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Nicholas C. Maliszewskyj

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Structural phase transition in ultrathin films of disk-shaped molecules

NICHOLAS C. MALISZEWSKYJ, OKSANA Y. MINDYUK,
PAUL A. HEINEY*

Department of Physics of Astronomy and Laboratory for Research on the
Structure of Matter, University of Pennsylvania, Philadelphia PA 19104, USA

JACK Y. JOSEFOWICZ

Tyco Printed Circuit Group, 8636 Aviation Blvd., Los Angeles CA 90301, USA

PETER SCHUHMACHER and HULMUT RINGSDORF

Institut für Organische Chemie, Johannes Gutenberg Universität, 55099 Mainz,
Germany

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We have used grazing-incidence X-ray diffraction and atomic force microscopy to study Langmuir–Blodgett films of 2-(3-hydroxypropyl)oxy-3,6,7,10,11-pentapentyloxytriphenylene, a disk-shaped molecule which also forms a bulk liquid crystalline columnar phase. Upon heating, we observe a phase transition from a low symmetry ordered crystalline structure to a high temperature liquid crystal. The transition is reversible, with considerable hysteresis.

1. Introduction

Langmuir–Blodgett (LB) films have been studied for more than a century [1], but they continue to offer new surprises [2]. Although not manifestly amphiphilic, many of the disk shaped molecules which give rise to columnar liquid crystalline phases [3] have recently been demonstrated to spread as monolayers at the air–water interface in configurations such that adjacent molecules pack cofacially and individual molecules rest ‘edge-on’ to the interface [4–13]. Furthermore, when monomolecular films of discoid molecules are transferred to a solid support via the Langmuir–Blodgett vertical dipping technique, not only is the conformation at the air–water interface roughly preserved, but the molecules are often seen to organize in columns along the direction of deposition [4–6, 14, 15]. Such anisotropic films offer promise for applications as pressure sensors [16, 17], anisotropic conductors [18], and display devices [19]. The thermal properties of Langmuir and LB films are also of interest, due in part to the possibility of transitions between crystalline, liquid crystalline, and isotropic liquid phases. Two-dimensional melting of fatty acid LB films was recently observed via atomic force microscopy (AFM) [20], and melting of monolayer discotic

Langmuir films has been observed using Brewster angle microscopy and grazing-incidence X-ray diffraction (GID) [11].

Most structural investigations of these systems have been spectroscopic in nature. Other experiments have probed the layer structure of LB films of discotics using X-ray reflection techniques and have drawn indirect conclusions regarding the in-plane order [6, 21]. Existing studies of the in-plane structure have been performed almost exclusively on as-prepared specimens under ambient conditions. In this paper we present the results of *in situ* heating studies of ultrathin films of a disk-shaped compound in which the in-plane structure is monitored through X-ray diffraction (XRD).

We report a structural study of an ultrathin LB film of a discotic molecule. The liquid crystalline 2,3,6,7,10,11-hexa-alkoxytriphenylenes [22–24] generally form hexagonal columnar phases in the bulk, and were recently shown to be photoconductors with large and anisotropic charge carrier mobilities [25, 26]. If these derivatives are partially functionalized with hydrophilic side chains (e.g. with OH or carboxylic groups [12, 13, 27–29]), they form stable Langmuir monolayers at the air–water interface with a well-defined orientation of the molecules relative to the surface [12, 13]. We studied a 2,3,6,7,10,11-hexa-alkoxytriphenylene which was monofunctionalized with a C₃H₆OH group at the 2-position (figure 1). We

*Author for correspondence.

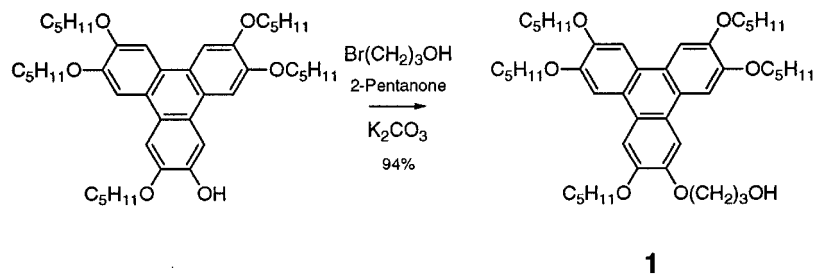


Figure 1. Structure and synthesis of compound 1.

used GID to monitor the inplane structure *in situ* as the film was heated, and AFM to explore the microstructure before and after heating. We observed a reversible melting transition from a two-dimensional crystal to a phase best described as liquid crystalline.

