Studies on ultrathin films of tricycloquinazoline (TCQ) based discotic liquid crystal molecules

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Abstract. The assembly of disk-shaped molecules on surfaces has drawn considerable attention because of their unique electro-optical properties. We have studied the monolayer of the tricycloquinazoline based disk-shaped (TCQCB) molecules at air-water and air-solid interfaces. The TCQCB molecules form a stable Langmuir monolayer at the air-water interface. The monolayer exhibits gas, low density liquid (L_1), and high density liquid (L_2) phases. In L_1 and L_2 phases, the molecules prefer edge-on conformation. The atomic force microscope study on the Langmuir-Blodgett films of the molecules reveals a structural transformation. The elongated domains in the film deposited in L_1 phase transformed to a compact grainy texture in the film deposited in the L_2 phase.

1. Introduction

The field of disk-shaped (discotic) liquid crystals has grown enormously because of the interesting electrical and optical properties of the molecules. Depending on the temperature, the discotic molecules assemble itself onto solid substrates yielding various columnar phases [1]. The charge mobility along the length of the column has been found to be enormously high when compared to its perpendicular direction. This makes such columnar system to act as a semiconducting material with a very high value of anisotropy in the conducting property. The discotic liquid crystals find potential industrial application in the fields of opto-electronics and photovoltaic devices such as light emitting diodes [2, 3], field-effect transistors [4], solar cells [5] and sensors [6]. Mostly, the cores of commonly studied discotic molecules are rich in π-electrons, and such molecules are known to behave as a p-type semiconductor with appropriate doping [7, 8]. The tricycloquinazoline (TCQ) based molecules are deficient in π-electrons and are reported to behave as a n-doped semiconducting material [9, 11, 12]. The nature of aggregation of the molecules on the surface is important for the device applications. The surface can induce an ordering in the bulk, and hence the material properties can be varied by varying the structure of aggregates on the surface [13, 14]. The surface behavior of such molecules are relevant and demands a systematic study. We have studied the behavior of TCQ core substituted with cyano-alkyloxybiphenyl (TCQCB) molecules on the surfaces like water and glass. A stable single layer of molecules at an air-water (A-W) interface is known as Langmuir monolayer [15]. The Langmuir monolayer at different phases can be transferred to a variety of solid substrates in a highly controlled manner by vertical dipping mechanism known as Langmuir-Blodgett (LB)

technique [15, 16]. There are numerous studies on the Langmuir monolayer of the disk-shaped molecules at the A-W interface [17, 18, 19, 20, 21]. Such systems are known to exhibit monolayer phases where the disk-plane of the molecules are either planar to the water surface (face-on conformation) or it is perpendicular to the water surface (edge-on conformation).

In a study on ethylenoxy substituted side chains of TCQ core, we have found a stable Langmuir monoayer at the A-W interface. Our studies have revealed a face-on molecular conformation in a low density liquid phase. Interestingly, the molecular conformation in a high density liquid phase were found to be both face-on and edge-on [22]. In this paper, we report our study on the Langmuir monolayer of TCQCB molecule. The Langmuir monolayer of the molecule at A-W interface exhibits a low density and a high density liquid phases where the molecules prefer edge-on conformation. The AFM images reveal a structural transformation from elongated domains to very compact grainy texture for the LB films deposited in the low and high density liquid phases, respectively.

2. Experimental

The cyano-alkyloxybiphenyl substituted TCQ based amphiphilic (TCQCB) molecule was synthesized in the laboratory [10, 11, 23, 24]. The chemical structure of the molecule is shown in Figure 1. The molecule possesses six polar cyano-alkyloxybiphenyl side-group symmetrically
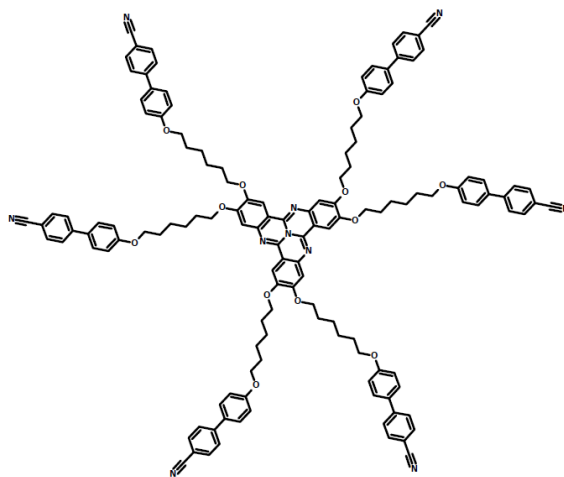

Figure 1. The chemical structure of the TCQCB molecule.

