Excited-State Properties of Trichromophoric Dye Molecules

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A new time-resolved laser-scanning-microscopy technique is used to measure the excited-state properties of two structural related rhodamine dyes and their 2,5-diphenyloxazole (PPO) derivates. The PPO antennas are separated by methylene bridges from the rhodamine chromophore. An efficient energy transfer from the excited PPO to the rhodamine chromophore is observed. Neither the fluorescence lifetime nor the fluorescence quantum yield of the rhodamine chromophore is affected by the PPO antennas. In contrast, the presence of the PPO antennas significantly influences the intersystem-crossing rate constant as well as the triplet−triplet and excited singlet absorption spectra of the rhodamine chromophore. This observation is clearly in contradiction to the simple model of separated individual chromophores, which is often used to describe multichromophoric dyes.

1. Introduction

Multichromophoric dye molecules (MCD) are of essential importance in widespread areas of science and technology. Owing to their special characteristics, even nature makes use of the concept of MCD, e.g., for photosynthesis.[1] For reasons of efficient energy harvesting, the design of an "ideal" multichromophoric laser dye has been discussed for a long time.[2,3] In modern technological areas, e.g., the manufacturing of efficient solar cells or organic semiconductors, intramolecular interchromophoric interactions are becoming more and more important.[4,5]

The interpretation of a molecule as being multichromophoric is not unambiguous. Usually one interprets a molecule as multichromophoric if it contains more than one spatially separated π-electron system. On this basis one may assume that the properties of the multichromophoric molecules are given by a simple model of separated individual chromophores. In this model a superposition of the individual chromophore properties and the interactions that are known from intermolecular processes are taken into account. These interactions, mainly charge and energy transfer, are basically understood.[6,7] Charge-transfer processes can be described by the Marcus theory.[8] The radiationless energy transfer over molecular distances of some nanometers may be described by the classical theory of dipole- dipole interaction, and the transfer rate constant can be calculated by the Förster formula.[9,10] For shorter distances, the electron orbits overlap and the exchange interaction[11] must be taken into account as well. Owing to the short distance between the chemically linked chromophores, intramolecular interchromophoric radiative transitions are presumed to be of secondary importance compared to the discussed radiationless processes.

If the simple model of separated individual chromophores is valid, MCD can be used as helpful model compounds. With the help of the closed neighbored chromophores, e.g., molecular interactions as energy and charge transfer can be studied in a well-defined way. However, for a valid interpretation of all investigations and applications concerning MCD, the answer of the following question is of elementary interest: Does the simple model of separated individual chromophores appropriately describe all the properties of MCD?

In the present paper we discuss the molecular dynamics and the excited-state absorption of trichromophoric dye molecules. The probability for intersystem crossing as well as the excited-state absorption of the multichromophoric dyes is not explicable by the simple model of separated individual chromophores. In contrast the ground-state absorption and the fluorescence of the multichromophoric dyes are in good accordance with the predictions of the simple model.[12,13]

2. Experiment

2.1. Chemicals. The investigated dyes are shown in Table 1. ClO_4^- was used as the counterion. The dyes were checked for purity by HPLC and did not contain a significant amount of impurities. In all experiments air-equilibrated ethylene glycol (Merck, puriss. p.a.) was used as solvent. All measurements were carried out at a solvent temperature of 20 °C. The dye concentration was aligned to a maximum absorbance of about 3 per mm.

2.2. Experimental Setup. The absorption spectra of the dye molecules in their ground state and fluorescence spectra are measured by a spectrophotometer (model Lambda 19, Perkin-Elmer) and a fluorimeter (model Fluorolog, Spex), respectively. The fluorimeter is calibrated for measuring photon spectra of fluorescence. The measured spectra are shown in Figure 1.

The investigation of the excited molecules is carried out with a new time-resolved laser-scanning-microscopy technique. Experimental details are described elsewhere.[14,15] Briefly, the sample consists of the dye solved in ethylene glycol, which is pressed through a nozzle producing a fast flowing jet stream (see Figure 2). This jet ($l = 100$ μm thickness) is commonly known from continuous dye lasers. The excitation beam (absorbed power ≈ 100 mW) is focused by a lens ($f = 50$ mm) onto the sample. This produces a characteristic distribution of transient states.

