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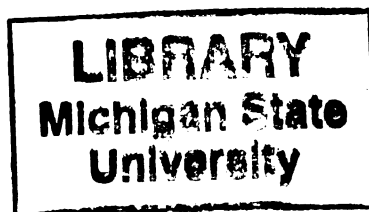
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ENERGY MIGRATION AND MORPHOLOGY CONTROL IN MULTILAYERS

By

Shawn Marie Mehrens

A THESIS

**Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of**

MASTER OF SCIENCE

Department of Chemistry

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ABSTRACT

ENERGY MIGRATION AND MORPHOLOGY CONTROL IN MULTILAYERS

By

Shawn Marie Mehrens

This thesis focuses on the construction and characterization of multilayers incorporating several different types of linking chemistry such as urea, urethane, amide, ester and coordinate bonds. Thin films are important because of their potential use in areas such as chemical sensing, optical information storage and nonlinear optics. By monitoring the fluorescence lifetimes of optical donor and acceptor molecules in different molecular layers, energy transfer between and within layers can be studied, which in turn presents valuable structural information about the layers. Optically active chromophores have been incorporated in covalent layered systems using amide linkages. These multilayers have been characterized using fundamental techniques such as ellipsometry, UV-visible spectrometry, FTIR spectroscopy and XPS. The population dynamics of the chromophores, both in solution and in layered assemblies have been studied. The fluorescence lifetimes of the chromophores on the surface are indicative of aggregation, a finding consistent with that found by Horne *et al.* We find that interlayer excitation transport does not occur efficiently in these systems, and we believe that this is due to more efficient donor-donor intralayer transfer within a single monolayer of chromophore. This work has demonstrated the complexity associated with the design of multilayer structures, and is a useful foundation for understanding interlayer excitation transport in covalently bound layered structures.

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Acknowledgements

The person whom I must thank first is my thesis advisor, Gary Blanchard. From the first moment I came to MSU he has always been encouraging, both in my research and in my life. I want to thank him for always being there, especially through all of my difficult decisions, and for giving me “doses of confidence” whenever the situation arose. Cheers Gary, and thanks for all of the good times!

I would also like to thank my committee members: Greg Baker, David Weliky and especially Merlin Bruening. Merlin: I appreciate all of your help, both as a professor and as my second reader, and especially your jokes, such as “Head TA Mehrens”. I also can’t forget Daniel Steffenson, my advisor at Albion College. Thank you for your continuing support and for answering all of my “cheesy” questions about topics varying from chemistry to life in general.

The next people who deserve recognition are my group members. To all of the past members who have gone on since I came here: Jen, Wendy, Scott and Punit; thanks for the fun times and all of the help! I can’t forget the current group members that I have worked with as well: Michelle, Jaycoda, Stephen, John, Joe and Lee. I’ll never forget you guys, we have a wealth of memories (I can’t mention the majority of them!), and I wish you all the best of luck in your futures. Joe and Lee deserve special recognition for all of their help with the “big laser machine,” without them I never would have gotten any useful data! Also to Michelle: please let me know when you have the “epiphany,” I’ll be waiting to hear about it!

I must also mention all of my friends at MSU. We went through this journey called graduate school together. Through the good times and the bad, thanks everyone

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for being there for me, as friends, teammates and scientific colleagues. To my other close friends, namely Grace, Heather and Colleen: you guys are the best!

Finally, I can't forget my husband Jared. His patience, understanding and ability to cook have kept me sane through the past 2 ½ years in graduate school. Without his love and support, this thesis would not have been possible. My parents also deserve credit. Thank you for always believing in me, and for raising a daughter who had confidence in her abilities and wasn't afraid to strive for her goals. I would not be the person I am today without you guys!

Last but not least, good luck to the future Blanchard group members! May your trip through the crazy world of graduate school be as rewarding and frustrating as mine was!

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Chapter 1

Introduction

The popularity of thin films and hence the amount of research currently being done in this area is due in part to the many potential applications of these materials. Just a few of the possible uses of thin films include chemical sensing,¹ synthetic light harvesting,² electronic, electro-optic, and photonic devices,^{3,4} and nonlinear optics.⁵ Much research has gone into synthesizing new molecular assemblies whose growth can be controlled in a layer-by-layer fashion. The ability to control the chemical composition within the layers is also important. By expanding the chemical functionalities that can be incorporated into multilayer structures, the utility of the resulting thin films increases.

The development of organized molecular assemblies on solid surfaces first began with the introduction of Langmuir-Blodgett films. These films are composed of amphiphilic molecules pre-assembled at an air-water interface. After their assembly, they are transferred from this interface to a solid substrate. Langmuir-Blodgett films were the first examples of monolayers constructed with a high degree of order, and have been studied in areas ranging from the optical characteristics of chromophores to chemical sensors.⁶ These films have proven useful for fundamental studies of molecular layers, but their utility is limited because of thermal instability and the weak van der Waals forces that bind the layers together.

The next development in the area of thin films was the self-assembling film, which was more chemically stable and did not have to be pre-assembled like Langmuir-Blodgett films. There are several types of self-assembled systems that result in organic



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monolayers. These systems include organosilicon compounds on hydroxylated surfaces (SiO_x on Si or Al_xO_y on Al),⁷ alkanethiols on gold,^{8,9} silver and copper,¹⁰ alcohols and amines on platinum,¹¹ and carboxylic acids on aluminum oxide.^{12,13} Early studies revealed that certain molecules would adsorb to a suitable substrate *in situ* and form crystalline-like monolayers, which could be further reacted to form a multilayer structure. In multilayers, the film is connected to the surface, the molecules in the monolayers are connected to each other, and the monolayers are bonded to one another by strong chemical bonds. In other words, this type of network, which forms a multilayer assembly, can be thought of as three dimensional, making these films significantly different than Langmuir-Blodgett films.¹⁴

Allara and Nuzzo were the first to publish work on the most common type of self-assembled monolayer, adsorbed alkanethiols on gold.¹⁵ In this type of system, alkanethiols adsorb to the gold surface, forming an actual chemical bond between the gold atoms and the sulfur head groups. Although alkanethiol monolayers have many advantages over Langmuir-Blodgett films, and have been studied extensively in the literature,^{16,17} issues such as oxidative degradation of the thiol head-group¹⁸ and lability of the gold-sulfur bond¹⁹ have limited their potential utility.

The most promising layered system to date has been metal phosphonate (MP) multilayers.^{20,21} Phosphonic acids form strong, sparingly soluble complexes with metal ions, giving them significant advantages over other systems such as Langmuir-Blodgett films and alkanethiols adsorbed on gold.²² The most widely implemented form of this chemistry employs a tetravalent Zr^{4+} that reacts with a phosphonate group to form the link between layers. Any type of molecule that can be functionalized to contain



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phosphonate groups can be used to build layers with this chemistry. These layers are more stable than the other systems mentioned mainly because of extended ZP sheets that connect adjacent layers, forming a cage-like inorganic structure. These systems are similar to self-assembling films in their ease of synthesis; the buildup of layers is accomplished by alternate immersion of the substrate in metal ion and bisphosphonate solutions. Due to the fact that there are two separate steps required for monolayer growth, the possibility of spontaneous layer growth is eliminated. ZP multilayers have been utilized in numerous studies, including nonlinear optics,^{5,23} electron transfer,²⁴ and surface modification.²⁵

New methods and routes for layer formation are constantly being sought. Two alternative types of linking chemistry that are currently being studied in the literature include covalent linking chemistry²⁶⁻²⁸ and polyelectrolyte deposition.^{29,30} Polyelectrolyte films are formed by the deposition of oppositely charged polymers onto charged substrates, with the binding force being the electrostatic attraction between the two charged species. This type of deposition chemistry has been used to study areas varying from electron and energy transfer³¹ to the permeabilities of membranes to ions.³² This is a robust method for layer deposition, but questions remain about the exact species that balance the charges between layers and the lack of order in these assemblies may be a potential problem in future applications. Covalent linking chemistry utilizes essentially the same chemistry as MP films, except that the interlayer linkage is a covalent bond such as an amide or ester linkage, as opposed to an MP functionality. This type of linking chemistry has not been studied as extensively in the literature, but due to the nature of our

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studies, this is the type of linking chemistry that we have solicited in our work (*vide infra*).

One application of multilayers that the Blanchard group has been interested in is optical information storage. In order to begin to understand this type of storage, fundamental studies using ZP chemistry were performed in our group. When visualizing optical information storage, it is important to understand both the interlayer and intralayer characteristics of the assembly. Information storage assemblies will be built using a series of layered assemblies that contain different chromophores in each layer; each chromophore absorbs light at a different wavelength. An explicit wavelength of light will be used to access a specific layer, and hence a specific piece of information. It is important to understand if any excitation transfer will occur between different layers, otherwise multiple layers may be accessed at once. The ideal situation is to hinder any excitation transfer from occurring between layers, thereby keeping each layer discretely accessible.

Horne and Blanchard studied energy transfer in ZP multilayer systems, and found that this was not the dominant means by which excited chromophores relaxed in these systems. Several reasons were cited for the inefficient energy transfer seen in the ZP multilayer system. The first entails intralayer energy transfer. In the system studied, the layers consisted of fixed concentrations of a donor molecule, and the concentration of acceptor molecule was varied. According to the Förster model, there should be a dependence of the donor lifetime on the amount of acceptor present. In other words, the fluorescence lifetime of the donor should decrease as the concentration of the acceptor increases. This phenomenon was not seen in these systems due to aggregation of the



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chromophores into islands that were spaced at distances larger than the critical radius.³³ Excitation transport between the same chromophore ($D_1^* + D_2 \rightarrow D_1 + D_2^*$) was also found to compete effectively with energy transfer between different chromophores ($D^* + A \rightarrow D + A^*$).

Interlayer excitation transport was also studied in ZP layers.³⁴ In these studies, different layers were prepared which consisted of 100% donor, 100% acceptor or 100% alkane spacer. Layers were designed to facilitate the highest efficiency energy transfer between donor-acceptor pairs. These studies revealed that efficient Förster energy transfer did not occur between layers of donor and acceptor molecules. One reason cited for this result is that the intralayer energy transfer between aggregates and monomers competes very effectively with interlayer transfer, lessening the likelihood of transfer between layers. One assumption of the Förster model for energy transfer is that the dielectric response of the space between the donor and acceptor is uniform. This is not the case for the ZP linkages. The presence of the ZP layer between the donor and acceptor acts as a “polarizable screen” which shields the oscillating transition dipole moment of the donor molecule from the transition dipole moment of the acceptor molecule. The basis of the Förster model for energy transfer is dipole-dipole coupling between the donor and acceptor molecules (*vide infra*). If the dipoles are somehow shielded from one another, then efficient energy transfer will not occur.

From this work it was concluded that in order to study energy transfer effectively, the use of another type of system was necessary. The next logical step was to link the layers covalently, thereby eliminating the need for the polarizable ZP moiety. In the Blanchard lab, covalent linking chemistry studied by Kohli was the starting point for

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the multilayer schemes used in this work. Kohli's work was begun using diphenylmethane derivatives³⁵ functionalized with amines or isocyanates, in which the relevant multilayer linking chemistry proceeds as follows. A diisocyanate-containing monomer is reacted with a diamine-containing monomer, and growth is controlled layer-by-layer by exposing the substrate to only one reactive monomer species at a time. The only time that uncontrolled growth was seen was in the presence of water. Isocyanates are water-sensitive, and water in the reaction may produce polyureas, due to the reaction of hydrolyzed isocyanate (an amine) with excess isocyanate. It is interesting to note that although layer growth is spontaneous when water is present, and thus thicker layers of material result, FTIR demonstrates that the same urea functionality is present as in the controlled growth layers.³⁵

Another type of covalent linking chemistry has also been used in our lab, which utilizes the formation of ester and amide bonds. In this case, diamine or dialcohol functionalized molecules are reacted with a diacid chloride to form either an amide or an ester linkage. This chemistry proceeds more efficiently and in less time, allowing a larger number of layers to be built more quickly. Using this chemistry, a multitude of different chromophores have been included in multilayer assemblies³⁶, and other work in our lab has utilized this chemistry in polymer assemblies, demonstrating the versatility of this linking chemistry. Another advantage to this type of linking chemistry, as opposed to the urea chemistry, is the controlled growth of the assembly. Although the reactions are performed under anhydrous conditions, if some water is present, uncontrolled growth will not occur. The only consequence is the hydrolysis of the acid chloride to a carboxylic acid, which will impede the reaction. The carboxylic acid can be converted

back to an acid chloride by reacting it with thionyl chloride, thereby allowing the reaction to further proceed. The layer-by-layer control seen with this scheme and the shorter reaction times are the main reasons that we have used this chemistry in our work.

There are two main goals in this project, the first of which is to build new types of multilayer structures, which has been done using a variety of different linking chemistries. The second is to better understand the local environment which molecules sense in a multilayer, and this has been accomplished by studying the fluorescence lifetimes of the molecules of interest. Utilizing fluorescence lifetime measurements, and studying energy transfer within a multilayer assembly, two things can be accomplished. First, the local environment of the molecules can be probed, demonstrating this technique's usefulness as a characterization method. Second, we believe that energy transfer can be utilized in other applications as well. For example, this technique can be a useful tool for irradiating a surface at one initial excitation wavelength. With layers constructed appropriately, excitation could propagate unidirectionally through a thin film by means of excitation transport. Such a structure could function as a broadband optical antenna. Another useful application is enhancing photoelectric effects in solids by optically sensitizing them with layers of fluorophores.³⁷ In this case, a molecule in contact with a solid absorbs energy and then transfers it to the solid substrate. The transfer of energy excites the solid, producing free carriers in the material. Sensitization is useful when a solid is not absorptive in a region of interest; by coating it with a thin film, the efficiency of the resulting photoelectric effect can be increased.⁶

In this work the chromophores 2,7-diaminofluorene, 3,3'-methylenedianiline (MDA) and 4,4'-diaminoazobenzene were studied to analyze their potential use in energy

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transfer studies, based on their optical characteristics and chemical functionalities. An important characteristic to consider when choosing chromophores for energy transfer applications is the absorption and emission bands of the chromophores. It is important in these studies that the emission band of the donor molecule overlaps the absorption band of the acceptor molecule. The solution phase absorbance and emission spectra of these chromophores are shown in Figure 1.1. Initially the donor-acceptor pair that we were interested in consisted of 2,7-diaminofluorene as the donor molecule, and 4,4'-diaminoazobenzene as the acceptor molecule. After preliminary fluorescence lifetime measurements were performed, the donor molecule was changed to MDA, keeping the same acceptor molecule. The fluorescence lifetime studies and energy transfer in the context of the Förster model will be discussed in greater detail in Chapter 3.

We use fluorescence lifetime measurements as a characterization method to probe the local environments of molecules, but we also wish to better understand the results seen in the ZP multilayer systems. By using covalent linkages as opposed to ionic linkages, we hope to support the reasons cited previously for inefficient energy transfer. We want to conclusively determine if other factors may have been involved in impeding efficient interlayer energy transfer in the ZP systems.

In this thesis, the characteristics of covalently linked multilayer assemblies are studied. The multilayer structure, optical properties and local environment are all important issues which must be better understood before the real-life applicability of these covalent films can be realized. In Chapter 2, the synthesis of covalently linked multilayers and alternate multilayer chemistries is described. Included in this chapter are the fundamental characterization methods used, including ellipsometry, FTIR, UV-visible

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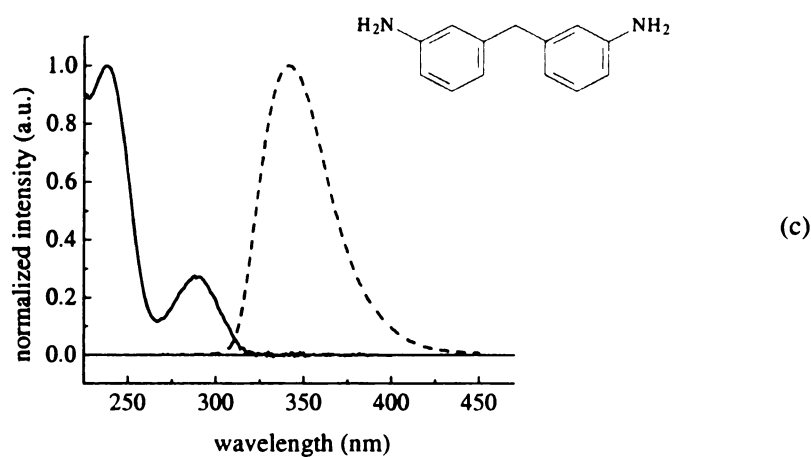
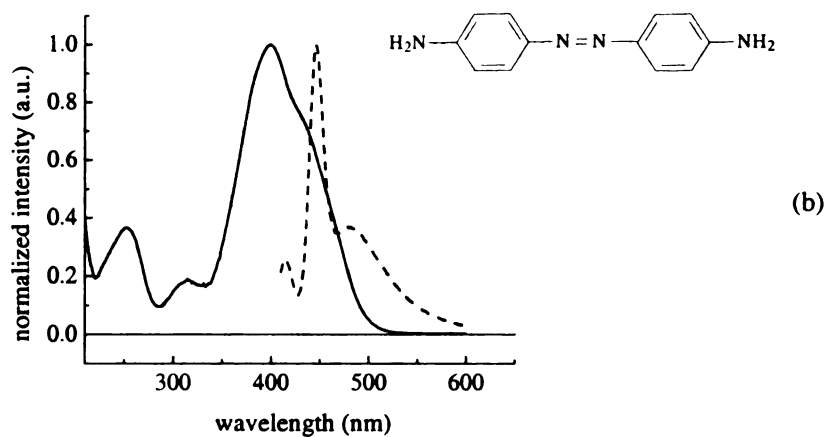
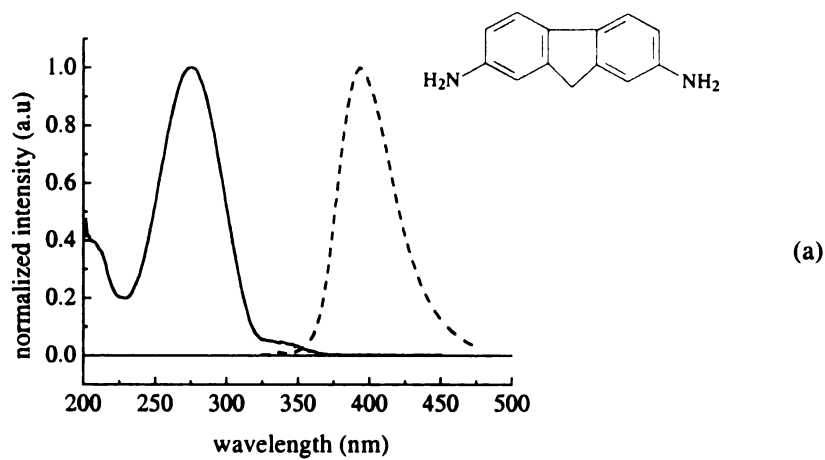


Figure 1.1 Structures and absorbance (—) and emission (----) spectra (10^{-5} M in ethanol) of (a) 2,7-diaminofluorene, (b) 4,4'-diaminoazobenzene and (c) 3,3'-methylenedianiline.

