Chapter 7

Monolayer of disk-like mesogenic molecules

7.1 Introduction

Discotic liquid crystals, which were discovered in 1977 [1], have drawn lot of attention. These liquid crystals exhibit various columnar phases [2]. The charge mobility along the length of the column has been found to be very high when compared to its perpendicular direction. This makes a columnar system to act as a semiconducting material with a very high value of conducting anisotropy. There are few studies on the bulk liquid crystalline properties of tricycloquinazoline (TCQ) based discotic mesogens [3–5]. The TCQ based molecules are electron deficient and are reported to behave as a n-doped semiconducting discotic liquid crystal [3, 6]. The TCQ molecule is also biologically active and is known to intercalate with DNA, leading to a carcinogenic effect.

This chapter deals with studies on the monolayer properties of the TCQ based amphiphilic discotic (AmTCQ) liquid crystal at the air-water (A-W) and solid-air interfaces.

7.2 Experimental

The TCQ based mesogenic molecule, 2,3,7,8,12,13-hexakis[2-(2-methoxyethoxy)ethoxy)]-tricycloquinazoline (AmTCQ) was synthesized in the chemistry laboratory of our Institute [7]. The chemical structure of the molecule is shown in Figure 7.1. The molecule possesses six polar ethylenoxy side-chains which are symmetrically attached to the TCQ
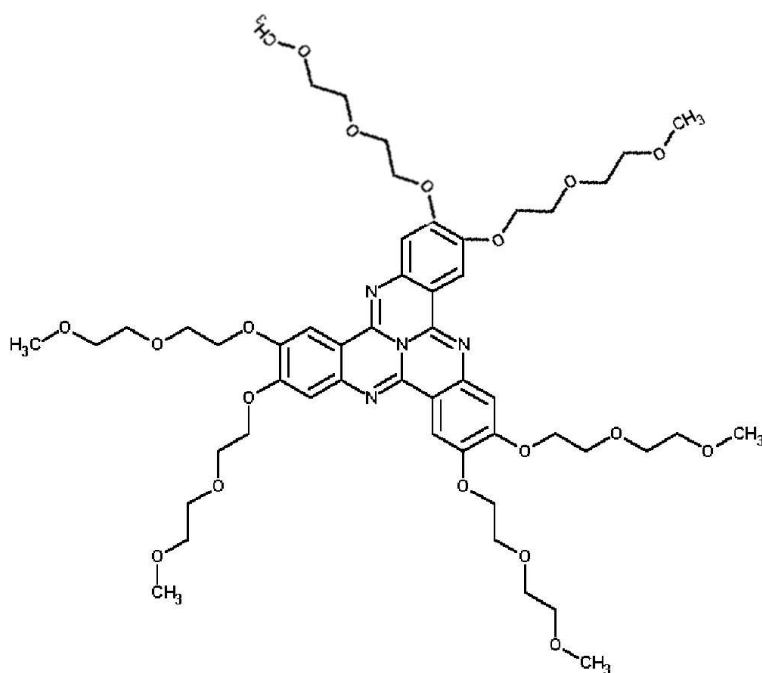
Figure 7.1: Chemical structure of AmTCQ molecule.

core so that it retains its C_3 fold symmetry. It shows a hexagonal columnar phase in the temperature range of 77 to 233 °C. The separation between the molecules in a column is 3.3 Å [4]. The radius of the central TCQ part of the molecule is about 5 Å. The length of the ethylenoxy side-chain is around 10 Å [8]. A solution of the AmTCQ was prepared in HPLC grade chloroform having a concentration of 9.7×10^{-5}M. The monolayer at the A-W interface was formed by spreading the solution on the ultrapure ion-free water surface. The monolayer was compressed at 25.6 (Å^2/molecule)/min. The area relaxation curve at a constant surface pressure was obtained by holding the surface pressure of the monolayer at a given value and monitoring the change in the A_m. The change in A_m is normalized by dividing the value of A_m at a time t (A_t) with its initial value at time equal to zero ($A_{t=0}$). The equilibrium spreading pressure (ESP) experiment was performed using a tensiometer (NIMA ST9000). The tensiometer along with a homemade mini teflon trough were housed in a sealed plexiglass box. The evaporation of the water from the mini trough was reduced by maintaining a high relative humidity inside the sealed box. The finely grounded crystalline powder of the AmTCQ molecule was sprinkled on the ion-free water surface and the surface

