



Reduction in fluorescence intensity and lifetime of Coumarin derivative MFBMC with an increase in temperature in non-polar and polar solvents

KEYWORDS

Fluorescence; Lifetime; Thermal deactivation energy; excited-state; solvents.

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ABSTRACT The influence of temperature (293-333 K) on the fluorescence emission of 4-[5-methyl-3-furan-2-yl-benzofuran-2-yl]-7-methyl-chromem-2-one (MFBMC) is recorded in non-polar (1, 4-dioxane, toluene), and polar (butanol, acetonitril) solvents. It is found that there is no shift in the position of fluorescence maxima, but the intensity decreases with increase in temperature, which depends on the polarity of the solvent. A mechanism of fluorescence quenching with rise in temperature is discussed in terms of the relative location of lowest ($\pi\pi^*$) and ($n\pi^*$) states, and the energy difference between them. The change in temperature brings about a change in the probabilities of radiative and non-radiative transition. The radiationless deactivation of excited-state in the absence of quencher is temperature-dependent and its thermal activation energy has been determined.

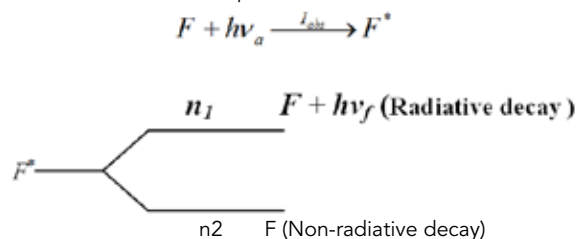
1. Introduction

The influence of temperature on the fluorescence emission intensity and lifetime of many organic compounds has been discussed rather extensively in literature for the 2H-chromen-2-one derivative [1-16], indole [17], anthracen [18-19], and rohdamine [20]. We have carried out measurements of the temperature dependence of fluorescence emission intensity of coumarin (2H-chromen-2-one) derivative, 4-[5-methyl-3-furan-2-yl-benzofuran-2-yl]-7-methyl-chromem-2-one (MFBMC) are well-known laser dyes for the blue-green region [21-23], which are applicable in different fields of science and technology. They exhibit strong fluorescence in the UV-VIS region that makes them suitable to use as a colorants, dye laser media and as non-linear optical chromophores.

In this paper the fluorescence intensities and lifetime of, 4-[5-methyl-3-furan-2-yl-benzofuran-2-yl]-7-methyl chromem-2-one (MFBMC) in polar and non-polar solvents, have been measured as function of the temperature and activation energy in all the solvents is also estimated.

2. Theory

In general, the natural fluorescence lifetime of fluorophore should be independent of temperature. But the intensities may vary due to other temperature dependent processes. The kinetic scheme for the fluorescence quenching in the absence of an external quencher can be written as



where F and F* represents the fluorophore in the ground-state and excited-states, Q is the quencher, the k's are the reaction-rate constants and n1 and n2 are the radiative and non-radiative transition probabilities, respectively.

The fluorescence lifetime of the excited molecule at t °C is given by

$$\frac{1}{\tau(t)} = n_1 + n_2(t) \quad (1)$$

where [1, 9] it is assumed that over a small range of temperature (10-70°C), n1 is independent of temperature. Further, if we assume that there is only one dominant radiationless deactivation process, then the temperature dependence of the lifetime can be expressed as

$$n_2(t) = n_2^0 \exp\left(-\frac{E}{RT}\right) \quad (2)$$

where n_2^0 is the frequency factor for deactivation process and involves the entropic component of the corresponding free energy of activation, E is the activation energy for the deactivation process, R is the gas constant, and T is the absolute temperature.

Equating Eqs. (1) and (2), we have

$$\frac{1}{\tau_0(t)} - n_1 = n_2^0 \exp\left(-\frac{E}{RT}\right) \quad (3)$$

A plot of $\ln[1/\tau(t) - n_1]$ versus 1/T should be linear, and the slope gives the value of E. This is fine as long as the fluorophore shows decrease in fluorescence intensity with increase in temperature. Thus it is clear that, temperature quenching indicates an increase in the radiationless de-activation of the excited-state. But what is not so obvious is the mechanism of these non-radiative processes, in order to find out plausible explanation for the variation of fluorescence intensity with temperature, it is necessary to examine various temperature dependent non-radiative de-activation processes. Some of these mechanisms are: i) Fluorescence intensity could decrease on increasing temperature, because of the increased conversion rate of electronic into vibrational energy (internal conversion). ii) Increase in temperature can cause a change-over from an excited singlet-state to a higher triplet-state (intersystem crossing), and thus decrease the fluorescence intensity. iii) There should be loss of planarity in molecular structure and dissociation of molecular complexes at higher temperature.

