

Effect of temperature on fluorescence quenching and emission characteristics of laser dyes

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Abstract

Effect of temperature on fluorescence quenching and emission characteristics of laser dyes (LD – 473) and (LD – 423) have been investigated in the temperature range 25°C - 65°C by steady state and transient methods. The fluorescence intensity of both dyes is quenched in the presence of quencher aniline at different temperatures. Stern-Volmer (S-V) plots are non-linear showing positive deviation. It has been found that dynamic quenching constant increases with temperature, whereas static quenching constant is independent of temperature. In both the dyes, Fluorescence emission intensity has decreased with increase in temperature and fluorescence band maxima is slightly shifted towards shorter wavelength. Further, fluorescence lifetime has decreased with increase in temperature for both the dyes. The possible deactivation mechanisms are discussed.

Keywords: LD-473, LD-423, Fluorescence quenching, Lifetime, Activation energy.

1. Introduction

Organic fluorophores have immense applications in bio research and other fields. They are used as chemical and biological sensors, and most frequently used for labeling target molecules. The two dyes in the blue region under study are 1,2,3,8-tetrahydro-1,2,3,3,8-pentamethyl-5-(trifluoromethyl)-7H-pyrrolo[3,2-g]quinolin-7-one (LD-473) and 1,2,3,8-tetrahydro-1,2,3,3,5-pentamethyl-7H-pyrrolo[3,2-g]quinolin-7-one (LD-423). These dyes have importance in pharmaceutical industry, dye industry and chemical industry [1-6]. The analytical and biological applications of these dyes prompted us to investigate the effect of solvents, quenchers and metal nanoparticles on photophysical properties of these dyes [7 - 10]. It has been found that these dyes are highly sensitive to solvent polarity, quenchers and metal nanoparticles. In the present study, authors have reported the temperature sensitivity of spectral properties of these dyes with aniline used as quencher and toluene as solvent.

2. Results and discussion

The absorption spectra are recorded at room temperature with different quencher concentrations and are given in Figure 1. There is no change in absorption maxima of both the dyes with the addition of quencher. The fluorescence spectra for both the dyes without quencher and with varying quencher concentration in the temperature range 25° C - 65° C are recorded and typical spectra at room temperature are shown in Figure 2. In both the dyes, there is an appreciable quenching of fluorescence and no apparent shift in the emission wavelength with the addition of different concentrations of quencher. The fluorescence lifetime $\tau(t)$ of both the dyes in the temperature range 25° C - 65° C is measured in the absence of quencher and the corresponding fluorescence decay life time data are given in Table 1.



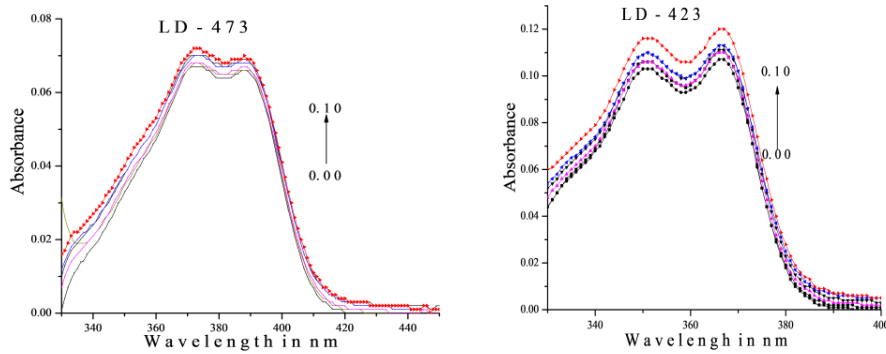


Figure 1: Absorption spectrum of LD-473 and LD-423 with varying quencher concentration [$Q = 0.00$ to 0.10 M] at room temperature