pressure was monitored with time. The temperature and the relative humidity measured during the ESP experiments were 24 °C and 90 %, respectively. The details of surface manometry and the microscopy experiments have been discussed in the previous chapters. The LB film was prepared on highly oriented pyrolytic graphite (HOPG) at a target surface pressure of 1.0 mN/m. On attaining the target surface pressure, the monolayer was allowed to equilibrate for 15 minutes. The dipper speed was maintained at 2 mm/min. Since HOPG is hydrophobic in nature, one layer of LB film was transferred by the first downstroke of the dipper. The details of one layer of LB film preparation on HOPG substrate have been discussed in chapter 6. The LB film deposited substrate was immediately transferred to the home built scanning tunneling microscope (STM) stage for imaging. Details of STM imaging are also discussed in chapter 6.

7.3   Results

The surface pressure (π) - area per molecule (A_m) isotherm of the AmTCQ monolayer is shown in Figure 7.2. The isotherm shows a lift-off area per molecule (A_i) at around
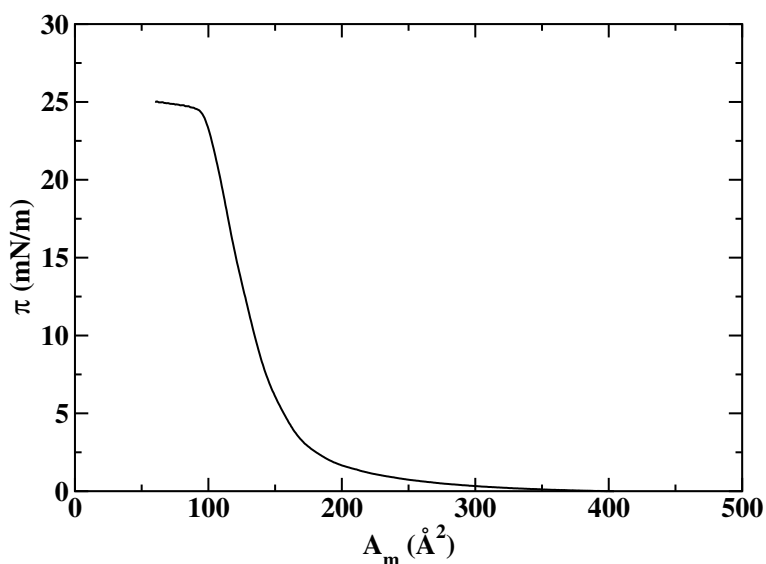

Figure 7.2: Surface pressure (π) - area per molecule (A_m) isotherm of the AmTCQ monolayer.

350 Å^2. With decreasing A_m, the surface pressure rises gradually, and at around 175 Å^2, it rises steeply. The monolayer collapses at around 96 Å^2 with a collapse surface pressure of

24.3 mN/m. The extrapolation of the region of the isotherm (at 250 Å^2) corresponding to the gradual increase in surface pressure yields an A_m (A_o^1) value of 314 Å^2. The extrapolation of the steep region of the isotherm yields the limiting area per molecule (A_o) to be 160 Å^2.

The Brewster angle microscope images of the monolayer of AmTCQ molecule at different A_m are shown in Figure 7.3. Immediately on spreading the molecules on the water surface, the entire field of view in the BAM shows an uniform gray texture. Figure 7.3(a) shows an uniform gray texture at a large A_m. This gray texture appears in the region of the isotherm corresponding to the gradual rise in surface pressure. On compression, the