Using Eq. (4), the values of fluorescence lifetime τ of fluorophore at different temperatures can be determined, provided τ at temperature 20° C is known from independent measurement.

$$\tau_0(t) = \tau_0^{20} \frac{I_0(t)}{I_0^{20}} \quad (4)$$

where τ_0^{20} and $\tau_0(t)$, I_0^{20} and $I_0(t)$ are the fluorescence lifetimes and emission intensities at 20° C and t °C in the absence of quencher respectively.

3. Experimental details

3.1 Materials

The solute, 4-[5-methyl-3-furan-2-yl-benzofuran-2-yl]-7-methyl-chromem-2-one (MFBMC) was synthesized by one of the authors [24]. The structures of the (MFBMC) are presented in Fig 1.

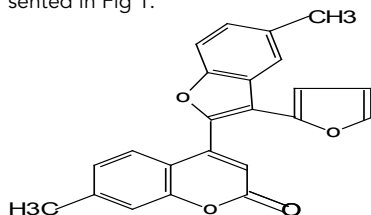


Fig. 1. The structural formula of 4-[5-methyl-3-furan-2-yl-benzofuran-2-yl]- 7- methyl-chromem-2-one (MFBMC)

The solvents 1, 4-dioxane (DX), toluene (TN), and butanol (BT), and DMSO were of HPLC grade (S-D-Fine chemicals Ltd, India) and were used without any further purification. The quencher aniline was double distilled and tested for its purity before use.

3.2 Steady-state measurement

Absorption spectra were recorded using UV-VIS spectrophotometer (PerkinELMER, LAMBDA-35) in a 1cm path length cuvette. The fluorescence intensity measurements were done on a Hitachi F-4500 spectrofluorometer. For temperature-dependent studies, we have used a hallow cell holder, through which water from a constant-temperature bath was circulated. The temperature in the cuvette could be controlled within ± 0.20 between 20 and 60° C, and was monitored directly by means of thermocouple immediately after the fluorescence measurement.

The excitation wavelength chosen was the absorption maximum of MFBMC. The concentrations of the fluorescent molecule in all the solvents were kept low $\approx 1 \times 10^{-4}$ M to minimize the inner filter effect for which the reliable and stable recording of the fluorescence spectra was ensured. The fluorescence intensity was usually determined by the measurement of relative intensity at the emission maxima, by varying the temperature from 20 to 60° C or by the addition of a quencher (0.00 to 0.01M) respectively. The shape and position of the emission spectrum were not noticeably altered by changing the temperature.

3.3 Lifetime measurement

The fluorescence lifetime of (MFBMC) was measured using computer controlled Time Correlated Single Photon Counting (TCSPC) picoseconds spectrometer (HORIBA JOBIN YVON, Model: 5000-U) with short pulsed diode light source Nano-LED at 337 nm excitation wavelength. The fluorescence lifetime measurements were performed in different solvent at temperature (20° C). The analysis of fluorescence lifetime data was carried out by using the software provided by IBH (DAS-6) which is based on reconvolution technique using iterative non linear least square methods. The reconvolution is preceded by the series of iterations until a reduced chi-square is obtained. In our measurements, the χ^2 values are less than 0.94. The experimental values are reproducible within 5% of the experimental error. The temperature dependence of the fluorescence lifetime at higher temperature was determined by using Eq. (4).

4. Results and discussion

The fluorescence intensities of MFBMC in 1, 4-dioxane, toluene, butanol, and DMSO have been measured as a function of temperature. The typical, fluorescence spectra in

1, 4-dioxane with different temperature is shown in Fig. 2.

