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Electronic spectral study of interaction of electron donor – acceptor dyes in the ground and excited state with a metal ion. Effect of molecular structure of the dye

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ABSTRACT

Interaction of manganese (II) ion with electron donor (D)–acceptor (A) dyes having symmetric D–A–D configuration of chromophores (ketocyanine dye) and the corresponding parent merocyanines (D–A configuration) in acetonitrile has been compared by monitoring the electronic absorption, and steady state and time resolved fluorescence characteristics of the dyes. Absorption spectral studies point to the formation of a 1:1 metal ion–dye (S_0-state) complex. Equilibrium constant (K_0) and other thermodynamic parameters for complex formation have been determined for all the systems. Symmetric ketocyanine dyes (D–A–D) form stronger complex than the corresponding dye with D–A configuration. Quenching of fluorescence is caused due to complex formation with the cation. However, for very low concentration of salts, where complex formation is insignificant, an enhancement of fluorescence intensity takes place due to addition of salt. The absorption band of the dye undergoes a slight blue shift in the same concentration range of the metal ion. Fluorescence life time of the excited state also increases with an increase in salt concentration in that concentration range. Results have been explained in terms of formation of a weak association complex where one or more cations replace equivalent solvent molecules in the cybotatic region around the dye. The binding constant of the association complex involving cation and the dye (S_1-state) has been determined. While the value of the binding constant is higher for a symmetric D–A–D dye relative to that for the corresponding dye with D–A configuration, the extent of fluorescence enhancement for the latter is larger. Values of decay constant for the different photophysical processes have been calculated. Formation of association complex in the S_1-state is characterised by a slower nonradiative decay of S_1-state of the dyes.

1. Introduction

Ketocyanine dyes form a class of compounds which are characterised by solvatochromic absorption and fluorescence properties [1–12]. The solvatochromism exhibited by the $S_0 \rightarrow S_1$ transition with the dye molecules can be attributed to an intramolecular charge transfer (ICT) from donor to acceptor centre. This property makes them good candidates for sensing the microenvironment properties of homogeneous and heterogeneous media [3,13–16]. These dyes also act as H^+ ion selective ionophores for use in integrated waveguides absorbance optodes [17,18]. The electronic spectral characteristics of these dyes are also modified due to interaction with metal ions. Basu et al. [19–22] and Doroshenko et al. [10] have studied the interaction of these dyes with alkali and alkaline earth metal ions. In a previous communication we have reported the study of interaction of Co^{2+} ion with a ketocyanine dye (the dye KD1 in Scheme 1) in which two N $(CH_3)_2$ electron donor (D) moieties are joined by a polyenic bridge to a carbonyl acceptor (A) moiety and thus forming a D–A–D configuration [23]. This study and a recent study [24] involving various metal ions and the parent merocyanine dye having similar D–A configuration reveal that these dye form a complex of various degree of stability with different metal ion in dipolar aprotic solvents e.g. acetonitrile and acetone. It has also been concluded that the interaction of the dyes with metal ions is mostly of electrostatic nature. Complex formation could not be detected in a protic solvent. Another interesting result of our studies is the enhancement of fluorescence intensity of the dye for the micromolar concentration range of the metal ions. Since the electronic spectral features and photophysics of a dye having D–A–D configuration differs from those of dyes with D–A configuration of the chromophores [15,25,26], it is instructive to compare the behaviour of these two classes of compounds with respect to complex

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formation with a metal ion. To this end we have monitored the electronic absorption, steady state, and time resolved fluorescence parameters of three (D–A–D, D–A) pairs of dyes viz. (KD1, DN1), (KD2, DN2) and (KD3, DN3) (Scheme 1) in polar aprotic (acetonitrile) and polar protic (methanol) solvents and their binary mixtures in presence of a particular metal ions, e.g. Mn^{2+} ion and compared the ability of sensing metal ions for the ketocyanine and the corresponding merocyanine dyes.

2. Experimental section

2.1. Materials

Dyes have been prepared following a literature procedure [1–3,25]. Purity of the compounds was checked by NMR, TLC, IR, UV–vis absorption and fluorescence spectral analysis. Acetonitrile and methanol, both of spectrophotometric grade (99.9%), were procured from Sigma-Aldrich and were used as received. Manganese (II)-perchlorate hexahydrate (Sigma-Aldrich) was dried cautiously in vacuum. The concentration of the dyes was in the range 10^{-5}–10^{-7} M in all spectroscopic measurements. The concentration of manganese (II) perchlorate solution varied in the range 10^{-2}–10^{-6} M.

2.2. Steady state spectral measurement

The UV–vis absorption and steady state fluorescence emission spectral studies were performed on CARY 300 BIO spectrophotometer and PERKIN-ELMER LS 55 spectrofluorimeter respectively. Temperature was controlled during the measurement using the temperature controller unit attached to the equipments.

2.3. Time-resolved fluorescence measurement

Fluorescence decay was measured by time-correlated single photon counting (TCSPC) technique using HORIBA JOBIN YVON time resolved fluorimeter. Excitation was done at 405 nm using a laser diode (model: NanoLED-405 L, Pulse duration: <100 ps, Serial number: 06808). Decay curves were analysed using IBH DAS-6 decay analysis software. In order to fit the decay curves, the following equation relating the fluorescence intensity at a time t, $F(t)$, with exponential decay functions has been used [27].

$$F(t) = \sum a_i \exp(-t/\tau_i) \quad (1)$$

where, a_i are the relative contributions to the lifetime component τ_i. The decay parameters were recovered using a nonlinear least square fitting procedure. Fittings with χ^2 values around 1 were taken as acceptable. For all these dyes the fluorescence decay was measured as a function of concentration of the metal ion. In the present study $F(t)$ for the dyes in pure solvent as well as in presence of Mn^{2+} ion solution, could be fitted with a single exponential decay equation.

