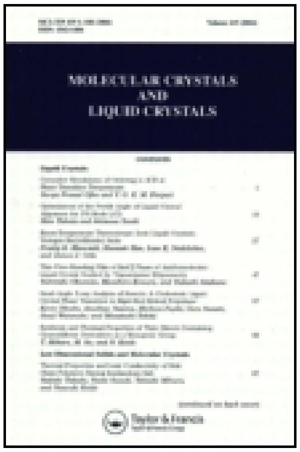

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Photophysical Behaviors of J-Aggregates of Merocyanine in Langmuir-Blodgett Films

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PHOTOPHYSICAL BEHAVIORS OF J-AGGREGATES OF MEROCYANINE IN LANGMUIR-BLODGETT FILMS.

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Abstract J-Aggregates of a long-chain merocyanine can be formed in the mixed monolayers with glycerol derivatives, phospholipids and cholesterol. Its morphologies observed by a fluorescence microscopy are dependent on the matrix agents and the compositions. The photoactive J-aggregates in LB films were characterized by the weak exciton-phonon coupling and the fluorescence occured by a radiative annihilation from the free exciton state. From measurements of the fluorescence decay curves for a single layer of the J-aggregates, the lifetine has been found to be 5 - 11 ps irrespective of the matrix agents. In the LB systems containing the J-aggregate as a donor combined with long-chain bipyridinium as an acceptor at a distance of 20.2 - 30.2 A, it has been found that the fluorescence decays more rapidly.

INTRODUCTION

Several J-aggregates of cyanine and squarylium dyes have been interested in view of photo-sensitizing function and photo-voltaic effects[1-4]. J-Aggregates are characterized by an intense narrow absorption band shifted to longer wavelength relative to the monomer band, and also by a strong emission band with a nearly zero Stokes' shift. Previously, we reported J-aggregates of a long-chain merocyanine dye in mixed mono- and multilayers with cadmium arachidate and methyl arachidate, and by applying an extended dipole model to the two-dimensional arrangement of the transition moments, the geometry and aggregation number of the chromophore in the J-aggregate was clarified[5,6].

In this paper, using another long-chain merocyanine substituted with chlorine we examined the J-aggregate formation in mixed monolayers with glycerol derivatives such as monostearin, distearin and tristearin, phospholipids such as dipalmitoylphosphatidyl-ethanolamine and choline, and cholesterol. From measurements of visible absorption spectra of the mixed mono- and multilayers as well as observation of the deposited monolayers by fluorescence microscopy, different extents of J-aggregate formation and various morphologies have been obtained in the mixed LB films, depending on the matrix agents and the compositions. And further, from temperature dependence of the absorption spectra for the J-aggregate has been considered by applying the Urbach rule.

EXPERIMENTAL

[Materials]

A long-chain merocyanine dye [Mc] containing benzothiazol substituted with chlorine at 5-position used in this work is indicated in Fig.1, which was obtained from Japanese Research Institute for Photosensitizing Dyes, Co. (Okayama, Japan).

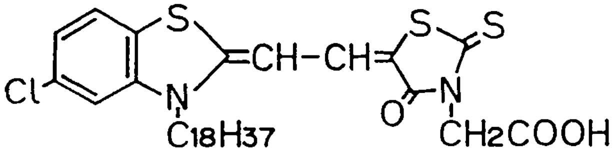


FIGURE 1. Long-chain merocyanine dye [Mc] used in this work.

As the matrix agents for the dye monolayer, glycerol-1-stearate [DL-MS: mp.81.3-82.3°C[SIGMA], L-MS: mp.75.3-77.0°C[Fluka]), glycerol-1,2-distearate (DL-DS: mp.71.7-72.4°C[SIGMA]), glycerol tristearate (TS: mp.72.0-73.1°C[Tokyo Kasei]), 1,2-dipalmitoyl-sn-glycero-3-phosphatidylethanolamine (PE: [Koch-Light Lab. Ltd., U.K.]), 1,2-dipalmitoyl-sn-glycero-3-phosphatidylcholine (PC: [Koch-Light Lab. Ltd., U.K.]) and cholesterol (Ch: mp.147.8-149.0°C[Tokyo Kasei]) were obtained commercially and were purified by recrystallization or thin layer chromatography.

[Procedures]

The monolayers of PE and PC were spread from the solution in mixed solvent of ethanol and chloroform (1:4 v/v) and the others from the chloroform solution onto the aqueous subphase with 3 x 10^{-4} M $CdCl_2$ and 5 x 10^{-5} M $KHCO_3$ (pH 6.3). Surface pressure - area isotherms were measured by a Langmuir-type film balance (Lauda) at 20°C.

