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Selectivity in changes of fluorescence emission of 1,4-naphthoquinone derivatives by manganese and cadmium ions

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ABSTRACT

Interactions of various metal ions with pyridine tethered 1,4-naphthoquinone derivatives (**1**–**4**) are studied by fluorescence spectroscopy. The fluorescence emission of 2-(pyridine-2-yl-methylamino) naphthalene-1,4-dione (**1**) is influenced by various metal ions and show highly selective fluorescence emission with Mn^{2+} ions and fluorescence ON and OFF states can be generated at different concentrations of Mn^{2+} ions. Sequential addition of Ni^{2+} and Mn^{2+} ions to a solution of **1** also generates ON and OFF emission states. The fluorescence responses towards the metal ions by two isomers 2-(pyridine-*n*-yl-methylamino)naphthalene-1,4-dione ($n = 3,4$) are non-specific. The 2-(pyridine-2-yl-ethylamino)naphthalene-1,4-dione (**4**) shows fluorescence response to various metal ions; but its fluorescence response upon interaction with cadmium ions is very unique. Three stages in emission upon increase in concentration of Cd^{2+} ions, namely OFF–ON–ON are observed.

1. Introduction

Small molecules are very useful for detection of metal ions [1–4]. Various fluorescent compounds are used for such studies, among them naphthalimides [5–11], xanthones [12], quinolines [13], dansyl-derivatives [14–17], rhodamine-derivatives [18–29] are common. Generally the fluorescent unit present at a close proximity of a metal ion is used for signal transduction. Host–guest complexes [30] are also used for detection of metal ions. Quinonic compounds such as anthraquinones [31–34], naphthoquinones [35,36] are used for detection of metal ions. Quinonic compounds bound to metal ions also play important roles in valence tautomerism [37] and in biological systems [38,39]. Naphthoquinone derivatives show switching properties under different redox conditions [40,41]. The ease of functionalisation of 1,4-naphthoquinone at α-position by amines [42] to attach a binding site makes it an attractive unit for metal binding. The quinone skeleton shown in Fig. 1 have close analogy to vitamin K, thus study of their interaction to metal ions will throw light on electron transfer processes. The visible spectroscopic study interactions of metal ions with 1,4-naphthoquinone derivatives was earlier reported [36]. Such studies were not performed with more sensitive tool such as fluorescence spectroscopy. Fluorescence switching, alternatively ON–OFF properties in different sequences and under different chemical conditions have application to design logic gate [43–47]. On the other hand, so far there are no comparative studies of metal ions binding effect on the position of the nitrogen atoms on the pyridine ring, as well as on the role of a methyl substituent on the naphthoquinone ring in fluorescence emission. Thus, we have taken up a series of compounds **1**–**4** [48–51] derived from 1,4-naphthoquinone (Fig. 2) to study their selectivity to bind metal ions and studied their fluorescence emission properties. Surprisingly, great differences are observed from the previous study [36] in terms of metal ion selectivity by our ligands and we have found that just by changing the substituent by methyl group metal ion, selectivity can be changed. For example, 2-(pyridine-2-yl-methylamino)naphthalene-1,4-dione (**1**) has highly specific fluorescence emission with the Mn^{2+} ions and the 2-(pyridine-2-yl-ethylamino)naphthalene-1,4-dione shows highly characteristic fluorescence emission which is specific to Cd^{2+} ions.

2. Experimental

2.1. Materials

1,4-Naphthoquinone, 2-(pyridine-2-yl)ethane amine, 2-picolylamine, 3-picolylamine and 4-picolylamine were obtained from Sigma Aldrich. HPLC grade solvents were purchased from Merck, India were used without further purifications. The UV–Vis spectra data were recorded using Perkin-Elmer Lambda 750 UV–Vis spectrophotometer. The fluorescence emissions were measured by a Perkin-Elmer LS-55 spectrophotometer. The ^1H NMR spectral data were recorded on a Varian-AS400 spectrometers. Infrared spectra obtained using Perkin-Elmer FT-IR spectrophotometer (4000–400 cm^{-1}). The compounds **1**–**4** were prepared by modifying

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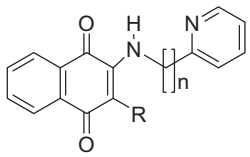


Fig. 1. Structural frame of 1,4-naphthoquinone derivatives (R = H or Me).

reported procedures [47–51]. The ESI-mass spectra were recorded on a micro mass Q-TOF (Waters) mass spectrometer using acetonitrile/formic acid matrix.