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spectrometry and X-ray photoelectron spectroscopy (XPS). We find that controlled growth of multilayer assemblies occurs using all of the linking chemistries utilized. Chapter 3 describes the investigations of the interlayer population dynamics of homogeneous and heterogeneous multilayer structures and also provides a discussion of the theory of Förster energy transfer. From these studies, we find that 2,7-diaminofluorene and 4,4'-diaminoazobenzene, the first donor-acceptor pair, do not exhibit efficient interlayer energy transfer. A decrease in the donor lifetime is seen in the second donor-acceptor pair, MDA and 4,4'-diaminoazobenzene, but this is not due to energy transfer. We believe that this decrease is a consequence of the structure becoming more ordered with the addition of the azobenzene. The incorporation of spacer layers did not affect the donor lifetime in this system and we conclude that inefficient energy transfer is occurring. It was discovered that although the dilute solutions of these chromophores exhibit single exponential decays, on the surface decays which are fit to a double exponential are recovered. The double exponential decay may be due to aggregation of the chromophores on the surface, and this will be studied in more detail in Chapter 3. Chapter 4 summarizes the current work and details some future work of this project, including the study of intralayer transfer within these covalent systems, rotational dynamics of these chromophores in order to study the freedom that the molecules have on the surface, and solution phase studies of model compounds which are analogous to the surface species.

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Chapter 2

Synthesis and Characterization of Multilayer Assemblies

2.1 Introduction

As stated in Chapter 1, the results recovered by Horne and Blanchard motivated the current work. Their studies involved incorporating optically active chromophores into zirconium phosphonate (ZP) multilayer assemblies in order to study the energy transfer within these systems. It was found that interlayer energy transfer did not proceed efficiently, in the context of the Förster model. It is believed that this result is due mainly to interlayer shielding of the transition dipole moments of the donor and acceptor molecules by the ZP functionality. It is also thought that intralayer transfer played a significant role in the lack of interlayer energy transfer. Förster energy transfer depends on dipolar coupling between the donor and acceptor molecules; if there is shielding of the transition moments of the two molecules, then energy transfer will not occur efficiently. In order to study energy transfer effectively in this type of multilayer system, the ionic ZP functionality must be removed, and energy transfer in the now covalent system should theoretically proceed efficiently. Systems that incorporate covalent linking chemistry, as opposed to the ionic ZP linking chemistry have been explored in the current work.

Another goal of this project has been the construction of novel types of multilayers, the focus of which has been covalent systems, but studies have not been limited to purely covalent systems. In order to fulfill this goal of the project, several different types of linking chemistry have been explored, and their potential utility evaluated. All of the systems constructed have provided useful information, but they are not necessarily appropriate for studying energy transfer. Some of the linking chemistries studied early

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on in this work were not as facile as necessary, or there were experimental limitations, and therefore these linking chemistries were modified. There are, in effect, two main categories of multilayer synthesis that have been studied in this work. The first entails a type of coordination chemistry, which is similar to ZP chemistry, but uses EDTA as the layered material, rather than a bisphosphonated molecule. In this case, the EDTA complexes with the Zr^{4+} , forming a coordinate bond as opposed to the ZP linkage. The second type of multilayer synthesis that we have studied includes the incorporation of two different types of covalent linkages, one that utilizes urea and urethane linkages, and another that utilizes the reactions that form esters and amides. In this Chapter, the synthesis of these different types of multilayers will be discussed. In addition, the fundamental characterization of these assemblies will also be presented, demonstrating the extent to which growth of these multilayer systems can be controlled.

2.2 Experimental

EDTA Multilayer Synthesis. Double-side polished, undoped Si(100) substrates (Boston Piezo-Optics) were used for multilayer synthesis. Substrates were cleaned in piranha solution (3:1 $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$) for approximately fifteen minutes and were then submerged in distilled water for approximately two minutes, producing a native oxide layer of ~ 15 Å, measurable by ellipsometry. The substrates were then rinsed with flowing distilled water and dried under a N_2 stream. The scheme that outlines multilayer deposition is shown in Figure 2.1. The silicon substrates were phosphorylated by immersion in a solution that was 0.2 M in both phosphorous oxychloride (Fluka) and 2,4,6-collidine (Aldrich) in anhydrous acetonitrile for 10 minutes. The substrates were then rinsed with reagent grade acetonitrile and distilled water. The resulting surface was

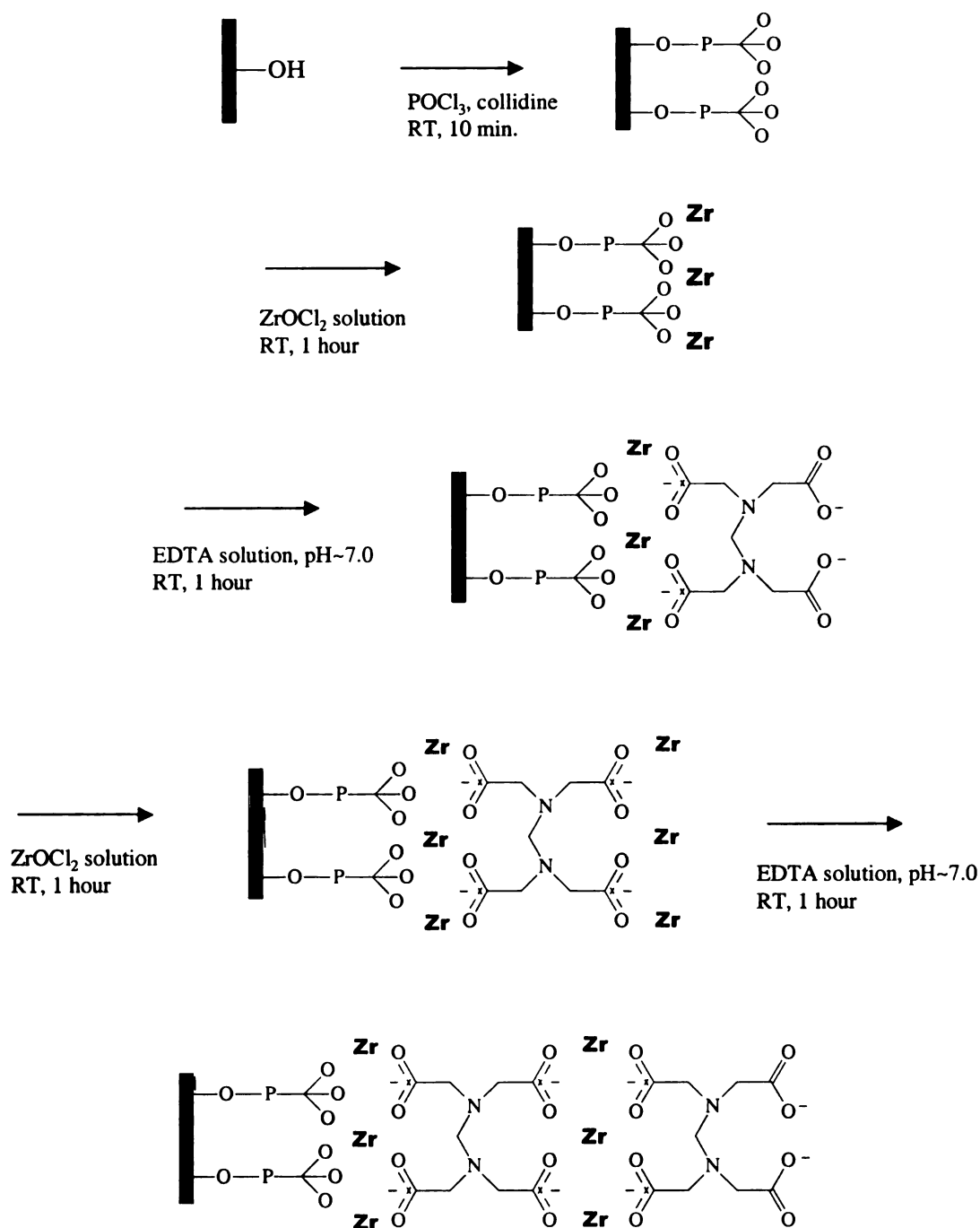


Figure 2.1 Scheme outlining the deposition of multilayers containing EDTA molecules, which chelate with Zr^{4+} ions to form multilayer structures. Note that the Y^{4-} form of EDTA is shown for simplicity, and does not necessarily imply that this is the form in the layers.

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exposed to Zr^{4+} by immersion in 5 mM ZrOCl_2 (Aldrich) in 85% EtOH/15% H_2O for one hour. After removal of the substrate from solution and rinsing with distilled water, it was placed in an aqueous solution of 0.1 M EDTA (pH $\sim$ 7.0). The pH of the EDTA solution was adjusted with 50% KOH. After reacting in the EDTA solution for one hour, the substrate was removed and rinsed with distilled water, dried under a N_2 stream and the thickness of the resulting layer was measured by ellipsometry (Rudolph Auto-El II). Subsequent layers were added by first zirconating the substrate, as discussed above, followed by immersion in the EDTA solution.

Urea Multilayer Synthesis. Single-side polished, undoped Si(111) substrates (Silicon Quest International) were cleaned in piranha solution for fifteen minutes. The substrates were then immersed in distilled water for two minutes, rinsed with flowing distilled water, and dried under a N_2 stream. Priming of the oxidized silicon substrates was carried out by reaction in a $\sim$ 1.0% v/v solution of 3-aminopropyldimethylethoxysilane (United Chemical Technologies) in reagent grade toluene overnight at room temperature. After priming, the substrates were rinsed with toluene, ethanol and distilled water, and dried in a N_2 stream. Priming yielded amine-terminated surfaces that were ready for further reaction.

The following conditions were used for bilayer formation (a bilayer consists of a diisocyanate layer capped with a diamine layer) and the scheme outlining the deposition of multilayers is shown in Figure 2.2. After priming, the substrate was placed in a $\sim$ 0.2 M solution of 1,6-diisocyanatohexane (Aldrich) in anhydrous DMF under Ar. The solution was allowed to react overnight at 60 $^\circ\text{C}$. This initial reaction forms a urea linkage between the amine-terminated substrate and the isocyanate, leaving a reactive isocyanate group at the surface. The reacted substrate was rinsed with hot DMF, and

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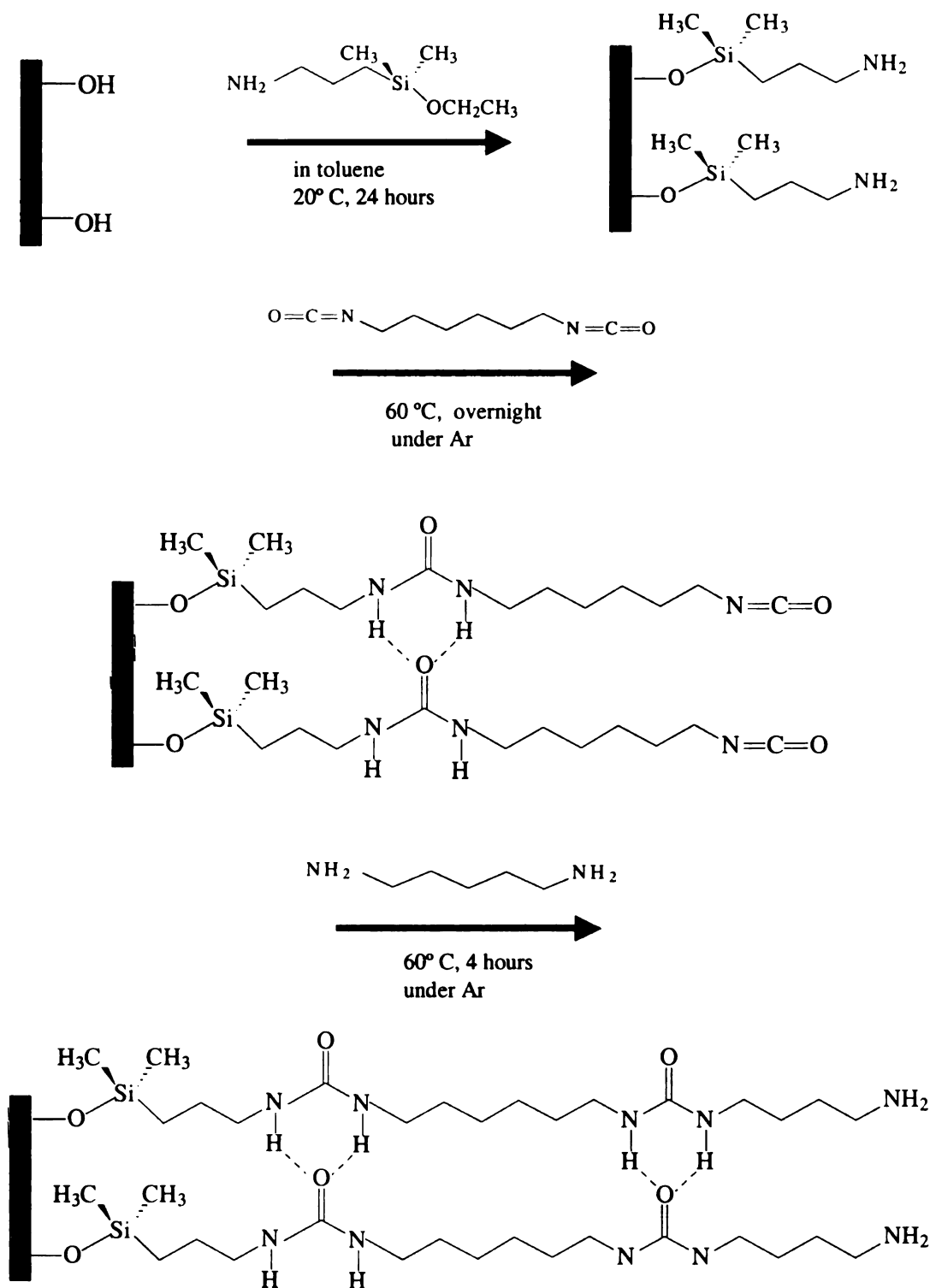


Figure 2.2 Synthetic scheme outlining the deposition of multilayers containing urea linkages. Note that the dashed lines between N-H and O-H groups indicate the possibility of hydrogen bonding. This hydrogen bonding, if it does occur, would give the multilayer structures an added degree of lateral stability not seen in other assemblies.

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reacted for four hours at 60 °C in a ~0.4 M solution of 1,4-diaminobutane (Aldrich) in anhydrous DMF under Ar. After reaction, the substrate was rinsed with hot DMF, distilled water, acetone, distilled water again and dried in a N₂ stream. At this point in the multilayer deposition scheme, when an amine-terminated surface was present, characterization of the surface was performed. This is due to the ease of hydrolysis of the isocyanate, which yields an amine, hindering further reaction.

Acid Chloride Multilayer Synthesis. Quartz substrates or double-side polished, p-doped Si(111) substrates (Silicon Quest International) were cleaned by immersion in piranha solution for fifteen minutes, rinsed with distilled water and dried under a N₂ stream. Clean substrates were primed immediately for further reaction. To prime the surface, the substrate was placed in a ~1.0% v/v solution of 3-aminopropyldimethylethoxysilane (United Chemical Technologies) in reagent-grade toluene overnight at room temperature. The resulting primed substrate was removed, rinsed with toluene, ethanol and distilled water and dried under a N₂ stream. The resulting amine-terminated surface was then ready for further reaction. The scheme that illustrates the formation of multilayers constructed using the acid chloride linking chemistry is shown in Figure 2.3.

The amine primer layer was reacted in a solution of ~0.2 M adipoyl chloride (Aldrich) and excess N-methylmorpholine (Aldrich) in anhydrous acetonitrile, under Ar, at room temperature for 25 minutes, to form an amide linkage. After this reaction, the acid chloride-terminated substrate was rinsed with ethyl acetate and placed under Ar once again. Either a ~10⁻³ M solution of diamine functionalized chromophore or a ~0.2 M solution of 1,3-propanediol in anhydrous acetonitrile was used for reaction, with an excess of pyridine added to neutralize any HCl that may be formed. This reaction

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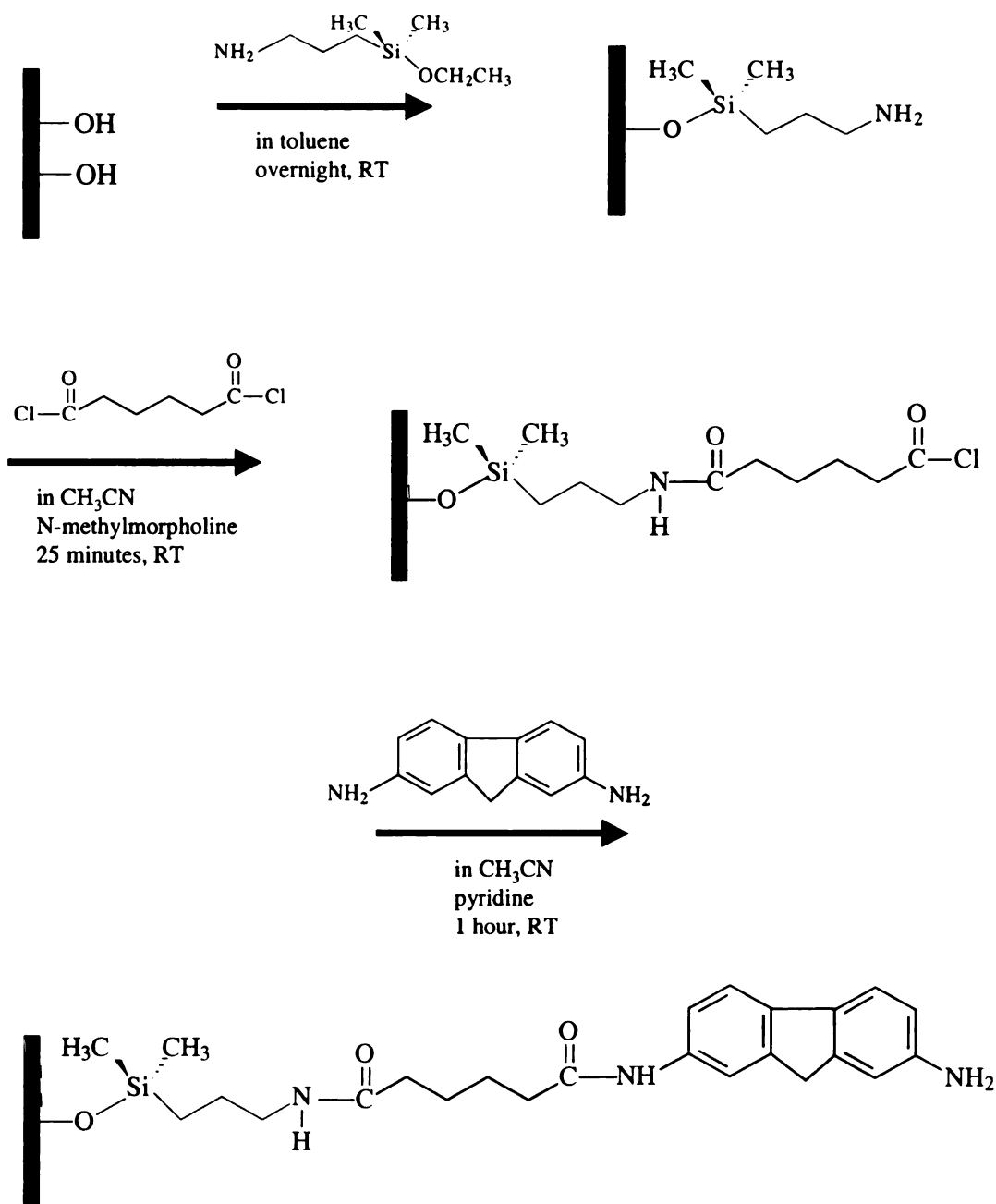


Figure 2.3 Synthetic scheme outlining multilayer deposition using amide linkages. When forming ester bonds as opposed to amide bonds, 1,3-propanediol was reacted instead of a chromophore, which is shown in this diagram.

