Dynamics of Intra- and Interlayer Energy Transfer in Langmuir−Blodgett Films of 5-(4-*N*-Octadecylpyridyl)-10,15,20-tri-*p*-tolylporphyrin Studied by Time-Resolved Fluorescence Spectroscopy

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Dynamics of electronic excitation energy transfer in the mono- and multilayer Langmuir−Blodgett (LB) films of 5-(4-*N*-octadecylpyridyl)-10,15,20-tri-*p*-tolylporphyrin on glass substrate has been investigated by means of picosecond time-resolved fluorescence spectroscopy using a single photon counting technique. The observed decay rate constants for the intra- and interlayer energy transfer are 1.2×10^9/s and $\sim 4.0 \times 10^9$/s, respectively, which are consistent with the relative fluorescence quantum yield for the LB films on the glass substrate.

Introduction

In our previous papers,[1,2] we reported the molecular orientation, substrate-dependent aggregation, and energy transfer in Langmuir−Blodgett (LB) films of 5-(4-*N*-octadecylpyridyl)-10,15,20-tri-*p*-tolylporphyrin studied by ultraviolet−visible (UV−vis), infrared, and steady-state fluorescence spectroscopies. Important conclusions drawn from these studies are (1) the porphyrin molecules form aggregates with the red shift of the Soret band in the LB films on glass, quartz, CaF_2, and gold-evaporated glass substrates where the chromophores assume nearly flat orientation to the substrate surface and (2) for the porphyrin LB films deposited on the gold-evaporated glass plates, apart from intra- and interlayer energy transfer, very efficient radiationless energy transfer from electronically excited porphyrin molecules to the metal surface takes place.

In addition to the structural aspects of adsorbates on substrates, deeper understanding of the interactions between the electronically excited molecular species among themselves as well as with the substrate surface is very important for microscopic description of the surface dynamical processes. The decay and trapping of the electronic excitation energy from adsorbates to substrates have been studied extensively, both theoretically and experimentally,[3−10] since the pioneering theoretical work of Förster[11] and Galanin[12] using the dipole−dipole and the exchange interaction models, respectively. During recent past, much attention has been focused on the dynamics of Förster-type excitation energy transfer explored by picosecond time-resolved techniques in organized molecular assemblies of restricted molecular geometries such as LB films.[3,4,7−10]

In a majority of the earlier studies on energy transfer in two-dimensional LB films of porphyrin-based species, a relatively low concentration of porphyrins dispersed in inert matrix of fatty acids, esters, vesicles, etc., in the monomeric form[13−16] has been used to explore their photophysical and photochemical properties.

We have investigated the relative importance of electronic excitation energy transfer (ET) among the porphyrin molecules within a single monolayer (intralayer ET) and among the monolayers in the multilayer LB films (in-

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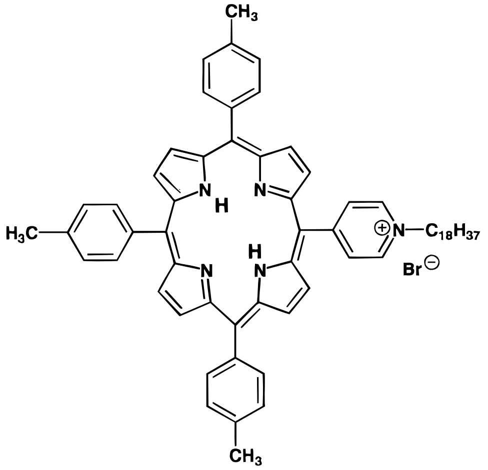

Figure 1. Structure of 5-(4-*N*-octadecylpyridyl)-10,15,20-tri-*p*-tolylporphyrin (porphyrin 338a).

