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# Aggregate Formation of Pyrene-1-Carboxylic Acid in an Ion-complexed Langmuir-Blodgett Film Induced by Contact with HCl Gas

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Ion-complexation between a cationic amphiphile and pyrene-1-carboxylate ($PyCOO^-$) dispersed the $PyCOO^-$ anions homogeneously in a Langmuir-Blodgett monolayer film. By bringing the film into contact with HCl gas, formation of fluorescent spots in the monolayer was observed by fluorescence microscopy. With an atomic force microscope, the spots were found to be topographically much higher than the monolayer level, and concluded to be aggregates formed by lateral diffusion of neutralized pyrene-1-carboxylic acid (PyCOOH) molecules in the monolayer.

Some cationic amphiphiles with an ammonium head group formed homogeneous ion-complexed Langmuir-Blodgett (LB) films with an anionic polymer[1)] or an anionic amphiphile[2)] added in a subphase. In a previous paper,[3)] we studied photoinduced proton transfer in an ion-complexed LB film between protonated 2-heptadecylimidazol cations and 2-naphthoate anions by fluorescence and IR absorption spectroscopies. Effects of acid vapor treatments on the properties of LB films of divalent metal salts of fatty acids were studied by X-ray diffraction[4-6)] and IR absorption spectroscopy.[5,6)]

In this work, we studied the structural changes of an ion-complexed LB monolayer between amphiphilic cations and pyrene-1-carboxylate ($PyCOO^-$) anions before and after an HCl gas treatment with UV-visible and fluorescence spectroscopies and fluorescence and atomic force microscopies.

Octadecylamine (OA) was purchased from Tokyo Kasei Co. Ltd., and purified by recrystallization. PyCOOH was synthesized from commercially available 1-pyrenecarbaldehyde by oxidation with silver oxide in a similar manner for the other aldehyde.[7)] Pure water from a Milli-Q system (Millipore Ltd.) was used for preparation of an aqueous subphase.

The ion-complexed monolayer was formed by spreading OA and compressed on an aqueous subphase containing $1 \times 10^{-6}$ mol $dm^{-3}$ $PyCOO^-$ (pH 6) at 10 °C. The monolayer on the subphase was simultaneously transferred onto three types of hydrophilic surfaces, i.e. a quartz, a silicone (Si(100)), and a cover glass plate. The cover glass and the silicone plate were used for fluorescence and atomic force microscopy, respectively. The quartz plate was used for absorption and fluorescence spectroscopy. During the transfer, the surface pressure of the monolayer was controlled at 25 mN $m^{-1}$. The lifting speed of the substrates was 2.5 mm $min^{-1}$

A Seiko SPA-300 AFM with a SPI-3700 probe station was used to observe the LB films. A triangular cantilever with a $Si_3N_4$ pyramidal tip (Olympus) was used. The HCl gas treatment was performed by dry HCl gas.

UV-visible absorption and fluorescence spectra of the monolayer on a quartz plate before and after the HCl gas treatment are shown in Fig. 1. In the absorption spectrum of the monolayer before the gas treatment, a relative peak height of a band at 284 nm against that at 350 nm is fairly high in comparison with the absorption spectrum of PyCOO$^-$ in an ethanol solution as shown in Fig. 2 (solid line). The peaks at 284 and 350 nm can be assigned to $^1B_b$ and $^1L_a$,[8,9] respectively. The difference between these absorption spectra can be attributed to high orientation of the pyrene moieties of PyCOO$^-$ anions in the monolayer. Because the incident angle of a light beam to measure the absorption spectrum was 0°, the $^1L_a$ band shows smaller absorbance than the $^1B_b$ band, if the long axes of the pyrene moieties are oriented perpendicularly to the surface.

