Picosecond Time-Resolved Fluorescence Spectroscopy of the Photochromic Reaction of Spiropyran in Langmuir–Blodgett Films

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The photochromic reaction of spiropyran + merocyanine has been studied with 1'-octadecyl-3',3'-dimethyl-6-nitrospiro-[2H-1-benzopyran-2,2'-indoline] (SSP) incorporated in Langmuir-Blodgett (LB) films prepared in a mixed film with stearic acid, arachidic acid, and tripalmitine. Time-resolved fluorescence spectra and decay curves of SSP and its photoisomer, merocyanine (SMC), were measured with a picosecond time-correlated, single-photon-counting apparatus. When SSP in LB films was excited at 360 nm, two fluorescence bands were observed: one has a maximum at 660 nm, and the other has a relatively weak band at 530 nm. We assigned them respectively to the fluorescence band of SMC and an intermediate X as a precursor of SMC. The rigidity of the medium surrounding photochromic molecules is an important factor in determining the rate of reversible photoconversion of SSP \leftrightarrow SMC.

Introduction

Recently, photochromic compounds, in which the absorption spectrum is changed reversibly by irradiating light at different wavelengths, have received much attention in view of the application to imaging technologies such as optical memories and optical computer devices.¹⁻⁵ Spiropyran is well-known as a typical organic compound exhibiting photochromism.⁶ Spiropyran in fluid solution, which is colorless in the dark, becomes colored upon irradiation of ultraviolet light but is bleached under visible light irradiation. This photocoloration and photobleaching cycle can be repeated many times. Time-resolved spectroscopic studies of the photochromic reaction of spiropyran and related compounds have been reported by several authors using the transient ab-sorption technique.⁷⁻¹⁰ However, very little is known about the photochromic reaction in the solid phase. It is of practical importance to investigate the kinetics of primary processes of the photochromic reaction in solid or molecular assemblies such as micelles, liquid crystals, and Langmuir-Blodgett (LB) films.

The LB film is typical of a two-dimensional molecular assembly that is prepared by transferring a compact monolayer spread on a water surface onto a substrate. We have recently studied the excimer formation and the excitation energy transfer in LB monolayers with picosecond time-resolved fluorescence spectroscopy.¹¹⁻¹³ The photochromic reaction of spiropyran in LB films was reported first by Polymeropoulos and Möbius.14

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Fundamental properties such as surface pressure-area isotherms and the possibility of the modulation of acceptor fluorescence have been presented.

In the present study, we have prepared the LB multilayer films using a spiropyran derivative, 1'-octadecyl-3',3'-dimethyl-6nitrospiro[2H-1-benzopyran-2,2'-indoline] (SSP). SSP was mixed with stearic acid, arachidic acid, or tripalmitine in appropriate mixing ratios. The photochromic reaction between SSP and its photoisomer, merocyanine (SMC), in LB films can be represented by eq 1.



Picosecond time-resolved fluorescence spectra and fluorescence decay curves were measured with a picosecond time-correlated, single-photon-counting apparatus.¹⁵ Kinetic behaviors of the photoisomerization were compared between the forward and reverse reactions; i.e., SSP \rightarrow SMC caused by UV light irradiation and SSP - SMC caused by visible light irradiation. The effects of the medium in the LB film upon the photochromic reaction were analyzed by use of three diluents; stearic acid, arachidic acid, and tripalmitine.

С ₁₇ Н ₃₅ СООН	stearic acid
с ₁₉ н ₃₉ соон	arachidic acid
CH ₂ O ₂ C - C ₁₅ H ₃₁ CH ₂ O ₂ C - C ₁₅ H ₃₁	tripalmitine
ĊH ₂ O ₂ C-C ₁₅ H ₃₁	

Experimental Section

SSP was purchased from Japan Research Institute for Photosensitizing Dyes Co. and used without further purification. Stearic acid, arachidic acid, and tripalmitine obtained from Wako Chemical Co. were recrystallized several times from ethanol.