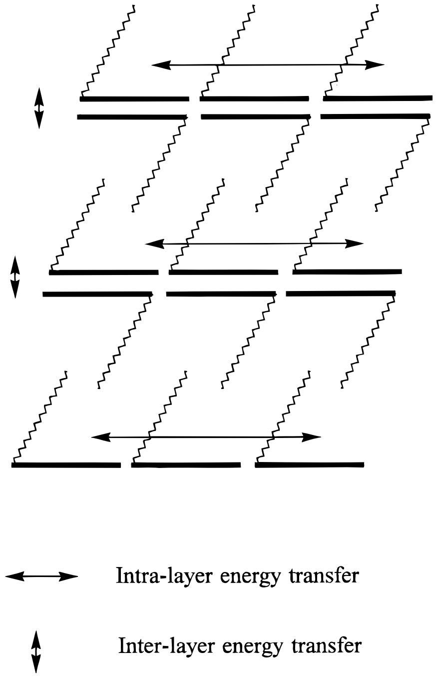

Figure 2. Schematic diagram of energy transfer processes in the LB films of porphyrin 338a.

terlayer ET) of porphyrin 338a on glass substrates by means of picosecond time-resolved fluorescence spectroscopy.

Experimental Section

The LB film forming material, 5-(4-*N*-octadecylpyridyl)-10,15,20-tri-*p*-tolylporphyrin (porphyrin 338a), is shown in Figure 1. The sample was dissolved in spectrograde chloroform (concentration 1.0 mM) and spread onto a pure water subphase at 20 °C. After the evaporation of the solvent, the monolayer film was compressed at a speed of 20 cm^2/min up to the surface pressure of 20 mN m^{-1} and then transferred by a typical vertical dipping technique onto glass plates.[1,2] The porphyrin LB films formed are Y-type LB films. (A schematic diagram of the structure of the porphyrin LB films is presented in Figure 2.) Steady-state fluorescence and fluorescence excitation spectra were measured by use of a Hitachi F-4000 spectrofluorometer with a cell holder in the front face configuration.

Fluorescence decay curves of the solutions and the LB films on glass substrates were measured by single photon timing spectroscopy.[17] A second harmonics (360 nm, pulse width 200 fs) of a hybridly mode-locked, dispersion-compensated femtosecond dye laser (Coherent Satori 774) pumped by a CW mode-locked Nd:YAG laser (Coherent Antares 76S) was used as an excitation source. A repetition rate of the excitation pulse was reduced to 3.8 MHz with an external pulse picker (Conoptics, model 360-80, 25D, and 305). A microchannel-plate photomultiplier (Hamamatsu, MCP R2809U) was used as a detector, which gave an instrument response function of 30 ps (fwhm). The fluorescence decays were detected at the peak of the $Q(0,0)$ band of porphyrin 338a at 660 nm, and the average power per pulse was kept minimal to avoid thermal decomposition of the LB films. The fluorescence decay curves were analyzed by a nonlinear least-squares iterative convolution method based on a Marquardt algorithm.

Results and Discussion

In our previous studies,[1,2] we found that the Soret bands of the one-, three-, five-, and nine-layer LB films of porphyrin 338a on glass, quartz, and CaF_2 plates show about 10 nm red shift compared to that in the chloroform solution. The red shift is associated with the formation of weakly fluorescent aggregates due to steric hindrance of long alkyl chains which result in loose packing and very weak excitonic coupling between porphyrin molecules in the aggregate unit.[1,2] On hydrophilic substrates such as glass and quartz, the fraction of monomeric species is also significant as evidenced by observation of strong fluorescence. A similarity of absorption spectra of the LB films on different hydrophilic substrates imply similar and regular structures of the organized species with nearly uniform distribution of molecules. The steady-state fluorescence spectra of the one-, three-, five-, and nine-layer LB films on glass substrates exhibit two bands centered at 665 and 720 nm with identical emission profiles by excitation at 436 and 480 nm, which correspond to the $Q(0,0)$ and $Q(0,1)$ transitions of porphyrin, respectively. The fluorescence emission spectrum of one-layer LB film of porphyrin 338a on glass substrate is given in Figure 3A. The comparison of the emission spectra between the one-layer LB film and chloroform solution (also shown in Figure 3A) indicates weak excitonic coupling of the porphyrin chromophores in the LB films due to lose aggregates of porphyrin molecules in the LB films. The fluorescence excitation spectra of all the LB films on glass plates monitored at 660 and 720 nm give excitation peaks centered at 433 nm (see Figure 3B), indicating that the emitting species in all the LB films is the same. This peak at 433 nm coincides with the absorption spectra of the Soret band of the LB films on glass, within the experimental error. All these results taken together provide clear evidence that a similar type of uniformly and randomly distributed aggregates influences the energy transfer processes in the LB films.

