STUDIES ON LAYER STRUCTURE OF MIXED LANGMUIR-BLODGETT FILMS DEPOSITED FROM SUPERMONOMOLECULAR LAYERS USING ENERGY TRANSFER

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The Förster energy transfer was applied to study layer structures of mixed LB films of 11-(9-carbazolyl)undecanoic acid and palmitic acid deposited from surface supermonomolecular layers. The structure of Y-type LB films composed of a monolayer unit, which was proposed previously for such systems, was confirmed by the present method. It was further shown that the energy transfer was able to specify the supermonomolecular LB films.

1. Introduction

We have recently reported the molecular orientation and photochemical properties of carbazolyl chromophores in mixed LB films of 11-(9-carbazolyl)undecanoic acid (CUA) and palmitic acid (PA)[1]. The carbazolyl chromophores in such LB films were aggregated and oriented with their short and long axes making an average angle of about 35° with respect to the substrate surface. We have also reported the molar fraction dependent energy transfer in mixed LB films of long chain fatty acids and CUA containing a very small fraction of acceptors[2]. A bilayer structure at the air/water interface due to the squeezing-out was also suggested in our previous study[1]. The structure of mixed LB films of CUA and PA which were prepared from monolayers squeezed-out at the air/water interface was shown to be a usual Y-type composed of a monolayer unit from X-ray diffraction and capacitance measurements[3]. Such structural information is very important in incorporating monolayer assemblies containing carbazolyl groups into photoinduced electron transfer systems, which we have been studying with various amphipathic redox compounds[4-9].

In the present paper we will propose a new method to elucidate the layer structure of mixed LB films deposited from squeezed monolayers (supermonomolecular layer) at the air/water interface based on the interlayer Förster energy transfer.

2. Experimental

Materials

The synthesis of pure CUA was reported previously[1]. 1-Pyrene dodecanoic acid (PDA,
MolecularProbes Inc.) was used without further purification. Palmitic acid (PA), stearic acid (SA) and arachidic acid (AA, Tokyo Kasei, reagent grade) were recrystallized several times from ethanol. The purity of each compound was confirmed by NMR, the elemental analysis, and/or the fluorescence spectroscopy.

**Measurements**

The surface pressure-molecular area isotherm ($\pi$-A isotherm) was measured by a Kyowa Kaimen Kagaku HBM-AP balancing meter with a Teflon trough at controlled temperatures ($+/-0.1\, ^\circ\text{C}$) and a compression speed of 2 cm/min. Distilled water was further purified by a Millipore Milli-Q Organex system. Optically polished quartz plates (13 mm x 76 mm x 1 mm) was cleaned ultrasonically in alkaline methanol for 15 min and was then thoroughly rinsed with purified water. Three monolayers of cadmium arachidate were deposited on solid substrates before depositing monolayers containing chromophores.

Fluorescence spectra were measured by a Hitachi F-4010 fluorescence spectrophotometer. All samples were deposited by a vertical dipping method at 15$^\circ\text{C}$ at 0.5 cm/min. Monolayers including CUA were deposited from aqueous subphase containing 0.25 mM CdCl$_2$, pH 5.0. Palmitic acid and mixtures of CUA/PA (1:2.7) were deposited at 20 mN/m. A 1:1 mixture of PDA/PA was deposited at 15 mN/m from an aqueous subphase containing 0.25 mM CdCl$_2$ and 0.05 mM NaHCO$_3$, pH 6.3. Alternate Y-type LB films for energy transfer measurements from CUA to PDA were constructed by depositing a monolayer of cadmium palmitate, CUA/PA, PDA/PA, and cadmium palmitate in this order. An LB film containing two monolayers of cadmium palmitate between CUA/PA and PDA/SA was also prepared. The deposition ratio was unity in all cases.

**3. Results**

Fig. 1 shows the $\pi$-A isotherms at 15$^\circ\text{C}$ for (a) PA, (f) CUA, and their mixtures CUA/PA, (b) 1:19, (c) 1:9, (d) 1:4 and (e) 1:2.7. These $\pi$-A isotherms were highly reproducible. The $\pi$-A isotherms below about 13 mN/m shifted to a larger area side with increasing molar fractions of CUA which occupies more area than PA. This result indicated that CUA and PA molecules were dispersed in the same monolayer at the air/water interface. At higher surface pressures all mixtures formed a solid condensed phase such as in PA alone, but the limiting area decreased with increasing molar fractions of CUA as shown in Fig. 1. The extrapolated limiting area normalized by the molar fraction of PA coincided with that of PA alone within experimental errors for all mixtures of CUA/PA as reported previously[1]. Compressed monolayers were collapsed at about 60 mN/m in all mixtures. The region of almost constant surface pressure (about 13 mN/m) shown in Fig. 1 increased with increasing molar fractions of CUA. These results strongly suggested the formation of a supermonomolecular structure by squeezing-out at about 13 mN/m. Schematic representation of LB films of CUA/PA deposited from supermonomolecular surface layers are
given in Fig. 2. LB films shown Fig. 2(A) and (B) are composed of a bilayer unit and that in Fig. 2(C) is composed of a mixed monolayer unit. In order to obtain information on the structure of mixed LB films of CUA/PA, the Förster energy transfer was studied by the use of PDA as an acceptor, which has a chromophore at the hydrophobic end. The \( \pi-A \) isotherm at 15°C for a mixture of PDA and SA with a molar ratio of 1:1 is shown in Fig 3, which showed the structural change of monolayers at about 25mN/m. The deposition was made at 15mN/m to...

