

Dimer Formation and Excitation Relaxation of Perylene in Langmuir–Blodgett Films

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Steady-state and picosecond time-resolved fluorescence spectra of perylene have been measured in order to examine the dimer formation and the excitation relaxation in restricted geometries of Langmuir–Blodgett (LB) films. In LB films, perylene forms two types of dimers, D₁ and D₂, which are assigned to the dimers where two chromophores are partially and fully overlapped, respectively. At the concentration of 0.05 mol %, only the monomer fluorescence is observed. As the concentration is increased to 1 mol %, the excimer 1 fluorescence (from D₁ site) can be seen in the time region after 40 ns. At a concentration higher than 10 mol %, all three components including the excimer 2 fluorescence (D₂) are observed from the early stage of time. Their contributions to the steady-state and the time-resolved fluorescence spectra are dependent upon the concentration. The excitation transfer from M (monomer) and D₁ sites to the D₂ site occurs with a time constant of ~50 ps at a concentration of 10 mol %, whereas it is ~10 ps in the case of 50 mol %.

Introduction

Recent studies on energy transfer and relaxation of photoexcited molecules have been directed toward their dynamics in restricted molecular geometries. In particular, Langmuir–Blodgett (LB) films have received much attention as two-dimensional monolayers or heteromolecular stacking multilayers where the molecular orientation and intermolecular distance between guest chromophores can be controlled.^{1,2} Functional guest molecules or chromophores in LB films are surrounded with fatty acids, such as stearic acid and arachidic acid, and compressed in a cage with significantly high pressure. It may lead to formation of dimers and excimers with specific configurations that do not appear in homogeneous and random media of solution and glass. In previous studies on LB films containing several types of molecules such as rhodamine, cyanine, and hydrocarbons,^{3–10} it has been shown that (1) nonhomogeneous distribution of guest molecules that can be expressed in terms of the fractal dimension, (2) formation of dimers and higher aggregates and/or excimers, and (3) energy relaxation process, predominantly the cascading hopping migration, take place among sites with slightly different energies.

In the present study, we focus attention on a typical aromatic hydrocarbon, perylene, in LB films. Previously, studies on molecular association of perylene, i.e., ground-state dimer and excimer, have been made under several conditions: in solution,^{11–13} in crystalline,¹⁴ in rigid media at low temperature,¹⁵ in thin polymer films,¹⁶ and in LB films.^{17–19} Perylene molecules form an E-type and a Y-type excimer depending on their environment, and their intermolecular interaction and excitation relaxation process have been discussed. In the study of Petty et al.,¹⁷ perylene molecules were doped into LB films, and their aggregation was discussed in terms of steady-state and nanosecond time-resolved fluorescence spectroscopy. Willig et al. extensively studied the temperature effect on the luminescence and its lifetime of 1:1 mixed layers of 12-(3-perylenyl)dodecanoic acid and arachidic acid in the spectral range of E- and Y-type excimers.¹⁸ They revealed that E-type emission occurs at 1.5 K with a lifetime of 69 ns and can be

generated through the partially forbidden transition to the lowest excited dimer state. On the other hand, Y emission occurs with 2.5 ns and shows a very weak temperature dependence. Multilayer mixed films of perylene-4-octadecanoic acid and stearic acid were studied by Sluch et al.¹⁹ Acylation of perylene to derive a long alkyl chain precludes excimer formation. Only monomer and dimer emissions were observed in their research.

To examine the behavior of perylene in LB films, we prepared LB monolayers with concentrations widely ranging from 0.05 to 50 mol %. The formation of two types of excimer, the distribution of perylene molecules in LB films, and their dynamical energy relaxation process after photoexcitation are investigated by means of a picosecond time-resolved fluorescence spectrophotometer. The result is discussed in the light of the behavior under different conditions and other types of molecules in LB films reported in previous papers.

Experimental Section

12-(3-Perylenyl)dodecanoic acid (from now on called PD) was obtained from Molecular Probes Co. and used without further purification. Arachidic acid, which was used as a matrix, was purified by repeated recrystallization from acetone solution. A Milli-Q water purification system (Millipore Co.) was used for the purification of water for the subphase. The conditions of the subphase containing 3×10^{-4} M CdCl₂ were maintained at 20 °C and pH 6.5 by adding NaHCO₃ buffer solution. A structure of the LB-deposited film is shown schematically in Figure 1. Nonfluorescent quartz substrates were precoated with three layers of cadmium arachidate to make the surface hydrophobic and uniform. A toluene solution of PD and arachidic acid was spread on the water subphase in a Langmuir trough (San-Yesu Instrument Co., FSD-20). A monolayer containing PD was deposited on a substrate at a surface pressure of 30 mN/m and a transfer rate of 4 mm/min. The concentration of PD was changed, ranging from 0.05 to 50 mol %.

