Dimer Formation of Naphthalene in Langmuir-Blodgett Monolayer Films Probed by Time-Resolved Fluorescence Spectroscopy

Kei Abe, Sachiko Suzuki, Ikuo Mukai, Seiji Akimoto, Nobuhiro Ohta, and Iwao Yamazaki*
Department of Molecular Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060

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Naphthalene incorporated in LB monolayer films has been found to exhibit two types of fluorescence emissions due to the monomer and the dimer. The dimer fluorescence corresponds well to those observed in crystal under extraordinary high pressure and in naphthalene paracyclophanes.

Photochemical processes under restricted molecular geometries, e.g., Langmuir-Blodgett (LB) films, have received much attention in view of exploiting new aspects of molecular photophysics.[1] In our previous works, the excitation energy relaxation in LB films was studied with rhodamine B,[2] oxacyanine[3] and pyrene[4] by means of picosecond time-resolved fluorescence spectroscopy. It was found that the LB film is characterized by (1) non-homogeneous distribution of guest chromophores with fractal or fractal-like structures,[3,4] (2) formation of dimers and/or aggregates of dyes in molecular cages compressed with fatty acid matrix,[2-4] and (3) excimer formation from the preformed dimers.[4] The present study is focussed on the molecular dispersion of a typical aromatic hydrocarbon, naphthalene, incorporated in LB monolayer films. Naphthalene is known not to give dimer or excimer state in ordinary conditions; the excimer forms only in extraordinary conditions like a crystal under high pressure[5] and paracyclophanes.[6] In this study, the dimer formation in LB films has been probed with time-resolved fluorescence spectroscopy.

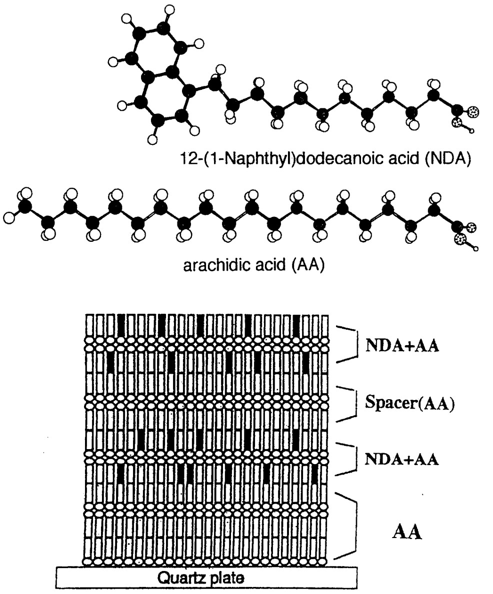

Figure 1. Molecular structures of NDA and arachidic acid, and a schematic illustration of LB multilayer structure.

12-(1-Naphthyl)dodecanoic acid (hereafter referred to as NDA, Figure 1) was synthesized by the Grignard reaction of 1-naphthyl magnesiumbromide with $CH_3OCO(CH_2)_{10}COCl$, followed by the Clemmensen reduction and the hydrolysis of carboxylic ester. The product was purified by repeated recrystallization from methanol. A toluene solution containing NDA and arachidic acid was spread on a water surface in a Langmuir trough (San-Yesu FSD-20) at 20 °C. In the water subphase, cadmium chloride (3×10^{-4} M) and sodium hydrogencarbonate (5×10^{-5} M) were contained. The π-A curves showed steep rises at occupied area around 0.18 nm^2, indicating that an LB monolayer incorporates NDA with its naphthalene ring being squeezed out partly from the monolayer surface. The monolayer was compressed at 10 mN/m, and then transferred onto a quartz plate at a transfer rate of 5 mm/min. The deposition ratios were 0.9 in 1 mol% and 0.8 in higher concentrations of NDA. The concentration of NDA in a matrix of arachidic acid was varied from 0.5 to 30 mol%. A schematic structure of the LB films is shown in Figure 1.

