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Investigations of energy transfer from some diolefinic laser dyes to Rhodamine 110

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Abstract

2,5-Distytyl pyrazine (DSP) and 1,4-bis(β-pyridyl-2-vinyl) benzene (P2VB) laser dyes have been studied with respect to energy transfer to rhodamine 110 (R110) laser dye in methanol and butanol by steady state emission measurements. The Stern–Volmer plots are linear, from which the second order-quenching rate constants of energy transfer (k_{ET}) were determined as 9.8×10^{12} and 13.4×10^{12} mol^{-1} dm^3 s^{-1} for DSP–R110, 2.17×10^{13} and 2.3×10^{13} mol^{-1} dm^3 s^{-1} for P2VB–R110 in methanol and butanol, respectively. The critical transfer distances (R_0) have been calculated from the emission of donor and absorption spectra of the acceptor using the Förster formula as 41.4 and 41 Å for P2VB–R110, 55.5 and 52.7 Å for DSP–R110 in the same solvents, respectively. The large values of k_{ET} and R_0 indicate that the dominant mechanism responsible for energy transfer is due to long-range dipole–dipole interaction between excited donor and ground state acceptor molecules.

Keywords: Energy transfer; Laser dyes; Dipole–dipole interaction; Critical transfer distance

1. Introduction

Many reactions in radiation and photochemistry, physics and biology depend on the transfer of electronic energy. The radiationless energy transfer can occur in the gas phase, in liquid and solid solutions, and in crystals. Thus, any advance in the understanding of the energy transfer processes will find immediate application in many areas of research. The process of energy transfer is well observed experimentally by the emission characteristics of the quenching of emission associated with the donor and its replacement by the acceptor. This process may be represented by Eq. (1):

$$M^* + Q \rightarrow M + Q^* \tag{1}$$

where M and Q refer to donor and acceptor molecules, respectively; and the asterisk represents a molecule excited to its first singlet state.

It was suggested that certain standard reference parameters called R_0 and C_0 are useful in evaluating the effectiveness of resonance energy transfer between different compounds. The quantity R_0 is defined as a mean distance, in angstroms, between a donor molecule and an acceptor molecule where the probability for resonance energy transfer is equal to the probability for emission. A related parameter C_0 is the concentration of acceptor molecules in moles per litre wherein there is, on the average, one acceptor molecule inside a sphere of radius R_0 [1].

Computer calculations of an energy transfer dye laser (ETDL) output can be manipulated by varying the donor or acceptor concentrations. Experiments done on anthracene–perylene (ETDL) were also in agreement with the predictions of the illustrated calculation [2]. Resonance energy transfer in dyes such as rhodamine 6G–cresylviolet [3] and coronene–rhodamine [4] have been studied using fluorescence lifetime measurements.

In the present communication, we report the resonance energy transfer from 1,4-bis(β-pyridyl-2-vinyl) benzene (P2VB) and 2,5-distytyl pyrazine (DSP) laser dyes to

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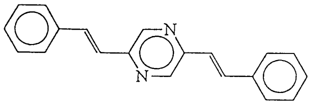
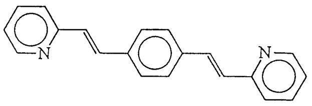
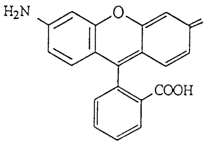
rhodamine 110 (R110) in methanol and butanol using steady state emission measurements.



DSP



P2VB



R110

2. Experimental

2,5-Distyryl pyrazine (DSP) and 1,4-bis(β-pyridyl-2-vinyl)benzene (P2VB) were prepared by the method described by Hasegawa et al. [5]. Purification was achieved by recrystallization and column chromatography on silica gel using methylene chloride as eluent. R110 was obtained from Aldrich and used as supplied. The solvents used are of spectroscopic grade. Steady state emission spectra were measured with a Shimadzu RF 510 spectrofluorophotometer using a rectangular quartz cell of dimensions 0.2 cm×1 cm. Electronic absorption spectra were measured using a Shimadzu UV-2100S spectrophotometer.

