Study of lateral electron transfer in Langmuir-Blodgett films containing cyanine and viologen amphiphiles

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Abstract

The efficiency of the lateral photo-induced electron transfer between cyanine (electron donor) and viologen (electron acceptor) amphiphiles (Cy and V, respectively) was examined by observing the absorption and emission spectra of V doped Cy LB films. The sharp J-band observed in the absorption and fluorescence spectra indicated the efficient formation of J-aggregate of the cyanine chromophore even in the mixed LB

monolayers with V. The fluorescence intensities of the J-band decreased monotonously with the increase of V concentration but the dependence of the electron transfer efficiency on the film composition was rather complicated. The efficiency of the lateral electron transfer estimated at the composition region of the lower V ratios, where V molecules are expected to disperse homogeneously into the Cy monolayer, was such that ca. 90 molecules of Cy would be quenched by one center molecule of V.

Key words: lateral electron transfer; cyanine J-aggregate; Langmuir-Blodgett film; fluorescence quenching

1. Introduction

Two dimensionally J-aggregated cyanine dyes in Langmuir-Blodgett films have been extensively studied and many experiments, theories, and models for the aggregation have been appeared. Especially for practical applications of the J-aggregate, the study of the sensitization of photo-electrochemical process is an important area.

In our approach for fabrication of an artificial photosynthetic system, we have synthesized acceptor-sensitizer-donor (A-S-D) type triad molecules as models for

photosynthetic reaction centers [1-4]. In the triad molecules, viologen, pyrene or perylene, and ferrocene moieties as A, S, and D, respectively, are covalently bonded with hydrocarbon bridges. In our previous study [5], we examined light-harvesting function of N,N'-dioctadecyl-oxacyanine (Cy in Fig. 1) LB film. In our design of an artificial photosynthesis, the J-aggregated cyanine dye as a light-harvesting antenna system should be integrated with our model reaction centers by a fabrication of a mixed LB monolayer including them. In such system, the light-harvesting antenna cooperates with a model reaction center via excitation energy transfer from photo-excited Cy (Cy*) to S moiety in the triad. In the preceding study, to focus only on the light harvesting process from the antenna to the sensitizer moiety of the triad, we doped small amount of perylene fatty acid (Pe) as the model S compound of the perylene type triad to the Cy LB film [5]. In that study, the antenna effect of J-aggregated Cy was estimated to be such that ca. 250 molecules of Cy would harvest light for excitation of one Pe molecule. This antenna effect is comparable to that of natural photosynthesis.

The efficiency of the energy transfer from Cy* to Pe is such good, but in the mixed monolayers of Cy and the perylene type A-S-D triad, however, Cy can act not only as an energy donor to S but also as an electron donor to A. Namely, in the Cy LB film doped with the triad, the unfavorable intermolecular electron transfer ($\text{Cy}^* + \text{A-S-D} \rightarrow \text{Cy}^+ +$

A⁻-S-D) can be expected besides the favorable energy transfer ($\text{Cy}^* + \text{A-S-D} \rightarrow \text{Cy} + \text{A-S}^*-\text{D}$).

The electron transfer between cyanine dye and viologen in layer-by-layer assemblies had been reported by Möbius [6]. In that study, the electron transfer quenching of an excited cyanine by an electron acceptor viologen had never observed in the case of donor-acceptor separation by an arachidate bilayer, corresponding to a distance of 54 Å. Considering the molecular area of Cy (ca. 0.6 nm² molecule⁻¹), 250 molecules of Cy, available for the light-harvesting in our previous result, arrange in the area of ca. 150 nm² on the monolayer surface. If we employ a rather crude approximation of the Perrin like model [7], we can assume that one center molecule of Pe quenches Cy molecules lying within ca. 70 Å radius. The quenching radius of ca. 70 Å is much larger than the thickness of an arachidate bilayer film; therefore efficient light-harvesting might be expected also in the mixed Cy monolayers with the perylene type A-S-D. However, the difference in the relative arrangement of the Cy and viologen between the layer-by-layer assembly of the multilayer system and the side-by-side assembly of our mixed monolayer system should be affect the distance dependence of the electron transfer quenching. In addition, some unexpected surface structures may affect the energy and electron transfer processes.

In the present study, we focused on the lateral electron transfer in LB films including Cy and a model A compound, N,N'-dioctadecyl-4,4'-bipyridinium bromide (V in Fig. 1), to estimate the efficiency of the side electron transfer reaction. We will also check the miscibility of V molecule with the Cy J-aggregate.