attached to the TCQ core so that it retains its C_3 fold symmetry. Such a novel covalently linked rod-disk oligomer exhibited a nanophase segregated liquid crystalline phase wherein the rods and disks are segregated into separate layers to form a smectic phase (SmA). The TCQCB molecules exhibit liquid crystalline phase while cooling from isotropic phase (I): I 173.4 °C SmA 169.5 °C cubic 156.4 °C crystal. The diameter of the TCQCB molecule is found to be around 5.3 nm. A solution of the sample was prepared in HPLC grade chloroform having a concentration of 1.7×10^{-5} M. The monolayer at the A-W interface was formed by spreading the solution onto the ultrapure ion-free (Millipore, DQ5) water having the resistivity greater than 18 MΩ-cm. The surface pressure (π) - area per molecule (A_m) isotherms were obtained by compressing the monolayer at the A-W interface in a Langmuir trough (LB2004C, Apex Instruments). The compression speed was maintained at 0.5 (nm²/molecule)/min. A high resolution microscopy was done by transferring the monolayer onto very clean solid (glass coverslip) substrates, and obtaining the topographic images of the films using atomic force microscope (AFM). Prior to deposition, the glass coverslip substrates were treated hydrophilically by boiling them in piranha

solution (3:1, conc H_2SO_4:H_2O_2) for 1 minute, and then rinsed successively with ion-free water, absolute alcohol and acetone solvents. The substrates were then dried by blowing hot air at 70 °C. The average root mean square roughness of glass coverslip substrates were found to be $\sim$ 0.1 nm for a scan range of 1.0×1.0 μm^2. This indicate a reasonably smooth surface of the glass coverslip [25]. We deposited a single layer of LB films on these substrates at different surface pressures by a single upstroke of the dipper. The film deposited substrate was transferred to the scanning stage of AFM, (Solver P47-Pro, NT-MDT) for imaging. The AFM imaging were done in semicontact mode in ambient. The spring constants and the resonance frequencies of the Si tips were in the ranges of 10-20 N/m and 180-270 KHz, respectively. The experiments were carried out at the room temperature ($\sim$22 °C).

3. Results and Discussion

The surface pressure (π) - area per molecule (A_m) isotherm of TCQCB molecules is shown in Figure 2. The isotherm shows zero surface pressure at very large A_m. It shows a lift-off area
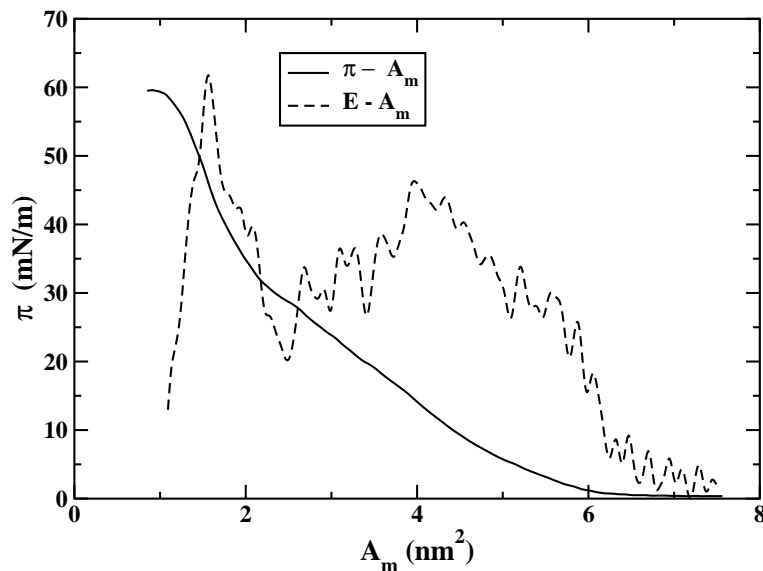

Figure 2. Surface pressure (π) - area per molecule (A_m) isotherm (solid line) and inplane elastic modulus (E) - A_m of the TCQCB molecule (dashed line).

per molecule (A_i) at around 7 nm^2. On decreasing the A_m, the isotherm indicates a change in the slope and then followed by a gradual rise in surface pressure. This region of the isotherm may corresponds to a low density liquid (L_1) phase. On further decreasing the A_m, another slope change is obtained at 30 mN/m. The surface pressure rises rapidly till the monolayer collapses at around 58 mN/m. This region of the isotherm may corresponds to a high density liquid (L_2) phase. The average molecular area in a phase can be estimated by extrapolating the corresponding region of the isotherm at the zero surface pressure [15]. The extrapolation of the region of the isotherm between 6 to 2.2 nm^2 to zero surface pressure yields an A_m value of around 5.6 nm^2 (=A_o^1). The extrapolation to the zero surface pressure of the rapidly increasing surface pressure region of the isotherm yields a limiting area per molecule of around 3.0 nm^2 (=A_o). The isothermal in-plane elastic modulus (E) is an appropriate quantity for distinguishing very weak phase transitions [26]. It is defined as $E = -A_m \frac{d\pi}{dA_m}$. The maximum value of E in the L_1 and L_2 phases were obtained as 46 and 61 mN/m, respectively. These are relatively smaller as compared to a commonly studied molecule, octadecanoic acid. The maximum values of E of

