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Emission characteristics and photostability of 1,4-bis[β-(2-benzoxazolyl)vinyl]benzene (BBVB) laser dye

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Abstract

The fluorescence efficiencies (Φ_f) of 1,4-bis[β-(2-benzoxazolyl)vinyl]benzene (BBVB) have been measured in various hydrogen bonding and non-hydrogen bonding solvents of different polarities on the π^* scale. In hydrogen bonding solvents Φ_f increases with increasing π^* value. The fluorescence has also been studied in other media, including micellar, microemulsion and acidic ones. BBVB solutions exhibit short excited state lifetimes in the range 0.5–0.7 ns.

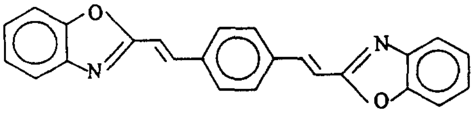
The second-order rate constant of oxygen and rhodamine 6G (R6G) quenching of BBVB fluorescence have been determined from Stern–Volmer relations. The critical transfer distances for the BBVB/R6G system have been determined as $R_0 = 46.8$ and 48.5 Å in ethanol and methanol respectively. The photochemical quantum yields (Φ_c) have also been determined in various organic solvents.

Keywords: 1,4-Bis[β-(2-benzoxazolyl)vinyl]benzene; Laser dyes; Lifetimes; Energy transfer; Medium effect

1. Introduction

Benzoxazole derivatives find several applications in many areas. They have been applied as fluorescent whitening agents [1,2] emitting in the wavelength region from 436 to 490 nm. Several benzoxazole derivatives are also reported as laser dyes of reasonable photostability [2–8]. Other applications are in UV stabilization of polymers [9], electrochromic display and optical imaging devices [10,11] and electroluminescent devices [4]. Certain benzoxazole derivatives act as antifungal and antibacterial compounds [12].

In this paper we report on the emission characteristics and photostability of 1,4-bis[β-(2-benzoxazolyl)vinyl]benzene (BBVB), which is the ancestor of several benzoxazole derivatives:



BBVB

2. Experimental details

BBVB was synthesized and characterized as reported previously [13]. Steady state fluorescence, fluorescence and photochemical quantum yields were measured using a Shimadzu RF 510 spectrofluorophotometer. The fluorescence spectra were corrected for the machine response using 10^{-5} mol dm^{-3} anthracene solution in benzene in correction as reported earlier by Melhuish [14]. UV–visible absorption spectra were recorded on a Shimadzu UV 160A spectrophotometer. Fluorescence quantum yields (Φ_f) were measured relative to 9,10-diphenylanthracene as a reference standard [15]. Low sample concentrations (less than 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:

$$\frac{\Phi_f(s)}{\Phi_f(r)} = \frac{\int I_s(\bar{\nu})d\bar{\nu}}{\int I_r(\bar{\nu})d\bar{\nu}} \frac{A_r}{A_s} \frac{n_s^2}{n_r^2}$$

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 and the subscripts "s" and "r" refer to the sample and reference respectively. Excited state lifetimes were measured using the facilities at

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the Chemistry Laboratory, Kyoto Institute of Technology, Japan, based on an experimental set-up described elsewhere [16]. The lifetimes in the presence of oxygen were measured for aerated solutions in which the oxygen concentration had been measured using an oxygen meter. Deoxygenation was then carried out by bubbling argon through the liquid sample until all the dissolved oxygen had been replaced. Photochemical quantum yields (Φ_c) were measured using a modified method that takes into account the decrease in absorbance at the excitation wavelength as photoirradiation proceeds. The methods is due to A.J. Lees of Binghamton University, New York and is summarized elsewhere [17]. The microemulsion system used was based on chloroform as the oil, water, sodium dodecyl sulphate (SDS) as the surfactant and butanol as the co-surfactant [18]. An oil-in-water (O/W) microemulsion system was prepared from water, chloroform, SDS and butanol in the ratio (by weight) 2.0:43.62:2.06:2.06. A water-in-oil (W/O) microemulsion system was prepared by mixing the same components in the ratio 37.075:4.308:4.308:4.306.