The time-resolved fluorescence measurement was performed with a picosecond laser system composed of a Nd:YAG laser and a dye laser (rhodamine 6G, λ=290 nm) and a time-correlated, single-photon counting system.[1]

Figure 2 shows the absorption and fluorescence spectra of naphthalene and NDA in ethanol solution; the NDA spectra are red-shifted by 5-10 nm relative to the spectra of parent naphthalene by an alkyl-group substitution at α position of naphthalene. Figure 3 shows the absorption (fluorescence excitation) and fluorescence spectra of NDA in LB films. The fluorescence spectra of low concentration (< 10 mol%) exhibit a maximum around 340 nm, and correspond to the spectrum in solution. As the concentration is increased, the spectrum is changed to the one with a peak at 360 nm. The fluorescence

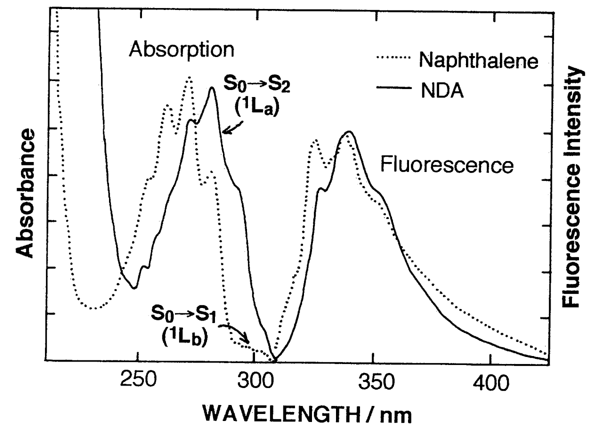

Figure 2. Absorption and fluorescence spectra of naphthalene and NDA in ethanol solution (3×10^{-4} M).

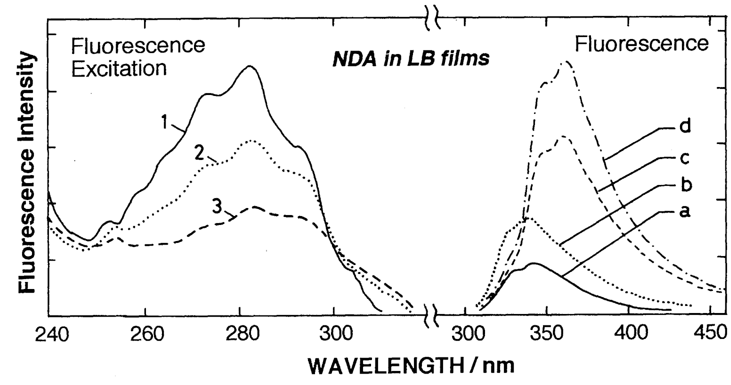

Figure 3. Absorption (fluorescence excitation) and fluorescence spectra of NDA in LB films. Curve (1) 10 mol%, λ_{obs} = 340 nm; (2) 30 mol%, λ_{obs} = 345 nm; (3) 30 mol%, λ_{obs} = 362 nm; (a) 1 mol%; (b) 10 mol%; (c) 20 mol%; (d) 30 mol%. The fluorescence spectra (a)~(b) were taken at λ_{exc} = 272 nm. The number of layers stacked were 20 layers for 1 mol% and 2 layers for other samples.

excitation spectra of low concentration (< 10 mol%) correspond well to the absorption spectrum in solution; the vibrational bands appear at 294, 283 and 273 nm. In higher concentration (>10 mol%), the spectrum changes with respect to the intensity ratio of the vibrational bands and also to an enhancement around 300-320 nm. These changes are pronounced much more upon changing the monitoring wavelength to the longer wavelength. The absorption spectra in 30 mol% are similar to those of naphthalene dimer in crystal under high pressure (>10kbar)[5] and also in paracyclophane.[6] The fluorescence spectra in higher concentration are similar to those of crystal which are red-shifted 10-20 nm from the monomer band. In paracyclophane, only an excimer fluorescence appears at much longer wavelength (390-420 nm). From these considerations, we assigned the fluorescence at low concentration as due to the monomer, while the fluorescence at higher concentraiton as due to the dimer which are formed in the ground state.

