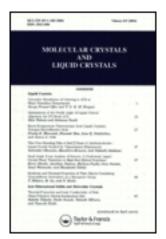
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Nematic Liquid Crystal Alignment on Phthalocyanine LB Films

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Two newly synthesized phthalocyanine compounds' Langmuir-Blodgett (LB) films were fabricated to align nematic liquid crystal (LC). Optical spectra were used to characterize the films and antiparallel type LC cells were constructed adopting SnPc and VOPc LB films as aligning layers. We found that LC molecules would align homogeneously on SnPc LB films along the deposition direction while those of on VOPc LB films align obliquely. The electrooptic effects of the cells were investigated and they showed an in agreement with LC alignment configurations. A TN type cell using SnPc LB films as aligning layer was also investigated. It has a better electrooptic effect than the antiparallel type. Since the two phthalocyanine compounds have a similar molecular structure but with different complex metals, and the corresponding LB films orient with the nearly same orientation angle on the substrates, ignoring other interactions, we think the alignment mechanism that results in different alignment configurations may be concerned with the interaction between LC molecules and oxygen atoms that are out of the macrocycle planes in VOPc LB films.

Keywords: Liquid crystal; aligning layer; Langmuir-Blodgett films

1. INTRODUCTION

Uniform and orderly liquid crystal (LC) alignment is an important criterion to determine the quality of liquid crystal display devices. It is usually by some kinds of surface treatment methods to get the required alignment. The commonly used methods are rubbing polymer films method and obliquely evaporated SiOx technique [1, 2]. Both methods have some disadvantages

and limitations, either for the static electricity effect or the inconveniences of vacuum requirement. Therefore, it is interesting to use an easy and flexible way-Langmuir-Blodgett (LB) technique to fabricate ultrathin and controllable LB films as LC alignment layers. It is valuable in the fundamental studies such as LC alignment mechanism on the interface of LC molecules and the aligning surface and the practical applications [3, 4]. Much work has been done on this area and the organic materials adopted are mainly polyimide (PI) serial compounds. Not only nematic LC alignment but also ferroelectric LC alignment on PI LB films has been studied intensively [5-7].

H. Ichinose and co-workers have used a series of phthalocyanine (Pc) derivative LB films to align nematic LC. They found that contrast ratio of the LC has a correlation with dichroic ratio of the LB aligning films [8]. Here we will adopt two newly synthesized Pc compounds, which have a good chemical and thermal stability, to prepare LB films. The films are characterized by UV-Visible and polarized UV-Visible spectra. The antiparallel (AP) and twist nematic (TN) type LC cells aligned by LB films are fabricated and the corresponding electrooptic effects are investigated. In addition, we discuss the possible alignment mechanism that results in different alignment configurations.

2. EXPERIMENTAL

2.1. Preparation of Pc LB Films

The Pc compounds are tin tetra-2,4-dimethyl phenoxy phthalocyanine (SnPc) and vanadium oxide tetra-2,4-dimethyl phenoxy phthalocyanine (VOPc). The chemical structures are shown in Figure 1. The monolayers of the compounds were spread from chloroform solutions (0.1 mg/ml) onto purified water at a subphase temperature of 20°C. The surface pressure-molecular area isotherms were recorded at the barrier moving speed of 4 mm/min. Five layers of Pc LB films were deposited onto indium tin oxide (ITO) conductive glass substrates, which were pretreated to be hydrophilic, by vertical depositing method at the surface pressure of 28 mN/m and the deposition speed 1.7 mm/min. The UV-Visible spectra and polarized UV-Visible spectra were measured with a Shimadzu UV260 spectrophotometer.

2.2. Fabrication of LC Cell

An antiparallel (AP) type cell was fabricated by placing ITO substrates together, whose conductive surfaces were coated with Pc LB films deposited

at the same time, with the deposition direction antiparallel, while that of a TN type was assembled with the deposition direction perpendicular to each other. The cell gap was controlled to be 12 µm. Nematic LC ZLI-1132 was injected into the cells by vacuum method. The alignment of LC was observed under a Leitz-Ortholux microscope. The electrooptic effects were recorded with a dual-channel oscilloscope and a photomutiplier.

3. RESULTS AND DISCUSSION

3.1. Properties of Pc LB Films

The surface pressure-molecular area isotherms of SnPc and VOPc are shown in Figure 2. Both isotherms have a relative wide "solid state" area, so it is suitable to transfer the monolayer onto the substrates at a surface pressure high above $20 \, \text{mN/m}$.

Figure 3 are UV-Visible spectra of SnPc, VOPc LB films. Compared with that of chloroform solution, the peak around 630 nm is lowered in SnPc LB films, while the 712 nm monomer peak is enhanced. indicating the occurrence of molecule aggregation in the film structure. In the case of VOPc LB films, there appears a shift of the two main absorption peaks towards long wave range, i.e. a red shift phenomenon. It means that VOPc LB film molecules coexist with a certain interaction [9].