Nonfluorescent quartz plates were precoated with five layers of cadmium arachidate to make a surface uniform and hydrophobic. A mixture of SSP and aliphatic acid or tripalmitine

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Figure 1. Surface pressure-area isotherms of SSP in mixtures with stearic acid (curve 1), arachidic acid (curve 2), and tripalmitine (curve 3) with molar ratios of 1:18, 1:18, and 1:6, respectively.

dissolved in chloroform was spread onto a surface of the water subphase containing 3×10^{-4} M CdCl₂. The subphase was conditioned at 10 °C and pH 6.5 by adding NaHCO₃ buffer solution. Mixed monolayers of 8–20 layers were deposited on a quartz plate under a constant surface pressure of 1.5×10^{-2} N m⁻¹. The surface was further coated with two layers of cadmium arachidate to prevent the multilayer structure of the LB film from being destroyed. These operations were carried out in a dust free and dark room to prevent any contamination of impurities and the photoisomerization from SSP to SMC.

Absorption and fluorescence spectra were measured with Hitachi U-3400 and Spex Fluolorog 2 spectrophotometers, respectively. The fluorescence decay curves and the time-resolved spectra were measured with a picosecond time-correlated, single-photon-counting method using a synchronously pumped, cavitydumped dye laser system.¹⁵ A proximity type of microchannelplate photomultiplier (Hamamatsu R2809U-01) was used to obtain an instrumental response function with a 30-ps pulse width (fwhm) for the scattered laser light. Fluorescence decays excited at 314 and at 576 nm were measured under the continuous irradiation of light at 632.8 nm by using a He–Ne laser (GLG 5211, Nippon Electric Co.) or at 365.0 nm by using a high-pressure Hg lamp (USH 500H, Ushio Electric Co.) and a band-path filter (Asahi Spectra Co.), respectively.

Fluorescence decay curves were analyzed by using a nonlinear, least-squares iterative convolution method based on the Marquardt algolism.^{16,17} The calculation was carried out with a Hitachi M-680H computer in the Computer Center of the Institute for Molecular Science.

Results

Surface Pressure-Area Isotherms. Figure 1 shows the surface pressure-area isotherms of SSP in mixtures with stearic acid (curve 1), arachidic acid (curve 2), and tripalmitine (curve 3) with molar ratios of 1:18, 1:18, and 1:6, respectively. It is shown that the surface pressure shows a steep rise at 0.19 nm² for the SSP-aliphatic acid monolayer and at 0.32 nm² for the SSP-tripalmitine. The maximum surface areas in the steep rising point were obtained only at these molar mixing ratios as discussed by Polymeropoulos and Möbius.¹⁴ The average surface area per SSP molecule was calculated from the molar mixing ratios and the molecular areas of aliphatic acid molecules (0.2 nm²) and triplamitine (0.6 nm²). The average surface areas of SSP in these mixtures are smaller than that of SSP itself estimated from a molecular model, 0.40-0.50 nm². This result indicates that a monolayer forms on the water surface with a large part of the spiropyran ring in SSP

Arachidic acid



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Figure 2. Diagramatic representation for the LB multilayer film used in this study. Twenty monolayers are deposited for the photochromic layers.



Figure 3. Absorption spectra of the LB films of SSP-tripalmitine mixture before (curve 1) and after (curve 2) UV light irradiation at 360 nm. The concentration of SSP is 14.3 mol %.

being overlapped with aliphatic acids or tripalmitine. Also one should note that the surface area of SSP is smaller in aliphatic acids than in tripalmitine, indicating that the SSP-aliphatic acid monolayer might be packed more tightly than the SSP-tripalmitine. The structures of LB films are illustrated schematically in Figure 2.

Absorption and Fluorescence Spectra. The absorption spectra are shown in Figure 3 for an LB film of 20 layers of the SSPtripalmitine mixture. The spectra were measured before and after UV light irradiation at 360 nm with a Xe lamp (240 mW m⁻²). Irradiation at this wavelength photoexcites SSP, and under a photostationary state it photoexcites a mixture of SSP and SMC. The absorption spectrum of SSP has a peak at 360 nm, and that of SMC has a peak at 565 nm.¹⁴ The same spectra were obtained for the LB films consisting of SSP and aliphatic acids. The average number of SSP molecules in unit area was calculated to be 1.0×10^{15} molecule/cm² from the molar extinction coefficient, and its value is in good agreement with those calculated from the area occupied by SSP and tripalmitine within an error of 10%. The linear relationship between the absorbance of SSP and the number of layers deposited was also obtained, indicating that the transfer of a monolayer onto a substrate from the air-water interface was made quantitatively.