2.2. Preparation of 2-(pyridine-2-yl) methylamino) naphthalene-1,4-dione (*1*)

To a well stirred solution of 1,4-naphthoquinone (0.31 g, 2 mmol) in methanol (20 ml) a solution of 2-picolylamine (0.2 ml, 2 mmol) was added drop wise. The reaction mixture was stirred at room temperature for 8 h. A golden yellow colour precipitate (**1**) was formed. The resulting mixture was filtered and dried in open air. Yield: 92%. IR (KBr, cm^{-1}): 3331 (s), 2923 (m), 2852 (m), 1677 (m), 1601 (s), 1593 (s), 1556 (m), 1503 (m), 1439 (w), 1415 (w), 1357 (m), 1339 (m), 1258 (m), 1126 (m), 786 (w), 733 (m), 699 (m), 609 (m), 548 (w). ^{1}H NMR (400 MHz, DMSO-d_6): 8.48 (broad s, 2H), 8.21 (t, J = 7.2 Hz, 1H), 7.98 (d, J = 7.6 Hz, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.80 (t, J = 7.6 Hz, 1H), 7.71 (t, J = 7.2 Hz, 2H), 7.31 (d, J = 4.4 Hz, 1H), 5.48 (s, 1H, NH proton), 4.48 (s, 1H) 4.46 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 181.5, 148.8, 148.4, 135.1, 134.8, 133.0, 132.3, 130.5, 125.9, 125.4, 123.6, 100.5, 42.7. UV–Vis: (λ_{max}) 438 nm, $\varepsilon = 3.9 \times 10^3\ M^{-1}\ cm^{-1}$. *m/z* (ESI): 265.09 $[M+H]^+$, 266.10 $[M+H+1]^+$. M.p. 153–155 °C.

The compounds **2** and **3** were prepared in similar procedure to **1** but 3-picolyamine and 4-picolylamine respectively were used.

2.3. Preparation of 2-(pyridine-3-yl) methylamino) naphthalene-1,4-dione (*2*)

Yield: 85%. IR (KBr, cm^{-1}): 3310 (bw), 2922 (m), 2851 (m), 1674 (m), 1611 (s), 1601 (m), 1568 (w), 1501 (w), 1425 (w), 1358 (m), 1339 (w), 1263 (w), 1161 (w), 1122 (w), 841 (w), 784 (w), 711 (m), 680 (m). ^{1}H NMR (400 MHz, DMSO-d_6): 8.57 (s, 1H), 8.43 (m, 1H), 8.19 (m, 1H), 7.96 (t, J = 7.2 Hz, 1H), 7.79 (d, J = 7.2 Hz, 1H), 7.74 (d, J = 6.4 Hz, 1H), 7.70 (m, 2H), 7.34 (m, 1H), 5.60 (s, 1H, NH proton), 4.47 (s, 1H), 4.45 (s,1H). ^{13}C NMR (100 MHz, DMSO-d_6): 181.6, 149.7, 148.6, 146.6, 134.8, 132.9, 132.4, 130.5, 125.9, 125.4, 122.2, 100.7, 44.1. UV–Vis: (λ_{max}) 441 nm, $\varepsilon = 8 \times 10^3\ M^{-1}\ cm^{-1}$. *m/z* (ESI): 265.08 $[M+H]^+$; 266.09 $[M+H+1]^+$. M.p. 202–205 °C.

2.4. Preparation of 2-(pyridine-4-yl) methylamino) naphthalene-1,4-dione (*3*)

Yield: 88%. IR (KBr, cm^{-1}): 3310 (bw), 3065 (w), 2922 (m), 2852 (w), 1740 (w), 1674 (m), 16111 (s), 1601 (s), 1568 (s), 1500 (s), 1481 (m), 1446 (m), 1425 (w), 1358 (m), 1339 (w), 1306 (w), 1215 (w), 1186 (w), 1122 (w), 1090 (w), 1072 (w), 1027 (w), 955 (w), 873 (m), 829 (m), 756 (m), 729 (m), 688 (m), 639 (w), 612 (w). ^{1}H NMR (400 MHz, DMSO-d_6): 8.59 (s, 1H), 8.45 (d, J = 4.4 Hz, 1H), 8.22 (t, J = 6.0 Hz, 1H), 7.98 (d, J = 7.6 Hz, 1H), 7.81 (d, J = 6.8 Hz, 1H), 7.77 (t, J = 8.8 Hz, 1H), 7.75 (t, J = 9.2 Hz, 1H), 7.49 (m, 2H), 7.36 (m, 1H), 5.62 (s, 1H, from NH), 4.49 (s, 1H), 4.48 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 182.1, 149.4, 149.1, 135.7, 135.5, 133.6, 132.9, 131.1, 126.6, 126.0, 124.3, 101.1, 43.3. UV–Vis: (λ_{max}) 439 nm, $\varepsilon = 4.6 \times 10^3\ M^{-1}\ cm^{-1}$. *m/z* (ESI): 265.09 $[M+H]^+$; 266.10 $[M+H+1]^+$. M.p. 208–210 °C.

