Exploring the Synthesis of Two-Dimensional Polymers: From Langmuir Films to Crystals

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry

By

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Abstract

Since the isolation of graphene the field of two-dimensional (2D) materials has become an intense research topic. Much of this work deals with naturally occurring 2D materials such as graphene, hexagonal boronitride, and molybdenum disulfide. While these materials have many unique properties and promising applications their structures are essentially fixed. This is one reason that interest in 2D materials that are synthesized using mild synthetic organic chemistry methods is growing. Using mild organic chemistry methods will allow for 2D materials with structures that have been designed to suit a specific application. These structures can be tuned and optimized in the same way small molecules can be. There are many promising applications such as separations membranes, surface patterning, and molecular electronics that will benefit from the realization of these materials.

In this dissertation I will explore the design principles, and methods for the synthesis of these materials, which we call two-dimensional polymers (2DPs). Chapter one will explore how we can classify 2DPs using the theory of tilings. Doing this not only provides a way to define 2DPs but also gives insights into the design of appropriate monomers for the synthesis of 2DPs.

Four different 2DPs will be presented in this dissertation. The first two are synthesized using amphiphilic shape-persistent tri-functional monomers that are confined at the air/water interface. Figure 1a shows antrip-DEG, which is one of the amphiphilic monomers used. These monomers are spread at the air/water interface and irradiated to give the 2DP (figure 1b and 1c). High resolution scanning probe
microscopy is used to show that both of the 2DPs made at the air/water interface are periodic and have pores ~0.9 nm in diameter.

![Figure 1](image)

**Figure 1.** a) Structure of antrip-DEG. b) UV irradiation of monomers on a Langmuir trough. c) SEM image of poly(antrip-DEG).

The last two 2DPs are made by a crystal approach. In this approach monomers are crystalized to preorganize them in 2D. The crystal is then irradiated with UV light to polymerize the 2D layers. Exfoliation of the layers provides the 2DP. We have characterized the crystals by X-ray diffraction, numerous spectroscopy techniques, and numerous microscopy techniques.
Acknowledgments

I would like to thank Benjamin King for providing me the amazing opportunity to work on this project. I will forever be grateful for the opportunities he provided me and the support he gave me.

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**Author’s Declaration**

Parts of the text presented in the abstract as well as chapters 2, 4, and 5 is taken or paraphrased from the following three papers


# List of Abbreviations

<table>
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<th>Description</th>
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<tbody>
<tr>
<td>1D</td>
<td>One Dimensional</td>
</tr>
<tr>
<td>2D</td>
<td>Two Dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>Three Dimensional</td>
</tr>
<tr>
<td>2DP</td>
<td>Two-dimensional Polymer</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>BAM</td>
<td>Brewster’s Angel Microscopy</td>
</tr>
<tr>
<td>COF</td>
<td>Covalent Organic Framework</td>
</tr>
<tr>
<td>GI-XRD</td>
<td>Grazing Incidence X-Ray Diffraction</td>
</tr>
<tr>
<td>PM-IRRAS</td>
<td>Polarization Modulated Infrared Reflection Absorption Spectroscopy</td>
</tr>
<tr>
<td>MMA</td>
<td>Mean Molecular Area</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<tr>
<td>SP</td>
<td>Surface Pressure</td>
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<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
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<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>UV/Vis</td>
<td>Ultraviolet / Visible</td>
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<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
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1. Introduction

1.1 General Introduction

Through the last century, chemists have brought the concept of polymers or macromolecules from theory into reality. Of course polymers have been around much longer than our human understanding of them. Nature has perfected the synthesis and uses of polymers long before us. However, chemists can now make polymers that are not found in nature and we can tune their properties to suit a vast number of applications. These polymers have come to dominate many aspects of our daily lives. They are key materials in simple applications to high-tech products and even to structural building materials. This increasing dominance of polymers can be seen from our global production of plastics, which was 310 million tons in 2014.¹

The polymers used in our everyday lives are all based on the linear growth of monomers into chain. Figure 1.1 shows three different classes of these polymers.

![Linear, branched, and network polymers](image)

**Figure 1.1.** Linear, branched, and network polymers. All are based on the linear growth of monomers to form chains.
If we disregard a polymer chain’s natural tendency to fold on itself we can consider it to be a one-dimensional (1D) object. Most of the polymers used today fall into this category. Their properties are dominated by chain-chain interactions and physical entanglement.

If one analyzes the dimensionality in small molecules one finds that their size is not more than a few nm and can, to an approximation, be considered zero-dimensional. The physical properties of these molecules are determined by their internal structure and the forces exerted between one another.

Jumping now to two-dimensional (2D) materials one finds that nature actually provides quite a few examples. These are materials that are composed of layers, which can be exfoliated down to individual 2D sheets. The most famous example of this is graphene. This 2D material was first discovered in 2004 by using Scotch tape to separate the individual layers of graphite. Because graphene has electronic and mechanical properties that are appealing for many applications it has gained much attention. It has also excited interest in other 2D materials such as hexagonal boronitride, molybdenum disulfide, various transition metal dichalcogenides, and transition metal carbides. This is just a small set of examples, and in fact, there are numerous of examples of 2D materials from natural sources.

Approaching 2D materials from a synthetic chemistry point of view results in a different story. Many of these inorganic 2D materials, such as graphene, can be made, however, their synthesis is limited to harsh thermolytic conditions that
prevent any practical structural design. For example graphene can grown on copper foil at 1000 °C from a mixture of methane and hydrogen. One can see that many of the ideals of synthetic chemistry (for example, rational structural design) are not compatible with this type of process. Realizing this one can ask the question: can 2D materials be synthesized in a rational, and mild way? It is this question that this dissertation seeks to shed light on. The following sections will provide the necessary background information needed in order to explore this question.

1.2. Two-Dimensional Polymers

The term two-dimensional polymer (2DP) has been used widely in the literature. The exact definition of the term, however, remains unclear. It was proposed by Schlüter et. al. that a 2DP should have all the characteristics of graphene. That is, one repeat unit thick, covalently bonded, and with long-range order. While this definition sets the stage for the synthesis of a material long sought after by chemists (a periodic, covalently bonded, molecularly-thin polymer) it leaves out many materials that are, in the author's opinion, worthy of the title.

To build a definition of a 2DP let's start with a definition of traditional polymers/macromolecules so we can build from it. From IUPAC's gold book a macromolecule is:
“A molecule of high relative molecular mass, the structure of which essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass.”

Let us consider linear polymers. Many of these are composed of one repeating monomer, such as poly(ethylene). Ignoring chain folding, one could say that poly(ethylene) is periodic in one dimension (1D). Let us now consider a random copolymer. In this polymer two or more different monomers are polymerized to form a chain. In a random copolymer the different monomers do not appear in the chain in any particular pattern. Therefore, a random copolymer is not periodic in one dimension yet it still fits the definition of a polymer. Using this logic one could argue that a two-dimensional material need not be periodic to be considered a 2DP.

Let us now consider linear coordination polymers. These are polymers with repeating coordination entities. While bonds holding these materials together are not all covalent, they are still polymers. They can be robust and functional materials.12

Taking all this into account, how then do we define 2DPs in such a way to encompass all the features of traditional macromolecules but still embrace the planarity of 2DPs? For this I will use the framework of topology and the field of tessellations to provide a precise definition.

A plane tiling is a set of tiles that cover a plane without gaps or overlaps.13 The tiles themselves are composed of vertices and edges. The vertices are connected by the edges to form a tile. This tile can then be patterned over a plane to give a
tiling. Figure 1.2 shows a tile being tiled to cover a plane without gaps or overlaps. In this figure vertices are represented by the black dots and the red lines represent the edges.

![Figure 1.2](image)

**Figure 1.2.** An example of a tile being tiled to cover a plane without gaps or overlaps to form a regular \(4^4\) tessellation. Edges are represented by the red lines and the vertices are represented by the black dots.

There are many classes of tilings such as Archimedean, regular tilings, semi-regular tilings, and random tilings, among others. Regular tilings are composed from congruent regular polygons. Semi-regular tilings are those that make use of more than one type of regular polygon. Random tilings are those that are not periodic and cannot be described by a repetition of regular polygons in any way. Figure 1.3 gives an example of these three types of tilings.
Now to apply this to 2DPs. We can define a 2DP as a tiling where the repeat units are the vertices and the bonds connecting them are the edges. The edges then outline a tile that can cover a plane without gaps or overlaps. This treatment has been explored in previously in crystallography. To put this definition into use let us describe graphene using this definition. The carbon atoms are the vertices and the C-C bonds are the edges. The edges outline hexagonal tiles, which cover the plane without gaps or overlaps.

Let us now consider the implications of this topological definition. First, considering a 2DP to be a tiling automatically restricts a 2DP to monolayers. If you have more than one layer the tiling then represents a structure that will have overlaps. This is consistent with other definitions of 2DPs.

Next, by this definition a 2DP need not be periodic. All that is required is that the bonds connecting the repeat units do not overlap in any way. This is not consistent with other definitions of 2DPs. Periodic 2DPs are just one class of 2DPs. It needs to be said, however, that periodic 2DPs will have benefits in many aspects. For example, structure elucidation will be greatly facilitated by periodicity. It allows for the use of powerful techniques such as X-ray diffraction, neutron diffraction,
scanning tunneling microscopy, atomic force microscopy, and transmission electron microscopy. There are many applications of 2DPs, such as membranes and surface patterning, that will benefit from periodicity. These applications will be discussed in detail later in the chapter.

This definition is not specific to the type of bond that forms the edges of the tile. All that is required for this is that the bond is robust enough to hold the structure together. From this we can see that 2D materials held together by metal coordination can still be classified as 2DPs. This aspect is also different than other definitions of 2DPs.

This definition also sheds light onto the design on monomers that can be used to form 2DPs. To be a tiling the valence (number of edges connected to the vertex) of each vertex must be at least three. Also, the edges coming from the vertex must be topologically planer. Let us now relate this to necessary features of a monomer. A 2DP must be made of a monomer that contains at least three reactive sites. Monomers can also have 4, 6, and 8 reactive sites. 5-fold symmetric monomers are excluded if they are to tile with regular pentagons because one cannot cover a plane with a pentagon without having gaps or overlaps. These reactive sites must also lie in a topological plane. This tells us that the monomer must be topographically flat. Not only must the monomer be flat it must also be shape persistent or rigid. This ensures that the functionality is always confined to the plane and cannot distort into 3D space. Figure 1.4 shows three examples of permissible monomers. One could imagine many other possibilities for designs.
Figure 1.4. Possible monomer configurations. Red blocks represent reactive binding sites and black lines represent unreactive parts of the monomer.

1.3. Synthetic Approaches to Two-Dimensional Polymers

Now that the definition of a 2DP has been laid out I will explore what has been done in attempting to construct this unique class of materials. As you will see many different approaches have been taken to achieve the synthesis of 2DPs. While some have yielded more results, all are valid methods.

1.3.1. Single Crystals

The use of single crystals for the synthesis of 2DPs has many appealing benefits. The structural perfection that is required to achieve a single crystal would insure structurally perfect 2DPs. Also, structural elucidation of the 2DP becomes achievable with the application of single crystal X-ray diffraction.
Figure 1.5. General outline of the strategy used to synthesize 2DPs using single crystals.

The general scheme used when synthesizing 2DPs using single crystals is presented in Figure 1.5. It starts with the crystallization of a monomer into a lamellar crystal. As outlined above this monomer must have at least 3 binding sites, as depicted in Figure 1.5. The lamellar monomer crystal is then polymerized to give a lamellar polymer crystal. The polymer crystal can then be exfoliated to give the 2DP. In this strategy there are many events that are difficult to predict. The monomer must not only crystalize in a lamellar fashion but it must have binding sites in close proximity to one another to allow polymerization to occur. If the polymer crystal can be successfully prepared it must then be exfoliated. For this to happen the forces holding the layers together must be sufficiently weak to allow separation. Exfoliations can be very unpredictable and require a large screening of conditions.

The first report of a 2DP synthesized following this strategy was reported in 2012 by Kissel et al. They used a photoreactive monomer bearing three 1,8-diethynylanthrylene (DEAs) units and three terphenylene bridges (TPBs) as seen in
Figure 1.6a. Crystallization from organic solvent gave sufficient quality crystals to allow the internal structure to be elucidated by single crystal X-ray diffraction. It was found that the monomer crystal was, indeed, a lamellar structure as planned. Within the layers the monomers adopted a hexagonal lattice in which the monomers alternated up and down (Figure 1.6b). An alkyne from an adjacent monomer overlapped with each anthracene at the medial positions. This arrangement would allow for a photopolymerization of the monomers by a [4+2]-cycloaddition between anthracene and the alkyne (Figure 1.6c). Upon irradiation with UV light it was found that polymerization did in fact occur by a [4+2]-cycloaddition. Transmission electron microscopy (TEM) imaging of the polymer crystal proved that order was retained through polymerization. These polymer crystals could be exfoliated down to single monolayers by heating in N-methylpyrrolidone for 3 days. Atomic force microscopy (AFM) imaging of the exfoliated sheets showed a thickness of ~2.5 nm which is consistent with the expected value for a monolayer. No X-ray diffraction structure of the 2DP was reported, however.
Figure 1.6. a) Monomer for the synthesis of 2DPs in single crystals. b) Arrangement of monomers in the monomer crystal. c) Depiction of the polymerization reaction.