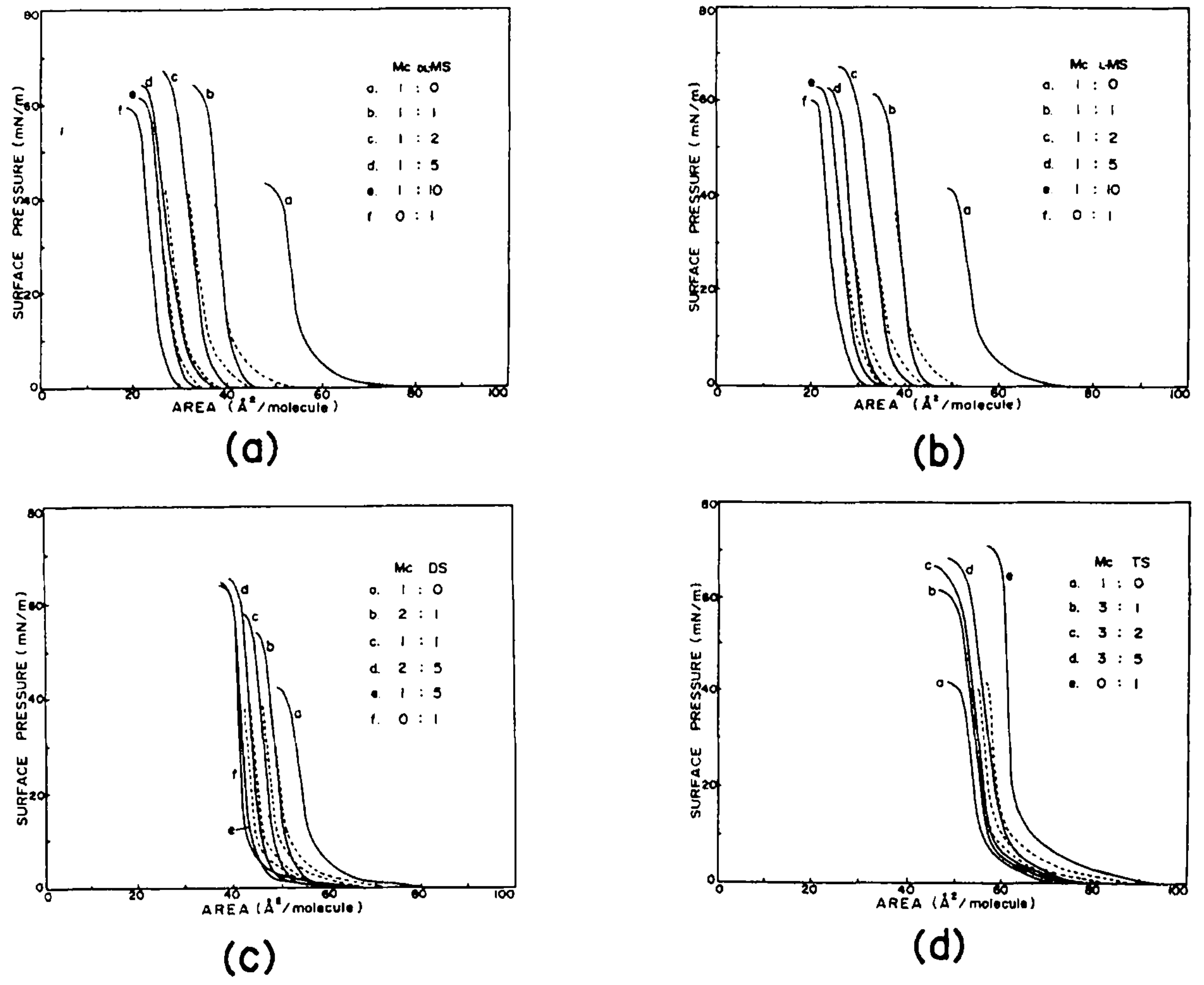
Absorption spectra of the monolayers at the air/water interface were measured by a multichannel photodetector (Otsuka Electronics) with reference to a spectrum obtained without the monolayer. The monolayers were transferred at the surface pressure of 30 mN/m according to the Langmuir-Blodgett method onto a quartz plate which was previously covered with cadmium arachidate films (3 - 5 layers) to make the surface hydrophobic. Absorption spectra of the single layer of built-up films were measured by a hitachi spectrophotometer (model 340) equipped with a cryostat in the temperature range of 120 - 300 K. And further, morphology of the deposited monolayers was observed by a fluorescence microscopy (Olympus ITM2) through irradiation of green light.

Fluorescence decay curves and time-resolved fluorescence spectra were measured by means of a picosecond time-correlated single photon counting system[7]. The picosecond laser as an excitation source was composed of a synchronously pumped dye laser and a mode-locked Nd-YAS laser.

RESULTS AND DISCUSSION

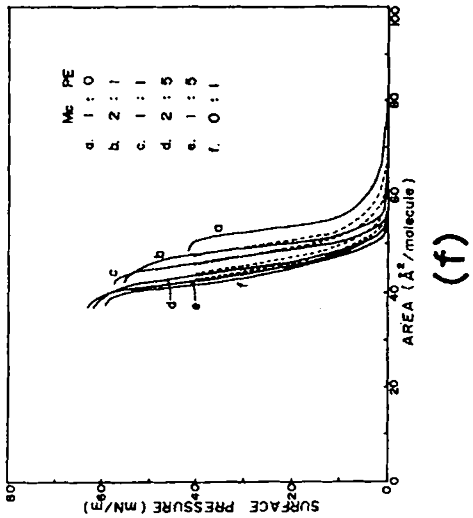
1. Mixed monolayers containing a long-chain merocyanine dye.

