

Fabrication and Femtosecond Optical Response of Langmuir–Blodgett Films with Two-Dimensional J-Aggregates

Makoto Furuki,* Osamu Wada, Lyong Sun Pu,[†] Yasuhiro Sato,[‡] Hitoshi Kawashima,[‡] and Toshiro Tani^{‡,§}

FESTA Laboratories, The Femtosecond Technology Research Association, 5-5 Tokodai, Tsukuba, Ibaraki 300-2635, Japan, Corporate Research Laboratories, Fuji Xerox Co. Ltd., 430 Sakai, Nakaimachi, Kanagawa 259-0157, Japan, and Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, Ibaraki 305-8568, Japan

Received: May 5, 1999; In Final Form: June 29, 1999

Fabrication and femtosecond nonlinear optical response of Langmuir–Blodgett (LB) films with two-dimensional J-aggregates are described. Single-layer LB-films were deposited on glass substrates from mono-molecular layers of squarylium dye J-aggregates at an air–water interface (Langmuir film). To obtain LB-films containing J-aggregates, deposition of the Langmuir film with compression slightly in excess of that required for monolayer occupation was necessary. Coating the surface of the LB-films with a glassy perfluorocarbon polymer soon after deposition was effective in enhancing the formation of J-aggregates and stabilizing their structures. The LB-films of squarylium dye J-aggregates exhibit a single J-band at 783 nm with an extremely large absorbance of 0.2/monolayer, which is comparable to that of the Langmuir films. The morphology of J-aggregates in the LB-films was characterized by transmission images obtained using a near-field scanning optical microscope (NSOM) at a resonant wavelength of 780 nm. The LB-films were comprised of randomly polarized two-dimensional domains in which transition moments of J-aggregates were oriented in a single direction on a sub- μm scale. Ultrafast nonlinear optical responses were characterized by means of resonant pump–probe measurements. The observed low absorption-saturation energy ($3.4 \mu\text{J}/\text{cm}^2\cdot\text{pulse}$) and ultrafast relaxation (time-constant of 200 fs) are indicative of delocalized excited states within highly organized structures of the squarylium dye J-aggregates in the LB-film which preserves the two-dimensional mono-molecular layer structures initially formed in the Langmuir films. Stable, solid-substrate-fixed, two-dimensional monolayers thus fabricated are promising for the realization of ultrafast planar all-optical switching devices.

1. Introduction

J-aggregates of molecules such as cyanine dye are known to be formed in highly ordered arrangements of 10 to 10000 molecules, which exhibit a sharp absorption band called the J-band at a wavelength longer than that of isolated molecules.^{1,2} Because of this intense, narrow absorption band, J-aggregates exhibit strong interactions with light at the resonant wavelength. Nonlinear optical properties, such as low absorption-saturation energy and ultrafast response, due to superradiant photoemission have been observed by means of optical measurements using short pulses. Studies on the dynamics of excited states in J-aggregates have become active during the past decade due to the possibility of using this large optical nonlinearity with ultrafast response in future all-optical devices.^{3–11}

The characteristics of J-aggregates are considered to depend on the ordering of molecular arrangements, since the above-mentioned optical properties are due to dipole–dipole interactions between the molecules. Since NSOM has ultrahigh spatial

resolution of 100 nm or less, the optical properties of mesoscopic structures, such as J-aggregates, can be characterized in more detail of molecular size.¹² Higgins observed morphology constituting intertwined fiber with diameters of less than 100 nm on the most well-known J-aggregates of pseudoisocyanine dispersed in polymer matrixes, which clearly suggested one-dimensional structures of the J-aggregates.¹³

As mentioned above, the J-aggregate dispersed in matrixes normally forms one-dimensional structures. The optical properties of such structures have been discussed on the basis of one-dimensional Frenkel exciton models. However, in the development planar optical devices using organic thin films, the J-aggregates with dense two-dimensional planar structures should be much advantageous in terms of effective interaction with incident light compared with that in a one-dimensional fiber structure, which must be difficult to utilize to cover a plane. Two-dimensional delocalization of excited states in LB-films of J-aggregates has been discussed by Kuhn and co-workers and others,^{14–17} but there has been no clear demonstration of ultrafast nonlinear optical responses in a film with a well-defined structure.

We have studied the forms of aggregate of squarylium dyes in connection with molecular structures, including the lengths and positions of alkyl substituents, and found a group of dye molecules that form J-aggregates in their Langmuir films.¹⁸ J-aggregates of squarylium dyes exhibit a sharp absorption band

* Corresponding author. Current address: Corporate Research Laboratories, Fuji Xerox Co. Ltd., 430 Sakai Nakai-machi Ashigarakami-gun, Kanagawa 259-0157, Japan. Phone: +81-465-80-2020. Fax: +81-465-81-8997. E-mail: furuki@rfl.crl.fujixerox.co.jp.

