

Organization of Discotic Mesogenic Amphiphiles at Air-Water and Air-Solid Interfaces

by

Alpana Nayak

**Thesis submitted to the
Jawaharlal Nehru University
for the award of the degree of
Doctor of Philosophy**

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***Raman Research Institute
Bangalore 560 080
India***

CERTIFICATE

This is to certify that the thesis entitled “**Organization of Discotic Mesogenic Amphiphiles at Air-Water and Air-Solid Interfaces**” submitted by Alpana Nayak for the award of the degree of DOCTOR OF PHILOSOPHY of Jawaharlal Nehru University is her original work. This has not been published or submitted to any other University for the award of any other degree or diploma.

Prof. Ravi Subrahmanyam

(Center Chairperson)

Director

Raman Research Institute

Bangalore 560 080 INDIA

Prof. Kattera A. Suresh

(Thesis Supervisor)

DECLARATION

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(Prof. Kattera A. Suresh)

(Alpana Nayak)

Raman Research Institute
Bangalore 560 080 - INDIA

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List of symbols used in the thesis

π	Surface pressure
π_c	Collapse pressure
π_t	Target surface pressure
A_m	Area per molecule
A_o	Limiting area per molecule
γ	Surface tension of water with monolayer
γ_0	Surface tension of water
$ E $	Compressional elastic modulus
τ	Transfer ratio
n	Number of cycles of LB deposition
d	Cantilever deflection
δ	Indentation depth
z	Piezo vertical movement
F	Load on the cantilever
k_c	Cantilever spring constant
ν	Poisson's ratio
E	Young's elastic modulus
f	Driving frequency of the cantilever
f_0	Resonance frequency of the cantilever
A_{sp}	Set point amplitude of the cantilever oscillation
A_0	Free oscillation amplitude of the cantilever
Q	Quality factor of the cantilever
ϕ	Phase shift angle in tapping mode AFM
E_{dis}	Energy dissipation in tapping mode AFM
h	Planck's constant
e	Electron charge
m	Electron mass
m^*	Effective electron mass
ϕ_b	Contact barrier height

List of abbreviations used in the thesis

PyTp	Pyridinium tethered with hexaalkoxytriphenylene
ImTp	Imidazolium tethered with hexaalkoxytriphenylene
TpImTp	Imidazolium tethered with hexaalkoxytriphenylene dimer
N-ImTp	Imidazole tethered with hexaalkoxytriphenylene (non-ionic)
DNA	Deoxyribo nucleic acid
HMDS	Hexamethyldisilazane
A-W	Air-water
A-S	Air-solid
LB	Langmuir-Blodgett
ESP	Equilibrium spreading pressure
BAM	Brewster angle microscope
FTIR	Fourier transform infrared spectroscopy
XRD	X-ray diffraction
AFM	Atomic force microscope
TM-AFM	Tapping mode atomic force microscope
CS-AFM	Current-sensing atomic force microscope
STM	Scanning tunneling microscope
<i>I-V</i>	Current-voltage characteristics

Preface

This thesis deals with the studies on organization of some novel ionic disk-shaped (discotic) liquid-crystalline (mesogenic) molecules at the air-water and the air-solid interfaces. Discotic mesogens are of interest for their intriguing supramolecular architectures [1]. They possess unique molecular electronic properties such as two-dimensional delocalization of electrons. Some of the known examples of successfully operating devices based on discotic semiconductors are field-effect transistor, light-emitting diode and photovoltaic solar cell [2]. In addition, there are some naturally occurring biological disk-shaped molecules such as vitamins, hemoglobin and chlorophyll. Therefore, studying the supramolecular organization of discotic molecules at interfaces are important from the point of view of technology as well as basic science.

The discotic mesogens used in this thesis work are; (i) pyridinium tethered with hexaalkoxytriphenylene with bromine as counterion (PyTp), (ii) imidazolium tethered with hexaalkoxytriphenylene with bromine as counterion (ImTp), (iii) a discotic dimer comprising of two hexaalkoxytriphenylene cores attached via flexible hydrocarbon chain and a imidazolium moiety with bromine as counterion (TpImTp), and (iv) imidazole tethered with hexaalkoxytriphenylene which is non-ionic (N-ImTp). These molecules were synthesized in our institute by Santanu Kumar Pal and Sandeep Kumar [3–5]. The chemical structure of these molecules are shown in Figure 1.

These molecules are amphiphilic in nature. Amphiphilic molecules consist of two parts; one part is hydrophilic and the other part is hydrophobic. When such molecules are put on water surface, the hydrophilic part of the molecules easily form hydrogen bonds with water molecules and hence get anchored to the water surface. The hydrophobic part of the molecules do not form hydrogen bonds with water and hence favors to stay away from the water surface. As a result, a monolayer of such molecules is formed at the air-water interface which is called Langmuir monolayer [6]. The Langmuir monolayers provide an ideal two-dimensional (2D) model system to study phase transitions depending on the nature of interaction among the molecules. For the molecules used in this thesis work, the discotic triphenylene core forms the hydrophobic part of the molecule.