The surface pressure - area isotherms for mixed monolayers of [Mc] with [DL-MS], [L-MS], [DS], [TS], [PC], [PE] and [Ch] are shown in Figs.2(a) - (g), respectively. For the monolayer of the dye only, the limiting area $A_{\pi \to 0}$ obtained from extrapolating of the linear part to zero pressure, is about 57 $\mathring{A}^2$/molecule which is rather condensed in comparison with that for the merocyanine dye without chlorine, previously reported[5]. In any matrix components the mixed monolayers of [Mc] are significantly stabilized with large compressibilities and higher collapsed pressures. For the [Mc] mixed films with [DL-MS] or [L-MS], the obtained isotherms are nearly consistent with the calculated curves from the molecular area of each component, though slightly condensed isotherms appear in the


SURFACE PRESSURE (mN/m)
AREA (Å²/molecule)
0
20
40
60
80
100
Mc αL-MS
a. 1 : 0
b. 1 : 1
c. 1 : 2
d. 1 : 5
e. 1 : 10
f. 0 : 1
Mc L-MS
a. 1 : 0
b. 1 : 1
c. 1 : 2
d. 1 : 5
e. 1 : 10
f. 0 : 1
Mc DS
a. 1 : 0
b 2 : 1
c. 1 : 1
d. 2 : 5
e. 1 : 5
f. 0 : 1
Mc TS
a. 1 : 0
b. 3 : 1
c. 3 : 2
d. 3 : 5
e. 0 : 1
a
b
c
d
e
f

(a) (b)

(c) (d)



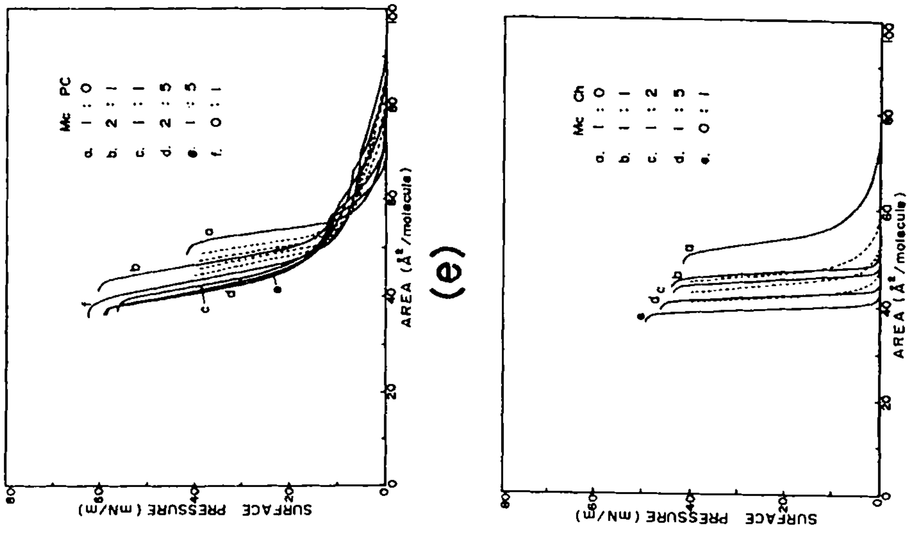
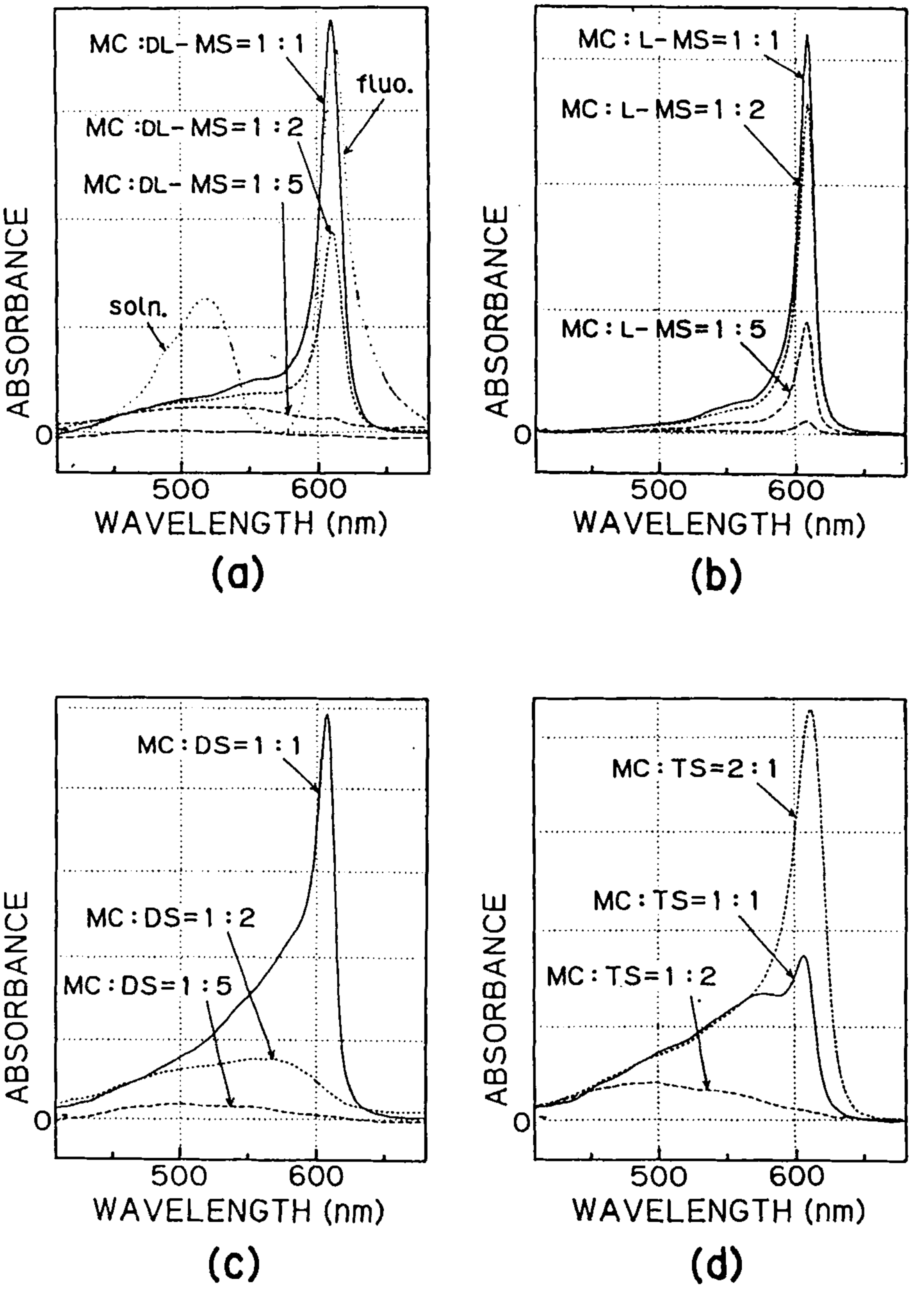


