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Formation of Porphyrin Domain Arrays at the Air-Water Interface

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Mixed monolayers of 5-(4-N-decylpyridinium)-10,15,20-tri-p-tolyl porphyrin (PyP) and arachidic acid were prepared, and their film textures were studied by fluorescence microscopy. PyP forms domain arrays by compression and expansion of the monolayer on pure water at neutral pH and at temperatures>24 ℃

The research activity on lateral textures in spread monolayer systems have been greatly enhanced by the introduction of fluorescence microscopic techniques,1-3) since they allowed a direct observation of micron-order structures at the air-water interface. Much attention has been predominantly paid so far to insulating lipid monolayers with their crystal-growth and phase-transition behaviors,4) except for a few studies on some cyanine monolayers.5,6) However, it is of practical importance to investigate two-dimensional structures of spread monolayers containing functional molecules since they may find promising applications in molecular electronic devices. Recently, we have found that domain structures in a porphyrin monolayer can be incorporated into micron-order photodiode arrays.7) In this letter, we describe the subphase conditions under which array-like patterns are successfully formed in the porphyrin monolayer.

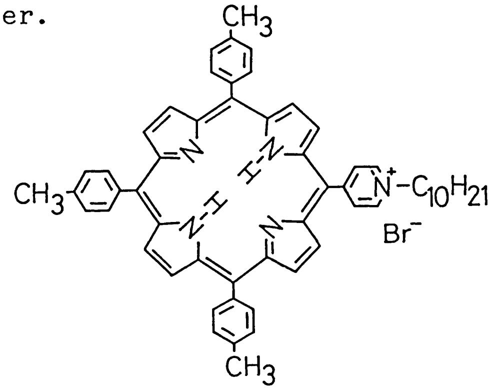

Fig. 1. Chemical structure of the porphyrin (PyP).

Figure 1 shows the structure of the functional material used, 5-(4-N-decylpyridinium)-10,15,20-tri-p-tolyl porphyrin (PyP). Mixtures of this compound and arachidic acid (AA) with a molar ratio of 1:10 were dissolved in chloroform and spread onto a water surface to form mixed monolayers. Lateral textures of the mixed monolayers were observed using a fluorescence microscope(Olympus BHMS) with the help of a SIT TV camera under various subphase conditions. The subphase pH was adjusted by the addition of HCl, KOH, and $KHCO_3$.

Figure 2 shows the pressure-area (π-A) isotherm of a mixed monolayer at various pH (23 ℃). The curve has a well-defined plateau below 40 mN m^{-1}. The appearance of a plateau was found for mixed monolayers containing a similar kind of pyridinium porphyrin by Nagamura et al., which was attributed to a pressure-induced squeezing-out of the porphyrin.[8] Therefore the PyP molecules are safely considered to be repelled out of the mixed monolayer at the plateau in the present case. The onset pressure of the plateau (π_p) is lower than the collapse pressure of pure PyP monolayer (about 40 mN m^{-1}) and depends greatly on the pH, indicating that an interaction between PyP and AA plays an essential role in the squeezing-out.

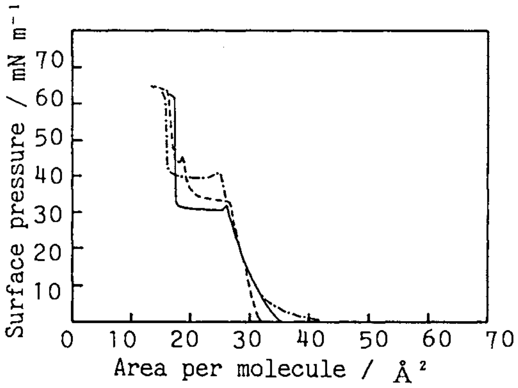

Fig. 2. π-A isotherms of a mixed monolayer at pH 2.8(--); at pH 7 (—); at pH 11(-·-).

