Novel Domain Structures in the Mixed Monolayer Films Identified by Atomic Force Microscopy

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Phase separation was observed by atomic force microscopy in the mixed monolayer films composed of arachidic acid (AA) and 5,10,15-triphenyl-20-(4-dl-α-phenylalanylamindo)phenyl porphyrin (TPPP). Under different preparation conditions, the mixtures exhibit only AA domains or a coexistence structure of AA domains, TPPP domains and downy structures constructed by AA and TPPP together. Different UV-Vis spectra were obtained in the two kinds of phase-separated structures.

Understanding the structures and properties of mixed monolayers as well as their transferred films is not only of fundamental interest but also find its application in the areas of electronics, nonlinear optics, and biosensors.[1-4] Recently, several research groups reported some interesting structures in binary mixed monolayer films by use of atomic force microscopy (AFM).[5-6] In their selected systems, domains of material A distributed separately in the monomolecular monolayer formed by material B. However, to our knowledge, no one has reported on such a structure that both material A and B can form their own domain structures in the mixed monolayer films. In this letter, we will report the microscopic structures and the macroscopic properties of a new mixed monolayer film composed of arachidic acid(AA) and 5,10,15-triphenyl-20-(4-dl-α- phenylalanylamindo)phenyl porphyrin (TPPP). In this particular study, the one- and two-domain structure mentioned above could be chosen to appear in the mixture by adopting suitable conditions during film preparation.

AA(analytical grade) and TPPP(synthesized in one of our laboratory,[7] structure shown in Figure 2) were dissolved separately in $CHCl_3$ (1.00×10^{-3}M) and mixed thoroughly before spreading. The mixing ratio is 2 mole AA to 1 mole TPPP. The subphase of pure water was from a Millipore Milli-Q system and the pH value of it was adjusted with HCl or NaOH. The standard spreading conditions were as follows: 100 μl of the mixed chloroform solutions of AA/TPPP was spread onto a surface area of 600 cm^2 and in this case the mean molecular area is 100$Å^2$ (π=0mN/m). Before deposition (15 minutes after spreading), the monolayer was either compressed at a controlled rate(Vc=20cm^2/min) to the expected pressure or just let alone in the original spreading conditions. Vertical dipping method was used to deposit the monolayer films on freshly cleaved mica substrates for AFM studies(Nanoscope III, Digital Instruments) and multilayer films on glass plates for UV-Vis spectrum measurements (UV-2201 model, Shimadzu, Japan). The dipping rate was controlled at 4 mm/min. The π-A isotherms of AA/TPPP mixed monolayers together with those of pure TPPP are shown in Figure 1. All experiments were carried out at 20^{0}C.

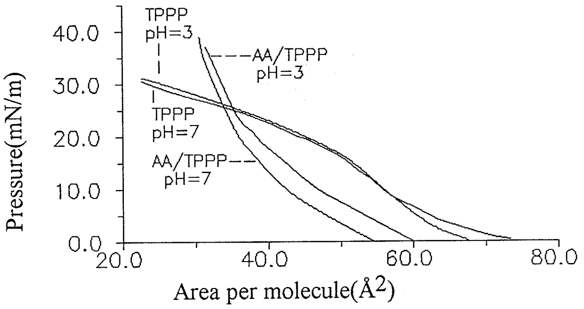

Figure 1. π-A isotherms of pure TPPP monolayer and AA/TPPP mixed monolayer(the mole fraction of TPPP is 0.33) under neutral and acidic conditions.

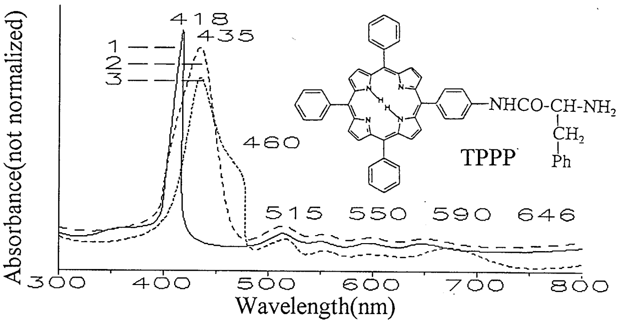

Figure 2. UV-Vis spectra of TPPP in Chloroform (1×10^{-5}M) (1), in its pure monolayer at pH 2.0-12.0 and mixed monolayer at pH 7.0-12.0 (2), and in the mixed monolayer at pH 3.0 (3).

It is well known that the free-base porphyrin has five maximum absorption peaks, a Soret band at about 420 nm, two Qy bands at about 500-550 nm and two Qx bands at about 600-650 nm.[8] In the case of TPPP monomer in chloroform (1.00×10^{-5}M), the absorption spectra exhibit the Soret band at 418 nm, Qy at 515 and 550 nm and Qx at 590 and 646 nm (see Figure 2). However, its pure mono- and multilayer LB films exhibit a red shift of Soret band from 418 to 435 nm, showing the formation of aggregates. No matter what pH values of the subphase are adjusted (from 2.0 to 12.0) during preparation(π=0 ~10mN/m), pure TPPP LB films exhibit the same absorption behavior. Same spectra were also obtained in the mixed monolayer films composed of TPPP and AA under neutral and alkaline conditions. This feature suggests that TPPP molecules have the same aggregation state both in its pure films and mixed films. Under acidic conditions, a new TPPP aggregation state is likely to appear in the mixture due to the occurrence of a shoulder absorption of Soret band at 460 nm. In this case, the interaction between TPPP molecules is much stronger than that in the films discussed above and TPPP molecules are expected to be in the more ordered state.[10] Further information will be provided by the following AFM studies.