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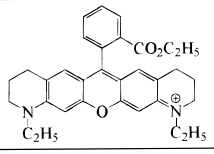
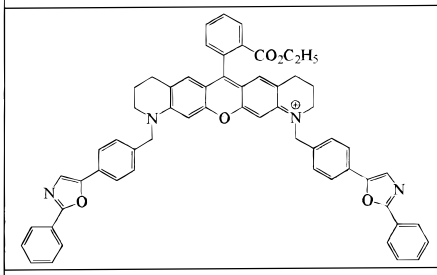
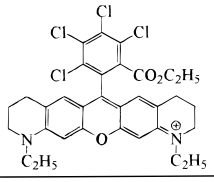
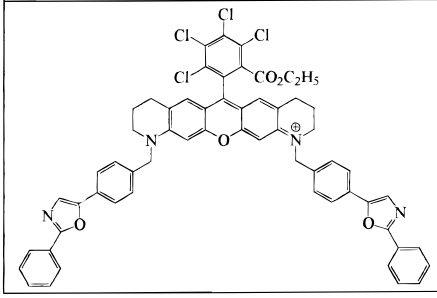
TABLE 1: Dye Structures

structure	name
	rhodamine 1
	PPO-rhodamine 1
	rhodamine 2
	PPO-rhodamine 2

The transmission of the sample is measured using a focused probe beam. Owing to the adjustable distance D between the foci of the probe and the excitation beam, the complete distribution of transient states in the sample is detectable. Because of the motion of the sample the spatial evolution of the transmission can be transformed into the time domain. Consequently it is possible to identify individual states by analyzing the temporal decrease of the transient absorption. The waist diameter $2a$ of the focused beams is 15 μm. A typical jet velocity v_{jet} is 15 m/s, which can be converted to a time resolution of $2a/v_{jet} = 1$ μs.

3. Theory

To measure the *transient* amount of total transmission, we compare the intensity of the transmitted probe beam, having transient states populated (excitation beam on), with the intensity I, having no transient states populated (excitation beam off). Owing to the polarization and orientation of excitation and probe beam, the orientation of the dye molecules in ground state and excited states can be anisotropical. To consider the effect of anisotropy, the transmission of the probe beam is measured for parallel and perpendicular polarization of excitation and probe beam, which is indicated by $i = \parallel$ and $\perp$. The change of the transmitted intensity

$$\frac{\Delta I^i}{I} = \frac{I_1^i - I}{I} \tag{1}$$

is recorded. Positive values indicate an increased transmission of the excited sample compared to the sample with just a ground-state population. From measured functions $\Delta I^i/I$, the signal $\Delta I/I$, which would be obtained if the probe molecules were oriented isotropically, can be calculated by[16]

$$\frac{\Delta I}{I} = \frac{1}{3}\left(\frac{\Delta I^{\parallel}}{I} + 2\frac{\Delta I^{\perp}}{I}\right) \tag{2}$$

The upper equation is valid for $\Delta I/I \ll 1$. This relation is fulfilled in all experiments. Typical measured signals are shown in Figure 3.

The analysis of the recorded signal is carried out on the basis of the Jablonski energy state diagram,[17] which is usually accepted for the characterization of organic dyes. The ground-state depletion as well as the excited singlet and triplet state absorption and the stimulated emission causes a change of the transmitted beam intensity. Owing to the short lifetime of higher excited states, only the first excited singlet S_1 and the lowest triplet state T are populated noticeably. Thus the value of $\Delta I/I$ can be expressed as[18]

$$\frac{\Delta I}{I} = 10^{l\cdot[c_1(D)\cdot(\epsilon_0+\epsilon_{SE}-\epsilon_1)+c_T(D)\cdot(\epsilon_0-\epsilon_T)]} - 1 \tag{3}$$