Following this report another example of a 2DP prepared by this same strategy was reported by Kory et al.\textsuperscript{16} While this work has pushed the field of 2DPs into high gear the crystal approach lacks the ability to provide 2DP sheets large enough for many applications.\textsuperscript{9}
1.3.2. Air/liquid interface

The air/liquid interface has been shown to be a promising candidate for the production of 2D layers. Indeed, ordered monolayers of fatty acids have been made at the air/water interface.\textsuperscript{17,18} The use of the air/water interface confinement of monomers in 2D space and subsequent polymerization dates back to 1935 when Gee reported the polymerization $\beta$-elaeostearin and its Diels-Alder adduct with maleic anhydride (Figure 1.7).\textsuperscript{19,20,21,22} While the technology for in depth structural elucidation of the polymerized film was not available they observed large changes in viscosity upon polymerization. This lead them to conclude that the molecules where crosslinking to form a network.

\textbf{Figure 1.7.} Monomers used by Gee for the formation of cross-linked networks at the air/water interface.
UV-induced polymerizations of an acrylate containing monomers at the air/water interface was reported in 1973 by Dubault. The resulting films were reported to be highly viscous insoluble films. Other notable contributions of materials of this type were made by Ruaudel-Teixier and Kloepner and Duran.

Figure 1.8. Michl’s strategy for the synthesis of 2DPs. a) Lanthanum sandwich complex of tetrapyridylphyrin. b) Coupling unit used to link the lanthanum sandwich complex. c) Idealized structure of the resulting polymer made at the air/mercury interface. The lanthanum sandwich complex is represented by the blue dots and the dibromo p-xylene is represented by the red rectangles.

Over several years the Michl group made progress on the synthesis of a 2DP at the air/mercury interface. They used a lanthanum sandwich complex (Figure 1.8a) that was designed so that one of the tetrapyridylphyrin rings adheres to the mercury surface and the other is extending above the mercury. IR spectroscopic studies of the molecule on the mercury interface showed that this molecule does in
fact adopt a structure in which the tetrpyridylphyrin rings are parallel to the interface.\textsuperscript{27} In order to link the rings dibromo p-xylene (Figure 1.8b) was added. This yielded a product that was still fixed to the interface. IR spectra showed that the product contained p-xylyene units and pyridinium rings just as they expected. In order to confirm the structure of the film scanning tunneling microscopy (STM) experiments were attempted. To do this the film had to be transferred from the mercury surface to highly ordered pyrolitic graphite (HOPG). This is not a trivial task and resulted in folding and mechanical deformation. However, some STM images were acquired and a hint of the expected structure (Figure 1.8c) could be seen.\textsuperscript{27} This system is a rational attempt at 2DPs and has potential for optimization in order to yield 2DPs.

Regan and co worker made a significant contribution to the field of polymerization of amphiphilic monomers at the air/water interface. They not only polymerized monolayers they also provided groundbreaking work on using these films for molecular sieving.\textsuperscript{28,29,30,31,32,33} Their general strategy is outlined in Figure 1.9.
**Figure 1.9.** Organization of amphiphilic calixarenes at the air/water interface followed by crosslinking.

They begin by spreading amphiphilic calixarenes at the air/water interface. After compression the calixarenes are crosslinked using either reaction of mercury trifluoroacetate moieties with malonate ion from the subphase, disulfide formation, or so called “gluing”. The latter is where calixarenes containing carboxylic acid groups are brought together by addition of water-soluble poly-electrolytes. After crosslinking the films were transferred to a macroporous support. Some of these films were shown to give permeation selectivities much higher than Knudsen diffusion. This indicates that the calixarene is acting as a pore that allows smaller gas molecules to pass but sieves out larger gas molecules.

Jumping forward, explorations into the synthesis of a 2D coordination polymer (still a 2DP under our definition) at the air/water interface have been made...
by Schlüter and co-workers.\textsuperscript{34} For this a hexafunctional terpyridine monomer, 1, was synthesized (Figure 1.10). The polymerization of this monomer is based on the complexation of the terpyridine units with a divalent cation (Figure 1.10). Monomer 1 was spread at the air/water interface on a Langmuir trough. Surface pressure/mean molecular area (MMA) isotherms gave an area per molecule of 520 Å\textsuperscript{2}/molecule indicating that the monomer lays flat on the interface. Addition of divalent metal ions to the subphase, under a compressed monolayer, resulted in a free-standing sheet with a measured thickness of \~0.8 nm. Even though internal structure of this polymer was never elucidated, this work is a step forward in the production of 2DPs.

\textbf{Figure 1.10.} Monomer used for the formation for 2D coordination polymers at the air water interface (right). Binding motif of the monomers.
1.3.3. 2D COFs

A thermodynamic approach to 2DPs involves monomer assembly and polymerization simultaneously under a dynamic bond forming condition. This approach provides materials known as covalent organic frameworks (COFs). This differs from the two approaches previously discussed where organization and bond forming are separate steps. COFs are normally synthesized by condensing two shape-persistent monomers that have directed functionality. One of the monomers must have at least three binding sites to avoid formation of linear chains. This condensation gives layered crystalline COFs that must then be exfoliated. This exfoliation, however, is very difficult. COFs normally have strong interlayer van der Waals interactions that prevent exfoliation down to single layers. Additionally, COFs are very rarely obtained as single crystals due to the kinetics of the crystallization competing with the kinetics of the bond formation. This normally results in the formation of microcrystalline material. Because most COFs are microcrystalline only very small sheets can be obtained if the COF is exfoliated. To date only, two COFs have been obtained as single crystals.

To circumvent some of the issues stated above, Dichtel and coworkers grew COF thin-films on single-layer graphene. Figure 1.11 shows the monomers used along with the resulting polymer. This work led to the formation of planer sheets of COFs that could be transferred to other substrates. Important to note however, that these are multilayers. In fact, COFs have yet to be isolated as single sheets.
Another major problem with most COFs lies in the linking chemistry. Most COFs rely on boronic esters or boroxines to hold them together. These linkers are both susceptible to hydrolysis which severely limits their utility. Many of these COFs will degrade simply by exposure to atmospheric conditions.\textsuperscript{41}

\textbf{Figure 1.11.} Surface assisted synthesis of planer multilayer COFs.
1.3.4. Solid Surfaces

The use of solid surfaces is being explored as a medium for the 2D confinement of monomers. Normally, monomers are deposited onto metal surfaces in ultra-high vacuum. The monomers can then be coupled using reactions known in solution chemistry, for example, the Ullmann coupling, Schiff-base formation, and boronic acid dehydration.\textsuperscript{42,43,44} An advantage of this approach is that it does not impose the constraint that the monomer must be amphiphilic as in the air/water interface approach. It also has the advantage that molecular level characterization by scanning probe microscopy becomes feasible.\textsuperscript{45}

![Diagram of Ullmann coupling via organometallic intermediates of Ag(111)](image)

**Figure 1.12.** Ullmann coupling via organometallic intermediates of Ag(111). Figure reproduced from reference 46 with permission from Royal Society of Chemistry.
Figure 1.12 shows the Ullmann coupling of 1,3-bis(p-bromophenyl)-5-(p-iodophenyl)benzene on Ag(111) in ultra-high vacuum. Room temperature deposition results in a not so well organized organometallic structure. This organometallic structure is formed by catalytic dehalogenation of the aryl halide upon deposition. A mild heating causes an annealing through the reversibility of the dehalogenation. The annealing results in an equilibration into a hexagonal organometallic structure. Further heating causes silver atoms to be eliminated converting the organometallic structure into a covalent structure. The conversion from an organometallic structure to a covalent structure causes a significant shrinkage in the structure that leads to the formation of very small domains.

Other notable contributions to this field were made by Grill et al., Bieri et al., and Blunt et al. While the results from these studies are impressive there are drawbacks to this approach. The largest challenge is the formation of extended sheets. All the systems reported to date are challenged to get uniform sheets over a few hundred nanometers on a side. On top of this, because the sheets are formed by adsorption to a solid surface a method for the removal and transfer of the sheet must be devised.
1.4. Potential Applications of Two-Dimensional Polymers

1.4.1. Separations

If the structure of a 2DP is porous, one can envision the use of these ultra-thin materials in membrane processes. Let us start by discussing why 2DPs are suited for use as a membrane and why current technology is not sufficient.

Declining water resources are one of the most serious problems of our time. The issues concerning water are wide spread: 1.2 billion people do not have access to safe drinking water and 2.3 billion people live in water-stressed areas.$^{50,51}$ By 2025, the number of people living in water stressed areas is expected to grow to 3.5 billion.$^{51}$ Freshwater demand is constantly increasing due to our ever-growing agricultural and industrial demand. Currently, only two methods exist to supplement our natural hydrological cycle: desalination and water reuse.$^{50}$ As seawater and saline aquifers account for 97.5% of all the water on earth, desalination seems to be the more viable option.$^{52}$

The most extensively used desalination technology is revers-osmosis (RO).$^{53,54}$ Traditional RO membranes are composed of homogeneous polymeric materials, such as polyamides or cellulose acetate. These membranes do not have defined pores and water must navigate the free volume of the membrane to reach the other side. Water transport occurs in a three step process: absorption onto the membrane surface, diffusion through the membrane, and desorption from the opposite surface.$^{54}$ This is called the solution diffusion model. Separations in this
model occur simply because salts (or small molecules) diffuse much slower across the membrane than water.

The use of 2DPs as RO membranes is very appealing for two main reasons. First, a 2DP can be designed to contain pores of a particular size. This immediately transitions 2DPs into a different class than traditional RO membranes, which do not contain pores. If 2DP RO membranes can be realized they will no longer function by the solution-diffusion model. Instead they will function by a size exclusion-viscous flow model. The advantage here is that water flux will not be limited by the diffusion coefficient of the membrane as in solution-diffusion.

The second appealing feature of 2DPs is their absolute thinness. The flux across a membrane is inversely proportional to its thickness. This is true for membranes that follow the solution-diffusion model and membranes that follow a viscous flow model. Because 2DPs are inherently as thin as materials can be, the flux across them should be enormous. This enhanced flux due to absolute thinness is supported by computational and experimental studies using nanoporous graphene.55,56,57,58,59,60
Figure 1.13. Illustration of a membrane made from a monolayer (left) and a membrane made from bulk material.

Figure 1.13 shows a representation of a monolayer membrane and a membrane that is much thicker. Assuming both of these membranes have pores that are smaller than the mean free path of a gas molecule they will both fall in the Knudsen flow regime. However, because the monolayer membrane does not have an appreciable thickness, molecule-pore wall collisions are minimized. Because of this the flux across the membrane cannot be described by Knudsen diffusion. To model the flux of a monolayer membrane the theory of effusion is used. In this model the flux across the membrane is only limited by the probability of a molecule hitting the
1.4.2. Functionalized surfaces

2DPs are an appealing platform for the patterning of functional groups on a surface. Imagine a 2DP with a hexagonal array of functional groups. Transfer of this 2DP to a solid surface would provide a surface that can be functionalized in many ways. These functional groups could be used for a variety of things like attachment of a catalyst, growth of polymers, or attachment of biosensors.

1.5. Aim of the Dissertation

This dissertation will seek to cover the synthesis of four different 2DPs. The first two 2DPs that will be described are made at the air/water interface. Next will come the two made through the use of single crystals.

In this dissertation I will present four 2DPs that are all structurally similar but differ in several key aspects. All of these 2DPs are made from rigid, shape persistent, 3-fold symmetric monomers that have directed functionality. These monomers are presented in Figure 1.14.
The first two monomers, antrip-DEG and carboxy fantrip, are amphiphilic and thus, are used to make 2DPs at the air/water interface. Monolayer films were formed by spreading the respective monomer at air/water interface using a Langmuir trough (described in the following section). After compression of the monomers, irradiation of the film with UV light polymerized the films through a [4+4] cycloaddition of the anthracene blades (Figure 1.15). Following polymerization the films are transferred off the interface for characterization. A
more in-depth discussion of the air/water interface and the dimerization of anthracene are provided in the following sub-chapters.

![Diagram of anthracene and tetrafluoroanthracene dimerization](image)

**Figure 1.15.** The photochemical dimerization of anthracene and tetrafluoroanthracene by a [4+4] cycloaddition.

Characterization of the amphiphilic 2DPs was accomplished using spectroscopic and many different microscopic techniques. Notably, scanning probe microscopy was pushed to its limits of resolution to provide information on the internal structure. In Chapter 2, the exploration into the synthesis of 2DPs from antrip-DEG will be presented. The results will show that this initial monomer makes polymer films that have an ordered array of nanopores. I will also present the techniques used for film handling/manipulation, sample preparation, and imaging that allowed for the synthesis and characterization of the first periodic 2DP made at
the air/water interface. A discussion of the limitations and shortcomings of this system comes at the end of chapter 2.

In Chapter 3, I will present the results on the second generation of 2DPS made at the air/water interface. This uses the carboxy fantrip monomer. Although the carbon framework is the same as antrip-DEG, some very important modifications have been made. The outer rim of each anthraceno blade has four fluorine atoms attached. This is done to take advantage of the co-facial, antiparallel packing often seen in end-fluorinated acenes.\textsuperscript{62,63} This will provide a larger driving force for the monomers to form an ordered structure at that air/water interface. The other change is that the polar part of the molecule was changed to a carboxylic acid. This allows for tuning of the film by adjusting the pH of the subphase and/or the addition of salts to the subphase. Through all of this, I will show that carboxy fantrip makes ordered nanoporous 2DPS much more readily than antrip-DEG when it is spread and polymerized at the air/water interface. To take a step farther I will present the first measurements of mass transport in a 2DP.

In Chapters 4 and 5, I will switch from the air/water interface approach to the crystal approach to 2DPS. This involves antrip and fantrip monomers. These are the same as the monomers in the last two chapters except that they are not amphiphilic. Here, monomers are crystalized to form a preorganized structure. They can then be irradiated with UV light to induce the [4+4] cycloaddition of the anthraceno blades and then exfoliated to provide the 2DP. My role in these projects involved the characterization and exfoliation of the polymer crystal so I will focus
my effort on that. The necessary information to tell the complete story of the 2DPs will, however be included.

In Chapter 6 I will provide a summary of all the experimental results. Along with this I will also discuss the outlook for the specific work and the 2DP field in general.