2.5. Preparation of 2-(2-(pyridine-2-yl) ethylamino) naphthalene-1,4-dione (*4*)

To a well stirred solution of 1,4-naphthoquinone (0.31 g, 2 mmol) in methanol (20 ml) a solution of 2-(pyridine-2-yl)ethane amine (0.24 ml, 2 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 6 h. A dark red colour precipitate (**4**) was formed. The resulting mixture was filtered and dried in open air. Yield: 95%. IR (KBr, cm^{-1}): 3444 (bw), 3338 (s), 3042 (w), 2921 (w), 2844 (w), 1673 (m), 1661 (s), 1604 (s), 1569 (s), 1518 (m), 1465 (w), 1435 (w), 1357 (m), 1240 (w), 1123 (w), 780 (m), 724 (m), 595 (w). ^{1}H NMR (400 MHz, DMSO-d_6): 8.51 (d, J = 4.4 Hz, 1H), 7.94 (t, J = 7.6 Hz, 1H), 7.81 (t, J = 7.2 Hz, 1H), 7.70 (d, J = 6.8 Hz, 1H), 7.69 (d, J = 6.8 Hz, 1H), 7.32 (d, J = 7.32 Hz, 1H), 7.23 (t, J = 5.2, 1H), 5.70 (s, 1H), 3.55 (t, J = 6.4 Hz, 2H), 3.03 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): 181.6, 159.0, 149.4, 148.5, 140.5, 136.9, 135.1, 133.4, 132.4, 130.56, 126.1, 125.6, 123.6, 121.9, 99.8, 41.9, 35.6. UV–Vis: (λ_{max}) 450 nm, $\varepsilon = 4.3 \times 10^3\ M^{-1}\ cm^{-1}$. *m/z* (ESI): 278.09 $[M]^+$, 279.09 $[M+H]^+$; 280.10 $[M+H+1]^+$. M.p. 183–189 °C.

Fluorescence measurements were carried out by taking a solution (10^{-5} M for **1**–**3** and 10^{-4} M for **4** in methanol) of the corresponding compound. The excitations were done at wavelength slightly away from the corresponding absorption maximum of the parent compounds (to avoid saturation). The fluorescence emission titrations were carried out by adding different aliquots (10–100 μl) of metal ion solutions (10^{-4} or 10^{-5} M in methanol).

3. Results and discussion

The compounds **1**–**4** were synthesised according to conventional procedure by reacting corresponding amine with 1,4-naphthoquinone [36,42]. These compounds are fluorescent and the intensity of fluorescence changes on interaction with different metal ions. The fluorescence emission spectra of the compounds **1**–**4** are independently studied in the presence of different metal ions. Unless stated, perchlorate or nitrate salts are used in such studies. It is observed that while stipulated amount of these compounds interact with identical concentrations of metal ions, the non-coordinating anions such as the perchlorate or nitrate do not change the fluorescence emission of **1**–**4**. Thus, the role of anions in the fluorescence emission is not considered as long as solutions were prepared from metal salts of these two anions. The compound **1**

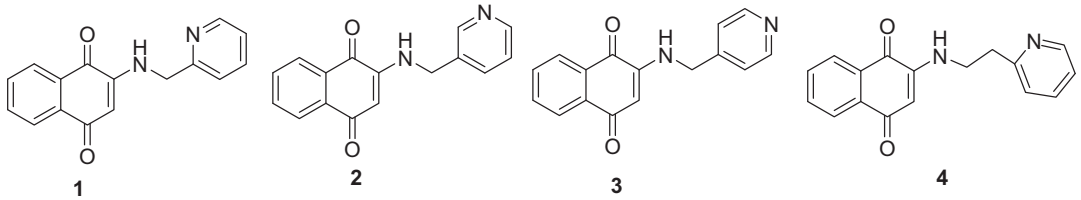


Fig. 2. Different compounds under investigation.

Table 1
Fluorescence lifetime measurement data for **1**.[a]

Compound	λ_{ex} (nm)	λ_{em} (nm)	τ^1 (ns)/(*f*)%	τ^2 (ns)/(*f*)%	τ^3 (ns)/(*f*)%	χ^2
1	445	538	0.084 (68.18)	3.178 (31.82)		1.168
1 + Mn^{2+}		(a) 515	0.050 (25.33)	3.829 (65.00)	0.373 (9.67)	1.277
		(b) 515	0.041 (22.98)	3.848 (66.17)	0.305(10.85)	1.075

[a] Compound **1**, (2 ml, 10^{-5} M, in methanol) alone and after addition of 100 μl; 10^{-5} M in methanol solution of Mn^{2+}; and after addition of 250 μl; 10^{-5} M in methanol solution of Mn^{2+}.

has visible absorption at 438 nm in methanol; whereas it emits at 538 nm upon excitation at 445 nm. This fluorescence emission is attributed to π^*–π emissions. The emission has two lifetimes (Table 1) associated with it suggesting it to have components from n–π emission too. One lifetime 0.084 ns (τ^1) contributes 68.18% of the fluorescence, and the other lifetime 3.178 ns (τ^2) contributes to 31.82% of the fluorescence.

Table 2
Fluorescence emission data for compound **1**–**3** with various metal ions.[a]

Compound	Absorption maximum (nm)	Added metal ion[(i)]	λ_{em} (nm)	Stokes shift (nm)
1	438	None	538	100
		Mn^{2+}	514	76
		Fe^{3+}	509	71
		Co^{2+}	517	79
		Ni^{2+}	515	77
		Cu^{2+}	514	76
		Zn^{2+}	512	74
		Cd^{2+}	515	77
		Hg^{2+}	517	79
2	441	None	558	117
		Mn^{2+}	553	112
		Fe^{3+}	550	109
		Co^{2+}	554	113
		Ni^{2+}	553	112
		Cu^{2+}	556	115
		Zn^{2+}	556	115
		Cd^{2+}	557	116
		Hg^{2+}	513	112
3	439	None	554	115
		Mn^{2+}	551	112
		Fe^{3+}	523	84
		Co^{2+}	536	97
		Ni^{2+}	528	89
		Cu^{2+}	542	103
		Zn^{2+}	550	111
		Cd^{2+}	543	104
		Hg^{2+}	530	91

[a] Excitation in each case is done at 445 nm in each case (this is to avoid saturation). Fluorescence emission spectra were measured by taking 2 ml, solution of **1**, **2** or **3** in methanol (10^{-5} M) with or without addition of 0.1 ml of 10^{-5} M metal salt solution in methanol.