The room temperature fluorescence quantum yields ϕ_f (s) were calculated relative to the fluorescence quantum yield of 9,10-diphenylanthracene in ethanol using the relation [6]

$$\phi_f(\mathrm{s}) = \phi_f(\mathrm{r}) \frac{A_r n_s^2 \int I_s(\bar{\upsilon})\,\mathrm{d}\bar{\upsilon}}{A_r n_r^2 \int I_r(\bar{\upsilon})\,\mathrm{d}\bar{\upsilon}} \tag{2}$$

where the indices s and r refer to sample and reference respectively; the integrals represent the corrected fluorescence peak areas; A is the absorbance at the excitation wavelength (337 nm); and n is the refractive index of the solvent.

3. Results and discussion

The strength of interaction between donor (M*) and acceptor (Q) is usually expressed in terms of the critical transfer distance R_0. At this distance of separation between donor (M*) and acceptor (Q), the probability of intermolecular energy transfer is just equal to the sum of probabilities for all de-excitation processes of M* [7].

The critical transfer distance R_0 has been calculated according to the following equation [8,9]:

$$R_0^6 = \frac{9000 \ln 10 K^2 \phi_f}{128 \pi^5 n^4 N_0} \int_0^\infty \frac{F_D(\bar{\upsilon}) \varepsilon_A(\bar{\upsilon})}{\bar{\upsilon}^4}\,\mathrm{d}\bar{\upsilon} \tag{3}$$

where ϕ_f is the emission quantum yield of donor in the absence of acceptor; $F_D(\bar{\upsilon})$ is the spectral distribution of the fluorescence of donor normalized to unity; $\bar{\upsilon}$ is the wavenumber; ε_A is the molar extinction coefficient of the acceptor; N_0 is Avogadro's number; n is the refractive index of the solvent; and K^2 is the square of orientation factor assumed to be 2/3 for solution studies.

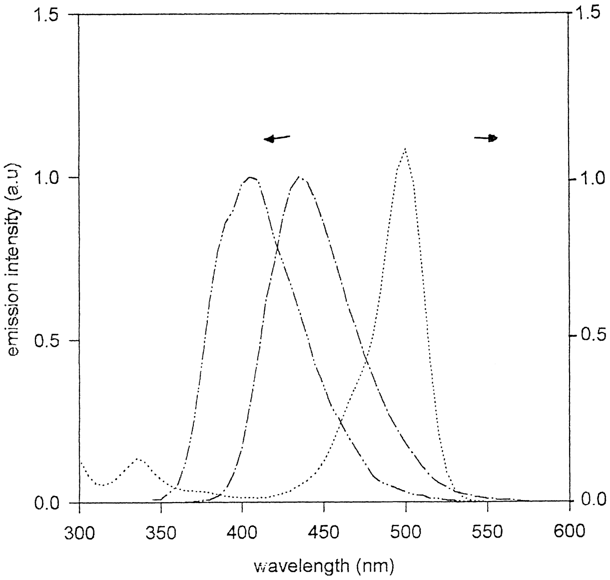


Fig. 1. Absorption spectrum of 1×10^{-5} mol dm^{-3} R110 (·····) and emission spectra of 1×10^{-5} mol dm^{-3} DSP (–·–) and 1×10^{-5} mol dm^{-3} P2VB (–··–) in methanol.

Fig. 1 shows the emission spectra of DSP, P2VB and the absorption spectrum of R110 in methanol. The values of R_0 for DSP–R110 and P2VB–R110 in methanol and butanol are summarized in Tables 1 and 2, respectively. These values are considerably greater than those normally obtained for collisional energy transfer in which R_0 is in the range of 4–6 Å [10].

Figs. 2 and 3 show the fluorescence quenching of 1×10^{-5} mol dm^{-3} DSP and 1×10^{-5} mol dm^{-3} P2VB by R110, respectively, in butanol. The electronic absorption spectra of DSP and P2VB show no changes upon the addition of R110 which indicate the absence of ground state complex formation between donor and acceptor. The emission spectrum of a mixture of donor and acceptor shows no new bands which is an evidence of the absence of exciplex formation between the excited donor and acceptor dye molecules.

Förster has shown that the energy transfer can be regarded as a bimolecular processes [11]. The quenching rate constant k_{SV} and the energy transfer rate constant k_{ET} can be determined from the Stern–Volmer relation [11,12]:

$$\frac{I_0}{I} = 1 + k_{SV}[\mathrm{Q}] = 1 + k_{ET}\tau_0[\mathrm{Q}] \tag{4}$$

where I_0, I represent the fluorescence intensity of the donor in the absence and in the presence of acceptor, respectively; [Q] is the acceptor concentration; and τ_0 is the fluorescence lifetime of donor in the absence of acceptor.

