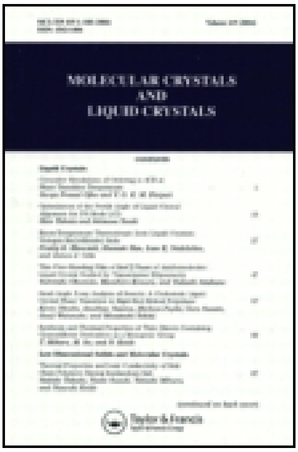

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Wenjun Zheng [a] , Cheng-Yan Chiang [a] & Ian Underwood [b]

[a] Photonics Department, National Sun Yat-Sen University, Kaohsiung, R.O.C.

[b] School of Engineering and Electronics, The University of Edinburgh, Edinburgh, UK

Version of record first published: 14 Jun 2011

To cite this article: Wenjun Zheng, Cheng-Yan Chiang & Ian Underwood (2011): Hybrid Molecular Orientation of Sandwich-Type Structure Discogen Hexaalkoxydibenzo[a,c]phenazine on the Surfaces Modified Using Silane Self-Assembly Monolayers, Molecular Crystals and Liquid Crystals, 540:1, 94-101

To link to this article: http://dx.doi.org/10.1080/15421406.2011.568344

Mol. Cryst. Liq. Cryst., Vol. 540: pp. 94–101, 2011
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.568344

Hybrid Molecular Orientation of Sandwich-Type Structure Discogen Hexaalkoxydibenzo[a,c]phenazine on the Surfaces Modified Using Silane Self-Assembly Monolayers

WENJUN ZHENG,[1] CHENG-YAN CHIANG,[1] AND IAN UNDERWOOD[2]

[1]Photonics Department, National Sun Yat-Sen University, Kaohsiung, R.O.C.
[2]School of Engineering and Electronics, The University of Edinburgh, Edinburgh, UK

Substrates were processed using hydrogen peroxide and coated with silane self-assembly monolayers to obtain different surface free energies. The face-on anchoring and edge-on anchoring of discogen 11,12-bisdodecyloxy-2,3,6,7-tetrakisoctyloxydibenzo[a,c]phenazine molecules were obtained on the peroxidized ITO surface and the surface covered by octadecyltrichlorosilane, respectively. It is demonstrated that substrates with patterned surface free energy template can be produced by stamp printing the silane onto and followed by a silanization process in situ on the substrates. Discogen domains with different types of columnar orientation are formed in a cell constructed using the substrates with patterned energetic template.

Keywords Columnar phase; columnar phase alignment; discotic liquid crystal; silane self-assembly monolayer

1. Introduction

Discotic liquid crystals (DLCs) that contain columnar superstructures formed by stacking of discotic molecules are versatile functional materials. In the one-dimensional oriented columnar structure, the parallel charge mobility along the column axes has been found to be much larger than the transverse one measured in the direction cross the disc surface [1–3]. Because of such superior conductivity in one direction, DLCs are considered to be useful materials for many important applications in molecular electronics and electrooptics devices, such as light emitting diodes [4–7], photovoltaic cells [8,9] and semiconductor transistors [10,11]. In most

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Address correspondence to Wenjun Zheng, Photonics Department, National Sun Yat-Sen University, 70 Lien-Hai Road, Kaohsiung 80424, R.O.C. Tel.: +886 7 5252000 ext 4445; Fax: +886 7 5254499; E-mail: wzheng@ymail.com

of above mentioned applications, a long range molecular ordering in a discogen is demanded in order to enhance the unidirectional charge-transport. For organic semiconductor devices, to manipulate different types of molecular alignment into a discogen layer to create effective charge transportation channels is crucial.

Over the years, great efforts have been made, and a variety of techniques, such as mechanical sheering [12], molecular growth in magnetic field [13], molecular epitaxial growth [14–16], use of friction pre-oriented poly(tetrafluoroethylene) (PTFE) [17,18], and the use of infrared laser [19,20] etc., have been tried in intending to form highly oriented structures in DLCs. Of the methods that exist for forming oriented columnar structures, however, few can be used to control stacking of discotic molecules locally to form columnar domains with desired orientational ordering. We approached this issue based on the consideration of surface characteristics of the substrate and the molecule/surface interaction.

