Interaction of alkali, alkaline earth and transition metal ions with a ketocyanine dye: A comparative electronic spectroscopic study

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Interaction of alkali, alkaline earth and transition metal ions with a ketocyanine dye: A comparative electronic spectroscopic study

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HIGHLIGHTS

► A ketocyanine dye with D–A configuration forms 1:1 complex with metal ions.
► DFT calculation has been done on dye–metal ion complexation.
► Slight blue shift of the absorption spectrum for low concentration of metal ions.
► Life time and fluorescence intensity increase for low concentration of metal ions.

GRAPHICAL ABSTRACT
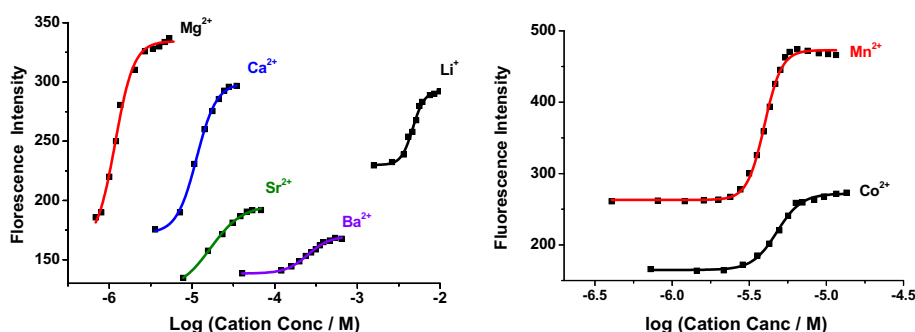
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ABSTRACT

Interaction of a dye which is structurally similar to a ketocyanine dye with metal ions (alkali, alkaline earth and transition metal) has been studied by monitoring the electronic absorption, steady state and time resolved fluorescence parameters of the dye. The dye (S_0 state) forms a 1:1 complex with cations as indicated by the appearance of a new band at a longer wavelength. Equilibrium constant and other thermodynamic parameters for complexation have been determined. The interaction between the dye and the cation is mostly electrostatic in nature. Spectroscopic results have been supplemented by DFT calculation. For very low concentration of cations, where complexation is insignificant, the absorption band of the dye undergoes a slight blue shift. Enhancement of fluorescence intensity has been observed in the same concentration range. Both phenomena have been explained in terms of formation of a weak association complex where one/more cation replace equivalent solvent molecules in the cybotatic region around the dye. The binding constant of the weak association complex involving cation and the dye (S_1 state) has been determined and has been found to depend on the charge-to-size ratio of the cations. Measurement of fluorescence lifetime of the dye indicates that the association complex is slowly decaying relative to solvated dye. At higher concentration of metal ions, however, fluorescence of the dye is quenched by the metal ions. A red shift of fluorescence maximum has also been observed in this concentration range.

Introduction

Photophysical and spectroscopic properties of dyes containing both donor and acceptor in the molecule has been the subject of intensive investigation [1]. Ketocyanine dyes provide an interesting system belonging to this class [2–4]. Due to the presence of an electron donor (D) e.g. amino group and an electron acceptor (A) carbonyl group, in the molecule, the electronic transition is

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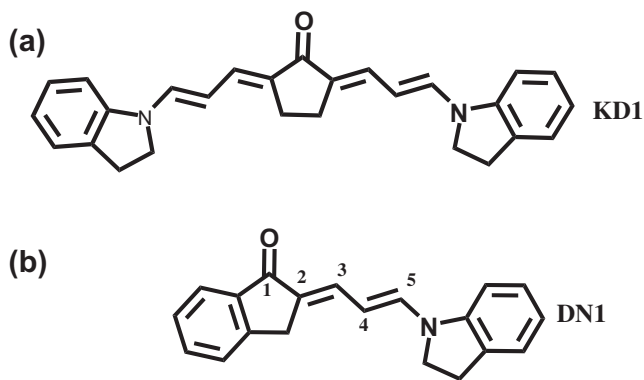
(a)

(b)

Fig. 1. Ketocyanine dyes: (a) KD1 and (b) DN1.

associated with intramolecular charge transfer (ICT) and as such the electronic spectral parameters of the molecule are very much sensitive to the nature of the immediate environment surrounding it. The pronounced solvent effects in both absorption and emission spectra of these dyes make them promising probes for monitoring micropolarity, hydrogen bond donating interaction, investigation of the cell membrane structures, and evaluating the microenvironmental characteristics of biochemical and biological systems [5–13]. Some of them are also used as laser dyes or photosensitizers and have found several industrial applications in photopolymer imaging systems [14–16]. 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 also changes significantly due to interaction with metal ions. Basu et al. [19–21] have studied the interaction of these dyes with alkali and alkaline earth metal ions. Crown ether substituted derivatives of ketocyanine dyes are efficient fluorophores for alkaline earth cation recognition. Doroshenko et al. have studied the interaction of bis-azacrown-substituted derivatives of ketocyanine dyes with Mg^{2+} and Ba^{2+} ions [22]. In a recent communication we have reported the study of interaction of Co^{2+} ion with a symmetrical ketocyanine dye (KD1, Fig. 1) having DAD configuration of the chromophores [23]. It has been observed that the Co^{2+} ion forms complex with the dye in both S_0 and S_1 electronic state in dipolar aprotic solvents like acetonitrile and acetone. Complexation could not be detected in a protic solvent. An enhancement of fluorescence intensity of the dye has been observed for the micromolar concentration range of the ion. It has been observed that the electronic spectral features are different for structurally similar dyes having D–A–D and D–A configuration of the chromophores [24], It is interesting to investigate whether the complexing ability of the dye also depends on the symmetric (D–A–D) and unsymmetrical (D–A) configuration of the chromophores. In the present work we have studied the interaction of the corresponding unsymmetrical dye, DN1 (Fig. 1) with several metal ion including alkali (Li^+, Na^+), alkaline earth (Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}) and transition metal ions (Mn^{2+}, and Co^{2+}) by monitoring the electronic absorption, steady state and time resolved fluorescence of the dye in acetonitrile (ACN) as a function of concentration of the metal ions. Spectroscopic and thermodynamic parameters have been determined for the system. Theoretical calculations at the DFT/TDDFT level have also been done on the dye–metal ion interaction.

