Effect of viscosity and temperature on some photophysical parameters of 9-phenyl-10-methoxy anthracene

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Abstract

9-Phenyl-10-methoxy anthracene (PMA) shows no significant change in the absorption spectrum on going from non-polar to polar solvents, indicating no change in dipole moment of dye molecules upon excitation. The fluorescence quantum yields (Φ_f) of PMA have been measured in different solvents. It was found that Φ_f and the lifetime (τ_f) increases with increasing the viscosity of solvent. It was also found that the fluorescence quantum yields (Φ_f) increased sharply by lowering the temperature. The quenching rate constants by molecular oxygen were measured using lifetime measurements.
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1. Introduction

Anthracene derivatives show high fluorescence quantum yield (Φ_f) and smaller fluorescence lifetimes than unsubstituted anthracene, consequently some of these molecules are used in scintillators and in dye laser as active media [1]. On the other hand there are some of anthracene derivatives characterized by very weak or practically absence of fluorescence [2–7] which can provide more information about the pathways which absorbed excitation energy is dissipated than can highly fluorescent molecules. The photostability and photophysical properties of anthracene derivatives varied from one to another according to the molecular structure and the positions of the substituents as well as the viscosity and temperature of the medium [8–10]. In the present article we study the photophysical behavior of 9-phenyl-10-methoxy anthracene (PMA) in different media. The effect of medium viscosity and temperature were also studied.

2. Experimental

9-Phenyl-10-methoxy anthracene was kindly provided by professor E. Daltrozzo, Faculty of Chemistry, University of Konstanz, Germany. Steady-state fluorescence was measured using a Shimadzu RF 510 Spectrofluorophotometer with band pass of 10 nm using a right-angle arrangement. The fluorescence spectra were corrected for the machine response using 10^{-5} mol dm^{-3} anthracene solution in benzene as reported earlier by Melhuish [11]. UV-Vis absorption spectra were recorded on Shimadzu UV-160 A Spectrophotometer with band pass of 5 nm. Fluorescence quantum yields (Φ_f) were measured relative to 9,10-diphenylanthracene as a reference standard [12]. Low sample concentrations ($\leq$0.1 absorbance units) were used to avoid reabsorption. The following relation has been applied to calculate the fluorescence quantum yields relative to those of 9,10-diphenylanthracene

$$\frac{\Phi_{f(s)}}{\Phi_{f(r)}} = \frac{\int I_s(v') \, dv'}{\int I_r(v') \, dv'} \frac{A_r n_s^2}{A_s n_r^2}$$

The integrals represent the corrected fluorescence peak areas. A is the absorbance at the excitation wavelength, n is the refractive index of the solvent used. The subscript 's' and 'r' refer to sample and reference, respectively, The fluorescence lifetime measurements were based on the time-correlated single-photon counting technique (TCSPC). The decay curves were analyzed using the method of iterative, nonlinear least squares [10]. The experimental details and the method of analysis are similar to those described in Ref. [13]. The lifetimes in the presence of oxygen were measured for aerated solutions in which oxygen concentration

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is known. Deoxygenation was then carried out by using argon that was bubbled through the liquid sample until all of the dissolved oxygen has been replaced. The microemulsion system used was based on chloroform as an oil, water, sodium dodecyl sulphate (SDS) as a surfactant and butanol as a co-surfactant. Oil in water (o/w) microemulsion system was prepared from water:chloroform:SDS:butanol in the ratio (by weight) 2.0:43.62:2.06:2.06, respectively. Water in oil (w/o) microemulsion system was prepared by mixing the same components in the ratio 37.075:4.308:4.308:4.308. Low temperature absorption spectra were measured using a modified commercial double beam UV-Vis Spectrometer of Varian (DMS 100). The probe holder is modified through a cooling head with a two-step closed cycle refrigerator kryostate (CTI). Low temperature emission were measured using a 150 W xenon high pressure lamp as light source followed by f/10 Gitter monochromator (Ziess, Modell MB3) as an excitation monochromator. The cooling of the sample is done through refrigerator kryostate (Leybold, ROK 10-300). A spex 1702-3/4m Gitter monochromator was used as an emission monochromator.

3. Results and discussion

3.1. Effect of solvent polarity

The electronic absorption and emission spectra of 9-phenyl-10-methoxy anthracene are carried out in organic solvents of varying polarities, namely, hexane, n-heptane, toluene, dioxane, carbon tetrachloride, chloroform, dimethylformamide, ethanol, butanol, ethylene glycol and glycerol. As shown in Table 1, PMA shows no significant change in both absorption and emission maxima on going from non-polar to polar solvents, indicating no change in the dipole moment and the polarity of the dye upon excitation.