3. Result and discussion

3.1. Absorption studies

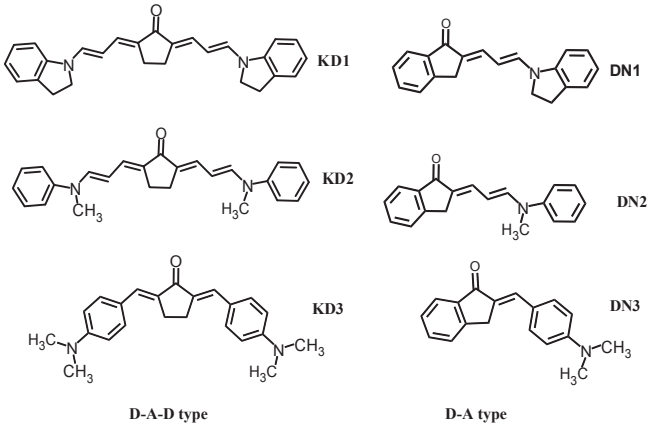
Absorption band of the dyes in acetonitrile appears as broad and structureless. Symmetric ketocyanine dyes having D–A–D configuration of chromophores show absorption maximum at longer wavelength than the corresponding parent merocyanine dyes (D–A configuration). The longest wavelength absorption band for the dyes is known to originate due to HOMO→LUMO electronic transition. The observed values of maximum transition energy for the dyes KD1 and DN1 (56.8 and 64.3 kcal mol^{-1} respectively) parallel the calculated HOMO–LUMO gap (3.0406 eV [23] and 3.3742 eV [24] respectively). In a dipolar aprotic solvent the dyes form loose solvated species. On addition of $Mn(ClO_4)_2$ to the dye solution, a new band forms at a longer wavelength and it gets enhanced in intensity as the concentration of the salt increases. For all dyes an isosbestic point appears in the absorption spectrum with gradual addition of the Mn^{2+} ion as shown in Fig. 1. Existence of isosbestic point indicates the presence of two species, namely, the solvated dye and dye–Mn^{2+} ion complex in equilibrium. While the lower wavelength band corresponds to the solvated dye, the longer wavelength band is due to the Mn^{2+}–dye complex. Values of E_S and E_C, (transition energy in kcal mol^{-1}, for the solvated dye and dye–Mn^{2+} ion complex respectively) for different dyes in acetonitrile have been listed in Table 1. Similar results have been obtained in our earlier studies [23,24], where a new band at longer wavelength appeared due to complex formation of the dye with a metal ion [23]. As reported in our earlier work, the difference between E_S and E_C parallels the extent of dye-metal ion interaction. The value of $(E_S - E_C)$ for KD1-Mn (II) system comes as 9.1 kcal mol^{-1} which can be compared with value 7.9 kcal mol^{-1} for KD1-Co (II) system. Thus the strength of interaction between KD1 and Mn (II) ion is similar to that between KD1 and Co (II) ion. Values of $(E_S - E_C)$ for the different dyes as listed in Table 1, indicate that, the value for a symmetrical dye (e.g. KD1, KD2) is greater than that for the corresponding parent merocyanine dye (DN1, DN2), indicating that the interaction of Mn^{2+} ion with a symmetric dye is stronger than that for the corresponding unsymmetric dye. It has been observed from quantum chemical calculation at AM1 level that the charge density of carbonyl oxygen in a symmetric ketocyanine dye is greater than that in asymmetric dye [2,3]. The strength of dye–Mn(II) interaction also follows the same order. Further, the spatial accessibility of the complexing centre, e.g., the carbonyl group, should be lower for the asymmetric molecule owing to the cation repulsion with ortho-hydrogen atom of the indanone moiety. Hence a stronger interaction with a symmetric dye is expected.

The absorption spectral observation can be rationalised in terms of existence of the following equilibrium in solution.

$$D\ldots..S + nMn^{2+} = D\ldots..(Mn^{2+})_n + S \quad (2)$$

The equilibrium constant (K_0)for complex formation of Mn^{2+} with the ground electronic state of the dye is given by:

$$K_0 = C_C/[C_S\,(C_{Mn}{}^{2+})^n] \quad (2a)$$



Scheme 1. Chemical structure of ketocyanine (D–A–D) dyes and corresponding merocyanine (D–A) dye used in the present work.

here $D....S$ and $D...(Mn^{2+})_n$ represent solvated dye and metal complexed dye respectively, n is the minimum number of Mn^{2+} participated in the equilibrium and C_S, C_C and $C_{Mn}{}^{2+}$ represent the equilibrium molar concentration of the solvated dye, metal-complexed dye and free metal ion in the solution respectively. Values of n and K_0 have been determined by a procedure as that described previously [23]. In all the cases the wavelength of maximum absorption corresponding to the solvated and complexed dye (λ_S and λ_C respectively) are widely different and it can be assumed that at λ_S and λ_C, the absorbing species are solvated dye and complex dye respectively. Denoting the absorbance at a wavelength λ_i by A_i, we have the following equation.

$$\log (A_C/A_S) = n\log C_{Mn}{}^{2+} + \log ((\varepsilon_c K_0)/\varepsilon_s) \quad (3)$$

where ε_c and ε_s are the molar absorbance of the complexed and the solvated dye at λ_C and λ_S respectively. If C_0 is the concentration of the total Mn^{2+} added, we can approximate $\log (C_{Mn}{}^{2+})$ by $\log (C_0)$ as we have $C_0 \gg C_C$ under the experimental condition [23]. The value of n determined from the slope of the plot of $\log (A_C/A_S)$ vs. $\log (C_0)$ comes in the range 0.85–0.98 for all the dyes indicating a 1:1 complex formation. The equilibrium constant for 1:1 complex formation can also be found out from an analysis of the spectral data as follows. Eq. (2) can be rearranged (with $n=1$) as

$$1 + K_0 C_{Mn}{}^{2+} = (C_C + C_S)/C_S = C_T/C_S \quad (4)$$

where C_T represents total dye concentration. If A_T and A_S represent the absorbance value for the total dye (solvated+complexed) and the solvated dye respectively at λ_S, we have the following equation:

$$A_T/A_S = 1 + K_0 C_{Mn}{}^{2+} \quad (5)$$

A_T is the absorbance of the solution when $C_0=0$. Table 2 lists the K_0 values for different dyes. Values of K_0 as obtained in the present

Table 1
Values of E_S, E_C and $E(F)$ for different dyes.

