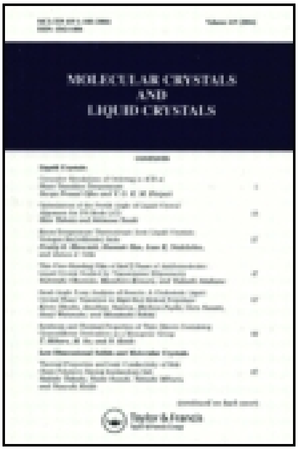

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Self-Organization in Stable and Metastable Langmuir-Blodgett Films of Liquid Crystalline Porphyrins

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SELF-ORGANIZATION IN STABLE AND METASTABLE LANGMUIR-BLODGETT FILMS OF LIQUID CRYSTALLINE PORPHYRINS

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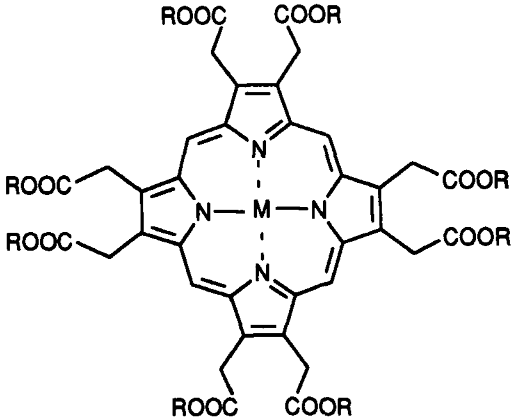
Abstract We report an AFM imaging study of molecular self-aggregation and organization in LB layers of mesogenic porphyrin derivatives. The images were taken from molecular resolution to the mesoscopic range, as a function of deposition pressure and of elapsed time after deposition. At the molecular level, from the images we were able to determine molecular dimensions and pseudo-mesomorphic structure, which was columnar. As a function of elapsed time, such images remained stable if the deposition was performed at the pseudo-solid part of the isotherm. For deposition in the coexistence, condensed liquid stage, as a function of time the images showed remarkable molecular self-organization processes, occurring over several length scales.

INTRODUCTION

Among the several types of molecular systems which can be deposited by the Langmuir-Blodgett (LB) technique,[1] particularly interesting are the mesogenic amphiphiles, i.e. molecules which yield bulk liquid crystalline phases.[2] In these systems in fact the monolayer structure and subsequent deposition are influenced not only by the "normal" interface forces, but also by the mesogenic potential which leads to the molecular self-organization characteristic of liquid crystals. Depending on the relative strength of these two types of forces, we may expect a complicated pattern of possible behaviours. In particular, some of the self-organization potential of the liquid-crystalline phase may persist in the solid LB film, allowing the self-organization dynamics to be studied as a function of preparation and deposition methods, and in the slowed down time scale of the solid state environment of the LB film.

From these points of view particularly interesting are amphiphilic porphyrin derivatives.[3] Porphyrin is a main constituent of chlorophyill and hemoglobin, and as such is involved in the energy transfer and photosynthesis processes.[4] Furthermore, it can readily complex with metals such as copper and zinc, and has been shown to have photoconductive[5] and semiconductive[6] properties which make it interesting for molecular electronics applications. For the subject matter of our work however, most important is that porphyrin derivatives presenting long chain substituents either in meso or β positions have been shown to self-organize in discotic or columnar mesophases.[7] Since molecular orientational order and intermolecular interactions determine the transport and optical behaviour, it may be possible to use the mesogenic potential to fine tune such characteristics by the detailed control of the molecular aggregation processes which is possible in the Langmuir monolayer.

To this end, we have studied octa-octyl-porphyrin **OOP-1** and its metal complex with zinc **ZOOP-2.**[8] Such molecules form stable columnar mesophases in a wide temperature range (I 160 D_1 104 D_2 86 K for OOP, I 201 D_1 106 D_2 84 K for ZOOP).



OOP-1 M = 2H, R = C_8H_{17}; **ZOOP-2** M = Zn, R = C_8H_{17}

In a previous work we have reported monolayer studies and the characterization of molecular stacking and orientation in the LB film by optical absorption spectroscopy.[9] In this work we report a study of the molecular ordering and self-organization processes from the molecular to the mesoscopic scale by Atomic Force Microscopy (AFM). In such study we have followed the behaviour in time of the AFM images of an LB layer deposited at different target pressures. For OOP we have found extensive self-organization processes in the films deposited from the coexistence region of the Langmuir isotherm. As shall be described later, in the time scale of days and weeks the molecules self-organize in a hyerarchy of structures ranging from the pseudo-mesomorphic columnar arrangement on the molecular scale to spirals, lattices of spirals and braids as time passes and the length scale increases. ZOOP instead was found to form stable LB films having columnar arrangement of the molecules, as evidenced by molecular resolution AFM images.