My overall goal in this dissertation is to show that ordered nanoporous 2DPs can be made at the air/water interface. I also hope that the results presented here would serve as a guide for others in their quest to synthesize 2DPs. The field of 2DPs is in its infancy and the applications of the films are of immense importance so I hope this work serves as a stepping-stone.

1.5.1. Molecules at the Air/Water Interface

Benjamin Franklin first described the spreading of oil on water. The story is described by Franklin in his 1774 paper to the royal society. I summarize the story below.

In 1757, Benjamin Franklin was travelling to England in a fleet of 96 sailing ships. During the journey he noticed that the wakes of two ships in front of his were remarkably smooth and that others were ruffled by the wind. When he inquired about this the ships captain told him that he supposed the two ships cooks had just been emptying their greasy water and it had greased the side of the ships. Intrigued by this Franklin resolved to make an experiment on the effect of oil on water.
In England, Franklin stayed at Clapham Common were there was a pond. On one windy day Franklin went to the pond with a vial of oil. He dropped a small amount on the surface of the pond to test his observations that he made at sea. When the drop hit the water he saw it spread itself with great swiftness. He notes that an instant calm came over a space several square yards and eventually spread itself all the way to the other side of the pond. He also observed the prismatic colors that are produced from the thinning oil and that the thinning oil would force debris away as it spread.65

Franklin did not calculate how thin the layer of oil became after it spread across the pond. If he had done this he would have calculated the size an oil molecule. It would not until the 1890’s that this calculation would be performed. The story resumes with Lord Rayleigh. In 1890 he began repeating Franklins experiments except, he did them in a laboratory this time.65 By spreading just enough oil on a fixed area of water Rayleigh calculated the thickness of the film to be 1.6 nm. This is surprisingly accurate by today’s standards.

The story will now pick up with Agnes Pockels. In 1891, Lord Rayleigh received a letter from a German lady, Agnes Pockels. In this letter Miss Pockels describes her own work of the effect of oil on water. She describes an apparatus she used for adjusting the surface area of the water and how she measured surface tension. All of this becomes even more astonishing when you learn that Miss Pockels had no formal training in science and that her experiments were conducted in her kitchen. Lord Rayleigh, recognizing the importance of the work, immediately sent the letter to the journal Nature to be published.66 Following this, Miss Pockels
published three more papers on the subject in *Nature*. With these papers Miss Pockels laid the groundwork for all of the subsequent work to come.

It was not until Irving Langmuir stepped in to the scene that a molecular picture of oil on water was provided. Langmuir studied the behavior of a vast number of different fatty acids at the air/water interface. For this he used a trough that he built based on Miss Pockels original design. Because Avogadro’s number was available to him, he was not only able to calculate the thickness of the film, but also the area that each molecule took up. From this he was able to show that molecules were not spherical, as was thought at the time, but had an asymmetric shape. In the case of fatty acids, they are much longer than the cross-sectional area of the molecule. Langmuir’s data also showed that for saturated fatty acids the cross-sectional-area remained constant regardless of the length of the hydrocarbon chain. From this he was also able to conclude that the polar head group must reside in the water and the non polar tail must be in the air. Remarkably, he was even able to provide evidence that condensed films of fatty acids adopt a tilted conformation at the interface. To do this he used the measured thickness of the monolayer film to calculate a C-C bond length in the fatty acid molecule. He calculated a value of 1.39 Å, which was smaller than the accepted value that was determined from X-ray crystallography. From this he concluded that the fatty acid chains must adopt a conformation such that they are tilted away from the surface normal.
Figure 1.16. Surface pressures vs. mean molecular area isotherm of stearic acid showing the three “phases” that are seen in compression isotherms. The stearic acid molecule with the polar group drawn in red is shown on the right. $A_{\text{calc}}$ is the cross sectional area of a cylinder drawn around the carboxylic acid group. A cartoon representation of a Langmuir trough and its function is show at the top of the image.

A cartoon representation of an amphiphilic molecule being spread and compressed using a Langmuir trough is presented in Figure 1.16. The change in surface tension of the underlying water upon compression of the surface is called the surface pressure. A plot of the mean molecular area vs. surface pressure at constant temperature gives valuable information about the behavior of the film.
This plot can be thought of as the 2D equivalent of a P-V diagram for a gas/liquid/solid. When the molecules are first spread on the interface they are said to be in the gas phase where they are far enough apart that they do not interact with each other. Upon compression of the film a liquid like phase is reached. In this phase the molecules start to interact via van der Walls forces between the fatty acid tails. In the liquid phase the hydrocarbon chains are in a random orientation. Further compression results in a transition to a solid phase. This is usually accompanied by a constant pressure region in the isotherm. Although this transition has been shown to not strictly follow the thermodynamics of a 1st order phase transition it is useful to make the analogy.\textsuperscript{71,72,73} Through the use of fluorescence and Brewster angle microscopy, the coexistence of both condensed and liquid phases has been observed.\textsuperscript{74,75}

1.5.2. The Anthracene Dimer

The dimerization of anthracene dates back to 1867,\textsuperscript{76} when Fritzsche discovered that if he left a saturated benzene solution of “photene” in the sunlight small crystals that adhered to the walls of the vessel would appear. He also observed that the photoproduct would revert back thermally to the starting compound. It was later discovered that “photene” and its photo product was actually anthracene and dianthracene, respectively.\textsuperscript{77,78} Figure 1.17 shows the photodimerization of anthracene.
The dimerization of anthracene is a $[4\pi + 4\pi]$ photocycloaddition that occurs between the 9,10-positions of one anthracene molecule and the 9'10'-positions of another. This reaction is driven forward by irradiation with UV light around 365 nm. The dimer can be reverted back to starting material with heat or UV light in the 270 nm range.

The mechanism of this reaction has been extensively investigated and is thought to proceed by the reactions presented in Scheme 1.1. First, anthracene absorbs a photon and is excited to the singlet-excited state ($^1A^*$). This excited anthracene then forms an excimer (excited state dimer) with an anthracene in its ground state. This excimer can then decay back to the ground state by undergoing
a cycloaddition to give the photodimer. There are many competing processes for the excimer, including non-radiative decay and fluorescence decay. These competing processes are more or less favorable depending on the substitution on anthracene.51

The dimerization of anthracene is very appealing for use in the synthesis of 2DPs for a few reasons. First, the fact that this is photo-initiated allows for preorganized assemblies to be polymerized without the need to incorporate another molecular species. Second, dimerization does not involve complicated conformational changes during bond formation. This allows for bond formation even when the monomers are confined to two-dimensions. Third, the dimer and a monomer sandwich pair occupy a comparable amount of space. Therefore, a lattice of an anthracene based monomer film will not have to shrink an apprehensible amount upon polymerization. This could lead to the formation of extended films with very large domains.
2. Poly(Antrip-DEG)\textsuperscript{82}

Our 2DP is prepared from antrip-DEG (Figure 2.1a), a rigid, amphiphilic monomer consisting of three anthraceno blades organized on a central triptycene core that has a diethylene glycol tail at one bridgehead. The diethylene glycol chain anchors the monomer to the water surface with the antrip body lying on the interface. Monomers link via dimerization of the anthraceno blades (Figure 2.1b). This design is an extension of the antrip monomer previously developed in our laboratories for 2DPs generated by photopolymerization in the crystal state, which are discussed in Chapters 3 and 4.\textsuperscript{83,84} By extension, we hypothesized that irradiation of a compressed monolayer of antrip-DEG on the interface should afford the 2DP as a large, single sheet.
2.1 Monomer films

An antrip-DEG solution in 1:1 chloroform:cyclohexane was spread at the air/water interface in a Langmuir-Blodgett trough. Compression isotherms (Figure 2.2a) at 1 °C exhibited a phase change at about 155 – 135 Å²/molecule and a second at ~80 Å²/molecule. This first phase change was not observed at 25 °C. The mean molecular area (MMA) of the low-pressure transition suggests the initial formation of a hexagonal packing (Figure 2.2b), a motif also observed in crystal packing of a fluorinated analog. We would expect a MMA of 155 Å² for this packing. Upon further compression, this lattice collapses to an unidentified denser packing.

![Figure 2.2. a) Surface pressure vs mean molecular area isotherm for antrip-DEG at 1 °C. b) Possible packing of antrip-DEG at the air/water interface.](image)

The structure of the dense packing is not obvious. The maximally dense packing for a trigonal star is the lattice shown in Figure 2.3 and suggests a MMA of
about 100 Å², which is significantly higher than we observe. It is not uncommon, however, for extended molecules to give a smaller MMA than would be expected. Because we are interested in the less dense, and thus porous, hexagonal packing, the subsequent experiments are of films made at 1 °C and 0.5 mN / m.

![Figure 2.3](image.png)

**Figure 2.3.** Maximally dense packing of antrip-DEG.

The compression process was also followed by Brewster angle microscopy (Figure 2.4). Aggregation into large domains with few defects was observed upon initial spreading at 1 °C, and these domains then coalesced into a homogeneous film upon compression to 0.5 mN / m. Once the film is compressed beyond 0.5 mN / m, a higher contrast in the film was observed. This is consistent with the initial formation of a loose packing that rearranges to a tight packing upon compression.
Figure 2.4. Brewster angle microscopy of the compression of antrip-DEG at the air/water interface.

Transfer of the monomer film to SiO₂ wafers allows the films to be imaged by polarized optical microscopy (POM) and atomic force microscopy (AFM). In order to prove that the monomer film is in fact a monolayer AFM images of cracks in the film were acquired. Figure 2.5 shows a step height measurement for the monomer film. From these measurements the monomer film is shown to have a thickness of ~1.2 nm which is the expected height of a monolayer.
Figure 2.5. AFM height image of antrip-DEG on SiO$_2$.

Imaging the monomer films by POM (Figure 2.6) shows that large areas of unbroken film can be transferred.

Figure 2.6. POM image of antrip-DEG on SiO$_2$. 

2.2. Polymer Films

The compressed film (1 °C, 0.5 mN/m, 150 Å²/molecule) was photopolymerized at the air/water interface using 365 nm light (see Materials and Methods for details). Attempts to measure the post-polymerization molecular area were impossible because the rigid 2DP could not be reversibly compressed. Indeed, the 2DP on water was sufficiently rigid to force the paper Wilhemy plate out of vertical alignment by up to ~30° when a single barrier trough was used.

![Polymerized film image](image1)

**Figure 2.7.** a) Polarized reflectance optical microscopy image of polymerized film spanning 20 × 20 μm² holes on a TEM grid. b) Crossed polarized optical microscopy image of the same area as a.

These poly(antrip-DEG) films can be transferred from the interface to a variety of substrates. Transfer to a TEM grid by the Langmuir-Schaefer method and subsequent imaging by optical microscopy (OM) reveals that the 2DP is free-standing. Figure 2.7 shows a reflected polarized optical microscopy (POM) image of the TEM grids with poly(antrip-DEG) spanning 20 μm × 20 μm holes. A few tears are
evident and likely form during transfer. Crossed polarizers (Figure 2.7b) reveal that these tears, in which the 2DP is no longer perpendicular to the optical axis, are birefringent. Nonetheless, pristine 1 mm² areas of unbroken 2DP are commonly obtained. A control experiment without irradiation fails to produce a freestanding film.

![AFM image of poly(antrip-DEG) on SiO₂](image)

**Figure 2.8.** AFM height image of poly(antrip-DEG) on SiO₂ with a height profile along the black line.

Transfer by the Langmuir-Blodgett method to SiO₂ wafers allows for imaging by reflectance POM and AFM. Long (mm), straight edges and cracks are observed by reflectance POM (Figure 2.9), indicating that the 2DP breaks along cleavage lines. AFM imaging (Figure 2.8) of single layer polymer films on SiO₂ reveals a thickness of ~1.2 nm, which is consistent with the expected height of a monolayer. This thickness is constant over large areas.
Figure 2.9. (a,b) OM images of poly(antrip-DEG) on SiO₂ (c) Water condensation on a SiO₂ wafer partly coated with poly(antrip-DEG). Large droplets show uncoated SiO₂ and small droplets reveal the coated portion.

The contact angle of water on a single layer of poly(antrip-DEG) on SiO₂ is 92°, which is comparable to conventional self assembled monolayers containing aromatic moieties. This angle indicates that the hydrophobic face of poly(antrip-DEG) faces out, as is expected from the direction of transfer off the interface. The unmasked SiO₂ has a contact angle of 50°. This difference in hydrophobicity enables visualization by water condensation (Figure 2.9c), with larger droplets forming on uncoated SiO₂ and smaller droplets forming on 2DP-coated SiO₂. The effect is
evident to the naked eye and may permit imaging of 2DPs on other supports. This method has allowed for the conformation that we can transfer sheets up to 1 cm² (Figure 2.10).

**Figure 2.10.** A ~0.9 cm² sheet of poly(antrip-DEG) imaged by selective condensation of water. The film starts at the blue arrow and extends down to the bottom of the image. The film is largely intact but some defects can be seen.

Polymerization via anthracene dimers is supported by UV-Vis spectroscopy. Transfer of the non-polymerized and polymerized films onto quartz slides permitted their spectra to be obtained. The changes upon polymerization⁸³ (Figure 2.11) are similar to those observed upon polymerization of crystalline antrip.
Figure 2.11. a) UV-Vis spectra of single layer antrip-DEG (----), and poly(antrip-DEG) (-----) on a quartz slide. b) Solid-state UV-VIS spectra of antrip (----) and polyantrip (---).

Scanning tunneling microscopy (STM) establishes the structure of the poly(antrip-DEG) 2DP. After numerous attempts at STM imaging in our laboratory, only low quality images could be achieved. A porous hexagonal structure can be seen in the imaging even though the quality is low (Figure 2.12).
Figure 2.12. a) Constant height STM image of poly(antrip-DEG) on HOPG. b) Line traces along the black lines in a. Analysis of the traces gives unit vectors of $a \approx 1.2$, $b \approx 1.6$. This image contains significant drift, which may skew the measured unit vectors.