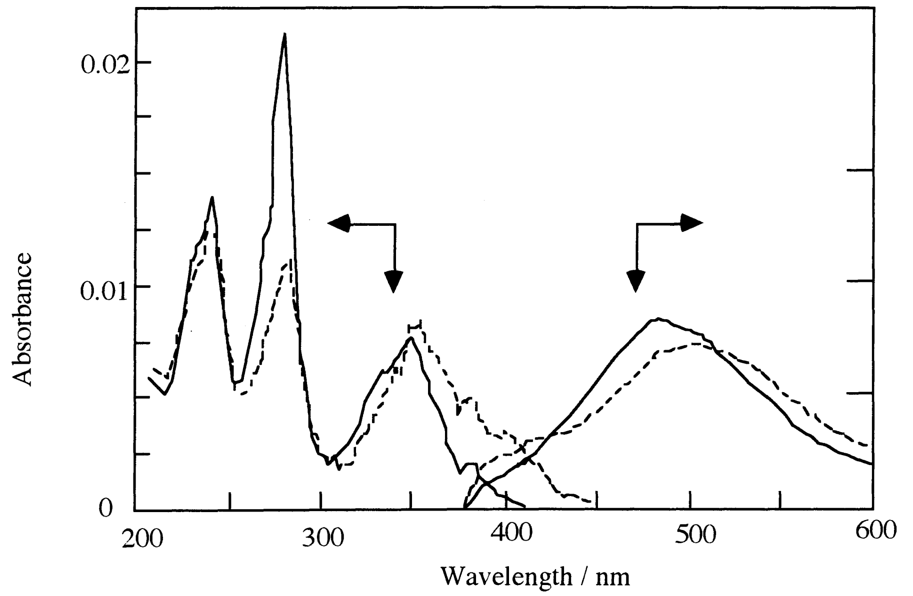

Fig. 1. Absorption and fluorescence spectra of the ion-complexed monolayer before ( —— ) and after (------) the HCl gas treatment.

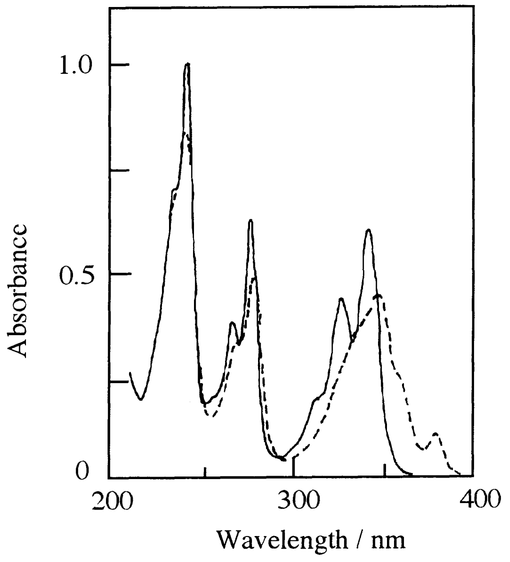

Fig. 2. Absorption spectra of PyCOO$^-$(——) and PyCOOH ( ------ ) in ethanol solutions. ($2 \times 10^{-6}$ mol dm$^{-3}$)

In the absorption spectrum of the gas treated monolayer (Fig. 1 (dotted line)), a relative peak height of a band at 284 nm against that at 350 nm decreased compared with that of the untreated monolayer (Fig. 1 (solid line)). The relative peak height between the two bands was similar to the spectrum of PyCOOH in an ethanol solution (Fig. 2 (dotted line)). This result suggests that the orientation of PyCOOH molecules formed by the HCl gas treatment was so perfectly randomized in the monolayer as that in the solution.

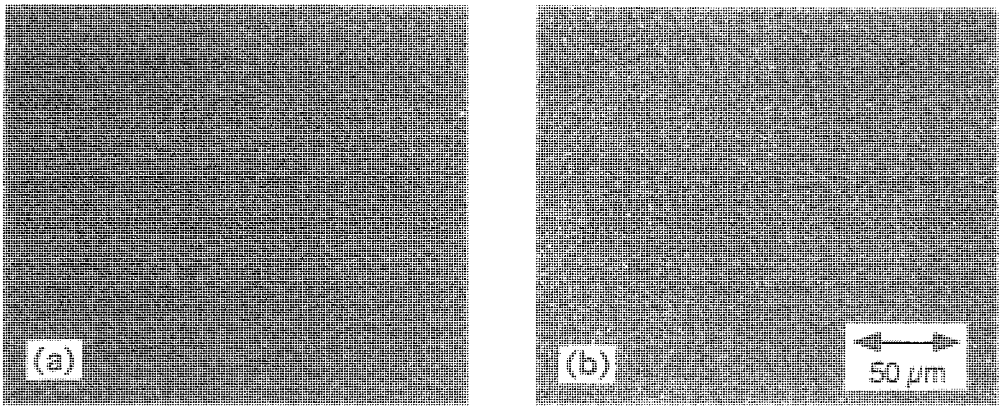

Fig. 3. Fluorescence micrographs of the monolayer before (a) and after (b) the HCl gas treatment.

