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Thermal Hysteresis in the Photoresponsivity of a Langmuir Film of Amphiphilic Spiropyran

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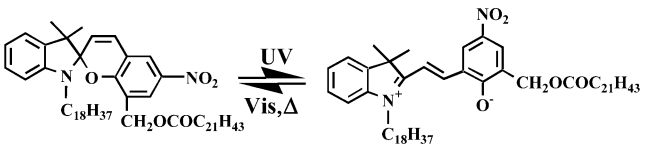
Hysteresis has been found in various phenomena such as magnetic properties of various materials,[1] chromatic properties of crystals,[2] contact angles of solid surfaces,[3] and adsorption isotherms.[4] Hysteresis related with bistability and phase transition has attracted much attention from the viewpoint of applications to switching and memory devices.

Phase transitions are reported for Langmuir and Langmuir−Blodgett (LB) films.[5] Only a few reports have connected thermal phase transitions with the functions of the films. The electrical conductivity of the LB film of a charge-transfer complex varies with the phases that appear at different temperatures.[6] The permeation of ions through LB films can be controlled using the thermal phase transition of the films.[7] However, hysteretic behaviors have not been reported.

J-aggregates of organic dyes have attracted considerable interest as materials for spectral sensitization, optical storage, and ultrafast optical switching.[8] We have been studying the light-induced and light-triggered J-aggregation in Langmuir and LB films.[9] Photoreaction of the Langmuir film of an amphiphilic spiropyran, 1′,3′-dihydro-3′,3′-dimethyl-6-nitro-1′-octadecyl-8-(docosanoyloxymethyl)-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SP) depends on the phase of the Langmuir film under isothermal conditions.[9f] In this paper we examine the changes in the structure and photoresponsivity of the Langmuir film of SP under isobaric conditions (at constant surface pressures). The Langmuir film of SP shows a thermal hysteresis in the photoresponsivity, whereas the structural change of the film is not detected using Brewster angle microscopy (BAM). This behavior should be related with the phase transition that occurs in the bulk of SP, and not with the phase transition between the phases of the Langmuir film of SP observed under isothermal conditions.



We examined the structural change of the Langmuir film of SP. SP showed an onset of surface pressure at an area per molecule of ca. 0.4 nm^2 at 13 °C, followed by a steep rise, characteristic of a condensed phase. BAM of the Langmuir film of SP revealed the formation of a continuous multilayer film at 10 mN m^{-1}. The morphology of the film did not change significantly on heating to 30 °C. On the other hand, the Langmuir film fabricated by spreading and compression at 30 °C consisted of multilayer domains embedded in a monolayer. These results show that the structure of the Langmuir film of SP depends strongly on the fabrication process, suggesting that the film shows hysteretic behaviors.

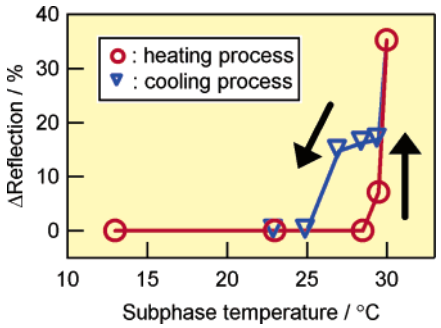


Figure 1. Increase in reflection of the Langmuir film at ca. 618 nm due to the light-induced J-aggregation as a function of subphase temperature.

We investigated the change in photoresponsivity of the Langmuir film of SP on varying the temperature after the fabrication of the film. SP was spread at 13 °C and compressed to 10 mN m^{-1}. The temperature of the film was then raised to a given temperature, or raised to 30 °C followed by cooling to a given temperature. The reflection spectrum of the heat-treated Langmuir film was measured after UV irradiation. The results are summarized in Figure 1. The ordinate is an increase in reflectivity of the film at ca. 618 nm due to the light-induced J-aggregation, which is a measure of the amount of J-aggregate formed in the film. In the heating process, only the photoisomerization of SP to merocyanine (MC) occurs in the temperature region from 13 to 29 °C. Light-induced J-aggregation proceeds when the temperature is raised to 30 °C. On the other hand, in the cooling process after the heating to 30 °C, light-induced J-aggregation proceeds down to 27 °C. J-aggregation is hindered when the film is cooled to 25 °C. A hysteresis is evident in the photoresponsivity of the Langmuir film. Similar hysteretic behaviors were observed when the temperature range was from 13 to 40 °C. To the best of our knowledge, this is the first report of a thermal hysteresis of the photoresponsivity of a Langmuir film. This type of hysteresis should be related with a certain phase transition in the Langmuir film.