where c_1 is the concentration of the molecules in the first excited

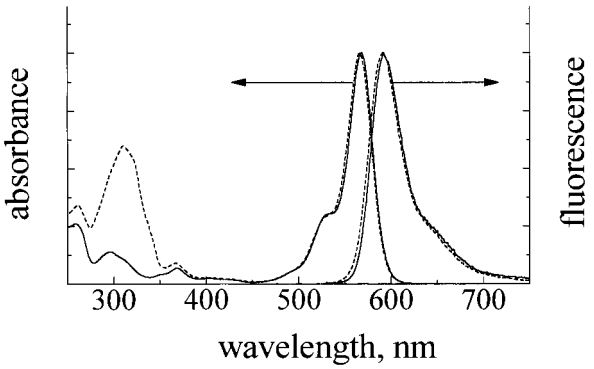


Figure 1. Normalized absorbance and fluorescence spectra of the investigated dyes in ethylene glycol: (—) absorbance and fluorescence of rhodamine 1; (- - -) absorbance and fluorescence of PPO-rhodamine 1. Excitation wavelength 530 nm.

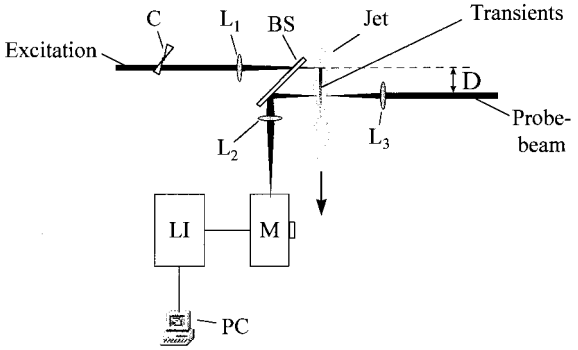


Figure 2. Experimental setup: jet, the dye jet is produced by a combination of a pump module (model 591, Coherent Radiation) and a nozzle (taken from a dye laser CR 599, Coherent Radiation); excitation, Kr-ion laser (model CR 3000K, Coherent Radiation) at 568 nm or Ar-ion laser (model Innova 400, Coherent Radiation) at 300.2, 302.4, and 305.5 nm (all-line UV); probe, dye laser (model CR 599, Coherent Radiation) or Kr-ion laser (model CR 3000K, Coherent Radiation) or Ar-ion laser (model Innova 70, Coherent Radiation); C, chopper (model 220A, HMS); M, monochromator (model H20, Jobin Yvon); LI, lock-in amplifier (model 5101, EG&G); L_1 and L_2, achromatic focusing lens ($f = 50$ mm); L_3, lens ($f = 100$ mm); PC, Computer; D indicates the distance between excitation and detection beam.