3. Results and discussion

Fig. 1 shows the emission ($\lambda_{ex} = 365$ nm), excitation and electronic absorption spectra of BBVB in two solvents of different polarities. The solvent polarity shows a slight effect on the position of the spectral maxima, indicating a small change in dipole moments on going from ground state to excited state. There is also a good mirror image relationship between absorption and fluorescence spectra. These facts are consistent with a strongly allowed transition with small geometry changes between electronic ground and excited states. In non-polar solvents, however, e.g. *n*-heptane, the fluorescence spectrum becomes more structured compared with polar solvents, e.g. dimethylformamide (DMF). In both cases the Franck–Condon peak occurs at the second vibrational peak. The fluorescence quantum yields (Φ_f) are much more affected by the solvent properties. Two types of behaviour are experienced in non-hydrogen bonding (NHB) and hydrogen bonding (HB) solvents. Fig. 2 shows a plot of Φ_f vs. the π^* scale of solvent polarities reported earlier by Kamlet et al. [19]. In HB solvents (including methylene chloride, which compares with chloroform) Φ_f generally increases as π^* increases. A modified relation of the form $\Phi_{max} = \Phi_0 + s\pi^*$ nearly applies to the present system with $s \approx 1.75$. The high Φ_f value associated with dioxane is presumably due to a specific solvent effect characterizing this solvent, leading to spectral anomalies as reported by other authors [19,20]. The high Φ_f values in dioxane have been confirmed by studying the variation in Φ_f in mixed dioxane–methanol and dioxane–acetonitrile solvents. The decrease in Φ_f as the proportion of methanol or acetonitrile increases is shown in Fig. 3 and can be attributed to efficient internal conversion and/or intersystem crossing by extensive mixing between the close-lying lowest $^1(\pi,\pi^*)$ and $^1(n,\pi^*)$ states.