To understand selectivity and differences in response of the emission signal of **1** on interactions with different metal ions, the fluorescence emission were measured by titrating methanolic solution of **1** with different solutions of metal ions, such as Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+} ions. From independent experiments it was observed that the fluorescence intensities increase in all cases with blue shifts (Table 2). The intensity changes in some cases are not very significant; yet they are good enough to implicate the presence of interactions with the metal ions. Among these ions, the fluorescence response of **1** towards Mn^{2+} ions was found to be exceptional. In this case, initially the fluorescence emission was increased on addition of Mn^{2+} ions, but with constant addition of the Mn^{2+} ions to the solution of **1**, the fluorescence intensity decreased from a certain concentration. The increase and decrease in the fluorescence intensity with the change in concentration of metal ions is shown in two separate figures (Fig. 3a and b).

We have also studied the fluorescence lifetime of solution of **1** by adding Mn^{2+} at two different concentrations and found that in each case there are three lifetimes of different magnitudes. The fluorescence lifetime of a solution of **1** with limited amount of Mn^{2+} (100 μl) showed three lifetimes, namely, 0.050 ns (25.33%), 3.829 ns (65.00%) and 0.371 ns (9.67%). This indicates that the percentage of n–π emission of the parent compound is enhanced by the Mn^{2+} ions, and a new path is generated by interaction of **1** with Mn^{2+} ions. Further the lifetime of the π^*–π emission is shortened; this supports the initial enhancement of fluorescence (Fig. 3a). When more Mn^{2+} ions are added to solution of **1**, three lifetimes were observed but they were with different magnitudes, the lifetimes are 0.041 ns (22.98%), 3.848 ns (66.17%) and 0.305 ns (10.85%), respectively. Thus, the lifetime of π^*–π emission slightly increases on increase in concentration of Mn^{2+} ions and the lifetime of n–π type and metal ions controlled path slightly decreases. But a slightly higher numbers of excited molecules pass through metal ions controlled path. So the π^*–π emission acts as the dominant path after interaction with metal ions [2]. The emission

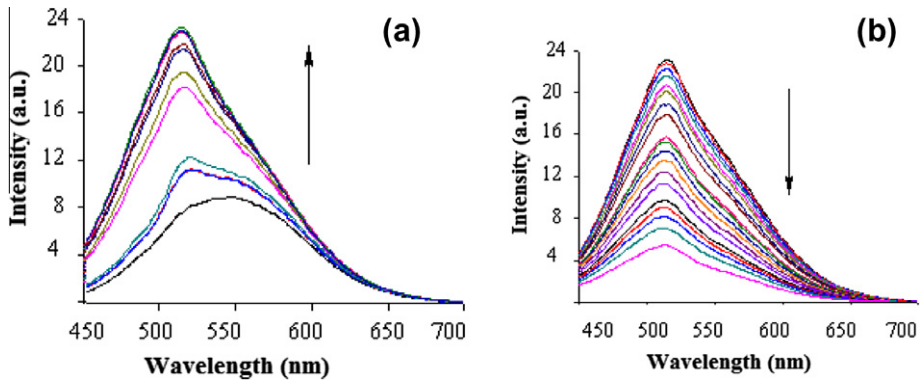
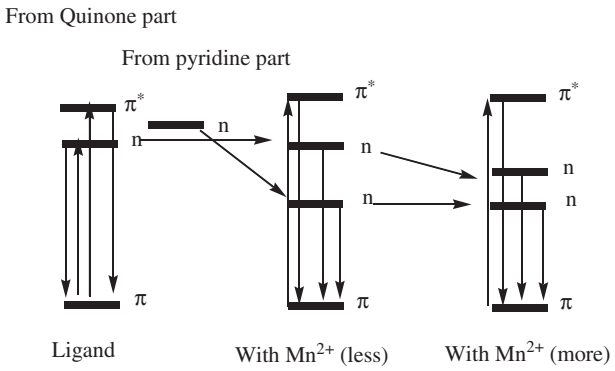


Fig. 3. Changes in fluorescence emission of **1** (2 ml, 10^{-5} M, in methanol) on addition of Mn^{2+} ions. (a) Initial increase in fluorescence intensity on addition of Mn^{2+} ions to the compound **1** (10^{-5} M in methanol; 10 μl in each aliquot). (b) Decrease in intensity after a particular concentration of Mn^{2+} ions.



