Fluorescence quenching of N,N'-bis(2,5-di-tert-butylphenyl)-3,4:9,10-perylenebis(dicarboximide) (DBPI) by molecular oxygen

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Abstract

The effect of the solvent viscosity on the fluorescence quenching of N,N'-bis(2,5-di-tert-butylphenyl)-3,4:9,10-perylenebis(dicarboximide) (DBPI) by molecular oxygen was investigated by measuring the fluorescence decay. The solvent viscosity was changed by using different solvents at 0.1 MPa and by application of hydrostatic pressure. The quenching rate constant k_q in non-polar solvents increased with increasing solvent viscosity η, whereas in polar alcoholic solvents it decreased with increasing solvent viscosity and followed a function of $A\eta^{-\alpha}$ with $\alpha = 0.48 \pm 0.12$. When the viscosity was changed by application of hydrostatic pressure, k_q of DBPI was also found to follow a function of $A\eta^{-\alpha}$ with α values of 0.71 ± 0.02 and 0.58 ± 0.08 in methanol and methylcyclohexane respectively. However, in n-hexane, the k_q values exhibited a convex shape vs. viscosity. The activation energies associated with the fluorescence quenching of DBPI were calculated to be $E_a = 9.87 \pm 1.2$, 14.1 ± 0.24 and -3.96 ± 0.6 kJ mol^{-1} in methanol, methylcyclohexane and n-hexane respectively. The negative activation energy and the convex shape of the viscosity dependence of k_q obtained in n-hexane indicate complex formation between DBPI* and molecular oxygen prior to fluorescence quenching. The large molecular size of DBPI does not increase the magnitude of k_q or influence its dependence on η.

Keywords: Fluorescence quenching; Pressure effect; Viscosity dependence; DBPI; Diffusion-controlled reaction; Diffusion coefficient; Ox_gen; Activation energy

1. Introduction

Molecular oxygen is an efficient quencher of many organic fluorophores [1–14]. In most cases, this quenching is so efficient that the reaction rate is believed to be diffusion controlled. It is often claimed that a given quenching reaction is diffusion controlled if its rate constant exceeds a value of approximately 10^{10} M^{-1} s^{-1} or sometimes smaller [4]. However, the quenching rate constant depends on various factors, such as the excited state energy of the fluorophore, the electronic configuration of the excited molecule, the redox properties of the excited molecule, the molecular structure and the solvent or molecular environment [15–21]. It is important to make a distinction between fully diffusion-controlled reactions and those that are nearly diffusion controlled since, in the latter case, the quenching reactions are not infinitely fast and encounter complexes with long lifetimes may be involved.

The great interest in quenching by molecular oxygen derives from the fact that it is ubiquitous in nature and possesses several unusual properties which account for its ability to quench electronically excited states efficiently, virtually without exception. The special properties include the triplet spin multiplicity of molecular oxygen in its ground state which can enhance intersystem crossing processes in organic molecules, the presence of two low-lying excited singlet states with energies of 94 and 157 kJ mol^{-1} which may be populated by the quenching of excited states via energy transfer [15] and the relative ease of reduction of molecular oxygen to superoxide ion. Various mechanisms for fluorescence quenching by molecular oxygen have been proposed related to these properties [1,19].

In previous papers [22,23], certain photophysical characteristics of N,N'-bis(2,5-di-tert-butylphenyl)-3,4:9,10-perylenebis(dicarboximide) (DBPI) have been reported, e.g. a fluorescence quantum yield of unity, high photostability, molecular aggregation in the ground and excited states, laser activity, effect of medium polarity and acidity on the electronic spectrum, energy transfer from certain blue laser

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Table 1
Fluorescence quenching of 5×10^{-6} M DBPI in different solvents