UV absorption spectra and steady-state fluorescence spectra were measured with a JASCO Ubest-50 spectrophotometer and a JASCO FP-770F spectrofluorometer, respectively. Time-resolved fluorescence spectra and fluorescence decay curves were measured with a picosecond time-correlated single-photon counting system. We employed a Hamamatsu microchannel plate photomultiplier (R3809) as a detector, a Nikon P-250

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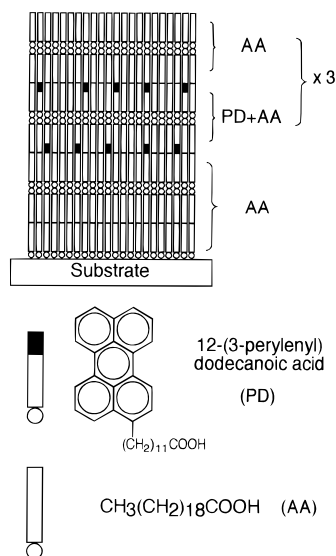


Figure 1. Schematic illustration of the perylene LB films.

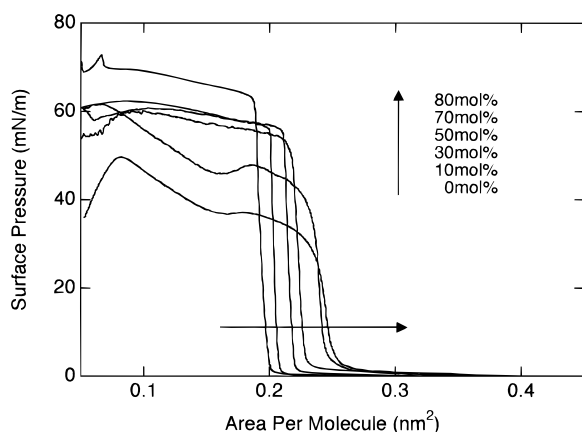


Figure 2. Surface pressure–area isotherms of mixtures of PD and arachidic acid at concentrations of 0–80 mol %.

monochromator, and a Ti:sapphire laser (Coherent MIRA 900) pumped by an Ar ion laser (Coherent INNOVA 310). The second harmonic of the Ti:sapphire laser was generated by a BBO crystal. The excitation wavelength was 390 nm corresponding to the $S_1 \leftarrow S_0$ transition of perylene. The sample was placed in a vacuum vessel with four quartz windows. The emission from the sample was collected at a right angle to the laser beam. All experiments were carried out at room temperature.

Results

Pressure–Area Isotherm. Figure 2 shows the surface pressure–area isotherm of mixtures of PD and arachidic acid with various concentrations of PD. Sharp increases are obtained in the surface pressure of the sample with PD concentrations less than 50 mol %, showing formation of compressed monolayers. However, the expanded monolayer is formed at concentrations of 70 and 80 mol %. We prepared LB monolayers with concentrations ranging from 0.05 to 50 mol % in the present research. The molecular area of perylene in the compressed monolayer was estimated to be 0.27 nm^2 on the assumption that the limiting area of arachidic acid is 0.198 nm^2 by averaging the values obtained from the compressed monolayers with a concentration of 10–50 mol %. The averaged value of 0.27 nm^2 is in good agreement with the area of side view along the short axis of the perylene chromophore, indicating that the short axis is parallel to the plate after deposition on a substrate.

