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Substrate-Dependent Aggregation and Energy Transfer in Langmuir−Blodgett Films of 5-(4-*N*-Octadecylpyridyl)-10,15,20-tri-*p*-tolylporphyrin Studied by Ultraviolet−Visible and Fluorescence Spectroscopies

Zhijun Zhang,[†] Anandi Lal Verma,*,[‡] Kenichi Nakashima,[§] Mitsuru Yoneyama,[‖] Keiji Iriyama,[⊥] and Yukihiro Ozaki*,[†]

Department of Chemistry, School of Science, Kwansei-Gakuin University, Uegahara, Nishinomiya 662, Japan, Department of Physics, North-Eastern Hill University, Shillong-790322, India, Department of Chemistry, Faculty of Science and Engineering, Saga University, Saga 840, Japan, Mitsubishi Chemical Corporation, Yokohama Research Center, 1000 Kamoshida-cho, Aoba-ku, Yokohama 227, Japan, and Institute of DNA Medicine, The Jikei University School of Medicine, Nishi-shinbashi, Minato-ku, Tokyo 105, Japan

Substrate-dependent energy transfer and aggregation in Langmuir−Blodgett (LB) films of 5-(4-*N*-octadecylpyridyl)-10,15,20-tri-*p*-tolylporphyrin (porphyrin 338a) have been investigated by ultraviolet−visible (UV−vis) and fluorescence spectroscopies. It has been found that the porphyrin molecules form different kinds of aggregates in the LB films on the glass and gold-evaporated glass substrates, evidenced by red shifts of about 10 and 25 nm, respectively, of the Soret bands compared to that of monomeric species in the chloroform solution. The two kinds of aggregates show different fluorescence characteristics. An additional feature of absorption around 480 nm of the LB films on the gold-evaporated glass substrate and marked quenching of fluorescence by the excitation at this wavelength suggest the formation of two different kinds of head-to-tail type J-aggregates in the LB films. Drastic quenching of fluorescence of the porphyrin LB films on gold-evaporated glass substrate and enhanced luminescence with increasing distance between the porphyrin and the gold-evaporated glass substrate by imposing arachidic acid LB films of known thickness may be explained due by efficient radiationless energy transfer from excited porphyrin molecules to the metal surface. An interlayer energy transfer has been observed for the multilayer LB films on both glass and gold-evaporated glass substrates.

Introduction

In the preceding paper,[1] we reported the molecular orientation and aggregation in Langmuir−Blodgett (LB) films of 5-(4-*N*-octadecylpyridyl)-10,15,20-tri-*p*-tolylporphyrin (abbreviated as porphyrin 338a), studied by ultraviolet−visible (UV−vis) and infrared (IR) spectroscopies. The following two conclusions were drawn: (1) The chromophoric part of the porphyrin molecules in the LB films deposited on the CaF_2 and glass plates assumes nearly flat orientation to the substrate surface. The hydrocarbon chain attached to the macrocycle has conformational disorder, including some gauche conformations. (2) The porphyrin molecules form aggregates in the LB films on CaF_2 plates characterized by a red shift of the Soret bands compared to that in the chloroform solution. Apart from the structural aspects of adsorbates on substrates, deep understanding of the interaction of the electronic and vibrational states of the adsorbates with the substrate surface is important for microscopic description of the surface dynamical processes. The excited states of molecular species in the proximity of the surface take part in many dynamical processes such as chemical reactions,[2] photochemical processes,[3] photoluminescence,[4] and nonlinear optical effects,[5] and therefore their nature

and mode of radiative and nonradiative relaxations are subjects of current keen interest.[6−9]

To gain a new insight into the interaction between porphyrin and substrates, we have undertaken detailed studies on substrate- and layer-dependent energy transfer and aggregation in the LB films of porphyrin 338a deposited on glass and gold-evaporated glass plates by using UV−vis and fluorescence spectroscopies. In order to differentiate the effects of interlayer energy transfer in the multilayer LB films from those of the energy transfer of the porphyrin to the metal surface, we have studied one-monolayer LB films of porphyrin 338a separated by 1-, 3-, 5- and 9-monolayer LB films of arachidic acid from the gold-evaporated glass substrate. On the basis of such studies, we have clarified various channels for nonradiative energy transfer and interactions between the porphyrin molecules and the substrates, in particular the metal substrates. This kind of investigation is particularly important for the development of the conducting porphyrin LB films because they are normally fabricated onto metal substrates.[10,11] The present studies may also provide a

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* To whom correspondence should be addressed.

[†] Kwansei-Gakuin University.