Collaboration with Markus Lackinger at TU München resulted in high-resolution imaging. This high-resolution STM imaging (Figure 2.13) of the 2DP reveals a porous structure that is consistent with the structure established by crystallography for related 2DPs.\textsuperscript{84} A split-image is shown in Figures 2.13c. In the upper part of the frame the 2DP was imaged, and at the scan-line marked by the arrow the tunneling parameters were abruptly changed during the scan for imaging the underlying HOPG in the lower part. This split-image scan demonstrates that the 2DP lattice image is real and not an artifact arising from a tip defect that gives a
distorted image of the HOPG lattice. The assertion that the 2DP images are real is further supported by the observation of domain boundaries (Figure 2.13d).

Figure 2.13. (a) STM image (+ 0.91 V, 28 pA) of poly(antrip-DEG) on HOPG under 1-phenyloctane. (b) Simulated poly(antrip-DEG) p6 lattice at the same scale as a. (c) Split image of monolayer poly(antrip-DEG) on HOPG showing both the 2DP lattice and the underlying HOPG lattice; the arrow marks the scan-line where the imaging parameters were changed (d) Wide view STM image (+ 1.0 V, 25 pA) of poly(antrip-DEG) on HOPG under 1-phenyloctane showing a domain edge at the lower right corner.
The observed unit cell parameters (calibrated from the split image) are $a = 1.3 \pm 0.2$ nm and $b = 1.3 \pm 0.2$ nm with $\gamma = 63.5^\circ$. This lattice constant is, however, smaller than the 1.8 nm expected from the simulated hexagonal $p6$ lattice shown in Figure 2.13b. The origin of this difference remains unclear. The structure might be subtly different from our expectations. For example, anthracene dimerization can occur between the 1,4 and 9,10 positions (Figure 2.14), as has been observed in constrained anthracene-anthracene systems.\(^8\) This linkage would give a lattice constant of 1.54 nm (Figure 2.15), which is within the uncertainty of these STM distance measurements. Or perhaps the lattice contracts by some deformation or distortion when mounted on the surface. Nonetheless, the important conclusion remains unchanged: the amphiphilic poly(antrip-DEG) 2DP forms a porous, honeycomb lattice.

**Figure 2.14.** 1,4-9,10 connectivity of two repeat units.
Figure 2.15. Simulated polymer lattice with 1,4-9,10 connectivity.

The pore density of this 2DP is enormous: $\sim 6.8 \times 10^{14}$ pores / cm$^2$. This is about three orders of magnitude higher than that reported for state of the art carbon nanotube membranes$^{90}$ and six orders of magnitude larger than polycarbonate track-etched membranes with 10 nm pores.$^{90}$ Moreover, this 2DP is three orders of magnitude thinner than the carbon nanotube membranes. STM imaging indicates that the pores have a narrow size distribution and are measured to be $\sim 0.7$ nm in diameter. The monodisperse, sub-nanometer pore size and monolayer thinness suggests that this 2DP might be useful in separations.
2.3 Conclusions

To conclude, we have prepared a 2DP by photopolymerization of antrip-DEG at the air/water interface. BAM imaging during the Langmuir-Blodgett compression shows that homogeneous monomer films can be formed. UV light irradiation of these films over the entire trough (~50 cm²) induces polymerization. The resulting 2DP can be transferred to both solid substrates, where cm² areas can be covered, and open lattices, where 20 μm × 20 μm holes can be spanned. The formation of a monolayer is confirmed by AFM. STM imaging shows that the polymer is periodic with a honeycomb lattice. We have observed boundaries by STM and suspect that the 2DP sheets comprise many domains.
2.4 Materials and Methods

Langmuir Film Preparation

Two different Langmuir troughs were used in this study, the first being a KSV 2000 System 2 and the other is a modified NIMA 312. Surface pressures were measured with a platinum or paper Wilhelmy plate. Both troughs are made from Teflon and the barriers are made from Delrin.

Antrip-DEG was dissolved in a 1:1 mixture of chloroform:cyclohexane to a concentration of 0.5 mg/mL. It was found that spreading from a pure chloroform solution resulted in the formation of a non-homogenous film. For spreading on the KSV 2000 System 2 60 μL was used and 10 μL was used for the NIMA 312. After spreading 45 minutes was allowed for solvent to evaporate if experiments were conducted at 1 °C and 30 min for isotherms at room temperature. Compression rates were 3 mm/min and 4 mm/min for the two troughs, respectively.
Brewster Angle microscopy

Brewster angle microscopy was performed with either a KSV MicroBAM or a home built microscope constructed following the details provided by Knobler et al. The KSV MicroBAM uses a 649 nm laser and the home-built BAM uses a 532 nm laser.

Polymerization and Film Transfers

For polymerizations at 1 °C, the trough was first cleaned at room temperature with chloroform and ethanol. The trough was then filled with milli-pure water and cooled to 1 °C. Antrip-DEG was then spread on the interface as described above. After spreading, the film was compressed until the start of the phase transition (~0.5 mN/m) and held at that pressure. A 40 W 365 nm light emitting diode (Led-Engin, LZC-70U600) was used for the irradiation (see Figure 2.16). The LED was placed ~5 inches above the interface and the compressed film was irradiated for 30 min. This setup allows the entire trough to be irradiated. Before transfer of the film, the subphase was warmed to 30 °C. It was found that warming the subphase was necessary for successful film transfer.

Transfer to TEM grids (PLANO G2780C) was accomplished by placing the grids horizontally on top of the irradiated film, much like a Langmuir-Schaefer film deposition. The grids were removed from the interface by placing a small piece of paper over them such that they adsorb onto the paper. The paper can then be pulled off the interface taking the grids with it.
For vertical transfer to SiO$_2$ wafers or any hydrophilic surface, substrates were immersed in the subphase before antrip-DEG was spread at the interface. Spreading, compression, and polymerization was performed as stated above. After polymerization was complete the substrate was pulled from the interface at a rate of 1 mm/min.

Transfer of a single layer to HOPG (ZYB Quality) with DEG tails facing down was achieved by modification of the subphase. HOPG has a hydrophobic surface, which classically inhibits single layer transfer on the up stroke. In order to achieve transfer in this manner, minimization of the surface energy difference between the subphase and the substrate is required.$^{92}$ This was accomplished by using a 0.2 M solution of 2-propanol in water as the subphase. This solution has a much lower surface tension than pure water and a lower contact angle on HOPG. The film was found to have all the same behavior on this subphase as on pure water.

The horizontal lifting method was used for the transfer. Freshly cleaved HOPG was placed on a home made wire “basket” and placed under the subphase which was held at 1 °C. Antrip-DEG was then spread on the interface, compressed, and polymerized. After polymerization the subphase was warmed to ~30 °C and the HOPG was lifted out of the subphase at a rate of 0.5 mm/min.
Atomic Force Microscopy

AFM imaging was performed either with a Nanosurf easyscan II AFM operated in contact mode in air or a pacific nanotechnology R2 operated in tapping mode. For the Nanosurf AFM, App Nano silicon SICONA cantilevers (Applied NanoStructures, Inc.) having a resonance frequency of 11-18 kHz and a spring constant of 0.1-0.6 N/m were used. A set point of 15 nN was used for both the monomer and polymer films. For the pacific nano AFM, Budget Sensors Tap300 probes with a resonance frequency of 300 kHz and a spring constant of 40 N/m were used.
Optical Microscopy

Optical microscopy was performed using a Leica DM2500P. Samples were prepared using the method described in the “polymerization and film transfer” section.

Contact Angle measurements

Figure 2.17. Homebuilt contact angle instrument employing a stereomicroscope.

Contact angle measurements were performed with a home built apparatus. A stereomicroscope was used for the optics and image capture. The microscope was focused on a right angle prism, which turned the optical path horizontal and permitted focusing on the sample. The sample was placed on a sample stage (see fig. 2.17) The syringe for drop application was controlled by a micromanipulator. Images were processed with Image J.
UV/Vis

UV/Vis spectra were obtained using a Perkin Elmer lambda 850 spectrophotometer. Samples were made by lifting a quartz substrate horizontally out of the interface. Spectra were recorded in transmission mode.

Scanning Tunneling Microscopy

STM images were acquired in constant current mode with a home-built microscope driven by a commercial ASC500 SPM controller (attocube Systems AG). The samples were imaged under ambient conditions in the dry state (i.e., without applying any solution) and under a drop of 1-phenyl octane using mechanically cut PtIr tips. The instrument was thoroughly calibrated with atomically resolved images of graphite.

Other images were acquired with a Nanosurf easyscan II STM operated in constant height mode. The samples were imaged under trichlorobenzene using mechanically cut PtIr tips.
Supplemental Isotherms

Figure 2.18. Isotherm of antrip-DEG at room temperature.

Supplemental BAM Images

Figure 2.19. BAM images of the compression of antrip-DEG at 1 °C. All scale bars are 1 mm.
Figure 2.20. BAM images of the compression of antrip-DEG at room temperature.

All scale bars are 700 µm.
Supplemental AFM images

**Figure 2.21.** AFM height image of non-polymerized antrip-DEG film made at 1 °C on SiO$_2$. The observed height of the monomer film is ~1.2 nm.

**Figure 2.22.** AFM height images of poly(antrip-DEG) made at 1 °C on SiO$_2$. Height analysis shows the observed height to be ~1.2 nm.
Supplemental STM images

Figure 2.23. Supplemental STM images a) Poly(antrip-DEG) deposited on HOPG imaged in air. b) Poly(antrip-DEG) deposited on HOPG imaged under 1-phenyloctane. c) Split image of poly(antrip-DEG) on HOPG. The upper portion of the image shows the 2DP, whereas in the lower half the underlying graphite was imaged by abruptly changing the tunneling parameters.
**Mean Molecular Area Discussion**

Figure 2.24 shows a simulated packing of antrip-DEG which was proposed because of previous work with non-amphiphilic antrip in the crystalline state. In this packing all anthracene blades are co-facially stacked and could give rise to the observed polymer lattice. This lattice is consistent with the observed area for the first phase transition in the low temperature isotherms. Figure 2.25 shows another possible lattice that correlates with the observed MMA of the first phase transition. This lattice, however, must undergo rearrangement in order to obtain a conformation in which polymerization can occur.

The observed MMA of the solid phase is much more dense and did not correlate with any lattices known to us. Due to this we began exploring more dense packings. Figure 2.26 shows a packing with the p2gg plane group which has an MMA of 100 Å² per molecule. This lattice has been shown to be the maximally dense packing for objects of this shape. This lattice is, however, still larger than the observed MMA of the solid state. Because of this the exact structure of the solid phase remains unclear to use for now.
**Figure 2.24.** Simulated potential packing of antrip-DEG on the interface. This packing has a p6 plane group and gives a calculated mean molecular area of 155 Å² per molecule.

**Figure 2.25.** Simulated potential packing on the interface. This packing has a p31m plane group and gives a calculated mean molecular area of 140 Å² per molecule.
**Figure 2.26.** Simulated maximally dense packing of antrip-DEG. This packing has a p2gg plane group and gives a calculated MMA of 100 Å² per molecule.
Contact Angle Images

**Figure 2.27.** Contact angle images monolayer polyantrip-DEG on SiO₂ giving a contact angle of 90° (left) and of bare SiO₂ giving a contact angle of 55° (right).

Wilhelmy Plate Deflection

**Figure 2.28.** Image showing the extent to which the Wilhelmy plate can be deflected during the course of a Langmuir experiment if a single barrier trough is used. If the surface is aspirated after compression the plate will fall back to normal position.
3. Poly(carboxy fantrip)

Carboxy fantrip (Figure 3.1a) was synthesized in 5 steps starting from 9-anthracenecarboxaldehyde. The synthesis was performed by other group members and will not be discussed here. The reactivity of this monomer lies in the three tetrafluoroanthraceno blades, which can photodimerize through the well known [4+4] cycloaddition. These tetrafluoroanthraceno blades are connected through a [2.2.2] bicyclic core. Arrangement of the tetrafluoroanthraceno blades in this fashion provides a shape persistent, rigid, trigonal star shaped molecule with a large internal free volume that hinders efficient packing of the molecules. The carboxylic acid moiety at one of the bridgehead positions of the central [2.2.2] bicyclic core anchors the monomer to the air/water interface in such a way that the tetrafluoroanthraceno blades lay perpendicular to the interface. This orientation allows monomers to stack their reactive blades in a face-to-face fashion permitting a [4+4] cycloaddition under UV irradiation. The use of tetrafluoroanthraceno blades facilitates the co-facial, anti-parallel packing of the monomers at the air/water interface.93

**Figure 3.1.** Structure of carboxy fantrip and its dimer.
3.1. Monomer Films

A 0.2 mg/mL solution of carboxy fantrip in 1:0.1 chloroform:2-propanol was spread at the air water interface and compressed. The resulting surface pressure/mean molecular area (SP/MMA) isotherm (figure 3.2) shows a steady rise in surface pressure starting around 200 Å²/molecule followed by a collapse of the film starting at ~25 Å²/molecule. The MMA is calculated to be 175 Å²/molecule, which is consistent with the area per molecule calculated from the crystal structure of a non-amphiphilic analogue.

![Figure 3.2. SP\MMA isotherm of carboxy fantrip at the air/water interface.](image)

Following the compression process by Brewster angle microscopy gives insight to the spreading and morphology at the interface. As shown in Figure 3.3, carboxy fantrip forms large islands with straight edges and sharp corners when initially spread at the interface. Upon compression these islands start to coalesce and a homogeneous film is observed by 10 mN/m. The features of these islands indicate that carboxy fantrip likely forms an ordered structure when spread at the air/water interface. From the calculated
MMA we can suggest that the structure is a porous, hexagonal lattice. This is the same lattice that is observed in the crystal structure of the non-amphiphilic derivative, fantrip.\textsuperscript{84}

Figure 3.3. Brewster angle microscopy showing the compression of carboxy fantrip at the air/water interface.