The monolayer absorption exhibits a significant change with compression. When the pH is above 3, the Soret band has a red-shifted peak at 430 nm below π_p compared with the corresponding band in chloroform solution (420 nm) due to an interaction between PyP and negatively-charged AA, while the monolayer has a monomeric absorption maximum at 415 nm below π_p at a lower pH (<3). On compression of the film above π_p, the Soret peak increases in intensity and shifted to about 440 nm irrespective of pH. This spectral change can also be explained by molecular squeezing-out:the PyP molecules are squeezed out onto the monolayer to form a porphyrin aggregate with an absorption peak at 440 nm.

The development of PyP domains by surface pressure control is clearly seen in Fig. 3, where the fluorescence micrographs of an expanded mixed monolayer on pure water (pH 7, 30 ℃) are depicted. In an as-spread state, AA tends to form solid circular domains with dimensions<10 μm which appear dark in the micrograph (Fig. 3a). The formation of AA domains is observed at any solution concentration studied (10^{-4} mol dm^{-3} to 10^{-2} mol dm^{-3}). These domains repel one another due to electrostatic forces arising from a difference in charge density between the AA crystallites and the surrounding PyP-dominated region. Increasing the pressure above π_p, new dark spots start to appear one after another in the PyP-dominated region, and at sufficiently high pressures (about 40 mN m^{-1}) they cover the entire monolayer, makig it practically impossible to observe clear fluorescence images. These new domains are attributable to the porphyrin aggregate produced by molecular squeezing-out.

On re-expansion of the film into an expanded state, the new domains disappear due to a destruction of the porphyrin aggregate, and the PyP-dominated region restores its fluorescence. However, the film texture differs greatly from the original one as shown in Fig. 3b:the PyP-dominated areas are surrounded by AA crystallites to form an array-like distribution of nearly circular domains. This structure remains fairly stable by repeated compression and expansion of the film, except for a slight increase in the domain size. The formation of the surrounding AA crystallites can be ascribed to compression-induced merging of the initial small AA domains, which is facilitated by the squeezing-out of PyP.

The formation of PyP domain arrays by compression and expansion is only observed under specific conditions. When the temperature is reduced

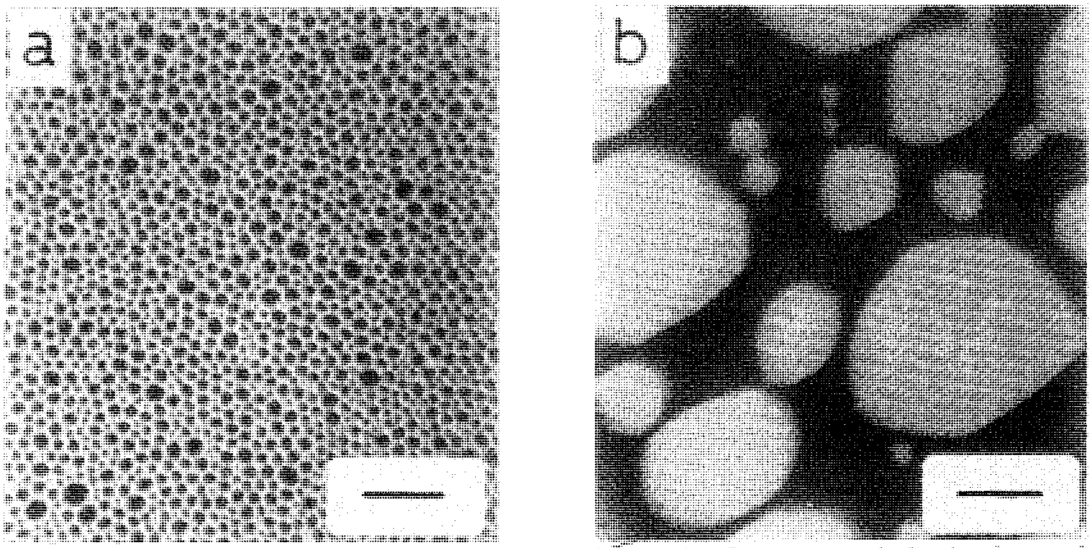

Fig.3. Fluorescence micrographs (scale bar, 20 μm) of an expanded mixed monolayer in an as-spread state (a) and after compression and expansion (b).