EXPERIMENTAL

The OOP and ZOOP molecules were synthesized using a short, high yield original procedure which is described elsewhere.[10] The details of the preparation of the Langmuir layer and of its deposition onto a solid substrate have already been published.[9] Here we only recall that to obtain good and reproducible results, hysteresis phenomena must be accounted for, and barrier compression and substrate dipping velocities must be slow or very slow respectively. We found that under such conditions Z-type films (i.e. films deposited on hydrophilic substrates only in the upstroke part of the deposition cycle) could be deposited with relative ease. The molecules were deposited on glass, quartz and silicon substrates.

Optical spectra were taken with a standard dual beam spectrophotometer. We verified linearity between optical density in the Soret band region and number of deposited layers (up to seven layers).

The microscopic and mesoscopic structure characterizations were performed with a Nanoscope III atomic force microscope, used mainly in the contact mode. Care was taken to verify the eventual damage or in any case modification of the soft LB monolayer by the microscope tip. We have used different tips and different scanners to cover the scan ranges from about 1 nm to over 50 microns. Thus we were able to obtain images from the molecular scale to the scale of the molecular superstructures which developed as a function of elapsed time from the deposition.

By selecting different regions of the LB film along the vertical dipping direction, we could obtain images reflecting the Langmuir monolayer structure and its time development in the coexistence region of the isotherm. We could do this, of course assuming that such structure was preserved upon deposition, since one deposition took about 4 hours (dipping speed 0.1 mm/min). Thus in this sense the vertical position on the sample corresponded to time spent in the coexistence region of the isotherm. Such assumptions were verified by optical spectroscopy; we found in fact that the Soret band substructure, related to the contributions of the different types of molecules (side-on and edge-on) varied with vertical position on the substrate, with the contribution from the edge-on molecules increasing with time spent in the coexistence region of the isotherm.[9]

From the isotherms we could deduce a mean molecular area (mma) of porphyrins **1** and **2** in the pseudo-solid phase (pressure 30 mN/m) of about 70-80 Å^2; this means that in this phase the molecules are oriented in the edge-on configuration, with the aliphatic chains sticking out of the water, but not in the the zone between the rings. In the case of OOP from the beginning of the two coexistence regions observed, we deduced a mma of 200 Å^2 and 120 Å^2 respectively, with corresponding pressures of 2.7 mN/m and 10 mN/m. These regions of the isotherm correspond to the vapor-expanded liquid and expanded liquid-condensed liquid transitions respectively. According to the classification proposed in the review by Laschewsky,[2] at the 2.7 mN/m transition the randomly oriented aliphatic chains of the molecules which lay flat on the surface orient perpendicularly away from the surface. In the following coexistence region, more and more rings orient away from the surface. This is the metastable region from which we deposited the metastable LB monolayer (usually at 2.7 mN/m). The behavior of ZOOP is different: only the expanded liquid-condensed liquid transition is observed at 10 mN/m, with a mma of 240 Å^2, followed by the transition to the pseudo-solid phase at 30 mN/m.

ATOMIC FORCE MICROSCOPY

In Figure 1 we show the direct image obtained at molecular resolution of a ZOOP three-layer LB film deposited on glass at 30 mN/m. We clearly see the horizontal columns formed by stacks of ZOOP molecules with the edge-on orientation relative to the substrate (white spots). A similar image was also obtained for OOP, and we found for both molecules good reproducibility of AFM imaging for many weeks after deposition. Section analysis of the AFM image of Figure 1 shows that there is a regular 5.7 Å stacking distance among the ZOOP cores in the columns, with an average width of 16.7 Å for each molecule. This last measure, confirmed in a Fourier filtered image of Figure 1, nicely matches the calculated value of 16 Å for ZOOP arranged edge-on, having the alkyl chains oriented upward with respect to the glass substrate. This implies that the columnar organization of ZOOP on water is predominantly retained upon deposition on glass.