When a discogen is put in contact with a surface, the way that the disc-like molecules anchored at the interface and the orientation of the discotic columns are determined by many factors, such as geometrical shape of the molecules, intra- and intermolecular interactions, surface topography of substrate, physicochemical and/or chemicophysical properties of the substrate, and molecule/surface interactions etc. It was shown that in the sandwich-type structure the discotic molecules tended to reside with the face-on anchoring at a high energetic surface, and to stand with the edge-on anchoring at a surface with low free energy [21,22]. This inspired us to modify the surface to obtain a substrate with patterned surface energy template for multi-domain alignment of DLC. Recently, we partially coated ITO glass substrates, which were peroxidized into highly energetic states, with a low surface free energy silane self-assembly monolayer (SAM) to produce surfaces consisted of regions with different surface free energies. We herein report the orientational stacking of discotic molecules in the cells constructed using such modified substrates. We demonstrate that with thermal conditions properly controlled, hybrid alignment discogen layers, with homogeneously and homeotropically aligned discotic columns co-existed, can be produced in a single cell.

2. Experimental

Substrates used in this study were flat ITO glass plates. The substrates were first immersed into freshly prepared 3:1 mixture of 96% sulphuric acid and 35% hydrogen peroxide (piranha solution) at 90°C for 30 minutes to increase the hydrophilicity of the substrate surface.

The silane compound octadecyltrichlorosilane (OTS), purchased from Alfa Aesar, was used for the preparation of SAMs. Solutions of 1 mM OTS was prepared by respectively dissolving the silane in anhydrous toluene. The monomolecular films can be grafted onto substrates by means of stamp-print technique. For this purpose, a slab of patterned polydimethylsiloxane (PDMS) was immersed into the silane solution for 30 seconds, and taken out and dried using a stream of nitrogen. The silane was then printed onto a peroxidized substrate by stamping the PDMS coated with the silane onto the substrate immediately after the silane solution being dried. To allow the silanization process to be completed, the PDMS stamp was kept on the substrate for 2 min by gently pressuring the stamp. The silanization processes for OTS SAM was taking 2 hours. After silanization, the substrates were washed by taking 5 min ultrasonic bath in anhydrous toluene, anhydrous ethyl, and deionized

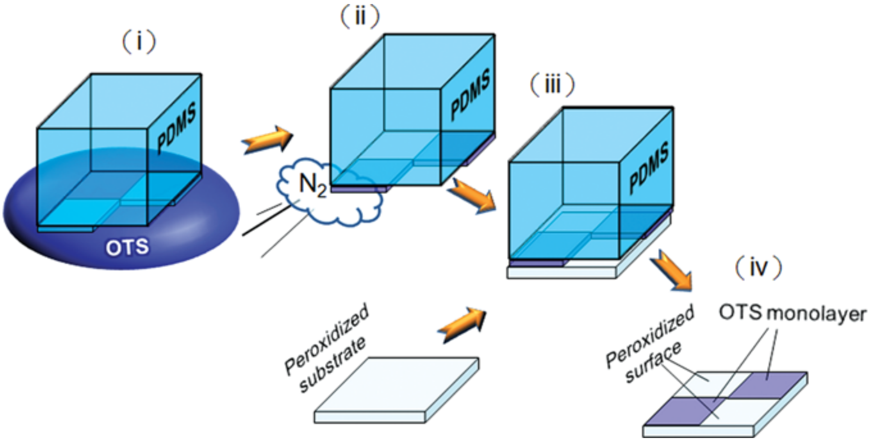


Figure 1. Procedure of stamp-print technique for the preparation of silane molecular monolayer on a substrate. (i) Immerse PDMS stamp in OTS solution for 30 seconds. (ii) Dry the stamp. (iii) Press PDMS stamp onto peroxidized substrate. (iv) Silanization and then clean and dry the substrate. (Figure appears in color online.)

water subsequently in order to remove surplus silane resided at the surface, and then dried in a 120°C oven for 5 min. In the stamp-print technique, the size and the shape of the silanized region on a substrate can be easily modified by patterning the PDMS seal. The procedure for the stamp-print technique is schematically shown in Figure 1. Surface free energy of the substrates was measured using a DSA100 surface tension meter (KRÜSS).

