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Electron transfer fluorescence quenching of napthalenediols by metal ions

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Fluorescence quenching of four naphthalenediols (1,5-; 1,7-; 2,7-; 2,3-NDs) by transition metal ions (Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}, Pb^{2+}) has been investigated in 95% water-ethanol mixture. The dynamic quenching is appreciable with all metal ions except Pb^{2+}. Cupric ion (Cu^{2+}) is found to be an efficient quencher with all naphthalenediols and the sensitivity of 1,7-ND fluorescence is much higher than other naphthalenediols. The quenching rate constants (k_q) have been analyzed for various possible mechanisms. A good correlation of log k_q values with the reduction potentials of metal ions reveals the electron transfer quenching mechanism via a non-emissive exciplex with electron transfer from excited fluorophore to the metal ions. The anomalous behavior of 1,7-ND is explained by its point group symmetry and polarity.

Keywords: Fluorescence quenching, Electron transfer quenching, Quenching, Transition metal ions, Naphthalenediols

Fluorimetry is a sensitive and accurate technique with instantaneous response, for sensing pH, temperature, light, redox potential and metal ions. Organic fluorescent compounds have been widely utilized as fluorescent probes in chemical, environmental, and biological fields. Changes in fluorescence characteristics of an organic compound reveal its property and interaction with other atoms/ions/ molecules and this property makes the organic fluorescent compound, a sensor for detecting the metal ions present[1-3]. Transition metals, accumulated in plants by water uptake, enter animal and human tissues through diet. Research on detection of metal ions has been focussed due to their importance in human and plant life[1-7]. The fluorescence quenching of highly fluorescent aromatic compounds in solution by various quenchers such as metal ions, has attracted many researchers in the last couple of decades to make use of them as sensors for the metal ions. Fluorescence quenching of aromatic fluorescent molecules by a series of metal ions have been reported[8-11]. Naphthalenediols (NDs) have excellent emission characteristics and can be used as fluorescent probes[12]. In the present work, we report the fluorescence quenching of four naphthalenediols (1,5-; 1,7-; 2,7-; 2,3-NDs) by some transition metal ions and have analyzed their quenching mechanism. The results may be utilized for using these compounds as sensors for reported metal ions.

Experimental

Four naphthalenediols (1,5-; 1,7-; 2,7-; 2,3-NDs) were obtained from Sisco Chemical Company, India and further purified by recrystallisation with suitable solvents. The concentration of fluorophore was 10^{-4} M in 95% water–ethanol system. This solvent system was selected as both naphthalenediols and metal ions are soluble in this solvent system. The metal chloride salts ($NiCl_2.6H_2O$, $CoCl_2.6H_2O$, $CuCl_2.2H_2O$, $PbCl_2$, $MnCl_2.4H_2O$, $ZnCl_2$) were purchased from E. Merck, Qualigens and SD Fine Chemicals. The salts were recrystallised from triply distilled water before use. Solutions of different quencher concentrations were freshly prepared using the respective stock solutions.

Absorption and fluorescence spectra were recorded with Hitachi U-2001 double beam spectrometer and JASCO FP-550 spectrofluorimeter respectively. The excitation wavelengths were the absorption maxima of the respective fluorophores. Measurements of lifetimes of the fluorophores were made on a time correlated single photon counting picosecond spectrofluorimeter (Tsunami, Spectra Physics, USA) with the excitation source Ti–Sapphire laser. The average output power of Tsunami is 680 mW with a pump power of 4.5 W. The pulse width of the laser is less than 2 ps. Fluorescence decay curves were monoexponential for all the fluorophores with and without quenchers. Cyclic voltammetric measurements were obtained using a Wenking potentiostat (model LB 75M) and voltage scan generator (model VSG-72). Half-wave potentials were measured as the average of cathodic and anodic peak potentials.

Results and discussion

Fluorescence quenching of naphthalenediols (1,5-; 1,7-; 2,7-; 2,3-NDs) by metal cations was studied in 95% aqueous ethanolic (5% ethanol) solution. It was observed in a separate experiment that NaCl had negligible effect on the fluorescence of naphthalenediols. Hence, all the metal ions taken were the salts of chloride.

