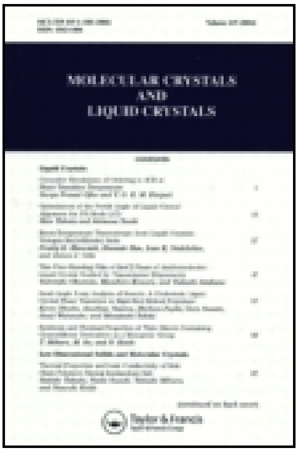

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Investigation of Alignment Mechanisms for Liquid Crystals on Phthalocyanine-Derived Langmuir-Blodgett Films by Scanning Tunneling Microscopy

Y.-M. Zhu [a], H. Chen [a], L. Wang [a], Z.-H. Lu [a], Y. Wei [a] & W. Yan [b]

[a] Laboratory of Molecular and Biomolecular Electronics, Southeast University, Nanjing, 210096, P. R. China

[b] Department of Physics, East China Institute of Chemical Technology, Shanghai, 200237, P. R. China

Version of record first published: 23 Sep 2006.

*Mol. Cryst. Liq. Cryst.*, 1995, Vol. 258, pp. 203–207
Reprints available directly from the publisher
Photocopying permitted by license only





# Investigation of Alignment Mechanisms for Liquid Crystals on Phthalocyanine-Derived Langmuir–Blodgett Films by Scanning Tunneling Microscopy

Y.-M. ZHU, H. CHEN, L. WANG, Z.-H. LU and Y. WEI

*Laboratory of Molecular and Biomolecular Electronics, Southeast University, Nanjing 210096, P. R. China*

and

W. YAN

*Department of Physics, East China Institute of Chemical Technology, Shanghai 200237, P. R. China*

*(Received December 15, 1993; in final form April 6, 1994)*

A homogeneous alignment of liquid crystal mixtures, E7, was produced by phthalocyanine (Pc)-derived Langmuir-Blodgett (LB) films. The Pc LB film was studied by scanning tunneling microscopy. Experimental results suggest that the molecular aggregates and molecular grooves between these aggregates may both be responsible for the alignment.

*Keywords: alignment of liquid crystals, phthalocyanine-derived Langmuir-Blodgett films, scanning tunneling microscopy, molecular aggregates, molecular grooves.*

## 1. INTRODUCTION

It is known that liquid crystals can be easily oriented by a solid surface.[1] Understanding this phenomenon is still a scientific challenge although it is very important for the applications of these materials. The main issue concerning the alignment of liquid crystals is to relate the observed alignment property with the structure of the solid surface and to find the microscopic mechanism for the alignment. Several techniques have proven to be very useful for this kind of study, among which are second harmonic generation,[2–4] scanning tunneling microscopy (STM)[5–7] and atomic force microscopy, and the Langmuir–Blodgett (LB) film technique.[7–10]

Ichinose *et al.* have shown that Phthalocyanine (Pc)-derived LB films can align liquid crystals both homogeneously and homeotropically by choosing the proper length of side chains.[11] In this paper we conduct a detailed study with the intention to understand the mechanism responsible for the alignment by STM observation of the Pc LB films.

## 2. EXPERIMENTAL DESCRIPTION

The Pc derivative used here is a tetrakis(neo-butyl)phthalocyaninato AlCl (PcAlCl), the chemical structure of which is shown in Figure 1. PcAlCl was dissolved in chloroform solvent to a concentration of about $1.0 \times 10^{-3}$ M. The solution was spread onto a clean water surface on a Langmuir trough to form a monolayer. Then the monolayer was compressed at a constant velocity (15 Å$^2$/(min·molecule)). The temperature of the subphase was controlled at 25°C within ± 0.5°C. The surface pressure was measured by a Wilhelmy balance with an accuracy better than 0.1 mN/m. To deposit Pc monolayers the surface pressure was kept at 15 mN/m, and the dipping velocity was fixed at 15 mm/min.

A liquid crystal cell was assembled using two glass plates coated with 5 layers of PcAlCl with their dipping directions antiparallel. The distance of the cell was controlled at 20 µm by glass spacers. Liquid crystal mixtures E7 were introduced into the cell above the clearing point of E7 in a vacuum. The alignment of liquid crystals *in the cell* was observed with polarizing microscopy. The cell could be rotated around the normal to the LB film coated glass plates.