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proceeded for one hour at room temperature. Following reaction, the substrate was rinsed with reagent grade acetonitrile, ethanol and distilled water, then dried under a N₂ stream. Subsequent layers were deposited by using the same sequence that is outlined in Figure 2.3. It is important to note that characterization of the surface was performed after the deposition of a bilayer. This bilayer consisted of an acid chloride-terminated group capped with either a diamine or dialcohol functionalized molecule. This is due to the reactivity of the acid chloride group to hydrolysis. In order to prevent hydrolysis of the acid chloride to a carboxylic acid group, which would be unreactive in this scheme, bilayers were deposited before characterization.

Optical Null Ellipsometry. The thicknesses of primed surfaces and monolayers were measured using an optical null ellipsometer (Rudolph Auto-El II) operating at 632.8 nm. The thickness measurements were determined using Rudolph DAFIBM software. For all film thicknesses measured, a value of $n = 1.462 + 0i$ was used as the film refractive index. It has been suggested by Ulman that a value of $n = 1.50$ should be used for monolayers of alkyl chains with chains of C₁₀ and longer, while alkyl chains of C₉ and shorter should use a refractive index of 1.45.¹ Tillman *et al.* determined that an increase of 0.05 in the refractive index translates to a decrease in thickness of only ~1 Å.² Given the small implications of a slightly inaccurate refractive index, the same value of 1.462 was used for both the native oxide (SiO_x) layer and the organic monolayers.

Brewster Angle FTIR. Infrared spectra of covalent films on silicon were obtained using a Nicolet Magna 550 FTIR spectrometer. The Brewster angle rotation stage and polarizer were obtained from Harrick Scientific Corporation. Spectral resolution was 4 cm⁻¹. The angle of the rotation stage was set at ~75°, which is the Brewster's angle for

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our specific p-doped silicon wafers. The Brewster's angle of a material can be calculated using the following equation:³

$$\theta_B = \tan^{-1}\left(\frac{n_2}{n_1}\right) \quad (2.1)$$

In this equation, n_1 represents the refractive index of the ambient, usually air, with a value of 1.00, and n_2 represents the refractive index of the medium itself. In the case of the silicon used, a value of $n_2 = 3.732$ was measured by performing ellipsometry on a clean, oxidized silicon surface, and this number was used to calculate the Brewster's angle. Substrates were prepared in the manner explained above, but double-side polished silicon wafers were used rather than single-side polished, a necessity in Brewster's angle studies. In the case of external reflection, there are two modes of reflection which must be considered, R_{TE} and R_{TM} . In a plot of reflectance versus incidence angle for a given material, the angle at which R_{TM} goes to zero is known as the Brewster's angle. Although R_{TE} is not zero at this point, and therefore some percentage of light is reflected, a polarizer was used in these studies, which should eliminate any contribution from this mode. The majority of the light is transmitted, allowing both sides of the surface to contribute to the signal. Since both sides of the surface are contributing to the signal, one rough side would cause a large amount of scatter, disrupting the signal. Therefore, in this type of spectroscopy, double-side polished wafers should be used. This technique is useful when performing infrared characterization on silicon substrates, as opposed to external reflection FTIR, a method used commonly to characterize gold substrates.

UV-visible Absorbance Spectrophotometry. Absorption spectra were taken using a Cary 300 Bio UV-visible absorption spectrophotometer. Solution phase spectra were obtained at a scan rate of 600 nm/min., while quartz surface measurements were obtained

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at a scan rate of 300 nm/min. Surface absorption spectra were obtained on a quartz surface, using clean, blank quartz substrates as the references.

External Reflection FTIR. In order to utilize external reflectance FTIR (Nicolet Magna 560), layers were also formed on gold-coated silicon substrates (2000 Å of Au on 200 Å of Ti, Silicon Quest International). These substrates were cleaned first in either a UV cleaner (Boekel) for 10 minutes, or in piranha solution for three minutes. The optical constants were immediately measured after cleaning by optical null ellipsometry. To functionalize the gold surface, the substrates were immersed in a 10^{-4} M solution of 11-mercaptoundecanol in ethanol at 20 °C for 24 hours. The hydroxyl-terminated surface was then reacted with 1,6-diisocyanatohexane to produce a urethane linkage, forming the first bilayer. Subsequent layers were grown using the same reaction scheme as that on silicon (Figure 2.2). It should be noted that this characterization technique was only used in studies where bilayers were grown on gold-coated substrates.

X-Ray Photoelectron Spectroscopy. XPS measurements on multilayer samples were performed using a Perkin Elmer Φ spectrometer with monochromatized Al K α radiation (1486.6 eV). All values that are reported are referenced to the C 1s line at 284.6 eV.

2.3 Results and Discussion

As discussed in the Experimental section, one method of layer formation that we have explored is the use of EDTA in a method similar to ZP linking chemistry. In these studies, the chelating characteristics of the EDTA molecule were utilized to build multilayers by complexation with Zr⁴⁺ ions. EDTA is most commonly used for metal ion analysis because it chelates 1:1 with many metal ions. In our experiments, we were

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hoping to utilize EDTA in its tetradentate form, Y^{4-} . In this structure, the four acidic protons are dissociated, allowing chelation at all four sites. The α plot of EDTA demonstrates that the Y^{4-} form is prevalent only above pH 10.0.⁴

We believed that monolayer formation would be dependent on the conformation that the EDTA molecule adopted in solution. In an attempt to optimize monolayer formation, a range of pHs was employed. The only pH that yielded monolayer growth was pH 7.0; layer growth was not seen when different pHs were used. According to the α plot, the species in solution at pH 7.0 are ~65% HY^{3-} and ~35% H_2Y^{2-} . Based on these values, it seems unlikely that more than one monolayer of EDTA would form, but multilayers were constructed, and a linear relationship between film thickness and the number of layers was seen for up to four layers. The plot of thickness vs. the number of layers is shown in Figure 2.4. Beyond four layers, linearity was not seen. Layer thicknesses were not reproducible, and growth did not always occur. Attempts to raise the pH to ~10.0, in order to increase the concentration of Y^{4-} in solution resulted in making the silicon substrates brittle. The exact reasons for this behavior are unclear. By increasing the pH of the Zr^{4+} solution, we tried to lessen the differences between the pHs of the two solutions. This caused the Zr^{4+} ions to precipitate out of solution as $Zr(OH)_4$, rendering the solution useless.

Although the idea of using EDTA and metal ions together to form multilayers was novel, in practice it was quite difficult. The chemistry itself is too pH sensitive, and high pH also seemed to have adverse effects on the silicon substrates. Although some layer growth was seen, the method was not as facile and reproducible as necessary. Due to the fact that growth was seen when the pH should not be conducive to this raises questions about the structure of the EDTA molecules in our solutions. Obviously the behavior of

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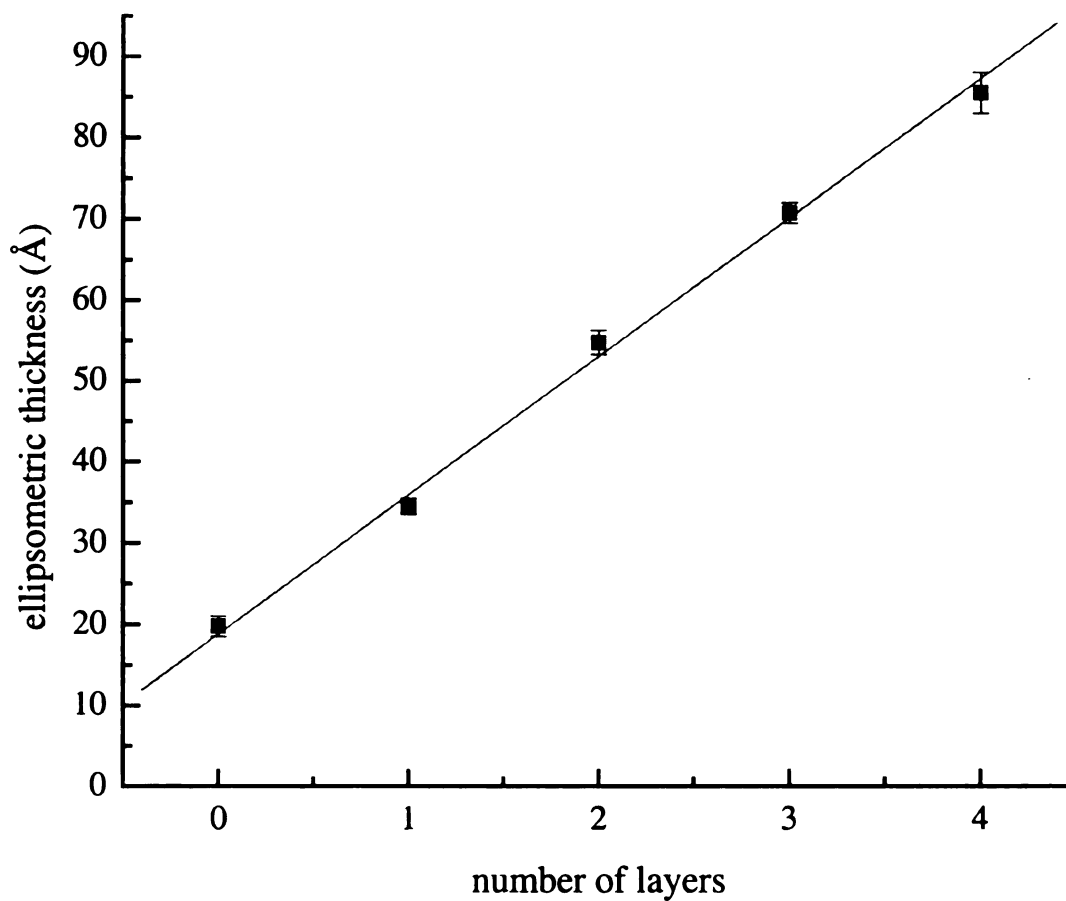


Figure 2.4 Ellipsometric thickness vs. the number of layers deposited for multilayers synthesized using EDTA as the layered material. The non-zero y-intercept is due to the native oxide that is present on the surface before the start of multilayer deposition. The error bars are the standard deviations of six measurements.

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the EDTA in the multilayers was more complex than we had originally believed, and the pH problems were too great to overcome. These facts combined to force us to seek a new route for multilayer synthesis.

At this point, we turned to the urea and urethane chemistry under development in our group. We were interested in modifying the original chemistry, which had involved copolymerization using diphenylmethane derivatives and we instead reacted individual monomer species. We first explored this method using alkane chains terminated with diamine and diisocyanate functionalities. The importance of demonstrating the alkane layer growth was two-fold. The first important point was determining if the chemistry was facile using diisocyanate and diamine terminated alkane groups. Once this proved fruitful, we could then incorporate these alkane functionalities as spacer layers in the energy transfer studies.

Characterization of the interfaces was performed after bilayer formation so that a stable, amine-terminated surface was present. It was imperative in all of the multilayer syntheses that water not be present. The step most vulnerable to hydrolysis was the addition of the diisocyanate. As previously stated, reaction of an isocyanate group with water yields an amine. The amines and excess isocyanate can then polymerize, resulting in uncontrollable layer growth. To protect against this, glassware was dried at 110 °C, then cooled in a dessicator. Furthermore, the 1,6-diisocyanatohexane and 1,4-diaminobutane were stored under Ar.

Linear growth of the multilayers was seen for up to 8 bilayers, and the average bilayer thickness (from the slope of the line) was ~13 Å. Figure 2.5 illustrates an example of a plot of thickness vs. the number of bilayers. As stated previously, the

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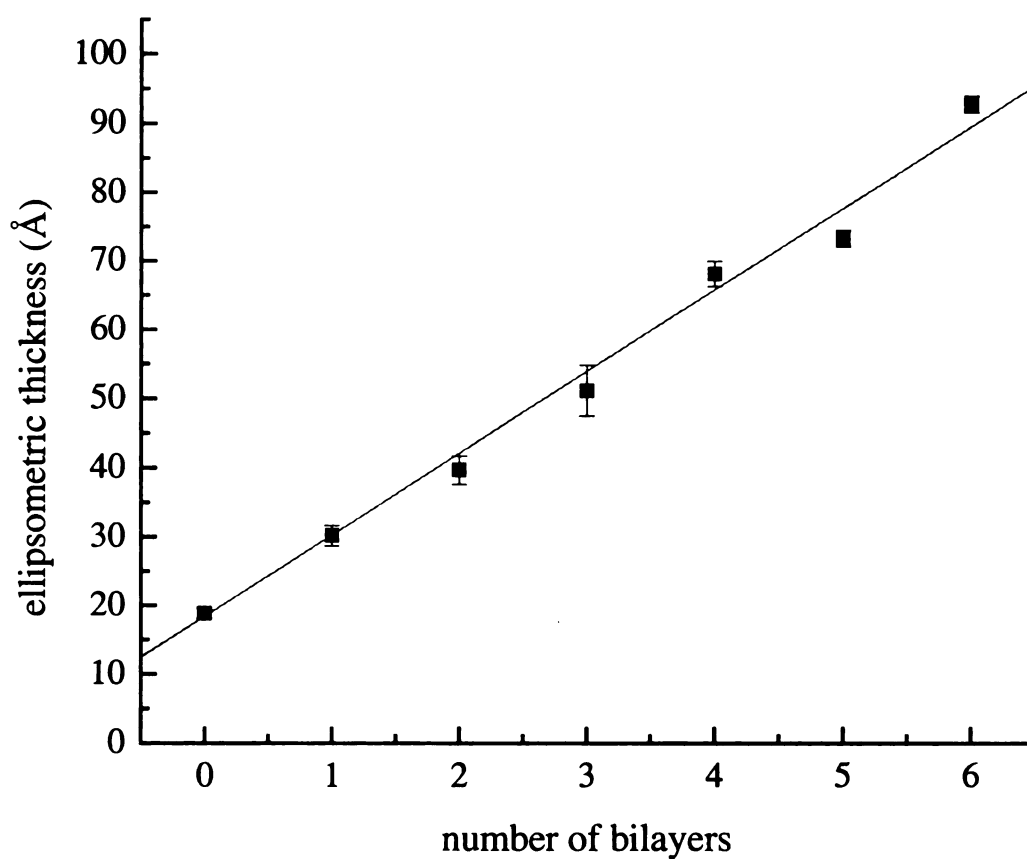


Figure 2.5 Plot of ellipsometric thickness vs. the number of bilayers deposited for multilayers constructed through the alternate deposition of 1,6-diisocyanatohexane and 1,4-diaminobutane. The relevant linking chemistry is a urea bond. The non-zero y-intercept is a result of a combination of the native oxide and the primer layer. The error bars represent the standard deviation of six different measurements.

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thickness of bilayers is reported because the stability of an amine-terminated surface is much greater than that of an isocyanate-terminated surface. The expected thicknesses are 19 Å/bilayer, as determined by HyperChem calculations, and this value is greater than the average thicknesses that we report. There are several possible reasons for this discrepancy. First, the HyperChem calculations are for a fully extended, all trans molecule, and no assumption is made about the tilt of the molecules with respect to the surface normal; it has been shown in the literature that molecules in a monolayer are not aligned with the surface normal.⁵ Another possible reason for the discrepancy between the expected and the experimental values may be due to incomplete surface coverage. The spot size of the He-Ne laser on the sample is large compared to the size of the molecules in the monolayer. Therefore when the beam is incident on the sample, a large number of molecules are contributing to the change in polarization of the light. The measured thickness is essentially an average of all of the contributing molecules, so a partially covered surface could yield a lower measured thickness because of the combinations of the bare and covered surface regions. The same result may occur if the molecules on the surface have a tilt angle. This tilt may make the molecular thickness appear lower than it actually is. These reasons must be considered any time that a lower than expected thickness is returned when using ellipsometry.

Although the ellipsometric data exhibit bilayer thicknesses that seem low, the FTIR spectra reveal that layers are being deposited, with the expected increase in absorbance with an increasing number of layers (Figure 2.6). In addition to demonstrating absorbance increases, FTIR data can also yield information about the species that are present within the assembly. These spectra illustrate that urea bonds are present. This fact is supported by peaks at $\sim 1634\text{ cm}^{-1}$ and $\sim 1582\text{ cm}^{-1}$, which represent

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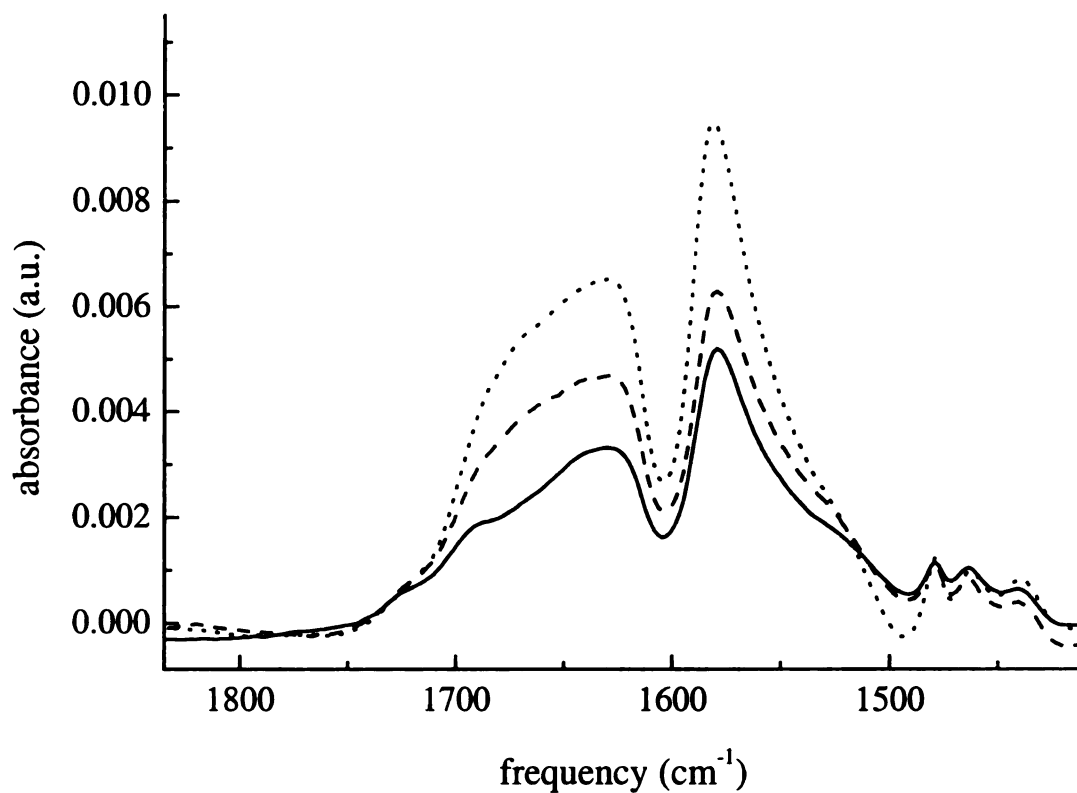


Figure 2.6 FTIR spectra of films composed of bilayers constructed using urea linkages. Note that the absorbance increases with an increasing number of layers, up to three bilayers, as shown. The peaks at $\sim 1634\text{ cm}^{-1}$ and $\sim 1582\text{ cm}^{-1}$ are characteristic of the amide I and amide II bands of urea compounds. The shoulder at $\sim 1680\text{ cm}^{-1}$ may be due to the carbonyl stretch of another type of urea moiety in the multilayers.

the amide I and amide II bands characteristic of urea compounds.⁶ As expected, the absorbance of these peaks increases in proportion to the number of bilayers. A broad peak centered at $\sim 3334\text{ cm}^{-1}$ (not shown) may represent numerous types of hydrogen bonding occurring amongst the N-H groups of the urea moieties.