Solvent	[O$_2$] [a] (mM)	η [a] (cP)	τ_0 [b] (ns)	τ [b] (ns)	$k_q/10^9$ (M^{-1} s^{-1})	$k_{diff}/10^9$ (M^{-1} s^{-1})
n-Hexane	3.09	0.313	3.83	3.65	4.2 ± 0.1	33
Isooctane	3.18	0.504	3.62	3.32	8.0 ± 0.2	21
Benzene	1.91	0.649	3.87	3.59	10.3 ± 0.3	16
Methylcyclohexane	2.50	0.734	3.76	3.38	12.0 ± 0.2	14.1
Methanol	2.12	0.550	3.69	3.36	12.0 ± 0.2	18
1-Propanol	2.30	1.078	3.59	3.39	7.4 ± 0.4	9.2
2-Propanol	2.16	2.256	3.58	3.41	6.2 ± 0.3	4.5
n-Butanol	2.11	2.859	3.58	3.44	5.5 ± 0.1	3.5
	1.80	2.948	3.48	3.38	4.7 ± 0.2	3.4

[a] Values taken from Ref. [25].

[b] Errors associated with the fluorescence lifetimes are ± 0.08 ns.

dyes and the deactivation of the excited singlet state by cobalt ions. DBPI is potentially useful in energy and electron transfer reactions, in site-selective spectroscopy experiments with biological systems, in p–n heterojunction solar cells and as a laser dye [23]. Another important feature of DBPI is its molecular size, which is more than three times larger than that of anthracene derivatives, for which the dependence of the fluorescence quenching by oxygen on the solvent viscosity has been studied extensively [2,14]. The reaction rate of collision-mediated fluorescence quenching, such as by oxygen, is dependent on the reaction distance (encounter distance) and the diffusion coefficient, both of which are determined by the molecular sizes of the reacting pair. Therefore DBPI is expected to provide an interesting system for the study of the dependence of the fluorescence quenching rate constant k_q on η.

In this paper, we report the deactivation of singlet excited DBPI by molecular oxygen in different organic solvents. The effect of hydrostatic pressure on k_q was also studied in methanol, methylcyclohexane and n-hexane using the time-correlated single-photon counting (TCSPC) method on a nanosecond time scale. The effect of the concentration of DBPI on the fluorescence quenching rate constant was also examined in chloroform.
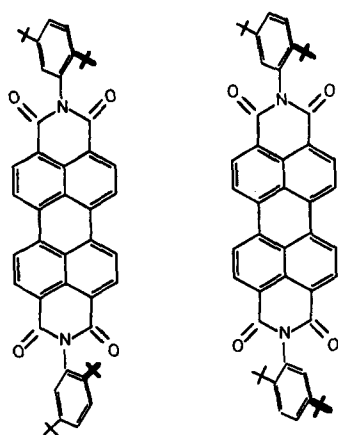
DBPI

2. Experimental section

DBPI was kindly supplied by Professor H. Langhals of Munich University. It was dissolved in a minimum volume of chloroform, the solution was filtered and the dye was precipitated by adding methanol. The precipitate was collected by filtration and dried in vacuum. All the solvents used in this work were of spectroscopic grade.

The fluorescence decay curves were measured using the TCSPC technique. The decay curves obtained were analysed using the method of iterative, non-linear, least squares [13]. The experimental details of the fluorescence decay curve measurements at high pressure and the analysis of the decay data have been described elsewhere [4]. The applied pressure was calibrated against a manganin gauge. The concentration of DBPI was kept below 1×10^{-5} M to avoid self-absorption effects [24]. The sample solutions were deaerated by bubbling with either solvent-saturated argon or nitrogen gas for 20 min. This procedure was found to be sufficient to remove dissolved oxygen by a comparison of the fluorescence lifetime measured at 0.1 MPa with that of a solution which had been degassed by repeated freeze–pump–thaw cycles. The temperature of the sample solutions was kept at 25 ± 0.1 °C using a thermoregulated water bath. The concentrations of oxygen in the solvents used in this work were obtained from Ref. [25] or determined by gas chromatography with a 5 Å molecular sieve column [4]. The change in the concentration of oxygen accompanying the volume change caused by the application of pressure was accounted for by using the compressibility of the solvents [26]. Diffusion coefficients at 0.1 MPa were measured by the Taylor dispersion method [27]. In this method, a small amount of a solution is injected into a solvent flowing through a capillary tube. The solute is dispersed along the tube as a result of a combination of convection and diffusion. By detecting the concentration profile at the end of the stream, the diffusion coefficient can be calculated.