Experimental section

Materials

DN1 has been prepared by a procedure described in a recent publication [24]. Acetonitrile and methanol, both of spectrophoto-

metric grade (99.9%), were procured from SIGMA–ALDRICH and were used as received. Perchlorate salts [SIGMA ALDRICH] have been used due to their higher solubility in the solvents. All the metal salts were dried cautiously in vaccum.

Electronic spectral measurements

The UV–Vis absorption and steady state fluorescence emission 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. 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-405L, Pulse duration: <100 ps, Serial number: 06808). Decay curves were analysed using IBH DAS-6 decay analysis software. The decay curves were fitted with exponential decay functions. The decay parameters were recovered using a nonlinear least square fitting procedure. The goodness of the fit was evaluated by χ^2 values and the plot of residuals. A fit was considered acceptable when plot of standard deviation was random about zero and χ^2 value was not more than 1.2.

Dye concentration in all the spectroscopic measurements varied in the range 10^{-6}–0^{-7} M. The concentration of metal salt solution varied in the range 10^{-2}–10^{-6} M.

DFT calculation

DFT calculations were done on the dye DN1 and the dye-M^{2+} system (M^{2+}: Mg, Ca, Sr, Ba, Mn, Fe, Co, Ni, Cu) using Gaussian 03 software [25]. Geometry optimisation calculations were done on the dye (DN1), metal ion solvated by ACN and dye–metal ion complex. Octahedral coordination of metal ion was considered in all the cases. Binding of M^{2+} ion on the oxygen centre of the dye has been considered. Calculations were carried out using the B3LYP functional [26–29]. 631G (d,p) basis set [30,31] was used for all the atoms except Mg, Ca, Sr and Ba where SDD pseudopotential [32] basis have been used. The comparison between the results obtained of different basis set could produce differences in the absolute values of a calculated parameter. But the trend would be the same. Geometry optimisation was done followed by frequency calculation to ascertain that the optimised structure was true minima. The default criteria for geometry optimisations were used in the process. The energy of formation (E_f) of the dye–metal ion complex is calculated assuming the following equation for the formation of the complex.

$$DN1 + M^{2+}(CH_3CN)_6 \rightarrow M^{2+}(CH_3CN)_5DN1 + CH_3CN \qquad (1)$$
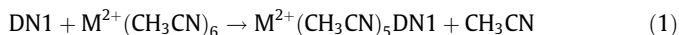
Thus E_f for a dye-M^{2+} system was calculated using the equation:

$$E_f = E[M^{2+}(CH_3CN)_5DN1] + E(CH_3CN) - E[M^{2+}(CH_3CN)_6] - E(DN1) \qquad (2)$$

Results and discussion

Theoretical studies on dye–metal ion interaction

The optimised geometry of DN1 has been shown in Fig. S1. Table 1 shows the relevant bond lengths. The C–C bond length from C_1 to C_5 carbon atoms of DN1 (Fig. 1) shows bond alternation. In dye–metal ion complexes, however, the bond alternation is significantly modified. Thus the bond length between C_1–C_2 and C_3–C_4 are shortened, while those between C_2–C_3 and C_4–C_5 are increased when the dye interacts with a metal ion. The carbonyl bond length

Table 1
Relevant bond lengths in the free dye and in dye metal complex calculated from DFT calculation. The numbering of atoms is similar to that shown in Fig. 1.

Metal	M–O	C_1–O	C_1–C_2	C_2–C_3	C_3–C_4	C_4–C_5	C_5–N
None		1.2275	1.4829	1.3559	1.4312	1.3648	1.3613
Mg	1.9616	1.2709	1.4348	1.3809	1.4063	1.3859	1.3369
Ca	2.1937	1.2753	1.4325	1.3816	1.4056	1.3861	1.3367
Sr	2.3533	1.2741	1.4342	1.3806	1.4065	1.3854	1.3373
Ba	2.5051	1.2744	1.4349	1.3801	1.4070	1.3852	1.3374
Mn	2.0176	1.2746	1.4318	1.3821	1.4045	1.3866	1.3357
Fe	1.9502	1.2795	1.4278	1.3844	1.4024	1.3883	1.3342
Co	1.9632	1.2748	1.4321	1.3824	1.4047	1.3869	1.3354
Ni	1.9995	1.2713	1.4373	1.3803	1.4063	1.3855	1.3366

is also increased. It has been suggested that the structure of the ketocyanine dye can be represented as a resonance hybrid of two valence bond structures, namely, the 'keto' and zwitterionic the 'enol' form [2]. Thus we can represent the structure of DN1 as shown in the Fig. S3.

