

An epifluorescence microscope (Olympus IX-FLA) was used to obtain all the fluorescence images of the monolayer at the air/water interface under different surface pressures. The Langmuir film was prepared with a Kibron minitrough (5.9 cm \times 19.5 cm, Kibron Inc., Helsinki, Finland) with a quartz window. Optronix Magnafire TM CCD camera was used to detect the fluorescence emission from the floating monolayer at the air/water interface.

In situ UV-vis absorption spectra of the Langmuir monolayer were recorded by a HP spectrophotometer model 8452A, set on a rail close to the quartz window of KSV trough. The fluorescence spectra of the Langmuir monolayer were recorded with a Spex Fluorolog 1680 spectrometer. An optical fiber probe was put 1 mm above the water surface, the excitation light from the fluorescence spectrometer and the emission light from Langmuir monolayer were transmitted through this fiber.

Study of the topography of a L-B film deposited on a mica plate was conducted by using a Philips/Electroscan Environmental Scanning Electron Microscope (Model XL 30-FEG), equipped with a field emission electron gun. All imaging has been performed in a "wet mode", using water vapor pressure in the range of 1.0 Torr as the imaging gas and protective atmosphere. Images presented herein are gaseous secondary electron images (GSE). A wide-range gaseous secondary electron detector was used without an external aperture.

AFM Mac mode was used to image the L-B monolayer, which was scanned in air. Mac mode is an oscillating cantilever method of imaging which uses a magnetic field as the cantilever driving mechanism. Like other AC techniques, the cantilever is driven at high frequencies and the surface is monitored by changes in the amplitude. Molecular Imaging PicoSPM microscope (Phoenix, AZ) with commercial sharpened tips attached to rectangular beams was used in this work. The Mac mode was immediately used to image sample after deposition. The L-B films (one monolayer) used in the AFM studies were prepared by vertical dipping method on mica surface from Langmuir films at the air/water interface, which were maintained at constant surface pressure.

Results and Discussion

Surface Pressure–Area Isotherm Studies of PPE4CN at the Air/Water Interface. Surface pressure–area isotherm is the most common method to describe the molecular arrangement at the air/water interface.¹² Surface pressure–area isotherms (20 °C) of PPE4CN are shown in Figure 2, from which two stages of molecular arrangements could be found. From 130 to 90 Å²/molecule, surface pressure began to increase from nil to about 5 mN/m, in this stage the random existing molecules began to orientate themselves to form a Langmuir film. Extrapolating the isotherm to nil pressure, a limiting molecular area of 120 Å²/molecule can be obtained from this part of isotherm. At around 90 Å²/molecule, a "peak-like" point appeared in the isotherm. This is a good indication of phase transition at this point (see below for details). After the "peak-like" point, the surface pressure was kept constant until about 60 Å²/molecule showing a flat line from around 90 to about 60 Å²/molecule. From 60 Å²/molecule, the surface pressure started to increase again until the Langmuir film collapsed at around 16 mN/m. A limiting molecular area of 63 Å²/molecule was obtained from this part of the isotherm.

As we pointed out the appearance of the "peak-like" point is a good indication of phase transition. This indicates that there are two different molecular orientations at the air/water interface shown as two different stages in the surface pressure–area

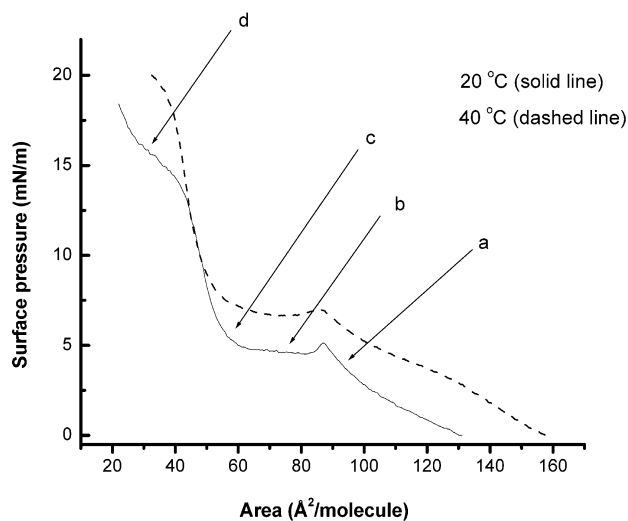


Figure 2. Surface pressure–area isotherms of PPE4CN at 20 °C and 40 °C. The arrows a–d indicate the surface pressures at which epifluorescence images were taken (see Figure 4).