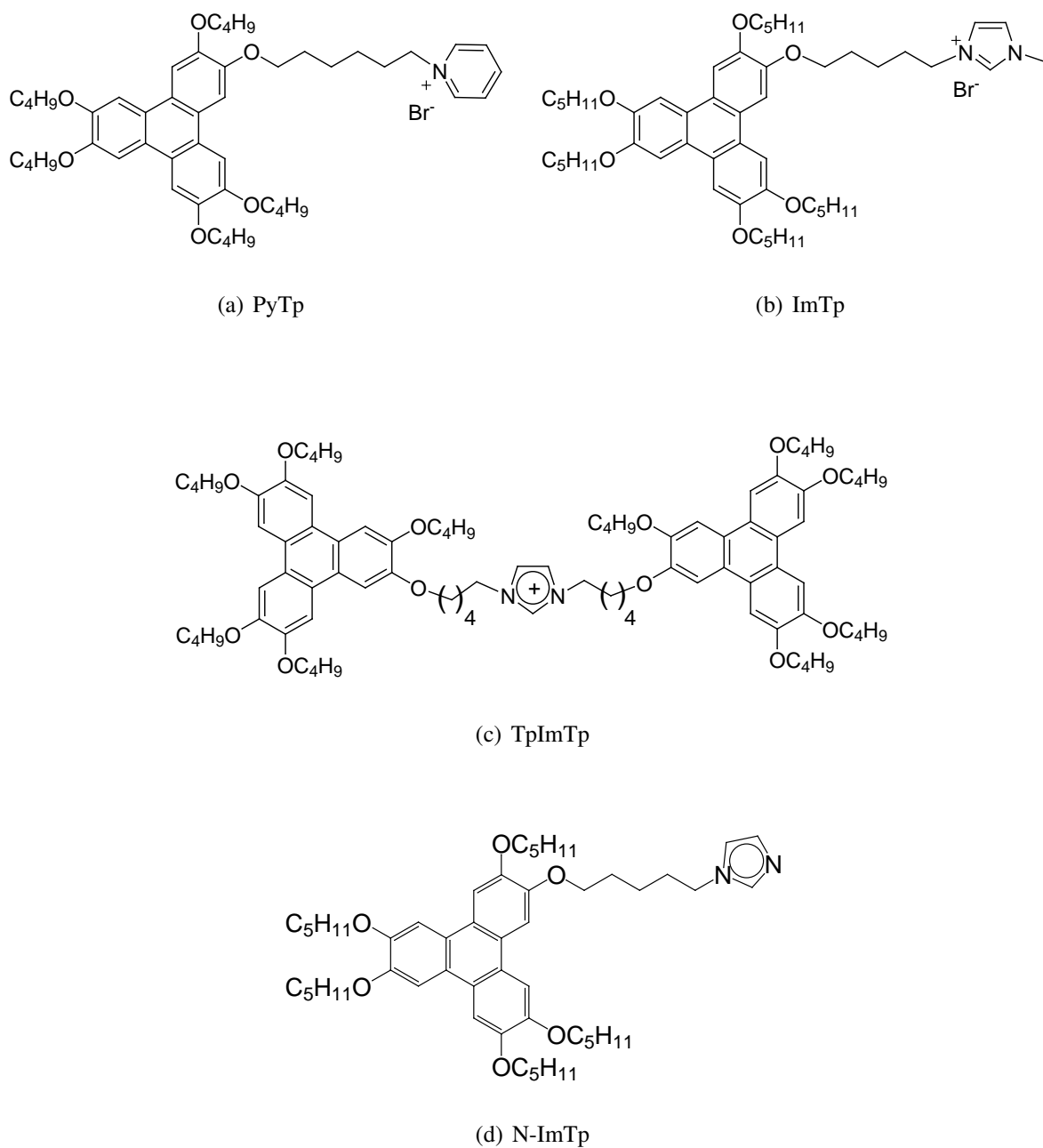


Figure 1: Chemical structures of (a) pyridinium tethered with hexaalkoxytriphenylene with bromine as counterion (PyTp), (b) imidazolium tethered with hexaalkoxytriphenylene with bromine as counterion (ImTp), (c) a discotic dimer comprising of two hexaalkoxytriphenylene cores attached via flexible hydrocarbon chain and a imidazolium moiety with bromine as counterion (TpImTp), and (d) imidazole tethered with hexaalkoxytriphenylene which is non-ionic (N-ImTp).

The pyridinium and imidazolium groups, attached to the triphenylene cores through alkyl chains, constitute the hydrophilic part of the molecules. The hydrophilic parts are highly polar with dipole moment of 2.2 D for pyridine moiety and 3.6 D for imidazole moiety. On the surface of water, the discotic amphiphiles can exhibit two types of configuration; face-on and edge-on (Figure 2). In face-on configuration, the discotic core lies parallel to the water surface and the hydrocarbon tails extend away from the interface. Such a configuration may be preferred if the core of the molecule is capable of hydrogen bonding. In edge-on configuration, the discotic core lies normal to the water surface with the polar end submerged in water. Such a configuration leads to the formation of a 2D analog of the columnar mesophase on the surface of water.

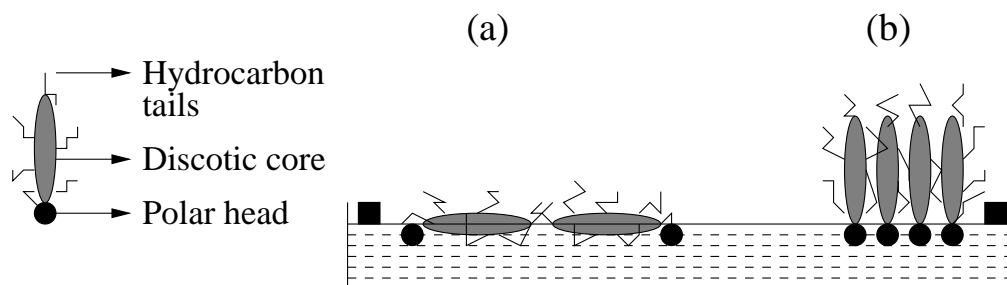


Figure 2: Schematic representation of (a) face-on and (b) edge-on configuration of discotic mesogenic amphiphiles at the air-water interface.

Langmuir monolayers can be transferred from the air-water interface onto solid substrates by vertical dipping technique. Such transferred films are called Langmuir-Blodgett (LB) films [7]. We have formed Langmuir and LB films of the novel discotic mesogenic molecules. We have studied these films at the air-water interface using surface manometry and Brewster angle microscopy. The films transferred on solid substrates were studied using different modes of atomic force microscopy (AFM). In Chapter 1, we have described the experimental techniques along with a brief introduction to the discotic mesogenic amphiphilic systems.

In Chapter 2, we have presented our studies on the organization of PyTp and ImTp molecules at the air-water and the air-solid interfaces. Both the molecules exhibited stable Langmuir monolayer which showed negligible hysteresis on expanding and compressing (Figure 3). Also, the collapsed state completely reverts to the monolayer state. As compared to the monolayers of non-ionic triphenylene derivatives reported so far [8], these cationic discotics showed higher limiting area

per molecule due to the direct electrostatic repulsion between the molecules within the film. These monolayer films transferred at different target surface pressures by LB technique were studied employing an AFM. The topography of these films, transferred at low and high surface pressure region of the isotherms, indicated a transformation of the monolayer from face-on to edge-on configuration (Figure 4). We find that the molecules PyTp and ImTp were arranged into columns in the bulk as seen by our X-ray studies. They exhibited two-dimensional columns at the air-water and air-solid interfaces as indicated by our surface manometry and AFM studies.