[‡] North-Eastern Hill University.

[§] Saga University.

[‖] Mitsubishi Chemical Corp.

[⊥] The Jikei University School of Medicine.

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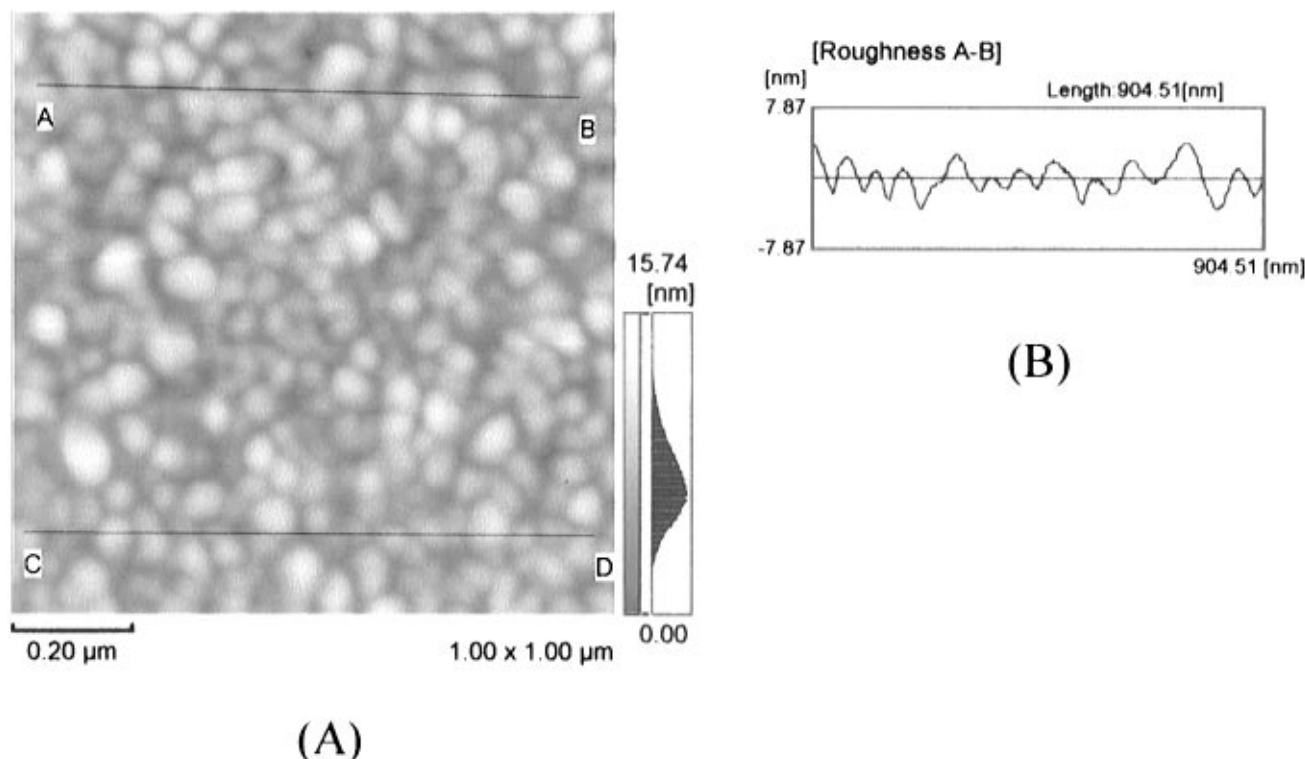
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Figure 1. Atomic force microscopy (AFM) image (A) and its cross section (B) of a gold-evaporated glass substrate.

new insight into various processes of energy transduction by porphyrins in the photochemical reaction center.[12]

Experimental Section

The porphyrin sample used is the same as that in previous paper.[1] Arachidic acid was purchased from Aldrich Chemical Co. and used without further purification.
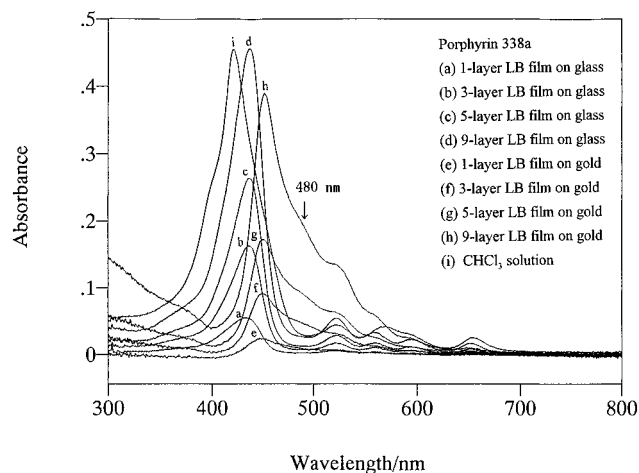
The gold- or silver-evaporated glass plates were prepared as follows: After chromium of 150 nm film thickness had been evaporated onto each glass plate, a gold or silver film having a thickness of 300 nm was evaporated onto it. Figure 1 shows the atomic force microscopy (AFM) image and its cross section of a gold-evaporated glass substrate. From the cross section, the average surface roughness was estimated to be about 2 nm.