Figure 4 shows the fluorescence spectrum of a SSP-tripalmitine LB film obtained with 360-nm excitation. The spectrum consists mainly of the SMC fluorescence band at 660 nm instead of the SSP fluorescence. SMC observed here might be generated by

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Figure 4. Fluorescence spectrum of the SSP-tripalmitine LB film. The excitation wavelength is 360 nm.



Figure 5. Fluorescence excitation spectra of the SSP-tripalmitine LB film monitored at 530 and 660 nm.

photoconversion from SSP during the LB film preparation. It should be noted that a very weak fluorescence band appears around 530 nm. The fluorescence spectrum of the SSP-aliphatic acid LB films is similar to that of the SSP-tripalmitine LB film but less pronounced in the 530-nm fluorescence band. Fluorescence excitation spectra monitored at 530 and at 660 nm are shown in Figure 5. These excitation spectra correspond well to the absorption spectra of SSP or a mixture of SSP and SMC (Figure 3). Therefore, the weak fluorescence band with a peak at 530 nm can be regarded as originating from SSP. An excited singlet state of SMC is also produced from SSP indirectly.

Quantum Yields of the Photochromic Reaction. The absorption spectrum is changed upon UV or visible irradiation associated with the photoconversion SSP \Rightarrow SMC (Figure 3). From analysis of the absorbance change, one can derive the quantum efficiency of the photochemical reaction. In Figure 6, the molar ratios of SSP and SMC in the LB films (Figure 2) are plotted as a function of irradiation time. The light source was a monochromatic light from a spectrograph with the intensity of 0.271 W m⁻² for 540 nm and 0.9 W m⁻² for 360 nm.

The quantum yields of the photochromic reaction of SSP \rightarrow SMC (Φ_1) and SSP \leftarrow SMC (Φ_2) can be formulated in a manner similar to that by Bertelson:⁶

$$\Phi_1 = (d[SMC]LN_A/dt)_{t=0}/I_0(1 - 10^{-A_{SSP}})$$
(2)

$$\Phi_2 = \{ (d[SSP]LN_A/dt)_{t=0} - k[SMC]LN_A \} / I_0(1 - 10^{-A_{SMC}})$$
(3)

where [SMC] and [SSP] are the concentrations of SMC and SSP, L is the effective cell length, N_A is the Avogadro's number, I_0 is the light intensity in unit area, and A_{SSP} and A_{SMC} are the absorbance of SSP at 360 nm and SMC at 540 nm, respectively. k is the first-order rate constant of the dark reaction from SMC





Figure 6. Changes in molar ratio among SSP and SMC as a function of irradiation time: (a) UV irradiation of the SSP-tripalmitine LB film and (b) visible irradiation of the SMC-tripalmitine LB film.



Figure 7. Decrease in the absorbance of SMC at 540 nm as a function of time under dark associated with the thermal reaction of SSP \leftarrow SMC.

to SSP. It is known that the reverse reaction SSP \leftarrow SMC occurs without irradiation.¹⁴ Figure 7 shows decrease in the absorbance of SMC at 540 nm as a function of time in the dark. k was estimated to be 1.44×10^{-4} s⁻¹ from the slope of straight line in Figure 7. Then the Φ_1 and Φ_2 values can be calculated from the initial amount of products in unit time under the irradiation of UV (360 nm) and visible (540 nm) light as follows: $\Phi_1 = 0.44$ for the ring-opening reaction and $\Phi_2 = 0.02$ for the ring-closing reaction.