Films of carboxy fantrip can be transferred to a variety of solid substrates. This can either be accomplished by Langmuir-Blodgett deposition or by Langmuir-Shafer deposition. This gives us the ability to have either side of the film exposed to air. Transfer of the film to SiO\textsubscript{2} using the Langmuir-Blodgett method allows for the film to be imaged by polarized optical microscopy (POM) and atomic force microscopy (AFM). POM images of the film show that large areas ( > 1 mm\textsuperscript{2}) of unbroken homogeneous film can be transferred off the interface (Figure 3.4). To confirm that the monomer film is a monolayer AFM imaging was performed. Figure 3.5a shows an AFM image of a film edge. A height trace along the black line in Figure 3.5a gives a step height of \(\sim\)1.3 nm which is consistent with the expected monomer dimensions. This thickness is uniform
over larger areas. Figure 3.5b shows a zoom of the outlined area in Figure 3.5a. This image reveals that the film is homogeneous on the nm scale.

**Figure 3.4.** POM image of carboxy fantrip on SiO$_2$.

(figure caption on next page)
Figure 3.5. a) AFM images of the monomer film on SiO$_2$. b) Zoom on the boxed area in a. c) height trace along the black line in a. The observed lines in this image most likely come from vibrational noise.

3.3 Polymer Films

Based on isotherm measurements and BAM studies, 10 mN/m was chosen as the surface pressure to perform polymerizations at. Polymerizations were performed at room temperature in ambient atmosphere. A 5 W 365 nm LED was used to irradiate the entire trough. Upon polymerization a sharp decrease in surface pressure is observed. The surface pressure is then restored to the starting value by a decrease in the trough area.

Figure 3.6. Change in surface pressure upon photopolymerization of carboxy fantrip at the air/water interface.

This can be attributed to a decrease in lattice size for the polymerized film. Figure 3.7 shows simulated monomer and polymer films. Measurement of the MMA for both
structures shows that the polymer film is 15 Å²/repeat unit smaller than the monomer film. Because the polymerization presumably happens faster than the barriers can close, a dip in surface pressure is seen until the barriers catch up with the polymerization reaction.

Figure 3.7. Change of MMA upon polymerization of carboxy fantrip.
The polymerization reaction was monitored by BAM to ensure no changes in film homogeneity occurred. Figure 3.8 shows BAM images of the film before and after polymerization at 10 mN/m. The images show no changes upon polymerization. If the barriers are opened after polymerization no changes are observed in the BAM indicating the film cannot be reversibly decompressed after polymerization. If, however, the interface is disturbed by vibration after opening the barriers long straight cracks are observed (Figure 3.8). This is indicative of a stiff, rigid film cracking under the application of mechanical force.

![BAM imaging of polymerization](image)

**Figure 3.8.** BAM imaging of the polymerization of carboxy fantrip at the interface. Scale bars are 1 mm.

The irradiated films can be transferred to a variety of substrates for analysis. Transfer by a “tilt transfer” method (see materials and methods for details) to SiO$_2$ wafers shows that large area (>1 mm$^2$) defect-free films can be transferred off the interface. Figure 3.9 shows two examples of polymerized film transferred to SiO$_2$. The transferred films often exhibit long straight cracks with clear corners. After observing many transferred films, corners of ~70° and ~110° are often seen. These angles are consistent with the unit cell angles that are seen in the crystal structure of the non-amphiphilic derivative of poly(carboxy fantrip). Consistent observation of these clearly defined edges
and corners gives another hint that poly(carboxy fantrip) possesses long range order. Because the angles are consistent with the crystal structure of the non-amphiphilic derivative, a porous hexagonal structure is likely.

**Figure 3.9.** POM images of poly(carboxy fantrip) on SiO₂.

The contact angle of water on a single layer of poly(carboxy fantrip) transferred to SiO₂ on the up-stroke of a Langmuir-Blodgett-type dipping is 95° indicating that the
film is transferred with the carboxylic acid tails facing the substrate. If a single layer film is transferred to silinated SiO$_2$ using a Langmuir-Shafer-type dipping the contact angle is $52^\circ$ indicating that the carboxylic acid tails are facing the air. Being able to transfer the film with carboxylic acid groups facing the air will enable future studies in post-polymerization modification of the films. These will involve using the carboxylic acid groups as a reactive handle. More details on this can be found in the Conclusion and Outlook section.

Imaging poly(carboxy fantrip) films on non-reflective substrates is not straightforward. It can be done by AFM but this can be very time consuming and imaging large areas is not possible. By taking advantage of the different contact angles of the polymer film and the bare substrate the film can be indirectly imaged. Figure 3.10 shows water vapor condensed onto a single layer of poly(carboxy fantrip) deposited onto quartz. The larger droplets show areas that do not have film and the smaller droplets show areas that are covered with the film. This technique allows for fast, large-scale imaging of the polymer film on non-reflective surfaces.
Poly(carboxy fantrip) can be transferred to copper TEM grids by a Langmuir-Schafer method. Imaging the grids by SEM shows that the monolayer film is able to span $25 \times 25 \text{ \( \mu \text{m}^2 \)}$ holes. Figure 3.11 shows SEM images of freestanding monolayer films. Most of the holes are covered with film but some show ruptured film. The ruptures occur either during transfer of the film off the interface or whenever the electron beam is

*Figure 3.10.* Water condensation on poly(carboxy fantrip) deposited onto quartz.
focused too much. Close inspection of the ruptured films shows that the monolayer folds up on themselves when that are not secured on all sides. Figure 3.11 shows a ruptured film were folds are clearly seen.

**Figure 3.11.** SEM images of poly(carboxy fantrip) spanning $25 \times 25 \, \mu m^2$ holes on a TEM grid.
Films transferred to TEM grids can also by imaged by polarized reflectance optical microscopy. If they are imaged under cross polarizers tears that are oriented so it is not perpendicular to the optical axis appear birefringent (Figure 3.12).

![Image](image.png)

**Figure 3.11.** Cross polarized optical microscopy image of spanning poly(carboxy fantrip).

In order to confirm that polymerization occurs by anthracene dimers the films were studied by UV/Vis spectroscopy. Monolayer films were transferred to fused silica optical flats in order to obtain their spectra. It is seen that the fine structure from 390 nm to 330 nm disappears upon polymerization. This is consistent with the spectral changes upon dimerization of anthracene.

In order to establish the structure of poly(carboxy fantrip) we use high-resolution atomic force microscopy (HR-AFM). Monolayer poly(carboxy fantrip) was transferred to freshly cleaved mica in order to permit high resolution imaging. Figure 3.13 shows HR-AFM phase images of poly(carboxy fantrip) on mica that show a distorted hexagonal
array of pores. Analysis of multiple images from multiple different samples gave observed unit cell parameters of \( a = 1.8 \pm 0.3 \text{ nm} \) and \( b = 2.0 \pm 0.3 \text{ nm} \) with \( \gamma = 71^\circ \pm 3^\circ \). Domain boundaries can be observed in some images (Figure 3.13c). Because the 2DP lattice can not be resolved if the scan size is larger than about 100 nm imaging a entire domain was not successful. We can conclude that poly(carboxy fantrip) consists of domains but we have no information on domain size.

The AFM phase images show pockets of dampened phase (dark spots in AFM images). Analysis of the height image shows that these correspond to mounds in the film a few angstroms high. This likely arises from ions or other contaminants that are trapped under the 2DP. Because imaging was performed in the repulsive regime it is likely that the film deforms when the tip moves over these regions causing a dampening of the phase. If the same region is imaged in the attractive regime these features are not observed but the 2DP lattice can not be resolved under these conditions.

The observed lattice parameters for poly(carboxy fantrip) are consistent with those found in the single-crystal XRD data of poly(fantrip) crystal \((a = 1.71 \text{ nm} \ b = 1.92 \text{ nm} \ \gamma = 70^\circ)\) (Chapter 5).\(^4\) Figure 3.14 shows the crystal structure for one layer of poly(fantrip). The 2DP adopts a distorted hexagonal lattice presumably to maximize intramolecular dispersion interactions between the \( \pi \)-stacked tetrafluorobenzene/benzene pairs.\(^4\) We observe that poly(carboxy fantrip) adopts this same distorted lattice at the air/water interface.
Figure 3.13. HR-AFM imaging of poly(carboxy fantrip). a) 70 × 70 nm phase image
b) 2D-FFT of the image in a c) 70 × 70 nm phase image were two domains can be seen.
Figure 3.14. Crystal structures of poly(fantrip) for comparison with poly(carboxy fantrip)

Transport measurements on free standing poly(carboxy fantrip) have been performed by measuring the flux of helium and nitrogen across the polymer. Because poly(carboxy fantrip) that is transferred to TEM grids consistently give a mixture of spanned and not spanned holes we transferred to a copper TEM grid which has a single 50 μm hole. This allows for simple determination of the spanning quality of the film. The hole is also large enough to give gas flow rates that are measurable by a capillary bubble flow meter. This grid is then placed in our flow cell and the flux of a gas can be measured using a capillary bubble flow meter.
Figure 3.15. a) Poly(carboxy fantrip) spanned over a 50 µm hole. b) Poly(carboxy fantrip) that ruptured on transfer.

To model the flow of gas across the 2DP we turn to the kinetic molecular theory of gases. Because the pores are much smaller than the mean free path of the gas molecule the probability of intermolecular collisions in the vicinity of the pore is low. In this system transport is in the molecular flow regime and can be explained using an effusion mechanism, which is only dependent on the probability of a gas molecule hitting the pore. Effusion flux in our 2DP can be described by the equation,

\[
Rate = \left(\frac{\Delta P A_p}{\sqrt{2\pi MR}}\right) N_p
\]

were \( P \) is the pressure, \( k_B \) is Boltzman's constant, \( T \) is the temperature, \( R \) is the gas constant, \( A_p \) is the pore area, and \( N_p \) is the number of pores in the membrane.
Table 3.1 shows theoretical permeance values calculated using Equation 1 and measured permeance values for nitrogen, helium, and carbon dioxide. The measured values are slightly lower than the theoretical presumably because a fraction of gas molecules will have a trajectory such that they will hit the pore wall. However the experimental values are in good agreement with theory.

### 3.3 Conclusions

We shown that photopolymerization of a Langmuir film of carboxy fantrip gives a nanoporous 2DP. Transfer of this 2DP to SiO$_2$ shows that large areas of homogeneous films are made. The 2DP is measured to be ~1 nm thick by AFM showing that poly(carboxy fantrip) exists as a one molecule thick sheet. Spanning the 2DP over holes on a TEM grid and imaging by SEM show that the film is mechanically coherent. HR-AFM imaging reveals that the 2DP is a periodic nanoporous 2DP. The structure is analogous to previously reported 2DPs made by single-crystal-to-single-crystal polymerizations. We also show that that gas
transport in poly(carboxy fantrip) obeys an effusion mechanism giving ballistic transport rates.

3.4. Materials and Methods

Langmuir Film Preparation

The Langmuir trough used in this study was a NIMA 312 modified to have two barriers and a larger trough. Surface pressures were measured with a paper Wilhelmy plate. The trough is made from Teflon and the barriers are made from Delrin.

Carboxy fantrip was dissolved in a 10:1 mixture of chloroform:isopropanol to a concentration of 0.2 mg/mL. It was found that addition of isopropanol was necessary to aid in solubility. For spreading on the NIMA 312, 20 μL was used. After spreading 30 minutes was allowed for solvent to evaporate. Compression rates where 3 mm/min.

Brewster Angle microscopy

Brewster angle microscopy was performed a home built microscope constructed following the details provided by Knobler et al. The home built BAM uses a 532 nm laser.

Polymerization and Film Transfers

The trough was first cleaned with chloroform and ethanol. The trough was then filled with milli-pure water and the surface of the water was aspirated to remove any contamination. Carboxy fantrip was then spread on the interface as
described above. After spreading the film was compressed to a pressure of 10 mN/m. A 5 W 365 nm light emitting diode (Led-Engin, LZC-70U600) was used for the irradiation (see Figure S1). The LED was placed ~5 in above the interface and the compressed film was irradiated for 30 min. This setup allows the entire trough to be irradiated. Films can be transferred immediately after polymerization.

Transfer to TEM grids (PLANO G2780C) was accomplished by placing the grids horizontally on top of the irradiated film, much like a Langmuir-Schaefer film deposition. The grids were removed from the interface by placing a small piece of paper over them such that they adsorb onto the paper. The paper can then be pulled off the interface taking the grids with it. A more gentle approach to transfer is accomplished by submerging a home built delrin “basket” under the interface before spreading and polymerization. The grids are then dropped onto the surface as described above. One the grids have been placed on the surface the basket is raised slowly (1 mm/min). the basket will lift the grids off the interface as it is lifted. Two hours are allowed for the grids to dry before they are removed from the basket.

For transfer to SiO$_2$ wafers or any hydrophilic surface, substrates were immersed in the subphase before antrip-DEG was spread at the interface. They are not held vertical as in a traditional Langmuir-Blodgett transfer but they are held at a 45 degree angle relative to the surface normal. This is made possible by using a home built Teflon clamp. Spreading, compression, and polymerization was performed as stated above. After polymerization was complete the substrate was pulled from the interface at a rate of 1 mm/min.
Figure 3.16. Setup for polymerization of antrip-DEG on the interface.