FIGURE 2. Surface pressure - area isotherms for the mixed monolayers of long-chain merocyanine [Mc] with (a)DL-MS, (b)L-MS, (c)DS, (d)TS, (e)PC, (f)PE and (g)Ch, with various compositions, together with the calculated curves (dashed lines) from each molecular area.

Lower pressure regions, The matrices of DL- and L-MS have little difference in the isotherms. In the [Mc] mixed monolayers with [DS] and [TS], a slightly condensed effect appears at the molar ratios of [Mc]:[DS] = 1 : 5 and [Mc]:[TS] = 3 : 2, respectively. The mixtures of [Mc] and [PC] give remarkable condensed films at the higher pressure region in the range of the molar ratio of 1 : ½ — 1 : 5. The transition point from the expanded to the condensed films changes depending on the mixing ratio. In contrast to this, the [Mc] mixed films with [PE] show little condensed effect. The mixtures of [Mc] and [Ch] form very rigid monolayers with less condensed behaviors.

2. Absorption spectra of the mixed mono- and multilayers.

Absorption spectra of the [Mc] mixed monolayers with various matrix lipids and the compositions, at 30 mN/m on the water surface, are shown in Figs.3(a) _ (g). A sharp and strong band shifted to the longer wavelength at about 610 nm in comparison with the monomer band of the solution at 630 nm is considered to be characteristics of the J-aggregate. Formation of the J-aggregate is found to be dependent on the matrix components and their compositions. For the [Mc] mixed films with DL- and L-MS the J-aggregate can be obtained with good reproducibility at the molar ratios of 1 : 1 — 1 : 2. Using [DS] or [TS] as the matrix, the J-bands are observed almost together with the monomer band and the other aggregate bands even at the molar ratio of 1 : 1 or 2 : 1. Further dilution with the matrices have considerably retarded the formation of the J-aggregate of [Mc]. In the cases of mixing with dipalmitoyl [PC] or [PE], the molar ratio of 1 : 1 is the most favorable for the J-aggregate formation and the optical density of the J-band with [PE] is very high. The mixtures of [Mc] and [Ch] give the narrow J-band with less the other bands and the most probability in the range of the molar ratios of 1 : 1 — 1 : 5. Taking the results of the pressure - area isotherms into account, the well-organized J-aggregate can be obtained in the case of appearance of less condensed effect in the mixed monolayers. It is suggested that a special interaction between the dye and the matrix molecules tends to hinder the chromophore aggregation


MC :DL- MS=1 : 1
fluo.
MC :DL- MS=1 : 2
MC : DL- MS=1 : 5
soln.
ABSORBANCE
0
500
600
WAVELENGTH (nm)
(a)
MC : L- MS=1 : 1
MC : L- MS=1 : 2
MC : L- MS=1 : 5
ABSORBANCE
0
500
600
WAVELENGTH (nm)
(b)
MC : DS=1 : 1
MC : DS=1 : 2
MC : DS=1 : 5
ABSORBANCE
0
500
600
WAVELENGTH (nm)
(c)
MC : TS=2 : 1
MC : TS=1 : 1
MC : TS=1 : 2
ABSORBANCE
0
500
600
WAVELENGTH (nm)
(d)