3. Results and discussion

3.1. Solvent effect on the fluorescence quenching

The fluorescence decays of 5×10^{-6} M DBPI were found to be single exponential under both aerated and deaerated conditions in the polar alcoholic and non-polar solvents used in this work. The rate constant for the quenching of the electronically excited singlet state of DBPI (DBPI*) by oxygen in homogeneous solution was obtained from

$$k_q[O_2] = 1/\tau - 1/\tau_0 \qquad (1)$$

where τ_0 and τ are the fluorescence lifetimes in the absence and presence of oxygen respectively, [O$_2$] is the bulk concentration of oxygen in solution and k_q is the second-order quenching rate constant. The k_q values obtained in various solvents are summarized in Table 1, together with other rel-
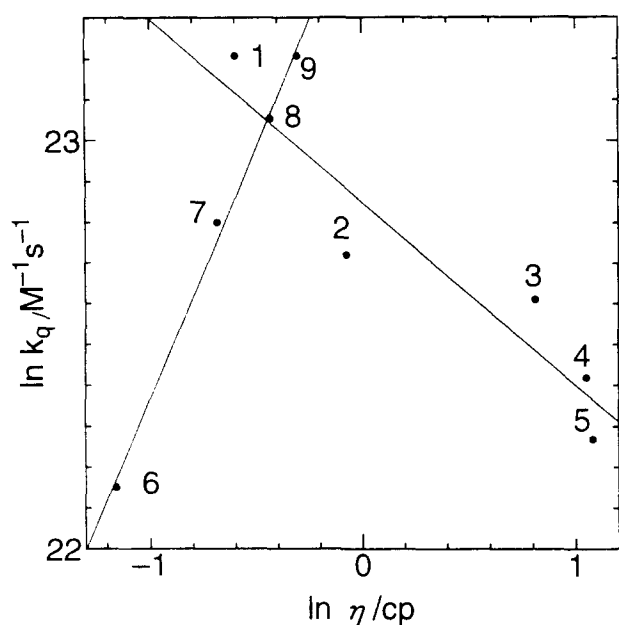
Fig. 1. Plot of ln k_q as a function of ln η for 5×10^{-6} M DBPI at 25 °C. The viscosity was changed by using different solvents at 0.1 MPa. The solvents are: (1) methanol; (2) ethanol; (3) 1-propanol; (4) 2-propanol; (5) n-butanol; (6) n-hexane; (7) isooctane; (8) benzene; (9) methylcyclohexane.

evant data. As can be seen from Table 1, the bimolecular quenching rate constant k_q increases with increasing viscosity of the non-polar solvents and the k_q values are significantly smaller than the diffusion-controlled bimolecular reaction rate constant k_{diff} given by $8RT/2000\eta$. However, in alcoholic solvents, the k_q values decrease monotonically with increasing solvent viscosity and are close to the corresponding k_{diff} values.

The viscosity dependence of k_q for diffusion-controlled bimolecular reactions is phenomenologically described by [2]

$$k_q = A\eta^{-\alpha} \tag{2}$$

where the parameters A and α are assumed to be constants that are invariant with η. Values for α ranging from zero to unity have been reported [1] for a number of bimolecular chemical reactions. A plot of ln k_q vs. ln η yields two straight lines as shown in Fig. 1. In alcoholic solvents, the value of α obtained from the slope in Fig. 1 is 0.48 ± 0.12, whereas the quenching of DBPI in non-polar solvents yields a negative value of -1.18 ± 0.08 for α. Such an anomalous trend, i.e. the negative value for α in non-polar solvents, has not been found at least for the anthracene derivatives studied so far [2,3,14].