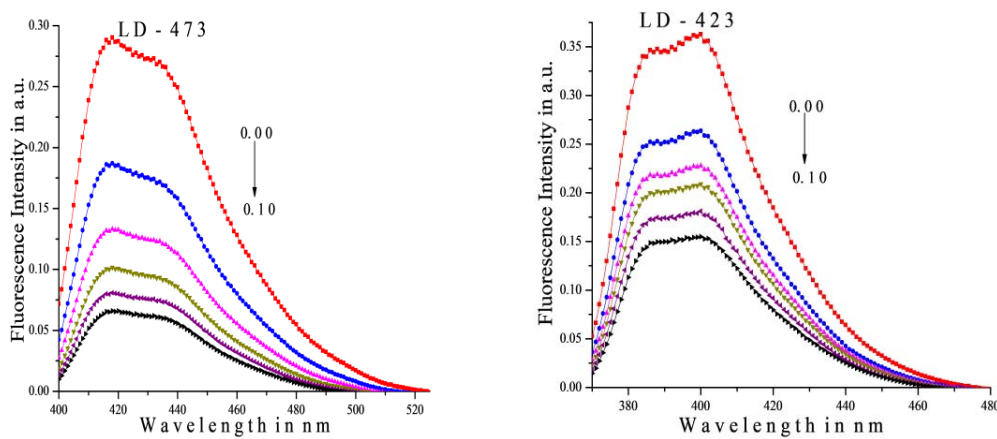


Figure 2: Fluorescence spectrum of LD-473 and LD-423 with varying quencher concentration [$Q = 0.00$ to 0.10 M] at room temperature

2.1 Fluorescence quenching by aniline in toluene

The Stern-Volmer (S-V) plots for both the dyes in the temperature range of 25°C - 65°C are plotted according to the S-V equation [11]

$$\frac{I_0}{I} = 1 + K_{SV} [Q] \quad (1)$$

where $K_{SV} = k_q \tau_0$ is called Stern-Volmer constant, k_q is the bimolecular quenching rate parameter, τ_0 is the fluorescence lifetime and quencher concentration $[Q]$. Eq. (1) is applicable when the experimental results are linear in nature. It is observed that S-V plots have positive deviation as shown in Figure 3. This suggests that quenching is not purely collisional and may be attributed to the presence of parallel quenching process. There is no appreciable change in shape or peak positions of the absorption spectrum of these dyes (Figure 1), the fluorescence quenching is without ground-state complex formation [12]. To check for the role of static quenching process, we have used the sphere of action static quenching model [13] and the modified

S-V equation is

$$\frac{I_0}{I} = \frac{1 + K_{SV}[Q]}{W} \quad (2)$$

According to this model only a fraction (W) of the excited state is quenched by the collisional mechanism and the remaining fraction ($1-W$) are deactivated instantaneously after being formed. The plots of $[1 - (I/I_0)]/[Q]$ versus I/I_0 are linear for both the dyes as shown in Figure 4. The dynamic quenching constant K_{SV} and the static quenching constant ' V ' are determined by using the equation $W = e^{-V[Q]}$ for both the dyes at different temperatures. These values are reported in Table 1. The dynamic quenching constant systematically increases with increase in temperature, where as static quenching constant ' V ' remains almost same at all temperatures. Further, the values of K_{SV} are more than the values of ' V ' at all temperatures. This indicates that the contribution of dynamic quenching is more with the presence of minor component of static quenching. The increase in K_{SV} with temperature is expected, because the number of collisions between quencher and excited molecules increases with temperature leading to deactivation of excited molecules by collisional mechanism. The bimolecular quenching rate parameter k_q are determined from the experimentally determined values of K_{SV} and fluorescence lifetime $\tau(t)$ at temperature t °C. The values of k_q are tabulated in Table 1. It is observed that k_q increases with increase in temperature for both the dyes.

