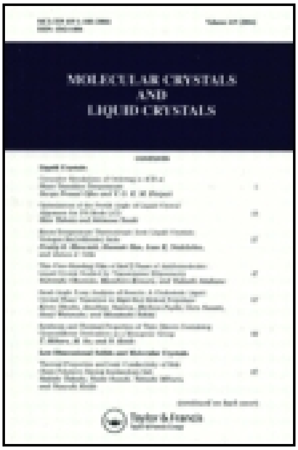

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# High-density J-aggregate Monolayer with a Squarylium Dye Exhibiting an Ultrafast Nonlinear Optical Response

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By analyzing the mechanism of J-aggregate formation with a squarylium dye on the water surface, we succeeded to obtain a mono-molecular layer with an extremely large optical density (>0.3). Because of the homogeneous and fine structure of this film, an ultrafast nonlinear optical response exhibiting a two-dimensional mono-molecular layer nature was observed at room temperature.

Keywords: squarylium dye; J-aggregate; mono-molecular layer; femtosecond; nonlinear optical response

## INTRODUCTION

A J-aggregate of a cyanine dye, such as pseudoisocyanine (PIC-J) exhibits large and fast optical nonlinearity because of a coherent effect of the one-dimensional Frenkel excitons.[1] However a complicated structure with intertwined PIC-J filaments was also observed for a dispersed film in a polymer matrix.[2] A two-dimensional J-aggregate would enhance the coherent effect,[3] and is extremely important for opening new applications because of its defined structure. Although there have been studies concerning the optical properties of two-dimensional J-aggregate molecular films[3], no ultrafast nonlinear dynamics has been observed. To achieve nonlinear optical signals, a high homogeneity of the J-aggregate and a narrow absorption band are required. This paper discusses the formation mechanism of a two-dimensional J-aggregate film with squarylium dye, and reports on the first observation of femtosecond nonlinear responses from a mono-molecular layer.

## EXPERIMENT

A monolayer of a J-aggregate was formed by spreading a chloroform solution of squarylium dye at a concentration of $8.31 \times 10^{-4}$ M on the surface of pure water. The occupied areas for one dye molecule were determined by the $\pi$-A isotherms of the monolayer in a Wilhelmy-type Langmuir trough along with a simultaneous measurement of their absorption spectra. The femtosecond excited-state dynamics was investigated by measuring the transient-absorption spectra using pump pulses with a center wavelength of 780 nm and probe pulses of a white-light continuum with 200 fs duration under a 1 kHz reputation rate. In the pump-probe measurement, a transparent trough formed on a glass substrate was used with the subphase temperature adjusted to 5 °C.

## RESULTS AND DISCUSSION

We studied the molecular structure of a squarylium dye suitable for preparing a Langmuir film with J-aggregates. By investigating the relations between the aggregation forms and the lengths of the alkyl substituents, a monolayer of squarylium dye with molecular structure shown in Fig. 1 (bis[4-(N-propyl-alkylamino) phenyl] squarylium), was found to exhibit a J-band. In these molecules, two propyl groups facing the water side control the stacking angle of the molecules to form the J-aggregates[4].

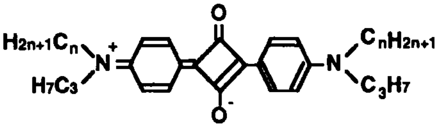
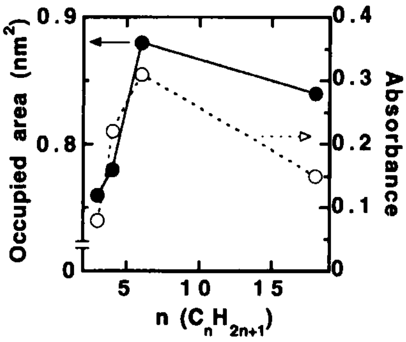


FIGURE 1 Chemical formula of squarylium dyes forming a J-aggregate.

In Fig. 2, clear correlations can be observed between the occupied area and the absorbance of the J-band in terms of the dependence on the length of the other two alkyl groups facing the air side. An increment of n from 3 to 6 results in an enlargement of the collapse pressure of the monolayer from 18 to 25 mN/m,[4] which means a stronger interfacial tension between the water and the monolayer. This interfacial tension causes an enlargement of the occupied area against dipole-dipole interactions between dye chromophores. On the contrary, dye molecules rather condense for longer alkyl chains from n=6 to 18 because of excessive hydrophobic interactions. Substituents of two hexyl groups seem to realize moderate hydrophobicity of the monolayer to achieve an intense J-band.