[†] Festa Laboratories.

[‡] Electrotechnical Library.

[§] Current address: Department of Applied Physics, Tokyo University of Agriculture and Technology, Naka-cho 2-24-16, Kogane-i, Tokyo 184-8588, Japan.

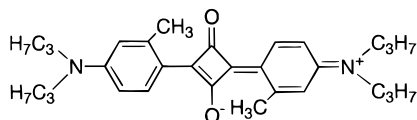


Figure 1. Chemical formula of squarylium dye (SQ33mM).

(J-band) at 750–790 nm, which is red-shifted from the absorption band of their isolated molecules at 630–650 nm. Among various types of squarylium dye, the squarylium dye with a propyl and a hexyl group at each end of its chromophore (SQ36) forms the narrowest (fwhm of 13 nm) and most intense (absorbance of 0.3 monolayer⁻¹) J-band. From an estimation of the oscillator strength of this Langmuir film based on absorption and reflection spectra, it has been clarified that almost all the molecules form J-aggregates and that the transition moments of the J-band are parallel to the water surface.¹⁹ One advantage of this well-defined two-dimensional structure can be seen in enhancement of the oscillator strength (1.5 times) compared to that of its solution because of the difference in average effective transition moment which is one-half for films and one-third for solution. Polarized fluorescence micrographs of this monolayer show mosaic-like morphology with randomly oriented domains with a diameter of 2–20 μm . The homogeneity of fluorescence brightness in each single domain suggests that these domains have a uniform two-dimensional structure. We have also observed the nonlinear optical response of this monolayer by femtosecond pump–probe measurement. The observed fast decay of absorption saturation (<300 fs) and low saturation energy (5 $\mu\text{J}/\text{cm}^2$) are indicative of exciton delocalization.^{19–21} However, the Langmuir film may not be stable enough for device applications. Therefore, a method for fixing this two-dimensional J-aggregate on solid substrates is required. We have succeeded in depositing squarylium dye LB-films on glass substrates that exhibit a single J-band similar to that of the Langmuir films on the water surface.

In this paper, we first summarize experimental details of the deposition and characterization of LB-films in section 2. Then, we discuss a novel method for depositing LB-films with a single J-band in section 3.1, morphology characterization of the LB-films through an NSOM in section 3.2, and results of femtosecond pump–probe nonlinear absorption measurements in section 3.3. Section 4 concludes the paper.

2. Experimental Section

2.1. Deposition of LB-Films. Squarylium dyes substituted at each end of their chromophores with a propyl group and an alkyl group longer than the ethyl group commonly forms J-aggregates in their Langmuir films. However, the shape of J-bands and the stability of monolayers observed in π -A isotherms depend on the length of the alkyl group and other substituents. In this work, squarylium with four propyl and two extra methyl substituents (SQ33mM: 2,4-bis-(4-(*N,N*-dipropylamino)-2-methylphenyl)squaraine) as shown in Figure 1, synthesized in accordance with the reported procedure,²² was used for the formation of LB-films. However, peak absorbance of the J-band observed for a Langmuir film of this dye (=0.2) is smaller than that of SQ36; this J-band is stable even when the film is compressed into an area less than that required for monolayer occupation. Langmuir films of the squarylium dye were formed by spreading a chloroform solution at a concentration of 8.31×10^{-4} M (i.e., 20 $\mu\text{L} = 1 \times 10^{16}$ molecules) on pure water containing 0.1 wt % of NaCl with the temperature maintained at 5 $^{\circ}\text{C}$. A moving-wall LB-film deposition apparatus (Nippon Laser & Electronics Lab., NL-LB240-MWA) with a

Wilhelmy balance was employed for the preparation of Langmuir films and LB-films. As substrates for the LB-films, Corning 1737 glass slides with a thickness of 1 mm and length and width of 50 mm (the same width as the LB-trough) were used after cleaning the surface by UV irradiation in oxygen gas flow at 200 $^{\circ}\text{C}$ for 20 min. For NSOM observations, cover-slips with a thickness of 150 μm and area of 20×20 mm², cleaned by the same procedure, were attached to the surface of glass slides and used as the substrates for LB-films. To stabilize their morphology, the deposited LB-films were surface-coated with glassy fluorocarbon polymer (Cytop, Asahi Glass). Cytop CTX-809AP was diluted by a special solvent of perfluorocarbon, CT-SOLV180, at the polymer concentration of 2 wt %, and spin-coated on the surface of the under at a constant rotation rate of 3000 rpm for 30 s, resulting in a polymer thickness of approximately 20 nm. In situ absorption spectra of the Langmuir films were obtained using a multichannel photodiode spectrometer (Otsuka Denshi, MCPD-100) combined with optical fibers. Absorption spectra of deposited LB-films were obtained using a dual-beam spectrophotometer.