The instrumentation and techniques for the fabrication of the LB films on glass, quartz, CaF_2 plates, and gold- and silver-evaporated glass substrates were the same as described elsewhere.[1] The UV−vis transmission spectra of the LB films on the glass, CaF_2, and quartz plates were performed with a Shimadzu UV-3101PC spectrophotometer, while the UV−vis reflection−absorption spectra of the LB films on the gold- and silver-evaporated glass substrates were measured by use of the above spectrophotometer with a reflection attachment. The fluorescence spectra were measured by using a Hitachi 4 spectrofluorometer with a cell holder in the front-face configuration.

AFM imaging of a gold-evaporated glass substrate was performed with a Shimadzu SPM-9500 atomic force microscope under ambient conditions using a 15 μm × 15 μm scanner and a silicon nitride tip on a cantilever with spring constant 0.16 N/m in contact mode.

Results

UV−vis Spectra. Spectra a−d of Figure 2 show UV−vis spectra of one-, three-, five-, and nine-monolayer LB

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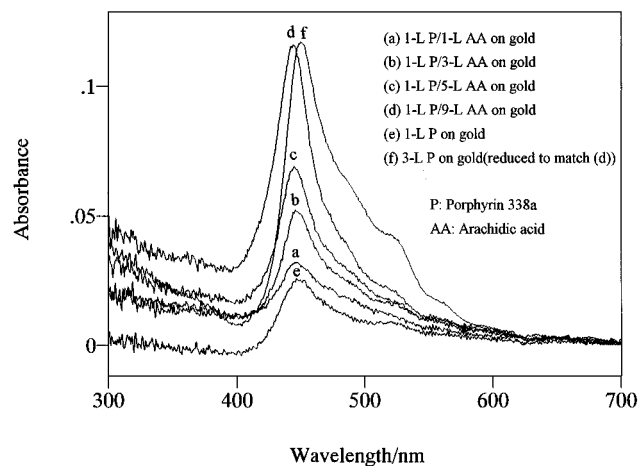

Figure 2. UV−vis spectra of (a) one-, (b) three-, (c) five-, and (d) nine-monolayer LB films of porphyrin 338a deposited on glass plates and corresponding spectra of the (e) one-, (f) three-, (g) five-, and (h) nine-monolayer LB films on gold-evaporated glass plates, respectively. For comparison, a UV−vis spectrum of porphyrin 338a in a chloroform solution is also plotted as (i).

films of porphyrin 338a on glass plates, respectively. The UV−vis spectra of the corresponding one-, three-, five-, and nine-monolayer LB films on gold-evaporated glass plates are displayed in spectra e−h of Figure 2, respectively; for comparison, a UV−vis spectrum of porphyrin 338a in a chloroform solution is also plotted (Figure 2i). The strong bands appearing in the 400−500 nm region are assigned as Soret or B bands.[12] The Soret bands of the mono- and multilayer LB films on the glass plates show a red shift by about 10 nm, compared with that in the chloroform solution, while for the mono- and multilayer LB films on the gold-evaporated glass substrate a red shift of about 25 nm is observed. Of particular note for the Soret bands of porphyrin LB films on the gold-evaporated glass substrates is the presence of an additional broad shoulder centered around 480 nm and sharp band shape on the high energy side.