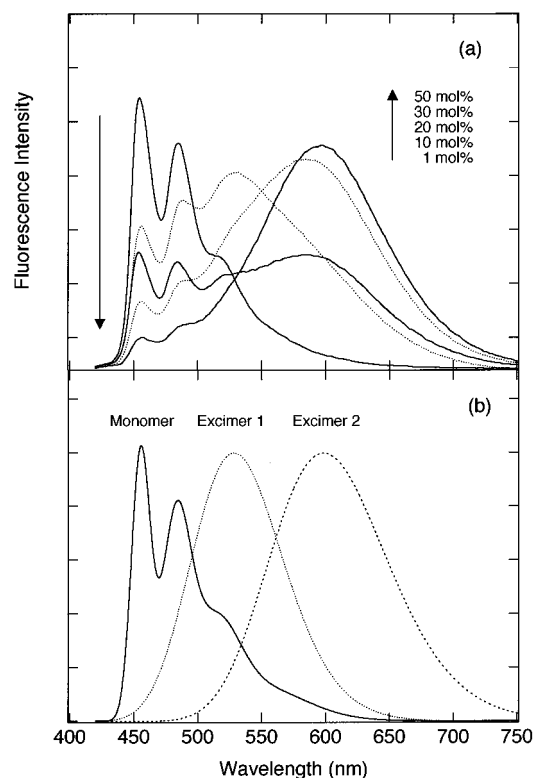


Figure 3. (a) Fluorescence spectra of PD in LB films at concentrations of 1, 10, 20, 30, and 50 mol % excited at 390 nm. (b) Fluorescence spectra of three components: monomer (solid line), excimer 1 (dotted line), and excimer 2 (broken line).

Fluorescence and Absorption Spectra. The fluorescence spectra of PD in LB films at concentrations of 1, 10, 20, 30, and 50 mol % excited at 390 nm are shown in Figure 3. The spectrum of 1 mol % shows well-defined vibronic bands at 455, 484, and 515 nm, and it is identical with that in benzene solution except for their slightly shifted values, 453, 482, and 516 nm, indicating that PD molecules exist as monomers. When the concentration is increased to 10 mol %, a broad structureless band peaked at 535 nm is also observed. The peak position of this broad band is the same as that of the Y-emission reported for an LB film¹⁸ and an α -perylenecrystal.²¹ With a further increase of concentration, an additional broad band around 600 nm, which is assigned to the ordinary sandwich excimer, appears and increases in intensity. All the fluorescence spectra are represented as the sum of a monomer and two broad bands. Figure 4 shows the contributions of three components of the fluorescence spectra observed for 10–50 mol %. Their contributions depend on the concentration, suggesting that the dimer formation and/or the energy transfer to the dimeric site effectively occurs at high concentrations. We consider these two broad bands as two types of excimers, and hereinafter, we refer to them as excimer 1 (peaked around 535 nm) and excimer 2 (600 nm), respectively.

Figure 5 shows the absorption spectrum of PD in LB films. The absorption spectra show vibronic features of the $S_1 \leftarrow S_0$ transition at 398, 421, and 449 nm. The 345 nm peak is assigned to the $S_2 \leftarrow S_0$ transition. When the concentration is increased, a shoulder is observed to the red of 450 nm.

The excitation spectrum of emission observed at 454 (monomer), 535 (excimer 1), and 600 nm (excimer 2) are shown in parts a, b, and c of Figure 6, respectively. The excitation spectra monitored at 454 nm also show the structured one independent of the PD concentration. On the other hand, in the case of the excitation spectra observed at 600 nm, a new band around 375 nm and a shoulder to the red of 450 nm appear and show an increase in their intensity with an increase of PD concentration,

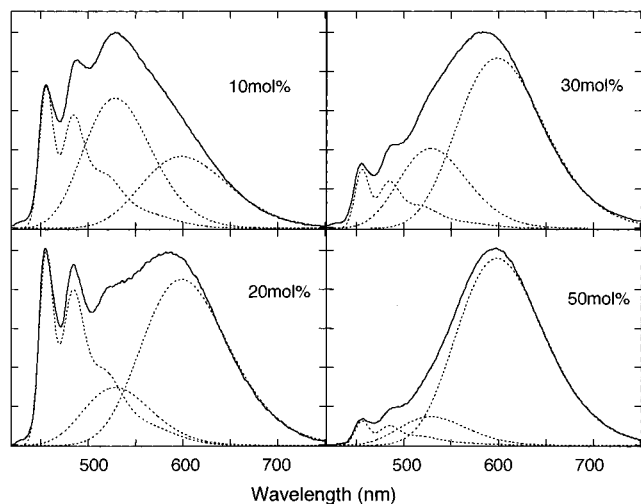


Figure 4. Contribution of three components to the fluorescence spectra of PD in LB films at concentrations of 10–50 mol %.