A highly oriented pyrolytic graphite (HOPG) substrate was cleaved by adhesive tape to give an atomically flat and clean surface for deposition of the PcAlCl two-layer LB film. The deposition was performed immediately after the HOPG was cleaved. The transferred LB film was then studied by STM in air and at room temperature. STM imaging was performed in constant current mode with a scan rate of 10 Hz, a tunneling current of 1 nA and typical bias voltage of 400 mV (tip positive).

## 3. RESULTS AND DISCUSSION

### 3.1. Surface Pressure-Molecular Area Isotherm

Figure 2 shows the surface pressure-area isotherm of the PcAlCl monolayer at the air-water interface at 25°C. The limiting molecular area is around 80 Å$^2$. The monolayer was stable during the whole compression process until it collapsed. Under surface pressure of 15 mN/m, the PcAlCl monolayer can be successfully transferred onto glass plates and onto the HOPG plate with deposition ratios close to unity. Y-type LB films were formed.

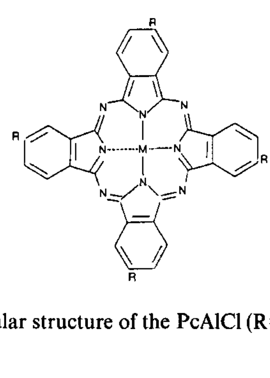


FIGURE 1 Molecular structure of the PcAlCl (R=C$(CH_3)_3$, M=AlCl).

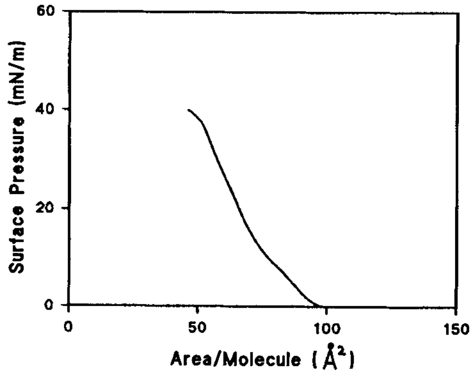


FIGURE 2 Surface pressure-area isotherm for the PcAlCl monolayer at the air-water interface at 25°C.

### 3.2. Liquid Crystal Alignment on Pc LB Films

Under a microscope with crossed polarizers, the light through the liquid crystal cell was uniform, implying that the liquid crystals were uniformly aligned. The intensity of transmission light changes with a period of 90° when the cell was rotated about the normal to the PcAlCl-coated plates. When the dipping direction was oriented at 0° with respect to the analyzer, the light transmission was optically dark as shown in Figure 3, and when the dipping direction was oriented at 45° with respect to the analyzer, a maximum transmission could be obtained. This indicates that the liquid crystals are aligned homogeneously along the dipping directions.

### 3.3. STM Observation of Pc LB Film

To understand the alignment mechanism, the PcAlCl LB film was observed by STM. Figure 4 shows a typical image of the PcAlCl LB film on HOPG. The image was stable during the imaging process with bright regions corresponding to the PcAlCl molecules. As revealed by this figure, the PcAlCl molecules form a column-like structure, as

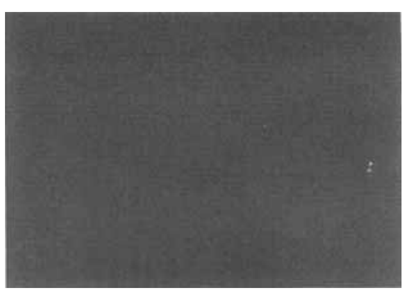

FIGURE 3 Optical micrograph of the liquid crystal cell when the dipping direction of the lower plate is oriented at 45° with respect to the analyzer.

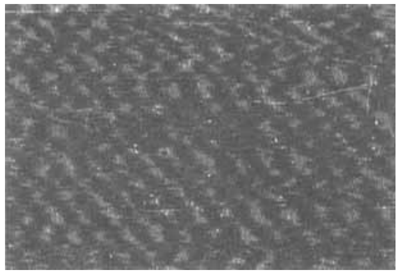

FIGURE 4 A typical STM image of the PcAlCl LB film on HOPG deposited at surface pressure of 15 mN/m. The scan size is about 45 × 30 $nm^2$. The dipping direction is shown by the arrow.

observed by an electron microscope.[12] The columns are almost parallel to the dipping direction (shown by the arrow in Figure 4). By changing the dipping directions, we have found that the PcAlCl columns are almost aligned in the dipping directions. This suggests that the arrangement of the PcAlCl molecules is due to the dipping process,[13,14] not induced by the graphite surface. The spacing between two adjacent columns is about 25 Å. The gap between two adjacent columns is comparable to the molecule size (ca. 17 Å). However, the resolution of the machine is not high enough to give the distance between two adjacent molecules in one column in the mentioned condition.