Dye	E_S/kcal mol^{-1} [a]	E_C/kcal mol^{-1} [a]	$E_S - E_C$/ kcal mol^{-1}	$E(F)$/kcal mol^{-1}
KD1	56.8 ± 0.1 (5 0 3)	47.7 ± 0.1 (6 0 0)	9.1	51.0 ± 0.1 (5 6 0)
DN1	64.3 ± 0.1 (4 4 5)	56.6 ± 0.1 (5 0 5)	7.7	55.0 ± 0.1 (5 2 0)
KD2	60.0 ± 0.1 (4 7 7)	51.2 ± 0.1 (5 5 8)	8.7	54.0 ± 0.1 (5 3 0)
DN2	67.3 ± 0.1 (4 2 5)	59.9 ± 0.1 (4 7 7)	7.4	57.8 ± 0.1 (4 9 5)
KD3	62.2 ± 0.1 (4 6 0)	51.5 ± 0.1 (5 5 5)	10.7	51.0 ± 0.1 (5 6 0)
DN3	68.6 ± 0.1 (4 1 7)	–	–	53.4 ± 0.1 (5 3 5)

[a] Absorption maximum values are given in parenthesis.

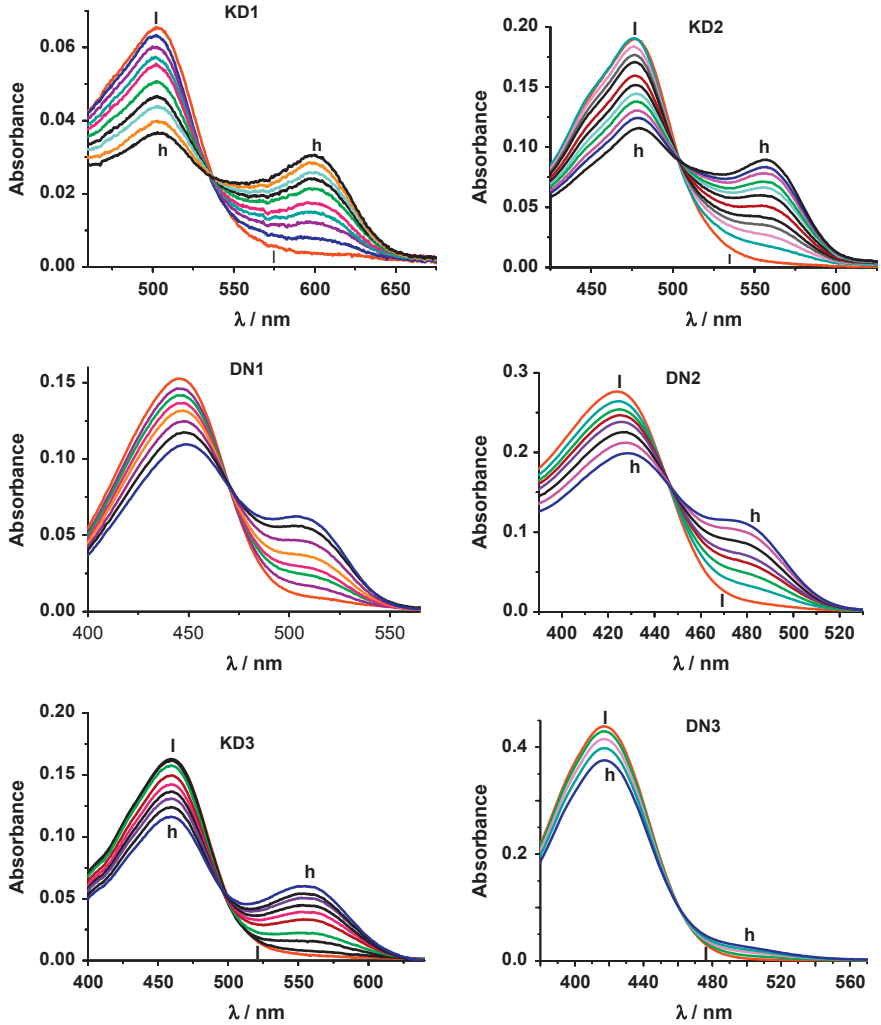


Fig. 1. Absorption spectra of different ketocyanine dyes in acetonitrile with varying concentration of Mn^{2+} ion. h and l indicate the highest and lowest concentration of Mn^{2+} ion. The ranges of concentration (h, l) for different dyes are: (6.8×10^{-4}, 0) for KD1, (8.5×10^{-4}, 0) for KD2, (1.25×10^{-2}, 0) for DN1, (1.31×10^{-2}, 0) for DN2, (1.35×10^{-2}, 0) for KD3 and (1.41×10^{-2}, 0) for DN3.

Table 2
Thermodynamic parameters for the ground state complexation of the dyes with Mn^{2+} ion in ACN solvent.