octadecanoic acid in the liquid expanded and liquid condensed phases were found to be 100 and 400 mN/m, respectively. This indicates that the observed L_1 and L_2 phases are more fluidic as compared to that of liquid expanded phase of octadecanoic acid. For a face-on conformation of the TCQCB molecules on the water surface, the average molecular area should be around 22 nm^2. However, the π - A_m isotherm of the TCQCB molecule indicates the average molecular areas in L_1 and L_2 phases to be around 5.6 and 3.0 nm^2, respectively. Such smaller average molecular areas in the different phases can be accounted for by the edge-on conformation of the molecules. Therefore, the L_1 and L_2 phases are low density and high density liquid phases wherein the TCQCB molecules exhibits edge-on conformation.

The stability of the Langmuir monolayer of TCQCB molecules on water subphase is studied by repeatedly compressing and expanding the monolayer and recording the corresponding surface pressures. The results from such isocycles are shown in Figure 3. The isocycle studies of
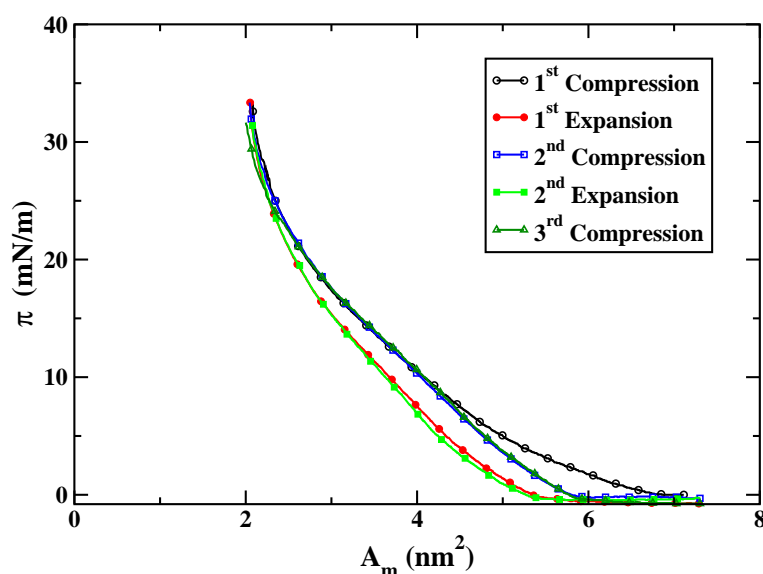

Figure 3. Isocycles obtained during repeated compression and expansion of the TCQCB monolayer at A-W interface.

TCQCB indicate that after the first compression, the expansion and compression curves remain unchanged at higher cycles. The isocycles also show negligible loss due to either dissolution or 3D aggregation. This indicates a better stability of TCQCB monolayer at the A-W interface.