2.2. Observation of Morphology Using a Near-Field Scanning Optical Microscope. An NSOM (Topometrix, Aurora) was used to visualize the morphology of the LB-films. To ensure stable scanning with low optical noises, the shear-force feedback apparatus supplied by the manufacture was modified. The laser diode used for the shear-force feedback was replaced with another laser diode module (Applied Techno) with an emission wavelength of 840 nm in order to avoid the excitation of fluorescence from the J-aggregates of the squarylium dye. Direction of the laser beam was also changed to direct-horizontal-illumination on dither-detection photodiodes through both sides of the probe tip form an oblique indirect-illumination of with single reflection on the sample surface. Because of these modifications, regulation of tip–sample distance is isolated from scanning of the sample. The morphology of J-aggregates was observed in illumination mode by coupling a beam emitted from a laser diode at the resonant wavelength for the J-band of 780 nm and by detecting the intensity of light transmitted through the sample and collected using an objective lens (N.A. of 0.6). A photomultiplier (Hamamatsu Photonics, R928) was used to detection of transmitted light. Polarized images were obtained by adjusting the rotation angle of a half-waveplate and a quarter-waveplate placed in front of a fiber-coupler for the illumination laser so that the linear polarization was achieved after collection by the objective lens. To avoid the polarization dependence of sensitivities, a quarter-waveplate was inserted between the objective lens and the photomultiplier, together with an analyzing polarizer with a rotation angle of 45 $^{\circ}$ to each optical axis, to illuminate the photomultiplier in circularly polarization. Images of the ideal J-aggregate morphology in Langmuir films were obtained by a microscope (Olympus, IX-70) with illumination provided by a Xe-lamp through a band-pass filter (780 nm, bandwidth 10 nm) and a polarizer.

2.3. Femtosecond Pump–Probe Measurement. Femtosecond optical pulses of signal (1.57 μm) and idler (1.63 μm) beams were generated from an optical parametric amplifier system (Spectra-Physics, OPA-800) using a 1 kHz Ti:sapphire regenerative amplifier. For pump–probe measurement, second harmonics of the signal beam (783 nm) and white-light continuum (approximately 400 nm to 2 μm) generated from a sapphire plate (thickness of 2 mm) by focusing the idler beam were used as pump and probe pulses. The cross-correlation width of each pulse was about 200 fs in the measured wavelength range. The illumination areas of pump and probe pulses at the sample were

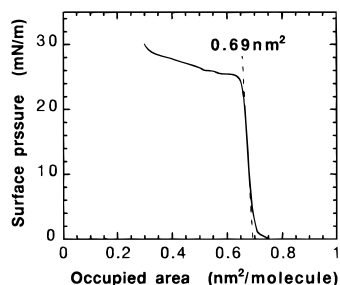


Figure 2. A surface-pressure vs area isotherm of an SQ33mM Langmuir film at 5 °C.

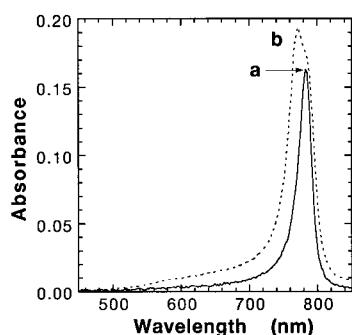


Figure 3. Absorption spectra of an SQ33mM Langmuir film at surface pressure of (a) 5 and (b) 20 mN/m.

5.0 and 3.0 mm², respectively. Transient absorption spectra were measured using a pair of spectroscopic diode array detectors, with one measuring the probe pulses transmitted through a sample and the other measuring the divided reference probe pulses. The intensity of the probe pulses was attenuated to about 30 μ W (corresponding to 1 μ J/cm² per pulse on the sample) until no bleaching of the absorbance was observed under illumination provided by only the probe pulse. To subtract optical noise resulting from self-diffraction and fluorescence by the pump pulses, the spectral signal observed under illumination of only the pump pulses was used as the background level.

3. Results and Discussion

3.1. Deposition of SQ J-Aggregate LB-Films. The form of aggregates in Langmuir films strongly depends on the surface pressure of the water containing the monolayer. In our previous studies, marked spectral changes depending on the surface pressure were observed during the formation of J-aggregates in Langmuir films.²¹ The initial absorption spectrum of isolated molecules just after the dye solution is dropped on the water surface changes into the J-band of 760 nm (J-blue) through broad inhomogeneous absorption spectra and then into a J-band of 780 nm (J-red) with a clear isosbestic point. These spectral changes, which are commonly seen in squarylium dyes forming J-aggregates, indicate that the molecular arrangement depends on the surface pressure, which increases as the solvent evaporates from the monolayer. Spectral changes of the opposite type are observed during the compression of Langmuir films, which is accompanied by an increase in the surface pressure.¹⁸ The surface-pressure vs area isotherm and absorption spectra observed during compression of the Langmuir film of SQ33mM are shown in Figures 2 and 3, respectively. Under a surface pressure greater than 20 mN/m, close to the collapse pressure, a part of J-red undergoes rearrangement of the form into J-blue. This spectral change can be understood as follows. The difference in absorption wavelength between J-blue and J-red might be due to the structure of each J-aggregate, such as the