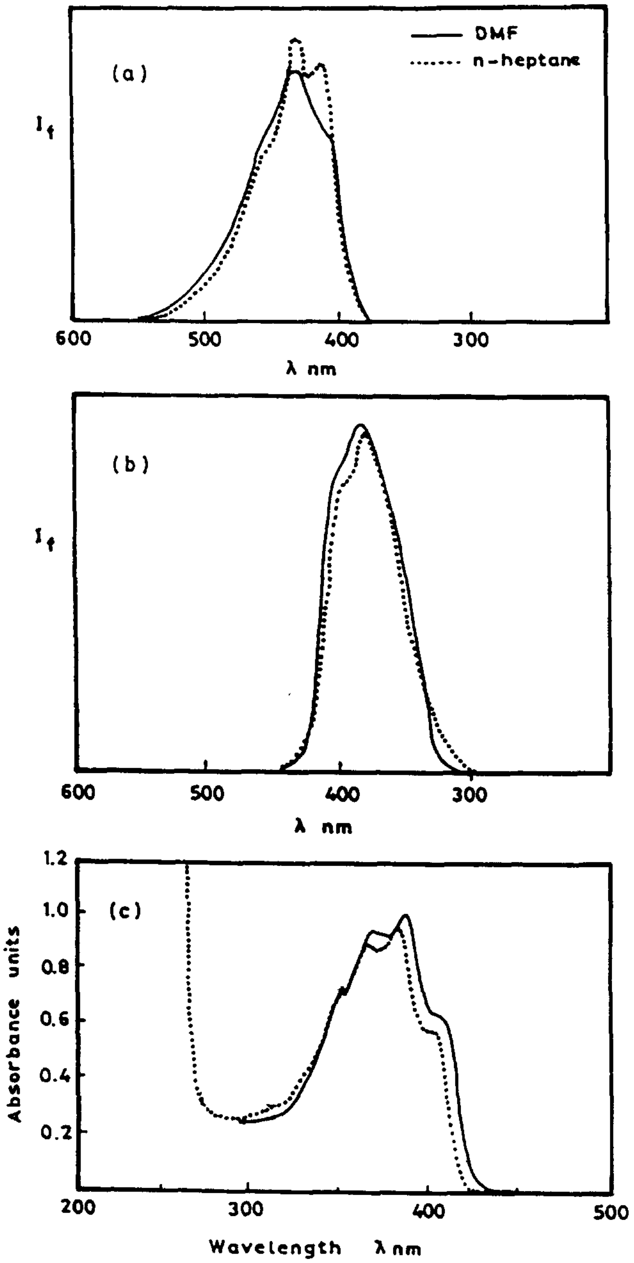

Fig. 1. (a) Emission ($\lambda_{ex} = 365$ nm), (b) excitation and (c) electronic absorption spectra of 5×10^{-6} mol dm^{-3} BBVB solutions in DMF and *n*-heptane. Excitation spectra were measured by following the emission maxima.

In addition, the non-radiative rate increases markedly in solvents with strong hydrogen bonding character and competes with fluorescence emission [21,22]. In NHB solvents, on the other hand, Φ_f decreases as π^* increases. (It has been reported [19] that chloroform usually acts as a non-hydrogen bonding solvent but has shown weak hydrogen bond donation properties with strong hydrogen acceptor indicator solutes.)

BBVB is insoluble in water. As expected, it undergoes solubilization in anionic micelles, e.g. SDS, with a subsequent increase in fluorescence intensity. An abrupt increase in fluorescence intensity is observed at a surfactant concen-

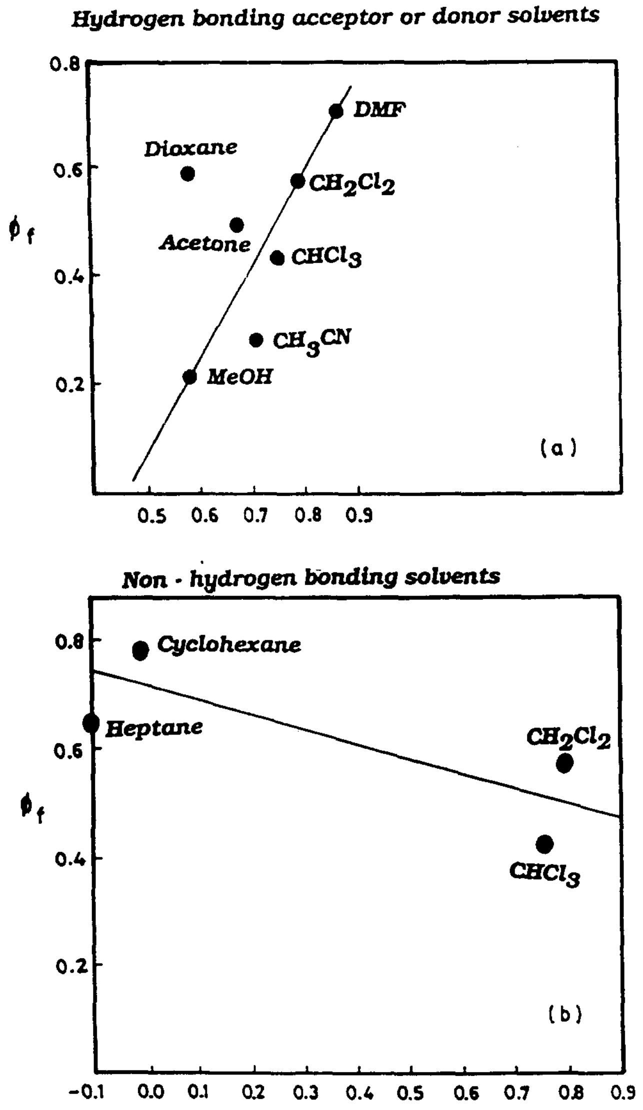

Fig. 2. Plots of Φ_f vs. π^* value for (a) hydrogen bonding and (b) non-hydrogen bonding solvents.

tration corresponding to the critical micelle concentration (CMC) as shown in Fig. 4.