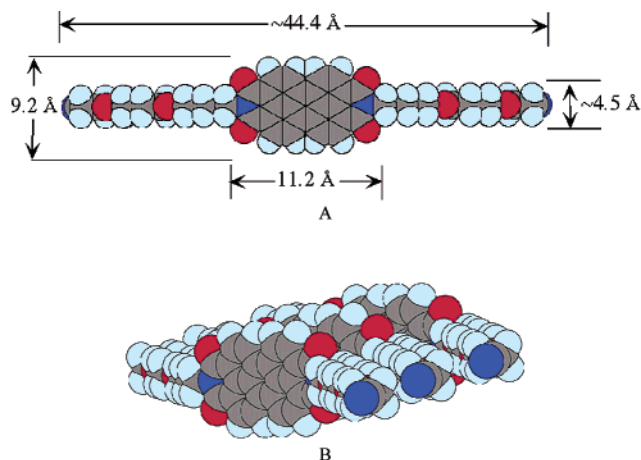


Figure 3. Energy minimized computer model of PPE4CN. (A) Face-on model. (B) Edge-on model.

isotherm. From the structure of PPE4CN, there is a rigid hydrophobic perylene core and two hydrophilic chains. There would be most probably two kinds of orientation for this molecule at the air/water interface: the plane of the perylene core is flat on water surface (face-on) or perpendicular to water surface (end-on). The two hydrophilic chains will be flat or merge into water in both cases. The energy minimized model would help us to understand the molecular orientation changes at the air/water interface. Calculated structures face-on and edge-on orientations are shown in Figure 3, which were optimized with MM2 force field using Chem3D program (CambridgeSoft Corp.).

If the PPE4CN molecules were flat on water surface (face-on arrangement, Figure 3A), the molecular area of water surface plane would be between 103.04 Å²/molecule (area of the perylene core) and 252.44 Å²/molecule (perylene core plus two chains). Face-on with two hydrophilic chains merging into water partly would be the most possible orientation. If these molecules were in edge-on orientation (Figure 3B) with perylene cores parallel to each other and perpendicular to water surface, the molecular area would be much smaller than that of face-on orientation because the molecules in edge-on orientation are more tightly packed than in face-on orientation. Compared these calculated results with limiting molecular area obtained from surface pressure–area isotherm, an orientation changing process