The Φ_2 value can be estimated in an alternative manner from the experiment under a photostationary condition, i.e., d[SMC]/dt = 0, with the following equation:

$$\Phi_2 = -A_p k N_A / (I_0 \epsilon_{\text{SMC}} (1 - 10^{-A_p})) + \Phi_1 \epsilon_{\text{SSP}} [\text{SSP}]_p / \epsilon_{\text{SMC}} [\text{SMC}]_p$$
(4)

 A_p is the absorbance at 360 nm in the photostationary state, and ϵ_{ssp} and ϵ_{smc} are molar extinction coefficients of SSP and SMC



Figure 8. Time-resolved fluorescence spectra of SSP LB films in the mixtures of stearic acid (a) and tripalmitine (b). The excitation wavelength is 314 nm. The time zero corresponds to the time in which the excitation laser pulse reaches maximum intensity.

at 360 nm, respectively. The subscript p indicates the photostationary state. From eq 4, Φ_2 is evaluated to be 0.04. Both sets of Φ_2 values estimated independently, i.e., 0.02 and 0.04, are significantly smaller than Φ_1 , by 1 order of magnitude. Polymeropoulos and Möbius¹⁴ have reported a value similar to that of our experiment by the analysis of energy transfer from thiacyanine to SMC: $\Phi_1 = 0.45$, $\Phi_2 = 0.03$.

For the SSP \leftarrow SMC ring-closing reaction, it is considered that the relative orientation and distance between the indole ring and the nitrophenyl ring of SMC must be specific to form a chemical bond between carbon and oxygen. This reorientation movement, necessary for the ring-closing reaction, must be responsible for smaller quantum yields relative to those in the ring-opening reaction. It is worth noting that the quantum yields of the SSP \rightleftharpoons SMC photochromisms are comparable to those in fluid solution: $\Phi_1 = 0.4$ and $\Phi_2 = 0.04$ in propanol at -50 °C¹⁸ and $\Phi_1 = 0.12$, $\Phi_2 = 0.10$ in ethanol solution at 26.5 °C.¹⁹ These results indicate that the observed large difference between Φ_1 and Φ_2 is characteristic not of LB films but of systems with high viscosity.

Time-Resolved Fluorescence Spectra. Figure 8, parts a and b, show the time-resolved fluorescence spectra of the SSP LB films in the mixtures of stearic acid and of triplamitine, respectively. The excitation wavelength is 314 nm, where SSP molecules are excited predominantly. The fluorescence spectra of the two LB films show a broad band at 620-660 nm, which can be assigned to be the SMC fluorescence. The peak wavelength is 616 nm in the short time region, but it shifts gradually to the red with time. After 2 ns, the spectra show a peak at 660 nm corresponding to the steady-state fluorescence spectra (Figure 4). In the tripalmitine LB films, additionally a weak fluorescence band around 530 nm can be seen in the short region (-10 - 20 ps), which corresponds to the spectrum observed in the steady-state fluorescence spectra (Figure 4, time region -10 - 20 ps). It disappears within 50 ps. The corresponding band is negligible in SSP-stearic acid.

Fluorescence Decays. Figures 9 and 10 show the fluorescence decay curves of the LB films obtained with excitation at 314 and 576 nm, respectively. The decay curves monitored at 530 and 660 nm (Figure 9a,b, respectively) are different; sharp decays are seen in the 530-nm decay curves, whereas there is a relatively slow rise in the 660-nm decays. The fluorescence decay profiles of SMC (Figure 10) depend on the diluents; it becomes faster in the order of stearic acid, arachidic acid, and tripalmitine.

These decay curves were analyzed in terms of a sum of exponential decays, $A_i \exp(-t/\tau_i)$. Analyses based on four or five components led to an acceptable curve fitting. The decay constants



Figure 9. Fluorescence decay curves of SSP LB films in the mixtures of tripalmitine (curve 1) and stearic acid (curve 2) and their respective weighted residuals (curves 3 and 4). The excitation wavelength is 314 nm and the monitoring wavelengths are 530 (a) and 660 nm (b). The decay curves of SSP-arachidic acid LB films coincide with those of SSP-stearic acid (curve 2).



Figure 10. Fluorescence decay curves of the SMC LB films in the mixtures of stearic acid (curve 1), arachidic acid (curve 2), and tripalmitine (curve 3), and their respective weighted residuals (curves 4-6). The excitation and monitoring wavelengths are 576 and 660 nm, respectively.

and amplitudes are summarized in Table I. The fluorescence decays following excitation at 314 nm show rise components for all the monitoring wavelengths. These rises are followed by the fast decays of 25-60 ps. On the other hand, the decays following excitation at 576 nm show no rise components; their decay constants are longer than those of 314-nm excitation.