We believe that this column-like structure could not be the alias image of graphite because we scanned different regions with different scales, and almost identical column spacing was determined. The similar orientation of the molecular columns suggests that this LB film has a good order on a large scale. The PcAlCl LB film deposited on glass may have a similar column structure because the deposition ratios are almost the same and the column structure is not caused by the graphite surface. The polarizing microscopy experiment shows that liquid crystals are aligned along the dipping direction. The molecular column and the molecular grooves between two adjacent columns should both play some role in the alignment. Because these grooves are extremely narrower and shallower than those induced by a rubbing or buffing treatment, and are comparable to the size of aligned liquid crystals, the geometrical configuration should be taken into account when elucidating the alignment property of the molecular grooves. Previous experiments[7,15–18] show that the alignment of liquid crystals on polymer LB films acts through the chain-chain interaction. Analogously, in our system reported here, the alignment may act through the molecular aggregates (columns) and the aligned liquid crystals. We argue that the ordered arrangement of molecules may form an ordered surface potential field. The aligned liquid crystals prefer the state with minimum energy. To elucidate this, a molecular dynamics simulation approach should be very helpful.

## 4. CONCLUSION

It has been found that the phthalocyanine-derived LB films can align nematic liquid crystals homogeneously along the dipping direction. A scanning tunneling microscopy observation reveals that the Pc molecules form column-like aggregates along the dipping direction in LB films and that the size of grooves between two adjacent aggregates are comparable to the size of molecular aggregates. All these data suggest that the alignment of liquid crystals may act through the molecular aggregates and the molecular grooves between aggregates.



## Acknowledgements

This work was supported by the Young Researcher Foundation of State Education Committee and the National Natural Science Foundation in China.

## References

1. B. Jerome, *Rep. Prog. Phys.*, **54**, 391 (1991).
2. P. Guyot-Sionnest, H. Hsiung and Y. R. Shen, *Phys. Rev. Lett.*, **57**, 2963 (1986).
3. W. Chen, M. Feller and Y. R. Shen, *Phys. Rev. Lett.*, **63**, 2665 (1989).
4. B. Jerome, J. O'Brien, Y. Ouchi, C. Stanners and Y. R. Shen, *Phys. Rev. Lett.*, **71**, 758 (1993).
5. J. S. Foster and J. E. Frommer, *Nature* (*London*) **333**, 542 (1988).
6. D. P. E. Smith and W. M. Heckl, *Nature* (*London*) **346**, 616 (1990).
7. J. Y. Fang, Z. H. Lu, G. W. Min, Z. M. Ai, Y. Wei and P. Stroeve, *Phys. Rev. A* **46**, 4963 (1992).
8. J. Y. Fang, Y. Wei and Z. M. Sun, *Mol. Cryst. Liq. Cryst.* **222**, 71 (1992).
9. Y. M. Zhu, P. Zhu, Q. H. Wei, Z. H. Lu, Y. Wei and Z. H. Luo, *Phys. Lett. A*, **176**, 141 (1993).
10. Y. M. Zhu, Z. H. Lu, Q. H. Wei, X. M. Yang, Y. Wei, X. X. Chen, J. H. Tang and W. Yan, *Phys. Lett. A*, **183**, 107 (1993).
11. H. Ichinose, M. Suzuki and T. Goto, *Mol. Cryst. Liq. Cryst.*, **203**, 25 (1991).
12. J. R. Fryer, R. A. Hann, and B. L. Eyres, *Nature* (*London*) **313**, 382 (1985).
13. N. Minari, K. Ikegami, S. Kuroda, K. Saito, M. Saito, and M. Sugi, *J. Phys. Soc. Jpn*, **58**, 222 (1989).
14. P. Karg, A. G. Patrov, E. Sackmann and A. Wunderlich, *J. Mol. Electronics*, **6**, 21 (1990).
15. J. A. Castellano, *Mol. Cryst. Liq. Cryst.*, **23**, 33 (1983).
16. J. M. Geary, J. W. Goodby, A. R. Kmetz and J. S. Patel, *J. Appl. Phys.*, **62**, 4100 (1987).
17. S. Baker, S. Seki, and J. Seto, *Thin Solid Films*, **180**, 263 (1989).
18. Y. M. Zhu, Z. H. Lu, F. Qian, X. M. Yang and Y. Wei, *Appl. Phys. Lett.*, **63**, 3432 (1993).