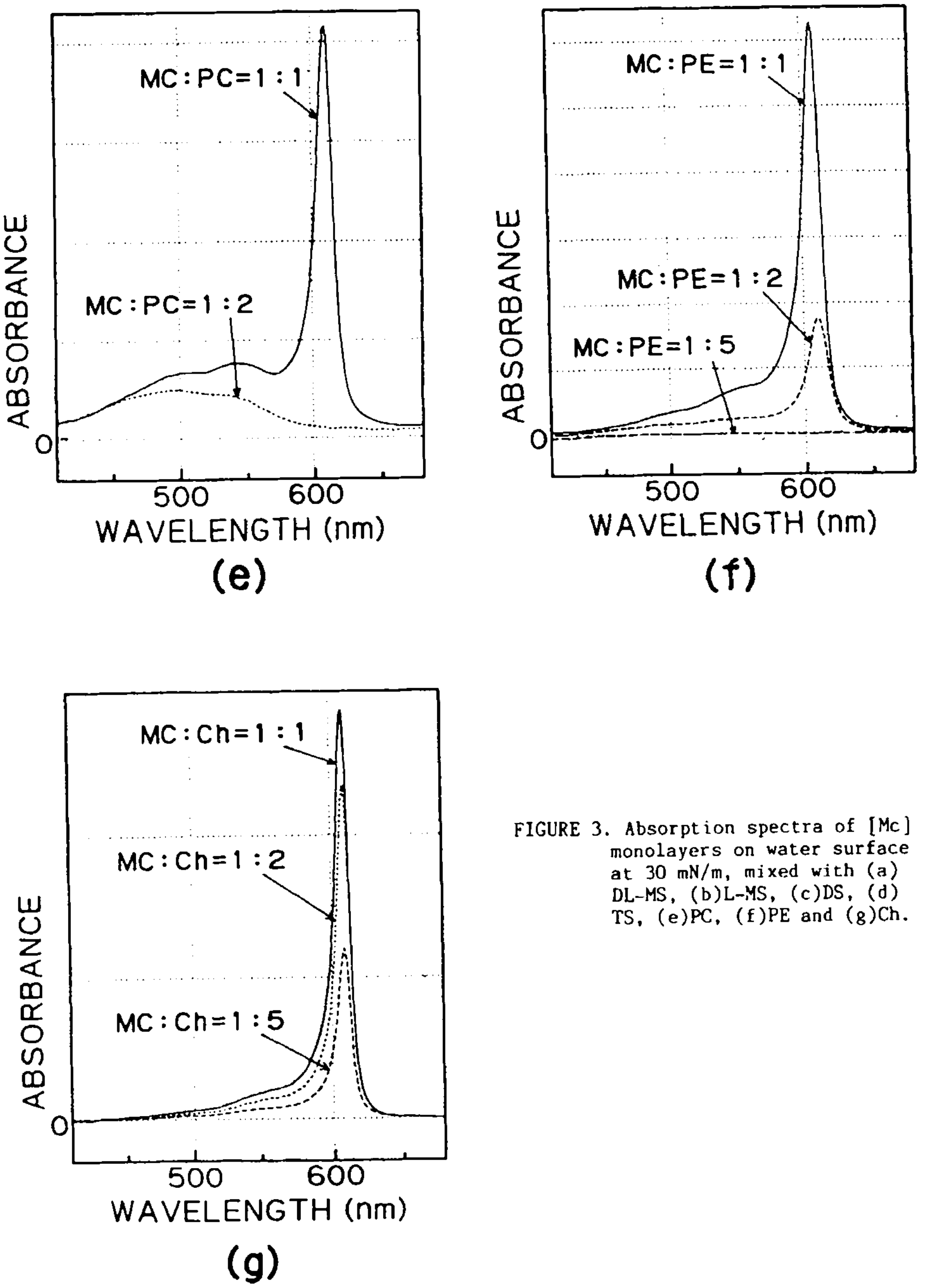


FIGURE 3. Absorption spectra of [Mc] monolayers on water surface at 30 mN/m, mixed with (a) DL-MS, (b)L-MS, (c)DS, (d) TS, (e)PC, (f)PE and (g)Ch.

with a well-defined arrangement. Appropriate matrices such as [MS], [PE] and [Ch] promote the formation of the more homogeneous J-aggregate exhibiting the J-band with the less half-band width, as compared with [Mc] pure monolayer.

Furthermore, absorption spectra for the built-up films of [Mc] mixed monolayers with the various matrices were almost very similar features to those for the monolayers on the water. In the cases of [Mc] mixed films with [DS], [TS] or [PC], the J-bands sometimes disappeared through the deposition procedure onto solid plates.

3. Morphology of J-aggregates in the mixed LB films.

The J-aggregate of [Mc] exhibits a red fluorescence by irradiation of green light. Various morphologies of the J-aggregates have been observed by a fluorescence microscopy, depending on the matrix components and the composions, as shown in Figs. 4(a) - (d). For examples, the mixture of [Mc] and [DL-MS] or [L-MS] forms J-aggregate domains composed by densely linked grains at the molar ratio of 1 : 1. With increase of the [MS] content, the grains are separated into small ones with diameter of about 3μm and further at the molar ratio of 1 : 10 changed to needle-shapes of which fluorescence is polarized to the long-axes oriented parallel to the dipping direction. In the case of mixture of [Mc] and [PE] the domains are emitted brightly over the film at the molar ratio of 1 : 1 and for the 1 : 5 mixture spherical domains are distributed separately and the weak emission due to the other aggregates is observed as a whole in addition to the strong emission of the J-aggregate. The film mixed with [PC] exhibits spindle-shaped domains with various sizes distributed randomly and at the molar ratio of 1 : 2 the domains (average 10 x 6μm) were much larger than those for 1 : 1, emitting fluorescence polarized parallel to the long-axes. The morphology of [Mc] : [Ch] = 1 : 1 film was similar to that of [Mc] : [MS], while with increasing [Ch] content the J-aggregate disappeared.