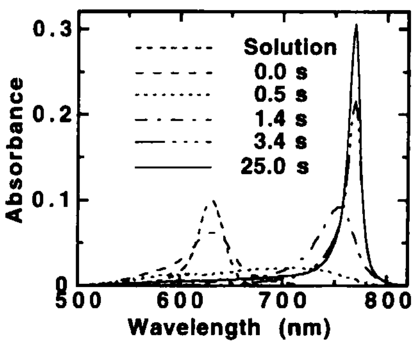


FIGURE 2 Influence of the substituted alkyl chain length on the occupied area and the absorbance of monolayers.

FIGURE 3 Sequential absorption spectra showing the formation of a J-aggregate in a monolayer on the water surface.

Figure 3 shows the time course of the observed absorption spectra for a Langmuir film (n=6) after dropping a chloroform solution on water. Due to the increasing interaction among dye molecules as the solvent evaporates, the initial absorption band of isolated molecules changes into an inhomogeneous broad band (t=0.5 s). After that, dye molecules are stretched due to the influence of increasing interfacial tension (observed for a decrease in the surface pressure). Finally, equilibrated interfacial tension effectively acts to form an ordered structure exhibiting a narrow J-band (t=25 s). The absorption spectra at t=1.4 s and 3.4 s were found to coincide with spectra of the dye molecules of n=3 and 4 at equilibrium, respectively[4]. This relation suggests that the poor homogeneity of aggregation formations is caused by either the small n of molecules or incomplete solvent evaporation, which equally reduces the hydrophobicity of the monolayers. The oscillator strength of the J-band calculated by O.D.=0.31 and FWHM=13 nm, as shown in Fig.3 is almost unity, which suggests the full formation of a J-aggregate with continuous structure of this monolayer.

Figure 4 shows the transient-absorption change spectra due to resonant pump-probe spectroscopy at a pump energy of 2.5x10$^{-6}$ J/cm$^2$, being as low as that for PIC-J. As the other J-aggregate, dispersion-type absorption change spectra containing a decrease in the absorbance at the longer wavelength side and an increase at opposite side of its absorption peak were observed in only a short time range. These spectra can be understood in terms of a three-level model. The decrease in the absorption is caused by either bleaching of the linear absorption of the transition from the ground state to one exciton state due to the pump excitation. The induced absorption at a shorter wavelength suggests the onset of a transition from the one- to two-exciton state, exhibiting an energy slightly larger than that for linear absorption. The time dependence of both bleached and induced absorption were analyzed by fitting the transient spectra using the linear-absorption curve. Over 60% of both observed absorption changes was found to decay with an identical femtosecond time constant in the range of 200~300 fs. The coincidence of the decay time constant implies that the both absorption changes depend only on the population of the one-excited states. This is consistent with the above-mentioned model. The high efficiency of the absorption change as well as the ultrafast decay of the excited states, as shown above, are indicative of the high-density, uniform two-dimensional nature of the Langmuir film prepared by the present method.

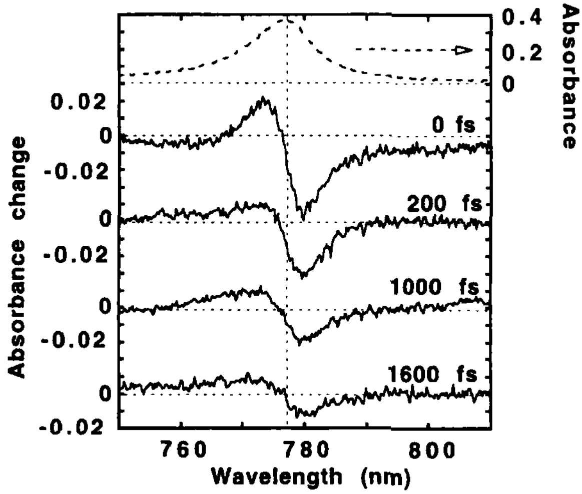


FIGURE 4 Linear and transient absorption spectra of the J-aggregate monolayer

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