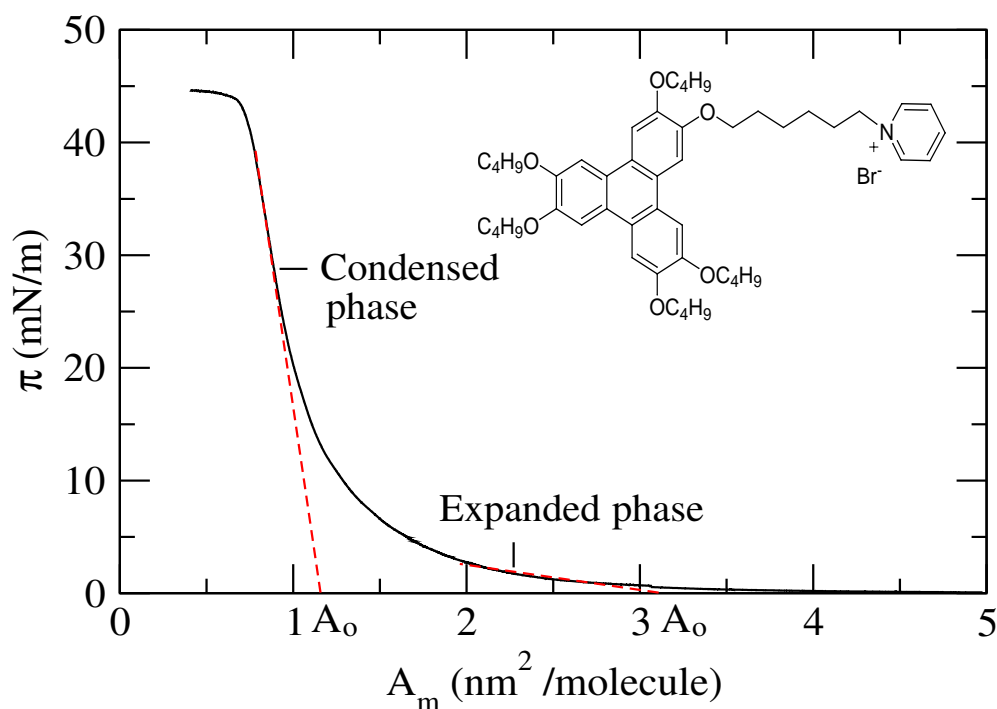


Figure 3: Surface pressure (π) - area per molecule (A_m) isotherm of pyridinium based discotic (PyTp) molecule. The extrapolation to zero surface pressure, shown by dashed lines, gives the limiting area per molecule A_o at the expanded phase and the condensed phase.

The presence of cationic moiety in the discotic molecules widens scope for studying electrostatic interaction between such a molecule and negatively charged species like DNA at interfaces. In Chapter 3, we have shown the supramolecular complexation between DNA and the cationic discotic mesogen PyTp at the air-water interface. The PyTp-DNA complex was formed primarily due to the electrostatic interaction between the pyridinium group of the triphenylene molecule and the phosphate group of DNA. Interestingly, we find that, compared to the pure PyTp monolayer, the PyTp-DNA complex monolayer exhibited a higher collapse pressure and lower limiting area,

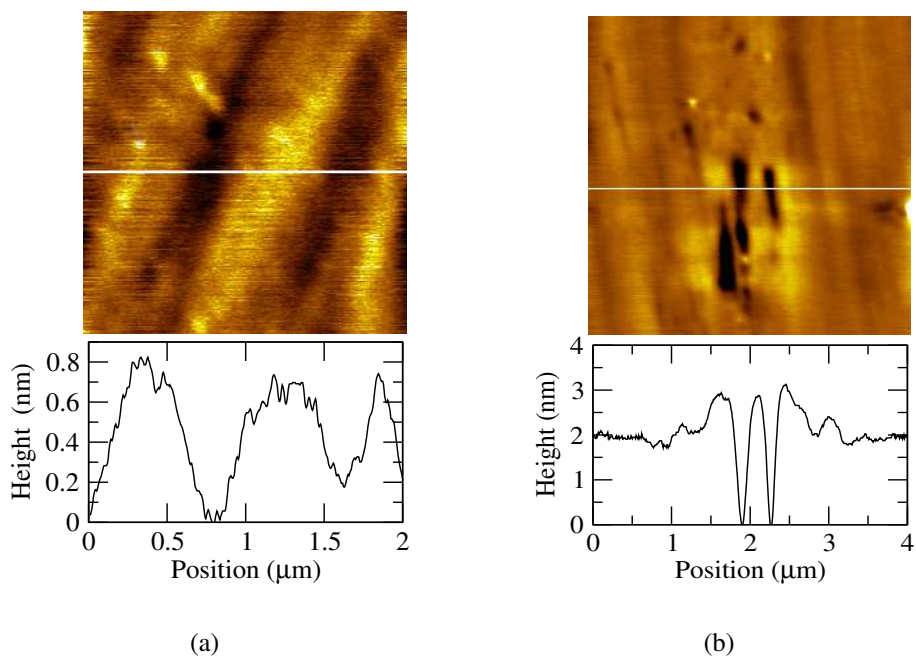


Figure 4: (a) AFM topography of ImTp monolayer transferred by horizontal method onto hydrophilic silicon substrate at a target surface pressure (π_t) of 5 mN/m. (b) Topography of ImTp monolayer transferred by LB technique onto hydrophilic silicon substrate at $\pi_t = 35$ mN/m. The respective height profiles corresponding to the lines drawn on the images are shown below.

indicating condensation and better stability (Figure 5). In addition, the formation of DNA complex has enhanced the transfer efficiency by LB technique to over several tens of layers (Figure 6). AFM studies on the LB films showed that the PyTp-DNA complex monolayer was thicker than the pure PyTp monolayer by about 1 nm. This thickness is reasonable for a DNA layer in a dried state and comparable to the reported values using neutron and X-ray reflectometry [9, 10]. The nanoindentation studies using AFM showed that the PyTp-DNA complex film was about two times harder than the pure PyTp film.

The ability of the PyTp-DNA complex to form multilayers on a substrate has potential application in the fabrication of devices like thin film transistors and nucleic acid-based biosensors. In the long-term and successful performance of devices, the mechanical stability of the materials play significant role. We have presented, in Chapter 4, a detailed and quantitative analysis of the nanoscale mechanical properties of pure PyTp film as well as the PyTp-DNA complex film. From the nanoindentation measurements, we have calculated the Young's elastic modulus values to be 54 and 160 MPa for the pure and complex films respectively (Figure 7). In addition, phase shift