4. Exciton-phonon interaction in the J-aggregate LB films.

The excited states and the exciton-phonon interaction in

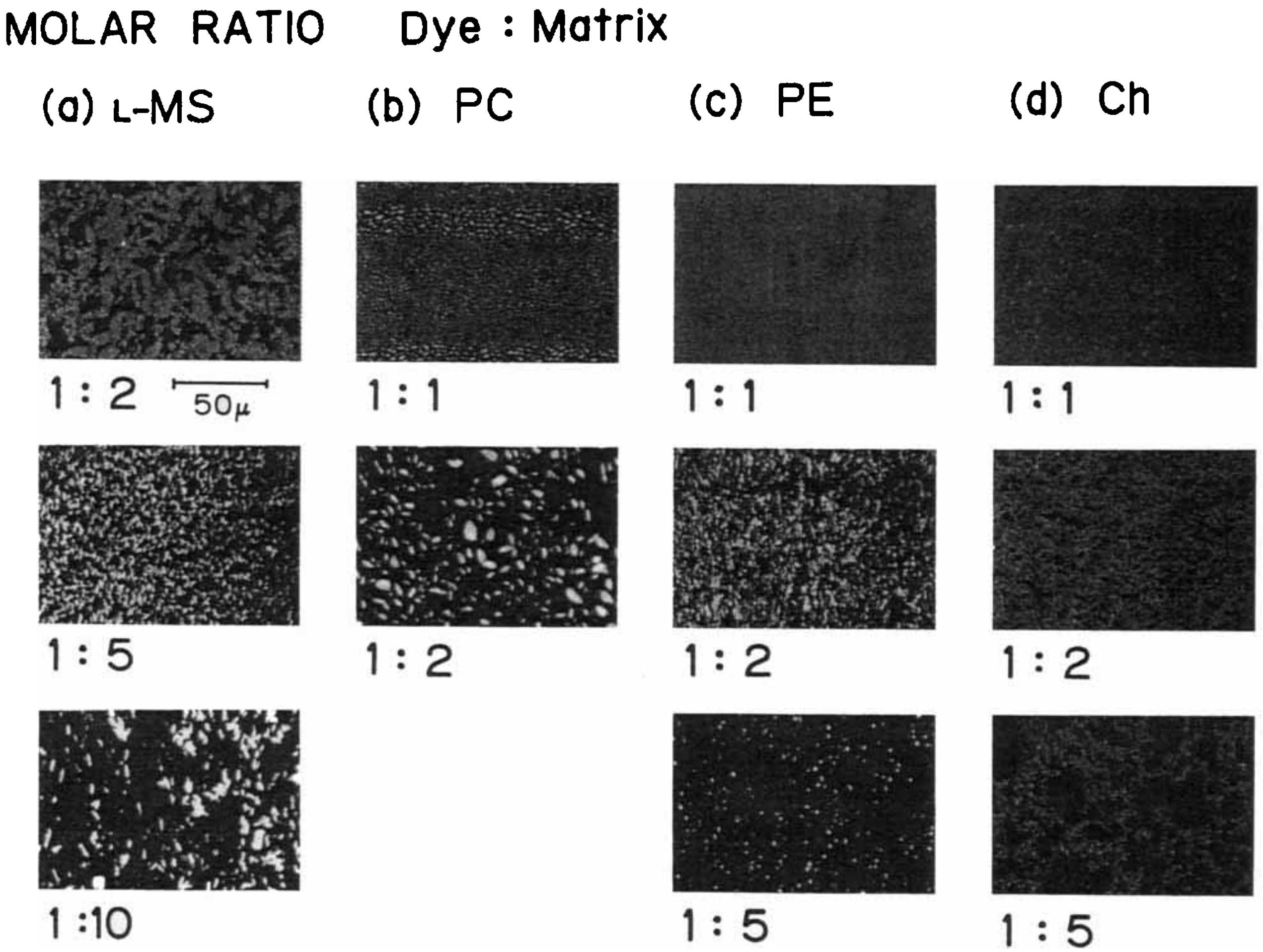


FIGURE 4. Morphologies of J-aggregates, observed by a fluorescence microscopy, in the mixed monolayers of [Mc] with (a)LMS, (b)PC, (c)PE and (d)Ch.

the J-aggregate LB films of [Mc] mixed with various matrix agents have been investigated by applying the Urbach rule[8] to temperature dependence of the J-absorption bands in the range of 296 – 136 K. A good linear relationship between the logarithmic absorption coefficient and the incident photn energy is observed for the low-energy tail of the J-bands, as an example of the [Mc] mixed film with [L-MS] shown in Fig.5 . The low-energy tail of the J-bands can be expressed by the Urbach rule with a steepness parameter (σ') of 1.34 – 1.49. Since the exciton-phonon coupling (g) is given by the ratio of a sttepness index (S) and σ', the values of S = 1.24 for the two-dimensional system[9] lead to $g < 1$. Consequently, for the J-aggregates in LB films it has been found that the exciton-phonon coupling is weak and the fluorescence occurs by a radiative annihilation from the free exciton state.

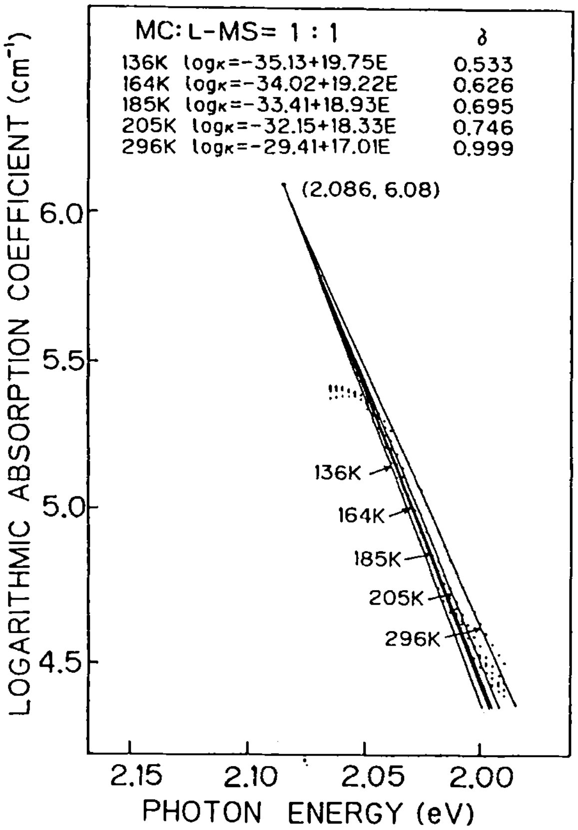


FIGURE 5.
Plots of logarithmic absorption coefficient and incident energy for the low-energy tail of J-band of [Mc] with [L-MS], at various temperatures.