The coincidence between the electronic absorption and excitation spectra of the dye in ethanol as in Fig. 1, together
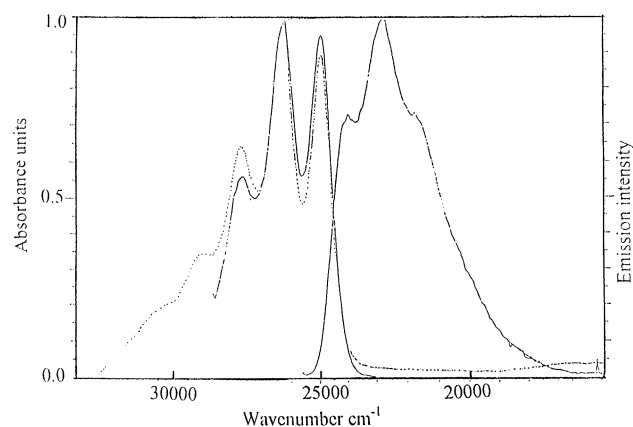

Fig. 1. Electronic absorption (···), excitation and emission spectra (-—) of 1×10^{-5} mol dm^{-3} PMA in ethanol. Excitation was monitored by following the emission maximum.

with the independence of emission maxima on the excitation wavelength reveals a high purity of sample and absence of tautomers. Fig. 2 shows the emission spectra of PMA in microemulsion media containing chloroform, sodium dodecyl sulfate (SDS) and butanol with different portions to form water/oil (w/o) and oil/water (o/w) microemulsion. PMA emission maximum in o/w is red shifted by ca. 13 nm compared with emission maximum in w/o. This is presumably due to excessive hydrogen bonding with dominant water molecules in o/w microemulsion.
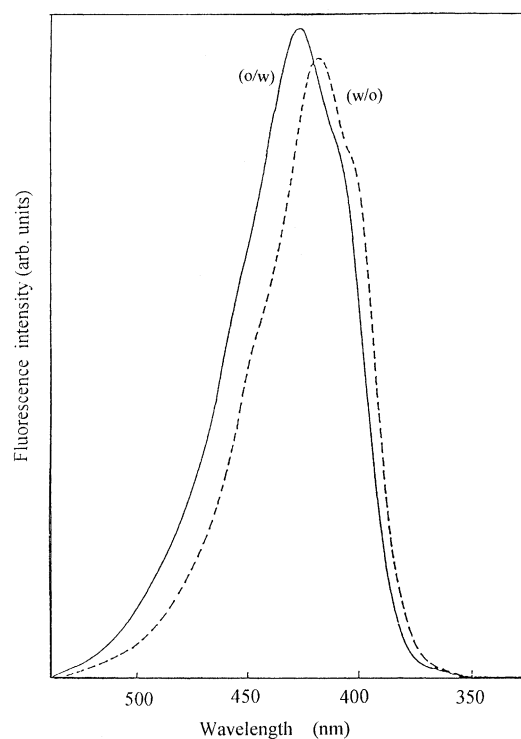
Table 1
Spectral data and Φ_f values of PMA in different solvents at room temperatures ($\lambda_{ex} = 365$ nm)

Solvent	λ_{ab} (nm)	λ_{em} (nm)	ε (dm^3 mol^{-1} cm^{-1})	Φ_f
BuOH	378	426	–	0.42
CHCl$_3$	378	426	9660	0.42
CH$_2$Cl$_2$	378	426	9500	0.40
CCl$_4$	376	426	9570	–
n-Heptane	376	420	–	0.32
Hexane	378	420	–	0.31
Toulene	378	419	–	0.31
Dioxane	378	424	10500	0.48
DMF	378	426	11250	0.37
EG	379	426	9860	0.42
Glycerol	378	426	10000	0.71
EtOH	378	426	–	0.20