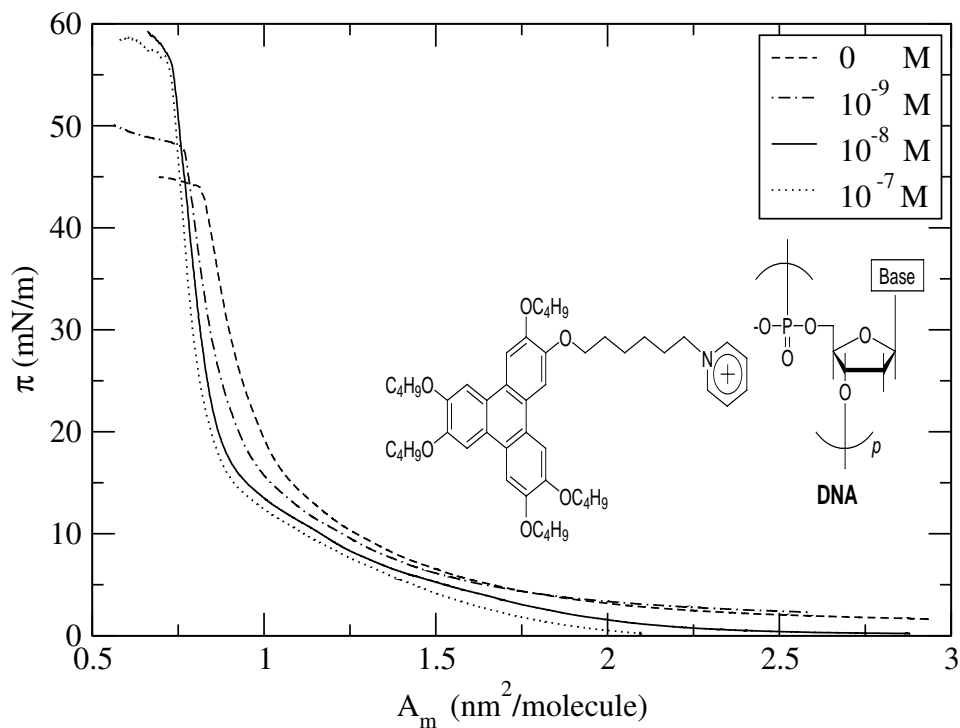
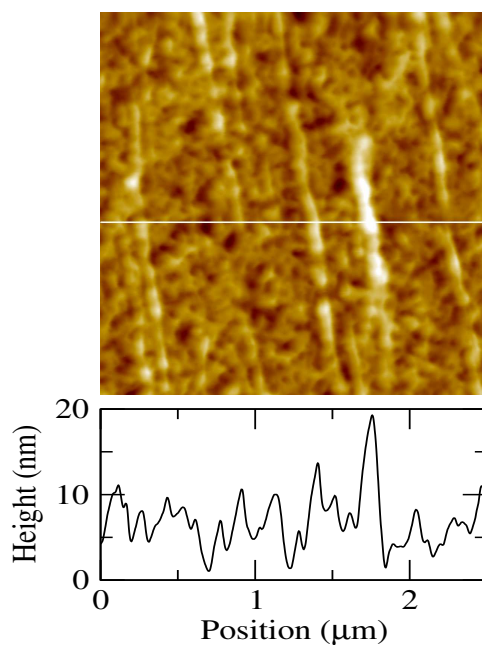


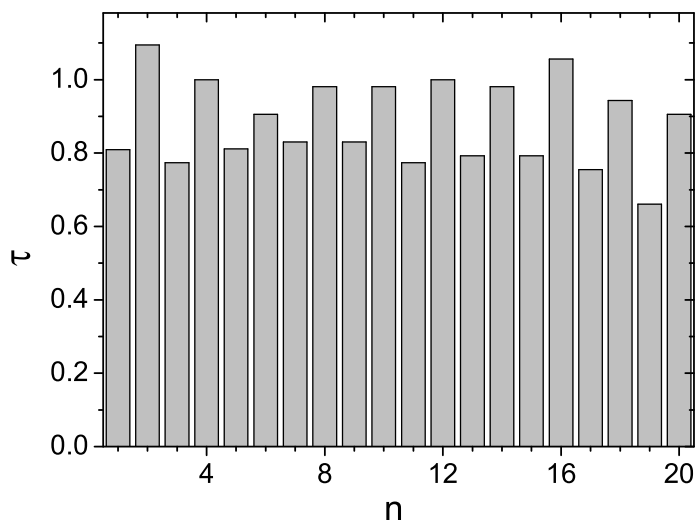
Figure 5: Surface pressure (π) - area per molecule (A_m) isotherms of PyTp-DNA complex mono-layer for different concentrations of DNA in the subphase. For comparison, we have shown the isotherm for pure PyTp molecule (dashed line).

measurements were carried out for these films and energy dissipation maps were constructed. By qualitative analysis of the energy dissipation maps, we find that the surface of the pure film is soft and uniform, whereas, the complex film surface is stiff and non-uniform (Figure 8). It is significant that nanoindentation measurements gave local elastic modulus of the film surfaces, whereas with the help of phase imaging, we could continuously map the variation in elastic properties over the film surfaces.

Discotic mesogens are considered as a new generation of organic semiconductors. They possess unique molecular electronic features that are not observed in linear oligomers and polymers. In addition, the DNA molecule has drawn lot of attention in nanoelectronic devices due to its intrinsic electronic properties. Since both DNA and discotic mesogens have their own intrinsic electronic properties, complexing DNA with cationic discogen molecules is a novel approach for developing advanced materials with interesting electronic properties. Therefore, the electrical property measurements of such films are of prime interest.

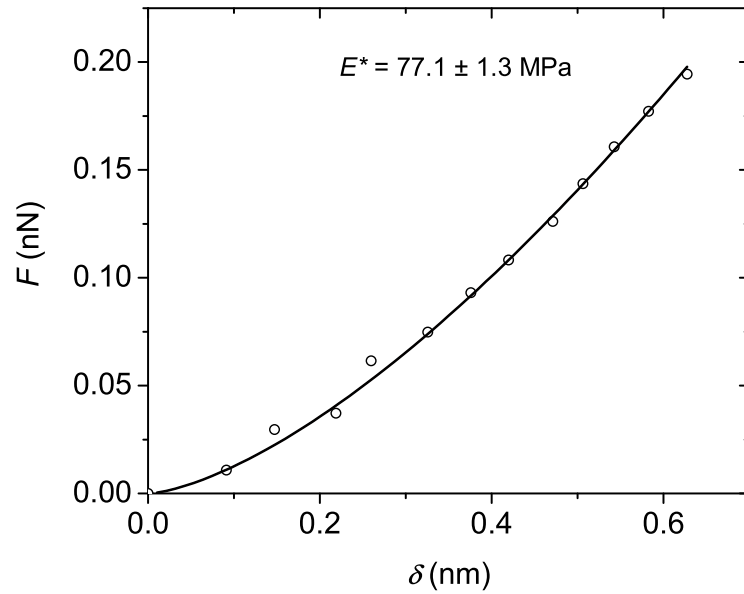


(a)