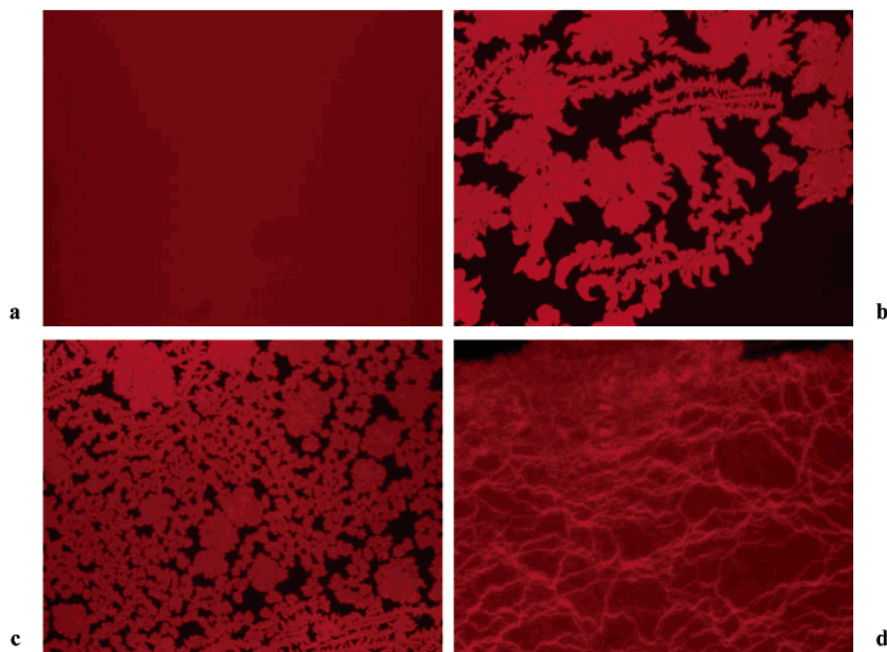


Figure 4. Epifluorescence images of PPE4CN monolayer at air/water interface under different surface pressures, which are labeled in Figure 2(a–d); image size $895\ \mu\text{m} \times 713\ \mu\text{m}$.

at the air/water interface with the increasing of surface pressure could be noticed. At pressure nil the molecules are in face-on random orientation. With the increasing of surface pressure, molecules began to orientate themselves until they are closely packed next to each other, from which limiting molecular area of $120\ \text{\AA}^2/\text{molecule}$ was obtained, which means that the two chains are partly merged into water subphase compared the calculated area. At the “peak-like” point the face-on configuration run to its limit, and the edge-on arrangement appeared. At this point, a phase transition from the face-on to the edge-on orientation occurred. This can be easily explained by the fact that the edge-on arrangement is a much more compact orientation than that of the face-on model, there is a relaxation of molecules at the air/water interface right after the phase transition. This is the reason the “peak-like” point in the isotherm is not a common phenomenon of surface pressure–area isotherms in surface chemistry studies. From $60\ \text{\AA}^2/\text{molecule}$ the surface pressure started to increase again while the monolayer with molecules in the edge-on configuration became more and more compact until the monolayer collapsed at about $16\ \text{mN/m}$.

Epifluorescence and Other Spectral Studies of PPE4CN in Langmuir Monolayer. The molecular orientation of face-on and edge-on are totally different, there should be clear topographic changes before and after the phase transition. The most direct and clear proof of the molecular orientation change and self-assembly process is from the epifluorescence images of the Langmuir monolayer of PPE4CN at the air/water interface. Epifluorescence microscopy is a perfect tool to study the formation of aggregates or domains of Langmuir films, especially for the chromophores.¹⁴ Excited by UV light, the fluorescence images of the Langmuir film of PPE4CN at the air/water interface at different surface pressures were shown in Figure 4. Figure 4A showed the image of Langmuir film at a surface pressure $4\ \text{mN/m}$. In fact, before the “peak-like” point in the isotherm the fluorescence images showed the same homogeneous monolayer at the air/water interface. With continuous compressing, just after the “peak-like” point in the isotherm, bright aggregates appeared as shown in Figure 4B,

symbolizing the orientation change before and after the “peak-like” point. At the “peak-like” point the self-assembly started, and the bright aggregates formed automatically from small random spots to large and more aggregates, until the image like in Figure 4C appeared, even the compressing of the Langmuir film was stopped. The bright aggregates became more and more compact with the continuous compressing of the Langmuir film, until the collapse of the monolayer. The image of collapse was exemplified in Figure 4D.