The absorption and fluorescence spectra of four fluorophores (with or without metal ions) have the following characteristics: (i) there is no change in the shape and position of absorption and fluorescence spectral bands with any of the metal ions, other than the decrease in fluorescence intensity, i.e., fluorescence quenching. Absence of a change in absorption spectra with metal ions indicates that there is no interaction between naphthalenediols and metal ions in ground state; (ii) there was no appearance of any new band either in absorption or fluorescence spectra at higher wavelength region, which reveals the non-formation of emissive exciplex, and, (iii) the excitation spectra resembles the respective absorption spectra. This shows that there is no change in the structure and geometry of fluorophore in the excited singlet state.

The Stern-Volmer (SV) plots were obtained according to Eq. (1),

$$(I_0/I) - 1 = K_{SV}[Q] \quad \ldots(1)$$

where I_0 and I are the fluorescence intensities with and without quencher [Q] respectively. The SV plot of $[(I_0/I)-1]$ versus [Q] for the fluorescence quenching of 1,5-ND by metal ions is displayed in Fig. 1. SV plots of 1,7-; 2,7-; and 2,3- naphthalenediols are given as supplementary data (Figs S1, S2 and S3 respectively). SV quenching curves for all NDs with all the metal ions are linear. The Stern-Volmer quenching constant, K_{SV}, was obtained from the slope of these curves. K_{SV} values for four naphthalenediols by metal ions in 95% water–ethanol mixture are given in Table 1.

Nature of fluorescence quenching may be static, dynamic or both combined together. The absence of static quenching is shown by (i) no change in absorption spectrum with quencher, and (ii) K_{SV} being independent of the excitation wavelength. Simultaneous presence of static and dynamic quenching leads to a positive deviation in the Stern-Volmer plot[17,18]. Linearity of all SV plots and the absence of positive deviation, imply that only one quenching mechanism is operative. Hence, quenching is purely dynamic and it is due to excited state reaction.

For dynamic quenching, $K_{sv} = k_q\tau_0$, where k_q is the bimolecular quenching constant (L mol^{-1}) and τ_0 is the excited singlet lifetime of the fluorophore. The k_q values calculated for all the metal ions are listed in Table 2 along with the lifetimes of fluorophores. Out of the six metal ions examined for quenching ability, it is found that copper (Cu^{2+}) is most efficient, while nickel (Ni^{2+}) comes next, with all the four naphthalenediols. Cobalt (Co^{2+}), zinc (Zn^{2+}) and manganese (Mn^{2+}) showed appreciable quenching. No quenching was observed for lead (Pb^{2+}) for all the fluorophores. Among the four naphthalenediols, fluorescence of 1,7-ND is more sensitive towards quenching.

There are different possible mechanisms for fluorescence quenching by metal ions, viz., (i) electronic energy transfer from the fluorophore to

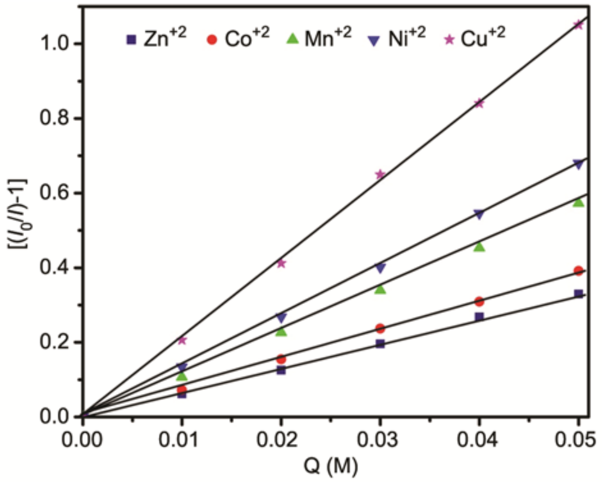

Fig. 1 – Stern-Volmer plot of 1,5-ND fluorescence quenching by various metal ions.