(a) A_m=250 Å^2 (b) A_m=180 Å^2

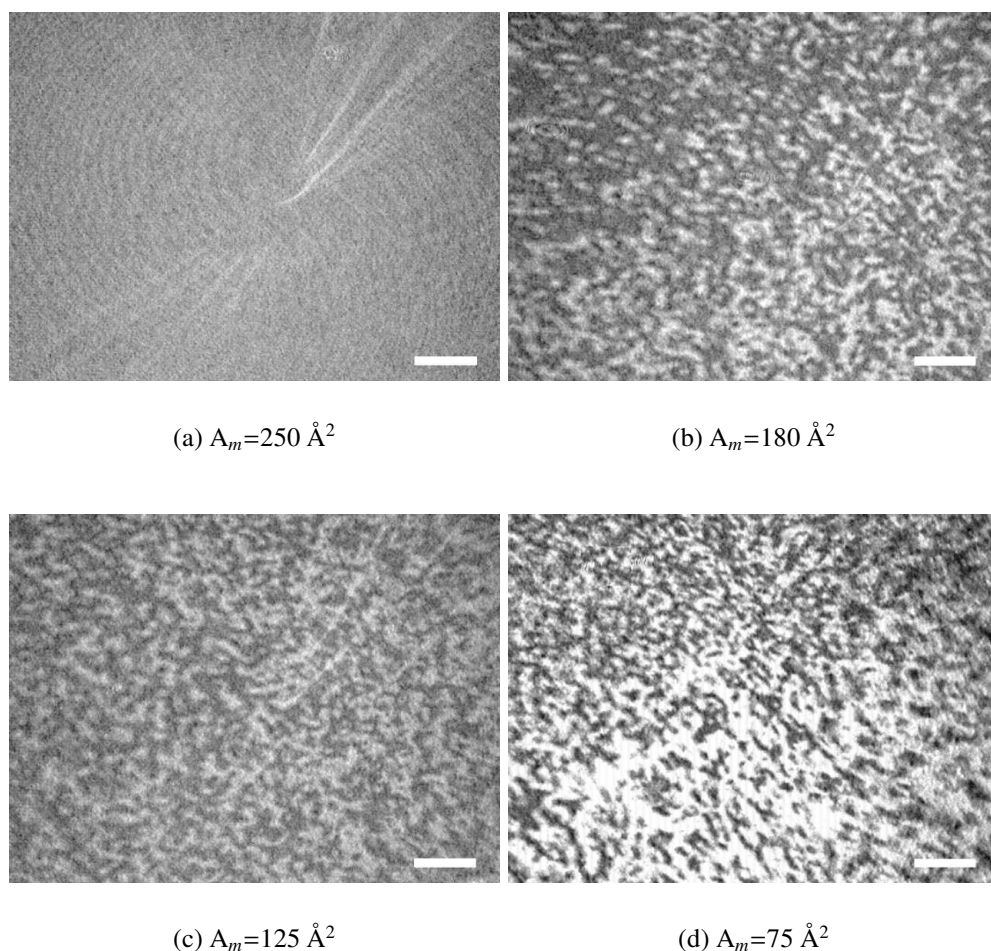(c) A_m=125 Å^2 (d) A_m=75 Å^2

Figure 7.3: BAM images of the AmTCQ monolayer on the ion-free water. The images were captured at an A_m shown below the respective images. (a) shows a very uniform gray texture. (b) shows a coexistence of bright domains in the gray background. (c) shows the coexistence of bright domains on the gray background in the steep region of the isotherm. (d) shows a collapsed state. In the collapsed state very bright 3D domains are seen to coexist with some gray domains. The scale bar represents 500 μm.

BAM image (Figure 7.3(b)) shows some bright domains growing on the gray background. This appears at a point corresponding to the onset of steep rise in surface pressure in the isotherm. The region of the bright domains was seen to increase with decreasing A_m. However, the gray region continues to exist even in the steep region of the isotherm (Figure 7.3(c)). The monolayer collapses on further compression, showing very bright 3D domains (Figure 7.3(d)) coexisting with gray region in the background.

The stability of the AmTCQ monolayer at the A-W interface was studied by monitoring the change in the A_m at a given surface pressure. Figure 7.4 shows a variation in the normalized area ($A_t/A_{t=0}$) with time (t). The variation in the normalized area with time
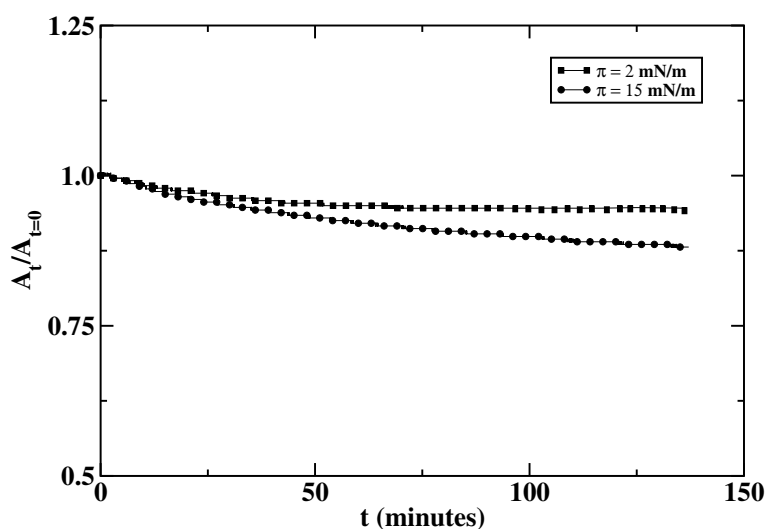