2. Experimental details

Cy used to fabricate LB films was purchased from Nippon Kanko Shikiso Co. and used as received. V was synthesized in our laboratory. The purity was confirmed by 270 MHz ^1H NMR. All other chemicals were reagent grade and used as received. Quartz plates from Fujiwara Scientific Co. were used for the substrates on which LB films were deposited.

The monolayer LB films were formed with a Langmuir-trough equipped with an electronic microbalance and a glass Wilhelmy plate (Kyowa Kaimenkagaku, HBM-AP). The subphase was pure water from a milli-Q system (Millipore Ltd.). The temperature of the subphase was maintained at 15 °C. The monolayers were spread from chloroform solutions containing Cy, n-octadecane (OD), and V in the molar ratios $\text{Cy:OD:V} = \text{X:X:1}$ ($\text{X} = 1, 2, 5, 10, 20, 50, 100, 200, 500, 1000, \text{ and } 2000$) and 1:1:0. OD just plays a role of a spacer in the hydrophobic part in a LB film. It contributes to the arrangement of the aliphatic region and not to the average surface area per molecule [8,9]. Thus OD

would not function as a barrier to block the electron transfer between the hydrophilic moieties. The compositions of monolayers given below will be described by the ratio Cy:V but it should be noted that OD exists equimolarly with Cy in all LB monolayers in this study. The monolayers were deposited on both sides of the quartz substrates at the constant surface pressure of 30 mNm⁻¹. The UV-vis absorption and the fluorescence emission spectra were taken with a Shimadzu UV-265FW recording spectrophotometer and a Jasco FP-777 recording fluorescence spectrophotometer, respectively. The spectral measurements on the LB films were carefully performed by following the similar methods used in the previous study [5].

3. Results and discussion

In Fig. 2, surface pressure-area (π -A) isotherms are shown for the molar mixing ratios Cy:V = 1:1, 2:1, 5:1, 10:1, 20:1, 50:1, and 100:1 (curves A, B, C, D, E, F, and G, respectively). The mixed Cy monolayers with V in the molar ratios Cy:V = 200:1, 500:1, 1000:1, 2000:1, and 1:0 gave almost the same π -A isotherms (not shown here) as curve G. Although, only at the highest concentration of V (curve A), the addition of V molecule attenuated the stability of the Cy monolayer, the other concentrations (curve B-G) successfully gave stable mixed monolayers as shown in Fig. 2. Among the wide

range of the mixing ratios from 2:1 to 50:1 (curve B-F), the π -A isotherms were very similar and some shrinking of the molecular area was observed. In contrast, the Pe doped Cy monolayers at the mixing ratios 20:1 ~ 100:1 gave expanded and similar isotherms [5]. In such cases, a small amount of V or Pe molecules of these mixed monolayers may affect the chromophore orientation of many Cy molecules composing J-aggregate .

Absorption spectra of the mixed Cy LB films represented by solid curve A, B, and C (1:1, 2:1, and 5:1, respectively) and of the pure Cy LB film by dashed curve are shown in Fig. 3. Although the addition of Pe to the Cy LB film had caused dissociation of the Cy J-aggregate even at the mixing ratio Cy:Pe = 50:1 [5], the sharp absorptions of the J-band (at 400 nm) were observed in the all absorption spectra of the Cy-V systems. As shown in this figure, a grow of the J-band with the decrease of the V concentration was observed, and finally, at the mixing ratio Cy:V = 10:1, the absorption spectrum (data not shown) reached to the same as dashed curve. It should be noted that these changes are almost linear to the surface concentration changes of Cy molecule. Although not shown, the absorption spectra of the mixed LB films at the concentrations of Cy:V = 20:1 ~ 2000:1, were also the same as that of the pure Cy LB film. These results suggests that V molecule would be easily embedded in the Cy monolayer without disturbing the

formation of the Cy J-aggregate.

Fluorescence emission spectra of the mixed and pure Cy monolayers are summarized in Fig. 4. The intensities of these spectra are normalized by the absorbance of the each mixing ratio at the excitation wavelength of 355 nm. The fluorescence J-band with a peak at 406 nm was commonly observed in the all emission spectra. The intensity of the J-band decreased monotonously with the increase of the V concentration. The decay of the J-band can be used as a measure of the electron transfer efficiency. Fig. 5 presents the plot of the peak emission intensity as a function of the molar concentration of Cy. We can see from Fig. 5 that the quenching of the J-band emission of Cy by the addition of V molecule is almost saturated at the mixing ratio $\text{Cy}:\text{V} = 10:1$. On the other hand at the concentrations of the lower V ratios, the rapid recovery of the J-band emission was observed but the dependence of the electron transfer efficiency on the film composition seems to be rather complicated. We presumably separate the emission change into four regions as indicated by four dashed lines of different slopes in Figs. 5 ($1:1 \sim 10:1$, $10:1 \sim 50:1$, and $100:1 \sim 500:1$) and Fig. 6 ($500:1 \sim 1:0$). Considering the constancy of the absorption spectra of the Cy J-aggregate, these complexities are not attributable to changes in the conditions of the Cy J-aggregate. Thus it is plausible that the complexities in the quenching of the J-band emissions are attributable to