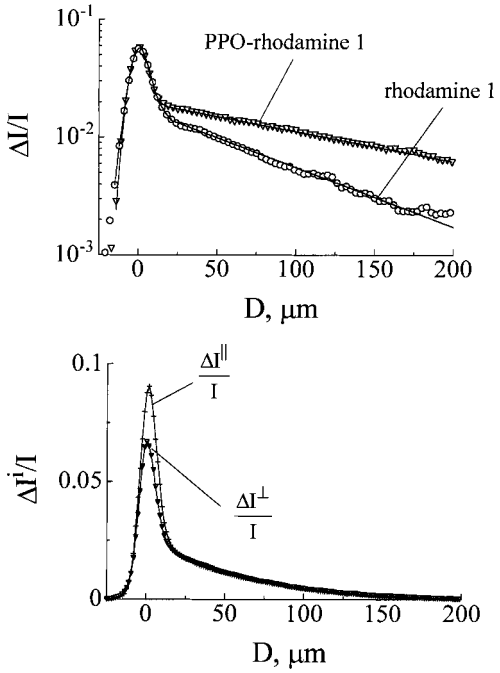


Figure 3. Typically obtained signals for an excitation and probe beam wavelength of 568 and 555 nm. (a, top) The symbols indicate the measured values for rhodamine 1 for 0.32 mM weight-in concentration, 60 mW absorbed excitation power, and $v_{jet} = 20$ m/s. The solid line interpolates the measured values. (b, bottom) The symbols indicate the change of transmission calculated from the measured values by using eq 2 for rhodamine 1 and PPO-rhodamine 1 for 0.32 mM weight-in concentration, 60 mW absorbed excitation power, and $v_{jet} = 20$ m/s. The solid lines are calculated by eq 4 with $\tau_T = 4.5$ μs, $a = 8$ μm, $M = 0.07$, $c_1(0) = 17.1$ μM, and $c_T(0) = 2.9$ μM for rhodamine 1 and $\tau_T = 8$ μs, $a = 8$ μm, $M = 0.04$, $c_1(0) = 16.9$ μM, and $c_T(0) = 3.4$ μM for PPO-rhodamine 1. With eq 5 one obtains $k_{ST} = 5.1 \times 10^5$/s and 6.5×10^5/s for rhodamine 1 and PPO-rhodamine 1 (see Table 2).

singlet state S_1, c_T is the concentration of the molecules in the triplet state T, ϵ_0 the molar decadic extinction coefficient for ground-state absorption, ϵ_1 the molar decadic extinction coefficient for S_1 state absorption, ϵ_T the molar decadic extinction coefficient for T state absorption, and ϵ_{SE} the molar decadic coefficient for stimulated emission.

The concentrations are to be interpreted as an average over the probe beam area.[18] The extinction coefficients are given for the probe beam wavelength. For the evaluation of both spectroscopic and kinetic data, it is useful to distinguish between the following different spectral regions.

3.1. Ground-State Depletion. If the wavelength of the probe beam is aligned within the main ground-state absorption band of the rhodamine chromophore, the ground-state depletion causes an increase of the transmitted beam intensity. With respect to the high extinction coefficient of the ground state, the absorption of the transient states at this wavelength usually can be neglected and eq 3 can be approximated as

$$\frac{\Delta I}{I} = 10^{l \cdot \epsilon_0 \cdot [c_1(D) + c_T(D)]} - 1 \tag{4}$$

For $D = 0$ (complete overlap between excitation and probe beam), the dye solution is bleached by the population of the S_1 and T states. Because of the short lifetime of the S_1 state (<10 ns, see Table 2), the ground-state depletion for $D > 30$ μm (no overlap between excitation and probe beam) is determined exclusively by the population of the T state. Therefore, the lifetime τ_T of the triplet state can be obtained by analyzing the signal in this region. The values of l and ϵ_0 are given from conventional absorption measurement. So from the recorded signal the functions $c_1(D)$ and $c_T(D)$ can be calculated by using eq 3. By comparison of the obtained concentrations, the intersystem-crossing rate constant k_{ST} can be calculated by[18]

$$k_{ST} = \frac{c_T(0)}{c_1(0) \cdot \tau_T \cdot M} \tag{5}$$

The excitation time is in the same order as the triplet lifetime. This fact is taken into account by introducing the factor M, which is given by[18]

$$M = \frac{2}{3} \cdot \left(1 + \frac{\gamma^2}{2 \cdot (\gamma^2 + \omega^2)} - \frac{\omega^5}{\pi \cdot \gamma \cdot (\gamma^2 + \omega^2)^2} \times \exp\left(-\frac{\pi \cdot \gamma}{\omega} \right) \sinh\left(\frac{\pi \cdot \gamma}{\omega} \right) \right)$$

with $\gamma = 1/(v_{jet} \cdot \tau_T)$ and $\omega = \sqrt{\pi}/a$.

