Dimer Formation of Anthracene in Langmuir-Blodgett Films as Revealed by Time-Resolved Fluorescence Spectra

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Anthracene incorporated in LB monolayer films has been found to show excimer fluorescence due to a dimer which is different from the so-called sandwich dimer or the so-called stable dimer, whose structure is known. Two types of excimer have been also found to be produced on excitation to the dimer.

The Langmuir-Blodgett (LB) techniques are very useful for examination of various molecular complexes since dimer or higher aggregates can be easily formed in the LB films. In a previous paper,[1] a dimer formation of naphthalene chromophore incorporated in LB films was reported. In the present study, photoexcitation dynamics has been examined for chromophoric anthracene distributed in the LB films on the basis of the steady-state and picosecond time-resolved fluorescence spectra and the polarization absorption spectra.

12-(2-anthryl) dodecanoic acid (12-ADA) was synthesized according to a reference.[2] All the samples of the LB films were deposited as a cadmium salt with a surface pressure of 22.5 mN/m. Stearic acid was used as a matrix for the mixed LB films of 12-ADA. A schematic structure of the mixed LB films is shown in Figure 1.

Steady state fluorescence spectra were measured with JASCO FP-770F fluorescence spectrometer, and fluorescence decays and time-resolved spectra were measured by using a femtosecond laser and single-photon counting system.[3] The laser system was an argon-ion laser pumped mode-locked Ti:Sapphire laser equipped with a BBO SHG crystal. Excitation wavelength was 368 nm.

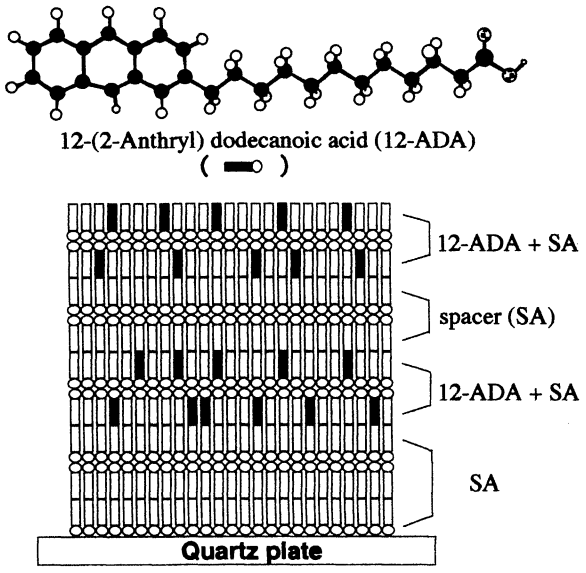

Figure 1. Molecular structure of 12-ADA , and a schematic illustration of LB multilayer structure of 12-ADA mixed with stearic acid (SA).

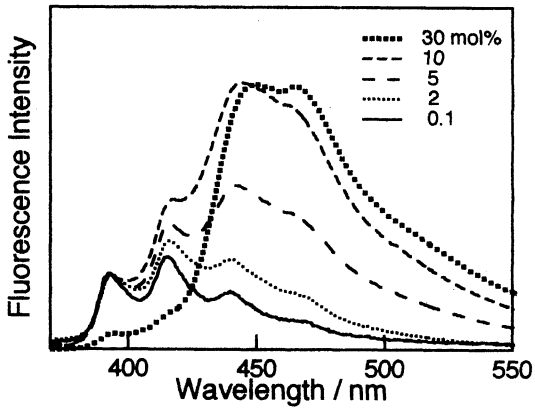

Figure 2. Fluorescence spectra of 12-ADA at different concentrations in mixed LB films.

Polarized absorption spectra were also measured with a JASCO U-best 50 spectrometer equipped with a sheet polarizer .[4]

Figure 2 shows the fluorescence spectra of 12-ADA distributed in LB films at various concentrations. At a low concentration of 0.1 mol%, only the fluorescence with a sharp structure is observed. This emission, whose spectrum is essentially the same as that in solution, is assigned to the fluorescence belonging to the $S_1 \rightarrow S_0$ transition of the monomeric anthracene chromophore. At high concentrations, on the other hand, a broad fluorescence with a peak at around 440 nm appears besides the sharp fluorescence. As the concentration increases, the relative intensity of the latter emission increases, and the broad emission gives two peaks at 440 and 460 nm at concentrations higher than 30 mol%. The broad fluorescence is assigned to the excimer emission. Figure 3 shows the fluorescence excitation spectra of

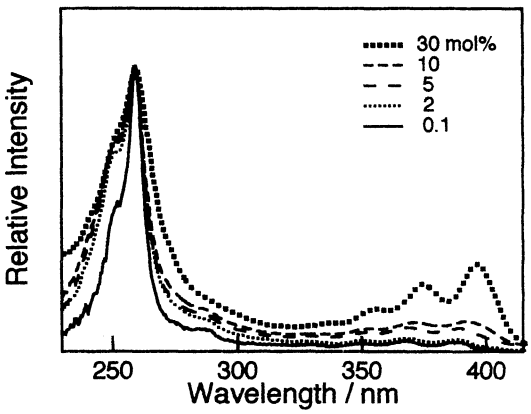

Figure 3. Fluorescence excitation spectra of 12-ADA at different concentrations in mixed LB films.