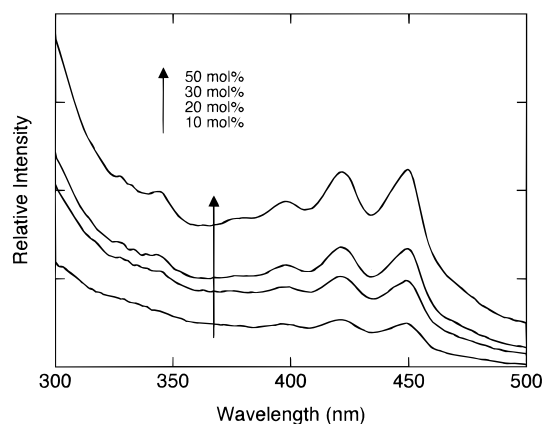


Figure 5. Absorption spectra of PD in LB films at concentrations of 10, 20, 30, and 50 mol %.

which corresponds to the absorption of the perylene dimer. The excitation spectra observed at 535 nm are essentially the same as that monitored at 454 nm except for the appearance of the dimer band. However, this is very weak compared to that monitored at 600 nm, and observed only in the highest concentration. The dimer absorption observed in the excitation spectra monitored at 535 nm, therefore, is thought to be caused by the tail of excimer 2 fluorescence band.

The intensity ratio of $S_2 \leftarrow S_0$ to $S_1 \leftarrow S_0$ absorptions in the absorption and excitation spectra is greater in LB films than in solution. The perylene chromophores are aligned with their long axes perpendicular to the surface of the LB film,¹⁸ contrary to the random orientation in solution. The peak around 345 nm that corresponds to the short axis transition, therefore, is increased against the transitions due to the long axis transition (>380 nm) in LB films.

Time-Resolved Fluorescence Spectra. Normalized time-resolved fluorescence spectra are shown in Figure 7 at concentrations of 0.05–50 mol %. These transient spectra are also represented as the sum of three components: a monomer and two types of excimers, as described in steady-state measurements. In the spectra of 0.05 mol %, no change was observed in the whole time region (0–44 ns) and these spectra correspond to a monomer spectrum obtained with stationary excitation as shown above. In the case of the spectra of 1 mol %, on the other hand, the excimer 1 band was also observed in the time region after 40 ns. At a concentration greater than 10 mol %, all three components were observed. Their contribution depends on the concentration and the delay time. In the spectra of 10

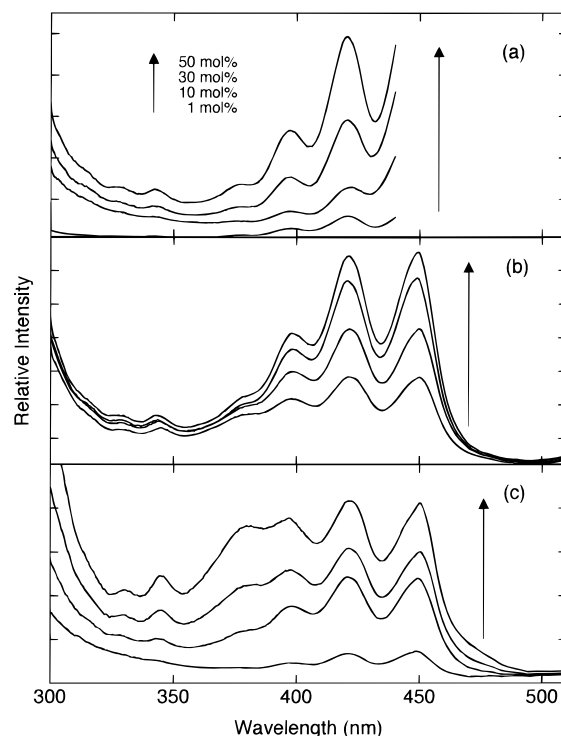


Figure 6. Fluorescence excitation spectra of PD in LB films at concentrations of 1, 10, 30, and 50 mol % monitored at (a) 454, (b) 535, and (c) 600 nm.

mol %, the excimer 1 band has a large contribution after 10 ns. With a further increase of the concentration, besides the monomer and excimer 1 fluorescences, the excimer 2 band can be observed just after laser excitation, and it becomes dominant earlier upon increasing the concentration.