Fig. 1 The surface pressure-molecular area isotherm at 15 °C for (a) PA, (f) CUA, and mixtures of CUA and PA with the molar ratio of (b) 1:19, (c) 1:9, (d) 1:4 and (e) 1:2.7

Fig. 3 Surface pressure-molecular area isotherm for a mixture of PDA/SA(1:1) at 15 °C

Fig. 2 Schematic representations of LB films for CUA(\( \bigcirc \)) and PA(\( \bigotimes \)) composed of a bilayer unit (A, B) and a mixed monolayer unit (C)

Fig. 4 Fluorescence spectra at \( \lambda_{ex}=296\text{nm} \) for a system containing (a) a monolayer of PDA/SA(1:1) directly deposited on a monolayer of CUA/PA (1:2.7) (b) further two monolayers of cadmium palmitate deposited between a monolayer of PDA/PA (1:1) and a monolayer of CUA/PA (1:2.7), (c) a monolayer of PDA/SA (1:1) alone deposited on three layers of cadmium arachidate
get usual Y-type mixed LB films. The excitation wavelength was set at 296nm so as to excite a donor CUA most effectively in comparison with an acceptor PDA, since it was difficult to excite a donor (CUA) alone owing to the overlapping of the absorption spectra. Fig. 4 shows the fluorescence spectra excited at 296nm for the systems containing (a) a monolayer of PDA/SA (1:1) directly deposited on a monolayer of CUA/PA (1:2.7), (b) further two monolayers of cadmium palmitate deposited between a monolayer of PDA/SA (1:1) and a monolayer of CUA/PA (1:2.7), and (c) a monolayer of PDA/SA(1:1) alone deposited on three layers of cadmium arachidate as schematically shown. Peaks at about 378 and 400nm were attributed to the monomer fluorescence of PDA. A broad excimer emission peak of pyrenyl chromophores was also observed at about 470nm. One of the donor(CUA) emission peaks was observed at about 358nm and another peak at 370nm overlapped with the tail of pyrenyl fluorescence. It should be noted that the monomer fluorescence of pyrenyl chromophores is very weak in Fig.4(c) in the absence of CUA. Fig.4(b) indicated that energy transfer from carbazolyl chromophores to pyrenyl chromophores occurred in LB films composed of an acceptor PDA/SA layer and a donor CUA/PA layer separated by two layers of PA. The intensity of pyrenyl fluorescence of both Fig.4(a) and Fig.4(b) is larger than that of Fig.4(c). This shows that the energy transfer from CUA to PDA enhanced both excimer and specifically monomer emission of PDA. The critical distance \( r_0 \) for the energy transfer from CUA to PDA was estimated to be 2.07nm from the fluorescence spectrum of CUA and the absorption spectrum of PDA in solutions. The value of \( r_0 \) coincided with the literature value for N-methylcarbazole and pyrene (2.08nm) [10].