Table 1
Measured values of photophysical parameters of DSP laser dye[a]

Solvent	R_0 (Å)	$k_{SV}\times10^3$ ($dm^3\,mol^{-1}$)	$k_{ET}\times10^{12}$ ($dm^3\,mol^{-1}\,s^{-1}$)	σ_e (DSP)$\times10^{-17}$ (cm^2)	α(DSP)$\times10^{-16}$ (cm^2)	ϕ_f
MeOH	55.5	14.7	9.8	7.03	1.09	0.55
BuOH	52.7	18.3	13.4	8.22	1.01	0.59

[a] λ_{ex}=337 nm.

Table 2
Measured values of photophysical parameters of P2VB laser dye[a]

Solvent	R_0 (Å)	$k_{SV}\times10^3$ ($dm^3\,mol^{-1}$)	$k_{ET}\times10^{12}$ ($dm^3\,mol^{-1}\,s^{-1}$)	σ_e (P2VB)$\times10^{-17}$ (cm^2)	α(P2VB)$\times10^{-16}$ (cm^2)	ϕ_f
MeOH	41.4	10	21.7	6.9	1.9	0.33
BuOH	41	14.7	23	8.5	1.92	0.44

[a] λ_{ex}=337 nm.

The values τ_0 are obtained from [13] and k_{SV} are the slopes of Stern–Volmer plots.

Figs. 4 and 5 show the Stern–Volmer plots of fluorescence quenching of DSP and P2VB by R110, respectively, in methanol and butanol. The values of k_{SV} and k_{ET} for DSP–R110 and P2VB–R110 are listed in Tables 1 and 2, respectively.

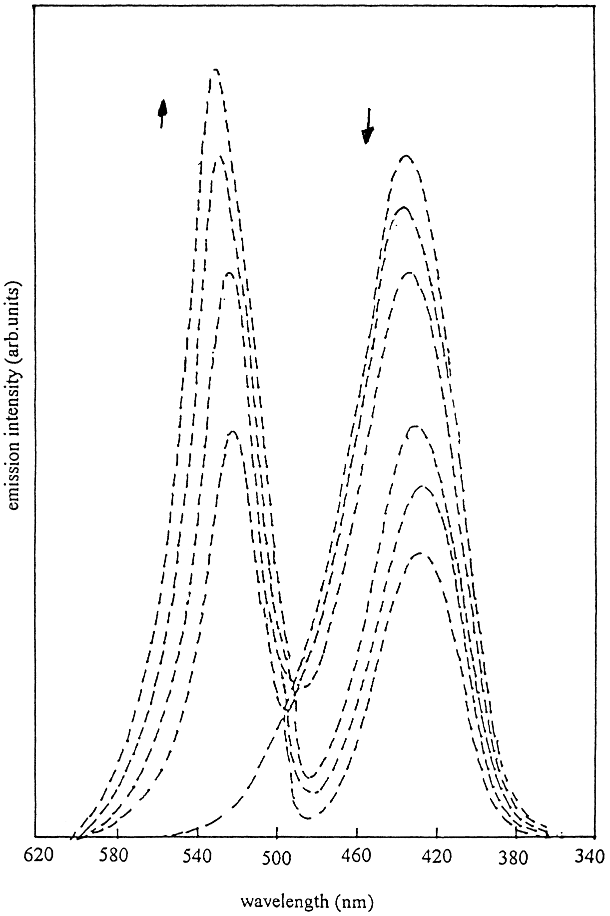


Fig. 2. Emission spectra of $1\times10^{-5}\,mol\,dm^{-3}$ DSP in butanol (λ_{ex}=337 nm) in the absence and in the presence of R110. The concentrations of R110 at decreasing intensities at 435 nm are 0.0, 1.0, 2.0, 4.0, 6.0, and $8\times10^{-5}\,mol\,dm^{-3}$.