3.2. Triplet−Triplet and Excited Singlet−Singlet Absorption. From the ground-state depletion measurement, the values of $c_1(D)$, $c_T(D)$, τ_T, and k_{ST} are given. An additional measurement of $\Delta I^{\perp}/I$ at a wavelength outside of the main ground-state absorption band of the rhodamine chromophore can be used to calculate (using eq 2 and 3) the value of ϵ_T and $(\epsilon_{SE} - \epsilon_1)$ at this wavelength. Thus the triplet−triplet absorption spectrum can be determined. To calculate the spectrum of the excited singlet absorption ϵ_1 from the difference $(\epsilon_{SE} - \epsilon_1)$, the value of ϵ_{SE} must be given. The spectrum of ϵ_{SE} can be calculated from the fluorescence spectrum by[19]

$$\epsilon_{SE} = \frac{1}{\tau_0} \cdot \frac{F(\lambda) \cdot \lambda^4 \cdot N_A}{8 \cdot \pi \cdot n^2 \cdot c^* \cdot \ln(10)} \tag{6}$$

where $F(\lambda)$ is the photon spectrum of fluorescence normalized of $\int F(\lambda) \cdot d\lambda = 1$, n is the refractive index of the dye solution, N_A is Avogadro's constant, and c^* is the vacuum velocity of light.

The radiative lifetime τ_0 of the S_1 state can be calculated from the quantum yield of fluorescence η_{fl} and the observed fluorescence lifetime τ_1 by[19]

$$\tau_0 = \tau_1/\eta_{fl} \tag{7}$$

Thus following the presented theoretical derivation the absorption spectra of the S_1 and T state as well as the rate constants for S_1-T and $T-S_0$ intersystem crossing can be investigated. As can be seen in Figure 3 the experimental obtained signals and the calculated data are in good agreement. For a more detailed discussion of data analysis, see ref 18.

TABLE 2: Molecular Dynamics[a]

name	τ_T/μs	k_{ST}/(10^6 s^{-1})	τ_1[b]/ns	η_{fl}/%
rhodamine 1	4.5	0.51	3.99	97 [12,13]
PPO-rhodamine 1	8	0.65	3.99	97 [12,13]
rhodamine 2	7.5	0.41	4.18	91 [23]
PPO-rhodamine 2	8.5	1.6	4.07	91 [23]

[a] Measured in air-equilibrated ethylene glycol at 20 °C. Excitation wavelength 568 nm. Probe beam wavelength 560 nm for rhodamine 1 and PPO-rhodamine 1. Probe beam wavelength 590 nm for rhodamine 2 and PPO-rhodamine 2. Each value is calculated by an average of five measurements. [b] Measured by S. Nord, University Heidelberg.

4. Results and Discussion

The ground-state absorption of the investigated multichromophoric dyes is represented exactly by the superposition of

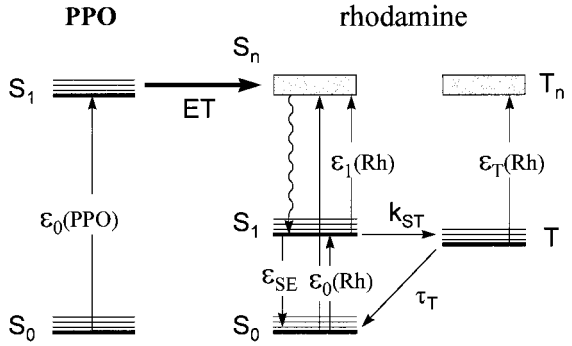


Figure 4. Energy level diagram for multichromophoric dyes that can be described by a model of separated individual chromophores. S_0, singlet ground state; S_1 and T, first excited singlet and triplet state; S_n and T_n, higher excited singlet and triplet states; ET, energy transfer.

the ground-state absorption spectra of one part of the corresponding parent rhodamine and two parts of the PPO molecules (see eq 8a). As shown in Table 2 the presence of the PPO antennas does not influence the S_1 lifetime of the rhodamine chromophore. Furthermore the fluorescence spectrum (not shown) and the fluorescence quantum yield (see Table 2) of the investigated multichromophoric dyes are also in accordance with that of the corresponding rhodamine molecules. This is the case even for excitation in the spectral region of strong PPO absorption. By the presence of the rhodamine chromophore, the fluorescence of the PPO chromophores is quenched to a high degree (quantum yield $< 10^{-3}$).[21] The quenching of the PPO fluorescence is probably due to Förster energy transfer from excited PPO to the rhodamine chromophore in the ground state. The critical distance for this process is approximately 3.5 nm,[20] whereas the distance of the center of the chromophores is only 1 nm. It follows with the Förster formula that a quenching of PPO fluorescence by a factor of $(3.5\ \text{nm}/1\ \text{nm})^6 \approx 1800$ can be expected. For rhodamine 1 this result is published in detail in refs 12, 13, and 20−22. All results discussed so far can be explained by the simple model of separated individual chromophores (Figure 4).