Figure 3. UV−vis spectra of the one-monolayer LB films of porphyrin 338a on a gold-evaporated glass plate separated by (a) one-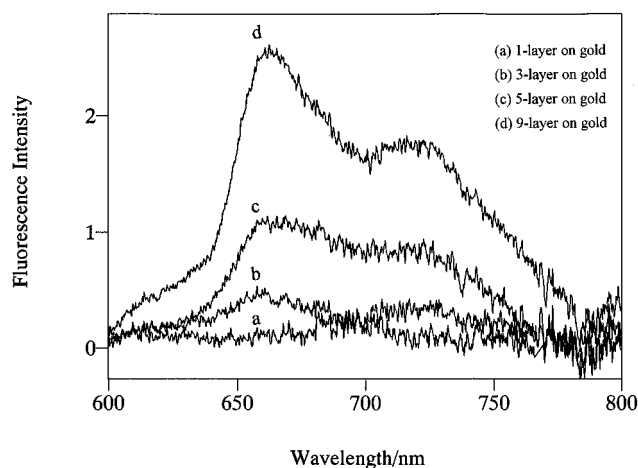, (b) three-, (c) five-, and (d) nine-monolayer LB films of arachidic acid from the substrates, respectively. The spectra of (e) one- and (f) three-monolayer LB films of porphyrin 338a deposited directly on the gold-evaporated glass substrates are included for comparison. Note that curve f is normalized to curve d.

Comparison of spectroscopic properties between the LB films on the glass and gold-evaporated glass plates provides important information about the nature of the interaction between the porphyrin molecules and substrates. The larger red shift of the Soret band and an additional band around 480 nm for the LB films on the gold-evaporated glass substrate indicate that the gold surface imposes much stronger influence on the molecular arrangement in the LB films. To investigate this effect, we prepared one-monolayer LB films of porphyrin 338a on the gold-evaporated glass plates onto which one-, three-, five-, and nine-monolayer LB films of arachidic acid had been deposited in advance. The UV−vis spectra of these LB films are presented in Figure 3. The spectra of the one- and three-monolayer LB films of porphyrin 338a deposited directly onto the gold-evaporated glass plate are also included for comparison (spectra e and f of Figure 3). It can be seen from Figure 3 that the band positions of the Soret bands of one-monolayer LB films of porphyrin 338a on the gold-evaporated glass plates blue-shifted to different extents upon the separating of the porphyrin LB films from the substrate, while the shoulder around 480 nm become weaker with the increase in the distance between the LB film of porphyrin 338a and the gold surface. It also is noticed that with the increase in the fatty acid monolayers, the absorbance the Soret bands of one-monolayer LB films of porphyrin 338a become stronger. This may arise from alteration of molecular orientation and aggregation, and interaction between porphyrin and gold surface, caused by insertion of fatty acid spacer between porphyrin LB film and gold surface. Further work to clarify this phenomenon is under progress now.

Fluorescence Spectra. Figures 4 and 5 present fluorescence spectra of one-, three-, five-, and nine-monolayer LB films of porphyrin 338a on glass and gold-evaporated glass plates, respectively. Two bands at ∼660 and 720 nm correspond to Q(0,0) and Q(0,1) transition of the porphyrins, respectively.[12−14] Note that the one-monolayer LB film deposited on the gold-evaporated glass plate shows very weak fluorescence emission, while the

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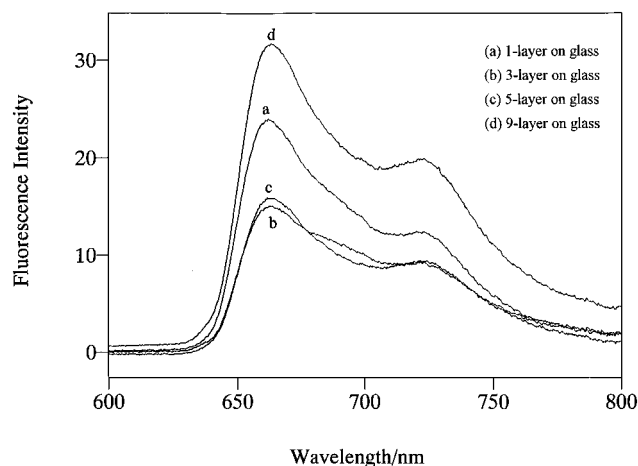
Figure 4. Fluorescence spectra of (a) one-, (b) three-, (c) five-, and (d) nine-monolayer LB films of porphyrin 338a on glass plates, respectively. The samples are excited at 425 nm.
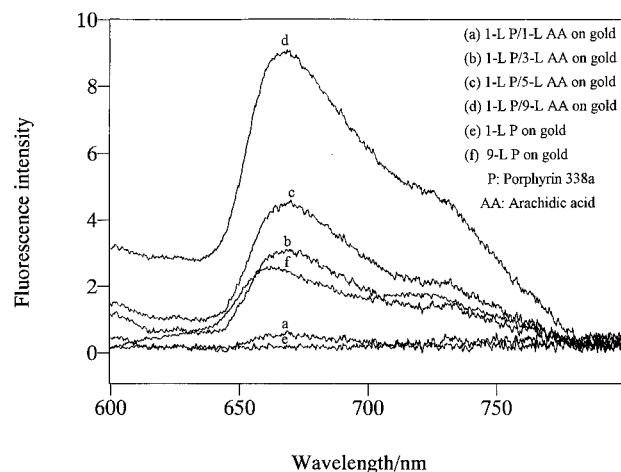