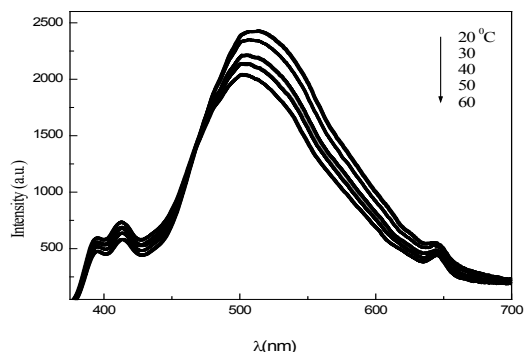


Fig. 2. Emission spectra of MFBMC (C = 1×10^{-4} M) in acetonitrile in the temperature range (20-60° C).

The values of relative intensities with respect to temperature in non-polar (1, 4-dioxane and toluene) and polar (butanol and Acetonitril), solvents are given in Table 1 and 2. Plots of relative fluorescence intensity $I_0(t)/I_0^{20}$ versus temperature in all the solvents are shown in Fig. 3. It is seen that the fluorescence intensity decreases by >50% in, non-polar and polar solvents when the temperature is raised from 20 to 60° C. It should also be noted that, the change in fluorescence intensity with temperature depends on the polarity of the solvent. A small decrease in intensity with a rise in temperature can be explained in terms of the increased conversion rate of electronic energy into vibrational energy. However, this certainly cannot explain the large change of >50% observed in all solvents. To explain this one must look for some non-radiative deactivation process such as tunneling from the excited to the ground-state, electron ejection to the solvent, proton transfer and intermolecular electron transfer to a quenching group, etc.

Table 1
Relative fluorescence intensity, lifetime and $\ln[1/\tau(t) - n_1]$ as a function of temperature at a fixed solute concentration in polar solvents.

Temp.(t)(°C)	$1/T \times 10^3$ (OK)	Acetonitrile			Butanol		
		I_t / I_{20}	τ (ns)	$\ln[1/\tau(t) - n_1]$ (s ⁻¹)	I_t / I_{20}	τ (ns)	$\ln[1/\tau(t) - n_1]$ (s ⁻¹)
20	3.41	-	3.39	18.37	-	1.39	18.91
30	3.30	0.969	3.28	18.49	0.975	1.36	19.02
40	3.19	0.910	3.08	18.63	0.953	1.32	19.11
50	3.10	0.881	2.98	18.73	0.925	1.29	19.20
60	3.00	0.840	2.84	18.84	0.904	1.26	19.28

Table 2
Relative fluorescence intensity, lifetime and $\ln[1/\tau(t) - n_1]$ as a function of temperature at a fixed solute concentration in non- polar solvents.

Temp.(t)(°C)	$1/T \times 10^3$ (OK)	1, 4-Dioxane			Toluene		
		I_t / I_{20}	τ (ns)	$\ln[1/\tau(t) - n_1]$ (s ⁻¹)	I_t / I_{20}	τ (ns)	$\ln[1/\tau(t) - n_1]$ (s ⁻¹)
20	3.41	-	2.13	19.02	-	1.22	19.37

30	3.30	0.933	1.98	19.20	0.865	1.12	19.57
40	3.19	0.851	1.81	19.40	0.705	0.95	19.73
50	3.10	0.778	1.65	19.58	0.604	0.84	19.92
60	3.00	0.711	1.51	19.74	0.467	0.71	20.08

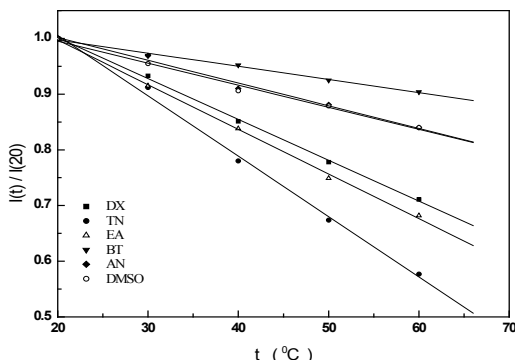


Fig.3. Relative fluorescence intensity $I(t)/I(20)$ of MFBMC versus temperature in solvents.