Dye	Temperature/K	K_0[a]/M^{-1}	ΔH^0/kcal mol^{-1}	ΔS^0/cal K^{-1}
KD1	293	1394	−1.877	7.98
	298	1320		
	303	1254		
	308	1192		
	313	1135		
KD2	293	825	−1.038	9.80
	298	802		
	303	778		
	308	756		
	313	736		
DN1	293	41	−0.586	5.36
	298	40		
	303	39		
	308	39		
	313	38		
DN2	293	35	−0.542	5.23
	298	34		
	303	34		
	308	33		
	313	33		
KD3	298	40		
DN3	298	15		

[a] Error ± 5%.

study follows the order: KD1 > KD2≫KD3 for the symmetrical dyes. For a given (D–A–D, D–A) pair the values of K_0 is in the order: D–A–D > D–A, indicating greater interaction of Mn^{2+} ion with the symmetrical dyes. This is also reflected by the $(E_S - E_C)$ values as discussed earlier. Values of K_0 have been determined at different temperatures for the dyes and are listed in Table 2. It appears that K_0 value decreases on increasing temperature for all the dyes indicating the dissociation of the complex at higher temperature. Calculated values of the thermodynamic parameters, ΔH^0 and ΔS^0, have also been listed in Table 2. Values of ΔH^0 show the same trend as K_0 for the different dyes.

Addition of Mn^{2+} ion to the solution of the dyes in methanol is not associated with any noticeable spectral change. Thus, the dyes do not interact significantly with Mn^{2+} ion in methanol solution. This is intelligible in view of fact that MeOH form hydrogen bond with the carbonyl oxygen of the dyes. This also provides further evidence that Mn^{2+} binds to the carbonyl oxygen of the dyes. When MeOH is added to the solution of the dyes in acetonitrile, both MeOH and Mn^{2+} ion competes for binding to the dyes. The extent of complex formation, as indicated by the relative absorbance at longer wavelength would decrease as the amount of MeOH increases. Experiments on complex formation have been carried out taking MeOH+ACN binary mixtures as solvent. The following equilibria may be assumed to exist in solution of the dyes in a mixed binary solvent containing ACN (S_1) and MeOH (S_2).

$$D\ldots\ldots S_1 + S_2 = D\ldots\ldots S_2 + S_1 \quad K_{12} \tag{6}$$

$$D\ldots\ldots S_1 + Mn^{2+} = D\ldots..Mn^{2+} + S_1 : \quad K_{01} \tag{7}$$

D……S_1 and *D*…….S_2 represent the dye solvated by S_1 and S_2 respectively, and K_{12} and K_{01} denote the equilibrium constants. Under this condition the Eq. (5) is replaced by the following:

$$A_T/A_S = 1 + K_{01}\, C_{Mn}{}^{2+}/[1+(K_{12}-1)x_2] \tag{8}$$

where x_2 is the mole fraction of MeOH in the mixed binary solvent. Thus a plot of (A_T/A_S) vs. $C_{Mn}{}^{2+}$ would give straight line. Fig. 2a shows a representative plot. The observed value of equilibrium constant (K_{obs}) at a solvent composition (x_2), as obtained from A_T/A_S vs. $C_{Mn}{}^{2+}$ plot, will be given by: $K_{obs} = K_{01}/[1+(K_{12}-1)x_2]$. Table 3 shows values of K_{obs} for KD1 as a function of x_2. The expression for K_{obs} can be rearranged to get the following equation:

$$1/K_{obs} = 1/K_{01} + [(K_{12}-1)/K_{01}]x_2 \tag{9}$$

Fig. 2b shows a plot of $1/K_{obs}$ vs. x_2. A linear plot has been obtained as expected from Eq. (9). Values of K_{01} and K_{12} as obtained from the plot, come as 1395 and 70 respectively at 298 K. The ratio K_{01}/K_{12} gives equilibrium constant for the process where S_2 (MeOH)-solvated dye interact with Mn^{2+} ion according to the following equation.

$$D\ldots\ldots S_2 + Mn^{2+} = D\ldots..Mn^{2+} + S_2 : \quad K_{02} = K_{01}/K_{12} \tag{10}$$

Thus the equilibrium constant (K_{02}) for the process represented by Eq. (10) comes as 20. The value is small compared to the value of K_{01} (1395). Thus, it can be concluded that Mn^{2+} ion can replace ACN molecule from the solvated dye easily, but replacement of MeOH molecule from the methanol-solvated dye is rather difficult. This is rationalisable in view of stronger dye–MeOH interaction due to H-bonding.

It is interesting to mention that for very low concentration of metal ion (micro molar range) no new band corresponding to the complex appeared, instead the absorption band of the dyes underwent a small but significant blue shift (3–5 nm) in acetonitrile. The concentration up to which the blue shift persists depends on the dye. No isosbestic point, however, could be observed. The continuous blue shift without appearance of any isosbestic point and the absence of new band in the longer wavelength due to formation of complex suggests that the solvation shell around the dyes is only modified due to the presence of metal ions. The interaction between the dye and cations in the surroundings is non-specific in nature and does not lead to a complex formation. Specific complex formation interaction takes place at a higher concentration of the cation.

3.2. Steady state fluorescence studies

Fluorescence band in acetonitrile for all dyes appears as broad and structureless. Symmetric ketocyanine D–A–D dyes show fluorescence maximum at longer wavelength than the corresponding parent merocyanine DA dyes. Values of the maximum energy of fluorescence, $E(F)$, for the dyes have been listed in Table 1. In presence of Mn^{2+} ion in the solution the observed position of the fluorescence maximum, when excited at the absorption maximum of the dye practically remains unaltered, but the intensity changes. No fluorescence is observed when the excitation is done at the absorption maximum of the dye-Mn^{2+} complex indicating that the complex formed between Mn^{2+} ion and the dye in the S_0-state is non-fluorescent. For the dyes KD1, KD2, DN1, and DN2 an enhancement of intensity of fluorescence at the μM level of concentration of Mn^{2+} ion has been observed. Table 4 shows the variation of intensity as a function of concentration for these dyes. Note that the fluorescence intensity practically remains unaffected in the concentration range 0–2 μM of Mn^{2+}. After that addition of Mn^{2+} ion leads to an enhancement of intensity. For a certain concentration of Mn^{2+} ion the fluorescence intensity reaches a maximum and quenching of fluorescence is observed beyond that concentration. KD3 and DN3 are exceptions, where quenching is observed practically at all range of concentration. Fig. 3 shows representative