Scheme 1. Schematic representations of the fluorescence emission by **1** in the presence and absence of Mn^{2+}.

process may be interpreted by the qualitative energy level diagram as shown in Scheme 1. Similar explanation holds good for enhancement of fluorescence emission by other transition metal ions. The exceptional behaviour of Mn^{2+} is attributed to formation of a six coordinated species via coordination through the lone pair of electrons on nitrogen atom (Fig. 4). This makes the lone pair of electron on the nitrogen unavailable for interacting with the excited state; thereby the enhancement of emission intensity is caused. For other metal ions also such arguments hold good. But in the case of Mn^{2+} ions there is a second step of quenching of fluorescence by Mn^{2+} ions on increase in concentration, this process is attributed to formation of new coordinated state of Mn^{2+} ions by coordination of the lone pairs of electrons present on the carbonyl group of naphthoquinone part as well as on the nitrogen atom of the pyridine ring. The seven coordination of manganese is often come across in literature [52,53]. However, in this case the fluorescence emission titration shows that the fluorescence enhancement increase take place up to a limit of 1:1 ligand to metal ion ratio whereas decrease occurs at the concentration range in which manganese ion to ligand ratio is 1:2. The binding constants for the mono (K_1) and di-substitution (K_2) on manganese(II) ion is determined (Supporting information Fig. S22) and they are found as 3.67×10^5 and 2.13×10^6/M respectively. It is also an established fact that the fluorescence lifetime thus serves as a sensitive parameter for exploring the local environment around a fluorophore [54].

Fluorescence titrations of **2**, as well as with **3**, with different metal ions such as Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2}+, Zn^{2+}, Cd^{2+} and Hg^{2+} in methanol show that the fluorescence intensity of the parent compounds increases with increase the concentration of the respective metal ions. The relative changes are listed in Supplementary

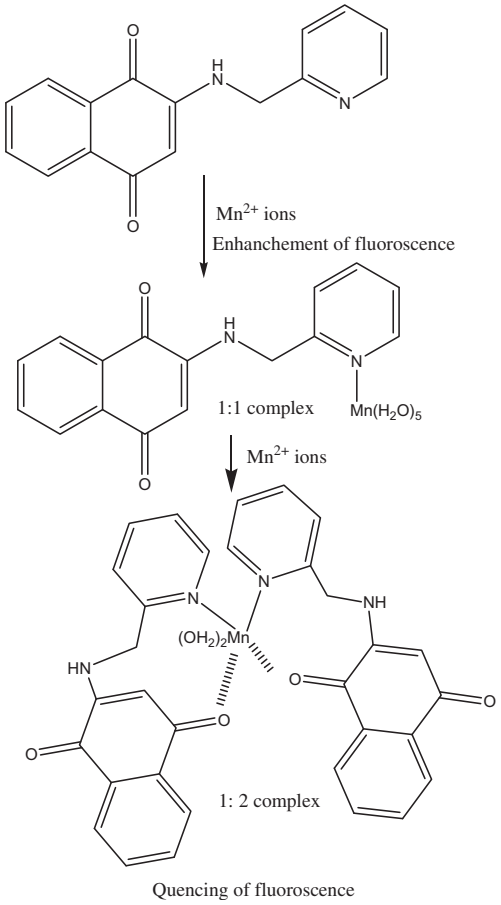


Fig. 4. Hypothetical coordination complexes of Mn^{2+} causing fluorescence changes.

materials. The Stokes shifts in all these cases were determined and the emissions with respect to absorptions were shifted to higher wavelengths than the absorption maximum. This suggests the role lone pair of electron present on the nitrogen atom of pyridine influences the fluorescence emission of the parent compounds and the lowering of its energy upon interaction with a metal ion causes π^*–π emission to predominate and this makes the emission absorption to shift. Accordingly, the π^*–π emission moves to higher wavelength and also intensity enhancement occurs as it was observed in other studies in related compounds [2].

Since fluorescence behaviour of Mn^{2+} and Ni^{2+} ions are quite different, and in case of the Mn^{2+} ions initial increase followed

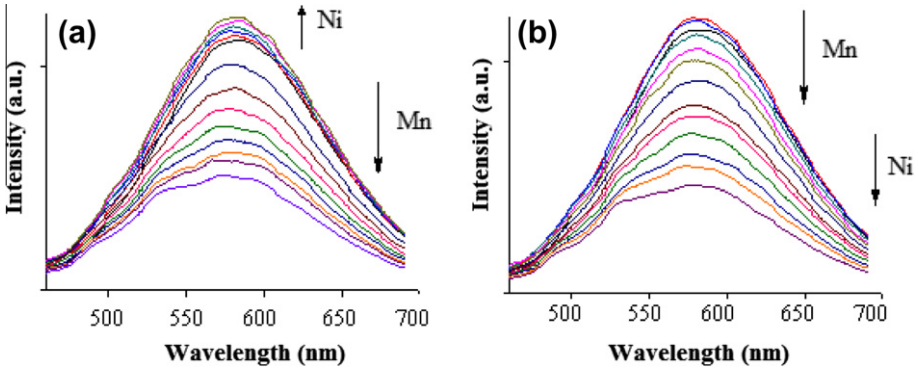


Fig. 5. (a) Changes in fluorescence spectra of **1** (10^{-5} M, 2 ml in methanol) on addition of Ni^{2+} (10^{-5} M in methanol, 10 μl in each aliquot ten times followed by addition of Mn^{2+} (10^{-5} M in methanol) 10 μl in each aliquot). (b) Changes in fluorescence spectra of **1** (10^{-5} M, 2 ml in methanol) on addition of Mn^{2+} (10^{-5} M in methanol, 10 μl in each aliquot ten times) followed by addition of Ni^{2+} (10^{-5} M in methanol) 10 μl in each aliquot.