Fluorescence Decays. Figure 8 shows the fluorescence decay curves of PD in LB films at several concentrations monitored at 454 nm. According to the time-resolved fluorescence spectra, the 454 nm decay curves correspond to those of the monomer. Then we are concerned with the excitation energy transfer from the excited monomer to energy acceptor sites. Contrary to the pyrene LB films,²⁰ the decay curve is not single-exponential even at the lowest concentration of 0.05 mol %. As the concentration of PD increases, the fluorescence intensity diminishes more quickly, suggesting that the excitation energy be efficiently transferred from the excited monomer to energy trap sites. In the time region after 30 ns, on the other hand, decay curves are almost parallel to each other with a decay time of 12–17 ns. This fact suggests that even at a high concentration of 50 mol %, isolated monomers that do not contribute to energy transfer still exist.

Discussion

Dimer Formation. As described in the previous section, two kinds of excimer fluorescences are observed in LB films: excimer 1 (peaked around 535 nm) and excimer 2 (600 nm). Their spectral band profiles are broad and structureless. The peak positions of excimer 1 and excimer 2 fluorescences are closely related to those of the Y- and E-type excimers, respectively, as reported for the LB film¹⁸ and the α -peryene crystal.²¹ In the α -peryene crystal, the Y- and E-type excimers are interpreted as the metastable one on two next-nearest parallel molecules and the stable one composed of card-packed dimeric units, respectively.²¹ Two types of excimers are also formed in pyrene LB films⁸ and the pyrene crystal.²¹ One is peaked around 470 nm, the other around 420 nm. They are assigned to a two-center sandwich excimer and a one-center or partial

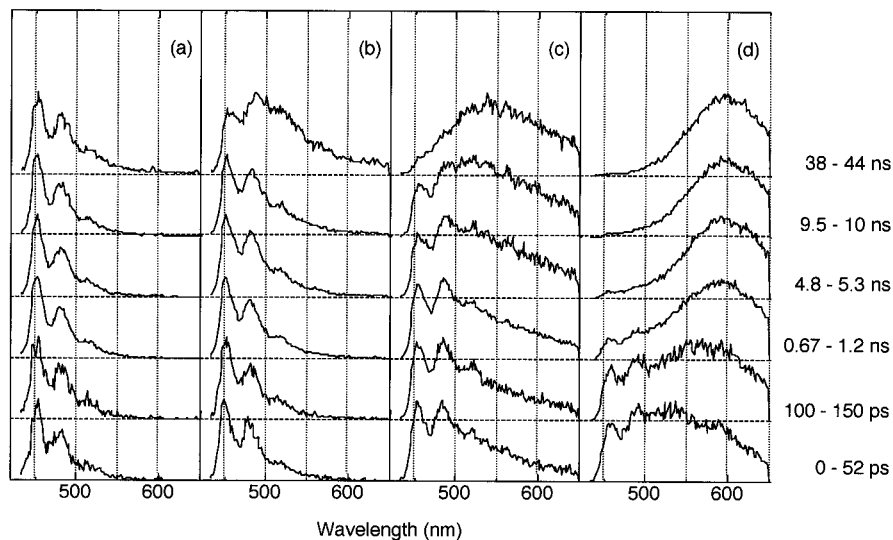


Figure 7. Time-resolved fluorescence spectra of PD in LB films at concentrations of (a) 0.05, (b) 1, (c) 10, and (d) 50 mol %. The excitation wavelength is 390 nm.

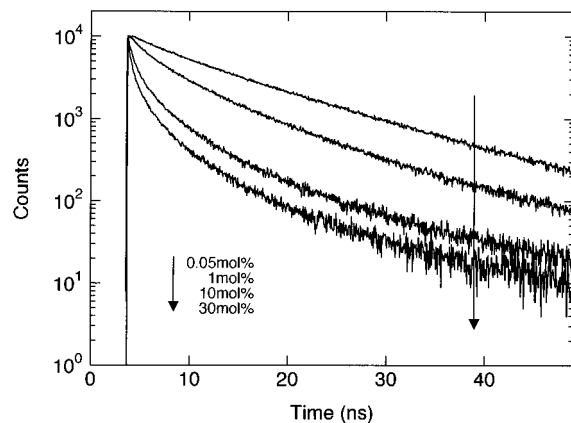


Figure 8. Fluorescence decay curves of PD in LB films at concentrations of 0.05, 1, 10, and 30 mol % observed at 454 nm (monomer fluorescence). The excitation wavelength is 390 nm.