To explore the details on the phase transition, differential scanning calorimetric (DSC) studies of SP have been conducted. The DSC thermogram of the heating process exhibits an endothermic peak at 28.4 °C (ΔH = 56.6 kJ mol^{-1}) due to the transition

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from crystal to isotropic liquid in the second and succeeding cycles. On the other hand, in the cooling process, exothermic peaks at 24.8 °C (ΔH = 45.8 kJ mol^{-1}) and 10.4 °C (ΔH = 1.9 kJ mol^{-1}) have been observed. These peaks could be attributed to phase transition from isotropic liquid to a mesophase and to a crystal, respectively. X-ray diffraction analysis of SP revealed the formation of higher order smectic liquid crystal with peaks at 3.186 and 0.409 nm. Details of the mesophase observed in the present case are under investigation.

The above results indicate that the phase transition temperatures of the bulk of SP resemble the temperature range of the hysteresis of photoresponsivity of the Langmuir film. This strongly suggests that the two phenomena are closely related with each other. We suggest that the phase transitions occur in the Langmuir film of SP at temperatures similar to those in the bulk. This is supported by the existence of phase transitions of the LB films in temperature ranges similar to those of the bulk.[5c,7] The hysteretic behavior shows that J-aggregation proceeds when SP is melted. This is because the photogenerated MC can undergo orientational change and/or diffusion necessary for the J-aggregation. On the other hand, the close packing in crystals and in highly ordered smectic structures prevents MC from forming J-aggregates due to the difficulties of such orientational change and/or molecular diffusion.

We used BAM to investigate the structural change accompanied by the J-aggregation. UV irradiation of the Langmuir film fabricated by spreading and compression at 13 °C and heating to 30 °C increased the reflectivity of the whole part of the film without any significant morphological changes.[10] The AFM image of the LB film fabricated from the above Langmuir film before irradiation shows that the LB film is a continuous multilayer with some defects. The AFM image did not show any significant morphological changes accompanied by J-aggregation. These results are completely different from the large morphological changes observed in light-induced or light-triggered J-aggregation in Langmuir and LB films of SP, where dendritic structures are formed around nucleation sites through the diffusion of molecules on the order of micrometers or several tens of micrometers.[9c−f] Large morphological changes also accompany light-triggered J-aggregation of other dyes.[9a,b] According to the literature, UV irradiation of a six-layer mixed LB film of SP/octadecane (1:2) at room temperature induces only the isomerization of SP to MC, whereas irradiation at 35 °C promotes the J-aggregation of MC.[11] Using AFM, we found no significant morphological changes accompanied by J-aggregation in the multilayer mixed LB film. This strongly suggests that the J-aggregation reported in the literature[11] occurs in a manner similar to that in the present study, compared with the J-aggregation in the LB films of SP fabricated under isothermal conditions at 30 °C, where large morphological changes occur.

The fact that no significant morphological changes occur during the J-aggregation in the present LB film suggests that this film is appropriate for pattern transfer. Figure 2 shows the polarizing micrograph of a single-layer LB film of SP after UV irradiation at room temperature through a photomask. The LB film is patterned with lines of J-aggregates (bright regions). The spatial resolution became worse for the LB films with larger layer numbers. When the LB film was fabricated under isothermal conditions at 30 °C, the spatial resolution was much worse because J-aggregates were formed around the nucleation sites through diffusion of molecules.

In conclusion, we have found hysteretic behaviors in the photoresponsivity of a Langmuir film for the first time. The hysteresis should be related with the phase transitions that occur in the Langmuir film. This indicates that hysteretic behaviors in various functions will be realized in Langmuir and LB films by appropriate selection of molecules and optimization of experimental conditions. Further, the LB films can be patterned with J-aggregates using a photomask. Patterning materials with J-aggregates will become important in the fabrication of optical switching and memory devices in the future.

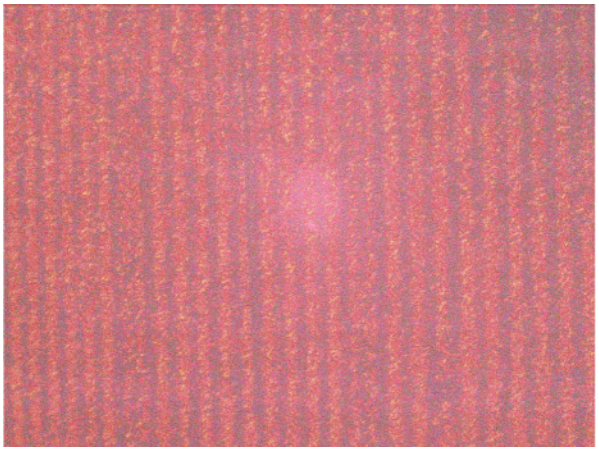

Figure 2. Polarizing micrograph of a single-layer LB film of SP after UV irradiation through a photomask of lines with a width of 5 μm each.