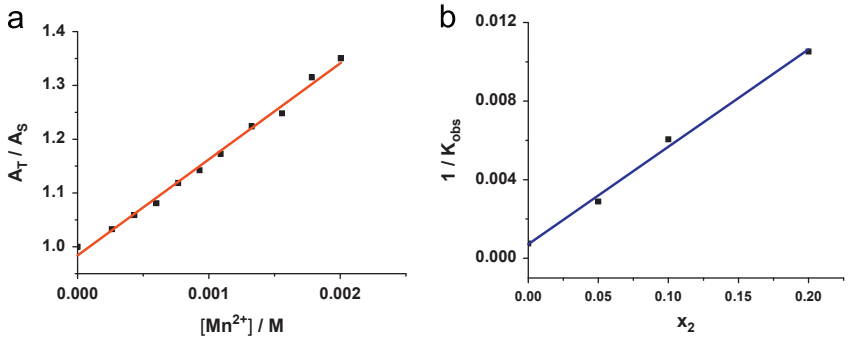


Fig. 2. (a): Representative plot of Eq. (8) in ACN+MeOH mixed solvent (mole fraction of MeOH=0.1); (b): Plot of $1/K_{obs}$ vs. x_2, the mole fraction of MeOH in binary mixture of ACN and MeOH for the dye KD1.

Table 3
Values of equilibrium constant (K_{obs}) for the KD1 in binary mixture of ACN and MeOH as a function of x_2, the mole fraction of MeOH at 298 K.

x_2	K_{obs}
0	1320 ± 65
0.05	346 ± 18
0.1	165 ± 8
0.2	95 ± 5

Table 4
Steady-state fluorescence intensity (F) of the various dyes with increasing concentration of Mn^{2+} ions in acetonitrile.

$10^6 \times [Mn^{2+}]$/M	Steady-state fluorescence intensity (F)			
	KD1	DN1	KD2	DN2
0	500.4	265.9	515.3	110.7
0.4059	499.0	264.0	515.5	110.7
0.8087	498.7	263.03	517.3	111.2
1.2082	498.8	264.30	518.6	113.8
1.6046	499.6	264.3	521.8	113.5
1.9978	501.6	263.4	528.0	114.1
2.3880	516.4	267.3	532.5	115.9
2.7752	521.2	277.7	535.3	120.2
3.1594	520.3	300.1	542.5	122.3
3.5406	515.8	325.9	550.2	133.1
3.9188	510.4	359.1	552.9	148.0
4.2942	509.2	393.7	554.5	162.4
4.6667	506.7	425.5	558.9	172.0
5.0364	503.6	445.4	556.9	183.0
5.4033	501.3	462.7	553.3	193.0
5.7674	498.7	470.4	551.4	201.4
6.4874	494.1	474.3	549.4	208.1
7.5474	483.9	472.0	546.2	215.3
8.9247	470.0	468.7	533.2	220.1
10.262	458.3	467.4	522.7	220.2
11.562	–	466.2	514.7	219.5
12.825	–	456.9	506.1	215.4

fluorescence spectra. Enhancement of fluorescence intensity needs special attention in view of the fact that the transition metal ions are very good quenchers. It is to be noted in this context that enhancement of fluorescence have been observed exactly in the range of concentration of metal ions where a small blue shift is observed in the absorption spectrum. The observed value of the equilibrium constant (K_0) for the ground state complex formation indicates that complex formation is insignificant in the concentration range (μM) where enhancement of fluorescence is observed.

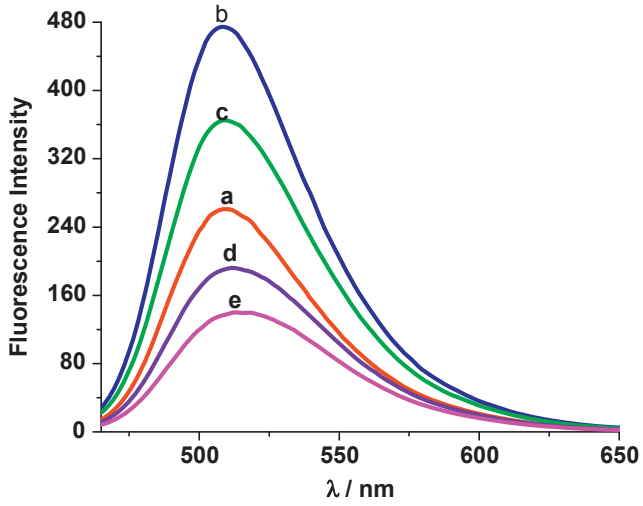


Fig. 3. Representative fluorescence spectra of DN1 in acetonitrile in presence of Mn^{2+} ion. Concentration of Mn^{2+} ion increases in the order: a < b < c < d < e.