5. Fluorescence lifetime of the J-aggregates in LB films.

For fluorescence decay curves of the J-aggregate LB films mixed with various matrix agents, measured by a picosecond time-resolved single photn counting system, three components of the lifetimes fitting to exponential terms in the following equation:

$$F(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3)$$

have been summarized in Table I.

TABLE I. Fluorescence lifetimes for J-aggregate LB films of [Mc] mixed with various matrices.

FILMS	τ_1(ps)	A_1	τ_2(ps)	A_2	τ_3(ps)	A_3
MC:AA=1:2	6.48	0.995	84.43	0.005		
MC:DL-MS=1:2	8.01	0.990	76.07	0.010	350.3	0.000
MC:L-MS=1:2	5.88	0.995	84.35	0.005		
MC:DS=1:1	6.66	0.979	51.65	0.020	213.5	0.001
MC:TS=3:2	7.97	0.980	62.06	0.019	261.7	0.001
MC:PE=1:1	7.62	0.971	50.48	0.027	195.6	0.002
MC:PC=1:1	11.11	0.951	50.32	0.046	188.8	0.003
MC:Ch=1:1	7.15	0.985	51.01	0.014	216.3	0.001

The fluorescence lifetimes (τ_1) observed at 610 nm for a single layer of the J-aggregates are obtained to be 5 — 11 ps in a large portion above 95 percent, irrespective of the matrix agents. The other slow components (τ_2 and τ_3) are minorities less than 5 percent. As shown in Fig.6 , in the time-resolved fluorescence spectra for the J-aggregate LB film of [Mc] : [AA] = 1 : 2, the fluorescence band at 610 nm decreases with time and its intensity is reduced to one-half the initial value at about 1 ns, while the 570 nm band due to the monomer is grown up. With increase of [AA] content in the mixed films, the decrease of 610 nm band and the rise of 570 nm band are more rapidly.

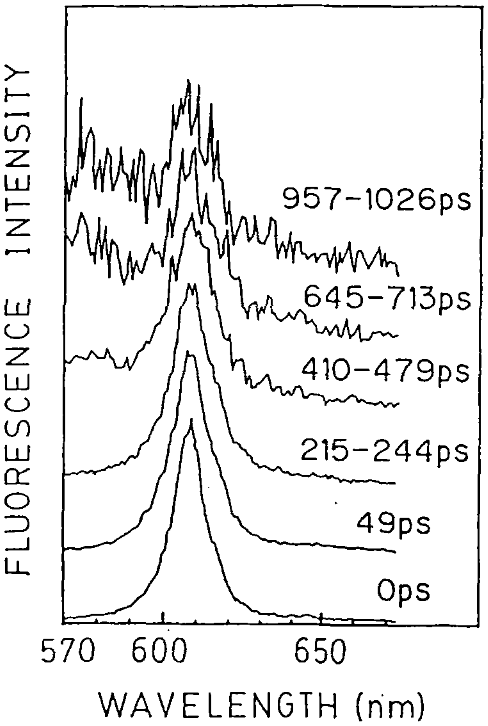


FIGURE 6. Time-resolved fluorescence spectra for J-aggregate LB film of [Mc] : [AA] = 1 : 2.

In the case of LB systems containing the J-aggregate ([Mc] : [AA] = 1 : 2) as a donor combined with long-chain bipyridinium as an acceptor layer at a distance of 20.2 — 30.2 Å, which was controlled by the insertion of a single layer of cadmium myristate, stearate or behenoate, the fluorescence decay curves of the J-aggregate are given in Fig.7. It has been found that the fluorescence of the J-aggregate decays more rapidly with the shorter spacing, as compared with no acceptor layer. From the time-resolved fluorescence spectra of these systems as shown in Fig.8(a) - (d), it can be seen that the fluorescence band at 610 nm disappears and the 570 nm band occurs more rapidly as the spacing between the donor and acceptor layers decreases. From these results, it is considered that the electron transfer from the J-aggregate in LB films occurs with a significantly high speed less than a few picoseconds.