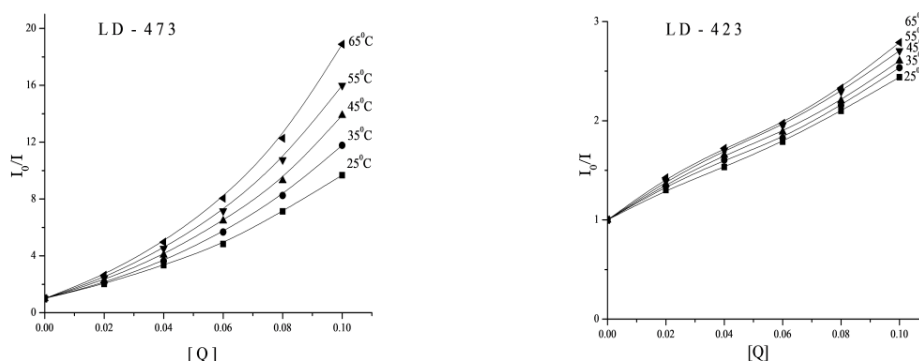


Figure 3: S – V plots for LD – 473 and LD-423 at different temperatures [25°C - 65°C]

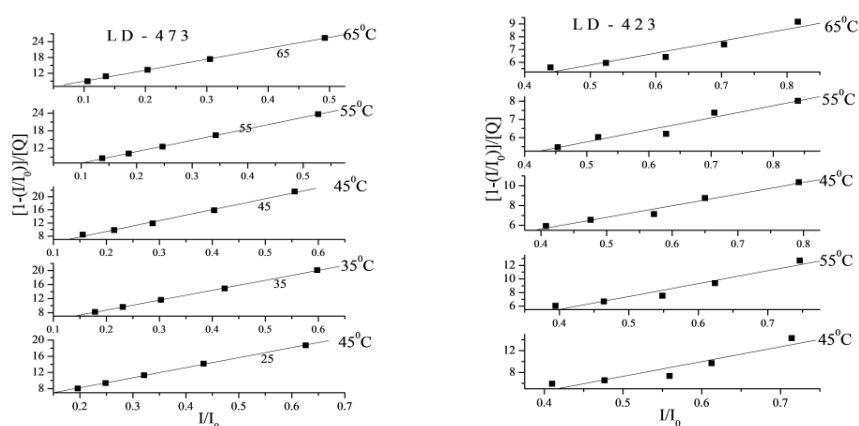


Figure 4: Plots of $[1 - (I/I_0)]/[Q]$ versus I/I_0 for LD – 473 and LD-423 at different temperatures [25°C - 65°C]

In order to support static and dynamic effects, we have determined radii ' r ' of sphere of action i.e., kinetic distance at different temperatures using $\frac{V}{N'} = \frac{4}{3} \pi (r)^3$ and values are given in Table 1. The encounter

distance or reactive distance r^* which is the sum of radii of dyes R_Y and quencher R_Q [14] are given at the bottom of the Table 1. Since $r > r^*$, the static quenching takes place irrespective of ground state complex formation provided reactions are limited by diffusion, indicating the sphere of action static quenching model [15].

In order to check for diffusion limited, the temperature dependence of rate constant k_q is examined. It has been assumed that k_q is proportional to $\exp(-E_q/RT)$ [16], where E_q is the activation energy for collisional process, R is the gas constant and T is the absolute temperature. The value of E_q can be determined from the slope of the plot $\ln k_q$ versus $1/T$ given in Figure 5. The values of E_q suggest that the rates of reactions are limited by diffusion of the reactants through the solvent [17].

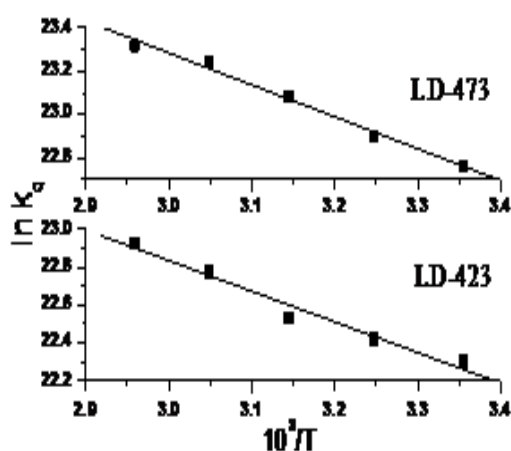


Figure 5: The Plot of $\ln k_q$ versus $10^3/T$ for LD-473 and LD-423

Table 1: The values of lifetime data, decay rate constant k_f , dynamic quenching constant K_{SV} , bimolecular quenching rate parameter k_q , static quenching constant V , kinetic distance r and activation energy E_q for both the dyes at different temperatures