Moreover, enhancement of dye fluorescence is observed upon addition of $NaClO_4$ which do not form a complex with the dye. Thus, the ground state complex formation has no role in the enhancement phenomenon. No enhancement of fluorescence intensity was observed when tetra butyl ammonium bromide was used in place of metal perchlorate. Fluorescence enhancement on addition of transition metal ions has been reported by other workers for fluorophore-spacer-receptor system [28–31]. In those systems the metal ion decreases the probability of photophysical interaction within the supramolecular system and consequently increases the fluorescence quantum yield. But no such intramolecular quenching mechanism supposedly exists for the dyes under study. As discussed in the earlier section, the blue shift in the absorption band at a very low concentration of metal ion can be explained in terms of modification of non-specific weak interaction between the dye and the surroundings in the presence of metal ion. Thus the characteristic features of the absorption and fluorescence spectrum presumably arises due to general solute solvent interaction. The analogous situation was described by Huppert et al. [32,33] and also by Maroncelli [34]. In one previous report we explained the observed enhancement of fluorescence of KD1 in presence of Co^{2+} ion at micro molar (μM) concentration level as due to formation of a different type of complex in the excited state in the relevant concentration range [23]. We propose a simple model involving dye-cation association for explaining the spectral changes in the concentration range discussed above. In

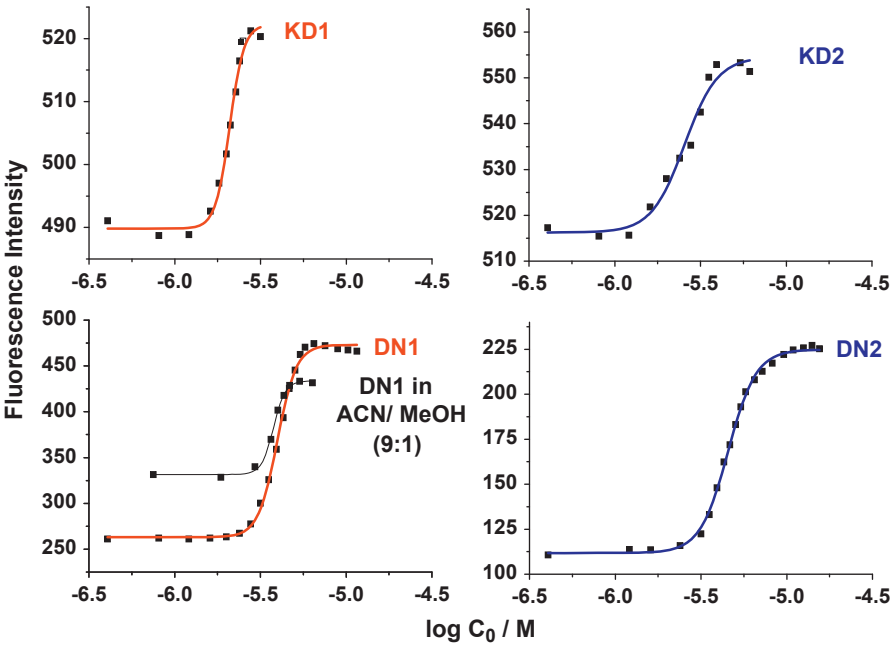


Fig. 4. Plot of fluorescence intensity of the representative dye with varying concentration of Mn^{2+} ion in acetonitrile. Filled squares represent experimental data, while the continuous line represents the best fit line according to Eq. (13).

solution phase the dye molecules will remain surrounded by solvent molecules. The interaction between the dye and solvent molecule leads to characteristic solvatochromism of the dye. Cations (M) can replace some of the solvent molecules (S) in the cybotactic region around the dye molecule (D). Thus the following multistep equilibria exist.

$$DS_n \rightleftharpoons DS_{n-1}M \rightleftharpoons DS_{n-2}M_2 \rightleftharpoons \cdots\cdots\cdots \quad (11)$$

In the above equation n is the number of sites on the dye available for solvent/cation contact. In a very dilute solution of cation ($10^{-6}-10^{-5}$ M in the present case) we assume that the first equilibrium is only important. Association at the acceptor centre of the dye would lead to a red shift in the spectrum. The observed blue shift suggests that the cation is statistically attached to the donor site (N-centre). Upon excitation the dye (S_1-state) will also form strong association complex involving the cations in the cybotactic region. Enhancement of fluorescence intensity indicates that the complex thus formed is also fluorescent. At higher concentration the ground state complexation predominates and overall result is a quenching of fluorescence. In the event of existence of equilibria (Eq. (2)) and Eq. (11) in the solute, the observed fluorescence intensity (F) is given by the following equation.

$$F=(F_0+F_cK_1[M])/\{(1+K_1[M])(1+K_0[M])\} \quad (12)$$

In the above equation F_0 and F_C are fluorescence intensity of the solvated dye (S_1-state) present as D^*S_n and the association complex, $D^*S_{n-1}M$ respectively and K_1 is the binding constant of the association complex. At low salt concentration where enhancement takes place, $K_0[M] \ll 1$ and Eq. (12) reduces to Eq. (13).

$F=\{(F_0+F_cK_1[M])/(1+K_1[M])\}$For the condition where the dye concentration is much less than the metal ion concentration, $[M]$ can be replaced by $[M]_0$, the total concentration metal ion added and a plot of F vs. $\log [M]_0$ would be sigmoid. Fig. 4 shows representative plots of F of the dye as a function of $\log [M]_0$ for different dyes. Values of K_1 as well as fitting parameters, F_0 and F_C as obtained from the sigmoid plot, are listed in Table 5. Note that the extent of enhancement, given by, $[(F_C-F_0)/F_0]\times 100$ is lower for the symmetric D–A–D dyes relative to the parent merocyanine (D–A) dyes. Note that the K_1 values for symmetric D–A–D dyes are greater than the corresponding D–A dyes. Thus, in general, Mn^{2+} ion binds more strongly with the S_1-state of a symmetric dye than with that of unsymmetric dye, but the per cent enhancement of fluorescence shows the opposite behaviour. It has been observed that the value of K_1 is higher for ACN+MeOH mixture than that in pure ACN and the per cent enhancement of fluorescent is lower (Table 5). Higher value of K_1 in ACN+MeOH mixture relative to that in pure ACN is intelligible in term of higher viscosity of binary mixture of ACN+MeOH over ACN. For KD3 and DN3 one of the double bonds in the wings is replaced by a benzene ring and the flexibility in the S_1-state is reduced. Thus due to geometric restriction the N-atom cannot come in proximity of Mn^{2+} ion for these dyes and no enhancement is observed.