12-ADA in the LB films at various concentrations. The absorption in the region of 350 - 400 nm is assigned to the vibronic bands of the $S_0 \rightarrow S_1$ transition, and the strong band at around 250 nm is assigned to the $S_0 \rightarrow S_3$ transition. At low concentrations, the excitation spectra are very similar to the absorption spectrum in solution. As the concentration increases, however, the $S_0 \rightarrow S_3$ band becomes broader, and its intensity relative to the $S_0 \rightarrow S_1$ band decreases. With increasing concentration, further, the $S_0 \rightarrow S_1$ absorption bands are red shifted, e.g., the 0–0 band is at 388 nm at 0.1 mol% and 396 nm at 30 mol%, though the peak wavelength of the $S_0 \rightarrow S_3$ absorption (259 nm) is nearly independent of concentration. These results indicate that a molecular complex is formed in the LB films at high concentrations, and the excimer fluorescence is emitted from this complex. Since anthracene is well known to form a dimer easily, we assign the molecular complex formed in the LB films as a dimer of chromophoric anthracene.

Two types of dimer are known in anthracene; the so-called sandwich dimer has a symmetric sandwich configuration, and the so-called stable dimer gives a configuration where the short in-plane axes make an angle of 55 degree with each other and the long axes are parallel to each other .[5] In comparison with the monomer spectra, the $S_0 \rightarrow S_3$ absorption of the former dimer gives a blue shift by about 40 nm, and the $S_0 \rightarrow S_1$ transition of the latter dimer gives a red shift by more than 20 nm. It is further known that the sandwich dimer gives a typical excimer fluorescence with a peak at 480 nm and that the stable dimer shows a fluorescence spectrum with a well defined vibronic structure. Therefore, the dimer formed in the LB films is different from the stable dimer since the excimer fluorescence is observed in the LB films. Further, the dimer formed in the LB films is different from the sandwich one because of the difference in position of the $S_0 \rightarrow S_3$ origin, though both the sandwich dimer and the dimer formed in the LB films give excimer fluorescence. Thus, a new type of dimer is regarded as formed in the LB films. The polarization spectra of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_3$ absorption bands observed for LB films at 30 mol% indicate that the in-plane long and short axes of anthracene chromophore tilt against the normal to the substrate by 56 and 62 degree, respectively, and both axes distribute equally about the normal to the substrate. These results of the polarization spectra suggest that anthracene chromophores partially overlap in the dimer formed in the LB films.

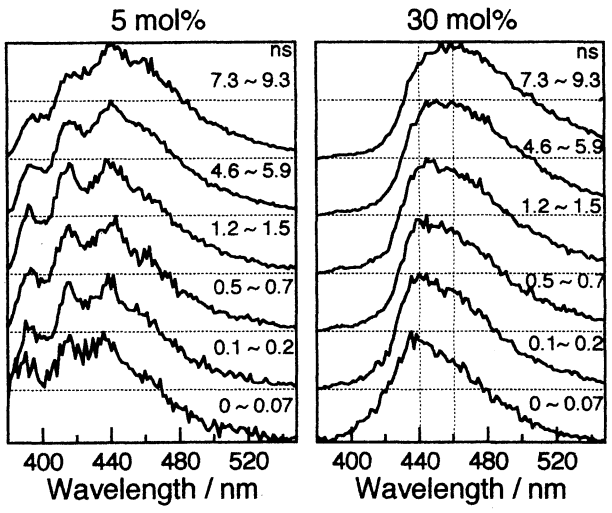

Figure 4. Time-resolved fluorescence spectra of 12-ADA at 5 mol% (left) and at 30 mol% (right) in mixed LB films.

It is also found that two types of excimer emission appear in the LB films. Figure 4 shows the time-resolved fluorescence spectra of the LB film at 5 and 30 mol% 12-ADA. At 5 mol%, both monomer fluorescence with a sharp structure and broad excimer fluorescence with a peak at around 440 nm are observed. The relative intensity of the latter emission becomes higher with a passage of time, indicating that the excimer fluorescence is emitted from the dimer following energy transfer from monomer to dimer besides the direct excitation to the dimer. Note that the time resolved spectra at 0.1 mol% show only the monomer fluorescence of anthracene in the whole time region. At 30 mol%, on the other hand, the spectra are dominated by the excimer fluorescence even at the initial stage of time, indicating that chromophores are dominated by dimers. Further, the excimer fluorescence becomes broader and shows a red shift with a passage of time, suggesting that there exist different types of dimer at high concentrations of LB films; one emits the 440 nm fluorescence and another emits the 460 nm fluorescence. The time-resolved spectra show that the concentration of the latter dimer is very low even at a high concentration of 30 mol% and that the excimer fluorescent state of this dimer is produced by energy transfer from the photoexcited state of the former dimer. Thus, the presence of two peaks in the steady state excimer fluorescence spectrum observed at 30 mol% (see Figure 2) results from an overlap of two spectra which show a different peak wavelength from each other.

Fluorescence measurements of anthracene chromophore have been reported also by Biesmans et al.,[6] mainly for 7-(2-anthryl) heptanoic acid monolayers (7-ADA). The fluorescence spectrum of 7-ADA monolayers was reported to be time independent between 0 and 11.5 ns. They also reported that no mixing occurs between 12-ADA and arachidic acid even at high dilution in the mixed monolayer of both compounds. As mentioned above, 12-ADA mixed with stearic acid shows a remarkable time dependence, indicating the presence of different types of excimer. Further, the concentration dependence of the fluorescence spectra shown in Figure 2 seems to show a mixing between 12-ADA and stearic acid at low concentrations of 12-ADA in mixed monolayer films. Thus, the present results in 12-ADA monolayer films mixed with stearic acid are very different from the results reported for 7-ADA and 12-ADA mixed with arachidic acid.

References and Notes

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