The fluorescence quenching of perylene, the parent moiety of DBPI, by molecular oxygen in different alcoholic solvents has been studied previously [1,6], and the values reported for k_q are 3×10^{10}, 2.7×10^{10}, 2.6×10^{10} and 1.9×10^{10} M^{-1} s^{-1} in methanol, ethanol, 1-propanol and n-butanol respectively. As shown in Table 1, the k_q values of DBPI are smaller than those of perylene by factors of 2.5, 3.6, 4.2 and 4.04

respectively in the same solvents. The diffusion coefficient D of DBPI was measured to be 0.59×10^{-9} m^2 s^{-1} in methanol at 25 °C and is smaller than that for perylene ($D = 1.37 \times 10^{-9}$ m^2 s^{-1} in methanol at 25 °C) by a factor of more than two. Schumpe and Lühring [28] measured the D values of oxygen in various solvents and plotted them as a function of η. A good correlation between D and η at 20 °C allows the D value of oxygen in methanol to be calculated. To correct for the temperature variation of D, the Stokes–Einstein equation can be used. The value thus obtained for the diffusion coefficient of oxygen in methanol at 25 °C is 4.01×10^{-9} m^2 s^{-1}. From this value and that measured for DBPI, the sum of the diffusion coefficients for DBPI and oxygen is calculated to be 4.60×10^{-9} m^2 s^{-1}, which is not much different from that calculated for perylene and oxygen. This is due to the large D value of oxygen. On the other hand, the molecular size of DBPI is more than twofold larger than that for perylene, but the quenching rate constant of perylene is about three or four times larger than that for DBPI. This indicates that every collision of oxygen with DBPI is not effective for quenching.

The effect of temperature on the fluorescence quenching of DBPI by molecular oxygen was also studied in methanol, n-hexane and methylcyclohexane in the range 15–50 °C. The activation energy values E_a associated with k_q were calculated by assuming the Arrhenius equation for k_q

$$k_q = B \exp(-E_a/RT) \tag{3}$$

The values obtained are 9.87 ± 1.2 kJ mol^{-1} and 14.1 ± 0.24 kJ mol^{-1} in methanol and methylcyclohexane respectively. Although these values are very close to the activation energy values associated with the solvent viscosity, $E_\eta = 10.4$ and 14 kJ mol^{-1} in methanol and methylcyclohexane respectively, this does not necessarily indicate that the fluorescence quenching of DBPI by oxygen is fully diffusion controlled [2,14]. On the other hand, the activation energy obtained in n-hexane is -3.96 ± 0.62 kJ mol^{-1}. This negative activation energy suggests the formation of a weakly bound encounter complex between DBPI* and molecular oxygen prior to fluorescence quenching [10,29].

3.2. Pressure effect on the fluorescence quenching

The application of pressure is a very useful technique for studying diffusion processes, since the viscosity of a solvent can be changed continuously over a wide range while other properties of the solvent remain practically constant. The apparent rate constant $k_q(p)$ for the quenching of DBPI* by molecular oxygen under high pressure was calculated using

$$k_q(p) = \{1/\tau(p) - 1/\tau_0(p)\}/[O_2]_p \tag{4}$$

where $\tau_0(p)$ and $\tau(p)$ are the fluorescence lifetimes of DBPI in the absence and presence of molecular oxygen at the applied pressure p respectively and $[O_2]_p$ is the concentration of oxygen at this pressure which was calculated using the known compressibility of the solvent.

Table 2

Pressure dependence of k_q for 5×10^{-7} M DBPI in methylcyclohexane at 25 °C

p (MPa)	η (cP)	$[O_2]/10^{-3}$ [a] (M)	τ_0 (ns)	τ (ns)	$k_q(p)/10^9$ $(M^{-1} s^{-1})$
0.1	0.661	6.26	3.76	2.87	12.0 ± 0.2
50	1.064	8.22	3.54	2.93	7.2 ± 0.1
100	1.622	8.22	3.51	3.04	5.4 ± 0.3
150	2.342	8.16	3.46	3.06	4.3 ± 0.1
200	3.631	8.61	3.45	3.09	3.8 ± 0.1
250	4.953	8.99	3.41	3.12	3.3 ± 0.2
300	7.413	8.99	3.44	3.19	2.7 ± 0.2
350	10.064	8.99	3.42	3.22	2.0 ± 0.1
400	14.125	8.99	3.42	3.25	1.6 ± 0.1

[a] Oxygen saturated at 0.1 MPa.