Transfer of poly(carboxy fantrip) to SiO₂ with carboxylic acids facing up can be accomplished using the Langmuir-Shafer method. The SiO₂ must first be made hydrophobic by reaction with trimethylsilyl chloride. The Langmuir-Shafer transfer of monolayer poly(carboxy fantrip) also works well using hydrogen passivated Si(111). This was generated by etching the native oxide layer from Si(111) in degassed ammonium fluoride solution. The hydrogen passivated Si(111) must be made immediately before use to avoid reoxidation.
Atomic force Microscopy

AFM imaging was performed either with a Asylum Research Cypher AFM operated in tapping mode or a Nanosurf easyscan II AFM operated in contact mode. For the Cypher ES AFM, Budget Sensors Tap150Al-G having a resonance frequency of 150 kHz and spring constant of 5 N/m. For the Nanosurf AFM, App Nano silicon SICONA cantilevers (Applied NanoStructures, Inc.) having a resonance frequency of 11-18 kHz and a spring constant of 0.1-0.6 N/m were used. A set point of 15nN was used for both the monomer and polymer films.

Optical Microscopy

Optical microscopy was performed using a Leica DM2500P. Samples where prepared using the method described in the “polymerization and film transfer” section.

Contact Angle measurements

Figure 3.17. Homebuilt contact angle instrument employing a stereomicroscope.
Contact angle measurements were performed with a home built apparatus. A stereomicroscope was used for the optics and image capture. The microscope was focused on a right angle prism, which turned the optical path horizontal and permitted focusing on the sample. The sample was placed on a sample stage (see Fig. 3.17) The syringe for drop application was controlled by a micromanipulator. Images where processed with Image J.

**UV/Vis**

UV/Vis spectra were obtained using a Perkin Elmer lambda 850 spectrophotometer. Samples were made by lifting a quartz substrate horizontally out of the interface. Spectra were recorded in transmission mode.

**HR-AFM**

High resolution AFM imaging was performed with a Asylum Research Cypher ES AFM. Olympus AC55TS probes with a resonance frequency of 1600 kHz and a spring constant of 85 N/m were used. Imaging was performed in tapping mode under a dry nitrogen atmosphere. No successful imaging could be performed in air. All images were obtained in the repulsive regime and it was found that the lattice of the 2DP could not be resolved in the attractive regime. Samples were prepared on mica using the method described above.
**Gas Transport**

For transport measurements poly(carboxy fantrip) was transferred to single orifice TEM grids with a 50 μm hole (Glider GA50). The transfer was done by the methods described above.

![Diagram](image.png)

**Figure 3.18.** Setup for gas flow studies.

After placing the sample in the sample holder the system was purged with the selected gas for 30 min. The pressure was then set at the desired pressure (normally 1.5 in H₂O). The valve to the bubble flow meter was then opened and the time for 25 μL of gas to pass through the 2DP membrane was measured. This was repeated 10X to ensure the flow had equilibrated.
Additional HR-AFM images

**Figure 3.19.** HR-AFM phase image of poly(carboxy fantrip)

**Figure 3.20.** HR-AFM phase image of poly(carboxy fantrip)
Figure 3.21. HR-AFM phase image of poly(carboxy fantrip)

Figure 3.22. HR-AFM phase image of poly(carboxy fantrip)
Figure 3.23. HR-AFM phase image of poly(carboxy fantrip)

Figure 3.24. HR-AFM phase image of poly(carboxy fantrip)
Figure 3.25. HR-AFM phase image of poly(carboxy fantrip)

Additional Optical Images
Figure 3.26. Optical image of poly(carboxy fantrip) on SiO$_2$.

Figure 3.27. Optical image of poly(carboxy fantrip) on SiO$_2$.

Figure 3.28. Optical image of poly(carboxy fantrip) on SiO$_2$. 
4. Poly(antrip)\textsuperscript{83,95}

![Diagram of antrip monomer and dimer]

**Figure 4.1.** Antrip monomer and its dimer.

The use of single crystals to preorganize monomers in two dimensions permits the synthesis of precisely defined 2DPs. Here a trifunctional monomer is

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**Declaration of Contributions**

My role in the poly(antrip) project involved the exfoliation of the polymer and the characterization of the exfoliated sheets. In this chapter I will cover the contributions from other project members in order to tell the complete story. The contributions from each author are listed below.

- **Radha Bhola**: monomer synthesis, crystallization, polymerization, X-ray, NMR, and IR.
- **Daniel Murray**: Exfoliation, SEM, AFM, depolymerization
- **Bharat Kumar**: X-Ray
- **Aaron Teator**: monomer synthesis
- **Sonja Hammer**: Powder X-ray

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used to make a 2DP through a solid-state photo-polymerization. The monomer, antrip (Figure 4.1), is composed of three anthraceno blades on a central triptycene core. This monomer is topologically flat, shape persistent, has directed functionality, and has three binding sites. These are the monomer design requirements that were laid out in Chapter 1. The approach to synthesize a 2DP from antrip relies on the preorganization of monomers in a monomer crystal. This monomer crystal can then be irradiated with UV light to induce a [4+4] cycloaddition of the anthraceno blades, creating the polymer crystal. The polymer crystal can then be exfoliated to give the 2DP.

4.1. Monomer crystal

Antrip can be crystalized from a variety of solvents. However, the $P2_1/c$ polymorph obtained from crystallization in benzene was used for all subsequent experiments because the polymerization was clean and the X-ray quality crystals could be grown easily. Single crystal X-ray crystallography was used to determine the structure of the monomer crystal (Figure 4.2). In the $P2_1/c$ polymorph hexagonal channels are formed the intersection of two rows of antrip molecules. The rows are tilted 35° relative to each other. In the structure each antrip molecule has two of its three blades in a co-facial arrangement with two other antrip molecules.
Figure 4.2. X-ray structure of antrip crystalized from benzene looking down the hexagonal channels (left) and across the plane of each row (right).

4.3. Polymer crystal

The $P2_1/c$ polymorph was irradiated with 400 nm light at 0 °C under nitrogen in order to photopolymerize the crystal. This process was followed by IR spectroscopy. The disappearance of anthracene can be detected by monitoring the C-H out-of-plane bend corresponding to the 9,10- positions. This bending mode shows up at 884 cm$^{-1}$ for anthracene and is shifted to 897 cm$^{-1}$ for antrip. Upon polymerization the anthracene blades dimerize across the 9,10- positions and this out-of-plane bend disappears. Figure 4.3 shows IR spectra of the antrip/polyantrip system (left) along with the anthracene/dianthracene system (right). These spectra
show that the 9-10- out-of plane band disappears upon irradiation for both antrip and anthracene.

**Figure 4.3.** IR spectra of the antrip/polyantrip system (left) and the anthracene/dianthracene system (right).

Confirmation of dimerization at the 9,10- positions in antrip is provided by deuterium labeling and solid state $^{13}$C NMR studies. For deuterium labeling studies $d_6$-antrip was prepared, were the 9,10- positions of each anthraceno blade is substituted with deuterium. The analogues deuterated anthracene was also prepared as a reference. Upon irradiation of labeled antrip the original C-D stretch
splits into two different stretching modes. This same change is observed for the conversion of d$_2$-anthracene to d$_4$-dianthracene.

Solid-state $^{13}$C NMR studies also provide valuable information on the polymerization process. When antrip is irradiated the intensity of the bridgehead resonance increases and a second bridgehead resonance appears in the $^1$H-$^{13}$C correlation spectra. This together with the deuterium labeling studies show that the polymerization of antrip occurs through the dimerization of anthracene across the 9,10-positions.

Even more evidence for the polymerization of antrip through anthracene dimers comes from fluorescence measurements. The fluorescence spectra of antrip crystals were continuously monitored during the irradiation. Initially a broad peak at 550 nm is observed. Upon irradiation this emission decays. Two pieces of information can be obtained from this. First, a broad emission at 550 nm is indicative of anthracene excimers. From this we can conclude that the anthraceno blades are in a co-facial arrangement. Second, a decay in the emission shows that the non-fluorescent dimer is forming.

Because antrip crystals crack upon polymerization single crystal X-ray diffraction analysis was not possible. However, powder X-ray diffraction was still viable. The powder X-ray diffraction pattern for poly(antrip) shows sharp reflections which indicate that it is crystalline. All attempts to elucidate a structure from the powder pattern failed. However, the patterns for antrip and poly(antrip)
are similar. This indicates that the fragments are in similar positions in both crystals.

4.4. Exfoliation

Figure 4.4. SEM micrographs of polyantrip that has been exfoliated in NMP.

Poly(antrip) is highly insoluble in organic solvents where antrip is soluble. Exposure of poly(antrip) to select solvents induces exfoliation. After a survey of solvents N-methylpyrrolidone and cyclohexanone were selected as the best for exfoliation. After a short, 15 min, treatment in NMP poly(antrip) crystals separate into sheets that can be observed by optical microscopy.

After several weeks in NMP, poly(antrip) separated into very thin sheets. These sheets can be imaged by SEM after they are deposited onto lacey carbon TEM grids. Figure 4.4 shows two examples of very thin poly(antrip) sheets. Red arrows provide guidance to the sheets, as they appear quite transparent. Close inspection of
the sheets show layering and folding indicating that these are sheets are at least a few layers thick.

Atomic force microscopy (AFM) provides even more information on the structure of poly(antrip). Solvent casting exfoliated sheets onto mica allowed for AFM imaging of the sheets. Figure 4.5 shows AFM imaging of multi-layer poly(antrip) sheets. In these images individual steps in the sheets can be seen. The overall thickness of the sheet corresponds to 5 to 10 layers. Height analysis of the steps show that some are monolayer and some are bilayer steps.

**Figure 4.5.** AFM height images of multilayer poly(antrip) flaks. Height traces follow the lines on the images.
Exfoliation of poly(antrip) for an extended time at ambient conditions results in the formation of single sheets along with some multi-layer sheets. Imaging them by AFM shows that they have a thickness of \(\sim 1.2\) nm which corresponds to a single molecular layer. Figure 4.6 shows AFM imaging of the single sheets and a multilayer sheet. It is not uncommon for the single sheets to have a lacy appearance.

**Figure 4.6.** AFM images and height analysis of few- and single layer sheets on mica.

This lacy appearance is most likely from depolymerization during the exfoliation process. This is supported by monitoring the release of antrip during exfoliation by UV/Vis spectrophotometry. Figure 4.7 shows a plot of the percent free antrip per unit time for exfoliations performed at 50 °C and 80 °C. The experiments
show that a few percent of free antrip is released quickly followed by a long slow release over a few weeks. Comparing the two temperatures shows that the depolymerization is about 8 times faster at 80 °C than at 50 °C.

**Figure 4.7.** Depolymerization of poly(antrip) during exfoliation in NMP at 50 °C (circles) and 80 °C (squares).

By piecing together all the data collected on poly(antrip) and applying the theory of tilings we can elucidate the structure of poly(antrip). From the experiments, we know that the polymer linkage is the anthracene dimer and that the repeat unit is the triple [4+4] adduct of antrip. AFM imaging proves that poly(antrip) is a lamellar material that can be exfoliated down to monolayer sheets. Powder X-ray shows that this material is periodic.
Using the information above, the definition of 2DPs (Chapter 1.2), and that antrip has a valence of three (the number of linkages to the repeat unit) we can reasonably conclude that the structure is that presented in Figure 4.8.

![Figure 4.8. Probable structure of poly(antrip).](image)

### 4.4. Conclusions

In summary, the monomer antrip can be crystalized and irradiated with UV light to give poly(antrip). Spectroscopic methods show that antrip polymerizes through a [4+4] photocycloaddition of the anthraceno blades. AFM and SEM show the presence of large flat layers within the polymer crystal. Exfoliation of the polymer crystal gave few- and monolayer sheets that can be deposited on mica and imaged by AFM. We used the theory of tiling and the above observations to propose that poly(antrip) has the structure presented in Figure 4.8.
4.5. Methods and Supplemental Information

**Exfoliation of Polyantrip:** To the irradiated crystals (13.3 mg), N-methylpyrrolidone (NMP) was added (2.8 mL). The mixture was left overnight at room temperature for exfoliation. The insoluble material was collected by centrifugation. The solids were washed with methanol (30 mL) and centrifuged. The process was repeated four times to remove any traces of NMP. The exfoliated solid was separated and dried under vacuum (8.5 mg). The insoluble irradiated crystals can be exfoliated down to few or single layer sheets by heating in cyclopentanone, or 1-methyl-2-pyrrolidone. Few layer sheets can be obtained by heating at 50 °C for 1 week. Exfoliation down to single layer sheets was accomplished by heating at 50 °C for 3 weeks. This method, however will give sheets that have started to depolymerize. A gentler exfoliation can be accomplished by slow rotation at RT in NMP for 5 days.

**Scanning electron microscopy (SEM):** Scanning electron microscopy was performed using either a LEO 1530 VP or a Hitachi S-4700II. As the samples are highly sensitive to radiation damage the acceleration voltage was kept at 3 kV or lower. For sample preparation, a copper TEM grid coated with a lacy carbon film (#01824, Ted Pella, Inc., Redding) was placed carbon side up on a Kimwipe. A dispersion of the exfoliated sheets was deposited, dropwise, on to the grip so that the solvent would pass through the grid and be absorbed by the Kimwipe. The grid
was then washed with four drops of chloroform. The sample was allowed to dry at room temperature for several hours before imaging.