In an aprotic solvent like acetonitrile the 'keto' form predominates. The observed change in the bond length indicates that the percent contribution of the 'enol' form increases due to complexation with metal ions. Result indicates a considerable bonding of metal ion to the oxygen centre of the dye. The HOMO–LUMO gap for the dye comes as 3.3742 eV, which is higher than that for KD1 (3.0406 eV) [23]. The value of the gap decreases on complex formation. TDDFT calculation provides with a value of 383.6 nm for the wavelength of maximum $S_0 \rightarrow S_1$ transition of DN1. The value can be compared with the experimental value of the absorption maximum (427 nm) of DN1 in a nonpolar solvent e.g. cyclohexane. The calculated values of the parameter for dye-M^{2+} ion complex come at a higher wavelength, as can be seen from Table S1. Thus the absorption band of the dye shifts to lower energies upon complex formation. Similar results have been obtained by Eilmes for interaction of Li^+ and Mg^{2+} ion with a dye of similar structure [33–35]. Values of energy of formation for the metal ion–dye complex have also been listed in Table S1. Negative value of E_f has been obtained for all the complexes. Due to the use of different basis sets for alkaline earth and transition metal ions the absolute values of E_f for the two series cannot be compared. However, the trend for a particular set of metal ions is meaningful. The stability follows the order: $Ba^{2+} < Sr^{2+} \approx Mg^{2+} < Ca^{2+}$ for the alkaline earth metal ions and $Ni^{2+} < Co^{2+} < Mn^{2+} < Fe^{2+} < Cu^{2+}$ for the transition metal ions complexes. Fig. 2 shows a plot of E_f as a function of charge-to-size ratio (q/r) of the cations. For the metal ions the value of E_f, in general, shows an increasing trend with an increase in the charge-to-size ratio of cation. In the present case the charge of

the cation is fixed. Thus E_f increases as the size of the cation [36] decreases. Mg^{2+} ion, however, shows somewhat different behaviours than the other alkaline earth metal ions. Of the transition metal ions, Co^{2+} and Ni^{2+} do not fall in the line with the others. Results indicate that although the interaction is mostly ionic in nature, the role of covalent bonding between the metal ion and the carbonyl oxygen cannot be ruled out.

Absorption study

The longest wavelength absorption band of DN1 in acetonitrile appears as broad and structureless with a maximum at 449 nm. This band can be assigned as due to intramolecular charge transfer transition (ICT) between N (donor) and carbonyl-O (acceptor) on the basis of the strong solvatochromic response of this dye. On addition of perchlorate salt of metal M, (M: Li, Mg, Ca, Sr, Ba, Mn, and Co), to the dye solution a new band grows at a longer wavelength and it becomes prominent as the concentration of the salt increases. No new band, however, grows when $NaClO_4$ or tetra butyl ammonium bromide is added. The observed spectrum for a particular concentration of metal ion can be represented as a sum of two Gaussian curves. Fig. S2 shows a representative plot. For a fixed dye concentration an isosbestic point appears in the absorption spectra of dyes in solutions containing varying concentration of the metal ion. Fig. 3 shows representative absorption spectra of the dye in acetonitrile containing varying concentration of metal perchlorate. Existence of isosbestic point indicates the presence of two species namely, solvated dye and dye–metal ion complex in equilibrium. Absorbance value at the maximum wavelength of the new band saturates at higher salt concentration. Thus, the new absorption band observed at longer wavelength is presumably due to a dye–metal ion complex. Thus, all the cations, except Na^+ and tetrabutyl ammonium ions, form complex with DN1. The observed position of the wavelength of the band maximum for dye–metal ion complex for different metal ions has been listed in Table 2. The shift of maximum wavelength of absorption to a higher value can be rationalised in terms of interaction of the cation with the acceptor centre of the molecule. The order of increasing λ_{max} would also parallel the order of strength of complexation. In the present case the order has been found to be: $Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Co^{2+}$ which is in accordance with Irving–William series [37]. Variation of E_C [=$28590/\lambda_{max}$ (in nm)], the maximum transition energy of the complexed dye, as a function of charge to size ratio of the cations is shown in Fig. 4. A linear correlation can be obtained for all the cations (except Li^+ and Mg^{2+} ions). Results indicate that the interaction between the dye and metal ion is mostly electrostatic in nature. Observed absorption spectral behaviour can be rationalised in terms of existence of the following equilibrium involving dye (D) and the metal ion (M) in solution.
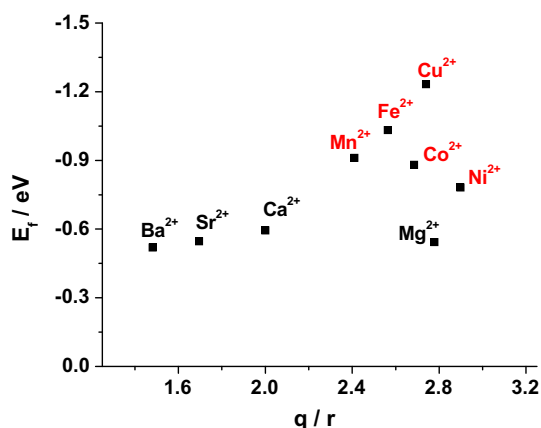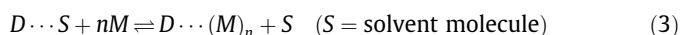
$$D \cdots S + nM \rightleftharpoons D \cdots (M)_n + S \quad (S = \text{solvent molecule}) \tag{3}$$