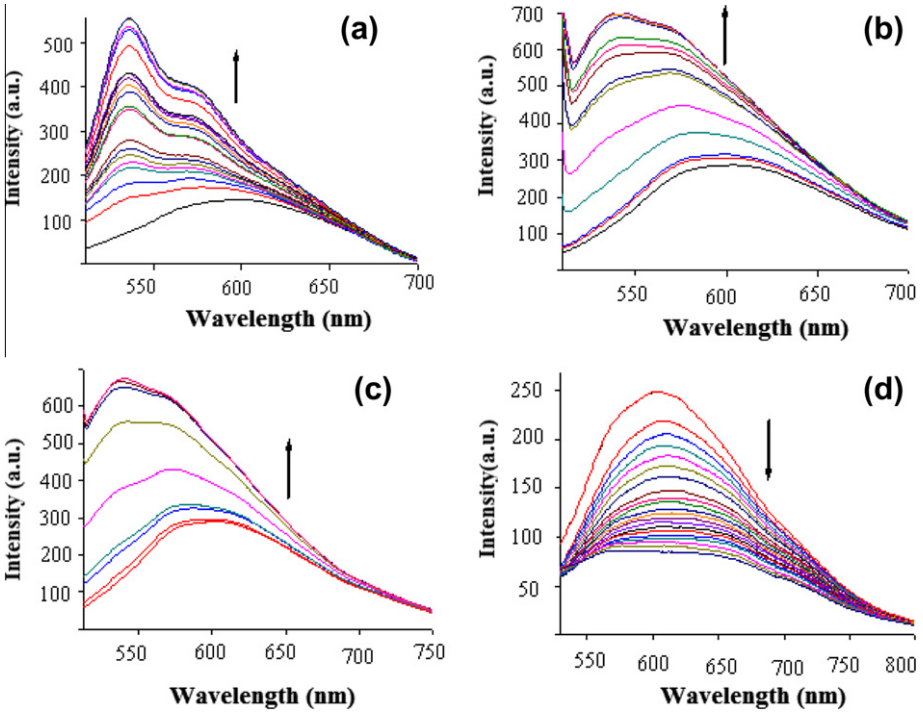


Fig. 6. Changes in fluorescence emission of **4** (10^{-4} M, 2 ml in methanol) on addition of (a) Ni^{2+}; (b) Hg^{2+}; (c) Ag^{+}; (d) Cu^{2+} (in each case 10^{-4} M in methanol 10 μl in each aliquot).

by decrease was observed, we studied whether a ON state generated by Ni^{2+} ions can be made OFF by excess of Mn^{2+} ions and vice versa. The fluorescence behaviour of **1** in the presence of Ni^{2+} and Mn^{2+} ions were studied with sequential addition of Mn^{2+} and Ni^{2+} ions to a solution of **1.** When Ni^{2+} ions were added first, followed by Mn^{2+} ions, it was found that the initial addition of Ni^{2+} ions to the solution of compound **1** enhanced the fluorescence intensity, but while to this solution Mn^{2+} ions were added, they caused quenching of fluorescence (Fig. 5). But in the reverse titration, namely, addition of Ni^{2+} ions to **1** containing Mn^{2+} ions could not enhance the fluorescence intensity. This suggests that the complex formed by Mn^{2+} ions is not converted to a nickel complex whereas the nickel complex can be transformed to manganese complex by displacement reaction. This further supported by the higher binding constant (refer to supporting Fig. S23) of nickel(II) ions with compound **1** ($K_1 = 7.69 \times 10^6$/M).

The fluorescence emission of **4** was also investigated with different ions such as Li^{+}, Na^{+}, K^{+}, Mg^{2+}, Ba^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2}+, Zn^{2+}, Cd^{2+}, $Hg^{2+}$and Ag^{+}. The compound **4** has an absorption maximum 450 nm due to π–π^* transition; it emits 600 nm upon irradiation at 480 nm. The fluorescence emissions of the compound **4** were changed upon addition of different metal salts. Addition of Li^{+} metal ion to a solution of **4**, causes an increase in intensity of emission but in the case of Na^{+} and K^{+} ions, the fluorescence intensity decreases. Further, the use of less ionisable salts such as potassium acetate causes insignificant change in the fluorescence emission of **4**. The fluorescence quenching by potassium and sodium is attributed to their ability to bind to carbonyl group rather than the pyridine nitrogen. Further lithium being small size has more covalent character, it tightly binds to two lone pairs on the two nitrogen atoms of **4** to form chelate. Addition of Mg^{2+} ions to **4**, causes very less change in fluorescence, but sharp decrease in the fluorescence intensity was observed in the case of Ba^{2+}. Among other metal ions Mn^{2+}, Co^{2+}, Fe^{3+}, Hg^{2+} ions cause enhancement of intensity. But Ni^{2+}, Zn^{2+} were found to be insensitive to **4.** Interestingly, the addition of Cu^{2+} to a solution of **4**, caused decrease in the fluorescence intensity as shown in Fig. 6. It may be mentioned that copper was also a special case in an earlier study with a similar compound derived from 2-methylnaphthoquinone [36] was found to bind tightly to Cu^{2+} ions. Complexation ability of **4** to Cu^{2+} ions is very clear from changes in visible spectra of **4** on addition of Cu^{2+} solution. There are two isosbestic points at 380 and 501 nm (refer supporting information). Other metal ions do not show such drastic changes in visible spectra (see Table 3).