It should be noted that the whole self-assembly process could be finished in several minutes which depends on compressing speed of the Langmuir monolayer and further more the whole process is reversible. With decreasing the surface pressure the monolayer recovered to the starting homogeneous stage. These images perfectly matched the molecular orientation changes analyzed from the surface pressure–area isotherm. Thus, the face-on orientated monolayer should correspond to the homogeneous epifluorescence image shown in Figure 4A. The compact edge-on orientated molecules corresponds to the bright aggregates shown in Figure 4C. In fact the self-assembly process we saw under epifluorescence microscopy was the self-assembly of the edge-on orientated PPE4CN molecules at the air/water interface. As we know in thin films, the self-organization property of perylene derivatives is due to the π – π interaction between molecules. The same reason may apply in the Langmuir monolayer at the air/water interface. When the molecules are in the face-on arrangement all the perylene cores are flat on water surface, which makes the π – π interaction between molecules impossible. In contrast to the face-on arrangement, the perylene cores of molecules in the edge-on orientation are parallel to each other, which allows the π – π interaction to occur. Obviously in the monolayer of amphiphilic liquid crystal perylene derivatives at the air/water interface, the edge-on configuration is the key element for the self-assembly process in the monolayer.

In addition to the fluorescence, there was also clear UV–vis absorption changes accompanied with the molecular orientation changes. The UV–vis absorption spectra and fluorescence emission spectra of PPE4CN in Langmuir monolayer at different

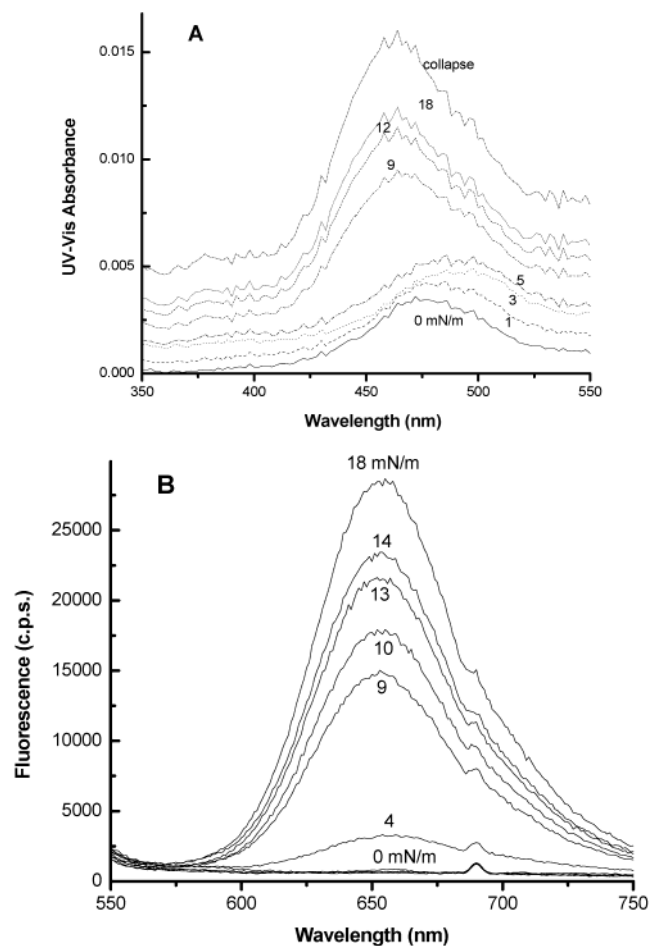


Figure 5. (A) UV-vis spectra of PPE4CN monolayer at the air/water interface under different surface pressures. (B) Fluorescence spectra of PPE4CN monolayer at the air/water interface under different surface pressures.

surface pressures were shown in Figure 5. In Figure 5A, some differences of the UV-Vis absorption spectra could be found before and after the “peak-like” point in the isotherm. First, the absorption peak shifted from 494 nm (before the “peak-like” point at about $90 \text{ \AA}^2/\text{molecule}$, 5 mN/m) to 460 nm (after the “peak-like” point), which suggested the configuration changes of the Langmuir film. In addition no matter before or after the “peak-like” point the absorption increased with the increase of surface pressure. However, the absorption intensity after the “peak-like” point was much larger than that before the “peak-like” point, indicating much more densely packed film formed.