Figure 5. Fluorescence spectra of (a) one-, (b) three-, (c) five-, and (d) nine-monolayer LB films of porphyrin 338a on gold-evaporated glass plates, respectively. The samples are excited at 450 nm.

one-monolayer LB film on the glass plate gives strong emission. For the LB films on the gold-evaporated glass substrates, the fluorescence intensity increases with the number of monolayers. In contrast, no such relationship is observed for the LB films on the glass slides.

Spectra a−d of Figure 6 depict fluorescence spectra of one-monolayer LB films of porphyrin 338a having the one-, three-, five-, and nine-monolayer LB film of arachidic acid as a spacer on the gold-evaporated glass substrates. The fluorescence spectra of one- and nine-monolayer LB films of porphyrin 338a fabricated directly on the gold-evaporated glass substrates are also shown in spectra e and f of Figure 6. It is clear from Figure 6 that with the increase in the distance between porphyrin LB film and gold surface, the fluorescence intensity of the one-monolayer porphyrin LB film increases. It is noteworthy that compared to the Q(0,0) band of the nine-monolayer LB film directly deposited on the gold-evaporated glass plate, the corresponding bands in the fatty acid-separated LB films of porphyrin 338a show a red shift by about 6 nm. It is observed that the one-monolayer LB film of porphyrin 338a on gold separated by either three-, five-, or nine-monolayer LB films of arachidic acid has fluorescence intensity stronger than a nine-monolayer LB film of porphyrin 338a directly deposited onto gold surface. These results demonstrate that the gold-evaporated glass substrate indeed imposes marked influence on the electronic state of porphyrin 338a in the LB films. In other

Figure 6. Fluorescence spectra of one-monolayer porphyrin LB films on gold-evaporated glass substrates onto which (a) one-, (b) three-, (c) five-, and (d) nine-monolayer arachidic acid LB films had been deposited in advance, respectively. Fluorescence spectra of (e) one- and (f) nine-monolayer porphyrin LB films fabricated directly on gold-evaporated glass plates are also included for comparison. All the samples are excited at 450 nm.
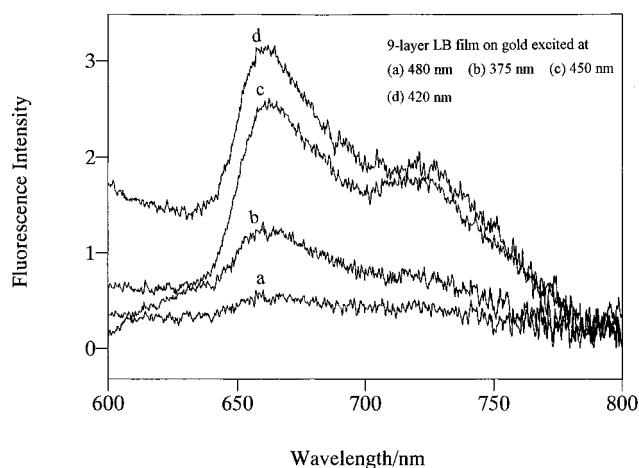
Figure 7. Fluorescence spectra of the nine-monolayer porphyrin LB film on a gold-evaporated glass plates excited at (a) 480, (b) 375, (c) 450, and (d) 420 nm, respectively.

words, the separation of the porphyrin LB film from the gold-evaporated glass substrate alters both the absorption and emission characteristics.

Spectra a−d of Figure 7 illustrate the emission profiles of the nine-monolayer LB film of porphyrin 338a on gold-evaporated glass plates excited at 480, 375, 450, and 420 nm, respectively. It can be seen that the contours of these spectra do not change significantly, though the intensities alter largely. It is noted that the species with the absorption maximum at about 480 nm is light absorbing, but nonfluorescent, as is evidenced from Figures 3 and 7.