Figure 3a shows the AFM topography of the mixed monolayer film AA/TPPP (π=0 mN/m and *A*=100 $Å^2$) prepared on the neutral subphase. There exist two distinctive structures in this figure: domains(brighter region representing higher height) and background(relative darker region and thus lower in height). Here, we assign domains to AA in the liquid-condensed(LC)

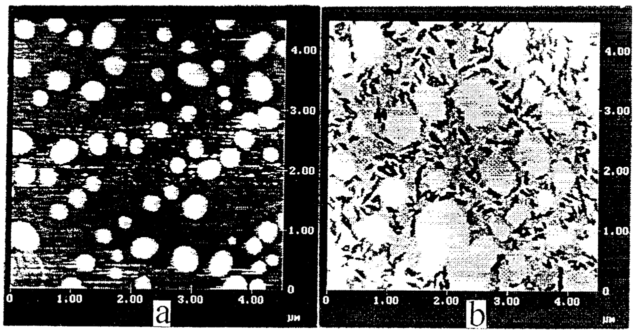

Figure 3. AFM topographies of mixed monolayer films (a)pH=7.0,π=0mN/m and A=100 Å^2. (b)pH=3.0 and π=5 mN/m

state and the background to TPPP monolayer based on the AFM studies of pure AA and pure TPPP monolayer films respectively. Pure AA monolayer films prepared on the neutral subphase show a homogeneous surface despite some defects. Cross sections across these defects enable the determination of the monolayer thickness experimentally with AFM.[11] At π=0 mN/m, the film is very thin near to 0 nm. With increasing the surface pressure, the film becomes thicker and finally reaches 2.5 nm in the LC and SC(solid condensed) phase state. As for pure TPPP monolayer films, AFM studies also show a homogeneous surface and a phase transition from gas to liquid-expanded(LE) to bulk aggregates on increasing the surface pressure. The correspondent monolayer height changes from 0 to 1.5 nm. The closely packed monolayer height 1.5 nm, smaller than the theoretical height 2.1nm (computed from the CPK model), means that TPPP molecules stand tilted. In Figure 3a, the circular domains, about 0.6 μm in diameter and 2.5 nm higher than the background, exhibit the molecular height of AA and so assume a liquid-condensed phase state. This assignment was further supported by the following experiments. First, the domain density increases with the increase of AA in the mixed monolayer. Secondly, three-dimensional ball-like structures due to the aggregation of TPPP molecules could be observed in the pure TPPP monolayer and the mixture's background when a relatively strong force was applied between the AFM tip and the monolayer film. No similar results could be produced in the mixture's domain structure.

As mentioned above, the transferred one-component monolayer film of AA shows a homogeneous surface at π=0 mN/m (A=100 Å^2). However, in our previous work,[9] we have observed some aggregation states of AA monolayer at the air-water interface by brewster angle microscopy. Why AA monolayer film on mica couldn't maintain the original structure of its precursor on water surface may be due to the fact that the interaction between AA molecules and water surface changes to that between AA molecules and the substrate surface during transfer owing to different interfacial energies involved. Then the film may have to change its structure in order to obtain new equilibrium. On the other hand, the line tension between AA domains and TPPP monolayers, which plays a dominant role in the mixture, is much stronger than that in a one-component monolayer. Thus, it is reasonable to consider that the mixed monolayer film could mainly maintain its original structure after the film transfer. It is also the line tension that makes AA domains behave the LC phase at very low surface pressure.

Under acidic conditions, the hydrophilicity of TPPP molecules was enhanced because the amino group(NH_2) on the end of TPPP changed to $(NH_3)^+$. Hence, TPPP could stand at a much bigger angle in respect to the air-water interface. This fact may result in the stronger interaction between TPPP and the larger solubility between AA and TPPP. This is the case here. Figure 3b shows the two-domain structure in the mixed monolayer film prepared at pH 3.0(π=5mN/m). Apart from the circular domains of AA, "footprint" domains appear in the mixture, about 0.2 μm in dimension and 1.8 nm lower than the circular domains. It is the pure TPPP aggregation state that contributed to the shoulder absorption at 460 nm. TPPP domains and AA domains are separated by some downy structure which have the same height as the circular domains. The downy region is loose and thus looks not as bright as the circular domains. This feature may mean the partly miscible aggregation of AA and TPPP. The interaction between TPPP in the downy region is weaker than that in the "footprint" domains but is considered to be similar to that in the mixed monolayer under neutral and alkaline conditions according to the UV-Vis spectrum. AA domains, TPPP domains and the downy structures could also be distinguished in the mixed monolayer film prepared at π=0mN/m under the acidic conditions, but they are not separated as clear as in Figure 3b.

In summary, through AFM studies of a mixed monolayer film of AA/TPPP, we have observed two kinds of phase-separated structures appeared in the mixture. Furthermore, these structures are possessed of different UV-Vis spectra. It is believed that AFM will represent a very powerful tool for macro- and microstructure studies on monolayer films.

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