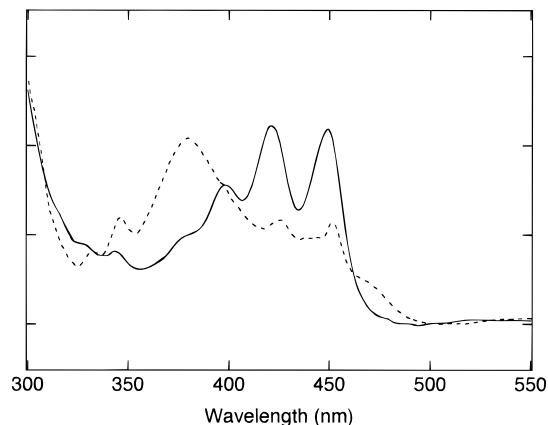


Figure 9. Absorption spectra of perylene monomer and perylene dimer in LB films.

overlapping excimer, respectively. By reference to the cases of pyrene LB films and crystal, the conformation of excimer 1 would be a one-center or partial overlapping type. A thermodynamical study will be needed to get an insight into the conformation of excimer 1 besides a time-resolved fluorescence study.

The absorption band of a ground-state dimer in LB films, on the other hand, is clearly obtained by subtracting the excitation spectrum of 10 mol % observed at 600 nm from that of 50 mol %. Figure 9 shows the spectra of a monomer and a ground-state dimer. The former is almost the same as that observed in solution, while the latter is a broad band peaked at 375 nm with a long tail to about 500 nm. The dimer absorption obtained in the LB film shows a good agreement with those in glass matrices¹⁵ and perylene-doped LB films.¹⁷

Here, we refer to the sites that give the monomer, excimer 1, and excimer 2 emissions as M, D₁, and D₂, respectively. The interaction between two perylene molecules in the D₁ site is very weak in the electronic ground state so that it gives the same absorption spectra as M. It is only in the electronically excited state where they interact with each other, resulting in the red-shifted fluorescence peaked at 535 nm. In the D₂ sites, the two perylene molecules have a strong interaction in both the ground and excited states, enough to show the dimer absorption to be different from the monomer absorption, and the further red-shifted and structureless fluorescence spectrum peaked at 600 nm. The M, D₁, and D₂ sites in LB films are

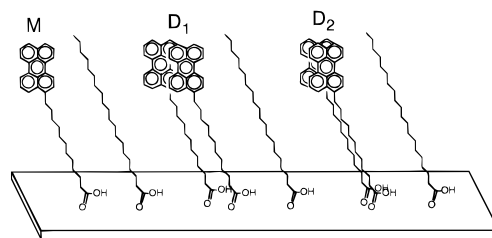


Figure 10. Schematic drawing of the M, D₁, and D₂ sites in LB films.

schematized in Figure 10. According to the concentration dependence of perylene fluorescence spectra in LB films, at concentrations less than 10 mol % an excimer where two chromophores are partially overlapped, i.e., D₁, and at higher concentration fully overlapped excimer D₂, becomes dominant. This indicates that the high-concentration stable modification has a structure similar to that of perylene with dimeric units in an α -peryene crystal.

Excitation Transfer from Monomer. In two-dimensional systems such as an LB monolayer, the fluorescence decays of energy donor molecules are analyzed by using the following equation²⁰

$$I(t) = A_1 \exp\left\{-\left(\frac{t}{\tau}\right) - K\left(\frac{t}{\tau}\right)^{1/3}\right\} + A_2 \exp\left\{-\left(\frac{t}{\tau}\right)\right\} \quad (1)$$

where τ is the lifetime of a donor molecule under the condition that the energy transfer does not occur. The second term on

TABLE 1: Results of the Fluorescence Decay Curve Analyses by Using Eq 1

| concentration mol % | A_2/A_1 | K | N molecules/cm ² |
|------------------------|----------------------|-----|----------------------------------|
| 0.05 | 3.2×10^{-1} | 1.0 | 1.5×10^{12} |
| 1 | 3.7×10^{-2} | 1.9 | 2.7×10^{12} |
| 10 | 1.6×10^{-2} | 4.0 | 5.9×10^{12} |
| 20 | 1.2×10^{-2} | 4.3 | 6.2×10^{12} |
| 30 | 9.0×10^{-3} | 4.8 | 7.0×10^{12} |
| 50 | 4.6×10^{-3} | 5.7 | 8.2×10^{12} |

