

A Study on GID Study of DMV-CS Monolayer

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Abstract - The monolayer arrangement is explored with tools including Grazing Incidence Diffraction (GID) from the liquid surface, isotherm investigations, Brewster Angle Microscopy (BAM), and X-Ray Reflectivity (XRR), Pressure-dependent In-situ GID experiments showed that 15mN/m, the ionic radicals of the CS begin to distort the head-head ordering, causing the DMV and CS molecules to slide out of their ordered position in the linear chain of the SAM, and 20mN/m, the tails begin to align in a hexagonal lattice.

Keywords - Grazing Incidence Diffraction (GID), Monolayer, Dodecyl methyl viologen (DMV), coronene tetracarboxylate (CS)

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INTRODUCTION

Investigations into molecular assembly at the air-water interface have long been fascinating. Molecular research including self-interaction, molecular orientation and interaction with water and other aqueous solutes, orientation as a function of temperature and PH, and so on, benefit greatly from molecules' 2D single-layer structures.(1) In recent years, charge transfer complex monolayers have gained attention as a promising system for use in both fundamental research and practical applications. These monolayers have been synthesised using the Langmuir Deposition technique and have found application in the fabrication of devices such as light-emitting diodes (LEDs), field-effect transistors (FETs), solar cells (SCs), and sensors (SENS). Using the Grazing Incidence Diffraction method developed for Langmuir monolayers, we have investigated the self-interaction of such DMV-CS molecules in this work. Since it was previously difficult to investigate the molecule in plane arrangement on the surface of a liquid by direct means like microscopy,(2) GID has emerged as a promising tool for studying such molecular monolayers. Sometimes the materials deposited on substrates have quite different properties from those at the air-liquid interface. With the development of Synchrotron Sources and improved measurement methods, scientists can now also examine the molecular arrangement of a langmuir monolayer in the in plane direction.(3) To determine if the self-assembling capabilities, which are obvious in the solution phase of DMV- CS, have any influence on the properties of the langmuir monolayer, we have employed GID to probe the structure of the monolayer and analysed the evolution of the monolayer with the trough pressure.(4)

Effect of Dimensionality in materials

Zero-dimensional (0D), one-dimensional (1D), and two-dimensional (2D) nanomaterials can be categorized based on their characteristic dimensions, which are in the nanometric range. The three dimensions of a 0D material (width, length, and thickness) are restricted in all three dimensions. Confinement occurs in just two dimensions, width and diameter, with a macroscopic third dimension, length, for single-dimensional (1D) nanomaterials. In this case, the material is considered to be 2D because of the macroscopic dimensions of its length and width. The substance is viewed as 3D if none of its dimensions are constrained. 3D materials having nanometric holes and structures are known as nanostructured materials, as well. Porous carbons, zeolites, and molecular sieves, for example, are all three-dimensional materials with nanoscale structures and pores. Internal length scale and related dimensions are more important than the overall size of an entity.(5)

Deviation from bulk properties

As a result of variations in the electron density of states, low-dimensional systems frequently have a lower total energy than their bulk counterparts. Thus, below a certain length scale, the most energetically advantageous state of such systems changes. A noticeable shift in the physical characteristics may be seen in the outermost electronic energy levels as a result of this. Metallic thin films with sub-monolayer coverage exhibit nonmetallic behavior and metal-insulator transitions when formed as thin films with a different crystal structure from the conventional bulk state.(6) Additionally, the substantial rise in surface-to-to-bulk atom ratio has an enormous impact on low-dimensional system physical characteristics, on top of the size effect. Surface atoms have fewer

nearest-neighbor atoms, causing bonding and electrical structural variations in low-dimensional materials. Surface atom density increases have an effect on system total energy, causing basic features of nanostructures to shift dramatically from their bulk state. Shape, structure, and arrangement of the nanostructures affect the interactions of the nanostructures with each other and the physical characteristics of the nanostructured materials.(7)

Self Assembly

Complex hierarchical structures that are built from pre-designed components can be described as self-assembly in the broadest sense, where an unordered system of pre-existing components forms an organized structure as a result of specific, local interactions among the components, without external bias. This type of nanostructure is called a Self-Assembled Nanostructure (SANS). Examples of self-assembled nanostructures, such as micells and reverse micells, liposomes, and Langmuir-Blodgett multilayers, include all of the aforementioned (SAN). Because of their surface properties, self-assembled nanostructures can be used as building blocks in more complex structures, which make them more useful than traditional top-down nanostructures. They can also be used to tune molecular structure and function, which makes them more useful as building blocks in more complex structures.(8)

Self-assembly nanostructures may be used in a wide range of applications because of their modular nature. If you want to use the SAN in technical applications, you must have a solid grasp of the SAN's development and structure. Due to the fact that most of the materials utilized in this study are monolayers, we will only employ Self-Assembled Monolayers (SAM).