4. Discussion

The plateau of \( \pi-A \) isotherms at about 13mN/m in Fig.1 and the limiting area at higher surface pressure normalized by the molar fraction of PA strongly suggested that the squeezing-out of CUA or PA occurred at about 13 mN/m and that a supermonomolecular layer (bilayer) structure was formed on the water surface at higher surface pressures. Several reports have been made on the formation of a supermonomolecular layer by the squeezing-out either at the air/water interface[11-19] or on solid substrates[14-19]. Kawabata et al.[14] reported the formation of a bilayer structure at the air/water interface for a mixture of arachidic acid and squarylium dye. From the thickness measured by a stylus method, and the capacitance, they concluded that LB films were composed of a bilayer unit which was formed on the water surface. Kim et al. [16,17] proposed a multi-stacked structure for \( J \)-aggregates of squarylium dyes with propyl groups in mixed LB films with arachidic acid from surface pressure-molecular area isotherms. Nagamura et al. [18,19] observed two solid condensed phases in mixed monolayer assemblies of amphipathic porphyrin and arachidic acid. They proposed a stacked structure of two porphyrins at higher surface pressure after the squeezing-out[19].
For the energy transfer between donors and acceptors located in layers separated by the distance \( d \), the fluorescence intensity monitored at the wavelength where only acceptors shows fluorescence is expressed by eq 1, where \( I_A \) is the fluorescence intensity of acceptors in the absence of donors, \( I_0 \) is the fluorescence intensity of acceptors in direct contact with donors, and \( d_0 \) is the critical distance for such two-dimensionally distributed donors and acceptors [20]. In the present case it is not possible to estimate \( d_0 \) directly using fluorescence data measured in LB films containing CUA and PDA as has been done before, because the structure of CUA/PA layer is unknown. The critical distance \( d_0 \) is related by eq 2 to the critical distance \( r_0 \) for statistically distributed donors and acceptors, which is estimated from the fluorescence spectrum of donors and the absorption spectrum of acceptors in solutions,

\[
d_0^4 = \frac{3}{2} \gamma \sigma r_0^6
\]

(2)

where \( \gamma \) is a constant dependent on the orientation of transition moments of donors and acceptors, and \( \sigma \) is the number of acceptor molecules per unit area [21]. The interaction of pyrenes at the ground state is weak and is known only to form a loosely coupled molecular pair showing the spectral shift of only a few nm [22]. Therefore we can use \( r_0 \) estimated in solution as a good approximation to evaluate \( d_0 \) in LB systems. The value of \( \sigma \) was estimated to be \( 1.88 \times 10^{14} \text{cm}^{-2} \) from the limiting area for PDA/PA(1:1). No estimation has been made for transition moments distributed over some range from a surface normal, although the value of \( \gamma \) was previously given for donors and acceptors specifically oriented in separated layers [21].

The carbazolyl chromophores were distributed in CUA/PA LB films making 50°-66° for a short axis and 42°-70° for a long axis transition with respect to the normal of a film plane [1]. The limiting values of the critical distance \( d_0 \) were estimated to be 3.63 and 4.32 nm from \( r_0 \) mentioned above and \( \gamma \) values (0.25 \( \pi \) and 0.49 \( \pi \)) for a donor CUA with experimentally determined distribution and an acceptor with transition moments parallel and perpendicular to the film plane as two extremes, respectively. Details of the estimation of \( \gamma \) taking the distribution of transition moments into accounts are shown in the Appendix.

The distance \( d \) is given by \( d = N \times d_0 \) for the model (A) or (C) and \( d = (N + 1) \times t_0 \) for the model (B) shown in Fig.2, where \( N \) is the number of cadmium palmitate monolayers deposited between a donor and an acceptor and \( t_0 (= 2.27 \text{nm}) \) is the thickness of a cadmium palmitate monolayer. The molecular lengths for CUA and PA, or PDA and SA were assumed to be almost equal from a Corey-Pauling-Koltun (CPK) molecular model. The ratio \( I(N)/I(N=0) \) is then given by the following equations for the model (A) or (C) and the model (B) in Fig.2, respectively.

\[
I(N)/I(N=0) = \frac{I_0/(1+(d_0/d_0)^4) + I_A}{I_0 + I_A}
\]

(3)

\[
I(N)/I(N=0) = \frac{I_0/(1+(N+1)^4) + I_A}{I_0/(1+(t_0/d_0)^4) + I_A}
\]

(4)

Observed values (filled circle) of \( I(N=2)/I(N=0) \) at \( \lambda_{ex}=296 \text{nm} \) are plotted in Fig.5 against the
fluorescence wavelength together with calculated dependences according to eq 3 (solid lines) and eq 4 (dotted lines) for two limiting values of $d_0$. Lower and upper curves are calculated for $d_0=3.63\text{nm}$ and $d_0=4.32\text{nm}$, respectively, in both cases. The results shown in Fig.4(c) and Fig.4(a) were used as $I_A$ and $I_0 + I_A$, respectively. The maximum experimental error was estimated to be about 1% in the calculation of these ratios. As shown in Fig.5 the observed ratios, $I(N)/I(N=0)$, are located in a region predicted by eq 3 for the model (A) or (C) which is clearly discriminated from a region between dotted lines for the model (B). The observed dependence of $I(N=2)/I(N=0)$ ratio on the fluorescence wavelength was attributed to the fact that the monomer fluorescence of PDA by the direct excitation shown in Fig.4(c) was much weaker as compared with those in Fig.4 (a) and 4(b) in the presence of CUA. Such difference in the fluorescence behavior of PDA might be attributed to more homogenous distribution of pyrenyl chromophores in the mixed monolayer of PDA/SA deposited on a CUA/PA monolayer either directly (Fig.4(a)) or with two spacer PA monolayers (Fig.4(b)).