Figure 7.4: Variation of normalized area ($A_t/A_{t=0}$) with time (t) at different surface pressures (π). Here, A_t is the A_m at a time t and $A_{t=0}$ is the initial A_m.

indicates a very small reduction in the value. Considering a linear dependence of the normalized area with time, we find rates of reduction in the area to be 0.05% and 0.092% per minute at the surface pressures of 2 and 15 mN/m, respectively. The variation of surface pressure with time to determine the equilibrium spreading pressure (ESP) of the AmTCQ molecule is shown in Figure 7.5. Within a minute after placing the AmTCQ crystallites on the water surface, the surface pressure rises to a high value of about 22 mN/m. Then, with increasing time, the surface pressure decreases slightly. Further, at a longer time, surface pressure saturates to a value of 20.5 mN/m. This is the ESP value of the AmTCQ molecule.
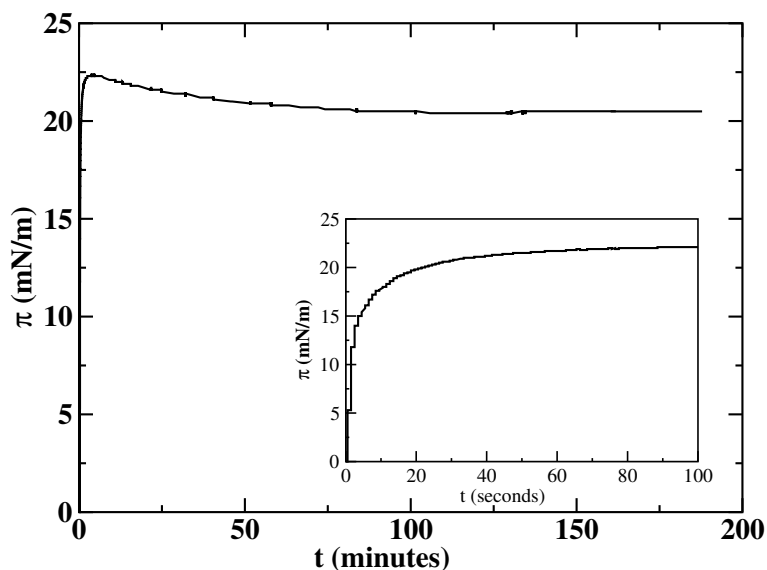
Figure 7.5: Variation of surface pressure (π) with time (t) during the determination of the equilibrium spreading surface pressure (ESP). The inset shows a rise in the surface pressure during the initial stage.

We have taken scanning tunneling microscope images of the Langmuir-Blodgett (LB) film of the AmTCQ molecules transferred onto a HOPG substrate at a target surface pressure of 1 mN/m. Figure 7.6 shows the STM image of the LB film of the AmTCQ molecules. The image shows a very high degree of ordering of the AmTCQ molecules.

7.4   Discussion

The surface manometry shows that the AmTCQ molecules form a stable monolayer on the ion-free water yielding a collapse pressure of about 24 mN/m. The AmTCQ molecules on the ion-free water surface yields a high value of ESP (20.4 mN/m). The kinetics during the measurement of ESP suggest a very high degree of spreading capability of the molecule at the A-W interface. The stability of a monolayer at A-W interface can be determined by monitoring the area-relaxation of the monolayer by holding the monolayer at a given surface pressure [9]. The variation of the normalized area at different surface pressures shows negligible rate of decrease. The small reduction in the value can be attributed to the relaxation of the molecules in the monolayer. These results show that the AmTCQ molecules form quite a stable monolayer at the A-W interface. The possible conformations

Figure 7.6: The scanning tunneling microscope image of the LB film of the AmTCQ molecules. The image was scanned in the constant-current mode with a bias voltage of 500 mV and a tunneling current of 1 pA. The size of the image is 6×6 nm^2

of the disk-like molecules on the water surface are depicted in Figure 7.7. The prependicular and planar conformations of the molecules are termed as edge-on and face-on, respectively. If the AmTCQ molecules lie planar at the water surface (face-on conformation) with the flexible side-chains being interdigited with the neighboring molecules, the area per molecule is expected to be around 305 Å^2. If the molecule confines itself in an edge-on conformation, the area per molecule could be around 90 Å^2. On compressing the monolayer of AmTCQ molecules, the surface pressure rises gradually upto 180 Å^2. In this region of the isotherm,

(a) Edge−on   **(b) Face−on**

Figure 7.7: A schematic diagram showing the conformation of discotic molecules at the air-water interface. (a) and (b) show an edge-on and a face-on conformation of the molecules at the interface, respectively.