Dye	Temp. (°C)	τ in ns	$K_f \times 10^9$ (s ⁻¹)	K_{SV} (M ⁻¹)	k_q ($\times 10^9$) (M ⁻¹ s ⁻¹)	V (M ⁻¹)	r Å	E_q (kJmol ⁻¹)
LD-473	25	3.23	0.31	24.79	07.67	3.38	10.70	12.29
	35	3.19	0.31	28.31	08.88	3.16	10.46	
	45	3.14	0.32	33.20	10.59	2.86	10.12	
	55	3.13	0.32	39.04	12.46	2.61	09.81	
	65	3.11	0.32	41.71	13.40	2.17	09.23	
LD-423	25	2.01	0.50	09.73	04.83	1.95	08.91	13.49
	35	1.94	0.52	10.59	05.46	0.28	04.67	
	45	1.93	0.52	11.75	06.10	0.94	06.98	
	55	1.91	0.52	14.92	07.81	2.49	09.66	
	65	1.74	0.58	15.72	09.06	1.14	07.45	

The encounter distance r^* (for LD-473 + AN) = 6.90 Å; r^* (for LD-423 + AN) = 6.75 Å

2.2 Temperature dependence of non-radiative deactivation processes

The fluorescence spectra at different temperatures are given in Figure 6. The shift fluorescence intensity decrease and band maxima shift towards shorter wavelength indicate that the emission states undergo changes on heating. The plots of relative fluorescence intensity $I_0(t)/I_0^{25}$ (where $I_0(t)$ and I_0^{25} are fluorescence intensities at temperatures $t^\circ\text{C}$ and 25°C respectively) versus temperature are shown in Figure 7. The change in fluorescence intensity with change in temperature can be explained in terms of possibility of change over from the excited singlet-state to a neighboring non-fluorescent triplet-state i.e., heating induces intersystem crossing of singlet (S_1) to triplet (T_2) and brings about a decrease in the fluorescence intensity.

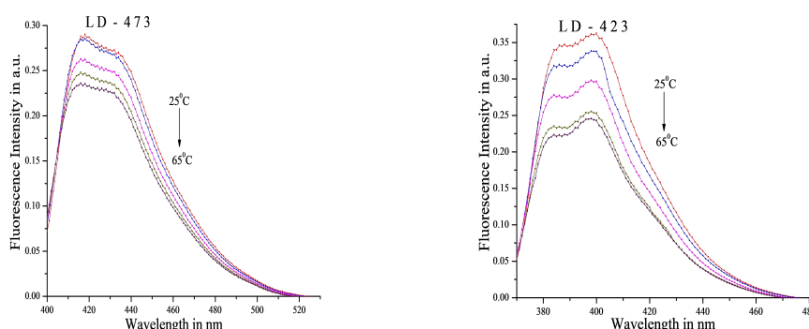


Figure 6: Fluorescence spectra for LD-473 and LD-423 at different temperatures [25°C - 65°C]

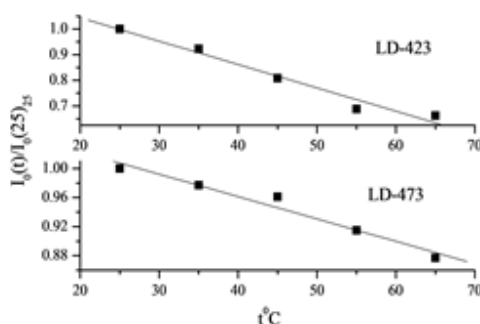


Figure 7: Plots of $I(t)/I_0^{25}$ versus temperatures for LD-473 and LD-423

In order to understand the temperature dependence of non-radiative deactivation processes, various rate parameters such as frequency factor for the thermally assisted de-activation process k' , fluorescence decay rate constant k_f , activation energy for the de-activation process ΔE and energy corresponding to S_1 and T_2 levels are determined. In order to understand the temperature dependence of k_f , we used equation $k_f = k^0 + k' \exp(-\frac{\Delta E}{RT})$ where k^0 is the temperature independent rate constant [18]. According to above equation, the plot of $\ln k_f$ versus $10^3/T$ should be linear with its slope equal to $(-\Delta E/R)$ and intercept equal to $\ln k^0$ as shown in Figure 8. The value of ΔE and k' are given in Table 2. From this table, the percentage change in lifetime with temperature is more where k' is high.