2. Experimental

2-(3-Hydroxypropyl)oxy-3,6,7,10,11-pentapentyloxytriphenylene (1, figure 1), was synthesized as follows. 2-Hydroxy-3,6,7,10,11-pentapentyloxytriphenylene (monohydroxytriphenylene [27]) was etherified with 3-bromopropanol according to the following procedure: 500 mg (0.74 mmol) of monohydroxytriphenylene, 0.16 g (1.11 mmol) of 3-bromopropanol, 2.05 g of potassium carbonate and 50 mg of potassium iodide were stirred for 5 h at 80°C in 15 ml of 2-pentanone. The mixture was filtered to separate non soluble inorganic materials. The residue was washed with dichloromethane, the combined filtrate dried over sodium sulphate, and the solvent evaporated. Column chromatography [(1) dichloromethane, (2) dichloromethane/acetic acid 19:1] yielded 509 mg (93.7%) of a white solid. The product was recrystallized from ethanol and petroleum ether.

Elemental analysis: Calcd. for $C_{46}H_{68}O_7$ ($M_w = 733.04$): C 75.37, H 9.35; found: C 75.26, H 8.01%; 1H NMR (200 MHz, $CdCl_2$): δ (ppm) = 7.83–7.79 (m, 6H, Ar-H), 4.43 (t, 2H, $OCH_2CH_2CH_2OH$, $J = 5.6$ Hz), 4.26 (t, 10H, OCH_2 , $J = 6.4$ Hz), 3.99–3.96 (m, 2H, $OCH_2CH_2CH_2OH$), 2.96 (s, 1H, OH), 2.27–2.15 (m, 2H, $OCH_2CH_2CH_2OH$), 2.01–1.88 (m, 10H, OCH_2CH_2), 1.60–1.39 (m, 20H, $OCH_2CH_2(CH_2)_2$), 0.96 (t, 15H, CH_3 , $J = 7.1$ Hz); FD-MS: m/z : 732.6 (100%) [M] † .

Langmuir films were prepared and surface pressure Π versus molecular area A isotherms were measured as previously described [8, 12, 13]. The sub-phase employed was Millipore purified H_2O (resistivity 18.2 $M\Omega$ cm). Small quantities (~ 100 μ l) of dilute solutions ($\sim 10^{-4}$ M) were delivered to the water surface using a Hamilton gas-tight syringe. Care was taken to prevent spreading drops from overlapping. At no point during the spreading process was the surface pressure observed to rise above 0.01 $mN\ m^{-1}$. Isotherms were measured several times at

10, 20, and 30°C and were found to be reproducible to within 5%. Films were transferred via the Langmuir–Blodgett vertical dipping technique at a surface pressure of 22.5 $mN\ m^{-1}$ onto Si wafers coated with a self-assembled monolayer of octadecyltrichlorosilane (OTS) [30]. Multilayer specimens were deposited through repeated insertion and withdrawal of the substrate through the Langmuir film. The transfer ratio for each layer was close to unity.

Atomic force images of the film surface were obtained using a Nanoscope III AFM [31] at 20°C, with a $1\ \mu m \times 1\ \mu m$ piezoelectric substrate translator having lateral and vertical resolution of less than 0.5 Å. The imaging experiments were performed using a silicon nitride tip in contact mode, with typical loads on the order of 10 nN. Images were recorded in several different areas on all samples. To determine that observed objects were not possible artifacts arising from AFM tip effects, the scan angle relative to the specimen was varied during the course of imaging.

Structural studies in both the bulk material and the LB films were performed using XRD. For studies of the bulk, small quantities (~ 10 mg) of dry power were loaded into a 0.7 mm glass capillary and the temperature controlled to within 0.25°C during the measurement. Powder diffraction measurements employed the $CuK_{\alpha 1}$ line at 1.5405 Å produced by an Elliott GX-13 rotating anode X-ray generator operating at 2.7 kW and monochromated using a singly bent LiF (2 0 0) monochromator crystal. The diffracted radiation was analysed with a flat LiF (2 0 0) crystal and collected in a scintillation counter. The resulting instrumental resolution was $\Delta q = 0.0045\ \text{\AA}^{-1}$ full-width-at-half-maximum (FWHM) † .

Studies of the in-plane structure were accomplished through XRD measurements in the grazing incidence geometry using beamline X9B at the National Synchrotron Light Source at Brookhaven National Laboratory, as previously described [12, 13, 32]. To minimize the effect of sample geometry, the samples were cleaved to a square shape before being mounted on the diffractometer.