BBVB emission efficiencies have been measured in microemulsion media containing chloroform as the oil, SDS as the surfactant and butanol as the co-surfactant. A Φ_f value as high as 0.59 is obtained in a W/O microemulsion, but a low value of 0.29 is obtained in an O/W microemulsion. The Φ_f value in W/O is higher than that measured in bulk chloroform, whereas the Φ_f value in O/W is lower than that measured in bulk chloroform ($\Phi_f = 0.42$). It seems that BBVB is solubilized at the oil–water interface in both cases, with a quenching role of water in the W/O system. Table 1 summarizes the Φ_f values and spectral data of BBVB in various media.

The effect of medium acidity on the absorption and fluorescence spectra of BBVB has been tentatively examined. Acidification of BBVB solution in DMF by adding drops of HCl leads to a decrease in absorbance at 405 and 381 nm and a relative increase in absorbance at 366 and 300 nm. This is obviously due to protonation of heterocyclic nitrogen atoms with subsequent masking of non-bonding electrons. The fluorescence intensity is substantially reduced upon protonation and this deprives the BBVB dye of the possibility of pH tuning as a laser dye.

The lifetime values of BBVB in various organic solvents are summarized in Table 2. The lifetimes are short (in the region of 0.6 ns) and become even shorter in the presence of dissolved molecular oxygen. From the lifetime values in the presence of dissolved oxygen (τ) and in the absence of oxygen (τ_0) the second-order quenching rate constant (k_q) has