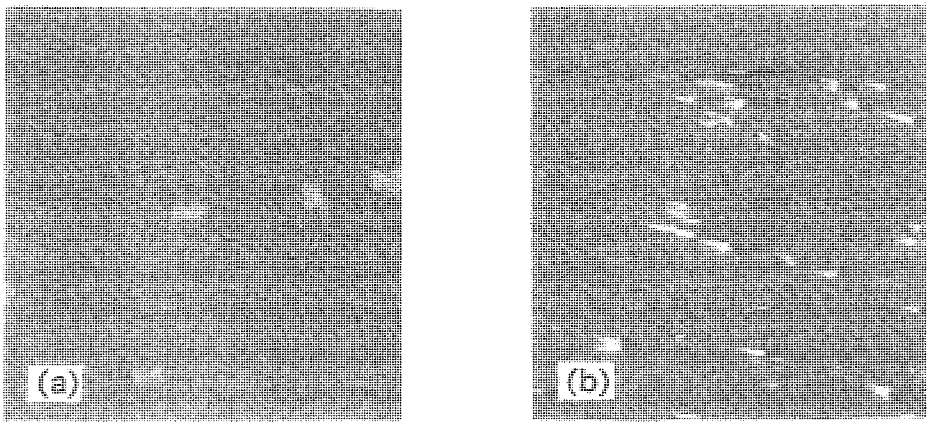

Fig. 4. AFM topographic images (15 x 15 $\mu m^2$) of the monolayer before (a) and after (b) the HCl gas treatment.

Figures 3a and 3b show fluorescence micrographs of the monolayer before and after the gas treatment, respectively. The monolayer before the HCl gas treatment fluoresces homogeneously, while many small fluorescent spots are observed in the gas-treated monolayer.

Figures 4a and 4b show 15 x 15 $\mu m^2$ AFM topographic images before and after the gas treatment, respectively. In the AFM image of the monolayer before the gas treatment, some higher parts (brighter parts) of ca. 1 μm in size were observed in a flat plane. Since heights of the higher parts from the flat plane of the monolayer were about 3-4 nm as shown in Fig. 5a, the higher parts can be assigned to collapsed bilayers on the monolayer. In the fluorescence micrograph of the corresponding monolayer (Fig. 3a), brighter spots corresponding to the higher parts are not clearly observed. As described later, the higher parts were obviously different in height from fluorescent aggregates of PyCOOH which were observed after the HCl gas treatment.

After the HCl gas treatment on the monolayer, a large number of much higher spots were observed in its AFM image. The heights of bright spots in the AFM image are larger than 10 nm as shown in Fig. 5b. In comparison with the fluorescence micrograph of the gas-treated monolayer, it can be concluded that the higher spots in the AFM images correspond to the fluorescent spots in the fluorescence micrographs.

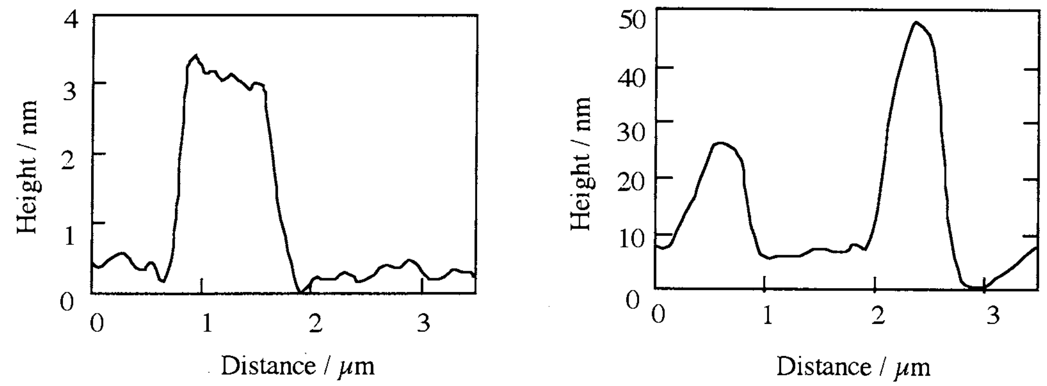

Fig. 5. Cross sections of the AFM topographic images of the monolayer before (a) and after (b) the HCl gas treatment.

In conclusion, it was confirmed from the present AFM observation together with the spectroscopic results that i) PyCOO$^-$ anions in the monolayer were neutralized by HCl gas, ii) the resulting PyCOOH molecules could diffuse more freely than the ion-complexed PyCOO$^-$ anions in the monolayer to form the aggregates, iii) the aggregated molecules oriented randomly in the monolayer, and iv) the higher density of PyCOOH in the aggregates gave images of the bright spots in the corresponding fluorescence micrograph.

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