The time-resolved fluorescence spectra are shown in Figure 4 for 10 and 30 mol%. In 10 mol%, the spectrum does not change with time, and it is almost the same as the monomer spectrum obtained with stationary excitation (Figure 3). On the other hand, the spectrum in 30 mol% changes with time; in 0-100 ps, the spectrum shows a peak at 350 nm, and assigned to a superposition of monomer and dimer spectra; after 100 ps, the spectrum shifts to the red with a peak at 360 nm, and assgined to the dimer spectrum. This means that at 30 mol% the excitation at monomer sites undergoes energy migration to the dimer sites in LB monolayer during 100 ps. The fluorescence decay curve of 1 mol% is almost single exponential with 37.0 ns lifetime, but the decay of 10 mol% is not exponential and can be fitted to the decay function ($\rho(t)$) of the fluorescence quenching in two-dimensional system.[2,3]

$$\rho(t) = \exp\left[-t/\tau_D - \gamma_A (t/\tau_D)^{1/3}\right] \tag{1}$$

where τ_D is the lifetime of NDA in the absence of trap sites (37.0 ns). By assuming homogeneous distribution of NDA in LB monolayer, $\gamma_A = 4/3\ n_A R_0^2$, where n_A is the surface density of trap sites, and R_0 is the Förster critical transfer distance. Then the n_A value can be estimated under an assumption of R_0 = 7 Å from the γ_A value obtained from curve fitting of fluorescence decay curves with eq 1. At the concentration of 10 mol%, as an example, the surface density of trap sites (dimer or oligomer) is calculated to be 1.2×10^{14} molecules cm^{-2}. By comparing this value with total number density of NDA (4.7×10^{14} molecules cm^{-2} at 10 mol%), half of molecules form dimers and/or oligomers and act as energy traps. Note that the ratio of the number density of aggregates to monomer (α) is 0.5 from a statistical calculation under an assumption of the random and uniform distribution. Then the experimental result $\alpha \cong 0.5$ is in agreement with the calculation, and indicates that naphthalene chromophores are distributed in LB monolayer films randomly as expected from the statistical calculation. In other words, naphthalene in LB films of low and medium concentrations (< 10 mol%) is dispersed uniformly and randomly as monomer much more than pyrene and ionic dyes like cyanine and rhodamine in which even in low concentration (1 mol%) dimer and/or excimer are formed.[2-4]

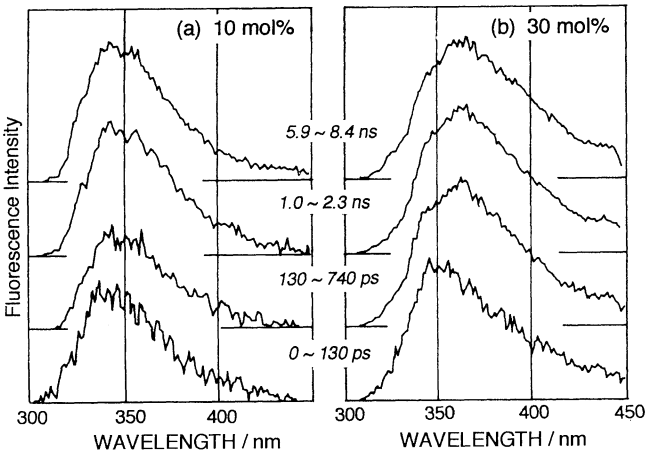

Figure 4. Time-resolved fluorescence spectra of NDA in LB films of 10 mol% (a) and 30 mol% (b). The excitation wavelength was 290 nm.

References

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