On addition of Cd^{2+} to a methanol solution of **4**, the fluorescence intensity initially decreases with increase in concentration of Cd^{2+} metal ions, after a particular concentration of Cd^{2+} ions, new emission band arises between 532 and 600 nm (Fig. 7). This dual characteristic of cadmium ions makes it unique to distinguish from other cations and makes it a potential chemo-selective cadmium sensor. Due to environmental concern, a large number of cadmium

Table 3
Fluorescence emission data for the compound **4** with or without metal ions.[a]

Added ions	Visible λ_{max} (nm)	λ_{em} (nm)	Stokes shift (nm)
None	450	600	150
Li^{+}		577	127
Na^{+}		570	120
K^{+}		600	150
Mg^{2+}		582	132
Ba^{2+}		600	150
Mn^{2+}		600	150
Fe^{3+}		600	150
Co^{2+}		585	135
Ni^{2+}		535	85
Cu^{2+}		600	150
Zn^{2+}		597	147
Cd^{2+}		532	82
Hg^{2+}		539	89
Ag^{+}		538	88

[a] Excitation in each case is done at 475 nm in each case. Fluroscence emission spectra were measured by taking 2 ml, solution of **1**, **2** or **3** in methanol (10^{-4} M) with or without addition of 0.1 ml of 10^{-4} M metal perchlorate solution in methanol.

sensors are prepared [54,55]. Cadmium sensors are widely used in industry, agriculture, and many other fields [56–58]. As Cd^{2+} can cause serious environmental and health problems, there is definite need for development of methods to monitor cadmium ions [59–61]. The present compound **4** might be first example of a naphthoquinone derived sensor showing concentration dependence fluorescence changes. Due to the simplicity and high sensitivity fluorescence is also a powerful tool to monitor in vitro or in vivo biologically relevant species such as metal ions [61,62]. Thus, the compounds having structural skeleton similar to the presented compounds here can be one candidate among them for such studies.

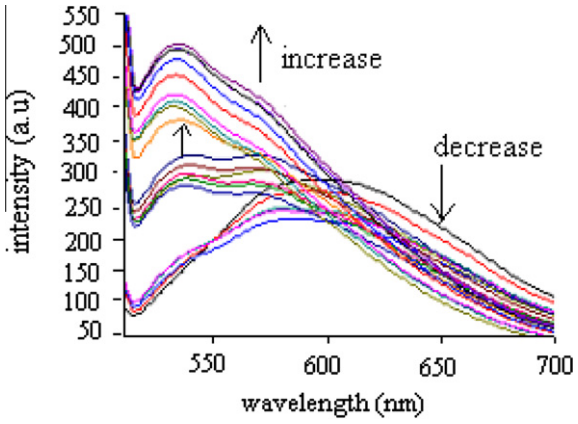


Fig. 7. Changes in fluorescence spectra of **4** (10^{-4} M, 2 ml in methanol) on addition of Cd^{2+} (10^{-4} M in methanol 10 μl in each aliquot; λ_{ex} = 475 nm) (intial decrease after that increase on gradual addition in two steps).

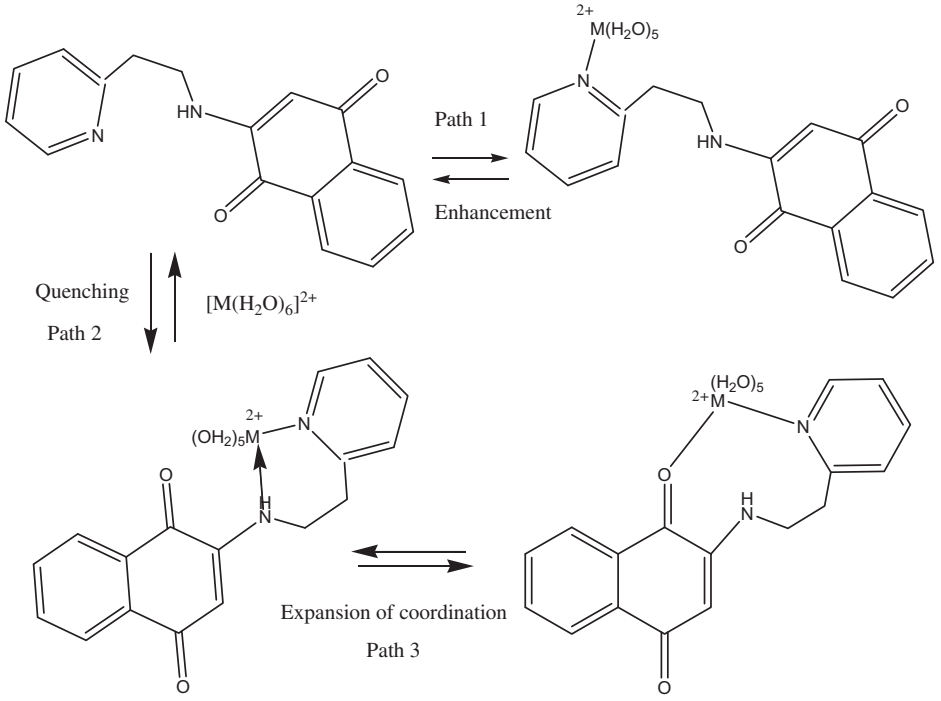
Table 4
Lifetime of fluorescence emission[a] of **4** without and with Cd^{2+} and Cu^{2+}.