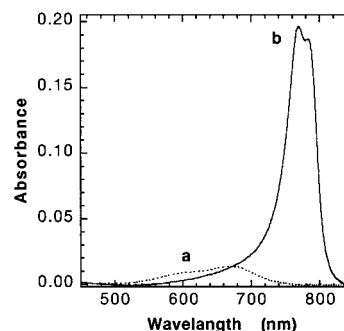


Figure 4. Typical absorption spectra of SQ33mM LB-films deposited under (a) constant surface pressure and (b) constant compression speed.

aggregation number and the molecular orientation. The structure of the J-red is speculated to have lower density of molecules than that of the J-blue because the J-red is stable under lower surface pressure and larger surface area. Compression of a monolayer causes an increase in the surface pressure which has the same effect as that the remaining solvent do in the process of monolayer formation from the solution. The transfer of a Langmuir film by the LB-technique is usually carried out under a surface pressure of around 30 mN/m in order to minimize the change in the surface pressure during the transfer process. However, the Langmuir film of SQ33mM collapses at a surface pressure of about 22 mN/m because of the low hydrophobicity of dye molecules with such short propyl substituents.

The deposition of an LB-film under a constant pressure of 20 mN/m at which the Langmuir-film still exhibits the J-red band (Figure 3a) results in deformation of the J-aggregates as shown in Figure 4a. This broad and weak absorption spectrum suggests that a higher compression force be required in order to maintain the molecular arrangements during the transfer process. LB-films containing J-aggregates were found to be deposited under the following particular conditions. Withdrawal of the substrate was started when the Langmuir film was compressed to an occupied area of 0.60 nm², where very little of Langmuir film collapsed, at a speed of 5 mm/min under 40% excess compression in a constant speed of 7 mm/min. This procedure resulted in the deposition of an LB-film exhibiting both J-red and J-blue (Figure 4b) which was similar to the Langmuir film under the collapse pressure (Figure 3b). The necessity of forced deposition by excess compression at a constant speed can be explained by variation in the surface pressure throughout the monolayer in the solid phase, the difference in surface flatness between the water and the glass substrate, or leakage of monolayer to the back of the substrate. Specific parameters of these deposition sequences may need to be altered slightly for Langmuir troughs with different geometry.

Unfortunately, the LB-films containing J-aggregates were not stable. The initial absorbance measured just after the deposition decreased by more than 50% in only 2 h as shown in Figure 5. To stabilize the monolayer structure of J-aggregates, we searched for inert coating materials for this squarylium dye and found a hydrophobic perfluorocarbon polymer of Cytop in perfluorocarbon solvent. In addition to the stabilization of J-aggregates, the enhancement of realignment from J-blue to J-red was confirmed for this coating material as shown in Figure 6b. Almost no spectral changes were observed for the coated LB-films over a period of one week. The bare surface of a two-dimensional monolayer exposed to atmospheric humidity can easily be deformed by the adsorption of water because the surface tension of the glass surface is less than that of water. When the surface is covered with hydrophobic polymer film,

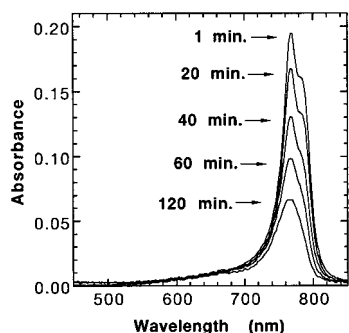


Figure 5. Temporal change in absorption spectra of an SQ33mM LB-film after deposition.

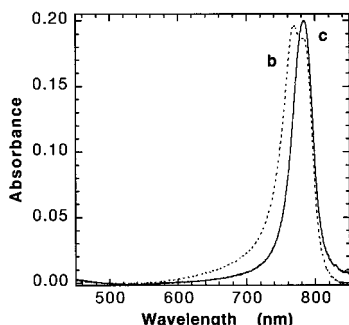


Figure 6. Absorption spectra of SQ33mM LB-films (a) with and (b) without surface coating.

the monolayer of squarylium dye is sandwiched between a hydrophobic polymer matrix and a hydrophilic glass substrate where the interfacial tension should be much higher than bare surface. Therefore, the recovery of J-red is considered to be caused by stretching force from the increase in interfacial tension. In our previous work,²³ we also have succeeded to form an LB-film containing J-aggregates form a mixed Langmuir film of squarylium dye and hydrophobic matrix of Cd-arachidate. Unfortunately, this mixing technique accompanies partial deformation of aggregation forms which resulting in broad J-band with 2–3 peaks. Our new coating technique is superior to the previous mixing technique in maintaining the aggregation structure of squarylium dye Langmuir films.