It is well-known that in a one-component system with overlapping absorption and emission spectra, excitation energy is transferred between molecules of the same kind. On the other hand, if energy trapping centers like aggregates are present, excitation energy can migrate among donors and finally get trapped by aggregates.[5] However, if the separation between the donors (say excited monomers) is large, the excitation energy from the donors can be transferred to the aggregates in a direct step. The donors are revealed through characteristic changes in the rate constants for exponential decay or in the appearance of multiexponential or nonexponential decays. As there are monomeric, aggregated species and other channels in the LB films that quench electronic excitation energy,

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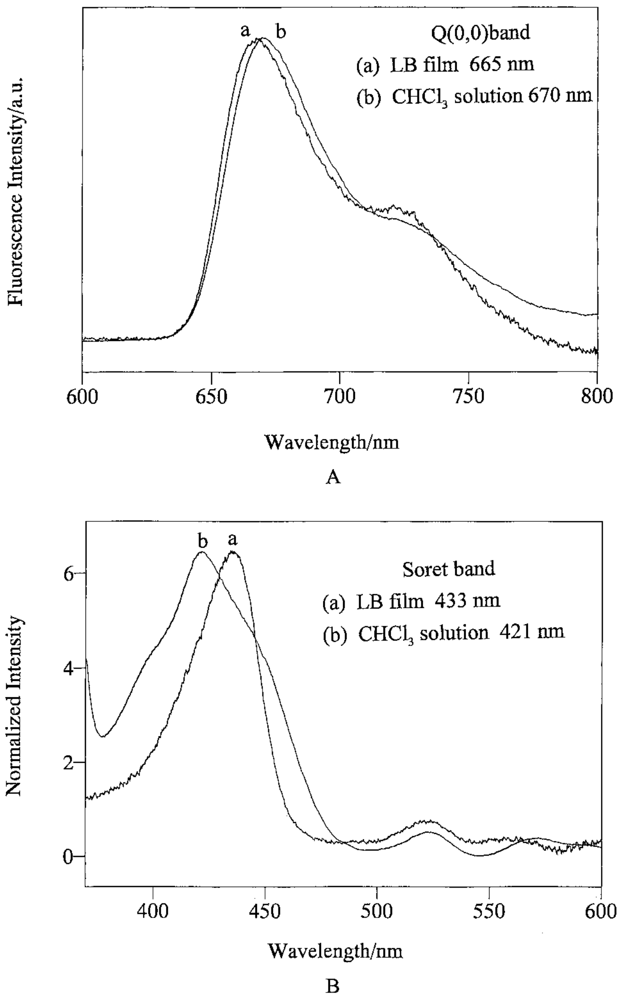

Figure 3. (A) Fluorescence emission spectra of (a) one-layer LB film of porphyrin 338a on glass substrate and (b) chloroform solution. (B) Fluorescence excitation spectra of (a) one-layer LB film of porphyrin 338a on glass substrate and (b) chloroform solution.

one would expect to observe either multiexponential or a nonexponential decay of fluorescence due to the Förster-type energy transfer from the excited porphyrin monomers to the aggregated species in a time-resolved fluorescence experiment.

Figure 4 shows the fluorescence decay curves of porphyrin 338a in chloroform and cyclohexane solution of $\sim 10^{-5}$ M. The decay curve for the chloroform solution is a single exponential with a lifetime of 4.2 ns, which is characteristic of monomeric species. In contrast to this, the fluorescence decay curve for the cyclohexane solution cannot be fitted to a single exponential, indicating the presence of at least two independent fluorescent species. The splitting of the Soret band into two bands at 385 and 436 nm in the absorption spectrum (data not shown) supports coexistence of the porphyrin monomeric and aggregated species in the cyclohexane solution. Figure 5 shows the fluorescence decay curves for the one-, three-, and nine-layer LB films of porphyrin 338a on glass substrates. Here again the decay profiles deviate from the single exponential form.