After the initial studies were performed using the alkane moieties, we chose molecules to incorporate into the layers for energy transfer studies. The obvious choice was organic laser dyes, due to their high fluorescence quantum yields and large extinction coefficients. Both of these factors are important when studying excitation transport in interfacial structures. Two molecules were chosen for these studies because of the amine functional groups that they possessed, a necessity to form a urea linkage. The two dyes which were chosen for these studies were rhodamine 6G and cresyl violet. Besides their amine functionalities, these molecules were also chosen because of their optical characteristics. The structures and solution phase absorption and emission spectra of these two molecules are shown in Figure 2.7. When studying energy transfer between molecules, their spectral overlap is an important characteristic to consider. For efficient excitation transport to occur, the emission spectrum of the donor molecule must overlap the absorption spectrum of the acceptor molecule. As seen in Figure 2.7, this requirement is fulfilled for this donor-acceptor pair.

The same conditions were used as for the alkane moieties in an effort to incorporate these dyes into the multilayers. These experiments were performed using both oxidized silicon (to study ellipsometric thickness increases) and quartz (to study absorption changes) as substrate materials. The formation of multilayers containing dye molecules did not proceed as expected. There are several possible reasons that this

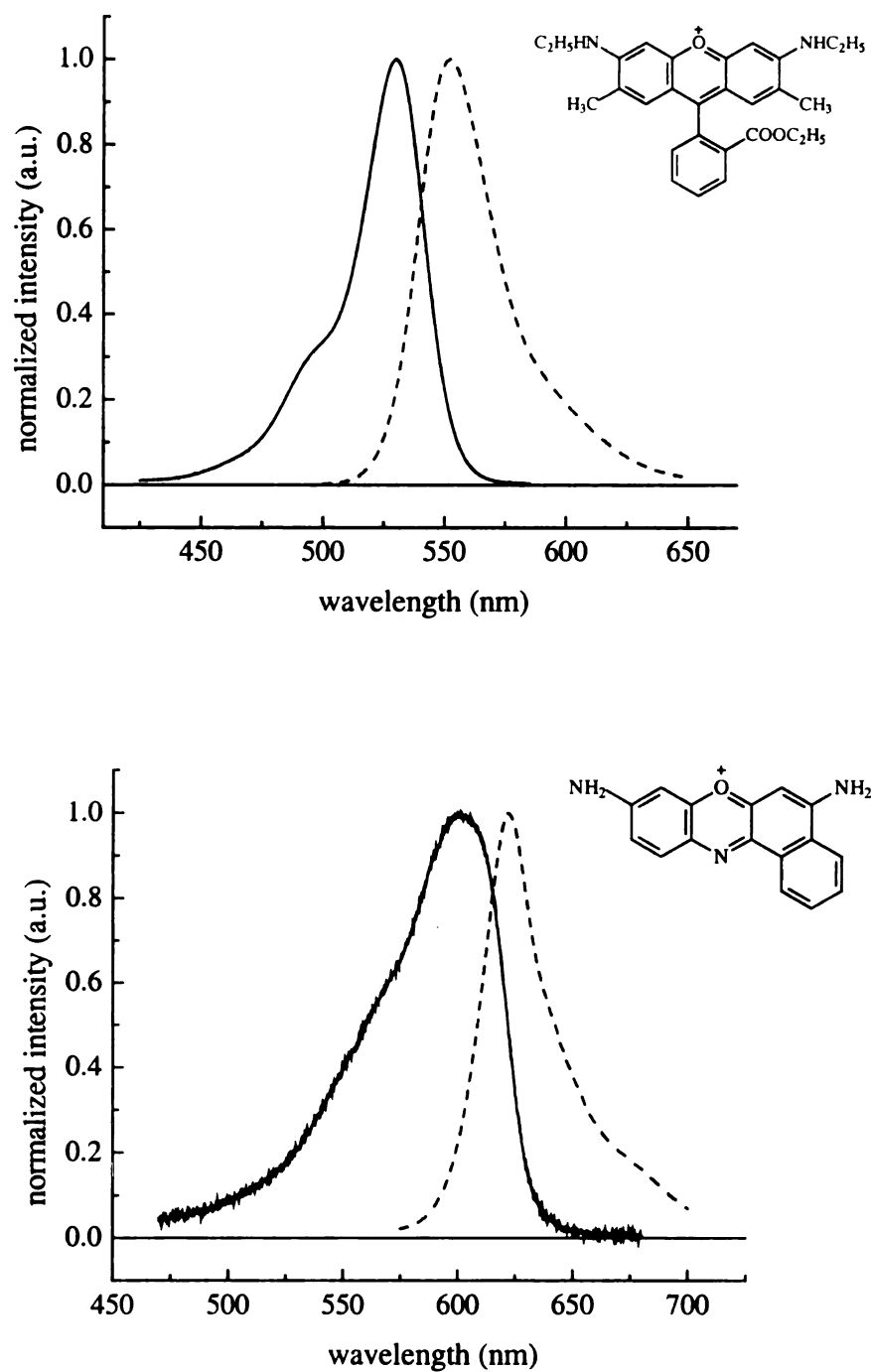


Figure 2.7 Structures and solution phase absorbance (—) and emission (----) spectra of the two dye molecule candidates for energy transfer studies. The top structure is rhodamine 6G, and the bottom structure is cresyl violet. Note that the emission band of the rhodamine 6G overlaps the absorption band of the cresyl violet.



chemical reaction scheme did not work. One reason deals with the reaction mechanism itself. In this reaction, the isocyanate undergoes nucleophilic addition with the amine functionality. The lone pairs located on the amine nitrogen attack at the partially positive carbon in the isocyanate molecule. After the addition at this carbon, a proton from the now partially positive amine undergoes a proton shift and moves to the nitrogen in the isocyanate. As stated this is a nucleophilic addition, and therefore the attempted addition of a cationic species would hinder the reaction. Unfortunately, we were unable to locate any dye molecules that not only fulfilled the requirement of being either anionic or neutral in nature, but also contained an amine functionality and had appropriate optical characteristics. Another possibility that we have considered is that the dye molecules are too sterically hindered and bulky to be incorporated into these assemblies. This situation does not seem likely though, given the range and size of molecules that have been used in multilayer assemblies reported on in the literature.

Although the alkane functionalized groups produced facile results using the urea chemistry, the incorporation of the laser dyes into the systems was not successfully accomplished. Along with exploring other chromophores that could be used in conjunction with the urea/urethane chemistry, we also explored other possible types of covalent linking strategies. The idea of using amide and ester bonds to link different layers became a possibility for building new types of layered assemblies. The main advantage to this type of chemistry was the facile nature of bond formation. In contrast to the ~16 hours necessary to build a bilayer using the urea chemistry, the formation of amides and esters was much quicker, requiring only ~1½ hours for bilayer formation. One obvious advantage to this linking strategy is that more layers can be built in less time.

To summarize the experimental details outlined before, the following occurs when building a bilayer with amide or ester bonds. Figure 2.3 outlines the synthetic scheme in greater detail. First, the substrate is functionalized to yield an amine-terminated surface. The amine groups are then reacted with adipoyl chloride using anhydrous conditions under Ar, which forms an amide bond. The next step is the reaction of the acid chloride-terminated surface with another group, either a diamine or dialcohol functionalized molecule, forming either an amide or an ester. As with the urea linking scheme, characterization is performed after the formation of a bilayer, for the reasons stated earlier.

Before moving on to more in-depth experiments with this type of multilayer linking chemistry, we performed some preliminary XPS measurements. We wanted to determine if the chemistry was occurring as we believed, starting first with the primer layer. The main technique used to characterize the primer layer was ellipsometry, which yields no chemical information about the species on a surface. FTIR is an alternative for getting chemical information, but good spectra of primed surfaces could not be obtained. Therefore we looked to XPS, which could give us useful information about the ratios and types of elements on the surface. The first surface that we performed measurements on was an amine-terminated surface, which contained only the primer layer. As shown in Figure 2.8, numerous peaks are seen in the XPS spectrum. As expected, peaks for oxygen, carbon and silicon were all seen. We were concerned about the presence of nitrogen on the surface, and the C/N ratio, if nitrogen was present. A small amount of nitrogen was seen, which we believe is due to the presence of the primer layer. The C/N ratio was calculated to be ~2.5:1, which is lower than the expected value of ~5:1. This is

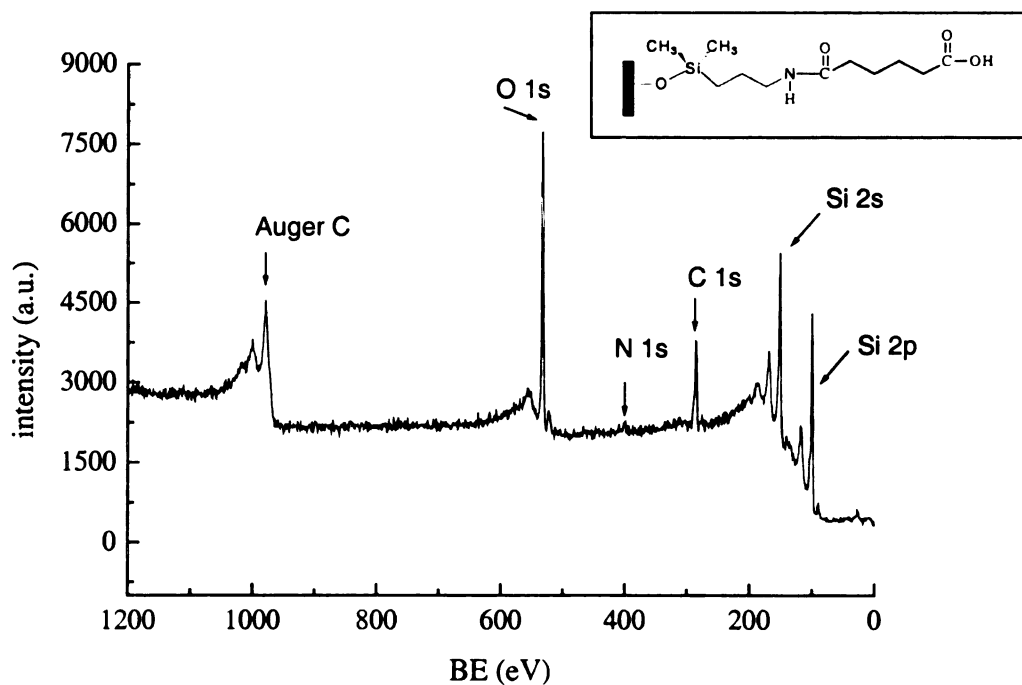
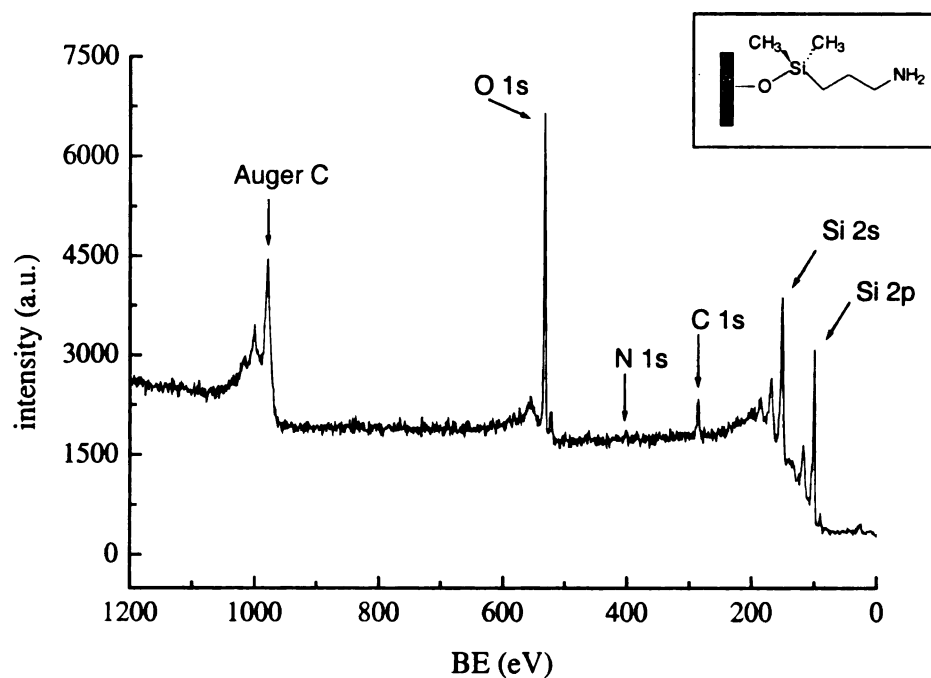


Figure 2.8 XPS spectra of surfaces that were primed with an amine-terminated silane group (top) and one that has been primed and then further reacted with an adipoyl chloride moiety (bottom). The insets depict the chemical functionalities present on the surface during the measurement.

Table 2.1 XPS peak areas, adjusted to the sensitivity factors of the instrument, for both a primed monolayer and an acid chloride terminated bilayer (contains both primer and acid chloride). The data show the presence of the expected elements, and also the proper ratios between different elements. While we still see the presence of C 1s, two peaks are observed, indicating two types of carbon with different binding energies.

	Carbon 1	Carbon 2	Nitrogen	Oxygen	SiO _x	Silicon
Primed	546.75	0	217.10	4994.91	787.52	4386.91
Acid chloride	1491.50	310.91	126.28	2734.92	621.5	3734.72

an unexpected result, but due to the large amount of noise compared with the small signal, the exact experimental ratio cannot be determined conclusively. On this surface we were mainly concerned about confirming the presence of nitrogen, and although the ratio was not exact, the presence of nitrogen was shown, and we moved on to the next sample, which also contained a primer layer, but in addition had been reacted with adipoyl chloride to form a bilayer. Figure 2.7 also depicts the molecules that should be on the surface after the priming of the substrate.

In the second sample, much more information was recovered. As expected, the relative peak areas of both Si and SiO_x decreased, indicating that the layer was thicker, and that the electrons could not penetrate through it. As shown in Figure 2.7, there should be two types of carbon that are distinguishable in this sample, carbonyl carbon, and methyl/methylene carbon. The overall carbon peak is larger in the second sample, and a shoulder is seen which was not present in the first sample. From the tabulated results shown in Table 2.1, we can see that there are in fact two different types of carbons present in the second sample, which is a result of a difference in binding energies. From this information, the ratio between the two types can be calculated, and it was found to be

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~4.5:1. This is the expected result, given that there are 9 methyl/methylene carbons, and 2 carbonyl carbons, which yields a ratio of 4.5:1. These results were extremely good, and demonstrated that the chemistry on the surface was occurring as we believed.

Prior to incorporating chromophores into these layers, we first needed to demonstrate that the linking chemistry was a reasonable route to multilayers. In order to determine this, initial studies were performed using diamine and dialcohol functionalized alkane chains. The molecules used in these studies included 1,3-propanediol, 1,5-pentanediol and 1,4-diaminobutane (all obtained from Aldrich). Initially, the use of the alkane chains presented difficulties in the experiments. During the reaction, the solutions were heated to 60 °C, and an excess of the appropriate reactive molecule was not used. Although growth was seen under these conditions, it was consistent for only the first two bilayers. Due to the freedom that is inherent when using these alkane chains, we believed that both ends of the molecules were reacting at surface sites. This process could, in effect, cap the layers, preventing further growth. To remedy this situation, the reaction was performed at room temperature, and the concentration of the amine or alcohol was increased. The concentration was increased in order to produce a large excess, which we hoped would speed up the kinetics of the reaction, allowing all of the sites to react before the molecules had a chance to cap the layer. One other change that we made was to use only the 1,3-propanediol in these experiments. The 1,5-pentanediol is a longer chain molecule with more flexibility and therefore has a greater chance of capping a layer. Although we tried using 1,4-diaminobutane to form amides, the formation of more than two bilayers was not seen. Even with the experimental changes, 1,4-diaminobutane and 1,5-pentanediol did not exhibit reproducible bilayer formation.

1

After these changes were made, continual layer growth was seen for up to four layers, which seemed to be the maximum number of layers that could be deposited. Due to the lower than expected thicknesses seen, capping of the layers may still have been an issue. To test this, we performed the following experiment. We used a solution that was more dilute (~ 0.05 M compared to ~ 0.2 M), and the same reaction conditions as outlined earlier. The first bilayer exhibited a slightly lower thickness than normal, and the second bilayer showed an ellipsometric increase of only ~ 3 Å, which is significantly lower than expected. The addition of a third bilayer did not show any increase, demonstrating that we had effectively capped the bilayer. It was not only important to demonstrate that the chemistry was reactive, but these studies laid the groundwork for the construction of the assemblies to be used in the energy transfer studies. In the energy transfer studies, the distance dependence of energy transfer will be explored using non-optically active spacer layers placed between the donor and acceptor molecules. It is important to understand the chemistry that occurs in the spacer layers, so that accurate distances can be approximated when separating the donor and acceptor molecules.