Table 5
Values of the fitting parameters of Eq. (12) for different dyes at μM level of Mn^{2+} ion concentration in acetonitrile. Values in the bracket correspond to DN1 in mixed 0.9 ACN+0.1 MeOH solvent at 298 K.

Dye	$K_b \times 10^{-5}$	F_0	F_C	$[(F_c-F_0)\times 100]/F_0$
KD1	4.8 ± 0.1	490	522	7
DN1	2.5 ± 0.1	262	481	85
KD2	3.8 ± 0.1	516	556	8
DN2	2.2 ± 0.1	112	225	100

At higher concentration of metal ions, however, quenching along with slight red shift of the fluorescence maximum has been observed. The shift in emission maximum at higher metal ions concentration indicates that it interacts differently with the dye in S_1 state than that at lower concentration of metal ion. For higher concentration of $C_{Mn}{}^{2+}$, we have $K_1C_{Mn}{}^{2+} \gg 1$ and $F_cK_1C_{Mn}{}^{2+} \gg F_0$ and Eq. (12) under this condition reduces to:

$$F=F_c/(1+K_0C_{Mn}{}^{2+}) \quad (14)$$

Table 6
Values of Stern–Volmer (S–V) quenching constant for the different dyes in pure ACN, MeOH and mixed (ACN+MeOH) solvents at 298 K. Values in the parentheses correspond to the equilibrium constant (K_0) for the ground state complexation.

Dye	KD1	DN1	KD2	DN2	KD3	DN3
Pure ACN	2540 (1 3 2 1)	60 (4 0)	1710 (8 0 2)	50 (3 4)	60 (4 0)	20 (1 5)
Pure MeOH	15	7	–	–	–	–

Table 7
Values of life time (τ/ps) for the dyes with varying concentration of Mn^{2+} ion.

$10^6 \times [Mn^{2+}]$/M	KD1	DN1	KD2	DN2	KD3	DN3
0	647	212	427	76	738	388
0.809	652	212	429	76	738	388
1.605	659	212	432	77	735	387
2.388	663	215	436	78	734	386
3.159	665	217	440	78	733	385
3.919	669	220	441	79	731	385
4.667	670	221	442	80	730	384
5.403	672	222	442	80	729	384
7.547	671	222	443	79	729	383

Thus for higher concentration one expects quenching. This is expected in view of the fact that a rise of Mn^{2+} content leads to a decrease in the concentration of the uncomplexed form of the dyes and quenching occurs. Eq. (14) is very similar to the Stern–Volmer (SV) equation, but F_c appears in Eq. (14) while F_0 appears in SV equation. A plot of $(1/F)$ vs. $C_{Mn}{}^{2+}$ would give a straight line from which value of K_0 and E_C can be obtained. The value of F_C is nearly the same as that obtained from fluorescence enhancement studies. Table 6 lists K_0 values for the dyes as obtained from SV plot in the mM concentration range of Mn^{2+} ion. For dyes KD3 and DN3 quenching is observed for all concentration ranges. Note that the value K_0 in ACN, as obtained from quenching study is always higher than that obtained from absorption spectral study. Probably the quenching may partly be of dynamic nature. Quenching has also been observed when Mn^{2+} ion is added to the solution of a dye in methanol. Analysis of SV plot gives values of the Stern–Volmer constant, which can be interpreted as the equilibrium constant for the ground state complex formation involving Mn^{2+} ion and the dye in MeOH. K values for KD1 and DN1 have been determined and listed in Table 6. It may be noted that K-values for KD1 comes as 15. The value is close to the value of K_{02} for dye–Mn^{2+} complexation in MeOH (according to Eq. (10)), as determined from studies in mixed ACN+MeOH solvents (vide supra).

3.3. Time resolved fluorescence studies

Fluorescence decay has been studied in acetonitrile for all the dyes in presence and in absence of Mn^{2+} ion. In all the cases the decay curves are best represented by a single exponential fit. The results have been given in Table 7. For DN2 the measured value of lifetime (τ) is close to the minimum measurable value for the instrument. Note that in a micromolar concentration range of Mn^{2+} ion the life time (τ) of the dye KD1, KD2, DN1, and DN2 increases as the concentration of Mn^{2+} increases, reaching a maximum value and after that, the value of τ remains practically constant. The range of concentration where the value of τ increases is very similar to the range of concentration where enhancement of fluorescence takes place as can be seen from Fig. 5. For the dyes KD3 and DN3, where enhancement of fluorescence intensity has not been observed, the τ value does not change significantly as Mn^{2+} ions are added to the solution. All these observations suggest

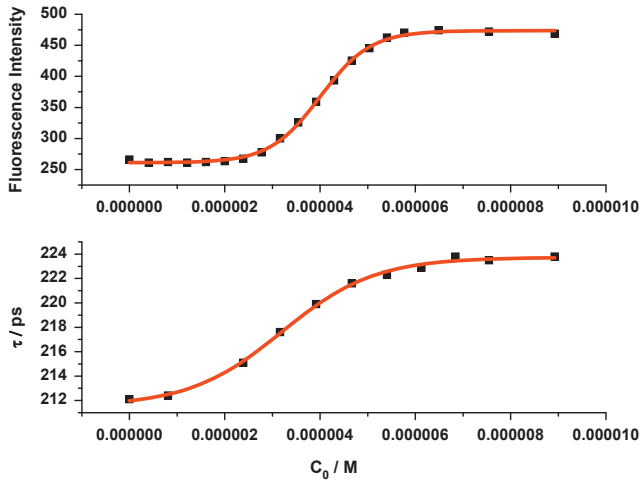


Fig. 5. Representative plot of fluorescence intensity (F) and excited state life time (τ) (ps) as a function of Mn^{2+} ion concentration in the μM range for DN1. Filled squares represent experimental data points. The continuous line is the best fit sigmoid line.