In order to check for the intersystem crossing mechanism, singlet state energies were determined from the absorption and emission spectra. The crossing point of the absorption and emission spectra is taken to be the close approximation for the 0 – 0 bands according to V. J. P. Srivatsavoy [19]. Hence, the singlet state energies of the dye molecules have been determined from the Figures 9 and the values are given in

Table 2. From the experimental values of ΔE and S_1 , T_2 energy state values are determined and are given in Table 2. T_2 energy state of both the dyes lies above S_1 , indicating that de-activation of excited molecules proceeds via the triplet state [20]. Hence there is a possibility of intersystem crossing $S_1 \rightarrow T_2$ with increase in temperature. Therefore, we conclude that in case of LD-473 and LD-423, thermally assisted intersystem crossing from S_1 to T_2 may be responsible for lifetime decay with increase in temperature.

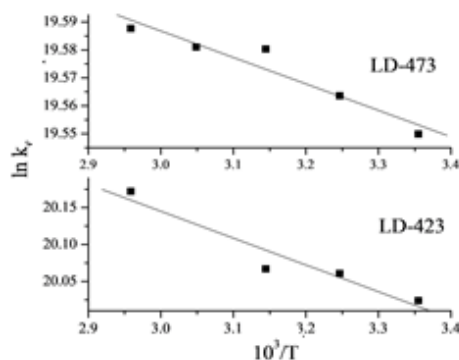


Figure 8: Plot of $\ln k_f$ versus $10^3/T$ for LD-473 and LD-423

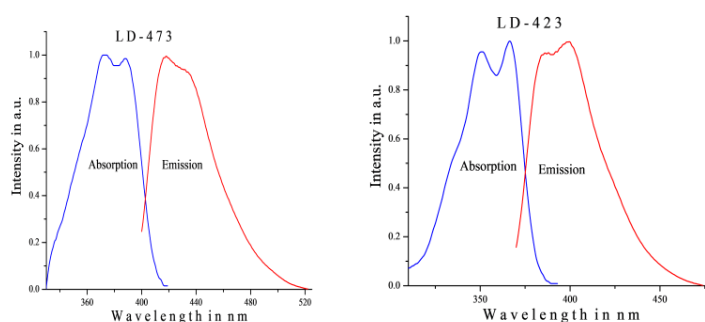


Figure 9: The crossing point of absorption and emission spectra of LD-473 and LD-423

Table 2: Energy separation ΔE , frequency factor k' and energy values of S_1 and T_2 levels

Dye	ΔE (kJmol ⁻¹)	r	k' 10 ⁹ (s ⁻¹)	S_1 energy (cm ⁻¹)	T_2 energy (cm ⁻¹)
LD-473	1.20	0.96	0.68	2481389	2481489
LD-423	3.03	0.89	1.67	2666667	2691928

3. Conclusion

The fluorescence quenching of laser dyes LD-473 and LD-423 by aniline in toluene at temperatures ranging from 25° C - 65° C has been studied. The quenching is appreciable and S-V plots are found to have positive deviation. This suggests that quenching is not purely collisional. The lack of change in the spectral shape or peak position indicates that the quenching has occurred without involving ground state complex formation. The contribution of dynamic quenching is more with the presence of minor component of static quenching.

The temperature dependent non-radiative process of de-activation has been studied. The fluorescence intensity has decreased with the shift in the band maxima towards shorter wavelength. This shows the sensitivity of emission states on heating. The fluorescence lifetime also has decreased with increase in temperature. The percentage change in lifetime with temperature is more where the frequency factor is high. Since T_2 energy state lies above S_1 , the de-activation of excited molecules takes place via the triplet state.

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