In Figure 5 the absorption spectra of the excited dyes are presented. These measurements are carried out twice, by excitation at a wavelength (568 nm) where the rhodamine chromophore absorbs exclusively and by excitation in a spectral region (303 nm) of high PPO absorbance. The results do not depend on the selected wavelength of excitation. The function of ϵ_{SE} that results from eqs 6 and 7 is also plotted. In the case of rhodamine 1 the values of ϵ_{SE} are nearly equal to those obtained for $(\epsilon_{SE} - \epsilon_1)$. Therefore no significant excited singlet absorption is obtained. From the accuracy of measurement the relation $\epsilon_1/\epsilon_{SE} < 0.1$ can be deduced. For the dye rhodamine 2 a measurable S_1-S_n absorption is obtained. Both trichromophoric molecules show a clearly higher S_1-S_n absorption than their parent dyes. A comparison between the $T-T_n$ absorption of the trichromophoric dyes and the corresponding parent molecules shows that the latter possess a lower ϵ_T. It is noticeable that this is the case even when the excitation takes place in a spectral region of no PPO absorption. These distinctions are clearly in contradiction to the discussed model of separated individual chromophores.

Table 2 shows the measured values of k_{ST}. It is shown that the trichromophoric dyes possess a higher intersystem-crossing rate constant. This result is obtained for an excitation that takes place in the main absorption band of the rhodamine chromophore as well as by a excitation wavelength of strong absorption of the PPO chromophores. These facts are also in contradiction to the model of separated individual chromophores.

As shown in Table 2, the presence of the PPO chromophores leads to a enhanced triplet lifetime τ_T. In air-equilibrated ethylene glycol the triplet lifetime is determined by the diffusion-