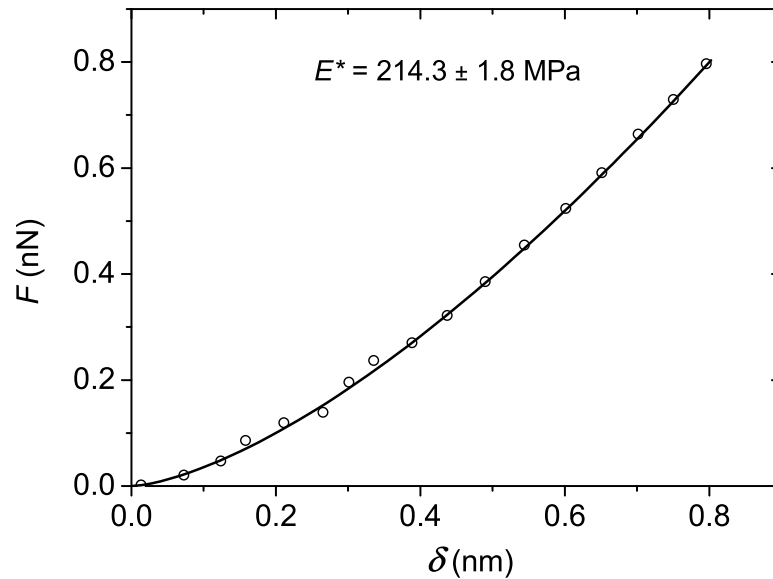


(b)

Figure 6: (a) AFM topography image of the PyTp-DNA complex LB film with 20 layers on hydrophobic silicon substrate transferred at a target surface pressure (π_t) of 35 mN/m. The height profile corresponding to the line drawn on the image is shown below. (b) Transfer ratio (τ) as a function of number of layers (n) of LB deposition at a π_t of 35 mN/m for the PyTp-DNA complex film onto hydrophobic silicon substrate.

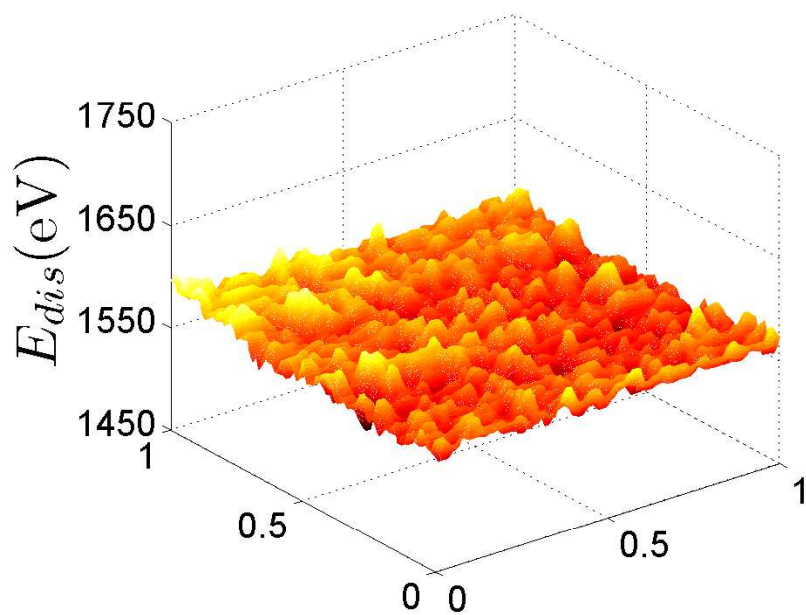


(a)

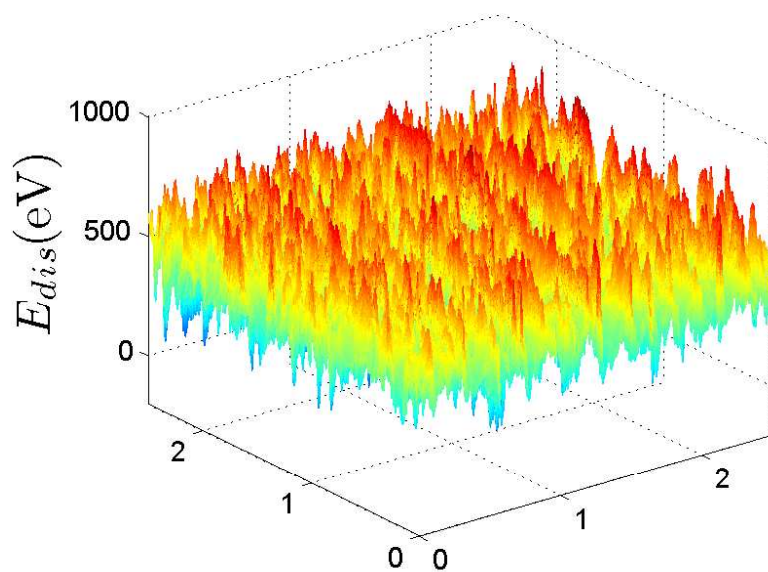


(b)

Figure 7: Typical load F versus indentation δ curves obtained for (a) PyTp film, and (b) PyTp-DNA complex film. The curves were fitted with the Hertz model (solid lines), yielding reduced elastic modulus E^* value of 77.1 ± 1.3 MPa for the pure film and 214.3 ± 1.8 MPa for the complex film.



(a)



(b)

Figure 8: (a) The energy dissipation (E_{dis}) map of the pure PyTp LB film with 2 layers with a scan range of $1 \times 1 \mu\text{m}^2$. (b) The E_{dis} map of the PyTp-DNA complex LB film with 20 layers for a scan range of $2.5 \times 2.5 \mu\text{m}^2$. Figures (a) and (b) were constructed using MATLAB software.

In Chapter 5, we have investigated the nanoscale electrical properties of pure PyTp film and the PyTp-DNA complex film using a special mode of AFM, i.e., the current-sensing AFM (CS-AFM). The conductive tip of CS-AFM, the LB film, and the metal substrate form a nanoscopic metal-LB film-metal (M-LB-M) junction (Figure 9).