the right-hand of eq 1 expresses the relaxation process of the isolated donor molecules. The first term, on the other hand, represents the survival probability of the donor based on the Förster-type energy-transfer process in two-dimensional systems.²² By use of the linear combination of these two factors, both random and inhomogeneous distributions are represented. K depends on the concentration of energy acceptor sites,

$$K = \frac{4}{3}\pi NR_0^2 \quad (2)$$

where N is the number density of acceptor sites and R_0 is the Förster radius. The Förster radius of perylene in solution is evaluated: $R_0 = 37.85 \text{ \AA}$.²³ Contrary to the random distribution in solution, the perylene molecules in the LB film are aligned with their long axes perpendicular to the surface of the substrates, resulting in a $(3/2)^{1/6}$ times greater value of the Förster radius than that in solution.²³ And then $R_0 = 40.5 \text{ \AA}$ is obtained for perylene molecules in the LB film. Here, we assumed that $\tau = 14 \text{ ns}$, which is evaluated by averaging the lifetimes of the monomer fluorescence at several concentrations in the time region after 30 ns.

Results of the decay curve analyses are listed in Table 1. The contribution of the second term of eq 1 becomes smaller with an increase of PD concentration. This trend indicates that as the concentration increases, the number of isolated PD monomer molecules decreases and the number of domains that contain both energy donor and acceptor sites increases, resulting in an effective excitation energy transfer. The concentration of acceptor sites stays about 10^{12} molecules/cm², although the concentration of PD widely changes from 0.05 to 50 mol %. This fact suggests that the concentration of acceptor sites in the domain does not depend on the PD concentration, but the number and/or size of the domain does. In addition, since the number of acceptors neighboring the energy donor is limited, the *effective* number of acceptor sites around the donor should be saturated, showing a gradual increase of the number density of acceptor sites against the concentration of PD.

Excitation Relaxation. The population decay curves of the three components are reconstructed by resolving the observed time-resolved fluorescence spectra into monomer, excimer 1, and excimer 2. Figure 11 shows the decay curves of each component, i.e., M^* , D_1^* , and D_2^* , at concentrations of 10 and 50 mol % in the time region before 500 ps. The dots and lines in the figure are the results of analyses and the curves simulated by convolution of the instrument response function and the sum of exponentials, respectively.

The decay curves of M^* and D_1^* have a fast component of 40–60 ps, which corresponds to the rise time of D_2^* at a concentration of 10 mol %. This behavior suggests that only M and D_1 are photoexcited at 390 nm, and then the excimer 2 emission is obtained as a result of (1) excimer formation between M and M^* , (2) conformation change in the D_1 site, and/or (3) excitation transfer from M^* and/or D_1^* to D_2 . At a concentration of 50 mol %, on the other hand, M^* and D_1^* diminish and D_2^* increases much more quickly with a time constant of 5–18 ps. In case 1, the rate of excimer formation is not dependent

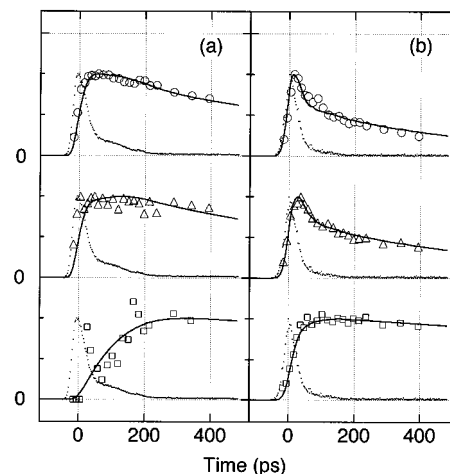
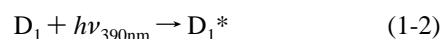
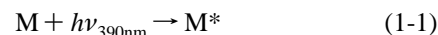


Figure 11. Population decay curves of three components. Dots (O, M^* ; Δ , D_1^* ; \square , D_2^*), dotted lines, and solid lines are the results of spectral analyses, the instrumental response functions, and the results of simulations, respectively. Part a is for 10 mol %. Part b is for 50 mol %.

on the concentration of PD, since translational diffusion does not occur in LB films in the time region we discuss. The conformation change, i.e., case 2, does not depend on the concentration either, since it is an *intrasite* process. On the other hand, the energy transfer process of case 3 is accelerated with concentration because the density of D_2 increases and the averaged distance between energy donor and acceptor decreases. Then the excimer 2 fluorescence is emitted because of excitation transfer from M^* and/or D_1^* to D_2 .