Table 1 – Values of K_{SV} of naphthalenediols fluorescence quenching by various metal ions in 95% water-ethanol mixture

Fluorophore	K_{sv} (L mol^{-1})					
	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Mn^{2+}	Pb^{2+}
1,5-ND	7.89	13.58	21.01	6.60	11.317	Nq
1,7-ND	9.78	11.76	14.82	8.33	9.34	Nq
2,7-ND	2.56	3.22	3.91	2.10	2.72	Nq
2,3-ND	5.29	6.76	12.58	5.01	6.02	Nq

Nq: No appreciable quenching.

Table 2 – Values of k_q and τ_0 of naphthalenediols fluorescence quenching by various metal ion in 95% water-ethanol mixture

Fluorophore	Lifetime τ_0 ±0.01 (ns)	k_q (L mol^{-1})					
		Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Mn^{2+}	Pb^{2+}
1,5-ND	8.57	0.92	1.59	2.45	0.97	1.32	Nq
1,7-ND	2.35	4.17	5.01	6.31	3.55	3.98	Nq
2,7-ND	6.19	0.41	0.52	0.63	0.34	0.44	Nq
2,3-ND	12.30	0.43	0.55	0.71	0.41	0.49	Nq

Nq: No appreciable quenching.

the quencher, (ii) static quenching by ground state complex formation, and, (iii) collisional quenching of excited state fluorophore by quencher which may occur via processes like heavy atom effect, paramagnetic interaction, quenching mediated through an emissive or non-emissive exciplex, and quenching by electron transfer.

Penzer and Radda[13] proposed a quenching mechanism by the conversion of electronic energy of the fluorophore to kinetic energy of the colliding species/quencher. In this mechanism, specific electronic characteristics of an ion is not relevant in determining its quenching ability, however its mass and diffusion coefficient are important in the determination of quenching efficiency. Analysis of k_q values reveals that there is no correlation between k_q and mass and diffusion coefficient of metal ions. Co^{2+} ($D = 7.3\times10^{-6}$ cm^2 s^{-1}) and Cu^{+2} ($D = 7.5\times10^{-6}$ cm^2 s^{-1}) and Zn^{+2} ($D = 7.3\times10^{-6}$ cm^2 s^{-1}) have comparable diffusion coefficients[14], but their quenching efficiencies are different. In fact all hydrated metal ions have almost the same radius, similar mass and diffusion coefficient, whereas the bimolecular quenching constant varies remarkably. So the mechanism of energy transfer electronically from fluorophore to the quencher is excluded from further discussion. Since there is no correlation between quenching constant and atomic number or spin multiplicity (Cu^{2+}:2, Co^{2+}:4, Ni^{2+}:3, Mn^{2+}:6, Zn^{2+}:1, Pb^{2+}:1), heavy atom quenching and paramagnetic interaction are ruled out[15,16]. As stated earlier, static quenching is also ruled out.

Bimolecular diffusion rate constant for the solvent (k_{diff}) was obtained using the Einstein-Smoluchouski equation,

$$k_{diff} = 8RT/2000\ \eta\ (\mathrm{L\ mol^{-1}}) \qquad \ldots(2)$$

where η is the viscosity of 95% water-ethanol mixture. k_{diff} was determined to be 1.06×10^{10} L mol^{-1} s^{-1}. The value of k_{diff} is approximate because of the assumption of equal molecular radii for fluorophore and quencher in Eq. 2 and does not hold true for diffusion-limited quenching. But the upper limit for the diffusion rate of the fluorophore and quencher is set by k_{diff} of the solvent and k_q can not exceed k_{diff}, even if every collision between the fluorophore and quencher results in quenching. The k_q values for all the fluorophores with the metal ions are closer to $k_{diff.}$ values. This indicates the collisional nature of the quenching. k_q value for quenching by Cu^{2+} is larger than the diffusion limit. No specific interpretation could be given for the large K_{SV}/k_q value of copper ion.

