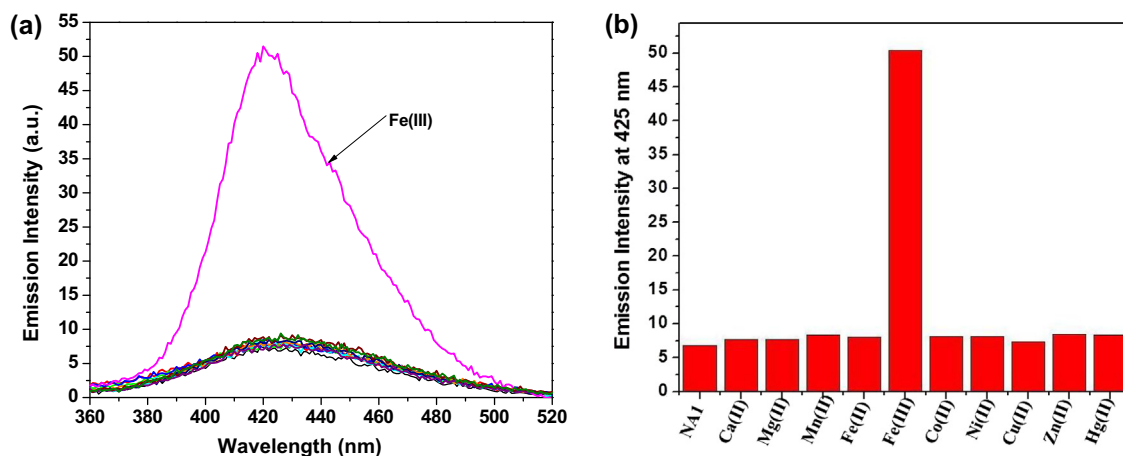


Figure 2. (a) Fluorescent emission spectra of **NA1** (50 μM) in methanol with 1 equiv of Ca(II), Mg(II), Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Hg(II). (b) Emission intensity of **NA1** at 425 nm after addition of 1 equivalent of selected metal ions in methanol at $\lambda_{\text{ex}} = 279$ nm.

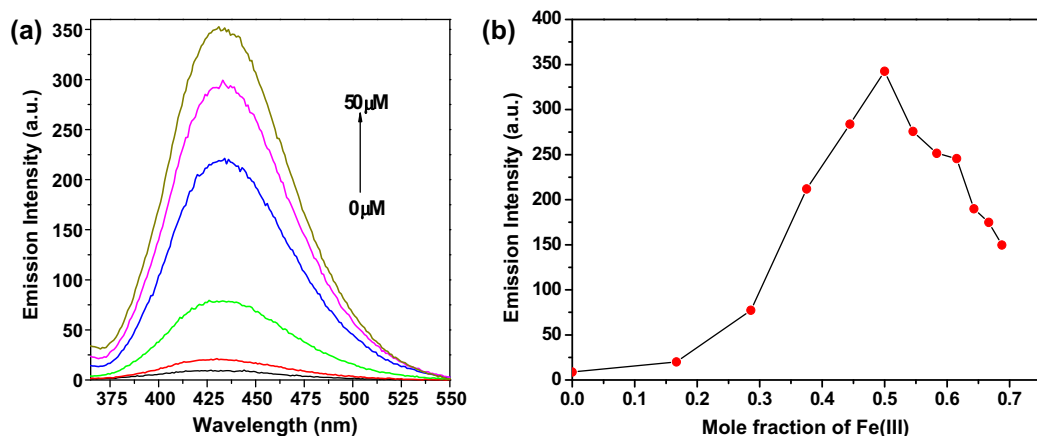


Figure 3. (a) Fluorescent emission titration spectra of **NA1** (50 μ M) in the presence of varying concentrations of Fe(III) in MeOH at λ_{ex} 279 nm. (b) Job's plot of **NA1** (50 μ M) and Fe(III) (50 μ M), where fluorescent intensity of **NA1** at 425 nm was plotted against the mole fraction of Fe(III).