Table 3

Pressure dependence of k_q for 5×10^{-7} M DBPI in n-hexane ($[O_2] = 11 \times 10^{-3}$ M at 0.1 MPa)

p (MPa)	τ_0 (ns)	τ (ns)	$k_q/10^9$ $(M^{-1} s^{-1})$
0.1	3.83	3.25	4.2 ± 0.1
25	3.80	3.20	4.4 ± 0.1
50	3.78	3.15	4.4 ± 0.3
100	3.70	3.12	4.5 ± 0.1
150	3.69	3.12	4.4 ± 0.1
200	3.67	3.13	4.2 ± 0.1
250	3.66	3.14	4.1 ± 0.1
300	3.59	3.14	3.6 ± 0.1
350	3.57	3.15	3.4 ± 0.1
400	3.52	3.18	2.7 ± 0.1

The quenched fluorescence decays from an aerated methanol solution of DBPI (8×10^{-6} M) and oxygen-saturated solutions of DBPI in methylcyclohexane and n-hexane (5×10^{-7} M) measured at pressures ranging from 0.1 to 400 MPa were found to be single exponential at each pressure. The values obtained for $k_q(p)$ are summarized in Tables 2 and 3, together with other relevant data. As shown in Table 2, the $k_q(p)$ values for DBPI in methylcyclohexane decrease monotonically with increasing solvent viscosity by the application of pressure. This is illustrated in Fig. 2. A similar behaviour is observed in methanol. The values for α calculated from the slopes of the plots of $\ln \eta$ vs. $\ln k_q$ are 0.71 ± 0.02 and 0.59 ± 0.08 for methanol and methylcyclohexane respectively. However, in n-hexane, as shown in Table 3 and Fig. 3, the k_q value increases from 4.2×10^9 M^{-1} s^{-1} at 0.1 MPa to 4.5×10^9 M^{-1} s^{-1} at 100 MPa and then decreases with increasing pressure to 2.7×10^9 M^{-1} s^{-1} at 400 MPa.