Based on the slope of the thickness vs. number of bilayers plots, an example of which is shown in Figure 2.9, the average thickness of the 1,3-propanediol/adipoyl chloride bilayers was found to be ~ 7 Å, which is significantly lower than the calculated thickness from HyperChem. Assuming no tilt of the molecules on the surface, HyperChem calculated a value of ~ 14 Å. One adipoyl chloride layer represents ~ 8 Å, and the 1,3-propanediol has an approximate length of ~ 6 Å. As discussed earlier, this discrepancy could be due either to the tilt of the molecules on the surface, or to a partially covered surface. Growth was seen consistently for up to four bilayers, yielding

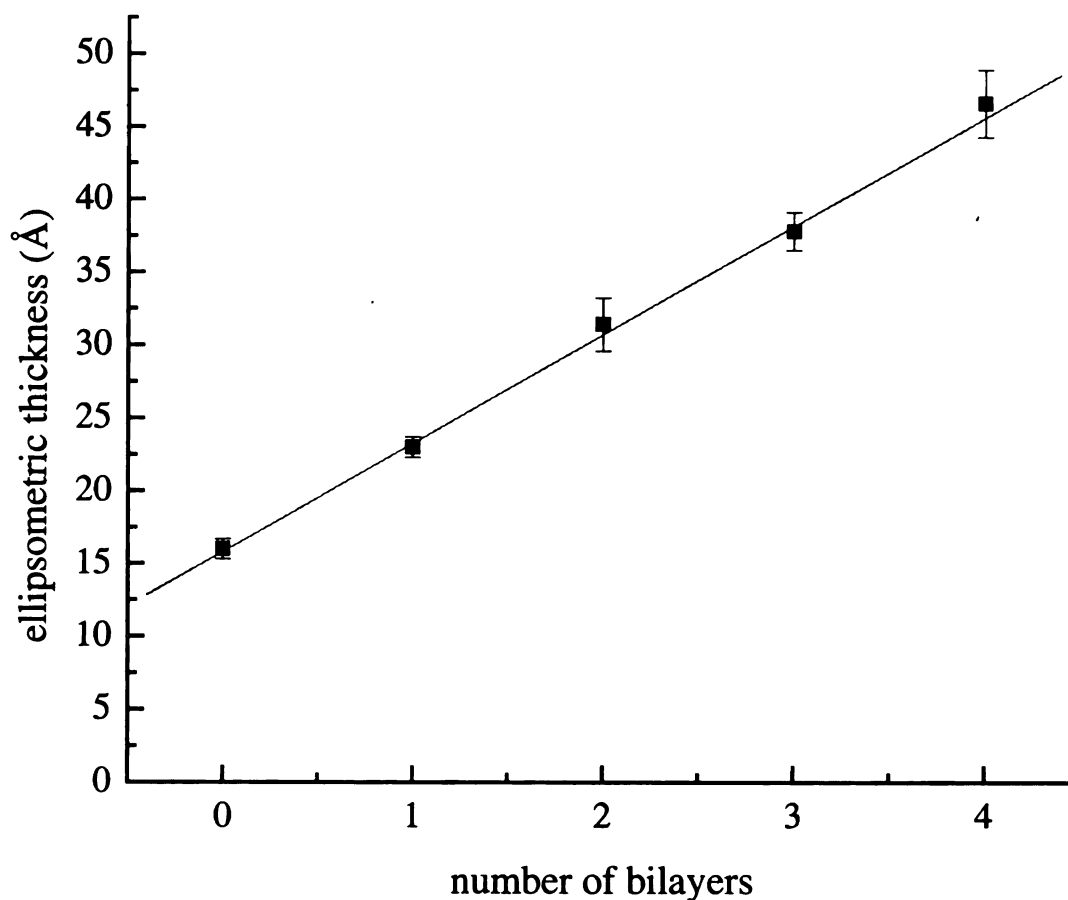


Figure 2.9 Thickness vs. number of bilayers for multilayers incorporating 1,3-propanediol reacted with adipoyl chloride to form ester linkages. Note that the y-intercept is not zero, and this is due to the combination of an initial priming layer and a native oxide. The error bars are the standard deviation of six measurements.

reproducible film thicknesses of 7 Å/bilayer. FTIR also confirms the growth of bilayers using this synthetic scheme. Figure 2.10 demonstrates that the carbonyl peak which is commonly seen for esters is located at $\sim 1725\text{ cm}^{-1}$ in these spectra. This peak increases linearly with the number of bilayers, but another peak, located at 1649 cm^{-1} does not show a linear increase. We believe that this peak is another type of carbonyl, perhaps an amide peak. This amide peak could be the result of the subsequent reaction of unreacted amines at the surface. Another possibility is hydrolyzed acid chloride, although the frequency seems low for this to be a possibility.

The next step was to incorporate optically active molecules into these assemblies. It was important that these molecules contained an amine functionality, but the optical characteristics of the molecules had to be considered as well. It must be reiterated that in order to study energy transfer effectively there must be spectral overlap of the donor emission and acceptor absorbance spectra. Another point to consider is how the optical characteristics of the molecules change once adsorbed on the surface. We therefore had to study the solution phase absorbance and emission spectra of different molecules, and also their spectra once adsorbed on the surface.

We chose diamine functionalized aromatic fluorophores for these studies, the linking chemistry being the formation of amide bonds. Several molecules including 1,5-diaminonaphthalene, aminoanthracene, 3,8-diamino-6-phenylphenanthridine, 4,4'-diaminazobenzene, 3,3'-methylenedianiline and 2,7-diaminofluorene were incorporated into multilayer assemblies using the covalent linking chemistry outlined in Figure 2.3. One problem we found with these molecules was the change in their absorption spectra upon attachment to the surface. In solution several of these molecules

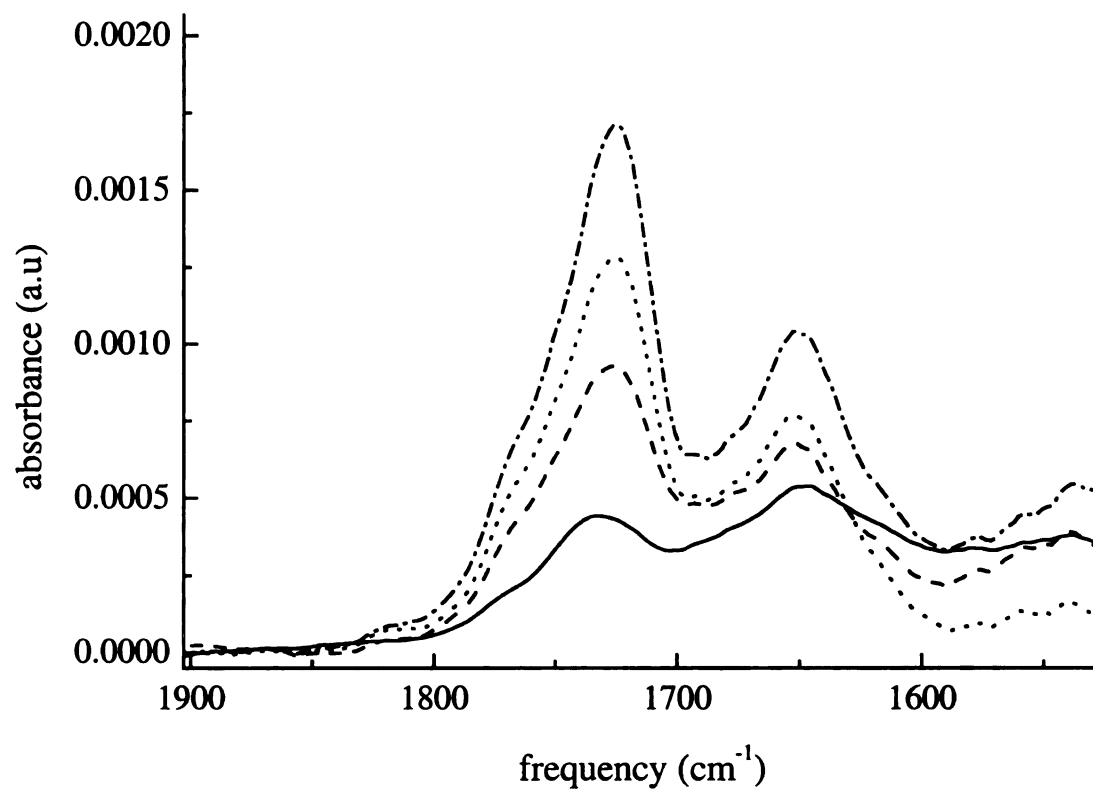
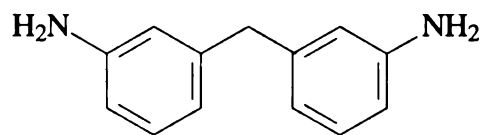


Figure 2.10 Brewster angle FTIR spectra of four bilayers composed of 1,3-propanediol and adipoyl chloride on silicon. Note the increase in absorbance with an increasing number of bilayers. The peak at $\sim 1725\text{ cm}^{-1}$ indicates the formation of ester bonds.

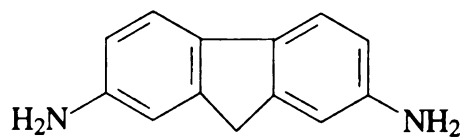
had promising absorption and emission characteristics. Another problem that we encountered was that many of these molecules, once adsorbed on the surface, exhibited only a peak at ~250 nm, or a peak further to the blue region of the spectrum. Also, other spectral features that were present in solution were not present on the surface, and therefore the absorbances were no longer optimal for inclusion in these studies. Other issues included irreproducible absorbance data, or solubility issues with the reaction solvent, acetonitrile.

After these initial studies, we chose three different chromophores, which exhibited promising optical properties, both on the surface and in solution. Although we were interested in a donor-acceptor pair, and therefore only needed to choose two of the three, all three chromophores were used. We then had several options available when we began the energy transfer studies. The three molecules that we chose were 3,3'-methylenedianiline (MDA), 2,7-diaminofluorene and 4,4'-diaminoazobenzene. The structures of these molecules are shown in Figure 2.11. The first step, after choosing the appropriate molecules, was to utilize fundamental characterization methods in order to study these molecules in the covalent multilayer assemblies.

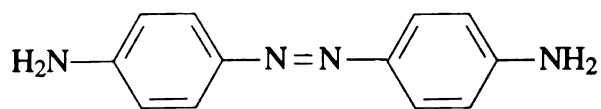
The first type of multilayer assembly that we studied incorporated 2,7-diaminofluorene as the chromophore. In solution this molecule has an absorbance maximum at ~275 nm, but once reacted with the surface this absorbance is red-shifted to yield a broad peak centered around 300 nm. The solution emission yields a peak at ~410 nm, and due to the red-shifting of the absorbance spectrum, we expect the surface emission spectrum to shift as well. Due to experimental difficulties, we were unable to measure the steady state emission spectra of the surfaces (*vide infra*). The absorption data for this molecule on the surface yield a linear absorbance increase for up to 9



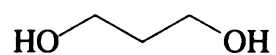
(a)



(b)



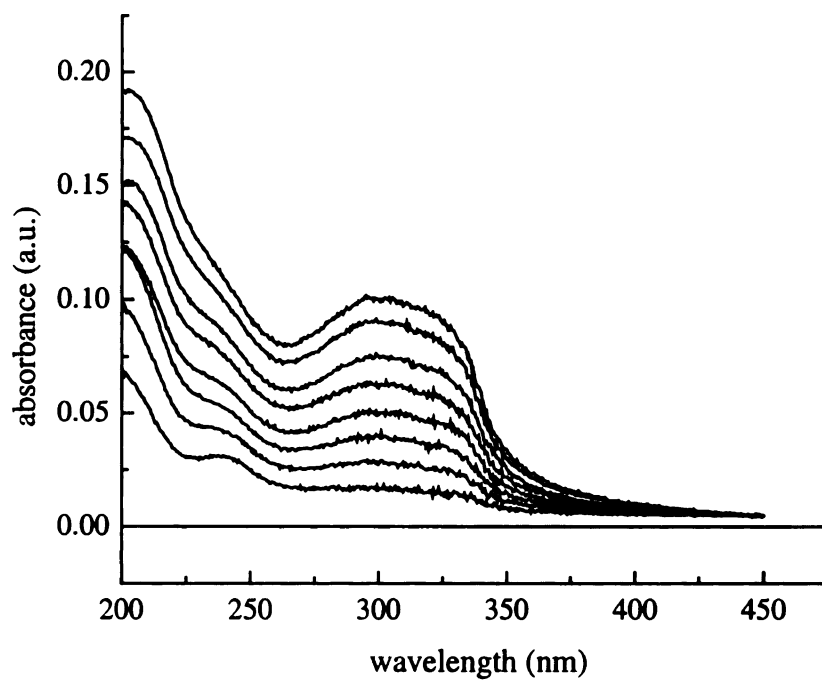
(c)



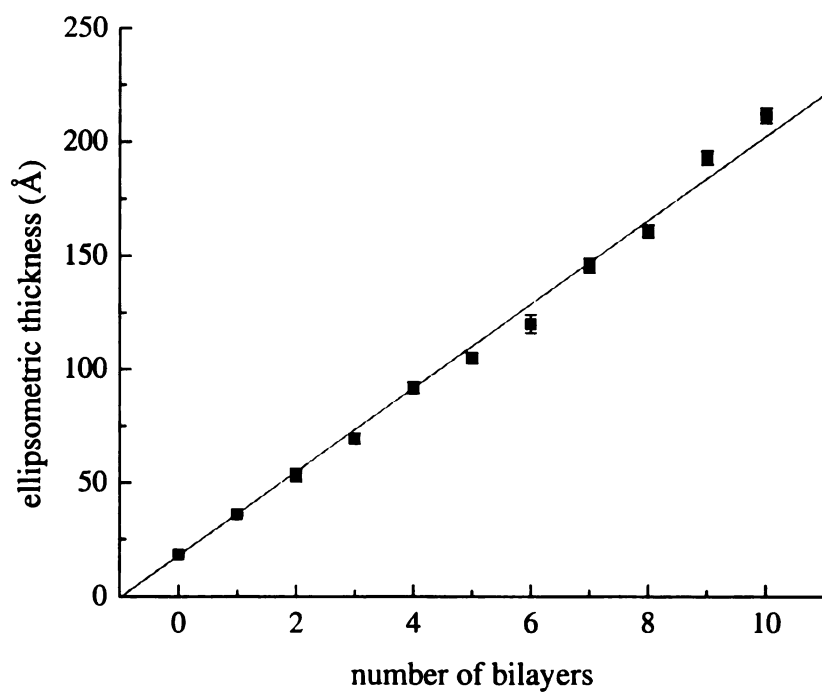
(d)

Figure 2.11 Structures of molecules used in covalent multilayers that incorporate amide and ester linkages: (a) MDA, (b) 2,7-diaminofluorene, (c) 4,4'-diaminoazobenzene and (d) 1,3-propanediol.

bilayers, demonstrating that equivalent amounts of material are being deposited during each reaction cycle. The ellipsometric data for this molecule also yield promising results. A linear increase in thickness was observed for up to 10 bilayers, demonstrating controlled growth. The absorbance and ellipsometric data are shown in Figure 2.12. The average bilayer thickness (from the slope of the line) was found to be $\sim 17 \text{ \AA}$, very close to the value of $\sim 18.3 \text{ \AA}$ which is predicted by HyperChem. The agreement between the theoretical and actual thicknesses is very good. One reason for this may be due to the rigidity of the molecule. 2,7-diaminofluorene consists of a five-membered ring sandwiched between two benzene rings; all three rings are fused to one another. Due to this rigidity, we would expect more ordered layers as compared to 1,3-propanediol, which had more flexibility within the bilayers. The FTIR data also support the growth of discrete, controlled bilayers. There are several peaks seen in the IR spectrum, all of which support the presence of amide bonds. A representative spectrum of these bilayers is shown in Figure 2.13. The largest peak is seen at $\sim 1723 \text{ cm}^{-1}$, and corresponds to the carbonyl carbon of an aromatic amide. Another large peak occurs in the spectrum at $\sim 1673 \text{ cm}^{-1}$. Both of these peaks increase linearly with an increasing number of bilayers. We are unsure of the nature of the peak at $\sim 1673 \text{ cm}^{-1}$. It may be indicative of the formation of another type of amide such as a disubstituted amide, but the mechanism by which this would occur is unknown. A peak in this region is present when forming both ester and amide bonds, so it may be the result of the formation of amides from initially unreacted primer amines, which would explain its presence in all of the spectra. Another large peak occurs at $\sim 1536 \text{ cm}^{-1}$ and can be attributed to the C-N-H stretch-bend mode, also referred to as the amide II stretch. The last large peak occurs at $\sim 1426 \text{ cm}^{-1}$



(a)



(b)

Figure 2.12 Absorbance (a) and ellipsometric thickness (b) data for bilayers formed by the reaction of 2,7-diaminofluorene with adipoyl chloride, which are linked by an amide bond. Note that growth of up to 9 bilayers is shown.

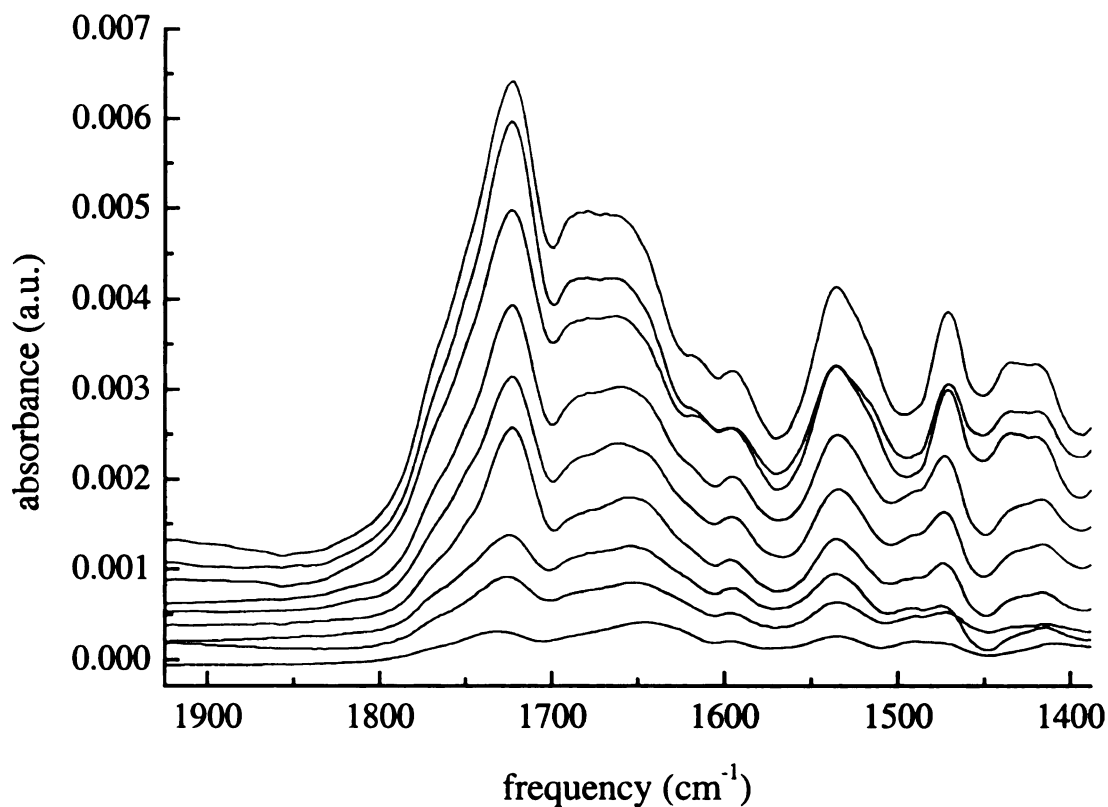


Figure 2.13 Brewster angle FTIR spectra of bilayers formed by the reaction of 2,7-diaminofluorene and adipoyl chloride. Note the peaks at 1723 cm⁻¹, 1536 cm⁻¹ and 1426 cm⁻¹, which are indicative of the formation of amide bonds. As expected, the absorbance increases with the number of bilayers, up to 9 bilayers, as shown. The spectra are offset for clarity.

and we assign this peak to C-N stretching. A large peak in the 3300 cm^{-1} range (not shown) is due to the N-H stretching mode.