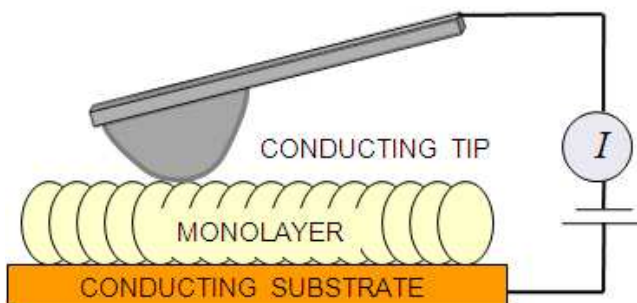
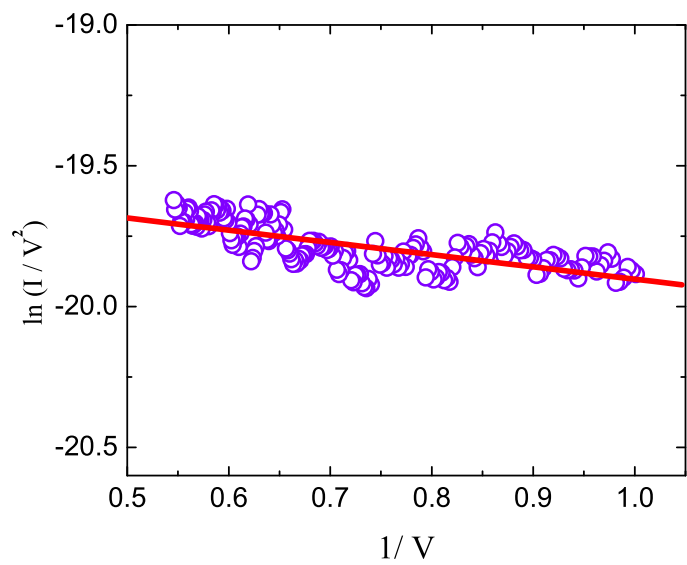


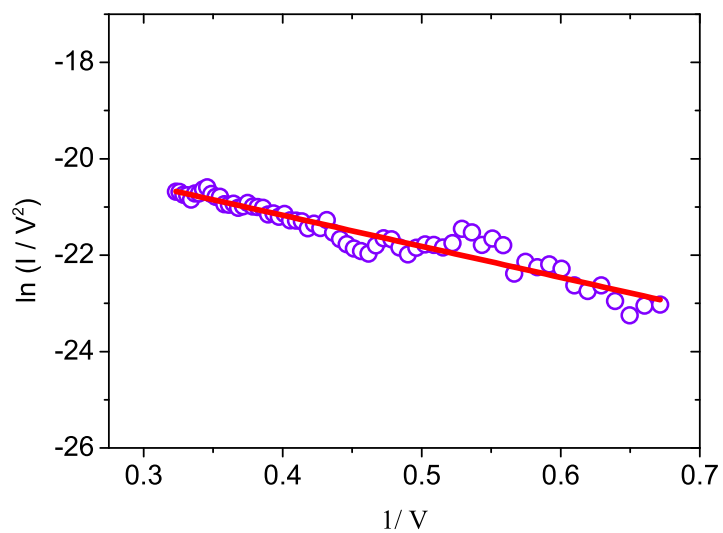
Figure 9: Schematic representation of a metal-LB film-metal junction formed by a conducting AFM tip in contact with a monolayer film deposited on a conducting substrate.

We have measured the current-voltage (I - V) characteristics for the M-LB-M junction using CS-AFM and have analyzed the data quantitatively. The ability to rationally design molecular electronic components hinges on a fundamental understanding of the charge transport mechanism in metal-molecule-metal junctions. To this end, we analyzed our data for a possible mechanism for electron transport at nanoscale in our M-LB-M system. Interestingly, we find that the I - V curves fit well with the Fowler-Nordheim (FN) tunneling model indicating the electron tunneling to be a possible mechanism for electron transport (Figure 10). Further, analysis of the I - V curves based on the FN model yields the barrier height of PyTp-DNA complex film to be three times higher compared to that of the pure PyTp film. The local electrical conductivity measurement of the films using CS-AFM provides better understanding of the electron transport properties at the nanoscale.

In the studies described in Chapter 2 to Chapter 5, the constituent discotic mesogen molecules were *monomers*. It is known in literature that the properties exhibited by a discotic *dimer* can be significantly different from the conventional low molar mass discotic monomers because of the restricted molecular motions [1]. We have presented, in Chapter 6, the organization of a novel discotic *dimer* TpImTp at interfaces, together with its complexation with DNA. The TpImTp molecule exhibited stable Langmuir monolayer. The collapsed state of the TpImTp film completely reverted



(a)



(b)

Figure 10: Fowler-Nordheim fitting for typical I - V characteristic curves measured for (a) pure PyTp monolayer film on a gold coated mica substrate at a constant force of 4 nN, and (b) PyTp-DNA complex monolayer film on a gold coated mica substrate at a constant force of 4 nN. Open circles represent the experimental data and solid lines represent the fit.