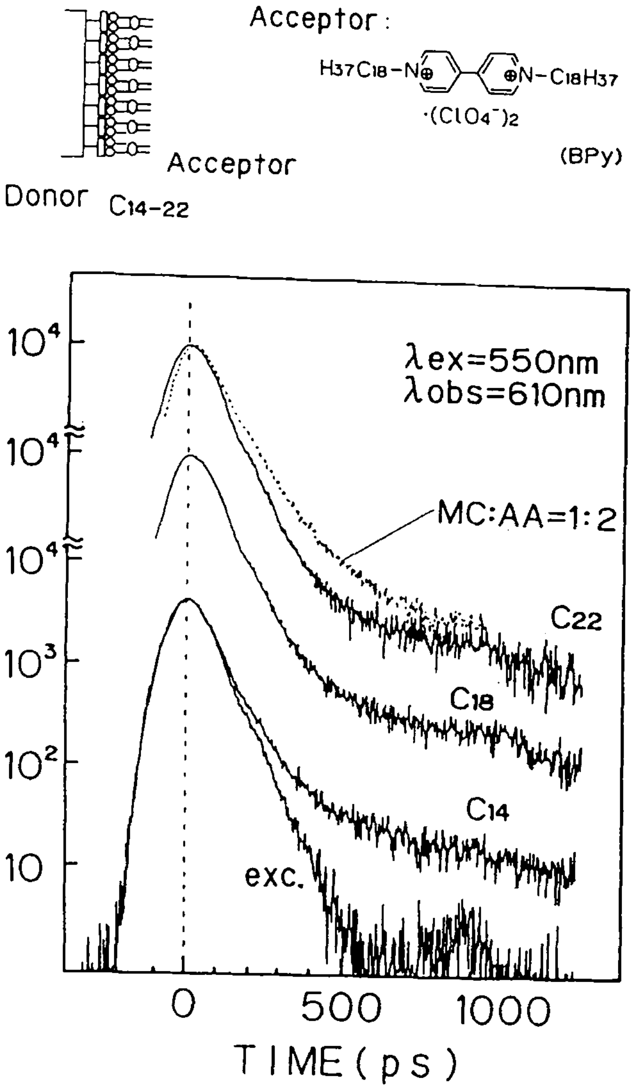


FIGURE 7. Fluorescence decay curves of J-aggregate ([Mc] : [AA] = 1 : 2) in LB films combining with spacer (C_n) and acceptor layers.

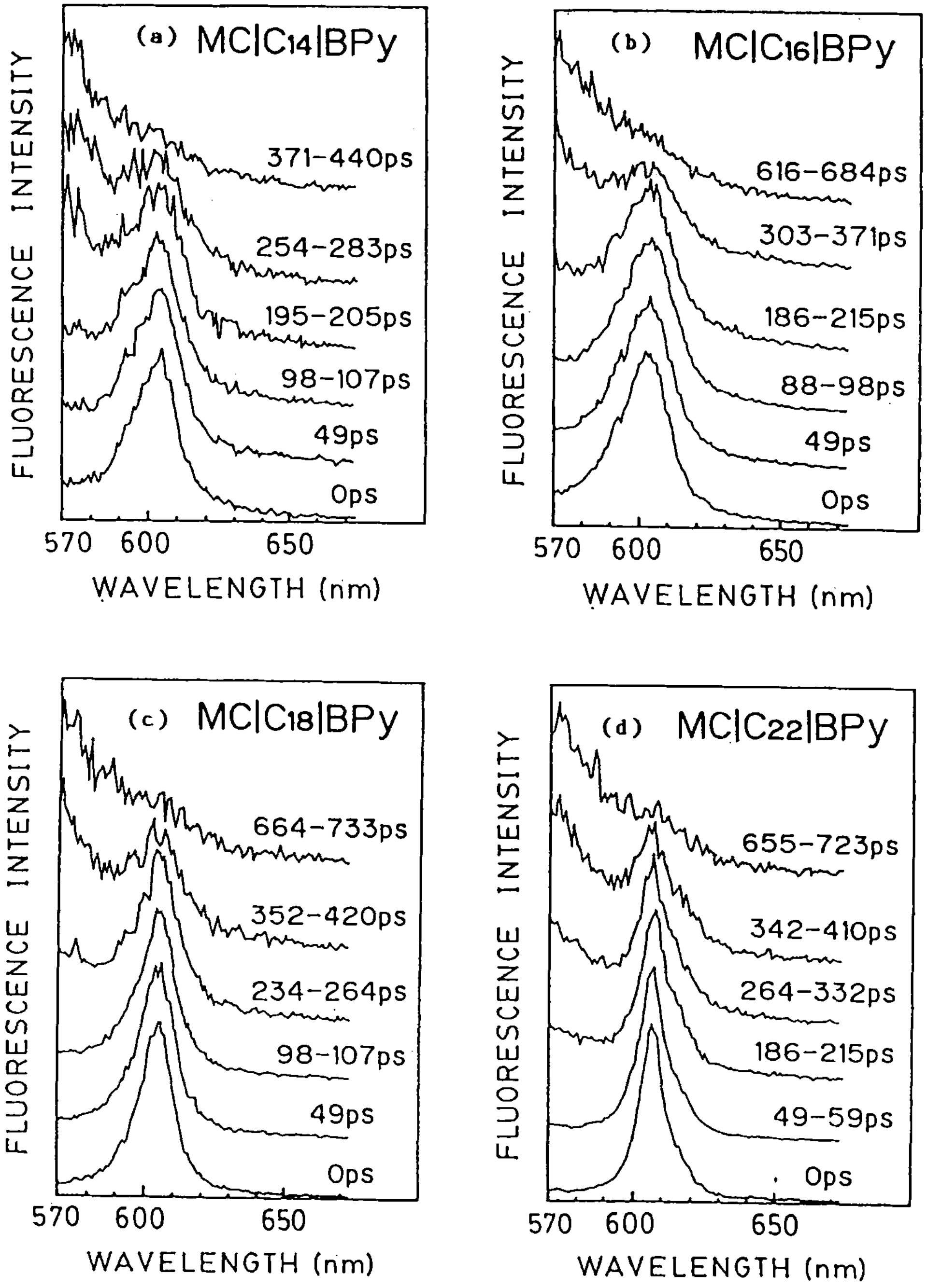


FIGURE 8. Time-resolved fluorescence spectra of J-aggregate ([Mc] : [AA] = 1 : 2) in LB films combining with spacer (C_n) and acceptor layers.

CONCLUSION

The J-aggregate of the long-chain merocyanine can be obtained in the mixed monolayers with glycerol derivatives, phospholipids and cholesterol. Its morphologies depend on the matrix agents and their compositions. The photoactive J-aggregates in the LB films are characterized by the weak exciton-phonon coupling and the fluorescence from the free-exciton state. The fluorescence lifetimes fall into the range of 5 — 11 ps and are further shortened by combining an electron acceptor layer at a distance of 20.2 — 30.2 Å in LB films.

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