Discussion

Substrate-Dependent Aggregation Behavior of Porphyrin Molecules in LB Films. It can be seen from Figure 2 that the Soret band in the UV−vis spectra of one-monolayer LB films of different solid supports shows a red shift to different extents, compared with that of the spreading solution. The red shift of the Soret band is due to the formation of aggregates in the LB films,[15,16] as discussed in the preceding paper.[1] On comparison of the

UV−vis spectra among the LB films of porphyrin 338a on CaF$_2$ (see Figure 3 in the preceding paper[1]), glass, gold, quartz, and silver (data not shown) plates, it may be concluded that the aggregates formed in the LB films on the surface of nonmetal substrates such as CaF$_2$, glass, and quartz have similar structure, while those formed in the LB films on the metal-coated substrates like the gold-evaporated glass substrate have quite different structure. The resemblance of the UV−vis spectrum of the porphyrin LB film on the silver-evaporated glass plate to those of the LB films on the nonmetal substrates may be ascribed to the formation of an oxide layer on the silver surface, as silver is highly prone to oxidation.[17] The influence of substrates on molecular arrangement has also been reported for LB films,[18−20] self-assembled films,[17] and evaporated films[21] by other researchers in the past.

It is very unlikely that the deformation in the porphyrin core or the formation of dication H$_2$P^{2+} (P, porphyrin 338a) is responsible for the red shift of the Soret bands of the LB films on the gold-evaporated glass substrates, because a LB film of the relatively rigid indium complex of porphyrin 338a also shows a similar red shift of the Soret band, and the LB films of porphyrin 338a give four Q bands characteristic of free base porphyrin. Blue and red shifts of absorption bands are very common for dyes forming aggregates due to excitonic interaction.[22] As per the excitonic model of chromophores in solution or organized assembles, the dipole−dipole interaction energy E_{dd} is given by[22]

$$E_{dd} = -\mu^2(1 - 3\cos^2\theta)/a^3 \qquad (1)$$

where μ is the transition moment and a is the center to center distance between the dipoles. The part in parentheses is the geometric factor related to the mutual orientation of the dipoles. The spectral shift of the absorption band for linear aggregates as a function of aggregate size N is given by[23]

$$\cos[\pi/(N+1)] = \Delta\nu_N/\Delta\nu_\infty \qquad (2)$$

where $\Delta\nu_N$ and $\Delta\nu_\infty$ are the spectral shifts for aggregates having N and ∞ number of units, with respect to the monomer, respectively. The absorption band width $\Delta\nu_{1/2}$ (A) of the aggregates is related to N as[24]

$$\Delta\nu_{1/2}(M)/\Delta\nu_{1/2}(A) = N^{1/2} \qquad (3)$$

where $\Delta\nu_{1/2}(M)$ is the absorption bandwidth of the monomer.

The larger red shift of the Soret band for the porphyrin LB films on the gold-evaporated plates compared to that on the glass substrates indicates that the separation of porphyrin units in the head-to-tail (J-aggregate) arrangement is smaller and/or that the number of molecular units is larger in the LB films on the gold-evaporated glass plates. The additional feature at 480 nm in the absorption spectra of porphyrin LB films on the gold-evaporated glass

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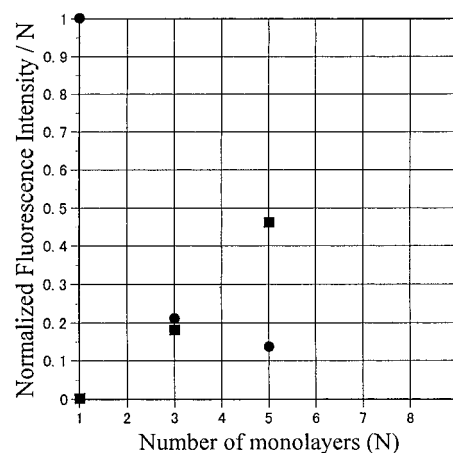(24) Knapp, E. W. *Chem. Phys.* **1984**, *85*, 73.

substrates may arise from the Soret band of another kind of J-aggregates (hereafter we refer them as J′-aggregates to differentiate them from the J-aggregates with the Soret band at 450 nm) having even larger number of units and a variety of interplanar porphyrin−porphyrin core geometries. The J′-aggregates do not show any fluorescence with the excitation at 480 nm (Figure 7a). The exciton model also predicts sharpening of absorption bands on the formation of J-type aggregates,[25] which is not observed in our case. The probable reasons for this are the loose packing of hydrocarbon chains and a variety of interplanar porphyrin−porphyrin core geometries.

Although the UV−vis spectra of porphyrin LB films on the glass and gold-evaporated glass substrates differ significantly, their emission profiles are very similar (Figures 2, 4, and 5). The absence of red-shifted fluorescence from any J-type of aggregates of porphyrin 338a on the glass and gold-evaporated glass substrates is understandable from the fact that the Soret transition occurs to the second single excited state S_2 which shows larger splitting, while the emission takes place from the first excited single state S_1 which does not show large splitting as the transition dipole moment is smaller for the transitions leading to Q bands.