For the 660-nm fluorescence band, the 576-nm excitation leads to much slower decay than the 314-nm excitation. In both excitations, the decay time becomes long as the monitoring wavelength is changed to the longer wavelength. These changes in the decay time are associated with the observation of the red shifts in the time-resolved spectra shown in Figure 8. The rise times also become long as the monitoring wavelength is shifted to the red.

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TABLE I: Fluorescence Lifetimes (τ) and Amplitudes (A) Obtained in Multiexponential Decay Analyses

diluents	λ_{exc} , nm	λ_{em}, nm	τ_1 (A ₁), ps	$\tau_2 (A_2), ps$	τ_3 (A ₃), ps	$\tau_4 (A_4)$, ps
tripalmitine	314	530	23 (-0.995)	25 (0.982)	230 (0.012)	940 (0.006)
•	314	620	31 (-0.997)	35 (0.961)	250 (0.027)	995 (0.011)
	314	660	41 (-0.996)	46 (0.908)	280 (0.058)	930 (0.032)
	314	700	51 (-1.000)	58 (0.900)	340 (0.065)	780 (0.028)
	576	620	, ,	67 (0.505)	390 (0.295)	1590 (0.200)
	576	660		130 (0.485)	550 (0.343)	1550 (0.172)
	576	700		230 (0.485)	855 (0.413)	2350 (0.130)
arachidic acid	314	530	22 (-0.994)	23 (0.983)	170 (0.011)	670 (0.005)
	314	620	30 (-0.998)	33 (0.959)	220 (0.027)	780 (0.012)
	314	660	40 (-0.998)	43 (0.945)	240 (0.033)	640 (0.017)
	314	700	49 (-0.998)	55 (0.903)	330 (0.064)	910 (0.029)
	576	620	· · /	110 (0.482)	560 (0.290)	2120 (0.228)
	576	660		150 (0.417)	710 (0.310)	2080 (0.274)
	576	700		200 (0.409)	1210 (0.532)	5530 (0.059)
stearic acid	314	530	22 (-0.991)	25 (0.973)	200 (0.018)	760 (0.008)
	314	620	30 (–0.998)	32 (0.961)	200 (0.027)	740 (0.009)
	314	660	43 (-0.997)	46 (0.941)	260 (0.040)	750 (0.017)
	314	700	49 (-1.000)	53 (0.932)	320 (0.045)	980 (0.022)
	576	620	· · · · · · · · · · · · · · · · · · ·	140 (0.496)	760 (0.288)	2420 (0.217)
	576	660		190 (0.371)	1350 (0.553)	4850 (0.077)
	576	700		250 (0.297)	1420 (0.682)	42000 (0.021)

Discussion

The present experimental results of the time-resolved fluorescence study might provide us with a mechanistic understanding for a primary stage of the photochromic reaction and the excitation energy relaxation pathways in the LB films.

We assume that a photoexcited SSP is converted in the first step to an intermediate, which gives a 530-nm fluorescence band in the time-resolved fluorescence spectra. One should note here that the band position of this fluorescence is largely shifted to the red compared to that of the absorption band of SSP and that it appears within only 20 ps after the pulsed excitation and decays with a time constant (25 ps) corresponding to a rise time of SMC (40 ps). These findings suggest that it is an intermediate as a precursor of SMC, hereafter referred to as X. The structure of X is considered as a nonplaner cisoid form. Krysanov and Alfimov⁷ also found out the intermediate corresponding to X from transient absorption spectra and reported that the species X is produced within 10 ps in solution.

Environmental conditions surrounding spiropyran in the LB films should be extremely different from those in solution, especially with respect to microscopic viscosity. The difference in the rise time between the LB film and the fluid solution systems might be interpreted in terms of microviscosity. Further, the rise times of SMC fluorescence in 314-nm excitation are somewhat longer than the decay time of X. From these considerations, we assume the following reaction mechanism. For the case of 314-nm excitation:

$$SSP + h\nu \to SSP^* \tag{5}$$

$$SSP^* \to X^* \tag{6}$$

$$\mathbf{X}^* \to \mathbf{SMC}^* \tag{7}$$

$$X^* + SMC \to X + SMC^* \tag{8}$$

$$X^* \to X + h\nu_F \tag{9}$$

For the case of 576-nm excitation:

$$SMC + h\nu \rightarrow SMC^*$$
 (10)

$$SMC^* \rightarrow SMC + h\nu_F$$
 (11)

$$SMC^* \rightarrow SSP + heat$$
 (12)

$$SMC^* \longrightarrow (SMC^*)' \longrightarrow \cdots \longrightarrow SMC^*$$
 heat (13)