3.2. Two-Dimensional Domain Structure of SQ J-Aggregates. Before discussing the morphology of LB-films, we present images of J-aggregates formed in Langmuir films, which are believed to have ideal two-dimensional structures. In a transmission image obtained at a wavelength of 780 nm without a polarizer (Figure 7a), dark regions of J-aggregate domains spread over the entire observation area except for gaps between domains. The relatively large ratios of the sizes gaps as expected for general Langmuir films must be due to this monolayer structure just floating on a droplet of water without any mechanical compression. In the two mosaic-like images (Figure 7b,c) obtained with orthogonal polarization directions, reversal of contrast in each domain is observed: this clearly indicates that the transmittance depends on the angle between the polarization of light and the orientation of transition dipoles of the J-band. Constant darkness within each domain suggests that the molecular arrangement is uniform over a diameter of 10–20 μm . Transmission images of bare and coated LB-films obtained by NSOM are shown in Figure 8 and Figure 9, respectively, together with their surface topographies of the films. From Figure 8, it is easy to understand the process of absorbance decay observed in Figure 5. Coagulation of dye molecules into three-dimensional dot structures with a height

of about 20–30 nm increases the ratio of transparent gap areas without dye molecules in the surface, resulting in a decrease in absorbance. The three-dimensional dots are observed for dark spots in transmission image, which suggesting that the dots still consist of J-aggregates, even when their morphologies change from two-dimensional structures into three-dimensional ones. Regarding the topographies of coated LB-films, the thickness of the polymers was identified to be about 20 nm, based on the depth of uncoated voids which appeared in images of a larger area of $20 \times 20 \mu\text{m}^2$. Even this polymer coating may weaken height nonuniformity, an almost flat topography down to a level of 1 nm is observed in Figure 9a. However, the size of domains are smaller than those of the Langmuir films in Figure 6, reversal of domain contrast was observed in the two images with orthogonal polarization (Figure 9b,c). The difference in domain sizes can be attributed to the stress applied in the deposition process and reconstruction during the coating. These results suggest that the LB-films with polymer coating comprise randomly oriented two-dimensional domains of J-aggregates in which the transition dipoles of the J-band are uniformly aligned.

3.3. Femtosecond Nonlinear Optical Response of SQ J-Aggregate LB-Films. Figure 10 shows typical transient spectra of absorbance change observed by femtosecond pump–probe measurement with a pump intensity of $3 \mu\text{J}/\text{cm}^2\cdot\text{pulse}$. Dispersion-type spectra with a decrease in absorbance at a longer wavelengths and an increase at a shorter wavelength, which are characteristic of J-aggregates, appeared upon illumination by pump pulses. Temporal absorbance changes at the valley wavelength of 790 nm on the delay time of the probe pulse illumination with respect to that of the pump pulse are plotted in Figure 11. Two exponential-decay time constants of 200 fs and 14 ps with intensity ratios of 70% and 30%, respectively, fit the decay curve of the absorbance change, which suggests that this LB-film has an ultrafast optical response. Because the two time constants are similar to those observed for the Langmuir films of SQ36, relaxation processes occurring on these time scales can be attributed to the same process of stimulated (fast) and spontaneous (slow) emission.²¹ Regarding the dependence of the absorption change at 790 nm on the pump energy as shown in Figure 12, the magnitude of bleaching increases with the pump energy and saturates at approximately 0.06 when the pump energy exceeds $5 \mu\text{J}/\text{cm}^2\cdot\text{pulse}$. From this curve, the pulse energy of absorption saturation is calculated to be $3.4 \mu\text{J}/\text{cm}^2\cdot\text{pulse}$, using a twice larger value for half saturation of $1.7 \mu\text{J}/\text{cm}^2\cdot\text{pulse}$. On the basis of the Frenkel-type exciton model of J-aggregates,^{3–11} the dispersion-type absorption-change spectrum is attributed to the superposition of a negative-absorption change of the bleached linear transition from the ground states to the one-exciton states and a positive-absorption change of the induced nonlinear transition from the one-exciton states to the higher exciton states. Because the negative and positive absorption spectra overlap each other because of homogeneous bandwidths at room temperature and a small difference in peak wavelengths, the saturation value in absorbance change reaches only one-third that of linear absorbance at 790 nm (0.18). In our previous work on Langmuir films of SQ36, the bandwidth of the linear absorption (13 nm) was considered to be bleached homogeneously by pump pulses with a bandwidth of 15 nm. In the case of this LB-film, the absorption bandwidth of 35 nm is larger than that of pump pulses. Therefore, the bleaching of absorption do not occur over the entire spectrum. If the fraction of excited J-aggregates excited by the pump pulses is estimated as 15/35, the saturation energy of $3.4 \mu\text{J}/\text{cm}^2\cdot\text{pulse}$ can be reevaluated as $7.9 \mu\text{J}/\text{cm}^2\cdot\text{pulse}$. The ratio of absorbance