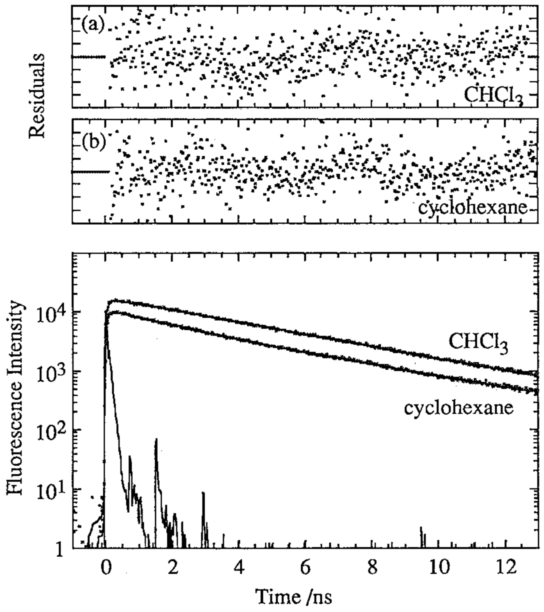

Figure 4. Fluorescence decay curves of porphyrin 338a in chloroform and cyclohexane solution ($\sim 10^{-5}$ M). The corresponding weighted residuals are given at the top of the decay curves. Excitation and detection wavelengths were 360 and 660 nm, respectively.

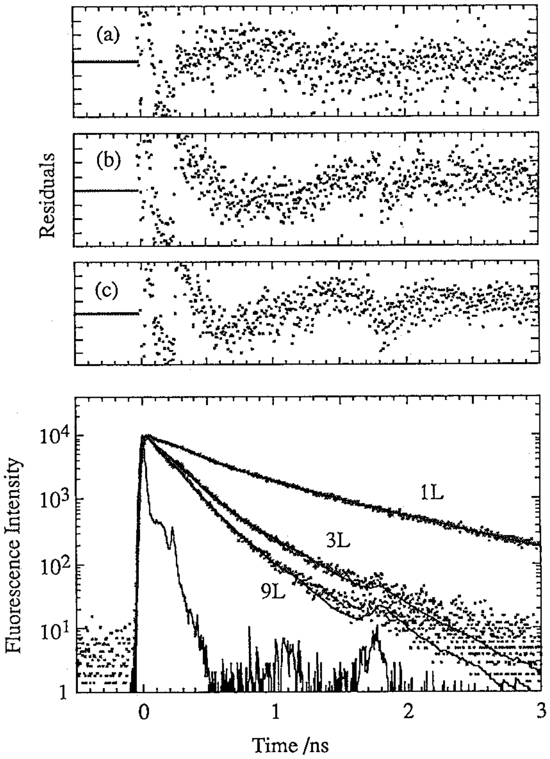

Figure 5. Fluorescence decay curves of one-, three-, and nine-layer LB films of porphyrin 338a on glass substrates along with the instrument response function using $\lambda_{ex} = 360$ nm and $\lambda_{em} = 660$ nm. Smooth lines are the theoretical best fit curves to the data based on two exponential decay functions with extracted parameters given in Table 1. Curves a, b, and c at the top give the weighted residuals for the decay curves of the LB films, respectively.

To analyze the decay curves, it is pertinent to note that many studies[4,7–9] on energy transfer in LB films of dyes reveal fractal behavior with respect to spatial distribution of chromophores or energetically hierarchical structures among different sites with slightly different energies. However, our absorption, steady-state fluorescence emission, and excitation studies on LB films of porphyrin 338a on glass substrates[1,2] indicate similar regular structures of the organized assemblies with nearly uniform distribution of molecules, and the emitting species is the same in all the films.