Fig. 2. Plot of calculated energy of formation (E_f) as a function of ionic potential (q/r) for alkaline earth and transition metal ions.
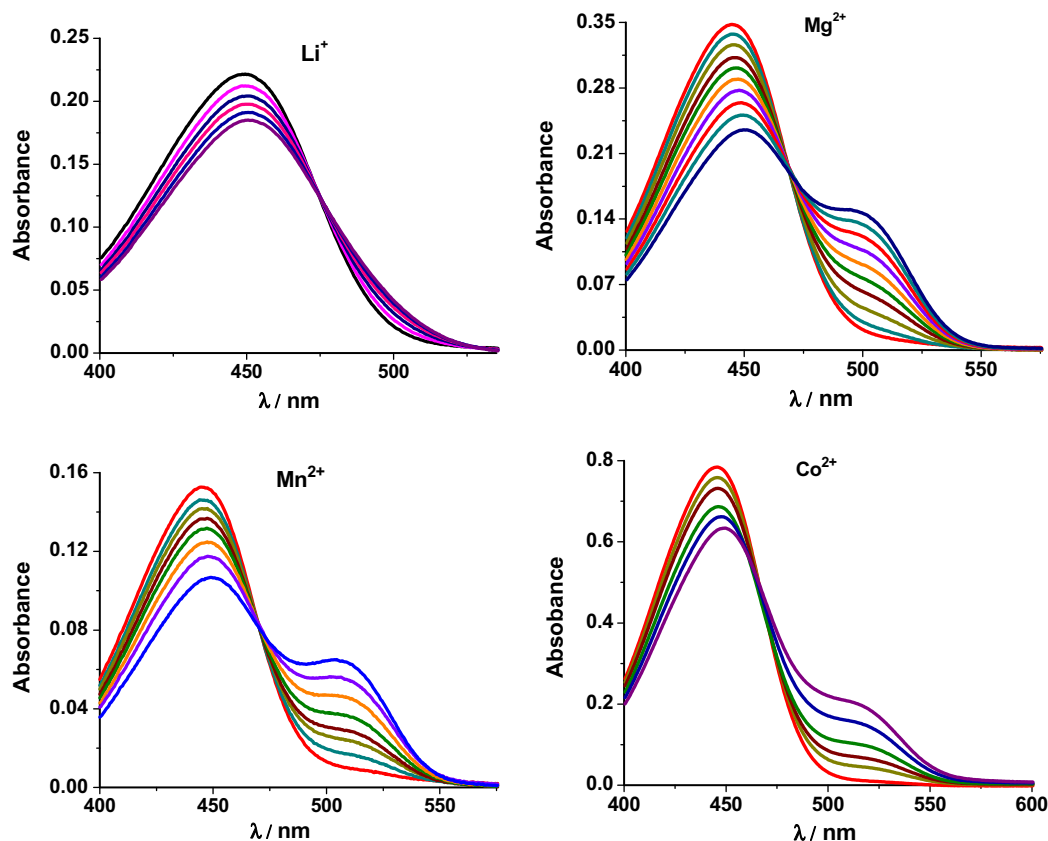
Fig. 3. Absorption spectra of the ketocyanine dye (DN1) in acetonitrile with varying concentration ($\sim$mM) of alkali and alkaline earth metal and transition metal ion.

Table 2
Values of spectroscopic and thermodynamic parameters for the interaction of DN1 in ground state (S_0) with different metal ion in ACN.

Metal ions	E_C (kcal mol^{-1})[a]	K (M^{-1})	ΔH^0 (kcal mol^{-1})	ΔS^0 (cal K^{-1})
Li$^+$	57.8 (495)	5	−0.86	0.3
Mg^{2+}	56.5 (506)	175	−0.23	9.4
Ca^{2+}	57.2 (500)	82	−0.14	8.3
Sr^{2+}	58.3 (490)	30	−0.40	5.4
Ba^{2+}	58.9 (485)	7	−0.37	2.6
Mn^{2+}	55.7 (513)	95	−0.6	7.1
Co^{2+}	55.2 (518)	30	1.11	10.5

[a] Values in the parenthesis are the corresponding value of absorption maximum (in nm) for the metal–complexed dye.

Here $D\cdots S$ and $D\cdots(M)_n$ represent solvated and metal complexed dye respectively, n is the minimum number of metal ion participation in the equilibrium. The equilibrium constant for the complexation of M with the S_0 state of the dye is given by:

$$K = [C]_e/[D]_e[M]_e^n \tag{4a}$$

where $[C]_e$, $[D]_e$ and $[M]_e$ represent the equilibrium molar concentrations of the metal complexed dye, solvated dye and metal ion respectively. Values of n have been determined by a procedure described previously [23] and come at around 0.9 ± 0.5 for all the metal ions, indicating a 1:1 complexation. The equilibrium constant for 1:1 complex formation can be found out from an analysis of the spectral data as follows. Eq. (4a) can be written (with n = 1) as:

$$K\{[M]_0 − [C]_e\} = [C]_e/\{[D]_0 − [C]_e\} \tag{4b}$$

where $[D]_0$ and $[M]_0$ are respectively the initial concentration of dye and the metal ion added. For the condition $[M]_0 \gg [D]_0 \cong [C]_e$ as
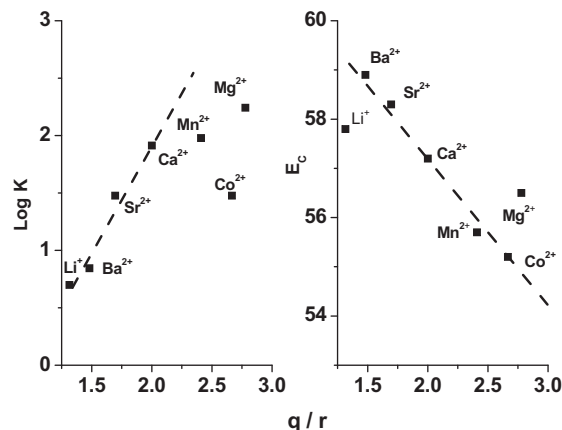

Fig. 4. Plot of log K and E_C as a function of charge to size (q/r) ratio of the cations.

used in the present study we can approximate $\{[M]_o - [C]_e\} \approx [M]_o$. Thus we have:

$$K[M]_0 = [C]_e/\{[D]_0 - [C]_e\} \qquad (4c)$$

Assuming that the complex obeys Beer's law we obtain:

$$1/A_c = \{1/(\epsilon_c[D]_0)\} + \{1/(\epsilon_c K[D]_0)\}(1/[M]_0) \qquad (5)$$

where A_c and ε_c represent the absorbance and the molar absorbance of the complex at the wavelength corresponding to the maximum absorption of the complexed dye. Plot of $1/A_c$ against $1/[M]_0$ would be straight line and the value of K can be obtained from the intercept and the slope. Values of equilibrium constant (K) as calculated using above procedure for the different metal ions in acetonitrile are listed in Table 2. We have studied the variation of ΔG^0 for complexation with the ion identity by examining the correlation of $\log K$ with the charge to size ratio (q/r) of the cation. Fig. 4 shows such a plot. It can be seen that ΔG^0, in general, increases with an increase in the value of q/r for the cations Li$^+$, Ba^{2+}, Sr^{2+} and Ca^{2+}. However, Mg^{2+}, Mn^{2+} and Co^{2+} ions show deviation from this behaviour. Values of ΔH^0 and ΔS^0 for complexation have also been listed in Table 2. ΔH^0 is characterised by negative values except for Co^{2+} system. The value of ΔS^0 for the complexation process comes as positive for all the systems.