- **Wetting control:** Organic monolayers were originally used to regulate the wetting qualities of surfaces. Changing the end group from hydrophilic to hydrophobic can readily control the wetting qualities.
- **Protective coatings:** SAM's protective layers are just "passive," yet they are crucial. Corrosion and mechanical protection of engineered metal surfaces have been effectively proved by their usage in coatings and surface treatments.(9)
- **Friction and lubrication control:** The "mechanical" qualities related to friction and lubrication issues may be adjusted by manipulating various end groups in the same way that end groups can be used to control the wetting properties of a material.
- **Adhesion:** Adhesion applications can benefit from the SAM's chemical flexibility.
- **Bio-related applications:** Filtering and analysis in biotechnology might benefit from selective adsorption. Bio-compatible applications have been the subject of a number of investigations.

- **Non-linear optical applications:** Functional groups that exhibit significant non-linear optical characteristics are capable of being attached to a surface using SAMs because of the modular design of molecules.(10)
- **Electronic properties:** SAM's use in electrical properties may be divided into two broad areas. Most fundamental investigations of electron transport through molecules are conducted with the use of a scanning autophoresis microscope (SAM) and then further studied with a scanning probe microscope (SPM).

Electronic transport in Nanostructures

As a result of the advancement of semiconductor technology, gadgets have been able to shrink in size throughout the previous century. There must be physical limits linked with the limit of how small a specific device may be made while still maintaining its dynamic and static responses authentic to the demand, no matter how good the concept of downsizing is for improving semiconductor device performance. The gate length of the transistor is the physical property that restricts the maximum density of devices that may be achieved in ICs or other devices. Once a threshold length scale is reached, such as the electron's De-Broglie wavelength in a particular material, quantum effects begin to take hold. A Mesoscopic System is one that exhibits the quantum effects of electronic transport in a solid state system. Neither is this a regime of atomic scale nor is it a typical regime for Bulk Materials. This topic is started with the example of semiconductor material since there is a lot of room for merging mesoscopic physics and building devices of a variety of various classes and uses. (11)

Electron Transport in Polymers

Nanostructure transport was discussed in general terms in the section above. As we've studied an organic system, it's vital that we have a fundamental grasp of electronic transport in organic systems. Even though it's impossible to cover all of the current model organic systems being explored for electronic transport, we'd want to talk about some of the aspects of transport in conjugate polymer systems because ours shares certain structural similarities with liner conjugated polymer chains. (12)

OBJECTIVES OF THE STUDY

- To study the GID of DMV-CS Monolayer

RESEARCH METHODOLOGY

Synthesis of DMV-CS and DMV monolayer: To recap, CS was produced using a two-step oxidative benzogenic Diels-Alder reaction of perylene with N-

ethyl maleimide and subsequent hydrolysis with KOH in methanol, whereas DMV was synthesised via a similar technique. DMV was produced by reacting 4, 4'-bipyridine with dodecyl bromide to form mono pyridinium ion and then with methyl iodide to form amphiphilic dicationic bipyridine (DMV).

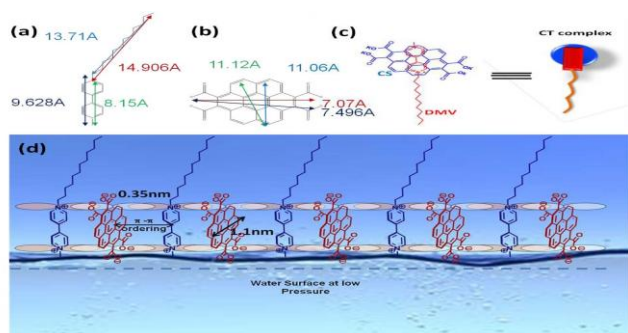


Figure 1: Length scales of DMV and CS molecules and the organization over in Air-Water Interface.