† We use the convention $q \equiv (4\pi/\lambda) \sin \theta = 2\pi/d$.

For temperature-dependent studies the sample was affixed to an MMR heating stage [33] using thermally conducting paste. The incident wavelength was 1.5405 Å. We define the [0 0 1] crystallographic direction to coincide with the normal to the plane of the specimen, the [0 k 0] direction to lie in the plane of the film and coincide with the dipping direction, and the [h 0 0] direction to lie in the plane of the film, perpendicular to the dipping direction. GID patterns were measured with the incoming beam with the incident beam parallel to or perpendicular to the dipping direction, thus obtaining maps of the h 0 l and 0 k l planes in reciprocal space. For most measurements, the diffracted radiation was collected using Fuji image plates [34] with an effective pixel size of $200 \times 200 \mu\text{m}^2$. The instrumental resolution was approximately $\Delta q_L = 0.004 \text{ \AA}^{-1}$ FWHM along the [0 0 1] direction and $\Delta q_H = 0.007 \text{ \AA}^{-1}$ FWHM in the plane of the film. For measurements of in-plane orientational distributions, the diffracted radiation was analyzed using a flat Ge (1 0 0) crystal and collected using a scintillation counter, resulting in a tighter resolution of $\Delta q = 0.0006 \text{ \AA}^{-1}$ FWHM.

3. Results

Differential scanning calorimetry measurements established that bulk **1** has four phase transitions, measured on second heating, at 0, 45, 59, and 108°C. Bulk powder XRD measurements were made at 55 and 80°C (figure 2). The diffraction pattern at 55°C can be indexed to a crystalline orthorhombic lattice with basal plane lattice parameters $a = 36.96 \text{ \AA}$ and $b = 23.27 \text{ \AA}$. The structure at 80°C is characterized by a strong peak

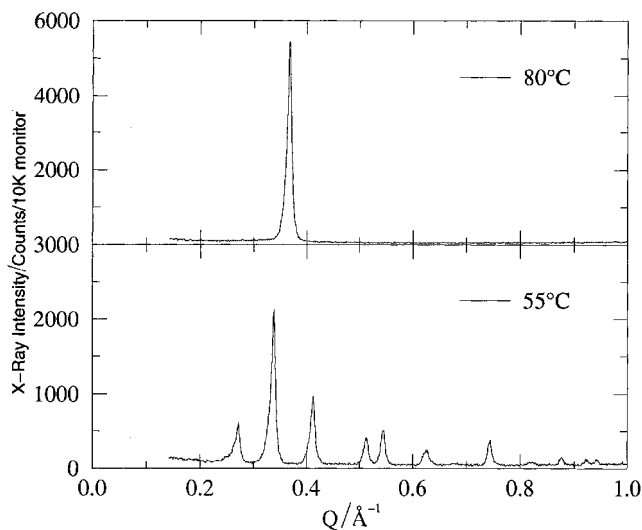


Figure 2. X-ray powder diffractograms of **1** at 55° and 80°C. The lower temperature structure is crystalline, probably orthorhombic; the higher temperature structure is that expected for a Col_{hd} hexagonal columnar liquid crystal.

at $q_0 = 0.3672 \text{ \AA}^{-1}$ and a very weak peak at $\sqrt{7}q_0$. These peaks clearly arise from a hexagonal columnar (D_{h}) liquid crystal [3], with a lattice parameter of 19.75 \AA , corresponding to a nearest neighbour distance of 17.1 \AA .

Surface pressure isotherms at the air–water interface were measured under conditions of varying temperature, as shown in figure 3. The relatively small molecular areas ($\sim 7\text{--}80 \text{ \AA}^2$) are consistent with a model in which the disks sit edge-on to the interface. They resemble those of the model hexapentyloxy compound and several of its derivatives [8, 12], which also exhibit a single rise to the collapse pressure. The relatively high ($\sim 55 \text{ mN m}^{-1}$) collapse pressures are most likely a consequence of the enhanced amphiphilic character of the molecule, brought on by the polarizable OH group at the end of one chain. The compressibility of the films is low, indicating the formation of a condensed (or solid-analogue) phase. As noted in other systems the collapse pressure increases with decreasing temperature, accompanied by a decrease in the film compressibility.