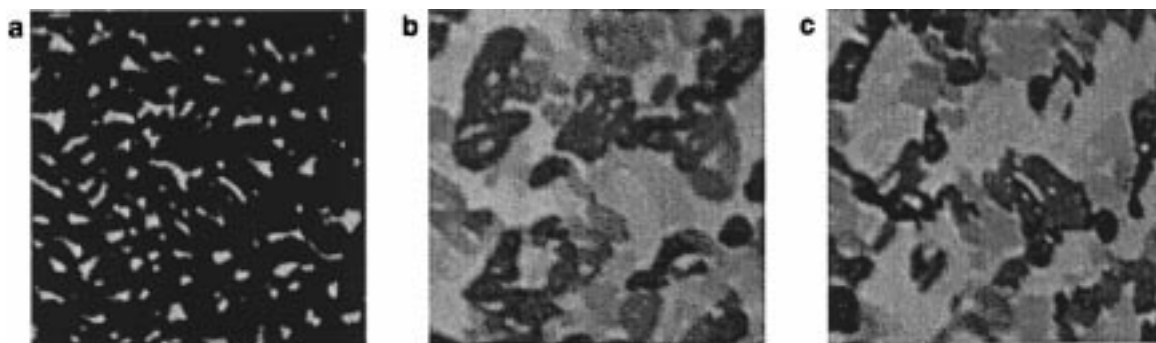


Figure 7. Transmission micrographs ($100 \times 100 \mu\text{m}^2$) of two-dimensional J-aggregates in a SQ33mM Langmuir film (a) without a polarizer and with a polarizer in (b) horizontal and (c) vertical directions.

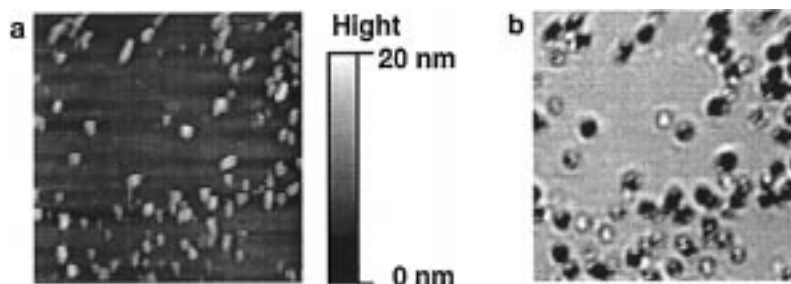


Figure 8. (a) Topography and (b) transmission NSOM images ($10 \times 10 \mu\text{m}^2$) of an SQ33mM LB-film without any coating.

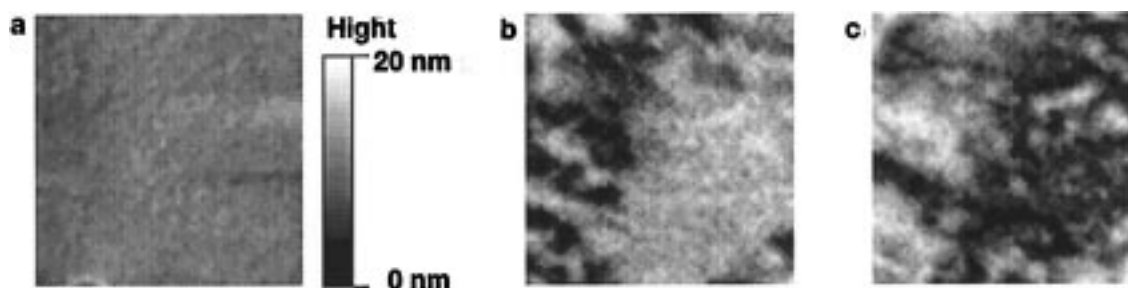


Figure 9. (a) Topography and transmission NSOM images ($8 \times 8 \mu\text{m}^2$) of an SQ33mM LB-film with polarized light in (b) vertical and (c) horizontal directions.