When the molecular size of a given fluorophore is much larger than that of oxygen, the sum of the diffusion coefficients can be approximated by the diffusion coefficient of oxygen. Therefore in the regime where k_{diff} is much less than the intrinsic rate constant for the quenching reaction k_{act} [3] (in the present case, in methanol and methylcyclohexane under high pressures), the dependence of k_q on the solvent viscosity is expected to be determined solely by the translational diffusion of oxygen and, hence, to converge to the same viscosity dependence. The values of α obtained for DBPI are not in good agreement with those obtained for 9,10-dimethylanthracene and 9-methylanthracene, i.e. 0.71 ± 0.02 vs. 0.98 ± 0.01 [14] in methanol and 0.59 ± 0.08 vs. 0.68 ± 0.06 [2] in methylcyclohexane. Since the fluorescence quenching by oxygen of these anthracenes is nearly
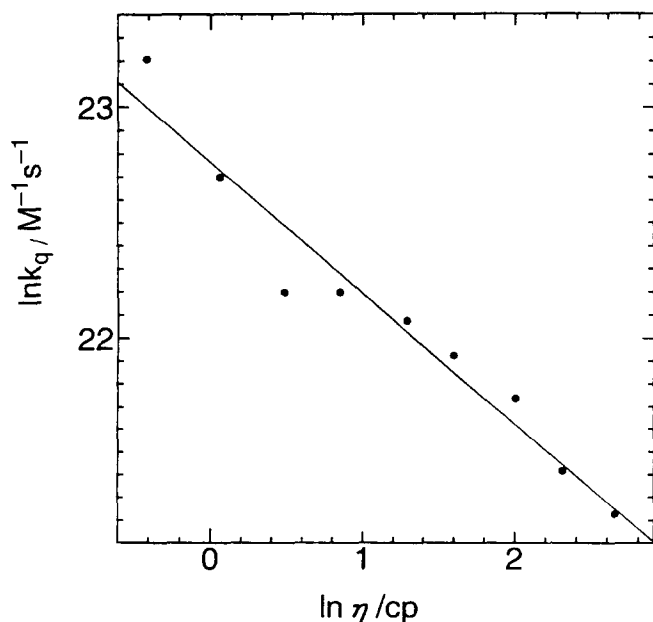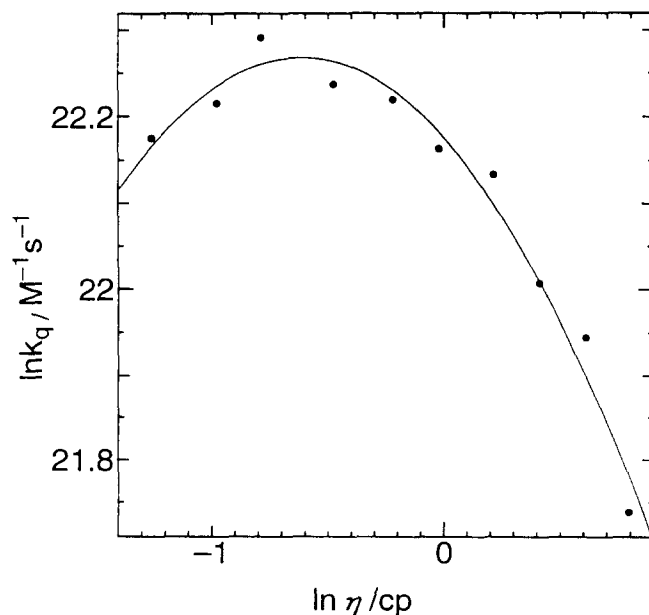

Fig. 2. Plot of $\ln k_q(p)$ as a function of $\ln \eta$ for DBPI in methylcyclohexane (5×10^{-7} M) at 25 °C. The viscosity was changed by applying hydrostatic pressure.

Fig. 3. Plot of $\ln k_q(p)$ as a function of $\ln \eta$ for 5×10^{-7} M DBPI in n-hexane. The viscosity was changed by applying hydrostatic pressure.

diffusion controlled, this may imply that the quenching reaction of DBPI by oxygen is not totally diffusion controlled and/or that the molecular size of DBPI is not sufficiently large to be able to neglect its translational motion relative to that of oxygen in the solvents examined in this work.

3.3. Mechanism of fluorescence quenching of DBPI

We consider the following scheme for the quenching of DBPI by molecular oxygen
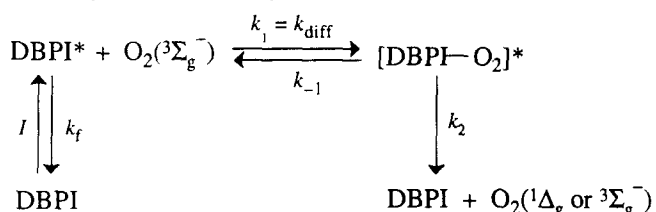
After pulse excitation, DBPI* interacts with $O_2(^3\Sigma_g^-)$ with the rate constant k_1 and forms a rather long-lived encounter complex [DBPI–O$_2$]*, which either dissociates into the reactants with the rate constant k_{-1} or results in quenching with the reaction rate constant k_2. The assumption of the formation of the encounter complex prior to quenching is based on the negative activation energy obtained in n-hexane. The yield of singlet oxygen was not measured, but the energy difference between the singlet excited state ($E_S = 218$ kJ mol^{-1}) and the lowest triplet state ($E_T = 108$ kJ mol^{-1}) of DBPI [30] is sufficient to produce singlet oxygen ($^1\Delta_g$) and DBPI in the lowest triplet state.