The substrates employed for LB film studies were Si wafers coated with monolayers of OTS. AFM studies of the OTS-coated surface showed that it was featureless with a root-mean-square roughness of $\sim 2 \text{ \AA}$. If kept in an inert atmosphere and in conditions of controlled humidity, LB films of **1** on OTS-Si were stable over a period of weeks, but were observed via AFM to have deteriorated significantly after having been stored in air for a year.

Figure 4 shows typical HOL GID patterns from an 8-layer LB film of **1** at different temperatures. We discuss first the pattern at 25°C, figure 4 (a); the higher temper-

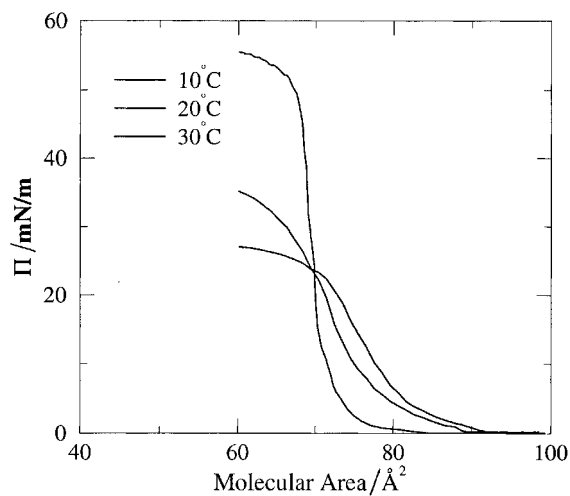


Figure 3. Pressure–area isotherms of **1** measured on pure water at different temperatures. The molecular areas are those expected for a structure in which the molecules are aligned edge-on to the air–water interface.

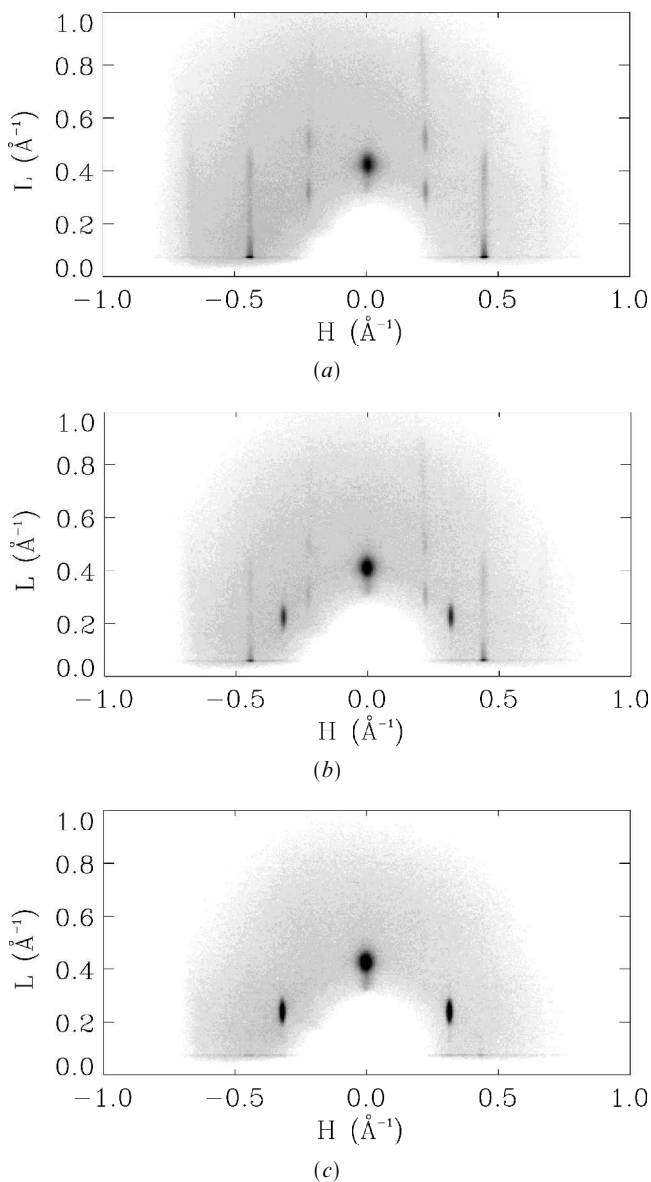


Figure 4. GID patterns from an 8-layer film of 1. (a) Pattern at 25°C; three orders of Bragg rods and a single 001 peak are visible. Modulations along the rods indicate strong interlayer correlations. (b) Pattern at 40°C, showing coexistence between low and high temperature structures. (c) Pattern at 45°C; Bragg rods at $\pm 0.342 \text{ \AA}^{-1}$ with sharp maxima at an azimuthal angle of 60° from the vertical indicate the presence of a hexagonal columnar phase with the columns parallel to the substrate.