The next molecule that we studied was 4,4'-diaminoazobenzene, which we were also considering for the energy transfer studies. We are grateful to Dr. Punit Kohli for synthesizing this molecule. The purity of the molecule was checked using TLC in three different solvents—ethanol, acetone and ethyl acetate, all of which yielded a single spot. The solution phase spectra seemed to be a good complement to the 2,7-diaminofluorene, but this was not the case once the molecule was adsorbed on the surface. In solution, the absorbance maximum is seen at $\sim 400\text{ nm}$, with an emission band at $\sim 450\text{ nm}$. On the surface the maximum absorbance shifts to $\sim 250\text{ nm}$, and a small peak is seen at $\sim 380\text{ nm}$. Once these molecules are covalently bound to the surface, their electronic structure and hence their absorbance spectra change. We expect emission to occur from the S_1 state, which corresponds to the peak at $\sim 380\text{ nm}$, and therefore emission should occur at a wavelength similar to the solution phase.

The same techniques used to characterize 2,7-diaminofluorene were used in characterizing 4,4'-diaminoazobenzene. The absorbance increases linearly with the number of bilayers deposited, indicating that controlled growth is occurring within these assemblies. Up to six bilayers were grown and characterized using UV-visible spectrometry. The ellipsometric data show a linear slope from a plot of thickness vs. the number of bilayers. Ellipsometric data were obtained for up to six bilayers, yielding an average bilayer thickness of $\sim 13\text{ \AA}$ (Figure 2.14). This experimental thickness is much lower compared to the predicted HyperChem value of $\sim 21\text{ \AA}$. The contrast between the theoretical and actual bilayer thicknesses could possibly be due to the reasons cited

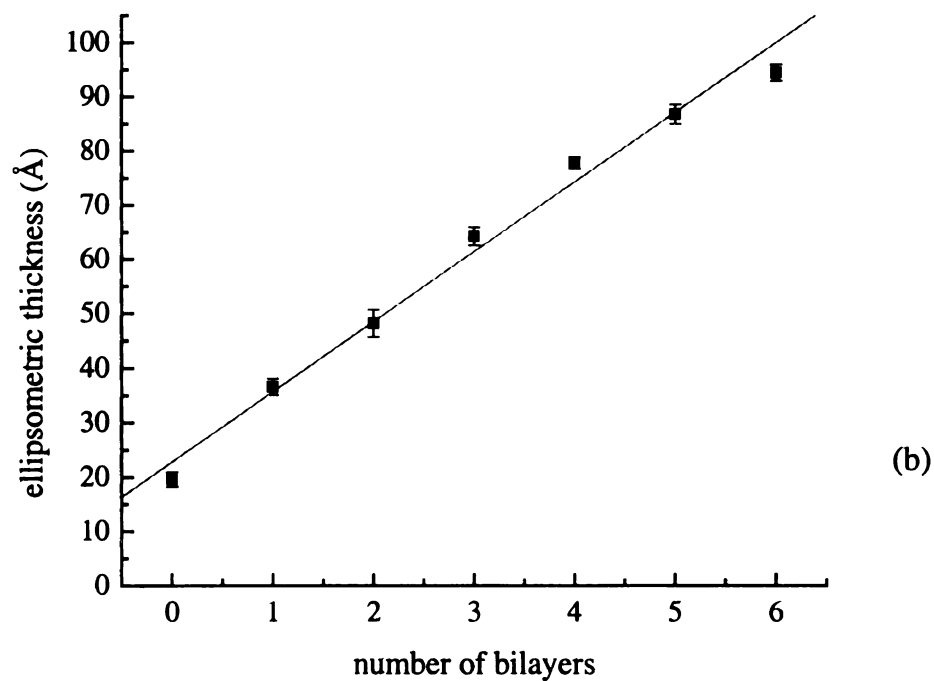
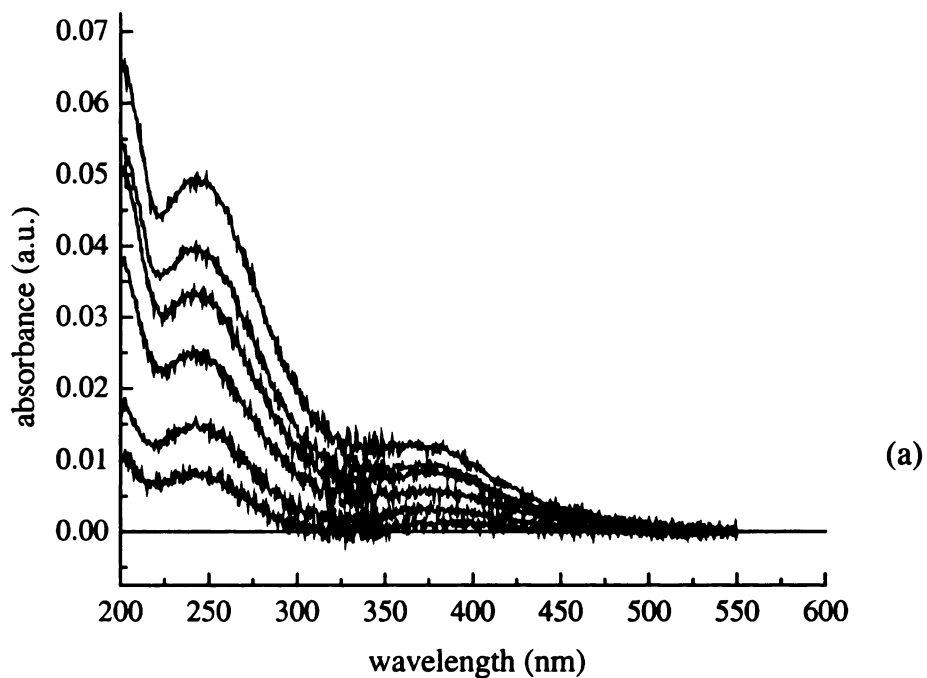


Figure 2.14 Absorbance (a) and ellipsometric thickness (b) data for bilayers formed by the reaction of 4,4'-diaminoazobenzene with adipoyl chloride. Note the linear increases in both sets of data. In the ellipsometric data, the average of six measurements is shown, and the error bars are the standard deviations.

earlier; a partially covered surface and/or a tilt angle of the molecules on the surface. One other possibility pertains to the flexibility of the azo bond within the molecule. The molecule has the ability to twist or rotate about this bond, which could lead to changes in thickness. Although the molecule should be “locked up” in the multilayer, there is still a small possibility that it could move within a layer; rotational dynamics studies on this chromophore in the future could help answer this question more definitively. Although this is a lower thickness than expected, the bilayer thicknesses are reproducible between samples. We also performed FTIR studies on these bilayers and discovered similar results to the 2,7-diaminofluorene bilayers. The expected carbonyl peaks are seen, indicating the presence of amides, and linear increases in absorbance were seen as well. At this point we moved on to the characterization of the third and final chromophore for these studies.

The last chromophore that we characterized was MDA. The absorbance spectrum of MDA in solution yields an absorbance maximum at ~240 nm, and a small peak at ~290 nm. On the surface, as with the other candidates, the absorbance peaks shifted. The peak at 290 nm was no longer present, except as a very small shoulder, and the primary peaks were located at ~245 nm and ~230 nm. The solution phase emission maximum was at ~350 nm. Due to the changes in the absorbance spectrum of MDA on the surface, we can expect a shift in its emission spectrum as well. Absorption studies on the surface showed that very reproducible bilayers were being deposited on the surface. Unlike the other chromophores, we were unable to perform ellipsometric thickness studies on this molecule, due to the unavailability of the priming solution, which occurred late in this work. The absorbance data demonstrate that linear growth is occurring within the assembly (Figure 2.15), and therefore the lack of ellipsometric data should not be an

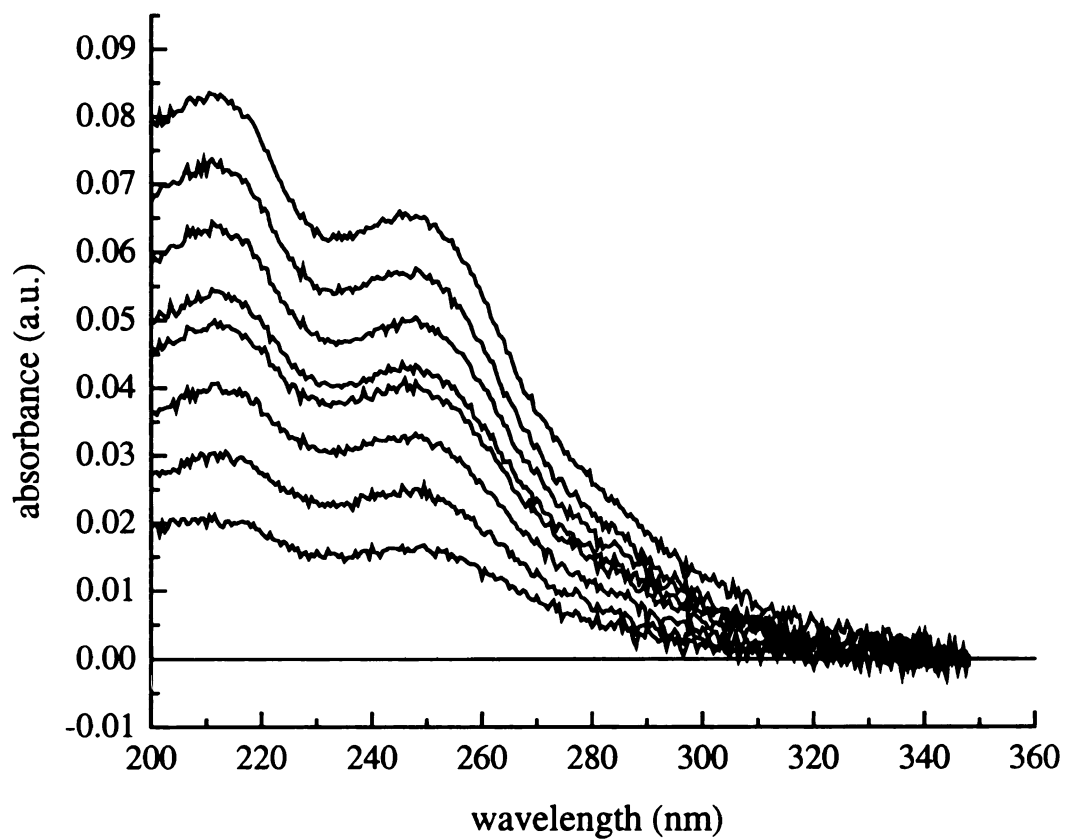


Figure 2.15 Absorbance data for bilayers formed by the reaction of MDA with adipoyl chloride, forming an amide linkage. Note that the absorbance increases linearly with the number of bilayers deposited.

issue. It is ideal to have both ellipsometric and UV-visible absorption data together to support the growth of multilayers, but the absorbance data are sufficient evidence for the controlled growth of this assembly.

2.4 Conclusions

One of the most stable multilayer assemblies to date are metal phosphonate assemblies, particularly those incorporating zirconium phosphonates. In an effort to explore different types of linking chemistry, multilayers were constructed by coordinating EDTA with Zr^{4+} , in a method similar to ZP chemistry. Although linear growth was seen for up to four layers, the exact mechanism of layer formation was not well understood. Based on the α plot of EDTA and comparison with our experimental conditions, we believe that there are complicating issues within these multilayers. The EDTA may have been adapting a different configuration than we had thought, but due to the complex nature of what we saw, we moved on to different types of linking chemistry that yielded more promising and understandable results.

The next type of multilayer scheme involved covalent linking strategies. In this case, two types of covalent linkages were used, urea/urethanes, and amide/esters. Using both schemes, reproducible and linear growth between samples was seen. Although we attempted to incorporate laser dyes into the urea assemblies, due to difficulties with the reaction mechanism this goal was not accomplished. The amide/ester linking chemistry proved to be more facile, and therefore a larger number of layers could be built in less time. Because of this, the amide/ester chemistry became the focus of our work. The incorporation of three different chromophores, 2,7-diaminofluorene, 4,4'-diaminoazobenzene and MDA into these assemblies yielded very promising results. UV-

visible spectrometry and ellipsometry prove that layer growth is controlled, and that equal amounts of material are being deposited during each deposition cycle. Linear increases in both absorbance and thickness, with an increasing number of layers, are evidence of this fact. FTIR also demonstrates the formation of amide bonds, as shown by the carbonyl stretches associated with amides. Linear increases in IR absorbances also indicate controlled growth. The synthesis of the multilayer assemblies incorporating the desired chromophores has been optimized, and evidence of discrete, controlled growth has been shown. In the next Chapter, the time-resolved and steady state optical properties of the three chromophores both in solution and on the surface will be studied.

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Chapter 3

Spectroscopic Studies of Covalent Multilayer Assemblies

3.1 Introduction

In the previous Chapter, the synthesis and characterization of several different types of multilayer structures was discussed. Characterization methods such as ellipsometry, UV-visible spectrometry, XPS and FTIR spectroscopy were used to better understand the synthesized layered assemblies. From these techniques, valuable information such as ellipsometric thickness and types of bond formation was recovered. The above techniques, while useful, are lacking in their ability to provide insight into the local environment that individual molecules in a monolayer sense. These techniques can reveal information about order within the layers, but they cannot tell us about aggregates on the surface or about the efficiencies of the various relaxation processes that occur when the molecules are excited. Currently, optical methods such as surface second harmonic generation (SSHG)¹⁻³ and fluorescence lifetime^{4,5} measurements are being used to probe the defect density and molecular environments within multilayer systems.

By monitoring fluorescence lifetimes, intermolecular energy transfer can be studied. Energy transfer measurements have been especially useful in characterizing proteins,⁶ aggregates of dye molecules,⁷⁻⁹ polyelectrolyte films,^{10,11} and Langmuir-Blodgett films,¹²⁻¹⁴ and the theory may be applied to other systems. The experiment is initiated when a donor molecule D is excited to its first excited singlet state, either directly or indirectly. If an acceptor molecule A is in the proximity of D*, then excitation transfer from the excited donor molecule to the ground state acceptor molecule will proceed. The efficiency of this process is determined by the distance and relative

orientations of D^* and A, as well as the spectroscopic properties of the molecules, as defined by the Förster critical radius, R_0 .¹⁵ Fluorescence lifetime measurements are very sensitive to the local environments of the molecules, whether in solution or in a monolayer. This technique was used in this work in conjunction with the aforementioned methods to better understand the way that molecules behave in a multilayer structure. In addition, the possibility of energy transfer occurring between different donor-acceptor pairs was also studied.

In this Chapter, the steady state and time-resolved spectroscopic behavior of three chromophores, 2,7-diaminofluorene, 3,3'-methylenedianiline (MDA), and 4,4'-diaminoazobenzene will be explored. These three chromophores were chosen because of their useful optical properties both in solution and within a monolayer. We are interested in studying the population dynamics of these molecules within multilayer assemblies in order to determine if energy transfer can proceed efficiently between a chosen donor and acceptor pair. To study these assemblies in the most effective manner, two different donor-acceptor pairs were chosen; the first pair consisted of 2,7-diaminofluorene and 4,4'-diaminoazobenzene, and the second included MDA and 4,4'-diaminoazobenzene. In solution, both of these pairs appeared to be good matches for energy transfer studies. The results of these studies, and the theory of Förster energy transfer, the model for dipolar energy transfer, will also be discussed in this Chapter. We find that interlayer energy transfer is inefficient in these assemblies, which could be due to spectral shifting of the molecules on the surface, making energy transfer less efficient, and/or aggregation of the chromophores, causing intralayer donor-donor transfer to dominate the observed response.

3.2 Experimental

Acid Chloride Multilayer Synthesis. The synthesis of covalently bound multilayer assemblies was discussed in detail in Chapter 2 (Figure 2.3), and will be outlined briefly here. Silica substrates, cut from sheets (Heraeus Optics) were cleaned by immersion in piranha solution (3:1 $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$) for fifteen minutes, rinsed with distilled water and dried under a N_2 stream. Clean substrates were primed immediately for further reaction. To prime the surface, the substrate was placed in a ~1.0% v/v solution of 3-aminopropyldimethylethoxysilane (United Chemical Technologies) in reagent-grade toluene overnight at room temperature. The resulting primed substrate was removed, rinsed with toluene, ethanol and distilled water, then dried under a N_2 stream. The resulting amine-terminated surface was then ready for further reaction.

The amine-terminated surface was reacted in a solution of ~0.2 M adipoyl chloride (Aldrich) and excess N-methylmorpholine (Aldrich) in anhydrous acetonitrile at room temperature for 25 minutes, under Ar in a roundbottom flask, to form an amide linkage. After this reaction, the acid chloride-terminated substrate was rinsed with ethyl acetate and placed under Ar once again. To functionalize the surface with an optically active chromophore, a $\sim 10^{-3}$ M solution of the diamine functionalized chromophore in anhydrous acetonitrile was used for reaction, with an excess of pyridine added to neutralize any HCl that may be formed. This reaction proceeded for one hour at room temperature. Following the reaction, the substrate was rinsed with reagent grade acetonitrile, ethanol, distilled water and dried under a N_2 stream. Optically inactive spacer layers of 1,3-propanediol (Aldrich) were incorporated in the same manner as the chromophore; the only difference was in the solution concentration.

Steady-State Optical Spectroscopy. The absorption spectra of solutions and covalent multilayers were collected as detailed in Chapter 2. Surface absorption spectra were obtained on a quartz surface, and blank quartz was used as the reference. In order to collect the absorbance spectra, the surfaces were placed perpendicular to the incident beam, and the beam was allowed to pass through the substrate, and into the detector. Emission spectra of solutions were collected using a Jobin-Yvon Spex-3 fluorescence spectrophotometer. The slits were adjusted based on emission intensity, but a five nm bandpass usually provided sufficient signal for the experiments. The emission of the solutions was collected at 90° with respect to excitation beam.