The reaction through eqs 6 and 7 is an adiabatic photoreaction,²⁰ in which a photochemical reaction occurs along an excited elec-

tronic energy surface. Equation 8 indicates a Förster energy transfer from X* to SMC, the latter of which is the preformed SMC under the repetitive irradiation of a picosecond UV laser. This process might compete with the fluorescence emission eq 9. Lenoble and Becker⁹ have reported that ground-state merocyanine is formed from triplet-state spiropyran with a rate of 10 ns and from X with a rate of 22 ns in n-hexane. In the LB films concerned here, the distance between chromophores is so close that the excitation energy transfer can occur even though the critical transfer distance is as short as 20 Å. The overlap between the fluorescence of X and absorption of SMC is favorable for the Förster excitation energy transfer. The most feasible mechanism of the formation of excited-state SMC is the excitation energy transfer from X* to SMC in LB films denoted by eq 8. On the other hand, for the case of 576-nm excitation, photoexcited SMC* undergoes a back reaction to SSP and excitation energy transfers to different sites in lower energies and finally quenched at trap sites.

Let us turn to discussion on fluorescence rise and decay curves. It is found from Table I that the fluorescence decay times of SMC monitored at 620–700 nm are much shorter for 314-nm excitation than for 576-nm excitation. The rate of the excitation relaxation of SMC is determined by two competing processes of the back reaction from SMC (process 12) and the excitation trapping by aggregates (process 13). The difference in the decay time can be interpreted in terms of the difference in the concentration of SMC* excited with UV or visible lasers.

In the visible (576 nm) laser excitation, the concentration of SMC is so small that the energy-transfer process (eq 13) does not occur. The main relaxation process is the back reaction from SMC* to SSP. On the other hand, in the UV (314 nm) laser excitation, the concentration of SMC is large enough to cause the energy transfer to neighboring SMC. The decays are mainly due to the excitation energy migration and trapping processes. Then it follows that the decay time of SMC fluorescence is much faster in UV excitation than in visible excitation.

Fluorescence decay profiles of SMC in LB films depend strongly on the microenvironment as shown in Figure 10 and Table I. The decay of SMC following excitation at 576 nm becomes faster with changing diluent molecule in LB film, in the order of stearic acid, arachidic acid, and tripalmitine; the decay constants of the dominant component are 1.55 ns in tripalmitine, 2.08 ns in arachidic acid, and 4.85 ns in stearic acid. Let us consider the microenvironment in LB films. The area occupied by a chromophore in the LB monolayer is significantly larger in tripalmitine than in the aliphatic acids. This means that the reaction cage containing SMC is larger in tripalmitine than in aliphatic acids, and therefore the reorientation of the indole ring and the nitrophenyl ring associated with the back reaction SSP \leftarrow SMC is much easier in tripalmitine film. Furthermore, in comparison among two aliphatic

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acids, stearic acid having a C₁₈ alkyl chain may fit more smoothly with SMC than arachidic acid having a C_{20} alkyl chain from a molecular model. Therefore, it is reasonable that the fluorescence decay time of SMC excited at 576 nm becomes shorter in the order stearic acid, arachidic acid, and tripalmitine; in other words, the reaction rate of SSP - SMC becomes larger in the same order. This result indicates that the volume and rigidity of reaction cage surrounding chromophores is essential to determine the rate of photoisomerization of SSP - SMC.

On the other hand, the fluorescence decay of SMC on excitation at 314 nm (Figure 9) is slightly faster in aliphatic acids than in tripalmitine. In the foregoing discussion, it is found that when SMC is irradiated with UV laser, the energy relaxation pathway in SMC is predominantly the excitation energy migration and trapping processes instead of the isomerization reaction. Since the excitation energy migration is sensitive to the interchromophore distance, the difference in the fluorescence decays can be interpreted as due to the slightly close average chromophore distance in aliphatic acids compared in tripalmitine.