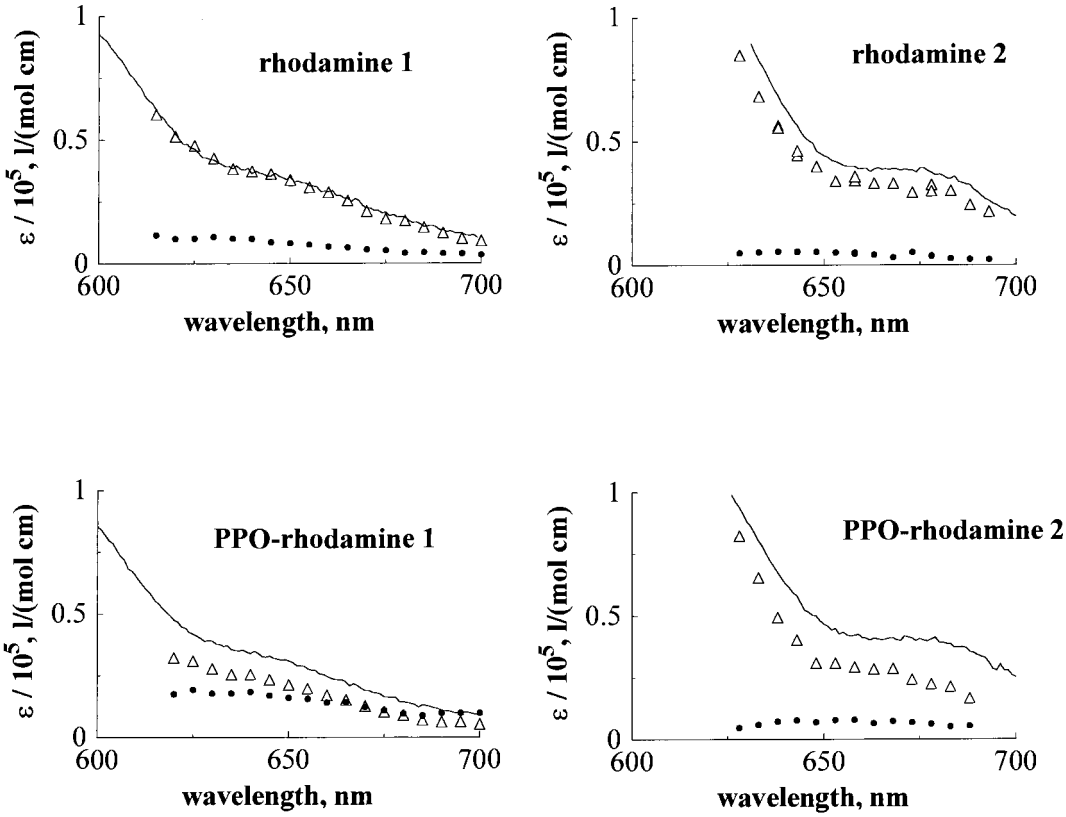


Figure 5. Spectra of excited molecules. (△) $\epsilon_{SE} - \epsilon_1$; (●) ϵ_T; (—) ϵ_{SE} calculated by eqs 6 and 7 with the values given in Table 2 and $n = 1.43$. (a, left) Rhodamine 1 and PPO-rhodamine 1; (b, right) rhodamine 2 and PPO-rhodamine 2.

TABLE 3: UV Absorption of the Dye Molecules in Ground and Excited States[a]

	$\epsilon_1 \cdot 10^{-5}$, L/(mol.cm)		$\epsilon_T \cdot 10^{-5}$, L/(mol.cm)		$\epsilon_0 \cdot 10^{-5}$, L/(mol.cm)
name	measd	calcd by eq 8	measd	calcd by eq 8	measd
rhodamine 1	0.10		0.10		0.13
PPO-rhodamine 1	0.45	0.48	0.4	0.48	0.51
rhodamine 2	0.14		0.09		0.16
PPO-rhodamine 2	0.51	0.52	0.53	0.47	0.54

[a] Measured at 303 nm (all-line UV of the used Ar-ion laser). The values are calculated with the assumption of a maximum ground-state extinction coefficient of 10^5 L/(mol•cm). For excitation wavelength see text.

controlled interaction between the solved molecular oxygen and the dye chromophore.[24] The diffusion of the small oxygen molecules is much faster than that of the relatively big dye molecules. Thus the triplet lifetime is exclusively determined by the diffusion rate of oxygen and the cross section of the dye chromophore. Obviously the increased triplet lifetime must be interpreted as a shielding of the rhodamine chromophore by the PPO chromophores.

In Table 3 the absorption of the excited molecules in the region of strong PPO ground-state absorption is shown. These results can be explained by the model of separated individual chromophores in the following way. As discussed above for the ground-state absorption the relation

$$\epsilon_0(\mathrm{MCD}) = \epsilon_0(\mathrm{Rh}) + 2 \cdot \epsilon_0(\mathrm{PPO}) \tag{8a}$$

is verified. Because of the efficient energy transfer from PPO to the rhodamine chromophore, the lifetime of the excited PPO chromophore is correspondingly short. Therefore the concentration of excited PPO chromophores should be neglectably low. Consequently the absorption of a multichromophoric molecule that contains a rhodamine chromophore in its S_1 and T state, respectively, can be calculated by

$$\epsilon_1(\mathrm{MCD}) = \epsilon_1(\mathrm{Rh}) + 2 \cdot \epsilon_0(\mathrm{PPO}) \tag{8b}$$

$$\epsilon_T(\mathrm{MCD}) = \epsilon_T(\mathrm{Rh}) + 2 \cdot \epsilon_0(\mathrm{PPO}) \tag{8c}$$

The model that leads to eq 8 is illustrated in Figure 4.

By using eq 8 the excited-state absorption of the MCD can be interpreted (Table 3). It can be seen that the excited-state absorption in the region of strong PPO ground-state absorption is in satisfying accordance with the model of separated individual chromophores.