The test for the orientational stacking of discotic molecules on the substrates was carried out using discotic compound 11,12-bisdodecyloxy-2,3,6,7-tetrakisoctyloxydibenzo[*a,c*]phenazine (HDBP) [23], whose chemical structures and phase sequence are shown in Figure 2.

Sandwiched cells were made using two silanized substrates. The thickness of all cells used in the present study was set at 10 μm. The DLC was injected in to the cells

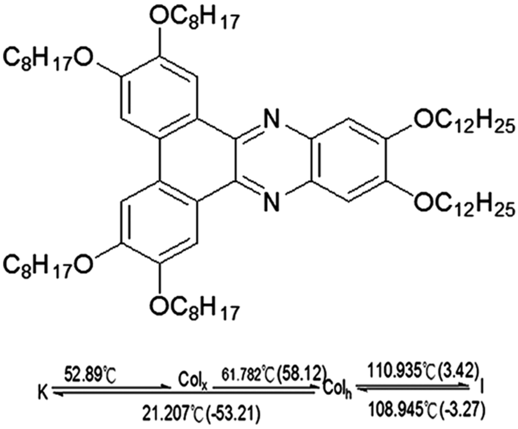


Figure 2. Chemical structure of 11,12-bisdodecyloxy-2,3,6,7-tetrakisoctyloxydibenzo[*a,c*] phenazine (HDBP) and the phase transition sequence of the discogen.

by capillary action at 120°C, which is well above the clearing temperature of the discogen. After the discogen was injected into cells, the samples were cooled down from the elevated temperature very carefully in a controlled way. The temperature of the samples was controlled using the Linkam TMS94 temperature system (Linkam Scientific Instruments Ltd). The texture of the samples was examined using a polarizing optical microscope (POM) Axioscop40 (ZEISS). Photomicrographs were taken using a digital camera (A620, Canon) that was mounted on the microscope.

3. Results and Discussions

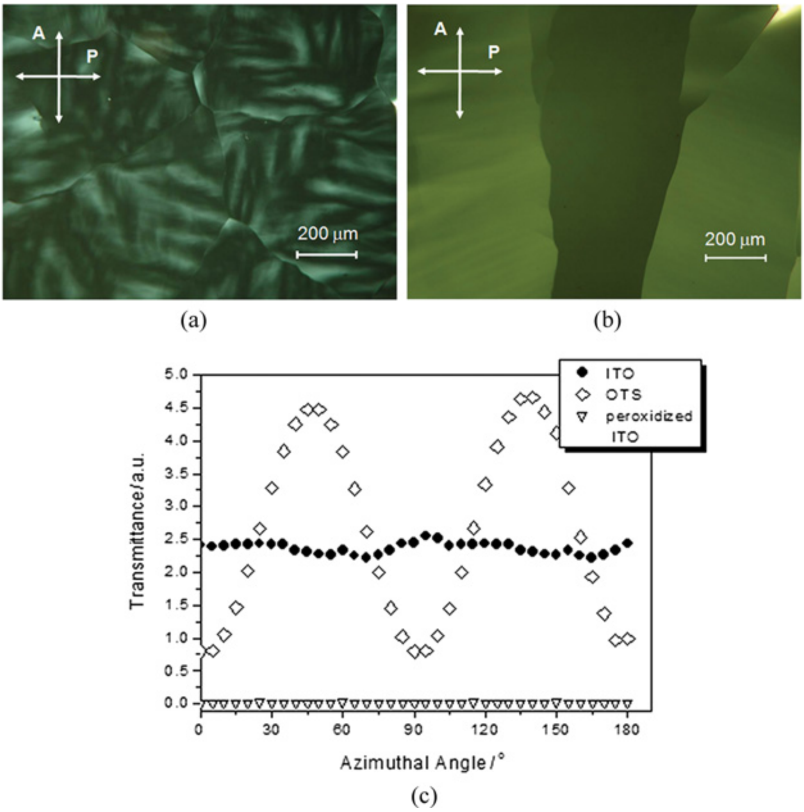
The surface free energies of the substrates treated by different materials were measured and are listed in Table 1. The ITO glass substrates used in the present study possess a surface free energy 40.98 mJ/m^2. The peroxidization treatment can markedly increase surface free energy to a value 65.26 mJ/m^2 and turned the ITO surface into a highly hydrophilic surface. On the other hand, the OTS monolayer can effectively reduce the surface free energy of the substrates to 20.8 mJ/m^2.