The time-resolved fluorescence spectra (Figure 8) show a large red-shift in the SMC fluorescence band with time; the maximum wavelength is 616 nm at 0 ps and 660 nm at 1 ns. Such a large time-dependent spectral shift is quite common in LB monolayer films containing organic dye chromophores such as rhodamine

B.²¹ Excited singlet dye chromophores in LB films undergo energy migration among energetically different sites and energy trapping by higher aggregates as trap sites. It is recognized that the electronic energy level of dye chromophores is slightly different with each other due to different conformation and different interaction with environmental molecules. In the case of rhodamine B, site-energy distribution arises from different relative angles of the phenyl ring. This interpretation will be adapted to the excitation energy relaxation of merocyanine in LB films. It is possible that chromophores of merocyanine caused by the C-O bond cleavage of spiropyran have different conformations in LB films. This will result in the energy level distribution of merocyanine among different sites. The energy migration among different sites is responsible for the time-dependent red shift of the fluorescence of SMC.

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Pulse Radiolysis of *trans*-1,2-Bis(4-pyridyl)ethylene in Aqueous Solution

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Pulse radiolysis with optical and conductometric detection techniques was used to study the reactions of hydrated electrons (ena⁻), H atoms, 2-hydroxy-2-propyl radicals, and OH radicals with trans-1,2-bis(4-pyridyl)ethylene (neutral form: M) and its conjugate acids HM⁺ and H₂M²⁺ in aqueous solution. Electron attachment to M leads to a transient with $\lambda_{max} = 455$ nm ($\epsilon = 4.0 \times 10^4$ dm³ mol⁻¹ cm⁻¹) at pH 11-12 and to another transient ($\lambda_{max} = 500$ nm, $\epsilon = 5.2 \times 10^4$ dm³ mol⁻¹ cm⁻¹) at pH 6-9. The 455-nm transient is assigned to a neutral H-adduct radical (HM[•], H attached to an N atom), formed via reaction of water with the radical anion. The 500-nm transient is assigned to H₂M^{•+}, the conjugate acid of HM[•], with both H's at the N's; $pK_s = 9.8$. At pH 4-6 H₂M⁺⁺ is also formed by reactions of e_{sq} or H atoms with HM⁺ in quantitative yield, whereas its formation at pH 2 occurs only in low yield. The 2-hydroxy-2-propyl radical reduces HM⁺ and H_2M^{2+} (at pH 1-5) quantitatively to H_2M^{++} but does not react with neutral M. Three OH-adduct radicals were observed in different pH regions. M°OH, a neutral radical ($\lambda_{max} = 392 \text{ nm}$), and its conjugate acid (HM°⁺OH, $\lambda_{max} = 410 \text{ nm}$) have a pK_a of about 6; at pH \leq 4.5 the latter radical is converted by acid catalysis into an isomer with $\lambda_{max} = 510$ nm. Structural assignments are presented for all radicals observed. Some results with trans-1,2-bis(n-pyridyl)ethylene (n = 2 or 3) are also reported.

Introduction

In the photochemistry of trans-1,2-bis(n-pyridyl)ethylenes (n,n'-DPEs, n,n' = 2-4) trans \rightarrow cis photoisomerization is the major process in "inert" solvents.¹⁻⁹ In H-donating solvents the

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photoreduction via an intermediate radical was observed.^{4,5,10} The major transient of trans-4,4'-DPE (M), observed by laser flash photolysis in organic solvents (e.g., cyclohexane or alcohols), has been attributed to the radical HM[•] (see formula below).¹⁰ This radical is formed by H-atom abstraction from the solvent (RH) involving the (n,π^*) state of the trans isomer of M. The radical decays by bimolecular termination. As stable photoproducts, PyCH₂CH₂Py and PyCHRCH₂Py (Py, 4-pyridyl; $R = (CH_3)_2$ -COH, if RH is 2-propanol) have been isolated.^{4,5,10} Additional radicals and reactions are expected in aqueous solutions due to acid-base equilibria (see below).11-14

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