**Atomic force microscopy (AFM):** AFM imaging was performed with a Nanosurf easyscan II AFM (Nanoscience Instruments, Inc.) operated in contact mode at room temperature in air. App Nano silicon SICONA-10 cantilevers (Applied NanoStructures, Inc.) having a resonance frequency of 11-18 kHz and a spring constant of 0.1 - 0.6 N/m were used. Samples were prepared by placing a copper TEM grid with a lacy carbon film (#01824, Ted Pella, Inc., Redding) on a Kimwipe with the coated side up. A dispersion of the exfoliated sheets was deposited, dropwise, onto the grid so that the solvent would pass through the grid and be absorbed by the Kimwipe. The grid was then washed with four drops of chloroform. The sheets were then transferred to a freshly cleaved mica substrate by turning the grid over and passing a few drops of chloroform through the grid and onto the mica. The chloroform was allowed to evaporate and the mica was washed with fresh chloroform and allowed to dry for several hours at room temperature.
Transmission Electron Microscopy (TEM)

Figure 4.9 TEM of polyantrip exfoliated in NMP

TEM was performed using a JEOL-JEM 2100F at 200 kV. Samples were prepared using the method described for SEM samples. All attempts at imaging the crystal lattice of the polymer were unsuccessful presumably due to swelling of the crystal by the NMP used in exfoliation. The lamellar structure can however be easily seen.
Differential Scanning Calorimetry

Figure 4.10. DSC thermogram of polyantrip

Differential scanning calorimetry was performed with a TA instruments model Q20. Starting at about 110 °C an exothermic peak corresponding to the depolymerization of poly(antrip) is seen.
Additional AFM Images

Figure 4.11. AFM images of monolayer poly(antrip)
Figure 4.12. AFM images of monolayer poly(antrip)
Additional SEM Images

Figure 4.13. SEM images of partly exfoliated poly(antrip)
Fluorescence

Figure 4.14. AFM images of monolayer poly(antrip).
5. Fantrip\textsuperscript{84}

Due to many problems with the production of poly(antrip) (chapter 4) we sought to develop a new generation of 2DP that met they expectations we had for antrip. The application of single crystal X-ray diffraction (XRD) to not just the monomer crystal but to the polymer crystal would provide unambiguous proof of structure. The polymerization of antrip resulted in crystals fragmenting. This presumably is because of the large rearrangement necessary to give a lamellar polymer crystal. To overcome this a system must be developed in which the monomer crystal has a lamellar structure and binding sites that are close enough to each other to minimize any rearrangement.

The monomer, which we call fantrip (Figure 5.1a), was developed in order to meet these needs. Fantrip has the same carbon framework as antrip. The key modification comes in the four fluorine atoms on the out rim of each anthraceneo

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declaration of Contributions

My role in the poly(fantrip) project involved the exfoliation of the polymer and the characterization of the exfoliated sheets. In this chapter I will cover the contributions from other project members in order to tell the complete story. The contributions from each author are listed below.

**Dr. Patrick Kissel:** monomer synthesis, crystallization, polymerization, X-ray, NMR, and IR.

**Daniel Murray:** Exfoliation, SEM, AFM.

**William Wulftange:** monomer synthesis

**Vincent Catalono:** X-ray structure elucidation
blade. This does two things. First, it takes advantage of the enhanced co-facial, antiparallel pacing that is observed in end-fluoronated acenes.\textsuperscript{93,97} This gives a larger driving force for fantrip to pack in a lamellar fashion. Secondly, it makes synthesis much more efficient. Fantrip is prepared in two steps where antrip is prepared in three. The reactive groups remain unchanged and the polymerization should occur by a triple [4+4] cycloaddition of fantrip.

**Figure 5.1.** Structure of fantrip monomer (a) and its dimer (b).
5.2. Monomer Crystal

Crystals of a high enough quality for single crystal XRD were grown from chloroform. Figure 5.2 shows the crystal structure of the monomer crystal.

**Figure 5.2.** X-ray crystal structure of fantrip monomer from the top down (a) and from the side (b). Solvent molecules are omitted for clarity. Fluorine atoms are in green and carbon atoms are in gray.

Single-crystal XRD shows that the monomer crystal is composed of layers. Within the layers each monomer adopts a face-to-face arrangement with three other monomers. This results in a quasi-hexagonal packing of the monomers. Distances from the 9,10-positions of each anthraceno blade are within 3.6-3.7 Å. This is within the distance needed for a [4+4] photocycloaddition to occur. As can be seen in Figure 5.2b the monomers anthraceneo blades lay in the plane of the respective
layer. Therefore all the reactivity lies in the plane of the layers and there should be no reactions between the layers.

5.3. Polymer Crystal

Irradiation of the monomer crystal directly with 400 nm light caused disintegration of the crystal. This made structure determination by single-crystal XRD impossible. Because of this a more gentle polymerization method was needed. We found when polymerization with 460 nm light at 223 K the crystal remained intact. Surprisingly, this irradiation resulted in a meta-stable dimer crystal (Figure 5.3a). This dimer crystal was not stable enough to be characterized by XRD at 223 K but could by characterized at 100 K.

Figure 5.3. X-ray crystal structures of the dimer (a) and polymer (b) crystals.
The polymer (Figure 5.3b) can be reached by irradiation of the dimer crystal with 400 nm light at 223 K. Once the crystal has been fully polymerized it becomes tough and can be dried in air without cracking. Single-crystal XRD analysis of dried polymer crystals show no residual solvent in the lattice (Figure 5.4). The crystal structure of poly(fantrip) gives a thickness of 6.88 Å for each sheet. These sheets are slightly offset from one anther resulting in tilted channels running through the crystal.

![Figure 5.4](image)

**Figure 5.4.** a) Three layers of the solvent free poly(fantrip) lattice. b) Crystal structure of one individual layer in the solvent free polymer.

### 5.4. Exfoliation

The polymer crystal can be exfoliated by treatment with 1-methyl-2-pyrrolidone. Initially the polymer crystals swell and start to separate into thinner sheets. This can be observed by optical microscopy (Figure 5.5). If the swollen sheets are sonicated they separate into thin plates, which retain their sharp edges (Figure 5.6).
Figure 5.5. Optical microscopy images of partially exfoliated crystals in NMP on a microscopy glass slide. Crystals were exfoliated in NMP at room temperature for one hour. **a**, 5 minutes and **b**, 60 minutes after addition of NMP. While crystals did not dissolve, clear signs of swelling were observed (red arrows).

Figure 5.6. Optical (**a**) and polarized optical microscopy (**b**) images of partially exfoliated crystals in NMP on a glass slide. Crystals were exfoliated in NMP at room temperature for 5 days, with direct sonication for 60 seconds after 3 days. Numerous fragments were observed that had kept sharp outlines and birefringence.
Poly(fantrip) can be exfoliated down to multi-layer and monolayer sheets by slow rotation in NMP at 50 °C for 6 days. This process uses mechanical shearing forces to facilitate delamination. UV/Vis spectroscopy of the exfoliation solvent showed no trace of depolymerization over the entire exfoliation. Deposition of the exfoliated sheets onto SiO₂ wafers allows for observation by reflectance optical microscopy. Figure 5.7 shows partly exfoliated poly(fantrip) on SiO₂.

![Figure 5.7. Polarized reflectance optical microscopy images of exfoliated sheets on a SiO₂ coated silicon waver. Crystals were exfoliated in NMP at 50 °C under slow rotation for three days. Numerous thicker sheets still exhibiting sharp outlines were observed, as well sheets already thin enough that they were hard to detect (yellow arrows).](image)
Deposition of the exfoliated sheets onto lacy carbon TEM grids allows for imaging by scanning electron microscopy. Very thin multi-layer sheets that show straight edges and sharp corners can be seen (Figure 5.8).

**Figure 5.8.** SEM imaging of poly(fantrip) exfoliated by slow rotation in NMP at 50 °C for three days. Crisp edges and sharp corners can still be seen.

Monolayer films can be found by depositing the exfoliated crystals onto mica and imaging by atomic force microscopy. Figure 5.9 shows films that have step heights of 0.8 -1.0 nm, which is consistent with what would be expected for a monolayer.
Figure 5.9. a) AFM image of poly(fantrip) monolayers on mica after exfoliation by slow rotation in NMP at 50 °C for 6 days. b,c) height profiles along the lines in a.

Multi-layer sheets were also found by AFM. Figure 5.10 shows three representative images. A step height of 0.8 nm is found for layers within the multilayer sheet. Partial exfoliation of polymer crystals into thicker multilayers was observed on a sample of crystals that were exfoliated in NMP at 50 °C under slow rotation for five days. Thicker features exhibiting step heights corresponding to ca. 7 to 20 layers were found (Figure 5.9a), as well step heights of 0.8 – 1 nm corresponding to an individual monolayer step (Figure 5.9b). Figure 5.9c shows a larger monolayer fragment among small monolayer fragments was obtained by
Exfoliation of crystals in NMP at room temperature for six days. Three days after start of the exfoliation, the sample was sonicated for 60 seconds. TEM imaging of the sheets was performed, however, little useful information was obtained.

**Figure 5.9.** Atomic force microscopy height images and corresponding AFM height profiles showing partially or fully exfoliated sheets on mica. Height profiles below the height images were recorded along the gray lines. A height of 0.8 nm is expected for a monolayer.

The individual sheets are composed of a quasi-hexagonal array of pores ~0.9 nm in diameter. There are $3.3 \times 10^{13}$ pore per cm$^2$ resulting in a porosity of 31%. The structure of these sheets suggests their use as a size selective filter. Due to the mono-disperse pore size only a single sheet would be needed to make a filter. The
problem with this, however, is that only very small sheets can be produced by this method and manipulation to make a membrane is very difficult.

5.5. Conclusions

In summary, we have prepared a nanoporous 2DP by a single-crystal-to-single crystal photopolymerization. The monomer fantrip crystalizes into a lamellar crystal that polymerizes to a lamellar polymer crystal by a photo induced [4+4] cycloaddition of its anthraceno blades. Single-crystal XRD reviles the structure of the monomer crystal, the polymer crystal, and a intermediate dimer crystal. The polymer crystal can be exfoliated down to monolayers. AFM imaging of these sheets shows a thickness of 0.8 nm for the monolayer. The 2DP is comprised of a quasi-hexagonal array of monodisperse subnanometer pores.
5.6 Methods and Additional Figures

Exfoliation of polymer crystals

For the exfoliation, irradiated polymer crystals were dispersed in N-methylpyrrolidone (NMP). Different degrees of exfoliation were obtained depending on the individual samples and conditions applied during the exfoliation process. Heating was found to promote the exfoliation process, as did the application of mechanical force through sonication or slow rotation of samples during exfoliation. Short term sonication (30-60 seconds) of crystals dispersed in NMP led to the formation of multilayers. Full exfoliation of crystals down into individual monolayers was achieved by slowly rotating a dispersion of polymer crystals in NMP at room temperature or 50 °C for 6–9 days.

Optical microscopy (OM) and polarized optical microscopy (POM)

Optical microscopy was performed with a Leica DM 2500 P. For OM observations on silicon oxide substrates, silicon wavers coated with a 300 nm thick silicon oxide layer were used to visualize thin sheets by optical interference contrast of the reflected polarized light. Samples were prepared by drop-casting a dispersion of the exfoliated sheets in NMP (2 drops) on the silicon oxide waver. The samples were then dried at 50 °C for 4 hours under vacuum.

Scanning electron microscopy (SEM)

Scanning electron microscopy was performed using a Hitachi S-4700II. Images were recorded at an acceleration voltage of 3 kV because samples were sensitive to
radiation damage. Samples were prepared by placing a copper TEM grid with a lacy carbon film (#01824, Ted Pella, Inc., Redding) on a dust-free blotting paper with the coated side up. A few drops of a dispersion of the exfoliated sheets were deposited onto the grid such that the solvent was sucked through the grid into the blotting paper. The grid was then washed with a few drops (3 – 5) of chloroform and dried under ambient conditions.

**Atomic force microscopy (AFM)**

A Nanosurf easyscan II AFM (Nanoscience Instruments, Inc.) operated in contact mode at room temperature in air was used to perform AFM imaging. App Nano silicon SICONA cantilevers (Applied NanoStructures, Inc.) with a resonance frequency of 11-18 kHz and a spring constant of 0.1-0.6 N/m were used. All samples were imaged with 15 nN of applied force. For sample preparation, a diluted dispersion of exfoliated sheets in NMP was used. Samples were prepared by drop-casting the resulting dispersion (3 drops) on freshly cleaved mica. The mica samples were dried at room temperature or 50 °C under vacuum for several hours. After being removed from vacuum, samples were washed by dipping them three times in chloroform. The sample was then placed under vacuum for an additional hour.
**Figure 5.11.** Fluorescence spectra of fantrip in solution (black), in crystal (red), and poly(fantrip) (green). Poly(fantrip) exhibited little to no fluorescence.
Figure 5.12. UV/Vis spectra of fantrip monomer in NMP (blue), polyfantrip after exfoliation in NMP at 50 °C for 3 days (green), and after 6 days (red). No fine structure can be seen in the exfoliated polyfantrip spectra indicating there is no depolymerization to the monomer at this temperature.
Figure 5.13. Scanning electron microscopy images of exfoliated sheets. Crystals were exfoliated in NMP at 50 °C under slow rotation for three days and then deposited on a lacey carbon coated TEM grid. Larger features with a clearly visible lamellar structure were found (a) as well as many large but very thin sheets (b – f). Those features are thin enough such that the underlying lacey carbon support can be clearly seen through them. Many of those thin sheets still possessed crisp edges
(yellow arrows in b - d), indicating their origin from the initial polymer crystals. Many of the sheets found were thin enough to exhibit tablecloth-like folds or ripples (see red arrow in c and images e and f).

**Figure 5.14.** Atomic force microscopy height images and corresponding AFM height profiles showing bilayers and fully exfoliated monolayers on mica. A height of ca. 1.5 nm is expected for bilayers, and a height of ca. 0.8 nm for monolayers. Height profiles below the height images were recorded along the gray lines. a, Monolayers and bilayers up to 1.5 micrometer in size obtained by slow rotation in NMP at 50 °C for 5 days. Yellow arrows point towards monolayers, red arrows towards bilayers. b, Monolayers obtained by exfoliation of a single crystal in NMP at room temperature during 9 days. 3 days after start of the exfoliation, the sample was
sonicated for 60 seconds. A large number of monolayers were found on the mica with dimensions up to 3 μm. Some of the monolayers that appear to have retained hexagon-like outlines are indicated by the black circles.