Using polarized UV-Visible spectra of Pc LB films, we investigated Pc molecular macrocycle orientation on the substrate surface according to Yaneyama's equation [10]. The calculated orientation angle, which is the

FIGURE 1 Chemical structures of phthaleocyanine compounds.

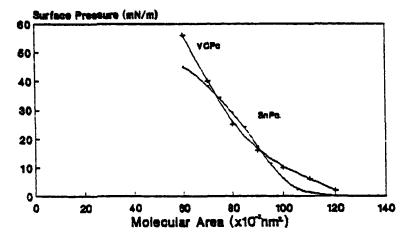
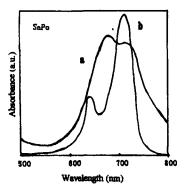


FIGURE 2 The surface pressure-molecular area isotherms of SnPc and VOPc.

angle between the Pc molecular macrocycle plane and the LB film deposition direction on the substrate, is 13.4° to SnPc and 10.2° to VOPc. (Detailed data and calculations will be reported elsewhere.) This demonstrates that SnPc and VOPc LB film molecules orient on the substrate surfaces with a similar orienting configuration.

3.2. LC Alignment on Pc LB Films

Under a ploarizing microscope, LC ZLI-1132 aligned by SnPc, VOPc LB films was arranged uniformly in both AP cells. The texture in SnPc aligned



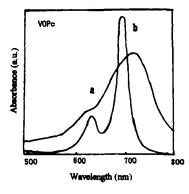


FIGURE 3 UV-Visble spectra of Pc LB films (a) and the chloroform solution (b).

cell was anchored along the deposition direction while that of VOPc aligned cell was extinguished as shown in Figure 4.

To further determine the LC alignment on Pc LB films, a Bertrand lens was exploited to obtain a conoscopic figure. No clear conoscopic figures appeared in the SnPc aligned cell. It indicates that LC molecules align in the cell homogeneously or little angle pretilted. In the VOPc aligned cell, a not complete dark cross was observed and the center of the cross would be deviated while rotating the cell along the incident light axis. This demonstrates that LC molecules are obliquely aligned with a higher pretilt angle on VOPc LB films. The corresponding conoscopic figure is shown in Figure 5.

3.3. LC Cell's Electrooptic Characteristics

Figure 6 shows the relationship of light transmission with the cell's rotation angle under crossed polarizers in the SnPc LB films aligned AP cell. When the deposition direction is fixed at 0° with respect to the analyzer, the transmission is about 5%. When the deposition direction is rotated to 45° with respect to the analyzer, the transmission reaches the highest value 85%. A extinction will occur every 90°. It can be concluded that LC molecules are aligned homogeneously along the deposition direction.

A similar phenomenon is also observed in the VOPc LB films aligned cell, expect that when the deposition direction is fixed 0°, there is a higher transmission 30%. This can be explained by the uniformly oblique LC alignment in the cell.

Figure 7 is the electrooptic response photographs of Pc LB films aligned AP cells observed on the oscilloscope. The applied rectangular waveform is 25 Hz. To the SnPc aligned cell, both the rise time and delay time are quick, which are 6.1 ms and 4.9 ms respectively, and the response curve is smooth under 10 v applied voltage. While in that of the VOPc aligned cell, the response intensity is lowered. The above mentioned electrooptic effects are concerned with the initial alignment of the LC molecules on different kind of Pc LB films.

Figure 8 shows the light transmission of the cells as a function of the applied voltage between crossed polarizers. There is a voltage threshold in either of the cells. The effective value is 1.6 v to SnPc aligned cell while 1.4 v to VOPc aligned one.

A TN type LC cell was assembled by placing two SnPc LB films coated substrates together with the deposition direction perpendicular to each other. When the applied rectangular voltage is 10 v, the rise time and

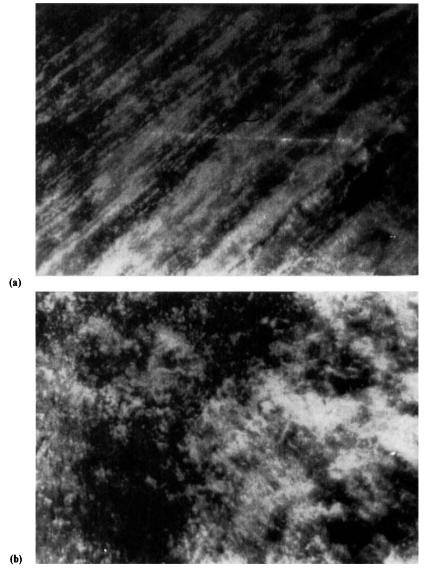


FIGURE 4 Polarized optical photographs of the cells aligned by different Pc LB films (a): SnPc (b) VOPc.

delay time are 5.0 ms and 3.8 ms respectively as shown in Figure 9. Compared with the AP type cell, it has a better electrooptic response.