ature profiles will be discussed in more detail below. The dark spot in figure 4(a) at $L \approx 0.64 \text{ \AA}^{-1}$ arises from the interlayer spacing, which ranges from 15.3 to 16.8 Å as the number of layers is increased. This is somewhat smaller than the bulk intercolumnar distance of 17.1 Å, and indicates either that there is substantial *gauche* character of the alkyl tails or, more likely, that the tails are splayed radially in the plane of the film rather

than extending radially from the core as would be expected in the bulk. Several orders of Bragg rods are observed, with the lowest order peak at $q_{10} = 0.2266 \text{ \AA}^{-1}$ ($d = 27.73 \text{ \AA}$). The most intense feature is seen at $q_{20} = 2q_{10}$, and lies on the equator rather than at finite L . Since a d -spacing of 28 Å is larger than any possible dimension of the molecule, the unit cell must contain several inequivalent molecules, possibly distinguished by different tilts [12]. Given the potential for hydrogen bonding of hydroxyl groups across adjacent layers, it is possible that molecules can dimerize out of plane as well. Modulations of the Bragg rods indicate substantial interlayer positional correlations. Although a detailed atomic structure could not be obtained from these measurements, the many orders of diffraction, the large size of the unit cell, and the presence of interlayer correlations are all consistent with an ordered crystalline structure of unknown but low symmetry. Since the transfer ratio was close to unity, and the molecular area at the air–water interface was roughly that expected for edge-on molecules, the structure is most likely columnar, with several columns per unit cell.

Figure 5 shows the orientational distribution of the diffracting planes within the film. This was determined by measuring the diffracted intensity in the second-order Bragg rod as the sample was rotated an angle ϕ about its normal. If the diffraction pattern arises from columns, as we anticipate, then a maximum at $\phi = 0$ would correspond to columns parallel to the dipping direction, as previously observed in monolayers of a closely related disubstituted triphenylene (“DBPOT” [14]) and other compounds [6, 7, 9, 10, 35–37]. Surprisingly, the intensity maxima are well away from $\phi = 0$, indicating that few if any of the columns lie along the dipping direction. We note, however, that AFM images of DBPOT bilayers [15] show square structures, which were interpreted as arising from sequential layers with the columns relatively

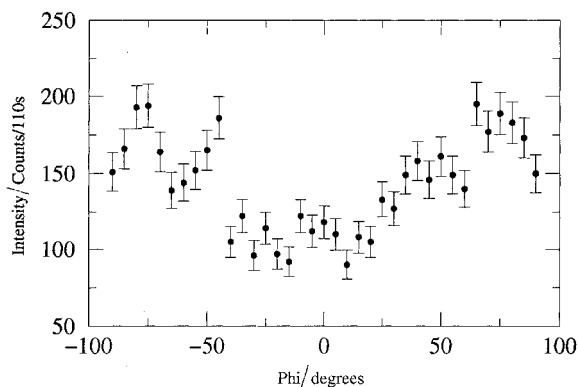


Figure 5. Orientational distribution of columnar order at room temperature, determined from the intensity dependence of the second intercolumnar Bragg rod as the sample is rotated by an angle ϕ about the normal to the surface.

perpendicular to each other. Clearly, the kinetics and energetics of LB film formation are complicated, and there is no simple rule that will allow one to predict the orientation of columns in an individual layer.

Figure 6 shows an AFM image of a 6-layer film of **1**, measured at room temperature. Since AFM is sensitive to the surface structure, the columns observed in this image reflect the structure of the topmost layer of the film. The columns have a 24 Å spacing, and are aligned along the dipping direction. The spacing is thus roughly consistent with the GID measurements, which averaged over the entire film, but the orientation of the topmost layer does *not* have the average orientation determined from GID.

On heating above 35°C, a second structure evolved. GID measurements at high temperature showed a pair of Bragg rods at $H = \pm 0.3240 \text{ \AA}^{-1}$ ($d = 19.40 \text{ \AA}$), together with a single strong maximum along the $0\ 0\ 1$ direction. The rods have strong maxima at $L = 0.187 \text{ \AA}^{-1}$, such that the angle between the rod maxima and the $0\ 0\ 1$ Bragg spot is close to 60°. The corresponding bulk structure at elevated temperatures is a hexagonal columnar D_{hd} liquid crystal, and the GID pattern we observe is that expected for a hexagonal columnar structure with the columns parallel to the substrate. While we have not unambiguously established the *lack* of intercolumnar correlations in the thin film, the absence of higher order diffraction peaks and the close congruence of our diffraction pattern with that expected for a hexagonal

columnar liquid crystal leads us to believe that the thin film should also be described as a confined D_{hd} phase.