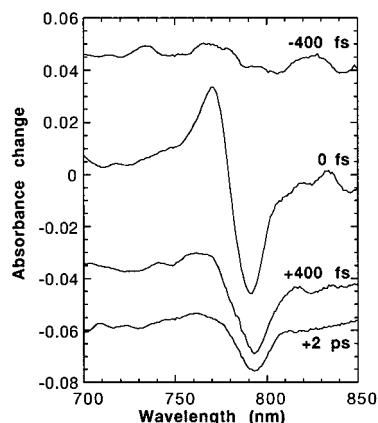


Figure 10. Transient absorption change spectra of a SQ33mM LB-film observed by the pump-probe measurement. The spectra have been shifted vertically.

calculated from the overlap of integrated pump and absorption spectra is 0.34. The number of photons concerning on excitation of the J-aggregates to saturate bleaching is $1.05 \times 10^{13} \text{ cm}^{-2}$, which corresponds to an absorption cross-section of $9.5 \text{ nm}^2/\text{photon}$. On the other hand, the area occupied by one molecule in LB-films calculated from the surface-pressure vs area isotherm of Figure 2 is $0.69 \text{ nm}^2/\text{molecule}$. Therefore, value obtained by dividing the absorption cross-section with occupied

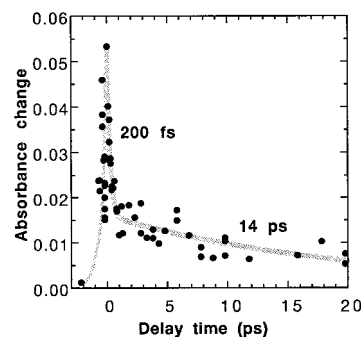


Figure 11. Temporal change of absorbance at 790 nm on the delay time of probe illumination compared to that of pump pulse. The thick grayline is the result of fitting a double-exponential curve with half-decay time constants of 200 fs and 14 ps.

area suggests that the number of coherently cooperating dye molecules in this J-aggregate film is 14. Although the degree of homogeneity of the absorption band and the domain size observed by NSOM are less than those for the Langmuir films, delocalization of excited states is indicated by the results of femtosecond pump-probe measurements. Regarding the difference in the coherent area of excitation (9.5 nm^2) and the size of single domains having identical orientation (sub- μm diameter), we argue as follows. For the J-aggregates, the size of the molecular arrangement in the identical orientation of the

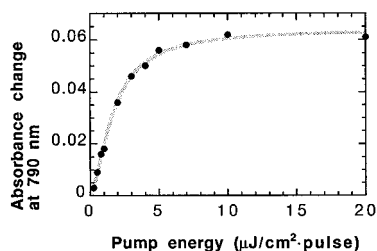


Figure 12. Dependence of absorption change (0 fs) at 790 nm on the energy of the pump pulse.

molecules means a single domain, and only a part of the single domain is excited over the coherent area by one photon. If the size of the single domain is less than that of the coherent size, the number of cooperation molecules is limited in a single domain, which should result in the blue-shift of the J-band. Compared to J-aggregates of SQ36 in Langmuir films, where the number of cooperation molecules was over 30,¹⁹ that of the LB-films with the SQ33mM is almost one-half. There are two different characteristics in J-aggregates of SQ33mM and SQ36 even in their Langmuir films. The absorbance of SQ33mM J-band is approximately one-half of that of SQ36 which is also reflected in the bandwidth. The occupied area of one SQ33mM molecule (0.69 nm²/molecule) is smaller than that of SQ36 in Lagmuir film (0.85 nm²/molecule) which means the more condensed structure of the J-aggregates with the SQ33mM. These differences clearly suggest molecular arrangement determined by stacking angles and by distances between molecules, which determine the number of cooperation molecules. Even the number of cooperation molecules is smaller; the important point of this work is the success in forming stable solid films of two-dimensional J-aggregates using the SQ33mM where it cannot be achieved using the SQ36.

4. Concluding Remarks

Squarylium dye J-aggregates have been transferred successfully from a monolayer at an air–water interface to a layer on a solid substrate by using the Langmuir–Blodgett technique and maintaining the two-dimensional structure of the J-aggregates. Coating the surface of an LB-film with hydrophobic polymer has been shown to be effective not only in stabilizing the morphology but also in enhancing the interfacial tension, resulting in realignment of the molecules, which form J-aggregates in two-dimensional structures almost in the same way as Langmuir films. These effects of the surface coating have been also confirmed in observations by NSOM. Almost full coverage of domains of monolayer J-aggregates has been confirmed from a pair of transmission images obtained with orthogonal polarization directions. By femtosecond pump–probe measurement, fast decay of absorption saturation and low saturation energy has been observed. Such excellent nonlinear optical properties at room temperature are superior to those of other organic materials, such as phthalocyanines²⁴ and polydiacetylene,²⁵ and are comparable to those of inorganic semicon-

ductors operating in the femtosecond time scale.²⁶ A successful observation of a large nonlinear optical response with only monolayer coverage of dye molecules at room temperature is due to highly oriented two-dimensional structure of the aggregates. This demonstration of the fabrication and characterization of stable, solid-substrate-fixed, two-dimensional monolayers exhibiting ultrafast, large optical nonlinearity is expected to open the way to the construction of planar all-optical switching devices.