Studies of the fluorescence emission spectra (Figure 5B) gave the similar conclusion. Excited at 460 nm the fluorescence spectra of PPE4CN monolayer showed a strong emission peak at 652 nm. The fluorescence intensity increased with surface pressure, which means that there was no clear self-quench effect. Similar to the UV-vis absorption spectra, the intensity “jumped” just after the “peak-like” point at surface pressure 5 mN/m at $90 \text{ \AA}^2/\text{molecule}$. The molecules in the edge-on orientation could give stronger fluorescence than the face-on arranged molecules at the air/water interface, which explained the reason that the aggregates in the edge-on orientation were much more favorable than the homogeneous face-on orientated Langmuir monolayer.

To further confirm such a phase transition phenomenon, we recorded the surface pressure–area isotherms of PPE4CN Langmuir monolayer at different temperatures (Figure 2). It is clear from Figure 2 that both isotherms at 40 and 20 °C showed

the similar phase transition characteristics at around $90 \text{ \AA}^2/\text{molecule}$, but the phase transition at lower temperature appeared at lower surface pressure than that at higher temperature due to the upshift of the isotherm at higher temperature (about 5 mN/m at 20 °C vs about 7.5 mN/m at 40 °C), which might suggest that low temperature favors the edge-on orientation at the air/water interface.

Topographic Studies (Environmental Scanning Electron Microscopy and Atomic Force Microscopy) of L–B films of PPE4CN. Compared with the traditional SEM, high vacuum chamber of environmental scanning electron microscopy (ESEM) is separated from the sample compartment, which allows the research sample to be measured under controlled atmosphere instead of the high vacuum condition of SEM. Also a minimum water vapor can be maintained in the sample chamber to protect the sample from being damaged by the high vacuum of traditional SEM.¹⁵ ESEM have been successfully used in the configuration studies of L–B films.^{16,17} ESEM images of PPE4CN L–B film were presented in Figure 6. These L–B films examined in this study were prepared at constant surface pressure of 10 mN/m. Two kinds of aggregates were found from Figure 6A. One was 2–3 μm long line-like aggregates; while another kind was 5 μm size leaf-like aggregates. The leaf-like aggregates were exactly the same aggregates we observed from the epifluorescence images at the air/water interface (see above). The line-like aggregates were not found because the size of them was too small compared to the leaf-like aggregates. The enlarged ESEM images of both kinds of aggregates were shown in Figures 6B and 6C. In Figure 6B, among the line-like aggregates, there was a small leaf-like aggregate, which looked like the self-assembly product of the line-like aggregates. The relationship between the leaf-like and the line-like aggregates was shown more clear in Figure 6C, in which the enlarged leaf-like aggregate (middle) was obviously the combination of several line-like aggregates. In fact, the self-assembly also happened in the L–B monolayer. The aggregates were “soft” and “moving” under ESEM. Within a period of time more and more leaf-like aggregates appeared in the place where the line-like aggregates previously occupied. ESEM images at other surface pressures have also been investigated. The L–B deposition ratio higher than 5 mN/m was close to unity; while the L–B deposition ratio at surface pressures lower than 4 mN/m was very low, close to nil. Because at low surface pressure, the face-on model was the only orientation of the L–B film, and thus the face-on orientated Langmuir films were difficult to transfer to mica surface.

By using ESEM, the L–B films were studied at microscale, herein we also used atomic force microscopy (AFM) to study the L–B monolayer at nano scale. AFM technique is widely used in the studies of molecular orientation of L–B films of disk-shaped molecules because of its high resolution.^{16–19} AFM images of PPE4CN L–B film (prepared at 10 mN/m) were shown in Figure 7. Two kinds of aggregates could be identified from Figure 7A, the brighter compact aggregates and the darker loose aggregates. The color of the image showed the thickness of the monolayer. The thickness of the darker part of the monolayer was around 5 \AA ; while the brighter part was nearly 10 \AA thick. Comparing these data with the calculated model from Figure 2, apparently, the molecules in the brighter aggregates were in edge-on arrangement, while the molecules in the darker part were in the face-on orientation. This was the direct proof of the different orientations of the Langmuir and L–B films. The enlarged image of the compact aggregates was presented in Figure 7B, from which it is clear that the compact