GID patterns from an 8-layer film were measured at 5°C intervals between 25 and 55°C (figure 4). The low-temperature structure was observed between 25 and 40°C. The shape and positions of the peaks are essentially unchanged over this range. The high temperature structure was observed between 35 and 55°C (i.e. both sets of rods coexisted at 35 and 40°C). The high temperature peaks were observed to move and sharpen slightly as the temperature was increased, such that the d -spacing increased from 19.24(10) Å at 35°C to 19.49(10) Å at 55°C, and the correlation length increased from 90 Å to 115 Å over the same range. Similar effects were seen in a 6-layer film.

Over the 24 h time scale of the GID measurements the phase transition was *not* observed to be reversible. Indeed, the hexagonal phase persisted even after cooling to room temperature. Likewise, AFM measurements performed hours after a sample was heated revealed columns separated by $\sim 19 \text{ \AA}$ rather than $\sim 24 \text{ \AA}$, indicating the metastability of the high temperature phase. (These images were also considerably noisier than those measured before heating, and tended to indicate that the topmost layer had been oxidized or otherwise disturbed by the heating process). By contrast, AFM measurements performed a week or more after heating, on the same sample as used in the GID measurements, showed a columnar structure with an 24 Å spacing, showing that the film does eventually revert back to the low temperature phase. For example, the image in figure 6 was observed one week after heating and then cooling, but is virtually identical to images observed before heating.

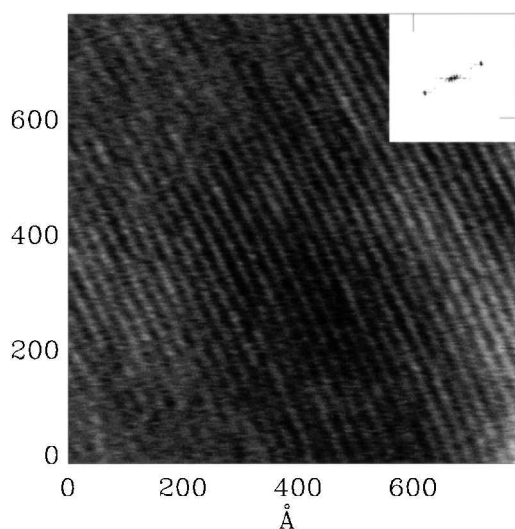


Figure 6. AFM image of a 6-layer film of **1**, measured at room temperature before heating. This image shows that the columns in the top layer are aligned along the deposition direction of the film, with an intercolumnar spacing of 24 Å. The inset shows a Fourier transform of the image; the sharp spots are indicative of coherence of the columnar order over the entire field of view.

4. Summary and discussion

We have made the first *in situ* observation of a thermally induced phase change in thin multilayer films of a disk-shaped molecule. At room temperature, as-deposited LB films of compound **1** exhibit a low symmetry structure with strong interlayer correlations. Upon heating above 40°C, we observe a phase transition to a structure analogous to the liquid crystalline columnar phase. The high temperature phase is metastable upon cooling over a several-hour time scale, but ultimately reverts to the original low temperature phase. This transition appears to mirror the 59°C transition observed in bulk samples of the same compound, but at a substantially lower temperature. The origins of the temperature difference are unknown, but presumably reflect the energetics of anchoring to the substrate.

Our observations provide an example of the extremely useful complementarity between AFM, which is a microscopic probe of surface morphology, and XRD, which is a macroscopic probe (in the sense that large surface

areas are probed) of structure throughout all layers of the film. The quantitative agreement in dimensions measured by these two techniques gives us added confidence in our results.

The factors governing column orientation remain an intriguing open question. Crystalline domains at the air-water interface are observed to be elongated streaks, with no average orientation in the absence of deliberately induced shear flow [11]. It is natural to expect that the columnar orientation along the dipping direction, seen in many columnar materials, arises from the reorientation of entire domains upon transfer to the solid substrate, but this may not always be the case. Molecule-substrate interactions, interactions between molecules in the same layer, and interlayer molecular interactions must all play a role. The role of the intralayer structure (crystalline, liquid crystalline, or liquid) in determining the structure and orientation of the deposited film should also be a subject for future investigation.

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