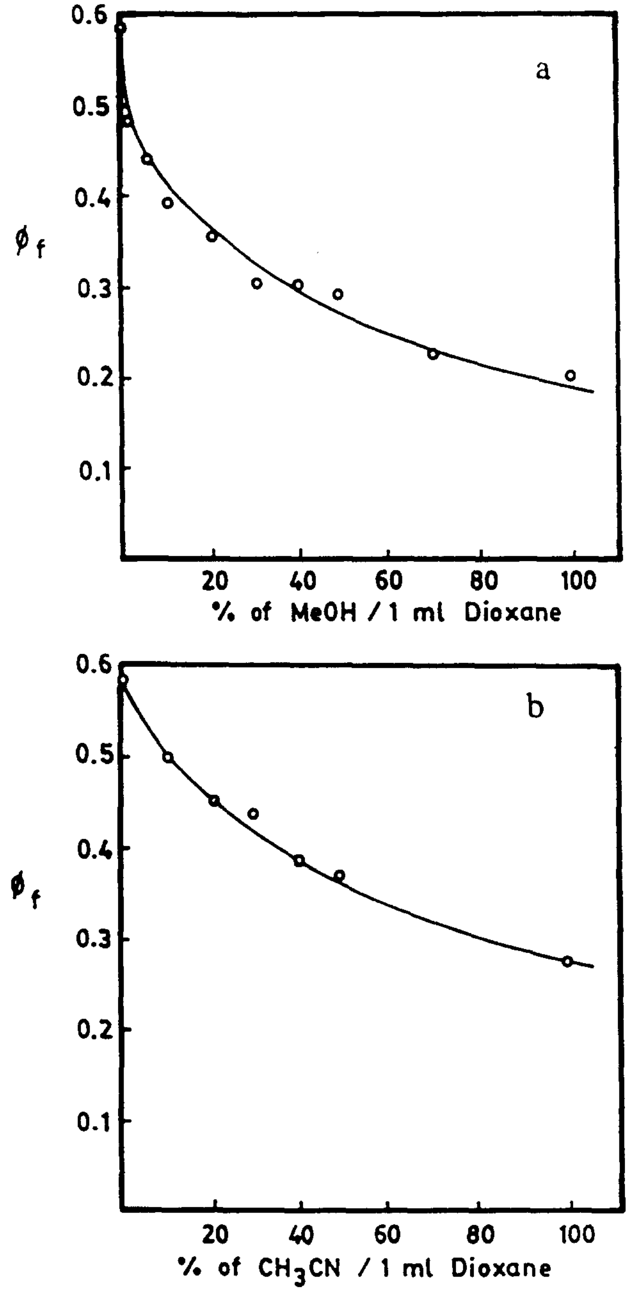

Fig. 3. Changes in Φ_f value in mixed (a) methanol–dioxane and (b) acetonitrile–dioxane solvents.

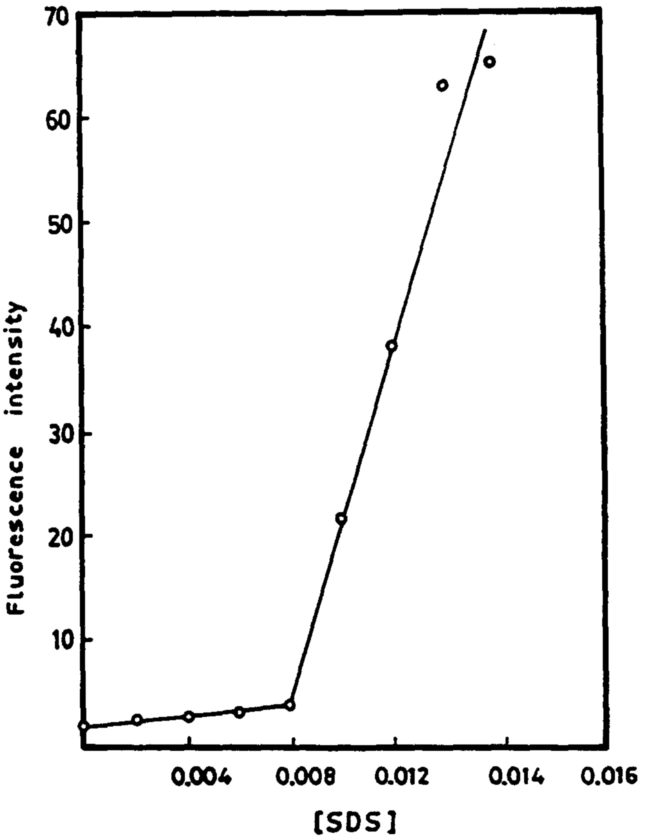

Fig. 4. Changes in fluorescence intensity in SDS solutions of various concentrations ($\lambda_{ex}=365$ nm, $\lambda_{em}=430$ nm).

been determined in various organic solvents by applying the Stern–Volmer relation

$$k_q[O_2]=\frac{1}{\tau}-\frac{1}{\tau_0}$$

where $[O_2]$ (mol dm^{-3}) is the concentration of dissolved oxygen in aerated samples. Table 2 summarizes the k_q values in the studied solvents. The quenching of BBVB fluorescence has also been studied using another laser dye as a quencher. Rhodamine 6G (R6G) has been applied as an excited state quencher. The BBVB/R6G system represents a useful energy transfer dye laser (ETDL) system achieving better harvesting of light photons at 337 nm (the wavelength of the pumping nitrogen laser). Fig. 5 shows the Stern–Volmer plot of BBVB fluorescence quenching using R6G as a quencher. The Stern–Volmer relation is of the form [23]

$$\frac{I_0}{I}=1+k_q\tau[Q]$$

where I_0 and I are the fluorescence intensities in the absence and presence of quencher of concentration [Q] (mol dm^{-3}) respectively, k_q (dm^3 mol^{-1} s^{-1}) is the second-order quenching rate constant and τ is the solution lifetime, taken as 0.62 ns in methanol. From the slope in Fig. 5, k_q has been calculated as 2.6×10^{13} dm^3 mol^{-1} s^{-1}. This value is much higher than the diffusion rate constant (k_{diff}) in methanol at room