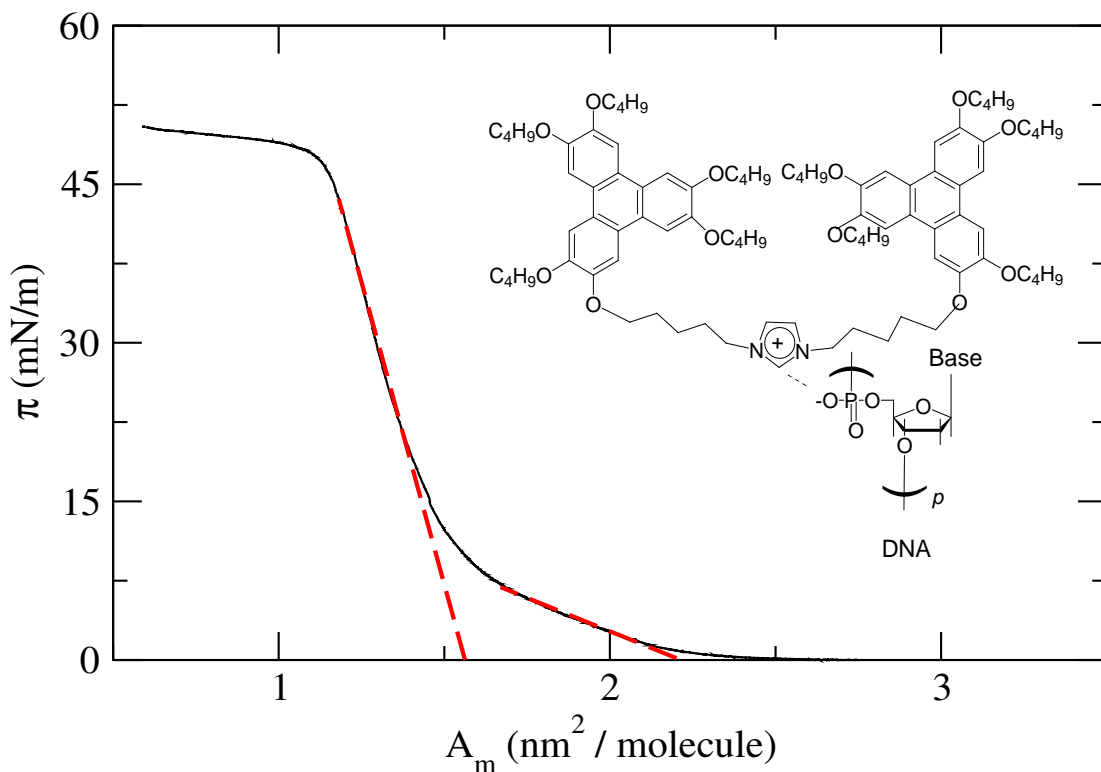
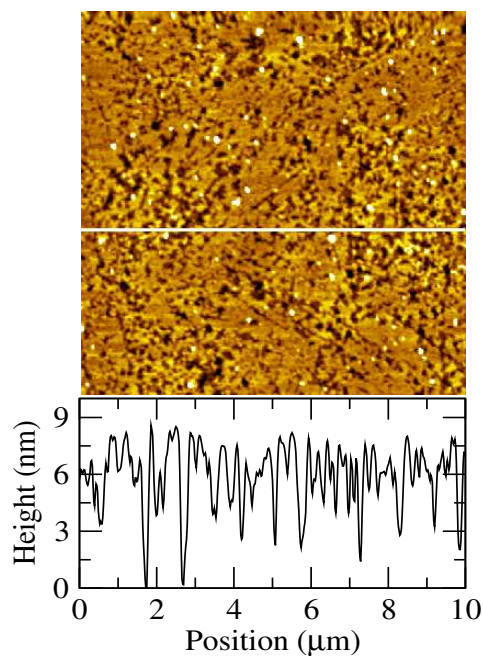
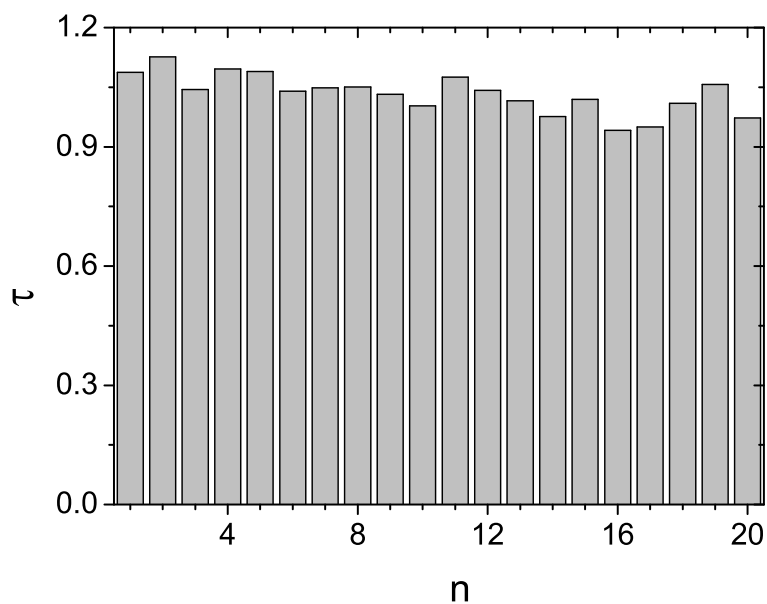


Figure 11: The π - A_m isotherm of the TpImTp-DNA complex monolayer with 10^{-8} M concentration of DNA in the subphase.

to the monolayer state on expansion. As compared to its monomer analog, the TpImTp monolayer exhibited higher compressional elastic modulus, indicating a much better packing of molecules in the monolayer. This is probably due to the two aromatic cores in a TpImTp molecule which enhances the π -stacking interaction. The complexation of the TpImTp monolayer with DNA at air-water interface results in a decrease in limiting area and an increase in the collapse pressure (Figure 11). In addition, DNA complexation facilitated the extremely efficient multilayer formation of the TpImTp monolayer on a substrate. Figure 12(b) shows the transfer ratio to be nearly 1 for deposition during the up and down strokes and practically no desorption. However, we find that, the TpImTp-DNA complex could not transfer large number of DNA molecules from the air-water to the air-solid interface. This may be attributed to the fact that the lone pair of electrons on one of the nitrogen atoms in imidazolium moiety screen the effective positive charge of the ring, thereby decreasing the strength of electrostatic interaction with DNA. In addition, the steric hindrance may play a significant role particularly in case of bulky groups like dimers.



(a)



(b)

Figure 12: (a) AFM topography of TpImTp-DNA complex LB film with 20 layers transferred onto hydrophobic silicon substrate at a target surface pressure (π_t) of 35 mN/m. The height profile corresponding to the line drawn on the image is shown below. (b) Transfer ratio (τ) as a function of number of layers (n) of LB film deposition for TpImTp-DNA complex on a hydrophobic silicon substrate. The film was transferred at a π_t of 35 mN/m and a dipping speed of 2 mm/min.

In the previous chapters, we have investigated discotic molecules which have ionic polar groups. We note that all these ionic systems share a common feature. The LB deposition was inefficient for these ionic systems and the efficiency drastically improved by the addition of DNA in the subphase. In literature, it is known that the deposition of charged Langmuir monolayer on a substrate by LB method involves complicated physical and chemical processes [11]. It would be interesting to study a non-ionic discotic system so that we can have a direct comparison between the properties exhibited by an ionic discotic system and a non-ionic discotic system at interfaces. In Chapter 7, we have presented our studies on a non-ionic discotic molecule (N-ImTp) to explore the effect of the absence of an ionic polar group on the properties of Langmuir monolayer and LB films.