Under the photostationary condition, the observed quenching rate constant k_q is given by

$$k_q = k_1 k_2 / (k_{-1} + k_2) \tag{5}$$

In solvents of low viscosity (e.g. the non-polar solvents in this work), where $k_{-1} \gg k_2$, k_q can be approximated

$$k_q = k_1 (k_2 / k_{-1}) \tag{6}$$

The observed rate constant will depend on the ratio k_2/k_{-1} (less than unity) and, hence, will be smaller than k_1, and the reaction is said to be activation controlled.

On the other hand, when the solvent viscosity is increased either by applying hydrostatic pressure or by changing the solvent until the relation $k_{-1} \ll k_2$ holds, k_q is approximated by the following equation

$$k_q = k_1 = k_{\text{diff}} \tag{7}$$

Therefore, at low viscosities, where the relation $k_{-1} \gg k_2$ holds, a slight increase in viscosity will lead to an appreciable decrease in k_{-1} and, hence, k_q will decrease with decreasing viscosity. At higher viscosities, where $k_{-1} \ll k_2$, the apparent rate constant is equal to k_1 and the quenching reaction becomes diffusion controlled and, hence, k_q decreases with increasing solvent viscosity. A similar mechanism has been proposed previously for the quenching of 9,10-dicyanoanthracene by oxygen whose k_q value at 0.1 MPa is much smaller than that of k_{diff} [14]. The anomalous viscosity

Table 4
Effect of concentration on the fluorescence quenching rate constant by oxygen in chloroform

[DBPI] (M)	τ_0 (ns)	τ (ns)	$k_q/10^9$ (M^{-1} s^{-1})
1×10^{-6}	3.71	3.65	1.66 ± 0.2
5×10^{-6}	3.72	3.64	1.69 ± 0.2
1×10^{-5}	3.92	3.85	2.07 ± 0.1
5×10^{-5}	5.10	4.88	3.58 ± 0.1
1×10^{-4}	5.53	5.27	3.68 ± 0.2
5×10^{-4}	7.42	6.64	6.55 ± 0.5
1×10^{-3}	8.52	7.22	8.30 ± 0.2

dependence of k_q on η found for DBPI in non-polar solvents can be interpreted in the same way. Thus it may be generalized on the basis of kinetic arguments that, when the value of k_q measured in a given solvent is significantly smaller than that of k_{diff} in the same solvent, a bell-shaped dependence of k_q on η will be observed.

3.4. Effect of concentration on the fluorescence quenching of DBPI

The fluorescence lifetimes of highly fluorescent molecules are often increased by the reabsorption of emitted photons unless the concentrations are sufficiently low. The effect of reabsorption is extraordinarily large for DBPI and the (apparent) fluorescence lifetime obtained by fitting the decay curve to a single exponential function increases rapidly with increasing concentration. As can be seen from the values given in Table 4, the fluorescence decay time varies from 3.70 ns at 10^{-6} M to 8.52 ns at 10^{-3} M in deaerated chloroform solutions. Caution should be exercised for a distortion of this sort, since erroneously large k_q values may readily be obtained if values of τ and τ_0 obtained in insufficiently dilute solutions are used to calculate k_q as in Table 4. Therefore the concentration of DBPI should be lower than 10^{-5} M when fluorescence lifetimes are measured in a conventional 1 cm cuvette. It was confirmed that the k_q values are independent of the concentration of DBPI over the range 10^{-6}–10^{-3} M by measurement of the τ and τ_0 values of solutions in a thin glass capillary with a fluorescence microscope, for which the effect of reabsorption is practically absent as described in detail in Ref. [31].

References

[1] J.B. Birks, *Photophysics of Aromatic Molecules*, Wiley-Interscience, London, 1970, p. 497.