The LB films of the TCQCB molecules are deposited on glass coverslip at different target surface pressure (π_t), and scanned using an AFM. The LB films are deposited in the L_1 and L_2 phases. These are shown in Figure 4. The AFM image of the LB films deposited at 10 mN/m (Figure 4A) shows the bright domains grown over a less bright background. The average height of such bright domains is 5.2±0.3 nm. This height corresponds to a vertical orientation of TCQCB molecules. The average height of the less bright region is around 3 nm. This can be accounted for by a tilt of the molecules. The bright domains do not show any preferential growth direction, and are found to be grown randomly. The morphology of the domains are found to be changed with the increase in π_t. The less bright region appear to vanish whereas the randomly grown bright domains assemble to yield interesting pattern. The AFM image of LB films of TCQCB molecules at 20 mN/m (Figure 4B) shows the domains to be elongated and oriented in a preferential direction. The height variation data also reveal that the average height of such elongated domains to be around 5.5 nm. With the further increase in π_t (= 30 mN/m), the elongated domains appear to be vanishing. This can be observed from the Figure 4C. The
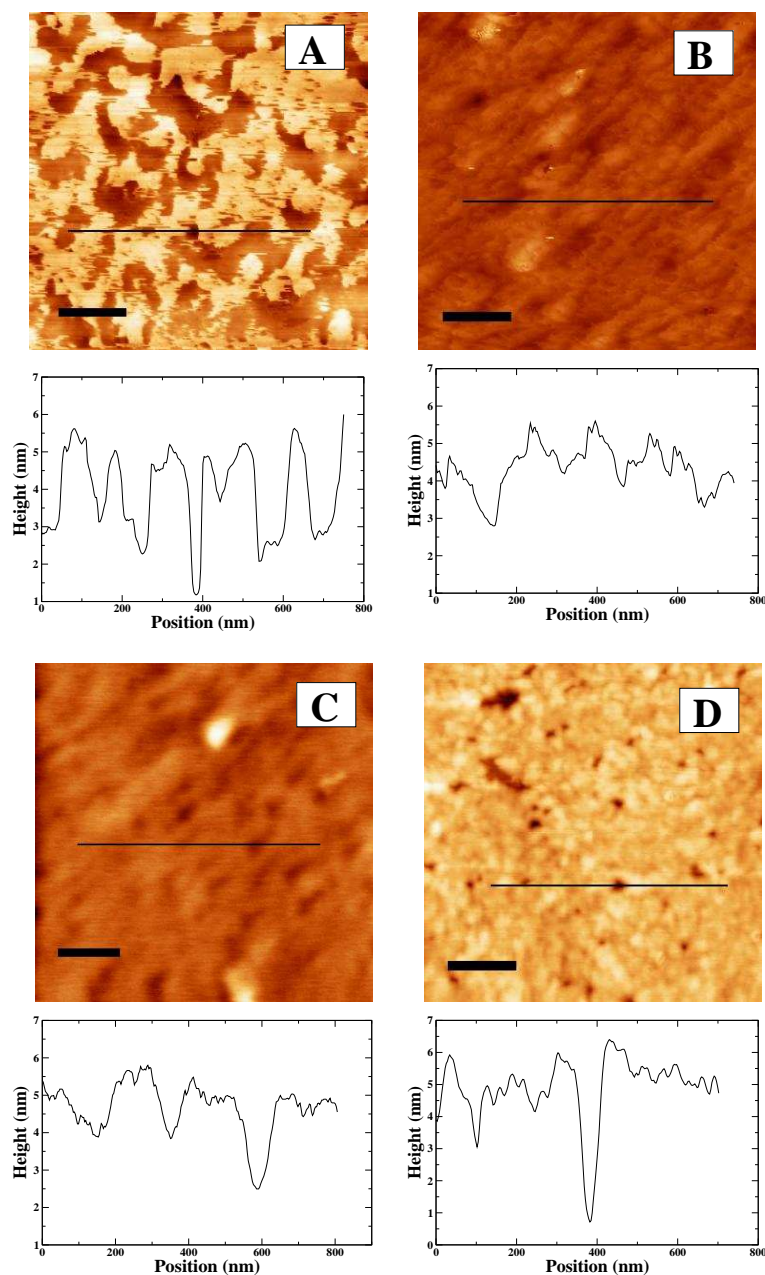
Figure 4. AFM images of LB films of TCQCB molecule. The target surface pressure (π_t) for LB films deposition corresponding to the images A, B, C and D are 10, 20, 30 and 35 mN/m, respectively. The height profile along the dark line drawn on the images are shown below the respective images. The scale bar represent a length of 200 nm.

AFM image at 35 mN/m (Figure 4D) reveal grainy texture wherein the elongated domains as observed in Figures 4(B - C) have completely transformed to isotropic small grain-like domains. The $\pi_t = 30$ mN/m is close to the L_1-L_2 phase transition. Therefore, the elongated domains as observed in the L_1 phase undergo a structural transformation to very compact grainy and isotropic texture in the L_2 phase.

The π-$A_m$isotherm of TCQCB molecules has indicated the low density L_1 phase where the molecules exhibit edge-on conformation. Because of the low density of L_1 phase, when the LB

films were deposited at the low surface pressure ($\leq$10 mN/m), two regions were obtained: region with vertically oriented molecules and region with tilted molecules. With the increasing π_t, the titled region vanishes and interesting domains with vertically oriented molecules were obtained. The LB films deposited in L$_1$ phase at a higher π_t (>10 mN/m) exhibited elongated domains. Such domains undergo a structural transformation to a compact grainy texture in the LB films deposited in L$_2$ phase.

4. Conclusions

We found a stable Langmuir monolayer of TCQCB molecules. The monolayer exhibits gas phase, a low density liquid (L$_1$), and a high density liquid (L$_2$) phases. The molecular orientation in L$_1$ and L$_2$ phases were found to be edge-on. The AFM images of the LB films deposited at $\pi_t \leq$ 10mN/m reveal the domains with vertical and tilted orientation of molecules. With increasing π_t, the elongated domains were observed. The elongated domains as observed in L$_1$ phase undergoes a structural transformation to form a dense grainy texture in L$_2$ phase.

5. Acknowledgments

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