we obtained a large value of A_o^1 (314 $\mathring{A}^2$) which indicates a face-on conformation of the molecules with the interdigited chains. Also, the BAM images in this region of the isotherm reveal a very uniform gray texture (Figure 7.3(a)). The isotherm (Figure 7.2) shows a steep rise in surface pressure below an A_m of 180 $\mathring{A}^2$. The A_o value was found to be 160 $\mathring{A}^2$ which is large for the edge-on and small for the face-on conformations, respectively. The BAM images in this region of the isotherm reveal the regions of two different intensity levels (gray and bright domains). The intensity of the BAM images depends on the thickness of the films and the orientation of the molecules [10]. The bright domains in the images (Figure 7.3(b and c)) may correspond to the domains of the molecules with edge-on conformation and the gray background may represent a face-on conformation. The large value of A_o can be accounted for a coexistence of domains with face-on and edge-on conformations. The conformation of the disc-like molecules at the A-W interface depends on the strength of their core-core interaction. It also depends on the interaction of the polar part of the molecules with water. It has been reported in literature that the triphenylene based amphiphilic discotic molecules prefer edge-on conformation. Such conformation was attributed to the strong π-π interaction of the core of the molecules [11, 12]. However, there are a few reports indicating the face-on conformation of the discotic molecules on the water surface [13, 14]. Such conformation was attributed to a strong core-water and weak core-core interactions among the molecules [15]. The AmTCQ molecule possesses hydrophilic side-chains which are attached symmetrically around the molecule. Though the core part of the molecule does not possess hydrophilic group, the weak core-core interaction leads the molecules to show a face-on conformation on the water surface. However, on compression, some molecules in the monolayer may orient to the edge-on conformation due to the weak core-water interaction and steric repulsion between the molecules. Both the conformations appear to coexist in the steep region of the isotherm. This is the first observation where a system of discotic monolayer at the A-W interface exhibits a stable phase of the coexistence of both the molecular conformations.

The STM images of the LB film of the AmTCQ molecules show a high degree of ordering. The central TCQ core of the molecule is considered as the electron deficient [3].

Hence, it may contribute less to the intensity in the STM images. Figure 7.6 shows dark region corresponding to the TCQ core of the molecule. On the other hand, the presence of external phenyl rings may yield brighter region in the image. We propose a possible arrangement of the molecules in the LB films as shown schematically in Figure 7.8.
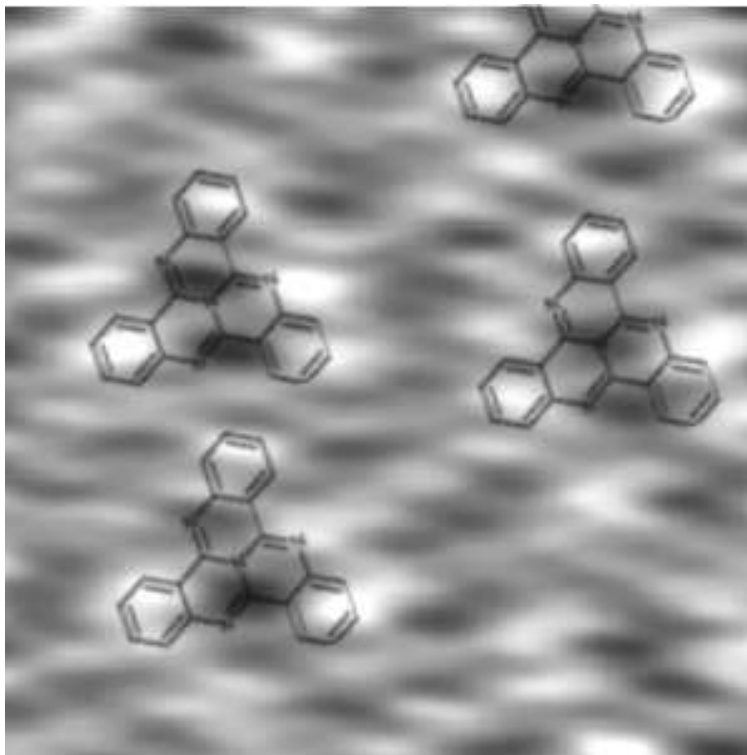

Figure 7.8: The STM image with a possible arrangement of the AmTCQ molecules in the LB film. Only TCQ core is shown for visual clarity. The size of the image is 3.6x3.6 nm^2.

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