Table 1. Fluorescence Decay Parameters[a] Extracted from Decay Profiles of LB Films of Porphyrin 338a on Glass Substrate Using a Two Exponential Decay Function Fit

no. of layers	τ_1	a_1	τ_2	a_2	$\langle\tau\rangle$	K_{inter}/ ns^{-1}	ϕ_f
1	257	60.6	888	39.4	693	–	0.165
3	136	78.1	374	21.9	240	4.1	0.057
5	138	76.5	332	23.5	220	3.9	0.052
9	77	62.0	228	38.0	191	4.3	0.046

[a] All the reported lifetimes are in ps; $\lambda_{ex} = 360$ nm, $\lambda_{em} = 660$ nm. The expectation value of lifetime $\langle\tau\rangle = (a_1\tau_1^2 + a_2\tau_2^2)/(a_1\tau_1 + a_2\tau_2)$, where the relative quantum yield of fluorescence ϕ_f is given by $\phi_f = \langle\tau\rangle/\langle\tau_m\rangle$.

Since the spatial and energetical distribution of the molecules in the LB films of porphyrin 338a and their relative orientation are not known, the exact decay function having different adjustable parameters[10,18] cannot be ascertained from our experimental data. The decay times were thus determined by fitting the experimental fluorescence decay curves to a convolution of the instrument response function with a combination of exponential functions given by

$$I(t) = \sum a_i \exp(-t/\tau_i), \qquad i = 1, 2, 3, ... \qquad (1)$$

where a_i and τ_i are the amplitude and the lifetime of the ith component, respectively. The fluorescence decay curves for different LB films of porphyrin 338a were satisfactorily fitted to two exponential functions. The lifetimes, amplitudes, and expectation value of the lifetime defined as $\langle\tau\rangle = \sum a_i\tau_i^2/\sum a_i\tau_i$ are given in Table 1. As shown in Figures 4 and 5, the artifacts at early times in the plot of residuals are due to improper compensation of scattered light. We also tried to fit the decay curves to three exponential functions. The results showed a marginal improvement in the goodness of fit parameters in a few cases but the lifetime and amplitude of the minor component varied substantially from experiment to experiment. The recovered parameters showed a responsible and consistent trend for the two exponential functions, and hence it was considered adequate for all the LB films investigated.

The decay curves for any of the monolayer LB films do not contain long decay component with lifetime in the 4 ns range (even three exponential fittings do not show any such component), suggesting absence of any isolated monomeric species in the LB films. Many authors in the literature[19−21] usually associate slow and fast decaying components of emission with monomeric and aggregated species, respectively. We shall try to understand the dynamics of energy transfer in the LB films, at least qualitatively, under limitations of applicability of this type of separation. With respect to the more than 10 nm red shift of the Soret band, but not the case of the Q-band for LB films compared to that of chloroform solution, and little changes in the fluorescence profiles of the LB films and chloroform solution, it is reasonable that for the LB films of porphyrin 338a, the molecular aggregation affects the Soret transition more significantly than the Q transition. This originated from the small value of the transition dipole moment of the Q-band as compared with that of the Soret band. On the other hand, the shorter lifetime of the aggregates compared to the monomers may be a result of resonant energy transfer quenching processes. Since we used a 360 nm excitation pulse, which mainly monomeric species absorb, the excitation energy may transfer among monomers, which may eventually be trapped by aggregated species. The expectation value of lifetime decreases with the increase in the number of monolayers as shown in Table 1. There could be minor changes in the interlayer spacings and/or relative orientation of the porphyrin units in different layers of the LB films that may not be responsible for systematic variation in the expectation value of the lifetime.

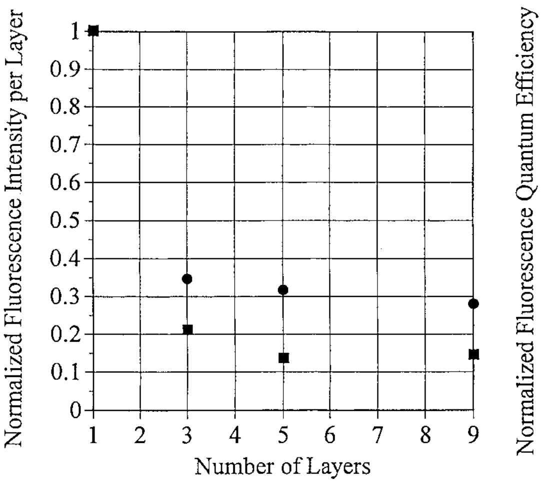

Figure 6. Plot of calculated (●) and observed (■) normalized relative fluorescence intensity versus the number of layers for the LB films of porphyrin 338a on glass substrates. The intensities were normalized for fluorescence intensity per layer as a function of monolayers for the LB films of porphyrin 338a on glass substrates.