The higher values of k_{SV}, k_{ET} and R_0 indicate that the dominant mechanism of fluorescence quenching is resonance energy transfer due to long-range dipole–dipole interaction between the excited donor and the ground state acceptor molecules. The values of R_0 for DSP–R110 are greater than those for P2VB–R110. This is because the

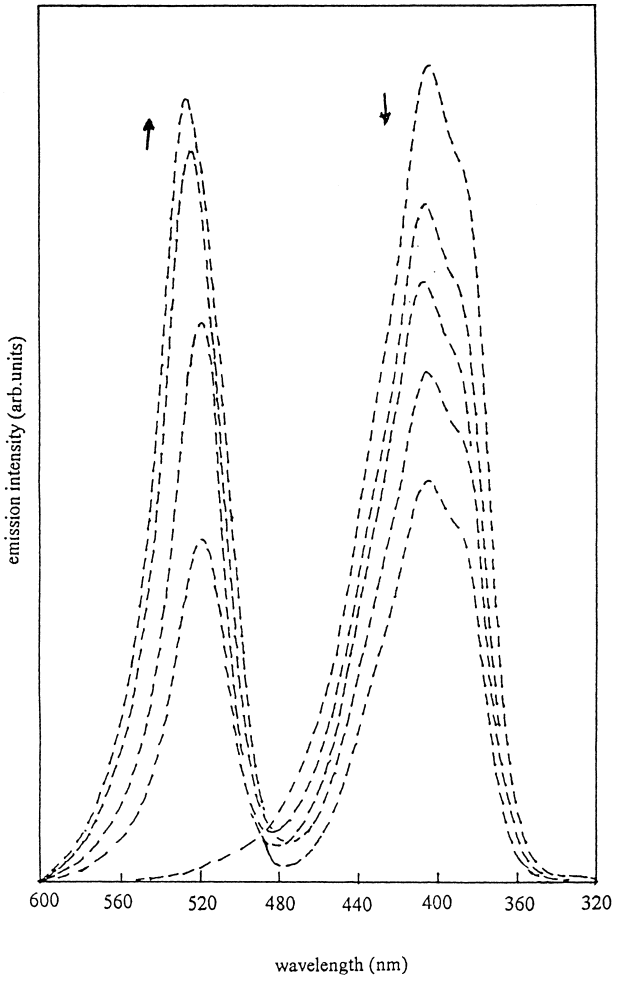


Fig. 3. Emission spectra of $1\times10^{-5}\,mol\,dm^{-3}$ P2VB in butanol (λ_{ex}=337 nm) in the absence and in the presence of R110. The concentrations of R110 at decreasing intensities at 410 nm are 0.0, 1.0, 3.0, 4.0 and $7\times10^{-5}\,mol\,dm^{-3}$.

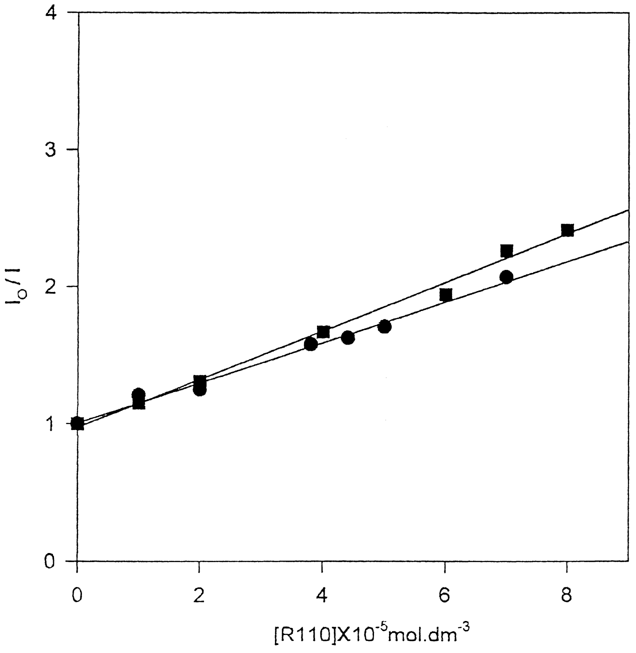


Fig. 4. Stern–Volmer plots for fluorescence quenching of 1×10^{-5} mol dm^{-3} DSP by R110 in methanol (●) and butanol (■).