[2] S. Hirayama, H. Yasuda, A.D. Scully and M. Okamoto, *J. Phys. Chem.*, 98 (1994) 4609, and references cited therein.

[3] A.D. Scully, H. Yasuda, M. Okamoto and S. Hirayama, *Chem. Phys.*, 157 (1991) 271.

[4] H. Yasuda, A.D. Scully, S. Hirayama, M. Okamoto and F. Tanaka, *J. Am. Chem. Soc.*, 112 (1990) 6847.

[5] J.R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Plenum, New York, 1983, p. 263.

[6] W.R. Ware, *J. Phys. Chem.*, 66 (1962) 455.

[7] M. Kristiansen, R.D. Scurlock, K.K. Iu and P.R. Ogilby, *J. Phys. Chem.*, 95 (1991) 5190.

[8] K. Kikuchi, C. Sato, M. Watabe, H. Ikeda, Y. Takahashi and T. Miyashi, *J. Am. Chem. Soc.*, 115 (1993) 5180.

[9] B. Stevens and B.E. Algar, *J. Phys. Chem.*, 72 (1968) 2582.

[10] F.A. Cebul, K.A. Kirk, D.W. Lupo, L.M. Pittenger, M.D. Schuh, I.R. Williams and G.C. Winston, *J. Am. Chem. Soc.*, 102 (1980) 5656.

[11] K.C. Wu and A.M. Trozzolo, *J. Phys. Chem.*, 83 (1979) 3180.

[12] R.C. Kanner and C.S. Foote, *J. Am. Chem. Soc.*, 114 (1992) 678.

[13] S. Hirayama and Y. Shimono, *J. Chem. Soc., Faraday Trans. 2*, 80 (1984) 941.

[14] K.K. Pandey, M. Okamoto and S. Hirayama, *Chem. Phys. Lett.*, 224 (1994) 417.

[15] F. Wilkinson, D.J. McGarvey and A.F. Olea, *J. Phys. Chem.*, 98 (1994) 3762.

[16] O.L. Gijzeman, F. Kaufman and G. Porter, *J. Chem. Soc., Faraday Trans. 2*, 69 (1973) 708.

[17] J. Saltiel and B.W. Atwater, *Adv. Photochem.*, 14 (1988) 1.

[18] D.J. McGarvey, P.G. Szekeres and F. Wilkinson, *Chem. Phys. Lett.*, 199 (1992) 314.

[19] F. Wilkinson, A. Olea and D.J. McGarvey, *J. Am. Chem. Soc.*, 115 (1993) 12 144.

[20] Y. Usui, N. Shimizu and S. Mori, *Bull. Chem. Soc. Jpn.*, 65 (1992) 897.

[21] S.K. Chattopadhyay, C.V. Kumor and P.K. Das, *J. Photochem.*, 30 (1985) 81.

[22] E.M. Ebeid, S.A. El-Daly and H. Langhals, *J. Phys. Chem.*, 92 (1988) 4565.

[23] S.A. El-Daly, *J. Photochem. Photobiol. A: Chem.*, 68 (1992) 51.

[24] Y. Sakai, M. Kawahigashi, T. Minami, T. Inoue and S. Hirayama, *J. Lumin.*, 42 (1989) 317.

[25] S.L. Murov, *Handbook of Photochemisry*, Section 9, Marcel Dekker, New York, 1973, pp. 85, 89.

[26] P.W. Bridgman, *The Physics of High Pressure*, G. Bell, London, 1949, p. 128.

[27] T. Tominaga and M. Nishinaka, *J. Chem. Soc., Faraday Trans.*, 89 (18) (1993) 3459.

[28] A. Schumpe and P. Lühring, *J. Chem. Eng. Data*, 35 (1990) 24.

[29] S.R. Logan, *J. Chem. Soc., Faraday Trans.*, 73 (1977) 592.

[30] W.E. Ford and P.V. Kamat, *J. Phys. Chem.*, 91 (1987) 6373.

[31] M. Kawahigashi and S. Hirayama, *J. Lumin.*, 43 (1989) 207.