It is interesting to mention that for very low concentration of metal ion no new band appeared, but the absorption band of the uncomplexed dye undergoes a small but significant blue shift. The spectral blue shift for various metal ions ranges between 2 and 5 nm in acetonitrile. No isosbestic point could be observed. The concentration up to which the blue shift occurs depends on the identity of the metal ion. In a solvent the dye forms a loose association complex with the solvent molecules. A red shift of the absorption spectrum of the dye with an increase in solvent polarity can be explained in this vein. Addition of a salt to a dipolar solvent is known to increase, in general, the polarity of the medium and a red shift of the ICT band of the dye is expected. The continuous blue shift without appearance of any isosbestic point can be explained in terms of a weak interaction between solvated dye and the metal ion.

Fluorescence studies

The fluorescence band of the dye appears as broad and structureless with a maximum around 510 nm in acetonitrile. Fig. 5 shows representative fluorescence spectra of the dye in acetonitrile containing different concentrations of metal perchlorates. Excita-

Table 3
Values of K_1 for the interaction of DN1 in the excited state (S_1) along with the fitting parameters (F_0, F_c) for different metal ions in ACN.

Metal	C_{max} (M)	$K_1 (M^{-1})$	F_0	F_C	$[(F_C - F_0)/F_0] \times 100$
Li(I)	2.0×10^{-3}	2.1×10^2	230	292	27
Mg(II)	5.9×10^{-6}	9.4×10^5	177	340	92
Ca(II)	3.5×10^{-5}	0.9×10^5	172	296	72
Sr(II)	6.8×10^{-5}	6.0×10^4	123	196	59
Ba(II)	5.3×10^{-4}	4.0×10^3	138	170	23
Mn(II)	6.5×10^{-6}	2.5×10^5	263	473	80
Co(II)	9.5×10^{-6}	2.1×10^5	165	272	65

tion in all the cases has been done at the wavelength corresponding to the absorption maximum of the free dye. No fluorescence could be observed when the excitation was done at the absorption maximum of the dye–metal complex. For Li$^+$ and alkaline earth metal ions a red shift of the fluorescence maximum has been observed. The extent of red shift increases in the order Li$^+$ ≈ Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+}. Similar red shift of fluorescence maximum has been observed for the KD1-alkali/alkaline earth metal ion system and was explained in terms of interaction of metal ions with the dye in the S_1-state [19–21]. For the transition metal ions the extent of red shift is very small. Initial addition of metal ion (very low concentration) to the solution of the dye leads to an enhancement of fluorescence intensity of the system and at certain concentration fluorescence intensity attains a maximum. Further increase in the concentration of metal ions causes quenching of fluorescence as expected along with a red shift of the fluorescence band. Although the enhancement of fluorescence intensity has been observed with all the metal ions under study, the concentration range of the metal ion for the fluorescence enhancement differs considerably from one metal ion to the other. Table 3 shows the value of maximum concentration (C_{max}) up to which enhancement could be observed. For Mg^{2+} ion, the enhancement of fluorescence of the dye is observed at μM concentration range of the metal ion, but for other alkaline earth metal ions, as we move down the group from Ca^{2+} to Ba^{2+}, enhancement is found up to a much higher concentration range whereas for alkali metal ion e.g. Li$^+$, Na$^+$ the fluorescence enhancement occur at mM concentration range. Transition metal ion like Mn^{2+}, Co^{2+} shows a considerable amount of fluorescence enhancement at μM range of concentration although the transition metal ions are notorious quencher of fluorescence. The position of fluorescence maximum however, practically remains unaltered in the concentration range where enhancement of fluorescence takes place. It is to be noted in this
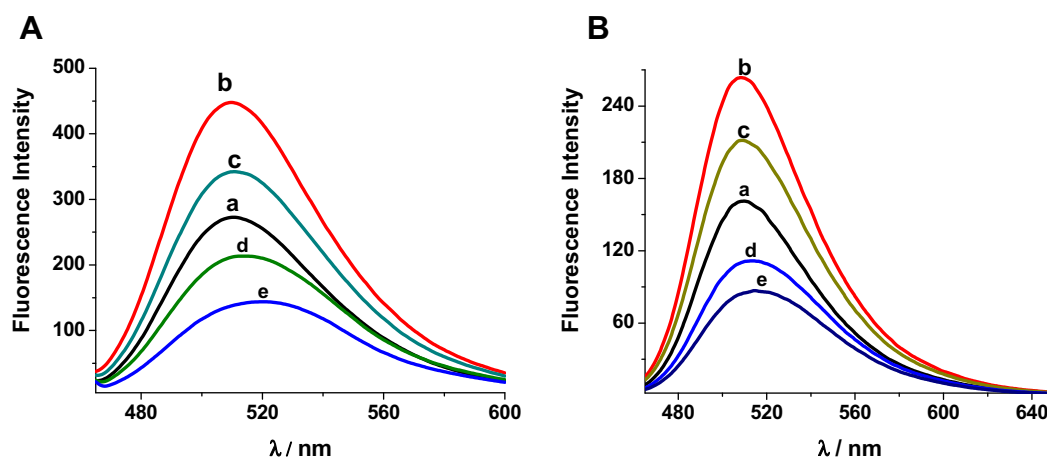