Cells were constructed using substrates treated using different materials, respectively. HDBP was then injected into the cells at 120°C. For routine tests, all samples were cooled down at a rate of 0.2°C/min to allow the discotic molecules to stack in the sandwiched structure. Figure 3a shows the optical texture of the HDBP in a cell constructed using ITO glass substrate. Domains can be observed in the sample. When the sample was rotated in the POM, the overall optical transmittance of the sample was nearly constant (Fig. 3c), however, the respective appearances for the domains became black and white alternately, and the changes in the appearance of the domains were out of phase from one domain to the other. Also a completed dark state for any domain cannot be reached because there is always certain amount of light leaking from these domains. The observed optical characters can be attributed to the molecular orientation of the columnar phase discogen. The periodical change in optical appearance of domains upon the sample rotating resulted from a molecular stacking structure in which the discotic columns arrange in the edge-on orientation in each domain. The non-vanished light transmittance of the domains is due to the optical axis, i.e., the discotic column axes, of each domain tilting a small angle (the pretilt angle) away from the substrate. The uniform appearance of each domain indicates that in each of these domains the dichotic columns orient in one direction, i.e., each domain has a unique orientational director with describes the average orientation of the columns in the domain. The non-synchronism azimuthal changes in light transmission for different domains indicate that the directors for different domains orient in different direction.

Figure 3b shows the optical texture of HDBP sandwiched between substrates covered by OTS monomolecular films. In this particular observed region of the sample, three major domains, all showing a very uniform optical texture, can be seen. The POM examination confirmed that the discogen in each of these domains are well

Table 1. Surface free energies of treated ITO substrates

Surface	Plain ITO	Piranha-treated ITO	OTS
Surface free energy (mJ/m^2)	40.98	65.26	20.8



(a) (b)

(c)

Figure 3. Optical textures of columnar phase HDBP layers sandwiched between (a) ITO glass plates, and (b) substrates coated with OTS monolayer, respectively. Both photomicrographs were taken while the samples were kept at 100°C. (c) Light transmittance for the columnar phase HDBP samples using ITO glass and OTS coated glass substrates, respectively. The measurement was carried out while the samples were kept at 100°C. (Figure appears in color online.)

homogeneously aligned with discotic columns orienting in a unique direction, however, the respective orientation directions for the three domains are not the same. When the sample was rotated in the POM, a periodical change in light transmittance was detected. Better contrast ratio of the maximum to the minimum optical transmission, as shown in Figure 3c, indicates that the enhanced edge-on anchoring of the discotic molecules and a better discotic column alignment can be obtained on the OTS monolayer coated surface whose surface free energy is much lower than that of plain ITO surface. To the other end, an increase in surface free energy of substrate will favour the face-on anchoring of the disc-like molecules and the formation of homeotropic alignment of discotic columns. This can be confirmed by allowing HDBP to stack in the test sample made using high energetic (65.26 $\mathrm{mJ/m^2}$) substrates peroxidized by the piranha solution. The discogen whose picture is not shown here exhibited a completed dark appearance, which was able to keep unchanged on rotating the sample, in the POM. This indicates that a truly homeotropic alignment of the columnar phase with all axes of discotic columns in the discogen parallel to the normal to the substrate.