Table 1

Spectral data and Φ_f and Φ_c values of BBVB in various media

Solvent	λ_{max} (nm)			ϵ (dm^3 mol^{-1} cm^{-1})		Φ_f			Φ_c		π^*
	Abs.	Ex.	Em.	λ_{max}	λ_{337}	λ_{max}	λ_{365}	λ_{337}	λ_{max}	λ_{337}	
n-Heptane	378	380	428	48864	35488	0.78	0.75	0.4	–	–	0.081
Cyclohexane	380	380	430	–	–	0.78	–	–	–	–	0.000
1,4-Dioxane	384	384	435	50468	38852	0.58	–	–	–	–	0.553
$CHCl_3$	384	392	440	52480	34909	0.42	–	–	0.032	0.024	0.750
CH_2Cl_2	382	385	440	51940	35594	0.68	–	–	–	–	0.802
Acetone	380	380	435	59477	42853	0.49	–	–	–	–	0.683
EtOH	381	381	435	54181	33163	0.5	0.4	0.3	0.023	0.014	0.540
MeOH	384	385	438	54180	33160	0.216	–	–	–	–	0.586
CH_3CN	384	384	434	58311	34241	0.32	–	–	–	–	0.713
DMF	381	384	436	58300	36771	0.73	0.73	0.42	0.029	0.017	0.875
W/O	383	384	438	52480	34211	0.589	–	–	–	–	–
O/W	383	384	438	52480	35084	0.29	–	–	–	–	–
EG	386	386	440	–	–	–	–	–	–	–	0.432

temperature. From the spectral data there is a significant overlap between the electronic absorption of R6G and the emission of BBVB. The critical transfer distance R_0 has been calculated for the BBVB/R6G system by applying the relation [23]

$$R_0^6 = 1.25 \times 10^{-25} \frac{\Phi_D}{n^4} \int_0^{\infty} F_D(\bar{\nu}) \epsilon_A(\bar{\nu}) \frac{d\bar{\nu}}{\bar{\nu}^4}$$

where R_0 is the distance at which the energy transfer and emission processes are equally probable. Φ_D is the emission quantum yield of the donor in the absence of acceptor, n is the solvent refractive index and the integral is the overlap integral for the fluorescence spectrum of donor normalized to unity (F_D) and the absorption spectrum of acceptor (ϵ_A) divided by the fourth power of the wavenumber ($\bar{\nu}$).

Accordingly, $R_0 = 46.8$ Å in ethanol and 48.5 Å in methanol. These values are much higher than those characterizing collisional energy transfer, for which R_0 is in the range 4–6 Å [24], indicating that the underlying mechanism of energy transfer is that of resonance energy transfer due to long-range dipole–dipole interaction between excited donor and ground state acceptor.

The photostability of BBVB in various organic solvents has been studied by measuring the photochemical quantum yields (Φ_c). Fig. 6 shows the effect of photoirradiation ($\lambda_{ex} = 381$ nm) on the electronic absorption spectrum of a 1.5×10^{-5} mol dm^{-3} solution of BBVB in DMF. A photoproduct is obtained with the build-up of absorbance at about 300 nm and a sharp single isosbestic point is obtained at 336 nm. At such low concentration of BBVB, bimolecular processes in the form of photodimerization are believed to be negligible. The prevailing photoreaction is thought to be a trans–cis photoisomerization reaction. Some benzoxazole derivatives are known to undergo a photodimerization process that involves the C=N double bond, but only at high concentrations of about 0.1 mol dm^{-3} [25]. The Φ_c values of BBVB in various organic solvents using two different excitation wavelengths are summarized in Table 1. Both Φ_f and Φ_c are wavelength dependent: lower Φ_f and Φ_c values are obtained upon excitation with 337 nm light than with 365 nm light. This can be explained in terms of the existence of various conformers exhibiting different photophysical and photochemical characteristics [26–28].