Fig. 5. A representative fluorescence spectra of the dye in acetonitrile in presence of high concentration range of (A) Mg^{2+} (B) Co^{2+} ion (~mM). Concentration of the metal ion increases in the order: a < b < c < d < e.
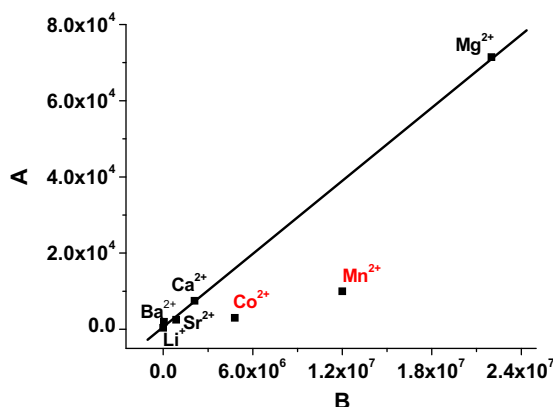
Fig. 6. Plot of enhancement of fluorescence per unit molar concentration of metal ion against shift in absorption (cm^{-1}) of the dye in acetonitrile for the different metal ions.

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. We have calculated the parameter $A = [\overline{U}(C_{max}) - \overline{U}(0)]/C_{max}$, where $\overline{U}(0)$ and $\overline{U}(C_{max})$ are respectively the wave number of absorption of the dye in acetonitrile without any added salt and that for the salt concentration C_{max}. The parameter supposedly characterises the shift in absorption band. For fluorescence enhancement, the parameter $B = (F_{max} - F_0)/(F_0 C_{max})$, where F_0 and F_{max} are respectively the fluorescence in absence of any added salt and the maximum value of fluorescence (at C_{max}), respectively. Fig. 6 shows plot of the two parameters A and B. It appears that there is good correlation between the parameters, particularly for alkali and alkaline earth metal ions. Transition metal ions (Mn^{2+} and Co^{2+}) do not fall in the line. This result suggests that the enhancement of fluorescence and slight blue shift in absorption band have the same origin, particularly for the alkaline earth metal ions. Enhancement of fluorescence intensity and the blue shift of the absorption band, taking place at lower salt concentration, do not originate due to formation of complexes between the dye (S$_0$ state) and the metal ion. The observed value of the equilibrium constant (K) for the ground state complexation indicates that the extent of complexation is insignificant in the concentration range where enhancement of fluorescence is observed. 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 complexation 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 [38–41]. 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 dye under study. As discussed in the earlier section, the blue shift in the absorption band at a very low concentration can be explained in terms of weak interaction between the solvated dye and the 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 and co workers [42,43] and also by Maroncelli [44]. In the previous publication we explained the observed enhancement of fluorescence of KD1 in presence of Co^{2+} ion at micromolar (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 a solution 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.

$$DS_n \rightleftharpoons DS_{n-1}M \rightleftharpoons DS_{n-2}M_2 \rightleftharpoons \cdots \tag{6}$$
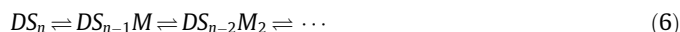
In a very dilute solution of cation ($10^{-6} - 10^{-5}$M in the present case) we assume that the first equilibrium is only important. In the above equation n is the number of sites on the dye available for solvent/cation contact. Association at the acceptor centre of the dye would leads to a red shift 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 an association complex with the metal ion 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. The observed fluorescence intensity (F), according to the above scheme, is given by the following equation.

$$F = (F_0 + F_c K_1[M])/\{(1 + K_1[M])(1 + K[M])\} \tag{7}$$

In the above equation F_0 and F_C are fluorescence intensity of the solvated dye present as DS_n and the association complex, $DS_{n-1}M$ respectively and K_1 is the binding constant of the association com-
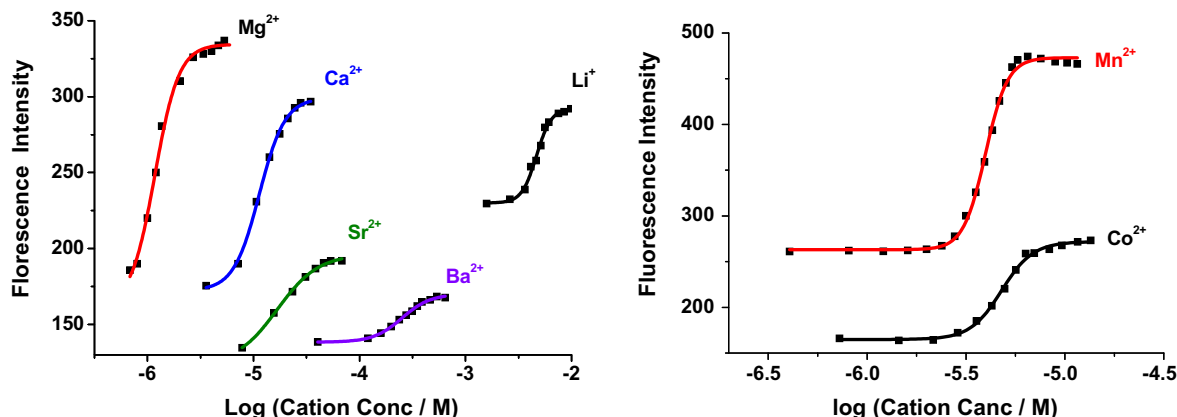