inhomogeneous dispersion of V molecule in the monolayer plane. However, at the mixing ratios of the extremely lower V concentrations, homogeneous dispersion of V molecule can be expected (Fig. 6). If a very small amount of V molecules are homogeneously dispersed into J-aggregate of large number of Cy molecule, the linear relation would be observed between the emission intensity of the J-band and the number of V molecule. Assuming this simple model for the plots corresponding to the mixing ratios Cy:V = 1:0, 2000:1, 1000:1, and 500:1, the linear relation was extrapolated as shown by dashed line in Fig. 6. The resulted value of the mixing ratio Cy:V $\approx$ 90:1 indicates that if V and Cy J-aggregate were uniformly mixed in the same manner as in the mixed LB monolayers with such lower V ratios ($< 1/500$), the complete quench of the J-band would be observed around the ratio Cy:V = 90:1. The surface area of 90 molecules of Cy (ca. 54 nm²) corresponds to the area of 42 Å radius. Namely one center molecule of V would be able to quench Cy* lying within the radius. The quenching radius estimated for the lateral electron transfer between Cy* and V is much smaller than that for the lateral energy transfer between Cy* and Pe [5].

4. Conclusions

We succeeded in fabricating the V doped Cy LB films without dissociation of Cy

J-aggregate. The observed electron transfer quenching of Cy* showed rather complex dependence on V concentration, which is probably due to inhomogeneous distributions of V molecules in the LB surfaces. The estimated electron transfer efficiency between Cy* and V molecules was such that ca. 90 molecules of Cy* would be quenched by one center molecule of V. The energy transfer efficiency between Cy* and the S moiety of the perylene type triad estimated in our previous work [5], where ca. 250 molecules of Cy was available for light-harvesting, is much greater than the efficiency of the electron transfer quenching of Cy* by the A moiety, therefore we can employ the J-aggregated Cy LB films as the light-harvesting antenna in our design of an artificial photosynthesis system.

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References

1. M. Fujihira, and M. Sakomura, Thin Solid Films 179 (1989) 471.
2. M. Fujihira, M. Sakomura, and T. Kamei, Thin Solid Films 180 (1989) 43.
3. M. Sakomura and M. Fujihira, Thin Solid Films 243 (1994) 616.
4. M. Sakomura, S. Lin, T. A. Moore, A. L. Moore, D. Gust, and M. Fujihira, J. Phys. Chem. A 106 (2002) 2218.
5. M. Sakomura, T. Takagi, H. Nakayama, R. Sawada, and M. Fujihira, Coll. Surf. A 198 (2002) 769.
6. D. Möbius, J. Am. Chem. Soc. 14 (1981) 63.
7. F. Perrin, Compt. Rend. 178 (1924) 1978.
8. H. Kuhn, D. Möbius, and H. Bücher, in: A. Weissberger, B. Rossiter (Eds.), Physical Methods of Chemistry, Part III B, vol. 1, Wiley, New York, 1972, p.577.
9. H. Bücher and H. Kuhn, Chem. Phys. Lett. 6 (1970) 183.

Figure captions

Fig. 1 Structural formulae of a cyanine (Cy) and viologen (V) amphiphiles.

Fig. 2 Surface pressure-area isotherms of the monolayers including Cy and V in the molar ratios Cy:V = 1:1, 2:1, 5:1, 10:1, 20:1, 50:1, and 100:1.

Fig. 3 UV-vis absorption spectra measured on the LB monolayers including Cy and V in the molar ratios Cy:V = 1:1, 2:1, 5:1 (solid curves), and 1:0 (dashed curve).

Fig. 4 Fluorescence emission spectra of the LB monolayers including Cy and V in the molar ratios Cy:V = 1:1, 2:1, 5:1, 10:1, 20:1, 50:1, 100:1, 200:1, 500:1, 1000:1, 2000:1, and 1:0. The peak intensity increases in the same order with the Cy concentration.

Fig. 5 The emission intensities of the mixed and pure Cy LB monolayers at the peak wavelength of fluorescence J-band (406 nm).

Fig. 6 A Plot in the region of the higher Cy concentrations in Fig.5 magnified for ease of viewing.

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