Fig. 2. Emission spectra of 2×10^{-5} mol dm^{-3} PMA in (---) w/o and (—) o/w microemulsion system ($\lambda_{ex} = 365$ nm).
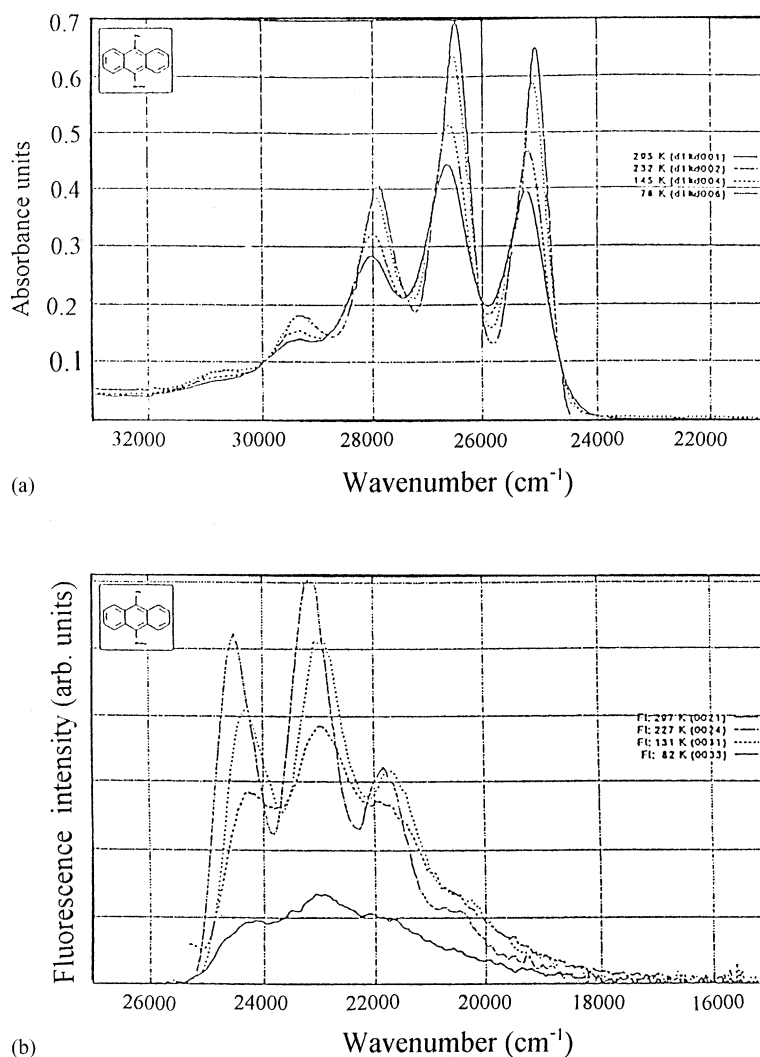
Fig. 3. (a) Low temperature absorption spectra of PMA in ethanol, the temperatures at increasing absorbance are 205, 232, 145, and 78 K. (b) Low temperature emission spectra of PMA in ethanol (5×10^{-5} mol dm^{-3}), the temperatures at increasing emission are 207, 227, 131 and 82 K.

3.2. Effect of temperature and medium viscosity

The electronic absorption and emission spectra of 1×10^{-5} M of PMA in ethanol were measured at different temperatures ranging from room temperature to 80 K. As shown in Fig. 3, there is a good mirror image relationship between low temperature absorption and fluorescence spectra of PMA in ethanol. On going with the temperature from room temperature to 80 K the electronic absorption spectra show a slight red shift and the spectral band width became narrow with 500 cm^{-1} at lowest temperature, indicating that no significant change in molecular structure of PMA, at least over the temperatures examined. In ethanol at 300 K PMA has low fluorescence quantum yield equal to 0.2 with decreasing temperature however the fluorescence quantum yield increase sharply ($\Phi_f = 0.9$ in ethanol at 82 K) as shown in Table 2. This is due to the lowering of twisting and molecular vibration which lead to the decrease

in radiationless processes. The relaxation processes in PMA molecules decreases with increasing the medium viscosity was observed by an increase of the fluorescence lifetime (τ_f) upon increasing solvent viscosity, as shown in Table 3.

Table 2
Fluorescence quantum yield of PMA in ethanol at different temperatures ($\lambda_{ex} = 365$ nm)

T (K)	Φ_f
300	0.20
240	0.73
210	0.75
200	0.82
180	0.82
160	0.84
130	0.85
100	0.87
82	0.90

Table 3
Lifetimes of PMA excited state in absence (τ_0) and in presence (τ) of molecular oxygen in different solvents ($\lambda_{ex} = 365$ nm)