Fig. 7. Plot of fluorescence intensity of the dye with varying concentration of metal ions in acetonitrile. Filled squares represent experimental data, while the continuous line represents the best fit line according to Eq. (8).
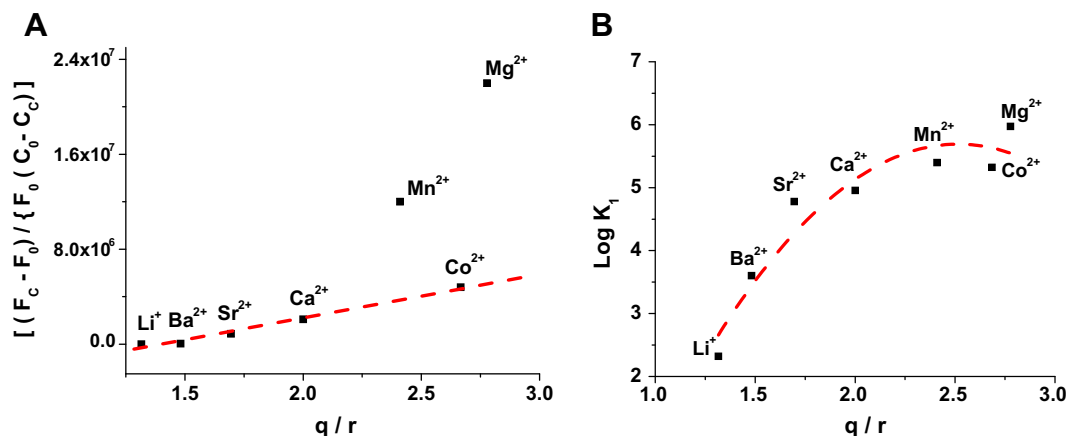
Fig. 8. Plot of (A) fluorescence enhancement $[(F_C - F_0)/\{F_0(C_0 - C_C)\}]$; (B) excited state equilibrium constant ($\log K_1$) as a function of ionic potential (q/r) for the metal ions.

plex. At low salt concentration where enhancement takes place, $K_0[M] \ll 1$ and Eq. (7) reduces to Eq. (8).

$$F = \{(F_0 + F_c K_1[M])/(1 + K_1[M])\} \qquad (8)$$

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 versus $\log[M]_0$ will be sigmoid. Fig. 7 shows representative plots of F of the dye as a function of $\log[M]_0$ for different metal ion. Values of K_1 as well as fitting parameters, F_0 and F_C as obtained from the sigmoid plot are listed in Table 3. Note that the extent of enhancement, given by, $[(F_C - F_0)/F_0] \times 100$ is lower for Li$^+$, and Ba^{2+} ions relative to other ions. The parameter $[(F_C - F_0)/\{F_0 (C_0 - C_C)\}]$ are shown in Fig. 8A as a function of charge to size ratio of the cations. Among the alkaline earth metal ions the highest fluorescence enhancement is observed for Mg^{2+} ion and the extent of fluorescence enhancement decreases on going down the group. The transition metal ion with d^5 electronic configuration causes greater enhancement of fluorescence of the dye than Co^{2+} ion. The parameter shows a linear correlation with the charge-to-size ratio of the metal ion, indicating that the nature of interaction leading to fluorescence enhancement is mostly electrostatic. Mg^{2+} and Mn^{2+} ions, however, fall outside the linear correlation. Fig. 8B shows a plot of K_1 as a function of the ratio of charge-to-size of the cations. A good correlation has been obtained indicating that the interaction between cation and the dye in the S$_1$ state is mostly electrostatic in nature. Moreover, it appears that the value of $\log K_1$ approaches a limiting value as q/r increases.

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. The red shift at higher concentration, can be explain on the basis of interaction metal ions at the O-centre of the dye molecule due to increased charge density on the carbonyl oxygen, leading to a stronger dye-M ion interaction in this state. The extent of red shift in fluorescence of the dye, however, depends on the identity of the cation. Thus, alkaline earth metal ions causes greater shift in fluorescence than the transition metal ions shown in Fig. 9.

Time resolved fluorescence studies

Fluorescence decay of DN1 has been studied in acetonitrile in presence and in absence of the metal ions. In all the cases the decay curves can be best fitted by a single exponential decay equation. The results have been given in Table S2. The value of lifetime (τ) for DN1 is smaller than that of the symmetric dye KD1 [24]. Note that in the micromolar concentration range of metal ion where enhancement of fluorescence is observed, the value of τ of the dye increases as the concentration of metal ion is increased, reaching a maximum value and beyond that, the value of τ remains practically constant. Although the variation is small, we have checked the results several times by repeating measurements. A representative plot showing the variation of $1/\tau$ as a function of $\log[M^{2+}]$
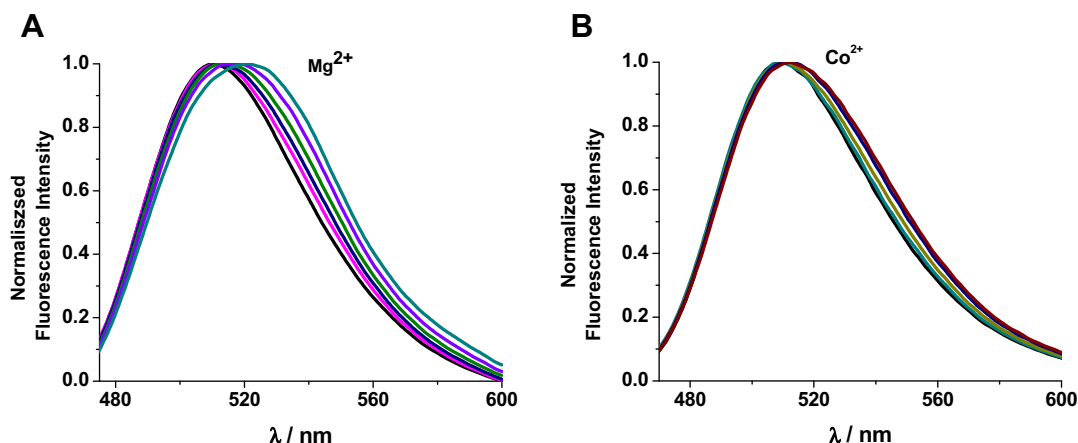