In order to explore the nature of the emitting species in the LB films of porphyrin 338a on the glass and gold-evaporated glass substrates, we measured fluorescence excitation spectra of the porphyrin LB films on these substrates by monitoring the fluorescence at 660 and 720 nm. The excitation spectra show intense peaks centered around 437 nm for the LB films on both substrates, indicating that the emitting species in both cases is of similar type. This peak in the excitation spectra coincides with the Soret band of the LB films on the glass substrate (∼436 nm). Probably, loose head-to-tail types of aggregates are formed in the LB films on both substrates. It is likely that these loose aggregates act as traps for the excitation energy of monomers. In other words, the excited monomers transfer the excitation energy to the aggregates absorbing at around 436 nm, which emit fluorescence. This interesting phenomenon remains to be fully understood.

Energy Transfer between Substrate and Porphyrin Molecules in LB Films. Energy transfer in LB films has been studied by several research groups.[26−34] The classic model proposed by Chance et al.[7] has been quite successful in predicting the rates of energy transfer from molecules to the metal surfaces. Chang has applied transition monopole theory of electronic excitation interaction to study energy transfer of chlorophyll molecules.[35] We have been interested in the effects of substrate and intermonolayer interaction on the energy transfer in the LB films of porphyrin molecules. The emission spectra of the porphyrin LB films deposited directly on the gold surface (Figures 5 and 8) and those of the one-monolayer

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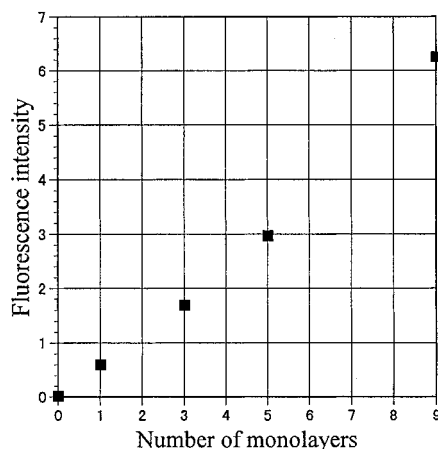(30) Kuhn, H. *J. Chem. Phys.* **1970**, *53*, 101.
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Figure 8. Plots of the normalized fluorescence intensity per monolayer versus the number of monolayers for the LB films of porphyrin 338a on glass (●) and gold-evaporated glass substrates (■).

porphyrin LB films on gold-evaporated glass substrates separated by fatty acid LB films (Figures 6 and 9) demonstrate distance dependence of effective energy transfer from the porphyrin molecules to the gold surface, as observed by Kuhn.[30]

Besides the efficient energy transfer from porphyrin molecules to the gold surface in the LB films of porphyrin 338a, the energy transfer between neighboring monolayers (inter-monolayer energy transfer) in the multilayer LB films is also considerably effective. This can be confirmed if we compare the fluorescence spectra of nine-monolayer LB films of porphyrin 338a directly deposited on the gold-evaporated glass substrates with those of one-monolayer LB films of porphyrin 338a separated by different monolayer LB films of arachidic acid on the gold-evaporated glass substrates (Figure 6). The fluorescence intensity of the nine-monolayer LB film is lower than that of the one-monolayer LB films of porphyrin 338a separated by the three-, five-, and nine-monolayer fatty acid LB films. Therefore, there exists competition between energy transfer from porphyrin molecules to the gold surface and that of intermonolayer interactions.

In contrast to the LB films on the gold-evaporated glass substrates, there seems to be no significant energy transfer from the porphyrin molecules to glass plates because the strong fluorescence is observed for the one-monolayer LB film of porphyrin 338a on the glass plate. To delineate the effects of the number of monolayers on the energy transfer in the LB films on the glass and gold-evaporated glass plates, plots of fluorescence intensity divided by the number of monolayers as a function of the number of monolayers are given in Figure 8. For the LB films of porphyrin 338a on the gold-evaporated glass plates, the increase in the number of monolayers reduces the effective energy transfer from the porphyrin to the gold surface due to the increased separation of higher monolayers from the gold surface. As a result, the fluorescence intensity increases. However, for the LB films on the glass plates, because of the lack of effective energy transfer from the porphyrin molecules to glass substrate, the fluorescence emission is fairly strong. With the increase in the number of monolayers, the fluorescence intensity per monolayer decreases sharply up to the three-monolayer film, and above it the intensity becomes almost constant (see Figure 8). The quenching of fluorescence in the multimonolayer LB films on the glass plates may be due to interlayer energy transfer.