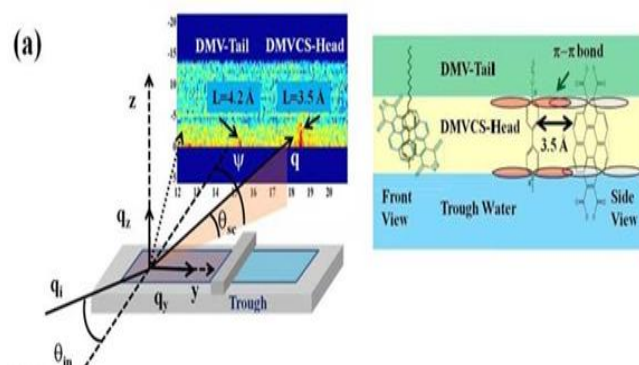
GID Measurement

Monolayer ordering development is notoriously hard to examine, although Grazing Incidence Diffraction (GID) measurements may help. We may also use the monolayer's surface pressure to investigate any in-plane ordering that may occur at the air-water interface. The SIRIUS beamline at the SOLEIL synchrotron in France was used to do the in-situ GID measurements with varied trough pressures of molecular monolayers at the Air-Water Interface. Data was collected at an incidence angle of $i=3$ milliradians into the beam, with the beam energy set at 8KeV. DMV monolayer generation on the water's surface required 15 minutes of sonication with 10 millilitres of a 1 M DMV solution in chloroform. Once the solute was well disseminated, it was added to the trough's water surface one drop at a time. To create the DMV-CS CT complex amphiphile monolayer, first a 1 M concentration of CS was added to the water in the LB trough, then the DMV monolayer production procedure was repeated, this time waiting 1 hr after adding the DMV dissolved in chloroform. Changing the height of the trough barrier allowed for the collection of GID data at a range of pressures. Images were combined along the channels to create the line scans, and an in-plane scanned 1-D Mythen detector with 2400 pixels was used to collect the data. The original raw 2-D detector file was integrated across a 20-pixel window to produce the 2D picture.

RESULTS

To learn more about the DMV-CS monolayer's interactions, we performed a Grazing Incidence Diffraction experiment at SIRIUS Beamline at SOLEIL France. Top of Figure 5.2 depicts the measurement geometry. The research was done on-site utilising through water with CS as a solute and DMV as a surface layer, allowing for charge transfer complexation at the Air-Water interface to create individual DMV-CS molecules. If equimolar aqueous solutions of DMV and

CS are combined together, a DMV-CS charge transfer complex is formed, and the DMV-CS molecules consolidate to form cylindrical micelle, which then self-assemble into highly ordered fibres. X-ray diffraction investigations of the fibres detected a peak of a length scale near to 3.4, which was determined to be the -DMV and CS molecules in the charge transfer moieties, the building block of such a higher order self-assembled structure. Other signs, such as the UV-Viz band for our system, are not visible for LB films owing to the extremely tiny quantity of sample present in the films, making it very difficult to verify the probability of charge transfer complexation at the Air-Water interface for our system. the growth of a peak at 10mN/m² trough pressure, with $q_{xy}=18.4\text{nm}^{-1}$, indicating a length scale in real space of 3.5, which is comparable to the - bond length of the DMV-CS molecule. This peak's appearance provides the experimental proof that charge conjugation between DMV and CS molecules is occurring in our system. As the pressure was raised to 15 mN/m², we saw that the peak's contrast in the 2D plot improved along with its intensity, as measured by the counts. According to the measurements, the DMV-CS head's organisation has improved as the barrier pressure has been applied across a broader region of the trough, as seen by a narrowing of the peak. When the pressure is raised to 20 mN/m², a second peak appears at $q_{xy}=15.1\text{nm}^{-1}$, corresponding to a real space length scale of 4.2. At high pressure, the Tail-Tail ordering of GdSt overcomes the gaseous nature of the isotherm, and this peak coincides with the GID peak found in a conventional Galulinium Stearate(GdSt) sample. Thus, the DMV-CS tails are likewise being ordered as a result of the applied pressure of 20 mN/m². It is interesting to note that the Head- Head(H-H) GID peak at 18.4 nm⁻¹ was obtained at low pressure (10mN/m), likely due to the onset of supramolecular ordering of the individual DMV- CS molecules after charge transfer complexation between DMV and CS.