In a previous report [24], we showed the effect of surface energetic state on the molecular anchoring and the orientation of the discotic columns. On a high surface free energy substrate, the molecules anchored with the disc faces of the molecules contacting the substrate surface, and further assembled into homeotropically aligned columnar phase. A decrease in the surface free energy of the substrate caused the discotic columns to tilt away from the normal to the substrate, and eventually the initial homeotropic aligned columns will degenerate into planar aligned columnar phase when the surface free energy is sufficiently low. The argument is again corroborated by the observed results of the disc-like molecules stacking on different substrates with different surface free energies.

In order to verify the possibility of producing different types of columnar arguments in single cell, we covered half of the peroxidized ITO glass with OTS monomolecular film to produce a substrate with half it becoming highly energetic and another half possessing very low surface free energy, and used the substrates to construct test cells. Figure 4 shows the picture of a sample in between two crossed polarisers. The type of molecular stacking of HDBP in the cell is clearly seen. In the high energetic region the dark appearance reflects a truly homeotropic alignment of discotic columns; whereas in the low surface free energy region covered with OTS the HDBP layer exhibits a fan shape texture, a typical optical image of a columnar phase in which the molecules anchor with disc edge contacting the surface and the discotic columns orient planarly [25]. While this report is writing up, experiments have been carried out on the use of substrates with certain surface energy patterns using different silane SAMs. Initial results show that similar results have been obtained by treating the substrate using combination of OTS and APS.

Efforts are still been making to achieve the homogenous alignment of the DLC with all columns orienting in a unique direction in the low surface free energy regions. Our preliminary results presented herein show that we are able to produce different types of columnar alignments, in terms of orientation of the discotic

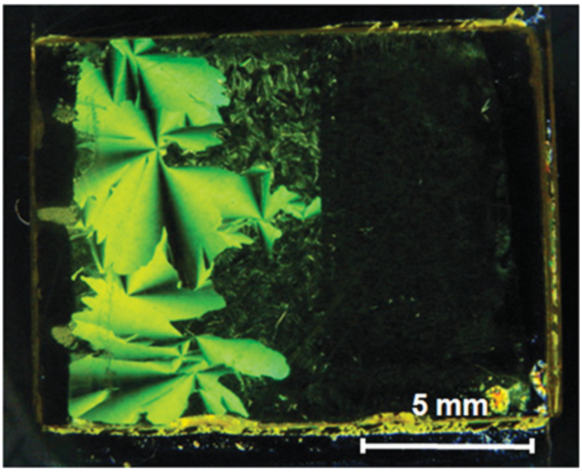


Figure 4. Photograph of HDBP layer in a cell constructed using substrates whose surfaces were preoxidized and then partially coated with OTS monolayer (on the left hand side of the sample in the picture). The sample was put between crossed polarizers, and kept at 100°C. (Figure appears in color online.)

columns, in a single cell. These results also show the possibility to attain a template for multi domain alignment of DLC by properly patterning surface free energy of the substrate.

4. Conclusions

We studied the molecular stacking of discogen HDBP in the sandwich-type structure, and show that the surface energetic state of the substrates is one of vital factors that determine the way the discotic molecules anchoring at the surface. At a substrate with a high surface free energy the discotic molecular will reside with disc surfaces touching the surface and form the face-on anchoring, whereas a low free energy surface can support an edge-on anchoring of the discotic molecules. A surface template comprising domains with different surface free energy levels can be produced by peroxidization process or coating the substrate with proper silanes. We demonstrate that domains with respective the edge-on and the face-on anchoring of HDBP molecules are attained on the surfaces covered with OTS SAMs and peroxidized by piranha in one cell. This provides the possibility of the multi domain hybrid molecular alignment for discotic molecular materials.

Acknowledgment

The authors acknowledge Prof Ong for kindly providing the discogen compound. The financial support from NEC of Taiwan through "Aim for Top Universities" scheme is also gratefully acknowledged. This study is funded by National Science Council of Taiwan (NSC982221E110008).

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