Time Correlated Single Photon Counting Spectroscopy. A schematic diagram of the spectrometer used for the fluorescence lifetime studies of the three chromophores is shown in Figure 3.1. A mode-locked CW Nd:YAG laser (Quantronix 416) produces ~11 W average power at 1064 nm, with 100 ps pulses at 80 MHz. An angle-tuned type I KDP (potassium dihydrogen phosphate) crystal is used to frequency double the output to 532 nm. The 532 nm light excites a cavity-dumped, synchronously pumped dye laser (Coherent 702-2) which is dumped at a repetition rate of 4 MHz, producing ~5 ps pulses. The output from the dye laser is divided using a 90/10 beam splitter into two paths: 90% of the light is used to excite the sample, and the other 10% is used for the reference. The beam sent to the sample is frequency doubled (SHG) with a Type I LiIO₃ (lithium iodate) crystal. The fundamental is separated from the second harmonic using color filters, and the excitation polarization is controlled using a polarization rotator (CVI). Emission from the sample is collected at 90° with respect to the incident light, and the polarization of the emission was selected using a Glan-Taylor prism (solutions only). Monolayer

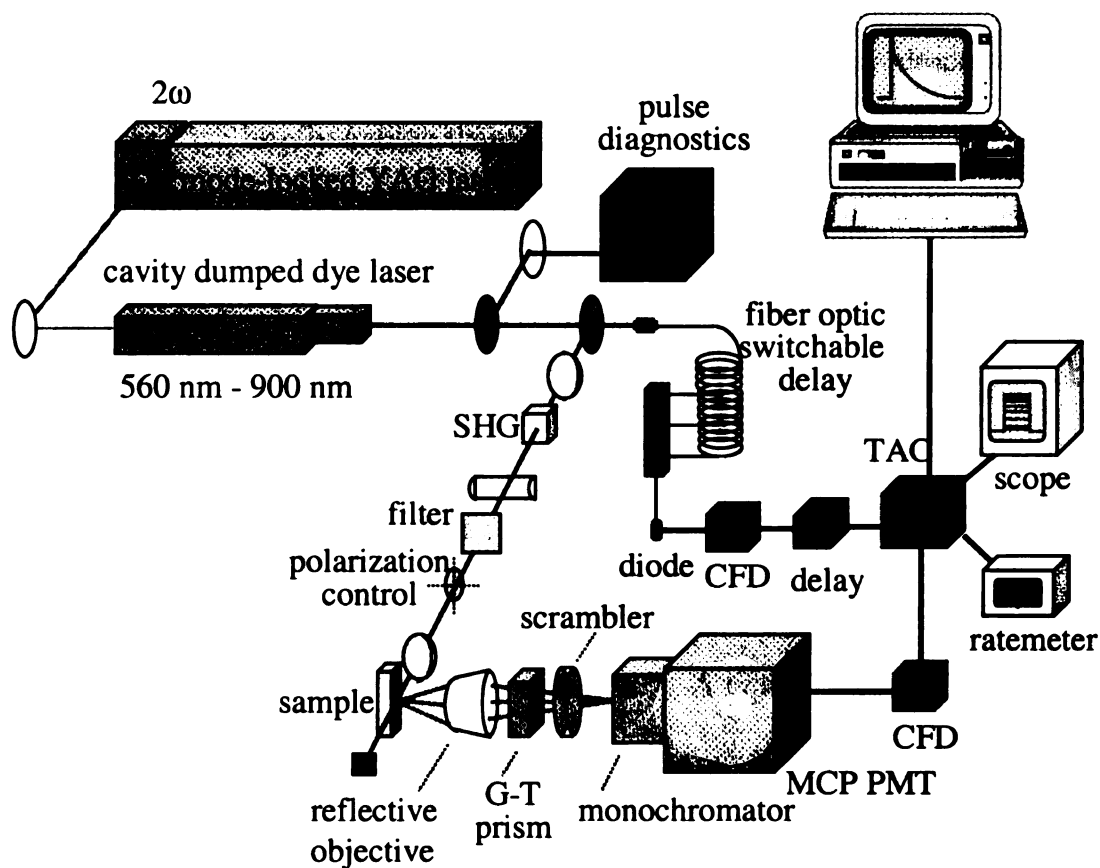


Figure 3.1 Time correlated single photon counting (TCSPC) spectrometer used in fluorescence lifetime experiments.

samples were held approximately horizontally, with 5° tilts away from the horizontal in two directions, toward the excitation beam and toward the detector. The polarization of the light is then scrambled, and collection wavelengths are selected using a subtractive double monochromator. The detection electronics have been described in detail elsewhere,¹⁶ and we briefly outline them here. The signal from the micro-channel plate PMT (MCP-PMT, Hamamatsu) is sent to a constant fraction discriminator (CFD, Tennelec TC454), where it is processed and sent to the time-to-amplitude converter (TAC, Tennelec TC864), operated in reverse mode. The TAC output counts are observed using an oscilloscope (Tektronix 2230) and are sent to a multichannel analyzer (MCA, Tennelec PCA-II) for collection. The reference consists of the remainder of the divided laser beam (10%), which is sent through a fiber optic delay line, where we control the time offset between signal and reference channels. A typical response function for the instrument was ~ 40 ps. Excitation was performed at 315 nm (doubled Kiton Red, Exciton) for both solution and surface measurements. The monochromator's slits were set at a 5 nm bandpass for solution measurements, and at 20 nm for monolayer samples. For all monolayer samples, emission was collected at 450 nm (*vide infra*), while solution emission was collected based on the maximum intensity from the emission curve.

Data Analysis. The lifetimes that we report here were fit to sums of exponentials or single exponentials using Microcal Origin v. 6.0 software. For solution phase lifetime measurements, the values reported are the averages of five measurements, with the uncertainty reported as 95% confidence intervals. For monolayer samples, the values are reported as the averages of between 15 and 40 measurements, and the uncertainty is

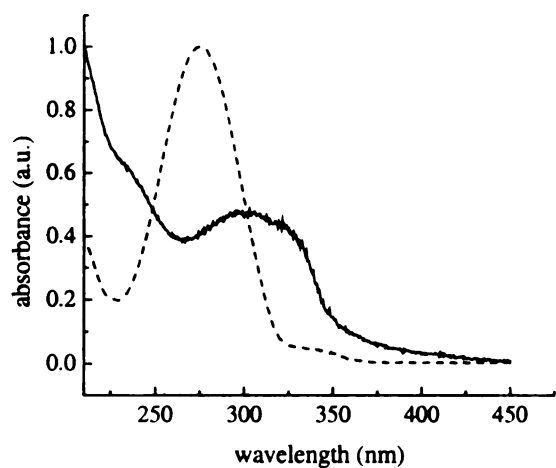
reported as the 95% confidence interval. The fits for all datasets were started at the point where the instrument response function was at 5% of its maximum value.

3.3 Results and Discussion

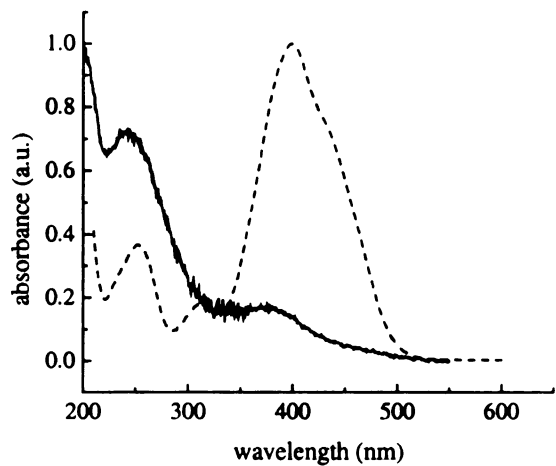
As discussed in Chapter 2, we discovered that the absorbance spectra of these chromophores changed significantly once bound to the surface. Figure 3.2 illustrates the change in absorbance of the solution phase of each chromophore compared with a five bilayer spectrum of the same molecule. This is an expected result, as the electronic configuration of the molecule should be altered once it is covalently bound to a surface and other molecules within a multilayer.

In these studies, we decided to use two different donor-acceptor pairs, the first consisting of 2,7-diaminofluorene (donor) and 4,4'-diaminoazobenzene (acceptor), and the second involving MDA as the donor, and the same acceptor molecule. In the initial studies, we began by measuring the solution phase lifetimes of the chromophores. We were able to measure the solution phase fluorescence lifetimes of two of the three chromophores, due to the excitation wavelength accessible with the dye laser. The wavelength of the incident beam was 315 nm, tunable from ~300-340 nm, and only 2,7-diaminofluorene and MDA absorbed significantly at these wavelengths. Since these were the two donor molecules that we were interested in using, it was most important to determine their lifetimes. In these interface studies, we were monitoring the lifetime of the donor, and its change in the presence of the acceptor. Knowledge of the acceptor's lifetime, while useful, was not central in these studies.

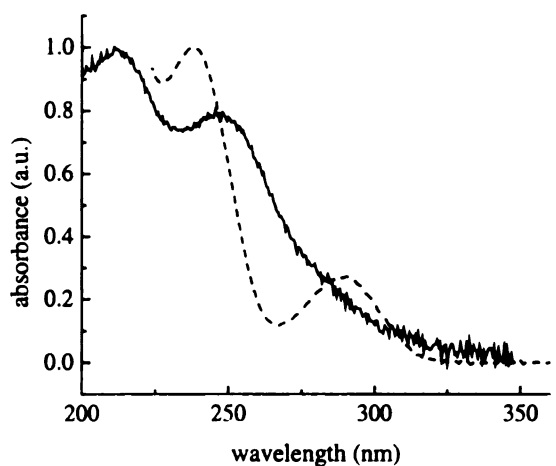
The steady state absorbance and emission spectra of the three chromophores in solution were presented in Figure 1.1. From these spectra, it is apparent that the



(a)



(b)



(c)

Figure 3.2 Wavelength shifts in the absorbance spectra of 10^{-5} M solutions (----) and 5 bilayer (—) samples of the three chromophores used in this work: (a) 2,7-diaminofluorene, (b) 4,4'-diaminoazobenzene, and (c) MDA.

absorbance spectrum of the acceptor overlaps the emission spectrum of the donor, which is essential for energy transfer to occur efficiently. If we assume though that the Stokes' shift for each of the chromophores on the surface is similar to that in solution, then the overlap between the donor and acceptor pairs may not be as great as in solution.

The ability to measure emission spectra from the quartz samples is an important piece of information for these studies. The emission spectrum may help to identify the presence of aggregates, and it is also revealing to measure the Stokes' shift of surface bound chromophores. Unfortunately, we were unable to measure emission spectra of the surface bound chromophores on quartz substrates. Every effort was made in an attempt to collect these emission spectra, but we were not successful. We believe that background fluorescence from the quartz slides was a problem, and that scattered excitation light was dominating the small signal from our monolayers. The quartz samples were measured at varying incidence angles to the excitation source, yet there was always a large background signal present. Up to eight bilayers of chromophore were built on quartz slides and measured, but the signal could not be extracted from the large background. To convince ourselves that this was not also an issue with the TCSPC system, we attempted to get emission from a blank quartz slide. We were able to collect only a very small signal from the blank quartz, and therefore this background signal was not an issue in the experiments utilizing the TCSPC spectrometer.

Although we were unable to obtain steady state emission spectra, by adjusting the monochromator of the TCSPC spectrometer, we were able to estimate the emission maxima for the two surface bound donor molecules. Both 2,7-diaminofluorene and MDA had emission maxima at ~450 nm on the surface. From the TCSPC spectrometer,

the data that we recover are not corrected for the sensitivity of the detector, nor are they corrected for any fluctuations in source intensity. Because of this, these maxima may not be exact, but these values should be very close to the actual ones. The large bandpass used in these experiments may also have an effect on locating the actual maxima. We were unable to elucidate information about the acceptor molecule, 4,4'-diaminoazobenzene, due to the excitation wavelength used. This is not a surprising result as we were unable to excite a 10^{-5} M solution at this wavelength, and therefore a much lower concentration of molecules would be less likely to become excited.

The solution phase lifetimes were collected using 10^{-5} M solutions made up in ethanol. The solutions were excited at 315 nm, and the emission from the samples was collected based upon the maxima from the emission spectrum. The monochromator bandpass was 5 nm. In dilute solutions, a single exponential decay is the expected result, and this was recovered for these solutions. Both chromophores exhibited a single exponential decay, with relatively long lifetimes. The lifetime of 2,7-diaminofluorene was measured as ~5.7 ns, and the lifetime for MDA was ~2.7 ns. It was very encouraging that such long solution phase lifetimes were recovered. An example of the instrument response function (~40 ps) and a representative plot of the solution phase fluorescence lifetime of MDA is shown in Figure 3.3.

The longer lifetimes should allow a greater amount of time for energy transfer to occur, on a timescale that we can easily monitor. The next step was to measure the lifetimes of the molecules individually on the surface. To do this, samples were made up which consisted of only one monolayer of the desired chromophore. It was important to note that the acceptor did not absorb at this wavelength. This is an important piece

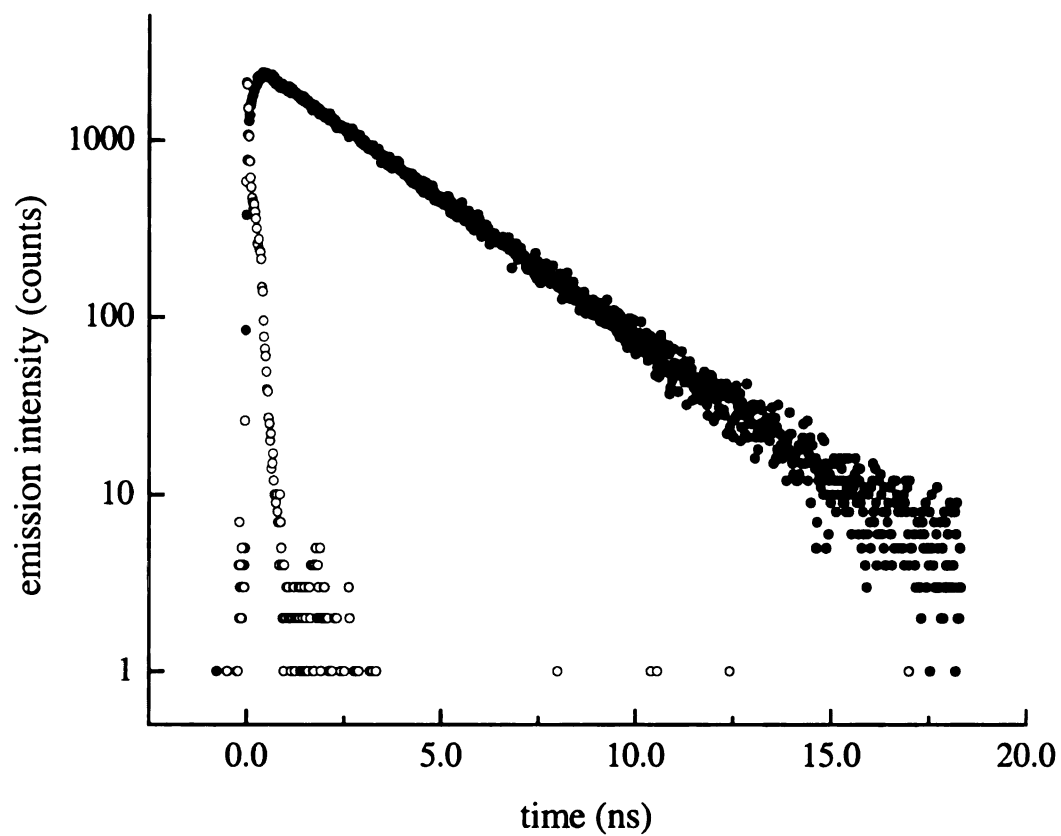


Figure 3.3 Representative instrument response function ($\circ$) and fluorescence lifetime of a 10^{-5} M solution of MDA in ethanol ($\bullet$). The data are plotted on a log scale for ease of presentation. Note that only a single exponential decay is seen.

of information because emission from this molecule could interfere with the collected emission from the donor molecule. We found that both 2,7-diaminofluorene and MDA exhibited double exponential decays on the surface. The fluorescence lifetimes of both of these molecules on the surface are shown in Figure 3.4. The recovery of a double exponential decay was not surprising, and the primary reason for this change is probably due to aggregation of the molecules on the surface (*vide infra*).

The lifetimes recovered from the monolayer samples contained both a short and a long lifetime component. The decay times recovered for both 2,7-diaminofluorene and MDA in homogeneous monolayers are shown in Table 3.1. To summarize, the short time component of the aminofluorene was measured as 336 ± 13 ps, with a long time component of 2189 ± 165 ps. The short time component of MDA was calculated as 434 ± 13 ps, while the long time component was calculated as 2648 ± 143 ps. Numerous measurements were made on these monolayer samples, and once we were confident about the lifetimes of the individual chromophores on the surface, we decided to determine what change, if any, would occur upon the incorporation of another optically active molecule into these assemblies. We believed that the incorporation of the acceptor

Table 3.1 Calculated fluorescence lifetimes for one monolayer of 2,7-diaminofluorene and one monolayer of MDA on quartz. The data were fit to the equation $y = y_0 + A_1e^{-t/\tau_1} + A_2e^{-t/\tau_2}$ using Microcal Origin 6.0 software. The uncertainties are the 95% confidence intervals for the measurements.

	τ_1 (ps)	A_1	τ_2 (ps)	A_2
diaminofluorene	336 ± 13	0.81 ± 0.06	2189 ± 165	0.19 ± 0.03
MDA	434 ± 15	0.76 ± 0.07	2648 ± 143	0.24 ± 0.03

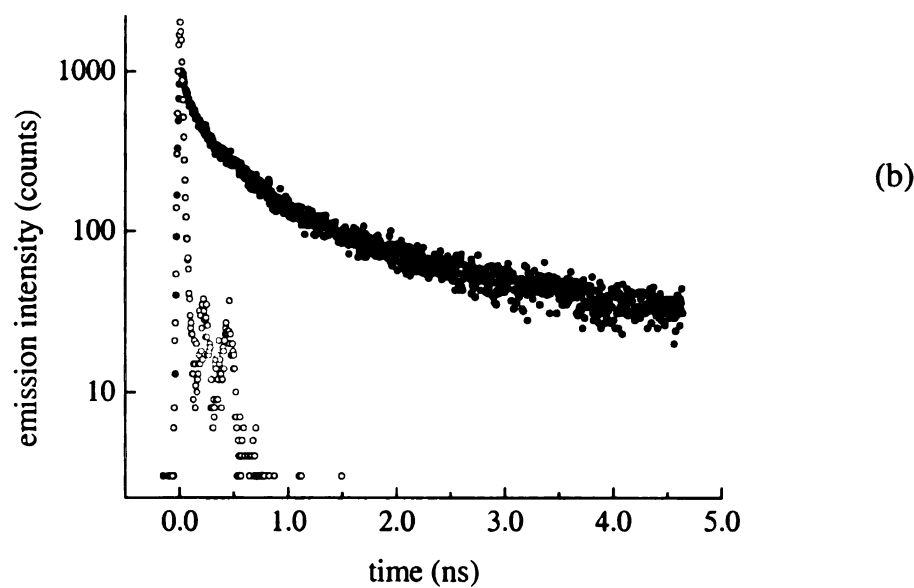
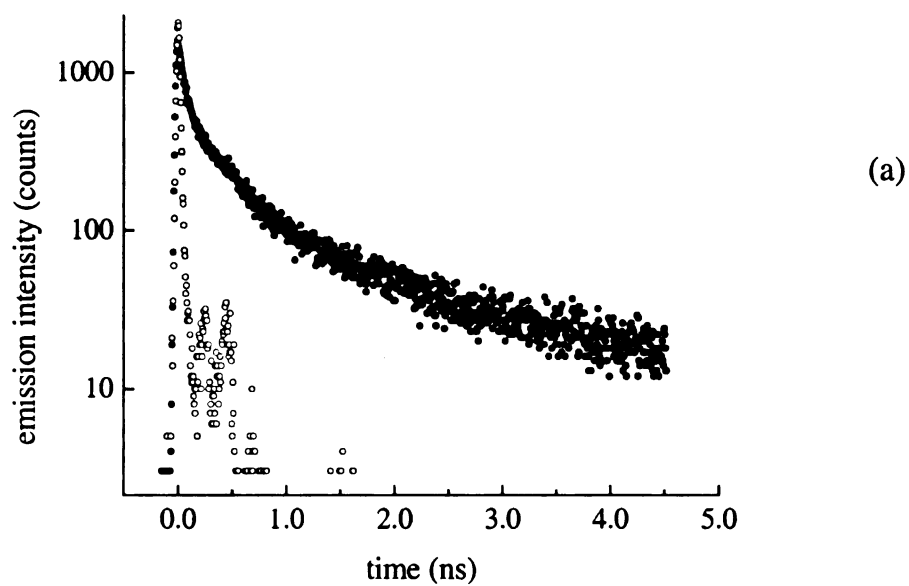


Figure 3.4 Representative instrument response functions ($\circ$) and fluorescence decays ($\bullet$) of (a) 2,7-diaminofluorene and (b) MDA on quartz surfaces. The data are plotted on a log plot for ease of presentation.

molecule, 4,4'-diaminoazobenzene, into these assemblies would produce a decrease in the lifetime of the donor molecule, due to facile interlayer energy transfer.