Table 8
Photophysical parameters for the dyes at 298 K.

Dye	τ_0/ps	τ_c/ps	Φ_0	$10^{-8} \times k_r$/s	$10^{-8} \times k_{nr}{}^0$/s	$10^{-8} \times k_{nr}{}^c$/s	$K_b \times 10^{-5}$
KD1	649	675	0.46	7.1	8.3	7.7	5.1
DN1	212	224	0.12	5.7	41.5	39.0	3.0
KD2	427	442	0.30	7.0	16.4	15.6	4.5

that the phenomena of increase of τ value and fluorescence intensity enhancement have the same origin.

As discussed in the earlier section, the two emitting species, viz., $D^* S_n$ and $D^* S_{n-1}M$ are present in solution at μM concentration level of Mn^{2+}. The τ value at zero Mn^{2+} ion concentration correspond to the $D^* S_n$ species and the limiting value of τ at higher Mn^{2+} ion concentration is characteristics of $D^* S_{n-1}Mn^{2+}$. Values of quantum yield (Φ) of fluorescence have been measured using rhodamine as standard. For the dye KD1, KD2, DN1 and DN2 the value of Φ increases with the addition of Mn^{2+} ion at the μM concentration range and the τ values parallel the Φ values. Parallelism of τ and Φ values indicate that the radiative decay constant k_r, as calculated by $k_r = \Phi/\tau$, is practically unaffected by complex formation. Values of the photophysical parameters for the dyes have been listed in Table 8. While the value of $k_{nr}{}^0$, the value for nonradiative decay constant (k_{nr}) at zero Mn^{2+} ion concentration is characteristic of the ($D^* S_n$) state, the limiting value of k_{nr} ($= k_{nr}{}^c$), calculated using limiting τ value (τ_c), corresponds to the complex ($D^* S_{n-1}$Mn). Note that the nonradiative decay of the ($D^* S_{n-1}$Mn) state is slower than that of the ($D^* S_n$) state. At any Mn^{2+} ion concentration the observed value of $1/\tau$ ($= k_r + k_{nr}$) would be given by mole fraction average of $1/\tau$ values of the two species. Thus we get

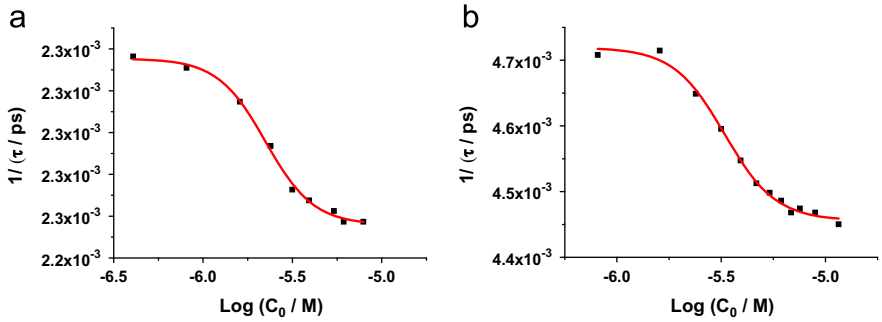


Fig. 6. Plot of $1/\tau$ for the KD2 (a) and DN1 (b) as a function of log C_0 in acetonitrile. Filled squares represent experimental data points. The continuous line is the best fit sigmoid line according to Eq. (16).

$$1/\tau = k_{r+}x_0 k_{nr}{}^0 + x_c k_{nr}{}^c \quad (15)$$

where x_0 and x_c represent the mole fraction of (D^* S_n) and ($D^*S_{n-1}Mn^{2+}$) respectively in solution. Considering the equilibrium scheme as given by Eq. (11), one gets Eq. (16).

$$1/\tau = [\{(1/\tau_0)+(1/\tau_c)K_1 C_{Mn}{}^{2+}\}/(1+K_1 C_{Mn}{}^{2+})] \quad (16)$$

Thus the plot of $1/\tau$ vs. log C_0 would be sigmoid in nature. Fig. 6 shows representative plots. The values of the binding constant (K_1) for the association complex for different dyes, as calculated from the sigmoid plot, have also been listed in Table 8. The values compare well the values of K_1 obtained from fluorescence intensity variation.

4. Conclusion

Absorption spectral studies indicate that Mn (II) ion forms 1:1 complex with the donor–acceptor dyes in their ground state (S_0) in acetonitrile solution. The strength of dye-metal ion complex is greater for symmetric dyes with donor–acceptor–donor configuration. The metal ion interacts presumably with the carbonyl oxygen of the dye. In methanol solution the dye forms hydrogen bonded complex with methanol and no complex formation could be detected in dye-Mn (II) ion system using absorption studies in methanol. Studies in mixed binary solvents containing methanol and acetonitrile, however, provide a small value of the equilibrium constant for dye-ion interaction in methanol solution. Similar value of equilibrium constant for dye-metal ion interaction in methanol has been obtained from quenching studies. Enhancement of fluorescence intensity has been observed in the micromolar concentration range of the metal ion. Value of fluorescence life time of the excited state also increases in that concentration range. These results have been explained in terms of formation of a different type of complex (solvato complex) involving the Mn (II) ion and the S_1 state of the dye. Fluorescence enhancement studies give the value of the binding constant (K_1) for the metal ion–dye (S_1-state) interaction, the value of K_1 being higher for a symmetric D–A–D dye relative to that for the corresponding unsymmetric D–A dye. However, the extent of fluorescence enhancement for an unsymmetric dye is greater. Complexation in the excited state is characterised by a slower decay of S_1 state of the dyes by a nonradiative path.

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