Table 2

Excited state lifetimes of BBVB solutions in the presence (τ) and absence (τ_0) of molecular oxygen ($\lambda_{ex} = 365$ nm, $\lambda_{em} = 420$ nm). The second-order quenching rate constants k_q in various solvents are also given

Solvent	τ_0 (ns)	τ (ns)	k_q (10^{10} dm^3 mol^{-1} s^{-1})
Acetone	0.56	0.51	7.3
CH_3CN	0.52	0.49	6.8
MeOH	0.69	0.62	7.7
EtOH	0.72	0.68	4.9
1-Propanol	0.52	0.50	3.7
2-Propanol	0.51	0.50	1.9
$CHCl_3$	0.63	0.61	4.7
Benzene	0.51	0.50	2.05
Iso-octane	0.56	0.53	3.2

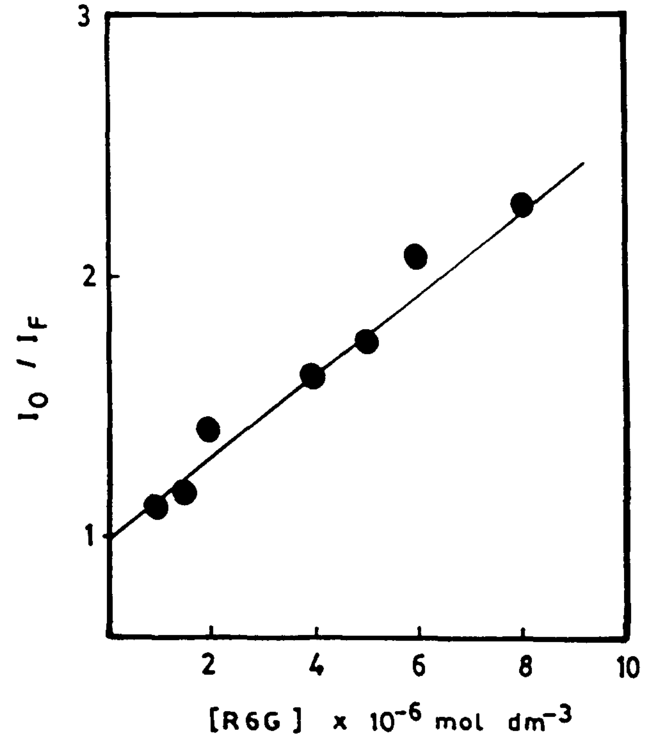

Fig. 5. Stern–Volmer plot of BBVB fluorescence quenching using R6G as a quencher in methanol at room temperature ($\lambda_{ex} = 365$ nm, $\lambda_{em} = 430$ nm).

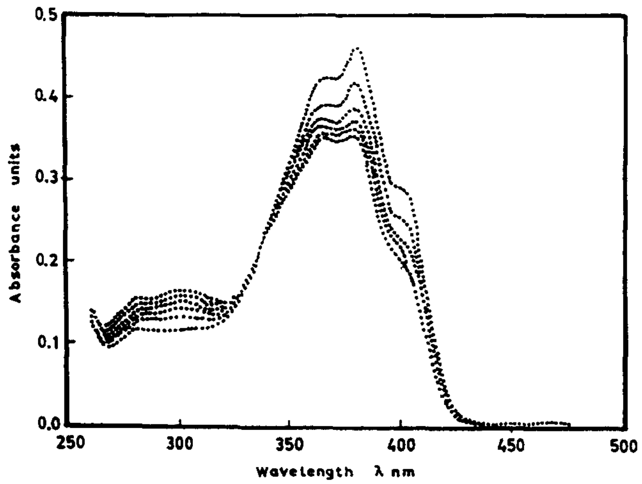

Fig. 6. Effect of photoirradiation ($\lambda_{ex} = 381$ nm) on absorption spectrum of 1.5×10^{-5} mol dm^{-3} solution of BBVB in DMF. The irradiation times for decreasing absorbance are 0, 5, 10, 15, 30, 50 and 81 min.

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