Solvent	η (cP)	τ_0 (ns)	τ (ns)	k_q ($\times10^{-10}$ M^{-1} s^{-1})
CH$_3$CN	0.36	1.38	1.23	6.6
n-Hexane	0.31	1.52	1.31	3.4
CH$_3$OH	0.55	2.04	1.99	5.9
iso-Octane	0.50	2.38	2.29	5.3
Methylcyclohexane	0.73	2.48	2.11	3.8
EtOH	1.20	2.90	1.93	8.4
2-Propanol	2.26	2.94	2.62	2.0
n-Butanol	2.95	3.70	3.19	1.9
Glycerol	1412	7.53	–	–

A systematic decrease in the emission intensity of PMA in n-heptane is observed upon increasing temperature whereas no detectable effect was found in case of glycerol upon heating up to 85 °C indicating that the rigidity of glycerol is enough to inhibit the rotation of the phenyl group at the nine-position of the anthracene ring either at room temperature or at relatively high temperature. This conclusion could be confirmed by high fluorescence quantum yield ($\Phi_f = 0.71$) and long excited state lifetime ($\tau_f = 7.53$ ns) in glycerol. Temperature variation experiments were performed to calculate the activation energy associated with fluorescence intensity in heptane. The value of activation energy E_a, was calculated using the following equation [10]:

$$\ln(1/\Phi_f - 1) = A + (E_a/RT) \qquad (1)$$

E_a was found to be 9.6 kJ mol^{-1} which is very close to the value of activation energy associated with solvent viscosity $E_\eta = 10.04$ kJ mol^{-1} indicating that the change in Φ_f value is mainly due to the change in the viscosity and this is confirmed by the high fluorescence quantum yield of PMA in glycerol ($\Phi_f = 0.71$) compared with that in ethanol ($\Phi_f = 0.20$).

3.3. Fluorescence quenching of PMA by oxygen molecule

The role of molecular oxygen in the deactivation of excited singlet state of PMA has been studied in different solvents of different viscosities. The bimolecular quenching rate constants k_q have been determined using the Stern–Volmer relation in the following form [14]:

$$k_q[O_2] = \frac{1}{\tau} - \frac{1}{\tau_0} \qquad (2)$$

where τ_0 and τ are the fluorescence lifetimes in the absence and presence of oxygen molecules, respectively. As shown in Table 3 the k_q values are in the range of k_{diff} indicating a collision mechanism is obeyed. Since the excited singlet state (s$_1$) of PMA has enough energy to populate $^1\Delta_g$ of oxygen molecule, the following mechanism has been
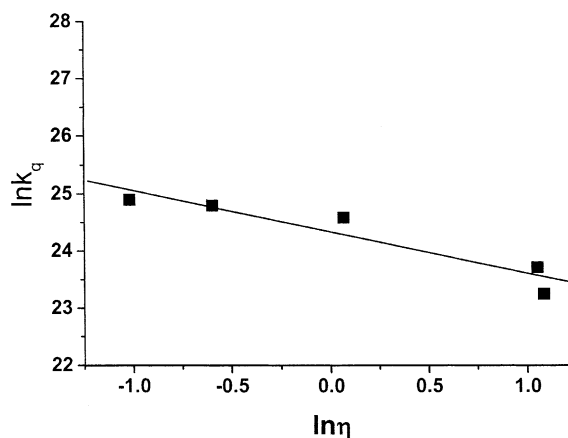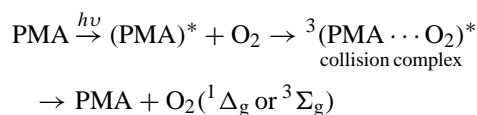

Fig. 4. Plot of $\ln \eta$ vs. $\ln k_q$ in polar solvents.

proposed for quenching by molecular oxygen:

$$PMA \xrightarrow{h\upsilon} (PMA)^* + O_2 \rightarrow {}^3(PMA \cdots O_2)^*_{\text{collision complex}}$$

$$\rightarrow PMA + O_2(^1\Delta_g \text{ or } ^3\Sigma_g)$$

The viscosity dependence of k_q for diffusion controlled bimolecular reaction is described by the following equation (3) [14]:

$$k_q = A\eta^{-\alpha} \qquad (3)$$

The $\ln k_q$ value decreases with increasing $\ln \eta$ (Fig. 4) and the slope (α) was found to be 0.72 in polar solvents indicating strong power dependence of k_q on the viscosity.

4. Conclusion

From our study we conclude that PMA has the same dipole moment in ground and excited state, the fluorescence lifetime and fluorescence quantum yield increase by lowering temperature of the medium or by increasing the medium viscosity and also the quenching by molecular oxygen is affected by the medium viscosity and obey the diffusion controlled mechanism in polar solvents.

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