Figure 5.15. TEM imaging of poly(fantrip) exfoliated in NMP on lacy carbon. a) low magnification image of exfoliated poly(fantrip). b) Zoom of the outlined region in a. No structure is observed presumably due to swelling of the crystal in NMP. Also, exfoliation causes layers to move relative to each other. This would mean the structure of each layer is not commensurate to other layers and thus the structure would appear disordered to transmitted electrons.
6. Outlook

Poly(antrip-DEG) and poly(carboxy fantrip) have been characterized using methods that were most available and most promising. However, other techniques could provide valuable information. In-depth information on the bonding could be obtained using tip-enhanced Raman spectroscopy (TERS). This has provided valuable information on bonding in covalent monolayer films produced by the Schlüter group.\textsuperscript{100,101,102} Polarization modulated infrared reflection absorption spectroscopy (PM-IRRAS) also can provide valuable information on monolayer systems. This technique can give information on the orientation of molecules at the air/water interface by distinguishing transitions that have their dipole oriented parallel to the surface normal and those that have it perpendicular to the surface normal. This been successfully used to give structural information in preorganized Langmuir films.\textsuperscript{103}

It would be useful to explore structure elucidation by grazing-incidence small-angle X-ray scattering (GI-SAXS). To get the necessary sensitivity to detect a monolayer a synchrotron light source would be needed. This method allows for detection of diffraction from thin films on surfaces.

Structure elucidation could also be explored by other methods in HR-AFM. We found that lattice resolution could be achieved by amplitude modulation phase imaging in the repulsive regime with a high Q cantilever. This has drawbacks such as fast tip destruction, sample destruction, and limited resolution. One method to
avoid this would be using a super-sharp tip (radius < 2 nm) in amplitude modulation imaging. In this case one could not only get information from the phase image but from the amplitude (height) image. For poly(antrip-DEG) and poly(carboxy fantrip) this would allow for the tip to penetrate the pores in the film and thus the topography could be mapped. Another method that could potently provide very high-resolution images is frequency modulation AFM (FM-AFM). In this method the cantilever is driven at its free resonance frequency. The cantilever is then scanned over the surface and the change in resonance frequency is used as the detection channel. The resonance frequency is shifted by short range interactions giving extremely high-resolution.\textsuperscript{104} This technique requires specific cantilevers and highly tuned imaging conditions making it a very difficult and time consuming process.

There are some limitations to the poly(antrip-DEG) system that should be touch on. The need to cool the trough to 1 °C for compression and polymerization and then warm to 30 °C for transfer is an inefficient and time consuming task which really limits this system. Because the polymerization and transfer needs to be performed at 0.5 mN/m it is hard to transfer large intact sheets. Therefore making a defect free membrane from this material would be very difficult. If methods can be developed to get around these issues this 2DP would have great potential. Currently poly(carboxy fantrip) has much more potential for application do to superior properties.

The application of these materials has only been touched on. To me the most promising application is in membranes for separations. We showed that gases flow
through the 2DPs with ballistic rates. This may be useful for gas separations. Much work needs to be done to transition to measuring the transport of liquids through the 2DPs. This includes construction of an apparatus and detection method along with developing methods for sample preparation. Due to the high forces involved with flow in liquids the sample preparation will be critical in performing these measurements. Along these as lines an understanding of the mechanical properties of the 2DPs will be necessary for proper sample construction. This is would be most easily performed by AFM Nano indentation of free spanning 2DP.105

For the poly(antrip) and poly(fantrip) systems, characterization by HR-AFM may provide useful results. With the proper instrument it would be possible to perform large area scans of exfoliated sheets deposited on mica to locate them and then zoom in to resolve the internal structure of the polymer. For the case of poly(antrip) this could be a way to prove the internal structure as single-crystal XRD was unsuccessful. This may by a time consuming experiment but it has the potential to prove that the exfoliated monolayers retain their structure. Additional work needs to be performed to optimize the exfoliation of both poly(antrip) and poly(fantrip). Although we were able to obtain monolayer sheets we could not do so in a high yield. If this could be done and dispersions of these small 2DP sheets were made applications in chemical recognition would open up.

The field of 2DPs is in its infancy and there is much work to be done. To date there has been only a hand full of 2DPs that have been rationally synthesized and characterized. There are many possibilities for new structures that could by tailored to fit many applications. The discovery of new liking chemistries will likely be
important to many applications of these polymers. With the increasing interest in this new field it should not be long before these things are realized.
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Appendix 1

Brewster Angle Microscope

Parts list

**Laser:** 50mW 520nm PL520 Green Copper Laser Module W/Microboost Driver & Aixiz Glass lens (purchased from ebay, seller ID: dtr-lpf)

**Laser mount:** custom made aluminum mount which fits into a 3 in Length, Ø1"

Stackable Lens Tube (Thor labs, SM1L30)
**Polarizers:** Laser side; glan laser calcite polarizer GL-10-A in a Lens Tube Mount (Thor labs, SM1PM10). Camera side; M25.5 x 0.5 Mounted Linear Glass Polarizing Filter (Edmund optics, Stock #46-575)

**Camera:** USB Microscope - 5MP interpolated 220x magnification / 8 LEDs (adafruit, product ID: 636)

The microscope needs to be modified in order to allow it to sit as close to the camera side mirror as possible. Also, the modification make mounting the analyzer much easier.

**Mirror mounts:** Newport P100-P Miniature Platform Optical Mount

**Polarizer/laser mount:** SM1-Threaded Cage Plate, Post Mountable (Thor labs, CP02)

**Translation stages:** The instrument height adjustment stage was taken from an old optical microscope and modified so that the base plate could be mounted to the height adjustment stage.

The translation stages for the usb microscope are two different stages that where modified so they could be bolted together. Both stages where both acquired from surplus equipment in the department.
Discussion

The Brewster angle microscope that we have developed was designed with two things in mind. The first is that it needed to be compact enough to fit over our relatively small trough and the second is that it needed to be inexpensive. In order to make the unit compact we used a design in which the laser and the camera are mounted in a vertical position as depicted in figure 1. This design was adapted from the work of Knobler et al.¹ The laser is deflected off a mirror such that it hits the subphase at 53°. The light reflected from the subphase is then directed into the camera with another mirror. The mirrors are mounted on miniature platform optical mounts so that the beam can be set exactly at the Brewster angle and steered directly into the camera.

![Diagram of the BAM](image)

**Figure 1.** Diagram of the BAM
To save money and space we decided to use a diode laser. A 50 mW 520 nm laser module with an Aixiz glass culminating lens was selected. The laser beam is sent through an aperture followed directly by a glan polarizer. Because the beam is polarized directly out of the laser diode the glan polarizer is used to enhance the polarization of the beam. The high level of polarization is needed to obtain a high quality image.

To further lower the cost we used a USB microscope for the imaging system. This also provides the long working distance needed with this set-up. The microscope is mounted on an x-z translation stage so that it can be positioned directly over the incoming beam. The microscope was shortened by ~0.25 in so a second polarizer (analyzer) could be mounted to the unit just before the objective. This polarizer need not be a glan polarizer but rather a cheaper linear glass polarizing filter.

All of the optics are mounted to a single plate of aluminum. This plate is then mounted to a Z-translation stage that holds the plate horizontally and allows the unit to be set at the proper height above the interface.
Figure 2. As built BAM. a) laser and mount b) glan polarizer in a lens tube mount c) usb microscope d) miniature platform optical mounts and mirrors e) instrument height adjustment stage f) x- and z- translation stages.

Note: The glan polarizer may be changed out for a less expensive laminated film polarizer. This should still be of high quality so that the image remains sharp.

Reference

Figure 3. Laser side of the BAM. a) laser b) laser mount c) 1” lens tube d) SM1-threaded cage plate, post mountable e) aperture f) glan polarizer in a lens tube mount g) analyzer h) usb microscope
Microscope Modification

In order to shorten the microscope the LEDs must first be removed. This is done by unsoldering the two pins that hold the LED circuit and pulling out the LED panel. The pins are indicated in figure 4.

![Image of LED panel](image)

**Figure 4.** Removal of the LED panel.

Next the body of the microscope needs to be cut down to the lip indicated in figure 5. This will leave a flat rim which the analyzer can be mounted to.
**Figure 5.** Cut part of the microscope which is indicated. This will leave a flat rim which the analyzer can be mounted to.
Appendix 2.

Advancements in light emitting diode (LED) technology over the last decade have enabled vast application. They are now used in space lighting, displays, and automotive lighting among others.\textsuperscript{1} LEDs that emit in the UV region have recently become viable options for light sources in applications such as UV curing, and UV water disinfection.\textsuperscript{2} LEDs offer increased efficiency, longer lifetimes, and lower cost compared to traditional light sources. Here we use low cost, high power UV LEDs to carry out photochemical reactions in the organic chemistry laboratory. These LEDs enable the completion of photochemical experiments in a single 3 hr laboratory session. Normally, expensive photoreactors or mercury lamps would be needed to perform most photochemical reactions in a short amount of time.

**Figure 1.** Photograph of the LED based photoreactor.

The photoreactor, Shown in Figure 1, consists of four high power 365 nm LEDs. Each LED provides 800 mW of output power giving 3.2 W of total output
power. The LEDs are mounted on an aluminum heat sink to dissipate heat. The reactor is enclosed with aluminum sheeting so not light is lost and to protect students from exposure to the UV light.

To demonstrate the effectiveness of our LED based photoreactor we developed an experiment based on the classical dimerization of anthracene. In order to provide extra opportunity for analysis we chose to perform the photodimerization of 9-(hydroxymethyl)anthracene (1). The use of 1 rather than anthracene allows for methanol to be used as the solvent rather than benzene. Scheme 1 depicts the dimerization, were two molecules of 1 come together to form the dimer as a mixture of isomers. The two isomers, head-to-tail (h-t) and head-to-head (h-h), both form when 9- substituted anthracenes are irradiated in solution. The h-t dimer is, however, normally favored do to electrostatic and steric effects.

\[
\begin{align*}
2 & \xrightarrow{\text{hν}_1} \text{h-t} + \text{h-h} \\
\text{hν}_2 & \text{or } \Delta
\end{align*}
\]

**Scheme 1.** Photochemical dimerization of 9-(hydroxymethyl)anthracene.

The ratio of h-t to h-h dimers can be determined by \(^1\)H NMR spectroscopy. Integration of the bridgehead signals from both isomers offers a convenient method for determining the ratio of isomers in the product. Figure 1 shows the \(^1\)H NMR
spectra of the bridgehead region in the dimer. The peak at 4.79 ppm corresponds to the h-h dimer and the peak at 4.54 ppm corresponds to the h-t dimer.  

Figure 2. $^1$H NMR spectra of the product from irradiation of 9-(hydroxymethyl)anthracene in degased methanol with 365nm light. Only the bridgehead region is shown.

Because of the high intensity of the photoreactor a 75% chemical yield can be achieved after only 40 min of irradiation. This allows for completion of the reaction and analysis all in one 3 hr laboratory period.

To conclude, we have developed a high power, cost effective photoreactor that can be used in a teaching laboratory setting. This reactor allows for shortened reaction times, allowing students to explore photochemical reactions in a single 3 hr period.
Photochemical reactions are those that occur under the influence of light. Molecules that have been excited by adsorption of a photon often exhibit different reactivity than molecules in the ground state. According to the Woodward-Hoffman rules a [4+4] cycloaddition is thermally forbidden but is photochemical allowed. For example, two molecules of anthracene will undergo a [4+4] cycloaddition at the 9,10-positions upon irradiation with 365 nm light as depicted below. This reaction will not occur without the addition of light because it is thermally forbidden.

A mechanism for the photochemical dimerization of anthracene is:

\[
{^1 \text{A}^* + A} \quad \underset{\text{hv}_1}{\rightleftharpoons} \quad {^1 (\text{AA})^*} \quad \underset{\text{hv}_2 \text{ or } \Delta}{\rightarrow} \quad \text{A}_2 \quad \text{(photodimer)}
\]

The mechanism begins by anthracene (A) absorbing a photon, exciting it to the singlet-excited state \( (^1 \text{A}^*) \). This excited anthracene then forms an excimer \( (^1 (\text{AA})^*) \) (excited state dimer) with an anthracene in its ground state. This excimer can then decay back to the ground state by undergoing a cycloaddition to give the dimer. There are many competing processes for the excimer, including non-radiative decay and fluorescence decay. These competing processes are more or less favorable depending on the substitution on anthracene.
In this experiment you will be performing the photodimerization of anthracene-9-methanol. Because of the substitution on the 9- position of the anthracene there are two possible isomers that can form. One is the head-to-tail (h-t) dimer and the other is the head-to-head (h-h) dimer. By analyzing the $^1$H NMR spectra of the product you will be able to calculate the ratio of h-t dimer to h-h dimer.

\[
\begin{align*}
2 \text{anthracene-9-methanol} & \overset{h\nu_1}{\underset{h\nu_2 \text{ or } \Delta}{\xrightarrow{\text{hv}}} 2 \text{ dimer}}
\end{align*}
\]

**Hazards**

UV light is damaging to your eyes. You should never operate the open photoreactor without UV protective eye wear.

**Experimental**

To a scintillation vial, add 50 mg of anthracene-9-methanol and 4 mL of methanol. Place the vial on a hotplate and bring the solution to a gentle boil for 2 min. remove the vial from the heat and immediately cap the vial tightly. This process will remove any dissolved oxygen from the solution. Once the vial is caped place the vial in the photoreactor for 30-40 min. A white solid will precipitate from solution.
during the irradiation. Collect this solid by vacuum filtration. Let the product dry in the vacuum filter for 5 min. Characterize the product by IR and $^1$H NMR.

**References**