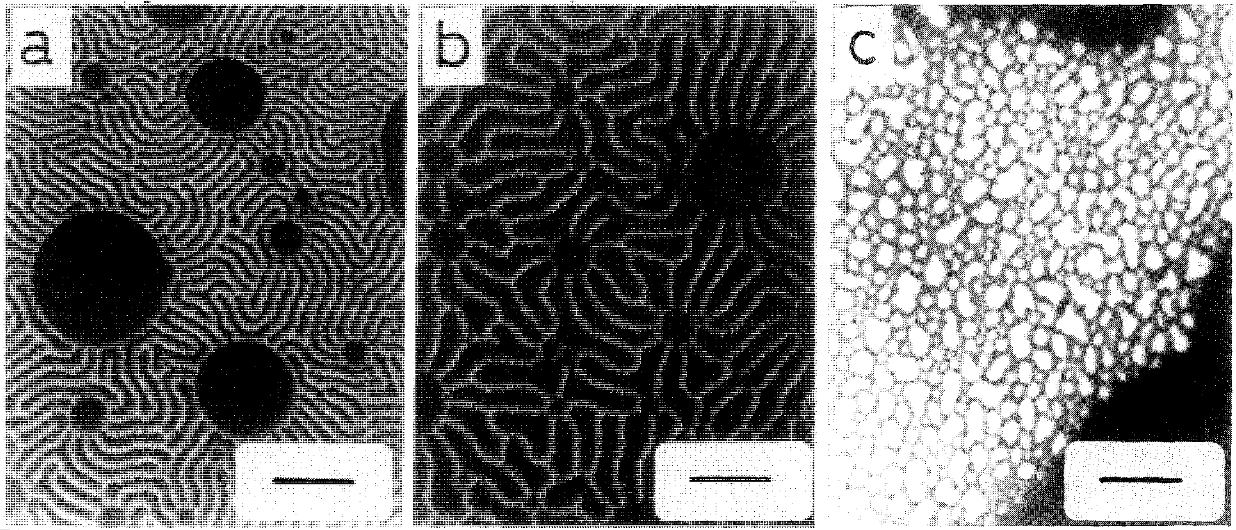

Fig.4. Fluorescence micrographs (scale bar, 20 μm) of an expanded mixed monolayer formed at pH 3.5 immediately after compression and expansion (a) and after aging for 1 minute (b), and formed at pH 2 (c).

to 20-23 ℃, the PyP domains have taints of AA spots left inside, which are impossible to remove by mere repetition of compression and expansion. At still lower temperatures (<20 ℃) the distribution of AA spots formed immediately after spreading is so stable that even the procedure of compression and expansion does not alter the original texture of Fig. 3a. Increasing the pH causes a strong interaction between PyP and AA, and it is hard to see if separate phases exist in fluorescence images. On the other hand, various types of microstructures are clearly observed on reducing the pH (Fig. 4). At a rather narrow pH window (3.5-4) network structures with thin elongated PyP domains are found to develop (Fig. 4a and 4b). At a lower pH (<3) small patches of PyP domains are formed, but they do not repel one another enough to be isolated by AA crystallites (Fig. 4c).

These features may be consistently interpreted in terms of an interplay between electrostaic forces due to excess charges or dipole moments of film-forming molecules and line tensions exerted on the boundary lines of contacting phases,[9,10] both of which drastically depend on subphase pH and temperature. We are therefore presently studying the film textures in more detail by changing environmental conditions with the hope of theoretically describing such behaviors.

In summary, we have obtained porphyrin domain arrays at neutral pH and at temperatures>24 ℃. This structure may be useful for organized microelectronic devices such as photodiode arrays.

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