Supporting Information Available: Surface pressure−area isotherms, DSC, X-ray diffraction pattern, and BAM images. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Fujita, W.; Awaga, K. *Science* **1999**, *286*, 261. (b) Shultz, D. A.; Fico, R. M., Jr.; Boyle, P. D.; Kampf, J. W. *J. Am. Chem. Soc.* **2001**, *123*, 10403. (c) Hayami, S.; Gu, Z.-z.; Yoshiki, H.; Fujishima, A.; Sato, O. *J. Am. Chem. Soc.* **2001**, *123*, 11644. (d) Ohkoshi, S.; Hashimoto, K. *J. Photochem. Photobiol. C: Photochem. Rev.* **2001**, *2*, 71. (e) Soler, M.; Wernsdorfer, Abboud, K. A.; Huffman, J. C.; Davidson, E. R.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **2003**, *125*, 3576.

(2) Koshihara, S.; Tokura, Y.; Takeda, K.; Koda, T. *Phys. Rev. Lett.* **1992**, *68*, 1148.

(3) Israelachvili, J. N. *Intermolecular and Surface Forces*, 2nd ed.; Academic: London, 1991; Chapter 15.

(4) (a) Lopez, R. H.; Vidales, A. M.; Zgrablich, G. *Langmuir* **2000**, *16*, 6999. (b) Kikkinides, E. S.; Kainourglakis, M. E.; Stubos, A. K. *Langmuir* **2003**, *19*, 3338−3344.

(5) (a) Gains, G. L. *Insoluble Monolayers at Liquid−Gas Interfaces*; Intersciences Publishers: New York, 1966. (b) Bell, G. M.; Combs, L. L.; Dunne, L. J. *Chem. Rev.* **1981**, *81*, 15. (c) Naselli, C.; Rabolt, J. F.; Swalen, J. D. *J. Chem. Phys.* **1985**, *82*, 2136. (d) Ulman, A. *An Introduction to Ultrathin Organic Films*; Academic Press: New York: 1991; p 133. (e) Kajiyama, T.; Oishi Y. In *New Developments in Construction and Functions of Organic Thin Films*; Kajiyama, T., Aizawa, M., Eds.; Elsevier: Amsterdam, 1996; p 1. (f) Sakai, H.; Umemura, J. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1027.

(6) Nakamura, T.; Tanaka, M.; Sekiguchi, T.; Kawabata, Y. *J. Am. Chem. Soc.* **1986**, *108*, 1302.

(7) Ariga, K.; Okahata, Y. *J. Am. Chem. Soc.* **1989**, *111*, 5618.

(8) *J-aggregates*; Kobayashi, T., Ed.; World Scientific: Singapore, 1996.

(9) (a) Matsumoto, M.; Tachibana, H.; Sato, F.; Terrettaz, S. *J. Phys. Chem. B* **1997**, *101*, 702−704. (b) Matsumoto, M.; Sato, F.; Tachibana, H.; Terrettaz, S.; Azumi, R.; Nakamura, T.; Sakai, H.; Abe, M. *Mol. Cryst. Liq. Cryst.* **1998**, 316, 113−118. (c) Terrettaz, S.; Tachibana, H.; Matsumoto, M. *Langmuir* **1998**, *14*, 7511−7518. (d) Tachibana, H.; Yamanaka, Y.; Matsumoto, M. *J. Phys. Chem. B* **2001**, *105*, 10282. (e) Tachibana, H.; Yamanaka, Y.; Matsumoto, M. *J. Mater. Chem.* **2002**, *12*, 938. (f) Matsumoto, M.; Nakazawa, T.; Azumi, R.; Tachibana, H.; Yamanaka, Y.; Sakai, H.; Abe, M. *J. Phys. Chem. B* **2002**, *106*, 11487.

(10) On the basis of the BAM observations, the reflectivity of the Langmuir film at the wavelength (632.8 nm) of the He−Ne laser used for our BAM increases in the order SP, MC, and J-aggregate of MC.

(11) Ando, E.; Miyazaki, J.; Morimoto, K. *Thin Solid Films* **1985**, *133*, 21.

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