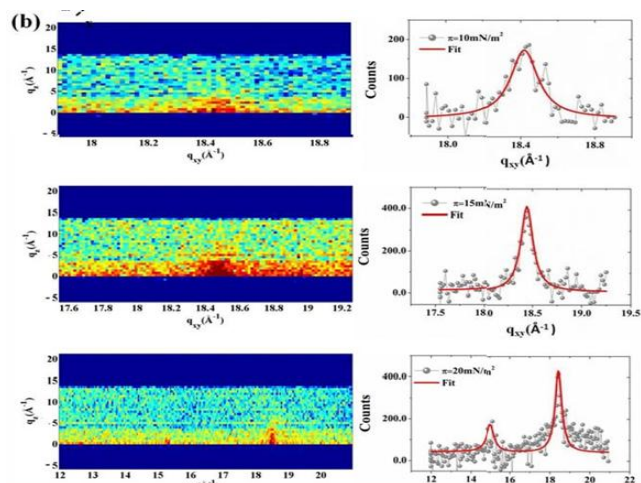


Figure 2: Grazing Incidence Diffraction setup used for the experiment

The results of a lengthy q_{xy} scan performed to determine how all of the important peaks changed in response to trough pressure. According to the procedures, a Mythen detector with 2040 vertical pixels was used to collect the information. The pixel was binned in 40 pixels in the vertical direction to increase the intensity of the peaks, and the summed intensity of those 40 pixels was used to create the 2D GID plot seen in the contour plot. You can see that there are problematic pixel patches throughout the detector because their intensity is uniformly high across the whole diagram, like a line. Such areas were disregarded from the statistical evaluation. The integrated intensity along the vertical pixels across the detector was used to create the line graphs. In the graph representing these three areas, we have shown three separate pressures. According to the isotherm, this molecule exists in a totally gaseous state at the air-water interface, which is what the plot at zero trough pressure (blue circles) shows.

The surface of a monolayer domain at moderate pressure, displaying both the head and CS peaks. To our eyes, it seems that the linear chains are piled in the q_{xy} plane, creating a 2D lattice with a length scale corresponding to the Head-Head distance. The DMV-CS molecular unit cell, with tails connected, is shown by the yellow circles. In addition, the tails, which may be orientated arbitrarily, do not exhibit a peak because of the weak pressure. The Tail-Tail ordering is only seen when the tails are subjected to much more pressure, which causes them to become considerably more stiff. From the diagram, we may deduce that the CS molecules are arranged in a linear chain, with the distance between any two such chains being the CS molecular distance. The Head-head peak and CS-CS peak in the GID data we have obtained may be explained by the presence of these randomly oriented domains in the 2D water surface. The DMV-CS heads' ordering improves and the peak intensity there rises with an initial increase in pressure. Nonetheless, when the pressure rises, the CS molecules begin to approach each other, resulting in an interaction of external pressure owing to the through barrier and the

electrostatic repulsion between the o- radicals in the CS molecule. As the pressure continues to rise, the linear chain connecting the DMV heads to the CS will begin to bend, and a circumstance may arise in which the DMV heads twist obliquely to shorten the CS's distance from the neighbouring chain. It is clear from the diagram that this setup severely disrupts the Head-Head Ordering present in the DMV-CS monolayer. Because of this, the maximum intensity of the Head-Head segment kept dropping as the pressure rose. This has also broken down the CS-CS ordering that existed in the monolayer before. Figure (b) shows that the head has no linked orientation if we follow the unit cells shown there. The 0.42nm Tail-Tail length scale of DMV-CS further supports this finding. If the tail formed a conformally stiff layer while the Head was being arranged, we would expect to see a scale of around 0.68 nm, or double the pi-pi distance. The shorter distance is the consequence of disordering of the head head linear stacking, where the CS in the head section are reorienting owing to electrostatic repulsion and the tails are moving closer to each other producing a stiff lattice at greater pressure. It can be shown in Figure 5.4(b) that the projected Tail-Tail hexagonal ordering in the DMV-CS monolayer is still there despite the loss of Head-Head ordering.

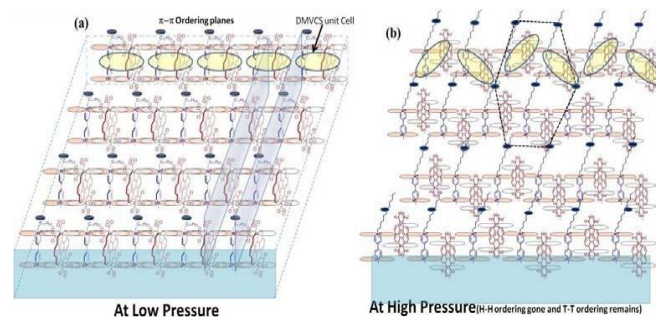


Figure 3: Schematic of monolayer evolution with change in orientation of DMV-CS moieties with increase in trough pressure

CONCLUSION

The GID study of the DMV-CS monolayer at the air-water interface revealed an intriguing property of a self-assembled monolayer: at low pressure, the monolayer consists of a rigid structure consisting of a linear chain of head groups forming a 2D lattice, but at higher pressure, the ordering of the head group is disrupted due to the interplay between the repulsion of the individual moiety of the DMV-CS charge transfer complex and the externally applied t . It was discovered that the head-head alignment disappeared altogether at higher pressure, leaving behind only the tail-tail ordering.

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