Figure 10 is the voltage dependence of light transmission in the TN cell with crossed polarizers. The curve can be divided into three regions I, II,

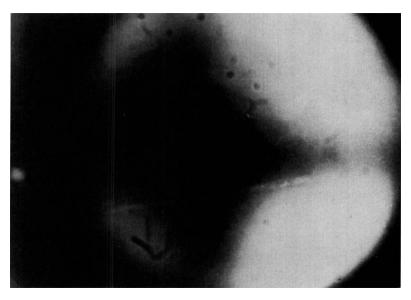


FIGURE 5 The conoscopic figure of VOPc LB films aligned cell.

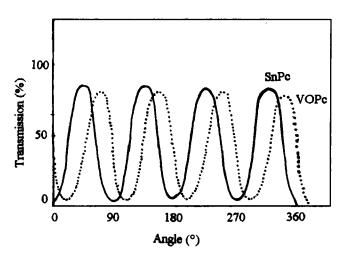
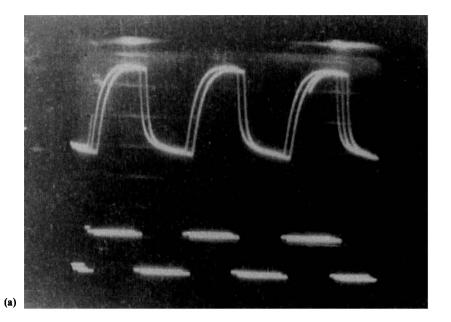


FIGURE 6 The relationship of light transmission with the cell's rotation angle between crossed polarizers in different Pc aligned cells.

III. In region I, there is no obvious response with the increase of voltage. When the applied voltage increases to 2.8 v, which is the threshold, the transmission begins to decline in region II. The transmission is almost extinguished in region III when the voltage is 5.7 v. The value is twice that of the threshold voltage.



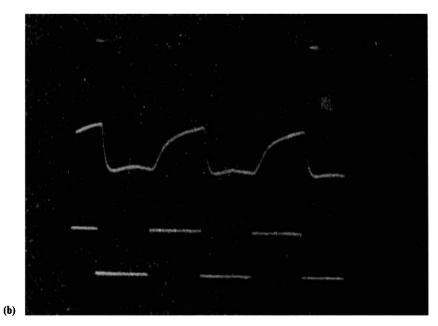


FIGURE 7 The electroptic response photographs of Pc LB films aligned AP type cells. The applied rectangular wave form is 25Hz. (a) SnPc (b): VOPc.

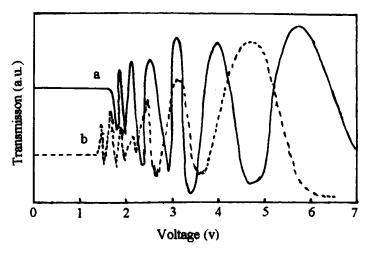


FIGURE 8 The curve of light transmission versus the applied voltage in Pc aligned AP type cells between crossed polarizers. (a): SnPc(b): VOPc.

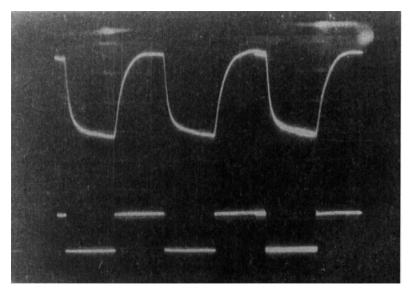


FIGURE 9 The electroptic response photograph of SnPc LB films aligned TN type cell.

4. CONCLUSION AND LC ALIGNMENT MECHANISM

We have adopted two Pc compounds, which have a similar molecular structure but with different complex metals, to fabricate AP type cells using the corresponding LB films as LC aligning layers. It is found that LC

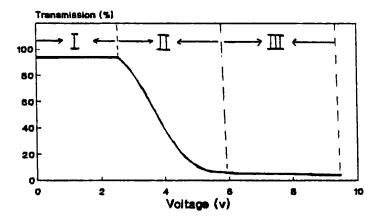


FIGURE 10 The voltage dependence of light transmission in SnPc aligned TN LC cell with crossed polarizers.

ZLI-1132 molecules are aligned homogeneously on SnPc LB films along the deposition direction while on that of VOPc LB films are aligned obliquely. SnPc LB films aligned cell shows a quiet good electrooptic effect.

Polarised UV-Visible spectra demonstrate that both SnPc and VOPc film molecules would orient with the almost same orientation angle on the substrates. Based on the experimental results, the mechanism that results in the different alignment configurations may be described as follows: Due to the existence of a complexed oxygen atom out of the Pc macrocycle plane in a VOPc molecules, the oxygen atoms in the LB films would have an instantaneous coupling with the injected polar LC molecules, and they can form a certain molecular interaction between them that belongs to the induced polar forces. Ignoring other types of interactions they may all have, the appearance of the above molecular interaction will make VOPc LB films have a stronger anchoring LC ability than SnPc LB films. Because the interaction is a short range force, it is not strong enough to anchor LC molecules a homeotropic orientation, but just shows an oblique alignment in the cell.

In addition, a TN type LC cell is realized using SnPc LB films as aligning layers. It is discovered that the cell has a quicker response time than an AP one. When the applied voltage is twice that of the threshold, the 90° twisting light ability will be exitinguished.

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