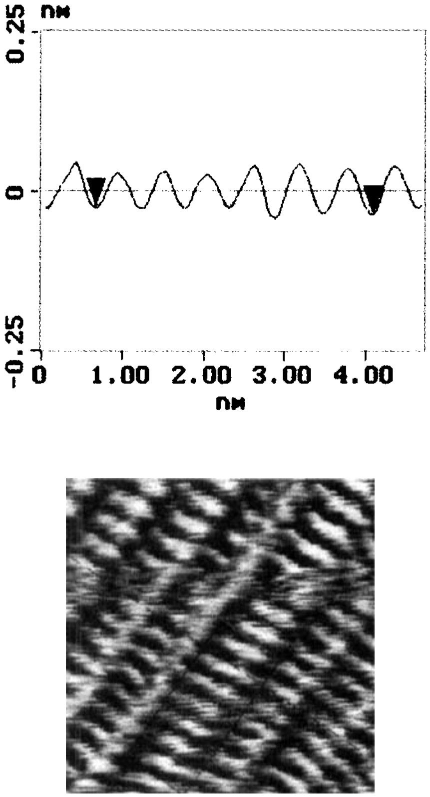


FIGURE 1 Topographical AFM image of a LB film of ZOOP with section analysis. Acquisition conditions: Si_3N_4 pyramidal tip; elastic constant of the cantilevers 0.12 N/m; A head scanner; scan size 6.405 nm; scan rate 42.72 Hz, number of samples 512. See Color Plate I.

In the case of ZOOP the columnar organization adopted in the monolayer is stable over time, in agreement with the general tendency of metal complexation to enhance porphyrin self-aggregation. This effect is also evident in the columnar mesophase: complexation with zinc widens the temperature range of the mesophase by 40°C in ZOOP with respect to OOP.[8,10]

From the optical absorption studies we obtained clear evidence that the monolayers of OOP deposited at 2.7 mN/m have a structure which is time and space dependent.[9] The changes observed in the optical spectra were paralleled by changes of the corresponding AFM images.

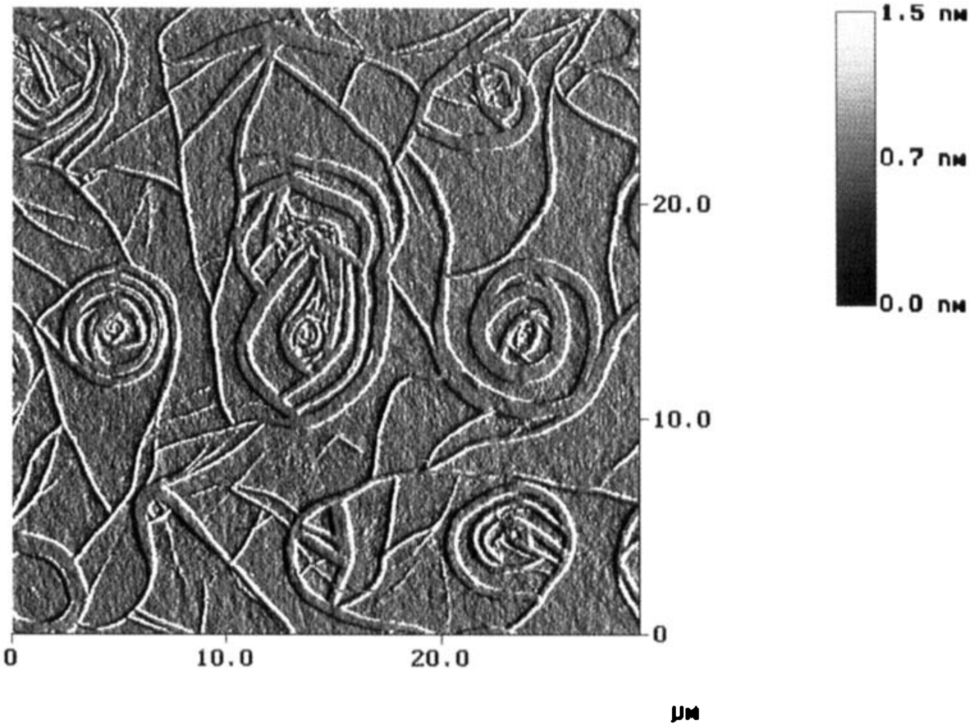


FIGURE 2 AFM image of a OOP monolayer four days after deposition. Acquisition conditions: Si_3N_4 pyramidal tip; elastic constant of the cantilevers 0.12 N/m; J head scanner; scan rate 10 Hz; number of samples 512. See Color Plate II.

In Figures 2 and 3 we show two images of the same OOP monolayer, taken at mesoscopic range, respectively four (Fig. 2) and fifteen (Fig. 3) days after the deposition on silicon. Note the appearance, over a fairly uniform background, of spiral structures: these correspond to the molecules which have risen form flat to edge-on orientation. As each molecule rises, there is an increase of interfacial energy with the other molecules which remain flat, probably due to two-dimensional steric effects: the edge-on molecules in fact occupy less than half the area of the side-on molecules. Such energy is minimized by adopting the shorter interface length, i.e. the circular shape which spirals away as more and more molecules rise. We feel that this is a beautiful example of molecular self-organization, which can be followed on the very convenient scale of days.