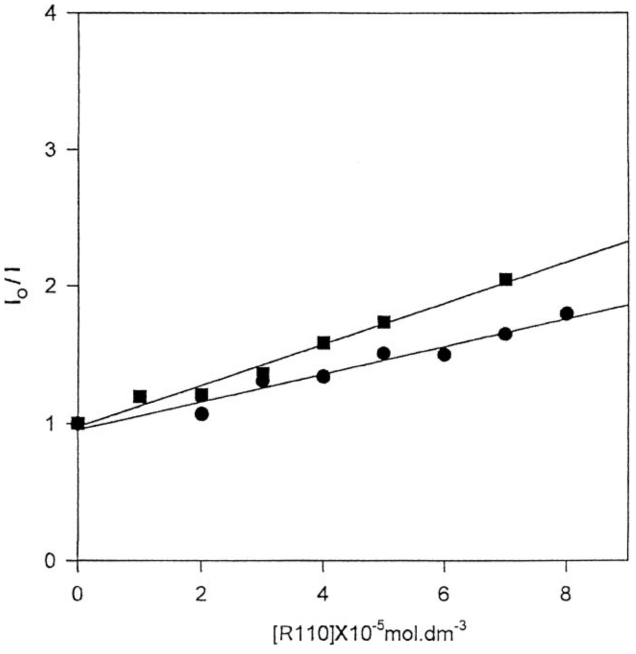


Fig. 5. Stern–Volmer plots for fluorescence quenching of 1×10^{-5} mol dm^{-3} P2VB by R110 in methanol (●) and butanol (■).

overlap area between the absorption spectrum of R110 and emission spectrum of DSP is larger than that between the absorption spectrum of R110 and the emission spectrum of P2VB.

An important indication for the quality of laser dyes is the absorption cross-section σ_a and the emission cross-section σ_e. A higher value of σ_a at the wavelength of pumping laser is desirable for a good laser dye [14]. The emission cross-section σ_e and the absorption cross-section σ_a are calculated according to [15,16]:

$$\sigma_e = \frac{\lambda_e^4 E(\lambda)\phi_f}{8\pi c n^2 \tau_f} \tag{5}$$

$$\sigma_a = 0.385 \times 10^{-20}\varepsilon \tag{6}$$

where λ_e is the emission wavelength; n is the refractive index of the solvent; c is the velocity of light; $E(\lambda)$ is the normalized fluorescence spectrum since $\int E(\lambda)\,d\lambda = \phi_f$; ϕ_f is the fluorescence quantum yield; and ε is the molar absorptivity.

The values of σ_a and σ_e for both donor and acceptor at the excitation wavelength (λ_{ex}=337 nm) are listed in Tables 1 and 2, respectively.

References

[1] R.G. Bennett, J. Chem. Phys. 41B (1964) 3048.
[2] S. Speiser, R. Katraro, Opt. Commun. 27 (1978) 287.
[3] C.E. Moelle, C.M. Verber, A.H. Adelman, Appl. Phys. Lett. 18 (1971) 278.
[4] R. Katraro, A. Ron, S. Speiser, Chem. Phys. Lett. 52 (1977) 16.
[5] M. Hasegawa, Y. Suzuki, F. Suzuki, H. Nakanishi, J. Polym. Sci. A-1 7 (1969) 743.
[6] J.N. Demas, G.A. Crosby, J. Phys. Chem. 75 (8) (1971) 1991.
[7] R.G. Bennett, J. Chem. Phys. 41B (1964) 3037.
[8] N.J. Turro, Molecular Photochemistry, Benjamin, New York, l967.
[9] A. Gilbert, J. Baggott, Essentials of Molecular Photo-chemistry, Blackwell, London, 1991, p. 168.
[10] F.B. Dunning, E.D. Stokes, Opt. Commun. 6 (1972) 60.
[11] T. Förster, Dis. Faraday Soc. 27 (1959) 7.
[12] O. Stern, M. Volmer, Z. Phys. 20 (1919) 183.
[13] S. El-Daly, S.A. Azim, H. El-Daly, K.A. Abou-Zeid, J. Chem. Phys. 92 (1995) 1195.
[14] B. Bangar Razu, T.S. Varadarajan, Laser Chem. 16 (1995) 109.
[15] O.G. Peterson, J.P. Webb, W.C. Mccolgin, J.H. Ebery, Appl. Phys. 44 (1971) 1971.
[16] A. Costela, J.M. Munoz, A. Douhal, J.M. Figured, A.V. Acuna, Appl. Phys. 49 (1989) 545.