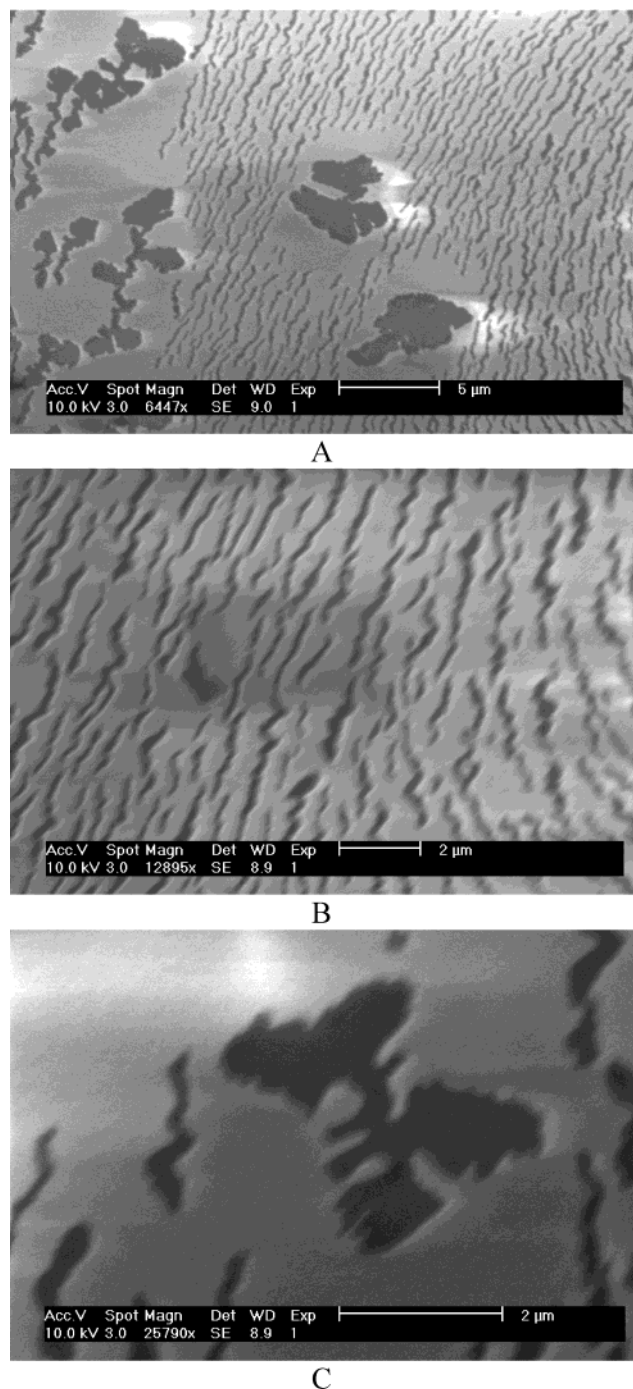


Figure 6. ESEM images of PPE4CN, one layer L-B film on mica prepared at surface pressure 10 mN/m. One layer L-B film on mica prepared at surface pressure 10 mN/m, wet mode, 1 Torr, magnification (A) 6447 \times , (B) 12895 \times , (C) 25790 \times .

bright aggregates were composed of many small line-like aggregates, whose size and form was similar to the line-like aggregates we observed in the ESEM images. There were small “gaps” between the line-like aggregates. From nano scale this proved that the leaf-like aggregates were the self-assembly product of the small line-like aggregates. The images in Figure 7A,B were measured right after the L-B films were prepared because the self-assembly also happened in L-B monolayer. After a period of time, the edge-on orientated aggregates became more and more compact and “homogeneous”. The gaps between the line-like aggregates disappeared. Figure 7C shows the image that was taken 3 h after the L-B film was prepared. In this image, only the self-assembly product, the homogeneous leaf-