One such possible mechanism is a change over from the excited singlet-state to a neighbouring non-fluorescent triplet-state. The lowest excited-state for a coumarin molecule is the $^1(n\pi^*)$ state, but due to the effect of substituents, the state order gets inverted making $^1(\pi\pi^*)$ the lowest state [25]. It is also known that with a given solute, a change of solvent causes a shift in the positions of $(\pi\pi^*)$ and $(n\pi^*)$ energy levels of the molecular system. The interaction of the solvent with the solute molecule perturbs the energy levels. In general, $(n\pi^*)$ level is affected more than the $(\pi\pi^*)$ levels [26] as shown in Fig 4.

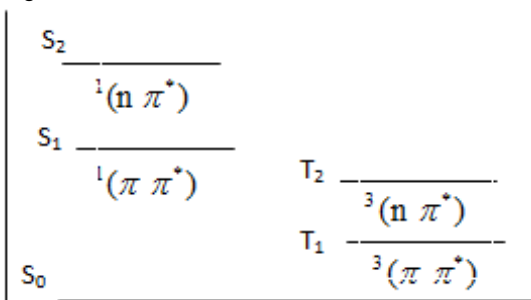


Fig. 4 Relative locations of the lowest lying $^1(\pi\pi^*)$, $^1(n\pi^*)$, $^3(\pi\pi^*)$, and $^3(n\pi^*)$ levels both polar and non-polar solvents.

The excited molecule in the state S1 deactivates (1) by allowed transition $S1 \rightarrow S0$ with the emission of visible or UV- fluorescence (2) by radiationless intersystem crossing to the nearby triplet state after which it may undergo internal conversion (radiationless) to the ground state or emit visible phosphorescence. It may further be noted that there is a high probability for the radiationless deactivation through the spin forbidden process $^1(\pi\pi^*) \rightarrow ^3(n\pi^*)$ (i.e. $S1 \rightarrow T2$) as compared to the spin forbidden process $^1(\pi\pi^*) \rightarrow ^3(\pi\pi^*)$ (i.e. $S1 \rightarrow T1$). Hence, the fluorescence intensity, which depends on the transition $S1 \rightarrow S0$ gets modified by the competing processes $^1(\pi\pi^*) \rightarrow ^3(n\pi^*)$. As the solvent polarity increases, due to dipole-dipole interaction, $^1(n\pi^*)$ and $^3(n\pi^*)$ levels are moved up and $^1(\pi\pi^*)$ and $^3(\pi\pi^*)$ levels are moved down. The lowering of $^1(n\pi^*)$ and $^3(n\pi^*)$ is much less as compared to the shifts in the positions of $^1(n\pi^*)$ and $^3(n\pi^*)$ (Fig. 4). Thus, the net effect of increase in the solvent polarity is to increase the probability $^1(\pi\pi^*) \rightarrow ^3(n\pi^*)$ transition and to decrease the fluorescence intensity/quantum yield ($S1 \rightarrow S0$ transition). In such case, activation energy of degradation in all the solvents can be calculated.

The fluorescence lifetime of MF in different solvents is measured at 20°C. The decay spectra in 1, 4-dioxane given in Fig. (5). The fluorescence lifetime of the excited molecule at t°C is given by Eq. (1).

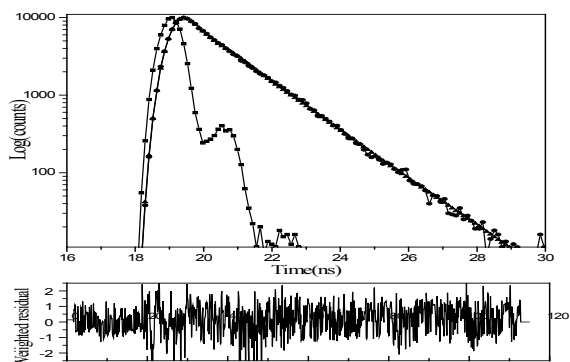


Fig. 5. Fluorescence decay profiles for MFBMC in acetonitrile at 20°C and the distribution of weighted residuals for the bi-exponential function ($\chi^2 = 1.1$).