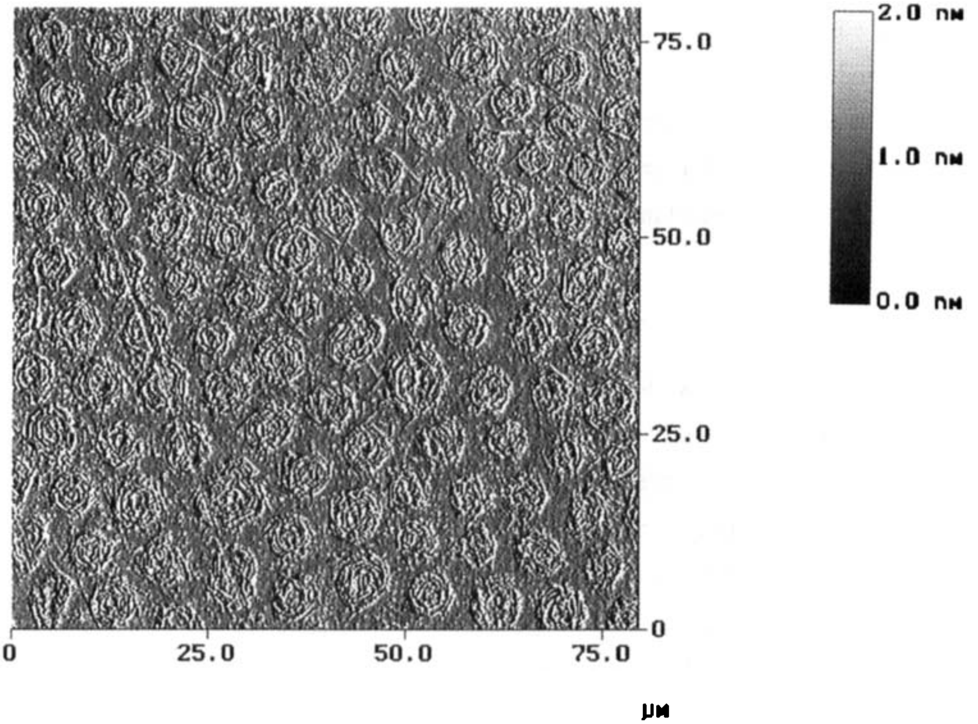


FIGURE 3 AFM image of a OOP monolayer fifteen days after deposition. Acquisition conditions: Si_3N_4 pyramidal tip; elastic constant of the cantilevers 0.12 N/m; J head scanner; scan rate 10 Hz; number of samples 512. See Color Plate III.

Note that the spirals seem to grow all to a very definite size: as time passes more and more such spirals form and filaments connecting them begin to appear. When the spirals density becomes sufficient, the spirals go through another self-organization process, forming an hexagonal-like lattice, as can be seen in Figure 3. At longer times eventually complex braid-like structures appear. The time kinetics of the aggregation processes reported in Figures 2-3 closely parallels the behaviour of the optical absorption spectra: the spiral structures in particular correspond to the appearance of the short wavelength component of the Soret band.[9]

We have also imaged the monolayer in different vertical positions on the same sample. We have found a close parallelism between the time behaviour observed for the images we reported and the vertical position dependence of the images: the images nearer to the bottom (i.e. initial times in the coexistence region) showed hardly any structures due to the presence of edge-on molecules; as distance from the bottom increased, more and more edge-on structures could be observed. From this we can deduct that the LB layer reproduces reasonably well the Langmuir monolayer structure as it is being deposited. Furthermore, we can also have a qualitative idea of the difference in relaxation times: over the liquid subphase, it takes hours for the molecules to reorient, whereas in the solid-like environment of the LB film, it takes many days.

CONCLUSIONS

In this paper we have shown that mesomorphic porphyrins are a very interesting system: they form stable monolayers which can be deposited well with some care; they have a strong self-organization tendency which is directly connected with their mesogenic properties. Such tendency can be followed very easily in the slowed down time scale made possible by the deposition of the Langmuir monolayer as an LB film. The tendency of the porphyrin molecules to self-organize in columnar mesophases in the bulk is reflected also in the monolayer structure, where the edge-on arrangement is favoured due to the possibility to form columnar stacks parallel to the water surface.

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