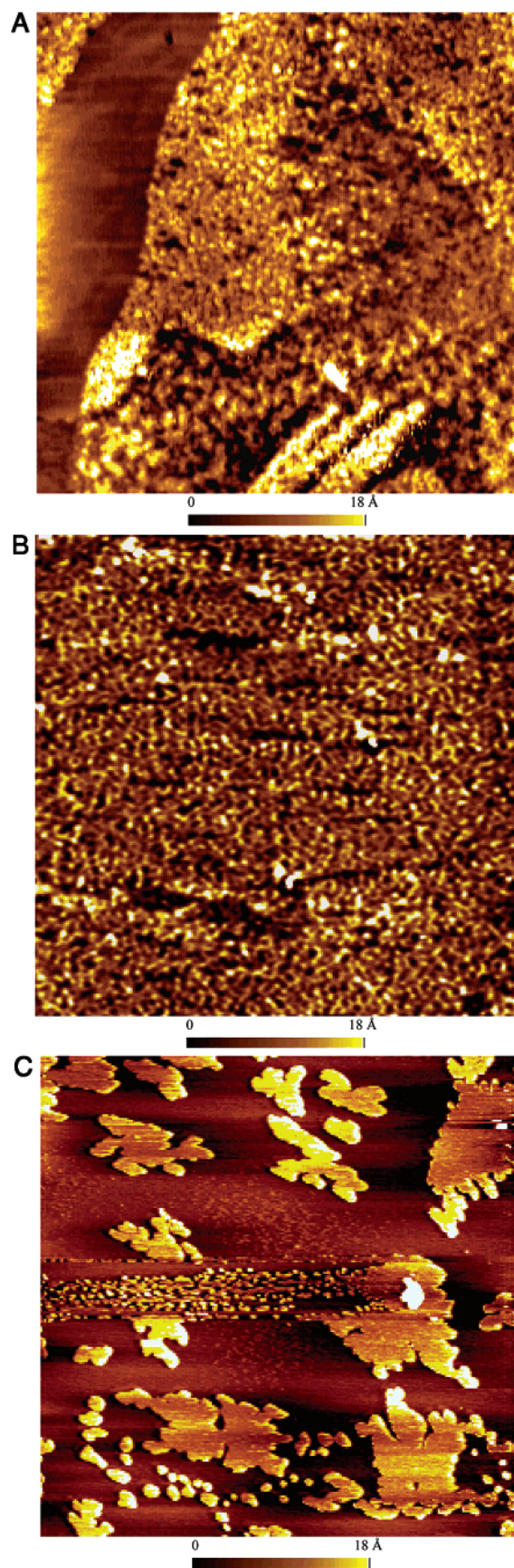


Figure 7. AFM images of PPE4CN, one layer L-B film on mica prepared at surface pressure 10 mN/m, (A) image size 2500 nm \times 2500 nm; (B) image size 350 nm \times 350 nm. (C) Image size 2500 nm \times 2500 nm. Topography of A and B were taken from a fresh L-B film, whereas topography C, 3 h after preparation.

like aggregates could be found, the line-like aggregates shown in Figure 7B could not be identified. The thickness of the aggregates was still around 10 Å, which means that the aggregates were composed of one edge-on orientated monolayer. The AFM images with time changing proved the self-assembly process in the nanoscale.

Summary

In this paper the orientation changes of PPE4CN Langmuir monolayer accompanied with its reversible self-assembly process has been studied. From the surface pressure–area isotherms and epifluorescence studies, it has been rationalized that the edge-on orientation is the key to the self-assembly for the liquid perylene diimide derivatives at the air/water interface. The topographic studies including the ESEM and AFM studies supported the orientation changes with self-assembly found from the epifluorescence studies. Also in monolayer of L–B film on mica the self-assembly process can also occur, which might follow the same rule as that in Langmuir monolayer at the air/water interface.

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