It is assumed that over a small range of temperature (20-60°C), nI is independent of temperature, $\tau^{(I)}$ can be estimated using Eq. (4). The values of $\tau^{(I)}$ at different temperature in different solvents are given in Table 1 and 2. As there is no change in optical density corresponding to the longest absorption wavelengths with temperature, the values of fluorescence intensities are used in Eq. (4) instead of quantum yields. The lifetime of the excited molecule is found to decrease with temperature (Fig. 6). As there is a shift in the maximum fluorescence wavelength towards shorter wavelength upon raising the temperature, it can be shown that the fluorescing state is altered on heating. Further, if we assume that there is only one

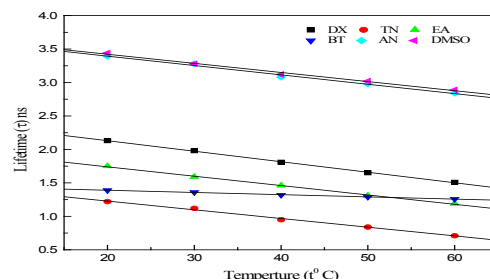


Fig.6. Temperature dependence of the fluorescence lifetime of MFBMC in non-polar and polar solvents.

dominant radiationless deactivation process, then the temperature dependence of the lifetime can be expressed and it is given by Eq. 3. By numerical fitting of Eq. (3) with the data in Fig.7,

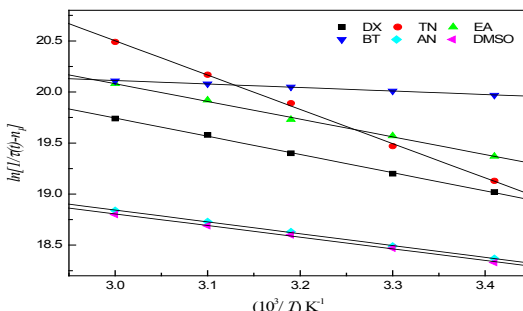


Fig. 7. Plot of $\ln[I(t)/I(0)]$ versus $1/T$ for MFBMC in different solvents.

the value of n_1 can be determined which gives a linear plot of $\ln[1/\tau(t) - n_1]$ versus $1/T$. Such plot is shown in Fig. 7; from the slope of this line we have obtained the E of Eq. 3. The actual lifetime, τ_0 , at 200 C, the radiative lifetime, $\tau_1 (= 1/n_1)$, the activation energy, E

A similar method has been used by some authors [1, 4-10] to obtain the value of activation energy, E of the fluorophore and correlation coefficient, r are given in Table 3.

Table 3
Actual and radiative lifetimes, activation energy for the radiationless transition process and correlation coefficient of MFBMC

Solvents	τ_0 (ns) ^a	n^{-1} (ns)	Activation energy E_2 (kJmol ⁻¹)	Correlation coefficient
1, 4-Dioxane	2.13	3.50	14.832	0.999
Toluene	1.22	1.62	27.893	0.999
Butanol	1.39	1.39	7.499	0.999
Acetonitril	3.39	3.39	9.619	0.999

a) The value at 200 C

5. Conclusion

On the basis of the result presented in this article, we can arrive at the following conclusions: the reduction in fluorescence intensity for fluorophore 4-[5-methyl-3-furan-2-yl-benzofuran -2-yl] -7-methyl-chromem-2-one (MFBMC), in non-polar and polar solvents strongly indicates that the molecule is under going rotation across the coumarins-benzofuran or benzofuran-aryl bonds which brings about the reduction in life time and fluorescence intensity. The reduction in fluorescence intensity with an increase in temperature which is due intersystem crossing ($^1(\pi \pi^*) \rightarrow ^3(n \pi^*)$). The relative position of $^1(\pi \pi^*)$ and $^3(n \pi^*)$ depend on the nature of the substituent's as well as the solvent. As the solvent polarity increases, due to dipole-dipole interaction, $^1(n \pi^*)$ and $^3(n \pi^*)$ levels are moved up, and $^1(\pi \pi^*)$ and $^3(\pi \pi^*)$ levels are moved down.

In view of these facts, we may conclude that, the reduction in fluorescence intensity with an increase in temperature in all solvents that takes place due to intersystem crossing ($^1(\pi \pi^*) \rightarrow ^3(n \pi^*)$).

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