According to the model for energy transfer from excited dipoles to the metal surface proposed by Chance et al.,[7]

Figure 9. Plot of fluorescent intensity as a function of the number of monolayers of arachidic acid LB films as a spacer (■).

at distances greater than ~100 Å, the radiative rate of the molecules is modified, leading to oscillations in lifetime and intensity due to interference between the radiative oscillating dipole moment of the electronically excited molecules and the reflected field from the metal surface. On the other hand, at distances below about 100 Å, the lifetime sharply reduces mainly in the form of nonradiative energy transfer from the near dipolar field to the metal surface via coupling through nonradiative surface plasmon modes of the gold. In that case, the lifetime decreases as reciprocal cubic distance (d^{-3}) for thick metal films (the thickness of metal is much larger than the distance of dipoles to the metal surface). On the other hand, for a thin metal surface (thickness of metal is smaller than the distance of dipoles from the metal surface) the lifetime is expected to show d^{-4} dependence.[7] The fluorescence yield is expected to behave similarly, if this is the only major channel for energy transfer.

In the case of the multilayer LB films of porphyrin 338a on the gold-evaporated glass substrates, there are at least three channels for nonradiative energy transfer: intra-layer, interlayer, and layer-to-substrate energy migration. In order to eliminate the effect of interlayer energy transfer, we carried out the experiments on the single monolayer LB films of porphyrin 338a separated from the gold surface by the one-, three-, five-, and nine-monolayer LB film of arachidic acid of known thickness of about 26.4 Å for each layer. We find nearly linear increase in the fluorescence intensity as a function of the distance (d) between the porphyrin LB film and gold surface (Figure 9), rather than a cubic distance (d^3) dependence for thick gold films reported by Chance et al.[7] This may be due to combined effects of intermolecular and surface specific nonradiative decay channels, as well as other energy traps due to impurities and defect sites. Another possible reason for this deviation is the effect of surface roughness of the gold-evaporated glass slides on the energy transfer from excited porphyrin molecules to the gold surface. Such an effect becomes more pronounced when the distance of the excited dipoles from the metal surface becomes comparable with the surface roughness, as pointed out by Alivisatos

et al.,[33] Garoff et al.,[36] and Arias et al.[37] We expect that the lifetime measurement would provide more precise and reliable information for energy transfer rate as a function of distance of porphyrin from gold surface. The investigation on the dynamics of energy transfer in the LB films of porphyrin by employing time-resolved fluorescence techniques will be reported soon.

Conclusion

The substrate- and monolayer-dependent energy transfer and aggregation of LB films of porphyrin 338a have been investigated. The UV–vis and fluorescence spectra of porphyrin LB films change substantially between nonmetal substrates such as the glass plate and metal-coated substrates like the gold-evaporated glass plate, indicating different forms of aggregates and energy transfer efficiency between the porphyrin molecules and substrates. In the LB films on the gold-evaporated glass plates, effective energy transfer from the porphyrin molecules to the gold surface takes place, evidenced by very weak fluorescence emission. The fluorescence intensity per unit monolayer increases nearly linearly with the number of monolayers for LB films of porphyrin 338a deposited directly on gold-evaporated glass substrates. The separation of the LB film of porphyrin 338a from the gold-evaporated glass substrate by the fatty acid LB films reduces, to a large extent, the energy transfer from the porphyrin LB film to the gold surface. In this case, the fluorescence intensity increases nearly linearly with the number of monolayers of fatty acid LB films for a one-monolayer LB film of porphyrin 338a separated by a LB film of fatty acid, due to decay of energy via other nonradiative channels. In contrast to the LB films on the gold-evaporated glass plates, no appreciable energy transfer occurs between the porphyrin molecules and the substrate surface for the LB films on the glass substrates. Instead, the energy transfer takes place between the porphyrin molecules through intra- and interlayer interaction. In summary, the present study on the energy transfer and aggregation in the LB films of porphyrin 338a by means of UV–visible and fluorescence spectroscopies has afforded much information about the nature of porphyrin–porphyrin and porphyrin–substrate interactions in the films.

In order to obtain deeper understanding of the energy transfer and the related phenomenon, a time-resolved fluorescence study on the dynamics of the energy transfer from porphyrin to the gold surface by use of porphyrin LB films with spacers of different thicknesses is now in progress and will be reported later. To our knowledge, this is the first report on the energy transfer from porphyrin to metal surface and interlayer energy transfer in LB films of porphyrin derivatives.

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