Acknowledgment. This work was supported by the New Energy and Industrial Technology Development Organization within the framework of the Femtosecond Technology Project. We thank Dr. Shyunsuke Kobayashi, Fumio Sasaki, and Tsuyoshi Kato of the Electrotechnical Laboratory and Taro Nambu and other members of the FESTA Laboratories for stimulating and fruitful discussions.

References and Notes

- (1) Jelly, E. E. *Nature* **1936**, *138*, 1009.
- (2) Scheibe, G. *Angew. Chem.* **1936**, *49*, 563.
- (3) Fidler, H.; Knoester, J.; Wiersma, D. A. *Chem. Phys. Lett.* **1990**, *171*, 529.
- (4) Knoester, J. *J. Chem. Phys.* **1993**, *99*, 8466.
- (5) Durrant, J. R.; Knoester, J.; Wiersma, D. A. *Chem. Phys. Lett.* **1994**, *222*, 450.
- (6) Spano, F. C.; Mukamel, S. *J. Chem. Phys.* **1991**, *95*, 7526.
- (7) Kopainsky, B.; Kaiser, W. *Chem. Phys. Lett.* **1982**, *88*, 357.
- (8) Kobayashi, S.; Sasaki, F. *Nonlinear Opt.* **1993**, *4*, 305.
- (9) Kobayashi, S.; Sasaki, F. *J. Lumin.* **1994**, *58*, 113.
- (10) Minoshima, K.; Taiji, M.; Misawa, K.; Kobayashi, T. *Chem. Phys. Lett.* **1994**, *218*, 67.
- (11) Minoshima, K.; Taiji, M.; Ueki, A.; Miyano, K.; Kobayashi, T. *Nonlinear Opt.* **1995**, *14*, 39.
- (12) Betzig, E.; Trautman, J. K.; Harris, T. D.; Weiner, J. S.; Kostelak, R. L. *Science* **1991**, *251*, 1468.
- (13) Higgins, D. A.; Barbara, P. F. *J. Phys. Chem.* **1995**, *99*, 3.
- (14) Kuhn, H.; Möbius, D.; Bucher, H. In *Physical Methods of Chemistry*; Weissbreger, A., Rossiter, B. W., Eds.; Wiley: New York, 1972; Vol. 1, Part III-B, p 577.
- (15) Nakahara, H.; Fukuda, K.; Möbius, D.; Kuhn, H. *J. Phys. Chem.* **1986**, *90*, 6144.
- (16) Nakahara, H.; Uchii, H.; Fukuda, K.; Tamai, N.; Yamazaki, I. *Mol. Cryst. Liq. Cryst.* **1990**, *183*, 345.
- (17) Nabetani, A.; Tomioka, A.; Tamaru, T.; Miyano, K. *J. Chem. Phys.* **1995**, *102*, 5109.
- (18) Furuki, M.; Kim, S.; Pu, L. S.; Nakahara, H.; Fukuda, K. *J. Chem. Soc. Jpn. Chem. Ind. Chem.* **1990**, *10*, 1121.
- (19) Furuki, M.; Pu, L. S.; Sasaki, F.; Kobayashi, S.; Tani, T. *Mater. Res. Soc. Symp. Proc.* **1998**, *488*, 777.
- (20) Furuki, M.; Pu, L. S.; Sasaki, F.; Kobayashi, S.; Tani, T. *Appl. Phys. Lett.* **1998**, *21*, 2648.
- (21) Furuki, M.; Pu, L. S.; Sasaki, F.; Kobayashi, S.; Tani, T. *Mol. Cryst. Liq. Cryst.* **1998**, *316*, 67.
- (22) Sprenger, H. E.; Ziegenbein, W. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 894.
- (23) Kim, S.; Furuki, M.; Pu, L. S.; Nakahara, H.; Fukuda, K. *Thin Solid Films* **1988**, *159*, 337.
- (24) Tokunaga, E.; Terasaki, A.; Valencia, V. S.; Wada, T.; Sasabe, H.; Kobayashi, T. *Appl. Phys. B* **1996**, *63*, 255.
- (25) Bolger, J.; Harvey, T. G.; Ji, W.; Kar, A. K.; Molyneux, S.; Wherrett, B. S.; Bloor, D.; Norman, P.; *J. Opt. Soc. Am. B* **1992**, *9*, 1552.
- (26) Kobayashi, H.; Takahashi, R.; Matsuoka, Y.; Iwamura, H. *Electron. Lett.* **1998**, *9*, 908.