No difference was found in the absorption spectra of PDA in the absence or the presence of a CUA/PA monolayer. Increased monomer fluorescence in CUA-sensitized cases appears that the enhanced monomer emission results from energy transfer from CUA to PDA monomer directly. The distance-dependent energy transfer from CUA to PDA can be used to study the layer structure because the spectral pattern did not change as shown in Fig.4(a) and 4(b). From these results one of the bilayer structures, the model (B) can be excluded. From X-ray and capacitance measurement, we previously reported that supermonomolecular layers on water surface were deposited as usual Y-type LB films composed of a mixed monolayer unit [3]. The present result gave another information supporting it. The energy transfer experiment can give solid information on the molecular arrangement in the bilayer structure which is not obtained from X-ray or capacitance measurements.

5. Conclusion

The Förster energy transfer method was proposed to study the layer structure of LB films deposited from supermonomolecular films on water surface. Although X-ray and capacitance measurements can distinguish LB films composed of a monolayer unit (model(C))
and a bilayer unit (model(A)), they can not determine the exact structure of LB films composed of a bilayer unit, the model(A) or the model(B). From the Förster energy transfer which is very sensitive to the relative orientation and distance between a donor and an acceptor, it is very easy to determine the exact location and orientation of chromophores in supermonomolecular layer structures.

References
Appendix

The factor $\gamma$ in eq 2 is estimated as follows for the case in which both donors and acceptors are oriented with respect to the surface normal over some range. The $\gamma$ values were reported in ref. 21 for specifically oriented donors and acceptors such that both or one of them are parallel or perpendicular to the layers or randomly distributed, which are the specific cases of our treatment. The unit vectors $\hat{q}_D$ and $\hat{q}_A$ of transition moments of a donor $D$ and an acceptor $A$ in layers separated by $d$ in a coordinate system shown in Figure A and vector $r$ connecting them are given as follows, $\hat{q}_D : (\sin(\theta_D), 0, \cos(\theta_D))$ $\hat{q}_A : (\sin(\theta_A) \cdot \cos(\phi_A), \sin(\theta_A) \cdot \sin(\phi_A), \cos(\theta_A))$ $r : (\rho \cos(\phi_r), \rho \sin(\phi_r), d)$ where $\theta_D$ and $\theta_A$ are the angles between transition moments and the surface normal, $\phi_A$ or $\phi_r$ are the angles between x-axis and the projections of an acceptor transition moment or the vector $r$. Donors and acceptors are assumed to be uniformly distributed in each layer. Projections of acceptor transition moments are assumed to be randomly distributed. Fig. A

The orientation factor $K$ in the Förster equation is given by
$$K = q_D \cdot q_A - 3(q_D \cdot r)(q_A \cdot r) / (\rho^2 + d^2) \quad \text{(A1)}$$

The total contribution from all acceptors are given by
$$\left( \frac{K^2 r^6}{\tau} \right)_{\text{total}} = \int \frac{K^2 r^6}{(\rho^2 + d^2)^3} \, d\phi_D \, d\phi_A \, d\rho / \int d\theta_A \quad \text{(A2)}$$

The integration over 0 and $2\pi$ for $\phi_r$ and $\phi_A$ and over 0 and infinity for $\rho$ using equation A 1 yields,
$$\left( \frac{K^2 r^6}{\tau} \right)_{\text{total}} = 12 + 3 \sin^2(\theta_D) \cdot \sin^2(\theta_A) + 3 \sin^2(\theta_D) \cdot \cos^2(\theta_A) \cdot \cos^2(\theta_D) \quad \text{(A3)}$$

If the orientation of both donors and acceptors are distributed in the azimuthal direction over specific range $\theta_{D1} < \theta_D < \theta_{D2}$, $\theta_{A1} < \theta_A < \theta_{A2}$, $\rho \cdot d \cdot \sin(\theta_D) \cdot \sin(\theta_A) \cdot r$, $\rho \cdot d \cdot \sin(\theta_D) \cdot \cos(\theta_A) \cdot \cos(\theta_D)$

The rate constant equation for the Förster energy transfer and eq 2, the $\gamma$-value is given by
$$\gamma = \pi \cdot \left\{ \frac{1}{(3/16)} \cdot \int \sin^2(\theta_A) \cdot \sin(\theta_A) \, d\theta_A \right\} \quad \text{(A4)}$$

This equation gave the same values of $\gamma$ as those in ref 21 for specific orientation of donors and acceptors considered therein.

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