For the discussion of the excitation relaxation in perylene LB films, we roughly divide the concentration region where our experiments were carried out into three: (i) the low-, (ii) the intermediate-, and (iii) the high-concentration regions. They are classified into ~ 0.05 , ~ 1 , and 10–50 mol %, respectively. As the photoexcitation at 390 nm and the following *intersite* energy transfer proceed, we are concerned with three pathways as follows: (1) photoexcitation at 390 nm



(2) energy migration (donor-donor energy transfer)

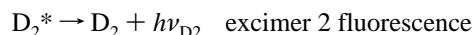
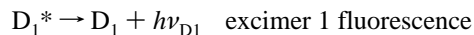
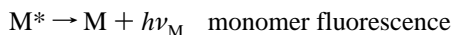


(3) energy transfer



In energy transfer process 3, the energy transfer from D_2^* to M and/or D_1 is negligible against the photoexcitation of M and D_1 , since the excimer 2 fluorescence spectrum is too red-shifted to be recognized to overlap with the monomer absorption (see Figures 3 and 7). The contribution of process 3-3 is much smaller than that of the process 3-1 because the spectral overlap between the excimer 1 fluorescence and the monomer absorption

is considerably small compared with that between the monomer fluorescence and the absorption of the D₁ site. As radiative relaxation proceeds, three types of fluorescence are observed:



(i) In the lowest concentration region i, the time-resolved fluorescence spectra show only the monomer band over the whole time range, suggesting that only the M sites exist. The nonexponential fluorescence decay of M* even in this lowest concentration region indicates that the energy migration among M sites (eq 2-1) efficiently occurs in perylene LB films.

(ii) As the concentration is increased up to 1 mol %, D₁ sites are formed, but their contribution is considerably small compared with that of M sites, so the excimer 1 fluorescence is observable only at a later time stage. The photoexcitation of M (eq 1-1) is followed by monomer fluorescence, energy migration among M sites (eq 2-1), and energy transfer to D₁ sites (3-1).

(iii) At a concentration of more than 10 mol %, the number of D₁ sites increases and D₂ sites are also formed. The photoexcitation of M and/or D₁ (eqs 1-1 and 1-2) is followed by monomer and excimer 1 fluorescence, energy migration among M and D₁ sites (eqs 2-1 and 2-2), and energy transfer to D₂ sites (eqs 3-2 and 3-4). The D₁ sites are formed effectively enough to accelerate the energy-transfer process (eq 3-1) and enough to make the direct photoexcitation of D₁ (eq 1-2) considerable against the energy-transfer process (eq 3-1).

Comparison with Pyrene LB Films. The Förster radius of perylene (37.85 Å) is much larger than that of pyrene (10.03 Å).²³ This causes a different feature of the relaxation process in perylene and pyrene LB films especially at the low-concentration region. The fluorescence decay curve of the perylene monomer is not single-exponential even in the low-concentration region. On the other hand, that of the pyrene monomer is single-exponential at low concentration and it deviates from the exponential form with an increase of concentration.²⁰ Because of its larger Förster radius, energy migration is more likely to occur in perylene LB films.

Summary

We prepared LB monolayers containing the perylene chromophores with different concentrations in the range 0.05–50 mol %. Besides the monomer fluorescence, two broad bands assigned to two types of excimers were observed. Their contribution to the fluorescence spectra is strongly dependent upon the concentration of chromophores included; as the concentration is increased, the main fluorescent band changes in the order of M, D₁, and D₂. This trend is closely related to

the concentration dependence of the dimer formation and the excitation transfer in LB films. The energy-transfer process after photoexcitation of M sites has been discussed using picosecond time-resolved fluorescence measurements. In the low-concentration region of 0.05 mol %, only the monomer fluorescence is observed. As the concentration is increased up to 1 mol %, the excimer 1 fluorescence can be seen in the time region after 40 ns, indicating that a small number of D₁ sites is formed and that it works as an energy trap in this concentration region. At a concentration higher than 10 mol %, the D₂ site is also formed and the excitation transfer to D₂ effectively occurs. The excitation transfer from M and D₁ sites to D₂ sites is observed with a time constant of ~50 ps at 10 mol %, whereas it ~10 ps at 50 mol %.

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