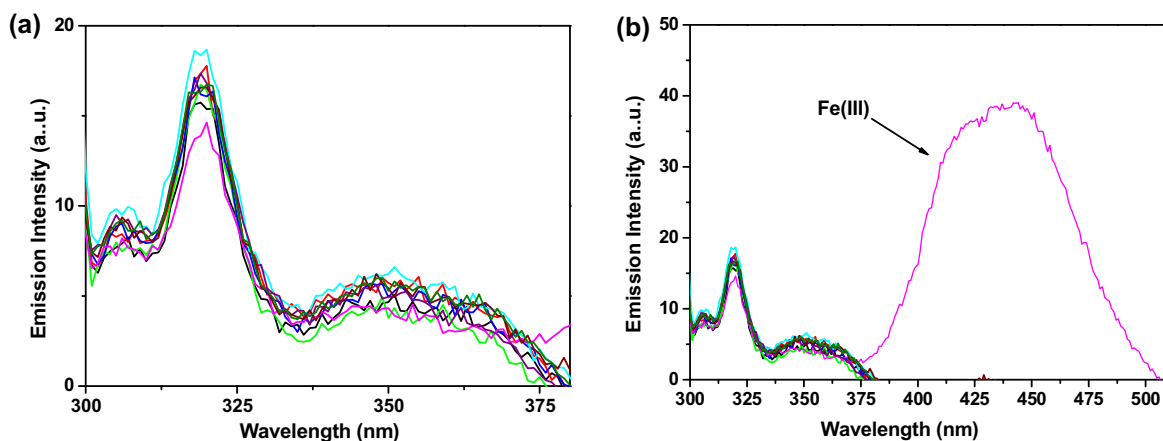


Figure 4. (a) Fluorescent emission spectra of **NA2** (50 μ M) in methanol with 1 equiv of Ca(II), Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) in the range of 300–380 nm (b) Fluorescent emission spectra of **NA2** (50 μ M) in methanol with 1 equiv of Ca(II), Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) in the range of 300–600 nm.

two probes are different. In case of **NA1** metal ion could sit near OH and OMe groups where the probe could act as a bidentate ligand or near imine nitrogen atom where the probe could

act as a monodentate ligand. On the other hand **NA2** probe could act as a bidentate ligand with phenolato and imine functions. The sensitivity curve indicated that the probe **NA2**

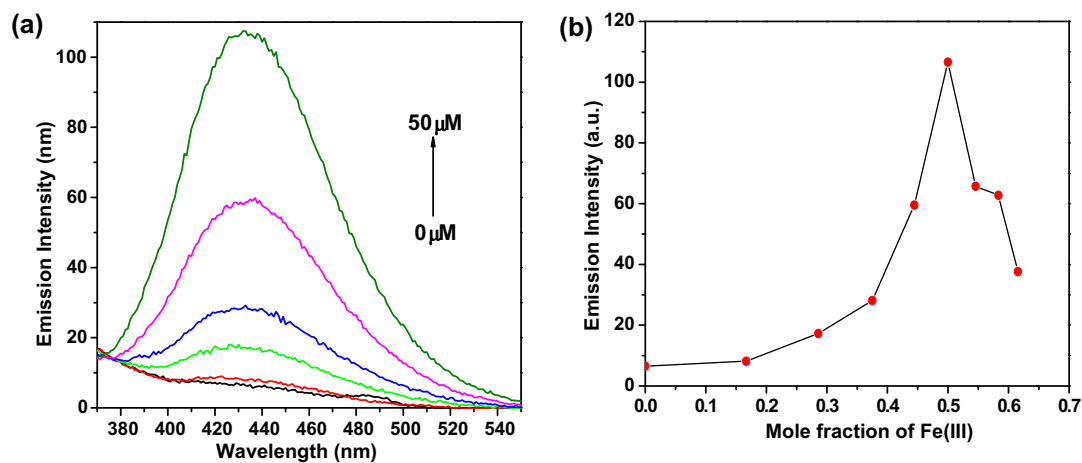


Figure 5. (a) Fluorescent emission titration spectra of **NA2** (50 μ M) in the presence of varying concentrations of Fe(III) in MeOH at λ_{ex} 290 nm. (b) Job's plot of **NA2** (50 μ M) and Fe(III) (50 μ M), where fluorescent intensity of **NA2** at 435 nm was plotted against the mole fraction of Fe(III).

maintained at a concentration of 50 μM , can be used for the analysis of micromolar concentrations of Fe(III) ions.

To examine the sensitivity of **NA2** fluorescence emission spectra were recorded with increasing concentration of Fe(III) from 0 μM to 50 μM . As shown in Figure 5a, **NA2** displays no fluorescence at 435 nm in the absence of Fe(III) at λ_{ex} 290 nm. But on the addition of Fe(III) a continuous increment in emission intensity was observed till 50 μM (Fig. S8). Job's plot according to the method of continuous variation showed 1:1 binding stoichiometry between **NA2** and Fe(III) (Fig. 5b). We observed that the emission intensity of **NA2** increases linearly with Fe(III) from 0 min to 52 min (Fig. S9).

In this Letter two Schiff bases have been synthesized and characterized by various spectroscopic techniques. Photophysical properties of these compounds **NA1** and **NA2** have been investigated to study the sensing of metal ions in solution. Both the compounds showed sensitivity and selectivity towards Fe(III) among the served metal ions. To the best of our knowledge **NA2** is the only naphthyl-based probe which exhibited turn-on fluorescence behaviour specific for Fe(III). The biological activities of these probes are under process.

Acknowledgements

K.G. and R.K. are thankful to MHRD, New Delhi, India for financial assistance. S.R. is thankful to UGC for financial assistance. The authors are thankful to the Institute Instrumental Facility, IIT Roorkee.

Supplementary data

Supplementary data (Supplementary material contains IR, UV–vis, ^1H NMR, ^{13}C NMR spectra, ESI-MS and Fluorescence emission spectra of **NA1** and **NA2**) associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tetlet.2013.09.066>.

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