Generally quenching occurs via the formation of an emissive or non-emissive exciplex with charge-transfer. Since there is no new emission at higher wavelengths, quenching may be due to non-emissive exciplex. To estimate the non-emissive charge (electron) transfer exciplex-mediated quenching, indirect methods are used[19,20]. Electron transfer occurs from a donor having lower ionization potential (IP) to an acceptor having higher electron affinity (EA)[21,22].

Quenching of fluorescence of aromatic hydrocarbons by inorganic anions takes place via the transfer of electrons[21]. Both directions of electron transfer are possible for metal ion quenching of flurophores. A Rehm-Weller plot of log k_q with half-wave potential of metal ions, shown in Fig. 2, gave a fairly acceptable linear fit which indicates the electron transfer from flurophore to metal ions[23]. The correlation between log k_q and $E_{1/2}$ (eV) of metal ions is fairly good for all naphthalenediols (Table 3). When charge transfer takes place from metal ions to fluorophore, then a plot of log k_q versus IP_D of various metal ions must be linear. The correlation coefficients of log k_q and IP_D of metal ions are given in Table 3. The correlation between log k_q and IP_D of metal ions is very poor for all naphthalenediols. This indicates that quenching occurs mainly through non-emissive exciplex with electron transfer from excited fluorophore to metal ions. This is further verified by the plot of log k_q against the oxidation

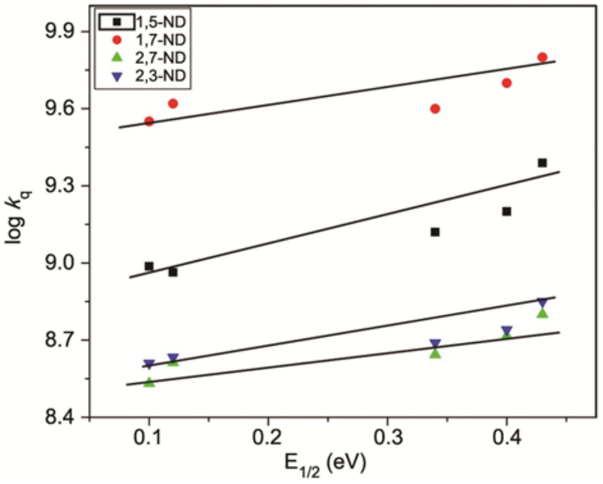

Fig. 2 – Plot of log k_q versus half-wave reduction potential $E_{1/2}$ (eV) of the metal ions for naphthalenediols.

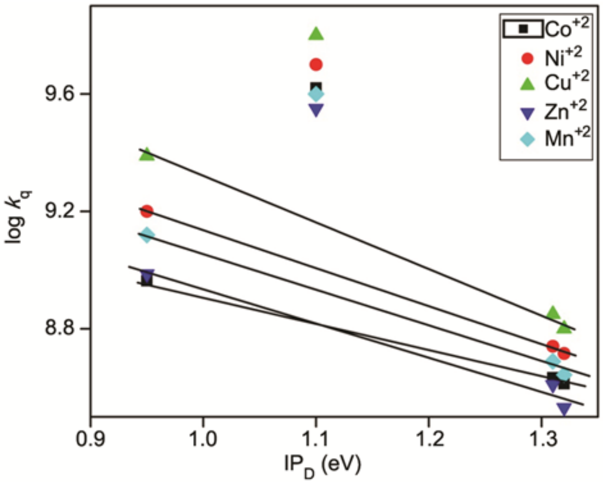

Fig. 3 – Plot of log k_q versus oxidation potential (IP_D) of the naphthalenediols fluorophores.

potential of the fluorophores (Fig. 3). In this plot the values of 1,7-ND are very much deviated. Quenching rate constants, k_q, for 1,7-naphthalenediols are higher than those for other naphthalenediols. Among the naphthalenediols, the 1,7-ND is reported to be more polar when compared to other naphthalenediols in the excited state due to its large stokes shift observed in water[12]. This behavior is explained by its point group symmetry, which is related to the polarity of the molecule. Point group symmetry of 1,7-ND (C_1h) is different from other naphthalenediols (C_2v, C_2h). The increase of excited state polarity of 1,7-ND may increase the formation of non-emissive exciplex. This is the reason why the correlation coefficient of 1,7-ND is slightly less, as shown in Table 3.