Compound	λ_{ex} (nm)	λ_{ems} (nm)	τ^1 (ns)/(*f*)%	τ^2 (ns)/(*f*)%	χ^2
4	475	600	0.039 (88.71)	2.522 (11.29)	1.303
4 With Cd^{2+}		(a) 600	0.039 (88.61)	2.542 (11.39)	1.277
		(b) 532	0.027 (60.93)	4.197 (39.07)	1.075
4 With Cu^{2+}		600	0.035 (89.66)	2.601 (10.34)	1.131

[a] Compound **4**, (2 ml, 10^{-4} M, in methanol) alone and after addition of 50 μl; 10^{-4} M in methanol solution of Cd^{2+}; and after addition of 200 μl; 10^{-4} M in methanol solution of Cd^{2+}. For Cu^{2+}, to a solution of compound **4**, (2 mL, 10^{-4} M in methanol) with 100 μl solution of Cu^{2+} (10^{-4} M in methanol).

Fluorescence lifetimes of 4 with or without Cd^{2+} ions were determined. Two lifetimes for compound **4** was observed; one 0.039 ns (τ^1) contributing 88.71% of the fluorescence, and the other 2.522 ns (τ^2) contributing the 11.29% of the rest of the fluorescence (Table 4). In related compounds, it was earlier shown that the relative contribution of each component of such lifetimes is dependent on the intramolecular electron transfer from the excited fluorophore to the adjacent quinone acceptor, or by the transfer of excitation energy to a low-lying non-emissive charge-transfer state [54]. The fluorescence lifetime of **4** was measured at two different emission wavelengths after addition of Cd^{2+} ions (50 μl of Cd^{2+} ions 10^{-4} M solution was added to 2 ml of 10^{-4} M **4** in methanol). When monitored at 600 nm the lifetime had two components, namely 0.039 ns (88.61%) and 2.542 ns (11.39%); but when the same lifetime was monitored at 532 nm after increasing the concentration of Cd^{2+} metal ions, a significant difference in the two lifetimes were observed. In the later case the lifetime had two components, one is 0.027 ns (of 60.93%) and rest 39.07% emission had lifetime 4.197 ns. We have measured the lifetime of the fluorescence emission of a solution of **4** containing Cu^{2+}, in this case, we did not see much difference in the path from the parent compound, other than slight changes in the lifetimes of the two paths compared to the parent compound (Table 4).

From this study it is clear that there are significant differences in emission patterns of the two compounds **1** and **4** by various cations. The emission processes are mainly guided by interactions of the lone pair of electrons on nitrogen of pyridine with the metal ions. The compound **4** has a better bite-angle to form chelate with



Scheme 2. Different possible ways of cadmium ions binding to compound **4.**

metal ions (Scheme 2). This results in the fluorescence quenching. When the complexation of the ligand is only through lone pair of electrons on the nitrogen atom of the pyridine ring, there is an increase in fluorescence. Thus, depending on the predominance of equilibrium as illustrated in Scheme 2; it may be suggested that the path 2 and path 3 predominates in the case of interaction of cadmium with compound **4**. There are good numbers of examples when pyridine coordination is observed in pyridine tethered fluorescent ligands [36,63,64]. The changes in chemical shifts due to coordination effect are also reflected in solution ^{1}H NMR of the 1,4-naphthoquinone derivative **4,** these are as depicted in Supplementary materials. The change of concentration of metal ions causes changes in the chemical shifts in different manners, which are also reflected in the fluorescence emission changes due to changes in concentrations.

In conclusion, the metal ion recognition by 1,4-naphthoquinone derivatives (**1**–**4**) has been investigated. The compound **1** shows unique behaviour towards Mn^{2+} ions. The fluorescence emission of **4** with different ions is guided by the ability and mode of coordination of different metal ions. A general trend of enhancement by participation of nitrogen lone pair in coordination is seen, but the exception of bivalent copper and barium are attributed to metal chelate formation. The exceptional behaviour of bivalent cadmium is attributed to the different coordination equilibriums. It may be mentioned that the compounds that shows higher than 100 nm Stokes shifts are less common in organic chemistry [61] and less often come across in inorganic chemistry [62]. In these study all the compounds **1**–**4** show large Stokes shifts and provides example of new set of organic fluorescent compounds which emits in visible range on excitation at relatively high wavelength. Importantly, the magnitude of the Stokes shift of the ligands can be tuned by different metal ions. The concentration dependent fluorescence intensity ON–OFF behaviour with **1** by Mn^{2+} ions and also concentration dependent OFF–ON–ON behaviour of Cd^{2+} ions with **4** makes this study unique.

Appendix A. Supplementary material

The visible spectroscopic titration of compound **4** with Cu^{2+} ions; the fluorescence emission titration of **4** with different ions; the fluorescence lifetime decay profiles of **1**, **4**, **1** with Mn^{2+} ions, **4** with Cd^{2+} ions and **4** with Cd^{2+} ions. ^{1}H NMR titrations of **4** with different amounts of Cd^{2+} ions are available. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2012.12.018.

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