In the case of multilayer LB films, in addition to the energy transfer within the same layer specified by the intralayer energy transfer rate constant K_{intra}, there is energy transfer between the porphyrin molecules among adjacent layers (K_{inter}), as illustrated in Figure 2. To obtain quantitative information about the relative importance of these two processes in energy transfer in porphyrin LB films, we can express the expectation value of lifetime of the initially excited porphyrin undergoing energy transfer with other chromophores in the LB films as

$$1/\langle\tau\rangle = [nK_{intra} + (n-1)K_{inter} + n/\tau_m]/n \qquad (2)$$

where $\langle\tau\rangle$ is the expectation value of lifetime of the porphyrin due to combined effects of the intra- and interlayer energy transfer processes in n monolayers, where n is the number of layers. τ_m represents the lifetime of the isolated monomeric unit taken as 4.2 ns for porphyrin 338a in chloroform solution.

For the one-layer LB film, eq 2 becomes

$$1/\langle\tau\rangle = K_{intra} + 1/\tau_m \qquad (3)$$

from the expectation value of the decay time $\langle\tau\rangle = 693$ ps for the one-layer LB film on a glass substrate, we calculate a value of 1.2×10^9/s for K_{intra}. Assuming that K_{intra} is nearly constant for all the porphyrin LB films and τ_m is 4.2 ns, we obtain the values of K_{inter} as 4.1×10^9/s, 3.9×10^9/s, and 4.3×10^9/s for the three-, five-, and nine-layer LB films, respectively. The observation of nearly comparable K_{inter} for the different multilayer films on the glass

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substrates is reasonable because the interaction between neighboring layers should not change significantly (see Figure 2) in the present case.

Dewey and Hammes[22] presented a general method for estimating fluorescence resonance energy transfer between distributions of donors and acceptors on surfaces. Specific approximations were derived for energy transfer within a plane consisting of the donors and acceptors and that between planes. The two kinds of the energy transfer can be expressed by the same equations except for the distance of closest approach of the donor and acceptor (*L*) and the distance between the planes (*h*). If *h* is smaller than *L*, the interlayer energy transfer is larger than the intralayer transfer and vice versa. In the case of the porphyrin LB films studied, *L* can be estimated to be much larger than *h*. Thus, the interlayer energy transfer is more efficient than the intralayer energy transfer.

The quantum efficiency of the steady-state fluorescence of the monomeric units is modified by the presence of intra- and interlayer energy transfer processes. For small fractional absorption of excitation light intensity in the films, the fluorescence intensity is proportional to the relative quantum efficiency Φ_f given by

$$\Phi_f = \langle\tau_n\rangle/\langle\tau_m\rangle \tag{4}$$

Using the value of 4.2 ns for τ_m and extracted values of $\langle\tau_n\rangle$ for different LB films given in Table 1, we calculate the relative fluorescence intensities for the one-, three-, five-, and nine-layer LB films as 0.165, 0.057, 0.052, and 0.046, respectively. We plot these calculated relative intensities (normalized as 1 for one-layer LB film) as a function of number of layers in Figure 6. A plot of the normalized fluorescence intensity per monolayer versus the number of monolayers is also given for comparison. The trends in the variation of the observed and calculated relative fluorescence intensities are very similar, justifying our method of analysis of the decay profiles.

In conclusion, the energy transfer of porphyrin 338a in LB films was analyzed by picosecond time-resolved fluorescence spectroscopy. The extracted values of the rate constants for the intralayer and interlayer energy transfer rates in the LB films of porphyrin 338a were obtained on the basis of energy transfer among porphyrin monomers and energy trapping by aggregates. It was found that the interlayer energy transfer dominates over the intralayer energy transfer process.

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