Table 3 – Correlation coefficients of log k_q of the fluorophores with $E_{1/2}$ and IP_0

Naphthalenediols	Corr. coeff. (*r*)	
ND	$E_{1/2}$ (eV)	IP_D (eV)
1,5-ND	0.93	0.59
1,7-ND	0.88	0.62
2,7-ND	0.90	0.57
2,3-ND	0.90	0.68

In conclusion**,** metal ions (Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}) are efficient quenchers of fluorescence exhibited by napthalenediols. The quenching is purely dynamic. The quenching occurs mainly through non-emissive exciplex, with electron transfer from the excited naphthalenediols to metal ions. This study may be useful for utilizing these compounds as sensors for the metal ions.

Supplementary data

Supplementary data associated with this article are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_57A(07)915-919_SupplData.pdf.

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References

1 Chai M, Zhang D, Wang M, Hong H, Yea Y & Zhaoa Y, *Sensors Actuators B*, 174 (2012) 231.
2 Zhao M, Zhou X, Tang J, Deng Z, Xu X, Chena Z, Li X, Yang L & Ma L J, *Spectrochim Acta A*, 173 (2017) 235.
3 Li G, Liu G, Zhang D B & Pu S Z, *Tetrahedron*, 72 (2016) 6390.
4 Kirubaharan C J, Kalpana D, Lee Y S, Kim A R, Yoo D J, Nahm K S & Kumar G G, *Ind Eng Chem Res,* 51 (2012) 7441.
5 Fu X, Lou T, Chen Z, Lin M, Feng W & Chen L, *ACS Appl Mater Interfaces*, 4 (2012) 1080.
6 Li H, Zhai J, Tian J, Luo Y & Sun X, *Biosensors Bioelectron,* 26 (2011) 4656.
7 Toal S J, Jones K A, Magde D & Trogler W C, *J Am Chem Soc*, 127 (2005) 11661.
8 Narayanaswamy N & Govindaraju T, *Actuators B: Chem,* 161 (2012) 304.
9 de Castro C S, Sergio Seixas de Melo J, Fernandez-Lodeiro A, Nunez C & Lodeiro C, *Inorg Chem Commun,* 47 (2014) 27.

10 Liu H, Li FX, Pi Y, Wang D J, Hu Y J & Zheng J, *Spectrochim Acta A,* 145 (2015) 588.

11 Udhayakumari D, Velmathi S, Boobalan M, Venkatesan P & Wu S P, *J Lumin*, 158 (2015) 484.

12 Rajendiran N, Radha N & Swaminathan M, *Indian J Chem,* 40A (2001) 331.

13 Penzer G R & Radda G K, *Quart Rev Chem Soc*, 21 (1967) 43.

14 Varnes A W, Barry Dodson R & Wehry E L, *J Am Chem Soc,* 94 (1972) 946.

15 Martinho J M G, *J Phys Chem,* 93 (1989) 6687.

16 Chang J H, Choi Y M & Kook Shin Y, *Bull Koran Chem Soc,* 22 (2001) 527.

17 Radha N & Swaminathan M, *Spectrochim Acta A,* 60 (2004) 1839.

18 Radha N & Swaminathan M, *J Chem Res,* 2001 (2001) 503.

19 Radha N & Swaminathan M, *Collect Czech Chem Comm,* 67 (2002) 1154.

20 Chitra H, Vijayasree V & Mishra A K, *J Lumin,* 75 (1997) 205.

21 Lakowicz J R, *Principles of Fluorescence Spectroscopy,* 3rd Edn, (Springer Science, New York, USA), (2006) 334.

22 Doose S, Neuweiler H & Sauer M, *Biophysics,* 10 (2009) 1389.

23 Rehm D & Weller A, *Ber Bunsen Phys Chem,* 73 (1969) 834.