Fig. 9. Fluorescence spectra the ketocyanine dye (DN1) in acetonitrile with varying concentration (0–10 mM) of (A) Mg^{2+} and (B) Co^{2+} ion, respectively.
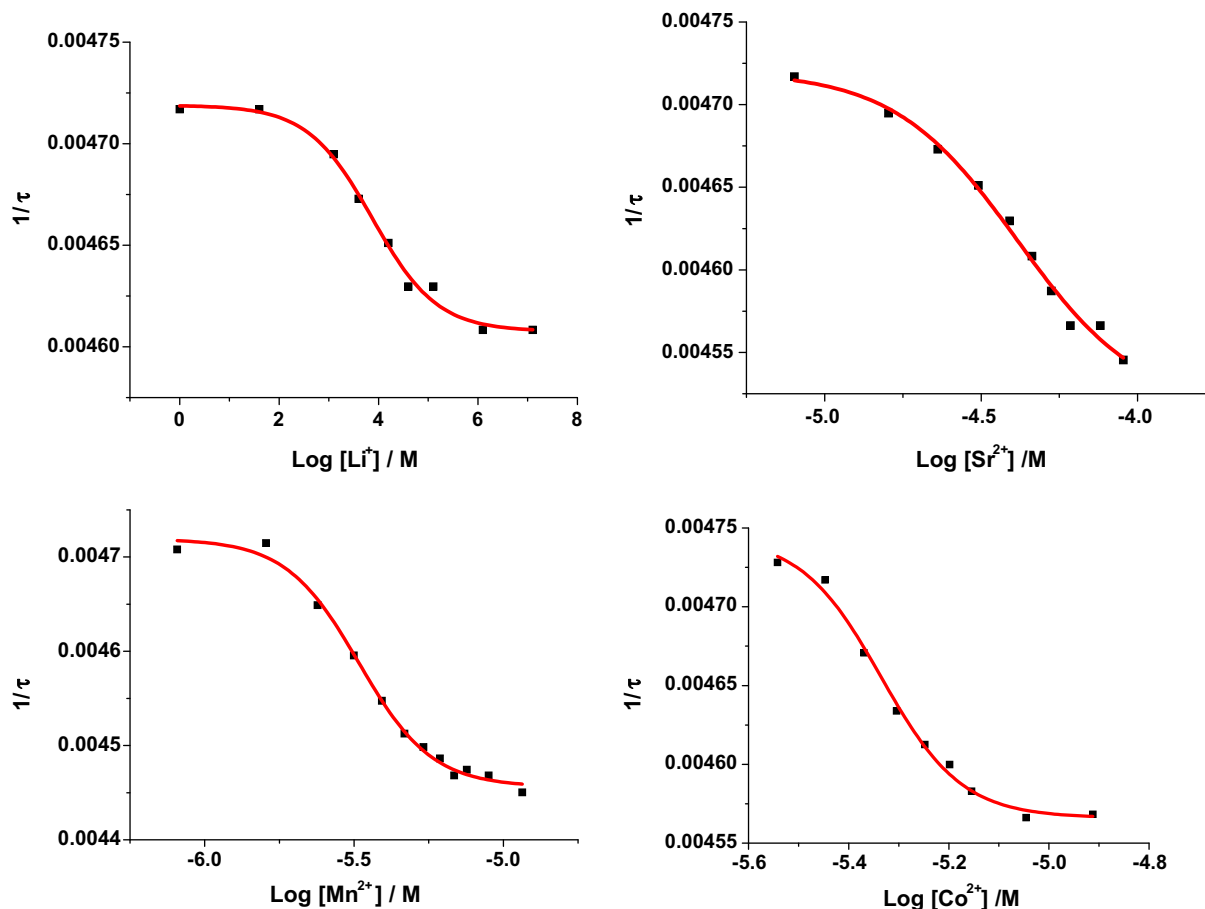
Fig. 10. Plot of $1/\tau$ for the dye (DN1) as a function of $\log C_0$ in acetonitrile.

has been presented in Fig. 10. Similar variation was noticed for interaction of KD1 with Co^{2+} ion. Thus for a very little concentration of cation the overall decay rate becomes slower. It is known that the radiative decay rate of DN1 is not very sensitive towards a change in its immediate environment [24]. Thus nonradiative decay becomes slower. According to the proposed model (Eq. (6)) the species DS_{n-1} is slower decaying than the solvated dye DS_n. Results suggest that the phenomena of increase of τ value and fluorescence enhancement have the same origin. The constancy of τ value after a certain concentration range indicates that quenching observed at higher salt concentration is static in nature.

Conclusion

(1) The dye forms 1:1 complex with metal ions. A new band, red shifted with respect to the band of dye, appears upon complexation. The equilibrium constant for complexation process and the position of the maximum transition of the complexed dye correlates well with the charge-to-size ratio of the cations. DFT calculation reveal that a considerable change in the bond alteration of the dye takes place on complexation with metal ion, indicating that the complexed dye exists predominantly in the enol form. Quenching of fluorescence of the dye takes place where dye forms a complex in the ground state. The metal cations induce a red shift of fluorescence, its extent being greater for Li and the alkaline earth metal ions than for the transition metal ions.

(2) For very low concentration of salt a slight blue shift of the absorption band is observed. An enhancement of fluorescence intensity is also observed in this region. Both the

two phenomena are related and have been explained in terms of formation of a weak association complex where one (or more) solvent molecules are replaced by cation in the cybotatic region around the dye. The binding constant for weak association complex involving the cation and the dye (S_1 state) has been determined. These values depend significantly on the charge-to-size ratio of the cation.

(3) In the concentration range where enhancement of fluorescence intensity is observed, the lifetime of the dye increases indicating that the weak association complex is slower decaying species relative to free dye.

Acknowledgements

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2012.09.015.

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