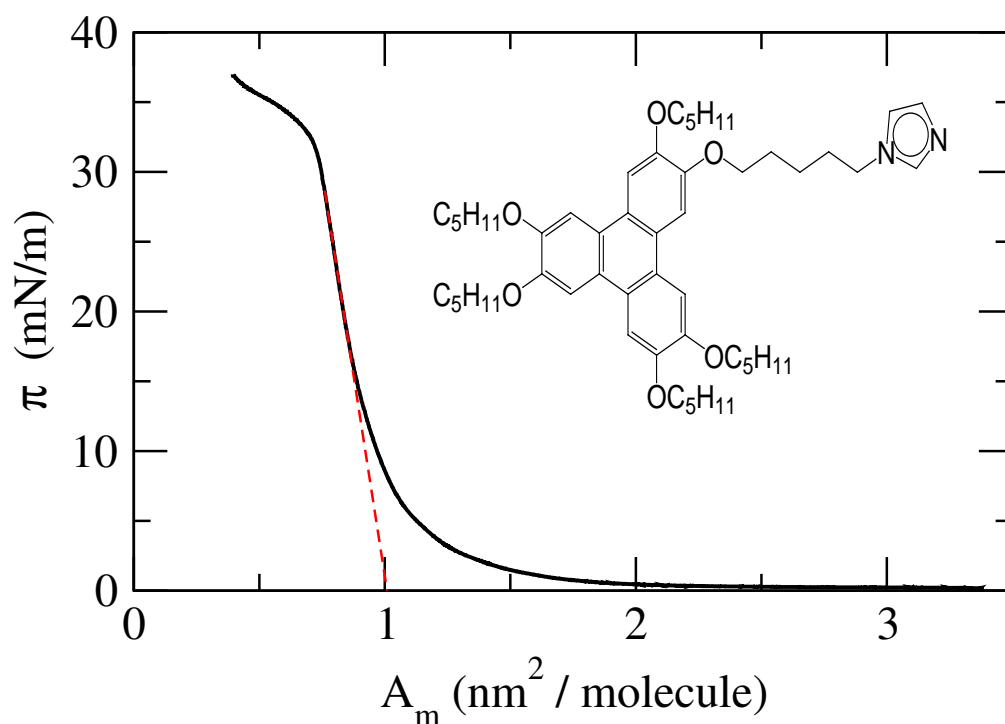


Figure 13: The surface pressure (π) - area per molecule (A_m) isotherm of N-ImTp monolayer on ultrapure water subphase. The dashed-line is drawn to obtain the limiting area per molecule.

We find that the N-ImTp molecule forms a stable monolayer at the air-water interface (Figure 13). As compared to the monolayer of ImTp described in Chapter 2, the N-ImTp monolayer exhibited decreased limiting area and increased compressional elastic modulus. This indicates a better packing of molecules in the N-ImTp monolayer due to the absence of electrostatic repulsion.

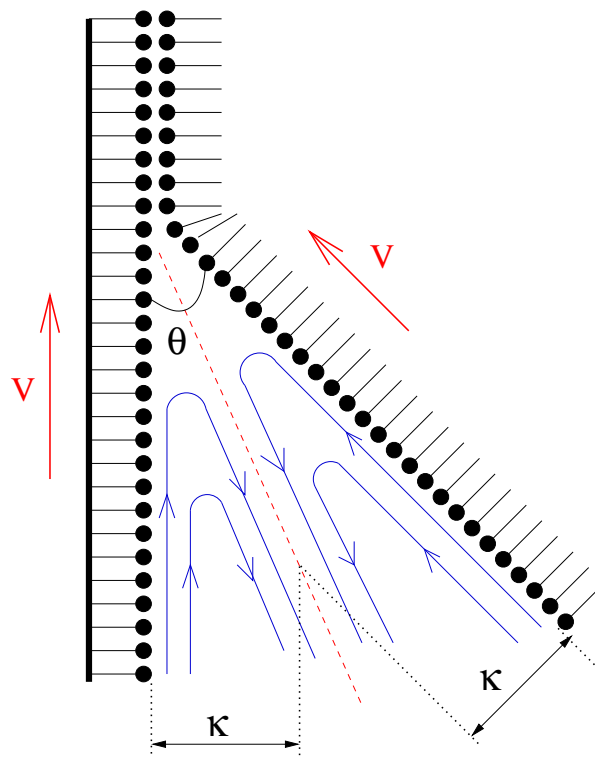


Figure 14: Schematic diagram of convective flow in the vicinity of the three-phase contact line. V is the velocity of the surface motion, θ is the dynamic contact angle, and κ is the thickness of the diffuse electric double layer (the Debye length).

Interestingly, the transfer of the N-ImTp monolayer to the solid substrate by LB technique showed a markedly different behavior. It was possible to build multilayer of N-ImTp film containing as many as 20 layers with good efficiency. On the contrary, its ionic analogs (ImTp and PyTp) could not form multilayers because of alternate adsorption and desorption over the successive strokes of LB deposition. This can be attributed to the fact that, on spreading the ionic discotic molecules on the surface of water, the small Br^- counterions dissolve into the subphase. The presence of these Br^- counterions in the subphase and the positively charged discotic monolayer at the surface form an electric double layer at the air-water interface. During LB deposition, the electric double layer overlaps in the same region where convective flow is induced by the moving surfaces (Figure 14). This generates a local redistribution of ions in the meniscus region and causes meniscus instability, thereby disrupting the multilayer formation. Such effects are absent in the case of the N-ImTp monolayer. Therefore, multilayers of N-ImTp monolayer could be formed successfully.

In summary, this thesis addresses to various aspects of organization of some novel ionic discotic mesogenic molecules at air-water and air-solid interfaces. The presence of cationic moiety provided opportunity to study the electrostatic interaction of such molecules with negatively charged biomolecule like DNA. Interestingly, the formation of stable multilayers of the complex film on a substrate provides scope for device applications like field-effect transistors and nucleic acid based bio-sensors. Further, such a system can act as a model to understand several biological discotic systems. We have investigated the nanoscale electro-mechanical properties like conductivity, hardness, elasticity and stiffness variation, of the films using an atomic force microscope. These are significant since the current trend in technology is towards miniaturization of products and devices. Thus, characterization of materials at the nanoscale becomes important. We expect that our studies on the organization of the discotic mesogens at interfaces and their electro-mechanical properties at nanoscale will lead towards research work of more interesting and novel molecular systems.

Publications during the course of this thesis work:

1. Films of novel mesogenic molecules at air-water and air-solid interfaces.
Alpana Nayak, K. A. Suresh, Santanu Kumar Pal, and Sandeep Kumar, *J. Phys. Chem. B* **111**, 11157 (2007).
2. Discogen-DNA complex films at air-water and air-solid interfaces.
Alpana Nayak and K. A. Suresh, *J. Phys. Chem. B* **112**, 2930 (2008).
3. Conductivity of Langmuir-Blodgett films of a disk-shaped liquid-crystalline molecule-DNA complex studied by current-sensing atomic force microscopy.
Alpana Nayak and K. A. Suresh, *Phys. Rev. E* **78**, 021606 (2008).
(This article has been selected for the September 1, 2008 issue of **Virtual Journal of Biological Physics Research** (<http://www.vjbio.org/>). Also, this has been selected for the September 8, 2008 issue of **Virtual Journal of Nanoscale Science & Technology** (<http://www.vjnano.org/>.)
4. Nanoscale mechanical properties of Langmuir-Blodgett films of a discogen-DNA complex.
Alpana Nayak and K. A. Suresh, *J. Phys. Chem. B* (under review).
5. Discotic mesogen-DNA complex films at interfaces.
K. A. Suresh and Alpana Nayak, *Mol. Cryst. Liq. Cryst.* (invited article).

Following manuscripts are under preparation:

- Langmuir-Blodgett films of a novel mesogenic discotic dimer and its complex with DNA.
Alpana Nayak and K. A. Suresh, (manuscript under preparation).
- A comparative study of ionic and non-ionic discotic amphiphiles on the effect of ionic polar group during Langmuir-Blodgett film deposition.
Alpana Nayak and K. A. Suresh, (manuscript under preparation).

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