5. Conclusion

In the present paper we discussed to what extent the properties of multichromophoric dyes can be described by a simple model of separated individual chromophores. The results show that the ground-state absorption and the fluorescence of the investigated multichromophoric dyes are given exactly by this model. In contrast the excited-state absorption and the rate constant of S_1-T and $T-S_0$ intersystem crossing are not explained. Obviously a more exhaustive interchromophoric intramolecular interaction must be taken into account. The nature of this interesting fact is so far unknown.

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References and Notes

(1) Renger, G. In: *Biophysik*; Hoppe, W., Lohmann, W., Markl, H., Ziegler, H., Eds.; Springer: Heidelberg, 1977; p 415.
(2) Schäfer, F. P. *Laser Chem.* **1983,** *3*, 265.
(3) Duarte, F. J., Hillmann, L. W. *Dye Laser Principles*; Academic: New York, 1990; p 301.
(4) Tasch, S.; Brandstätter, C.; Maghdadi, F.; Leising, G.; Foyer G.; Athonel, L. *Adv. Mater.* **1997,** *9*, 33.
(5) Hagfeldt, A.; Gräzel, M. *Chem. Rev.* **1995**, *95*, 49.
(6) Klessinger, M.; Michl, J. In *Lichtabsorption und Photochemie organischer Moleküle*; Verlag Chemie: Weinheim, 1989; p 203.
(7) Turro, M. J. *Modern Molecular Photochemistry*; Benjamin/Cummings Publishing Company: Menlo Park, CA, 1978; p 38.
(8) Marcus, R. A. *J. Chem. Phys.* **1956,** *24*, 966.
(9) Förster, Th. *Z. Naturforsch.* **1949,** *49*, 321.
(10) Förster, Th. *Discuss. Faraday Soc.* **1959**, *27*, 7.
(11) Renger, G. In *Biophysik*; Hoppe, W., Lohmann, W., Markl, H., Ziegler, H., Eds.; Springer: Heidelberg, 1977; p 183.
(12) Deltau, G.; Kringel, U.; Peros, D.; Runde, B.; Drexhage, K. H. In *Recent Developments in Molecular Spectroscopy*; Jordanov, B., Kirov, N., Simova, P., Eds.; World Scientific: Singapore, 1988; p 545.
(13) Arden, J.; Deltau, G.; Huth, V.; Kringel, U.; Peros, D.; Drexhage, K. H. *J. Lumin.* **1991,** *48/49*, 352.
(14) Thiel, E.; Drexhage, K. H. *Chem. Phys. Lett.* **1992**, 199, 329.
(15) Thiel, E. *Eigenschaften angeregter Rhodamin-Farbstoffe und deren Wirkung im Farbstofflaser*; Shaker: Aachen, 1996; p 23.
(16) Menzel, R.; Thiel, E. *Chem. Phys. Lett.*, in press.
(17) McGlynn, S. P.; Azumi, T.; Kinoshita, M. *Molecular Spectroscopy of the Triplet State*; Prentice Hall International: London, 1969; p 2.
(18) Thiel, E. *Eigenschaften angeregter Rhodamin-Farbstoffe und deren Wirkung im Farbstofflaser*; Shaker: Aachen, 1996; p 27.
(19) Peterson, O. G. In *Methods of Experimental Physics*; Tang, C. L., Ed.; Academic: New York, 1979; p 263.
(20) Verseckas, A. *Einfluss der UV−Vis-Absorption auf die Lasereffizienz von Rhodamin-Farbstoffen*; C. Görling: Merseburg, 1995; p 50.
(21) Thiel, E. *Eigenschaften angeregter Rhodamin-Farbstoffe und deren Wirkung im Farbstofflaser*; Shaker: Aachen, 1996; p 16.
(22) Peros, D. Ph.D. Thesis, University of Siegen, 1991; p 79.
(23) Arden-Jacob, J. Ph.D. Thesis, University of Siegen, 1992.
(24) Thiel, E. *Eigenschaften angeregter Rhodamin-Farbstoffe und deren Wirkung im Farbstofflaser*; Shaker: Aachen, 1996; p 66.