Before moving on to the results found in the heterogeneous multilayer studies, it is instructive to introduce the theory of Förster energy transfer because regardless of sample morphology, dipolar excitation transport will be operative in these systems and an understanding of the essential physics is important. Excitation transfer in the context of the Förster model is a phenomenon that does not explicitly involve emission and reabsorption of a photon. This process can occur whenever the emission spectrum of a donor molecule overlaps the absorption spectrum of an acceptor molecule. It should be noted that the acceptor does not need to be fluorescent for this transfer to occur, because the donor lifetime is monitored, not the acceptor's. The donor and acceptor transfer excitation by means of a resonance between their oscillating transition dipole moments, the intensity of which depends on the distance separating them and their relative orientations in space. The rate constant for Förster energy transfer is defined as:¹⁷

$$k_{DA} = \frac{3\kappa^2 R_0^6}{2\tau_D R^6} \quad (3.1)$$

In Equation 3.1, τ_D is the decay time constant of the donor in absence of the acceptor; R_0 represents the Förster critical radius and R is the distance between the donor and acceptor; κ^2 , the geometric factor, will be explained in more detail later in the discussion.

The critical radius, R_0 , is defined as the distance when 50% of the relaxation processes in the molecule will occur by energy transfer, and the other 50% will occur by other radiative or non-radiative means.⁶ To simplify this, we will assume that all processes which occur when $R > R_0$ are inefficient, and when $R < R_0$, we will assume that the process is efficient. As expected, when R becomes much greater than R_0 , the transfer

efficiency between the donor and acceptor decreases, and the number of molecules that relax by energy transfer lessens. The transfer efficiency can be equated by the following:⁶

$$E = \frac{R_0^6}{R_0^6 + R^6} \quad (3.2)$$

As shown in Equations 3.1 and 3.2, both the transfer efficiency and the rate of transfer have a R^{-6} dependence. This dependence stems from the dipole-dipole interaction energy which scales as R^{-3} , and therefore the probability of the donor and acceptor interacting is R^{-6} , yielding this distance dependence for dipolar energy transfer.

The term R_0 is unique for each donor-acceptor pair, and must therefore be determined for each individual case. The critical radius for a given donor-acceptor system can be calculated using the following equation:⁶

$$R_0^6 = \frac{9000 \ln(10) \kappa^2 \phi_D}{128 \pi^5 N n^4} \int_0^\infty F_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda \quad (3.3)$$

In Equation 3.3 several terms must be defined. The first is ϕ_D , the quantum yield of the donor in absence of the acceptor; N , Avogadro's number; n , the refractive index of the medium; F_D , the normalized fluorescence intensity of the donor in the wavelength region of interest; ϵ_A , the extinction coefficient of the acceptor at the wavelength of interest, and the geometric factor κ^2 , which describes the relative orientation in space of the transition dipole moments of the donor and acceptor. For solution phase studies, the value of κ^2 is typically assumed to be 2/3, which is appropriate for molecules that randomize rapidly by rotational diffusion compared to the timescale of energy transfer. The value of κ^2 is calculated using the following equation:⁶

$$\kappa^2 = (\sin \theta_D \sin \theta_A \cos \phi - 2 \cos \theta_D \cos \theta_A) \quad (3.4)$$

In Equation 3.4, θ_D and θ_A represent the angles between the transition dipole moments of the donor and acceptor with the vector joining them. The angle ϕ represents the angle between the donor and acceptor transition moments along the axis of the connecting vector. A schematic diagram illustrating these vector quantities is shown in Figure 3.5. Equation 3.3 contains an overlap integral, which describes the degree of spectral overlap between the donor emission spectrum and the acceptor absorption spectrum. This equation allows the Förster radius to be calculated from the spectral properties of the donor, acceptor and donor quantum yield.

There are several factors that have an effect on the critical radius R_0 and the rate of energy transfer. The two largest are the fluorescence quantum yield of the donor and the degree of spectral overlap between the two molecules. The quantum yield does have a large effect on the rate of energy transfer, which seems counterintuitive, due to the nature of the process. It was stated previously that Förster energy transfer is a non-radiative process, which does not involve the emission and reabsorption of a photon. The greater the fluorescence quantum yield of a molecule, the larger the number of molecules that will relax radiatively, and not by other processes. When energy transfer occurs, the energy is transferred from a state that would otherwise decay radiatively. The more excited molecules, the greater the probability that dipolar energy transfer will occur. If the quantum yield is lower, then there are fewer molecules that will remain in the state that is resonant with the acceptor, lowering the probability of dipolar excitation transfer.

The spectral overlap also plays a role in the determination of R_0 . In order for energy transfer to occur, there must be coupling between the donor and acceptor, which requires a resonance at a common energy for the two species. The spectral overlap is a

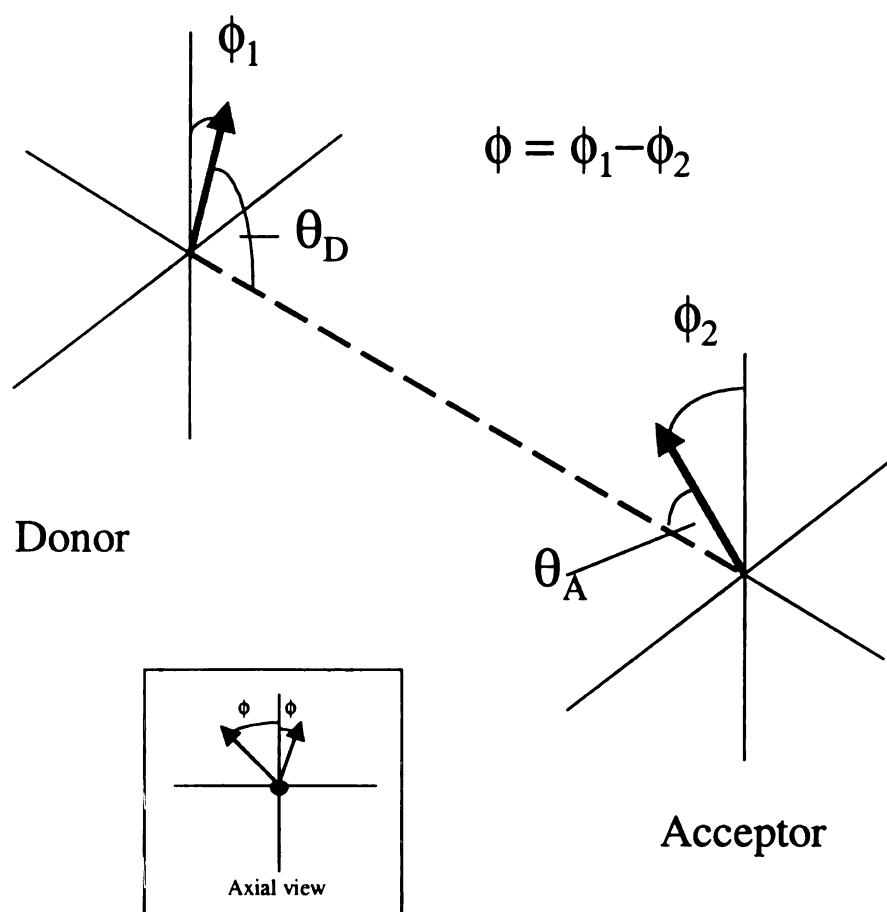


Figure 3.5 Vectors representing the different angles used to calculate κ^2 , the geometric factor in Förster energy transfer. The inset depicts the axial view of the vector joining the dipole moments of the donor and acceptor molecules.

measure of this resonance condition. Although there is no direct exchange of photons between the donor and the acceptor, their spectral characteristics are nonetheless reflective of this resonance condition.

The functionality of our decays is not what is expected from a simple Förster treatment. This form of the data is reflective of the morphology of the interface and we discuss this issue below. It is pedagogically useful to examine results found previously in our group from probing energy transfer in zirconium phosphonate (ZP) multilayer assemblies. The results obtained from those studies are also pertinent to our results in covalent assemblies, and conclusions about the lack of energy transfer may also be inferred from the previous work.

Horne and Blanchard studied both intralayer and interlayer energy transfer in ZP multilayer systems. In their work, they reported double exponential decays for their chromophores, although in solution the same chromophores yielded single exponential decays. It is well known that molecules aggregate into island-like formations once they are adsorbed on the surface, and the double exponential decay was attributed to monomers in different environments (*vide infra*). Horne and Blanchard did not observe interlayer energy transfer in systems where the multilayer structure should be conducive to it. They performed a series of experiments incorporating both spectroscopic and AFM data, which concluded that the chromophores were aggregated into islands ~50-100 Å in diameter, with nearest neighbor spacing varying between 40-100 Å.¹⁸ The apparent absence of intralayer energy transfer between the donor and acceptor molecules was reflective of the violation of a central assumption of the Förster model; the homogeneity of the monolayers and that the chromophores behave as individual entities. From these

studies, Horne and Blanchard concluded that the double exponential decay functionality of the donor emission was due to the contributions of monomers in two different environments. The first type of environment was a monomer in close proximity to an aggregate island, perhaps even within an island, but somehow isolated so that it is not participating in the aggregate structure. The second case is when the monomer is not in contact with the aggregate, and is residing at some point away from the island structure. An exciton hopping model was used to calculate the size and shape of the aggregate species.¹⁸

We believe, from the presence of a double exponential decay in our data, that aggregation occurs on the surface. In an effort to test this theory, we have used an exciton hopping model similar to the one proposed by Horne *et al.*¹⁸ In this model, depicted in Figure 3.6, an aggregated island of chromophores, A, is excited by a pulse of light. The excitation can decay radiatively, which is not a likely event, due to the dark state of the aggregate¹⁹, or it can “hop” about the aggregate island until it reaches a radiative monomer to which it can transfer its energy. The radiative monomer can be either present as a defect within or on the perimeter of the aggregate (M_1), or may be present outside of the aggregate (M_2). A series of coupled differential equations that describe the temporal evolution of monomer and aggregate populations are shown as Equations 3.5-3.9.

$$\frac{d[A^*]}{dt} = -k_{xt}[A^*]([M_1] + [M_2]) - k_{nr}[A^*] \quad (3.5)$$

$$\frac{d[M_1^*]}{dt} = -k_{M1}[M_1^*] + k_{xt}[A^*][M_1] \quad (3.6)$$

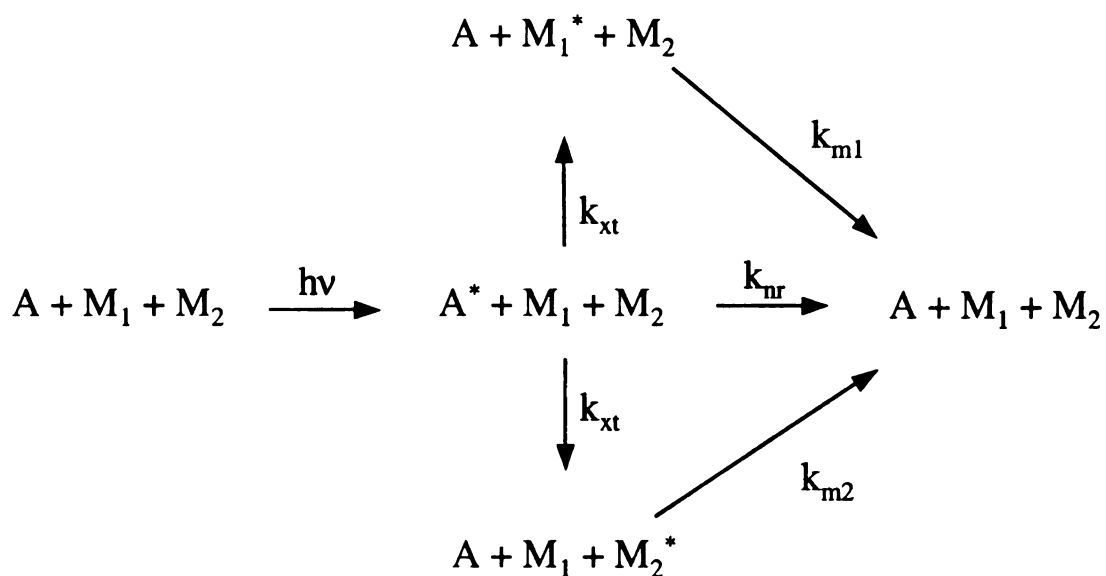


Figure 3.6 Scheme depicting the kinetic model used for population decay dynamics in the covalent monolayers used in these studies. In this scheme, A represents an aggregate species, and M_1 and M_2 represent monomers in different environments.

$$\frac{d[M_2^*]}{dt} = -k_{M_2}[M_2^*] + k_{xt}[A^*][M_2] \quad (3.7)$$

$$\frac{d[M_1]}{dt} = k_{M_1}[M_1^*] - k_{xt}[A^*][M_1] \quad (3.8)$$

$$\frac{d[M_2]}{dt} = k_{M_2}[M_2^*] - k_{xt}[A^*][M_2] \quad (3.9)$$

These equations can be solved numerically to yield the time course of the populations of M_1 and M_2 , as done by Horne *et al.* Two boundary conditions must be noted for these calculations. The first is that the concentration of A_0^* equals unity. The second condition is that at infinite times, $M_1 + M_2$ equals unity. The first quantity of interest in these measurements is k_{xt} , which is the transfer rate of excitation from an excited aggregate to a radiative monomer. Experimentally, this is a difficult quantity to measure because it is seen as a build-up in the single photon counting signal after time zero. Although our instrument response function is short (~ 40 ps), we are unable to resolve this build-up in the experimental data. Attempts to deconvolute the experimental data from the instrument response function were unsuccessful. Horne *et al.* were able to deconvolute the data, but the time constant was too short to be resolved clearly, and an upper bound value of 10 ps for the excitation migration time was reported. Based on this value, we estimate that our value of k_{xt}^{-1} must be less than 10 ps. Physically these small transfer times indicate the presence of small islands. We would expect a slow build-up in signal with the presence of large islands, which would allow the excitation to “hop” around the island for a longer period of time before transferring its energy to a radiative monomer, at which point emission would be seen. Although we were unable to perform the simulations, due to the fact that we could not resolve a build-up, we can place an estimate on the size of the aggregate islands. Assuming $k_{xt} = 10^{13} \text{ s}^{-1}$, consistent with excitation

hopping in LB films of stilbazolium dyes¹⁹, and a conservative estimate of $\phi_n = 0.10$ for aggregated MDA, with $\tau_n = 2700$ ps for MDA in solution, we estimate the nonradiative rate constant, $k_{nr} = 3.3 \times 10^9 \text{ s}^{-1}$ for the MDA aggregates. Although we did not perform the simulations ourselves, we can use the results found by Horne *et al.* and relate them to our measurements. This is relevant because we are using the same types of surfaces and analogous priming chemistry, so we expect similar environments on the surface.

In order to determine approximate island sizes, the time constant per excitation event, or hop is assumed to be 0.1 ps, so in 10 ps, which was the upper bound used by Horne *et al.*, an average of 100 hops can occur. Song *et al.* have published the results of a random walk simulation used to model the motion of an exciton within an H-aggregate.¹⁹ Using their results, the mean distance an exciton can travel in 100 hops is $\sim 40 \text{ \AA}$. Other simulations and estimates of ZP lattice sizes predict that the aggregate size is on the order of $50 \times 50 \text{ \AA}$. We estimate from these calculations that our aggregate islands have areas that are smaller, based on the faster value of k_{xt} .

The first step in the heterogeneous multilayer studies was preparing layers that consisted of donor and acceptor, separated only by the adipoyl chloride layer. The first donor-acceptor pair that we studied was 2,7-diaminofluorene and 4,4'-diaminoazobenzene. The fluorescence lifetimes recovered from this experiment demonstrated that there was not significant excitation transfer occurring between these two molecules. As discussed in Chapter 2, the overlap in the solution phase spectra of these two molecules seemed quite favorable, but due to the spectral shifting associated with covalently bonding the molecules to an interface, the efficiency of energy transfer was substantially reduced. The lifetimes recovered for samples containing both donor

and acceptor adsorbed on the surface suggest that the spectral overlap is no longer favorable for energy transfer. The recovered times were the same, to within experimental error, as those measured for a monolayer containing only donor. The results of these lifetime studies are summarized in Table 3.2. From these data we conclude that energy transfer between the two molecules is not efficient.

Table 3.2 Measured fluorescence lifetimes of 2,7-diaminofluorene in a monolayer, and capped with an additional monolayer of 4,4'-diaminoazobenzene. The uncertainties are the 95% confidence intervals of the acquired data. Note that within the experimental uncertainty, the values recovered are identical.

	τ_1 (ps)	A_1	τ_2 (ps)	A_2
aminofluorene (D)	336 ± 13	0.81 ± 0.06	2189 ± 165	0.19 ± 0.03
D + A	350 ± 10	0.80 ± 0.11	2154 ± 200	0.20 ± 0.02

At this point, we turned to the third chromophore that we had been studying, MDA. In these studies, we were interested in using MDA as the donor, and 4,4'-diaminoazobenzene as the acceptor molecule. The first set of lifetimes that we collected involved only the donor and acceptor, which were separated by a C₆ diamide (adipoyl chloride) layer. We recovered lifetimes that were shorter than a monolayer of MDA alone, a result that could indicate excitation transfer. Further studies demonstrate that excitation transport does not account for these data. As discussed earlier in this Chapter, the transfer of energy has an R⁻⁶ dependence. In an attempt to determine exactly what was occurring within these layers, we incorporated optically inactive spacer layers between the donor and acceptor layers. If energy transfer was proceeding according to the Förster model, then the lifetime of the donor molecule MDA should increase with

increasing donor-acceptor separation. Figure 3.7 illustrates the chemical functionalities that were present in each of the experiments incorporating the MDA and the azobenzene in multilayer structures.

Table 3.3 Lifetime measurements of a monolayer of MDA (donor, D); multilayers of MDA (donor) and 4,4'-diaminoazobenzene (acceptor, A) with no spacer layer; and one or two spacer layers incorporated between them. The uncertainties are the 95% confidence interval of the measurements. The spacer molecule used in these studies was 1,3-propanediol.

	τ_1 (ps)	A_1	τ_2 (ps)	A_2
MDA (D)	434 ± 15	0.76 ± 0.07	2648 ± 143	0.24 ± 0.03
D + A	369 ± 9	0.79 ± 0.14	2415 ± 152	0.21 ± 0.04
1 spacer	371 ± 16	0.82 ± 0.08	2332 ± 138	0.18 ± 0.03
2 spacers	372 ± 18	0.85 ± 0.51	2285 ± 216	0.15 ± 0.06

The results of the lifetime measurements of the donor-acceptor layers with zero, one and two spacer layers are shown in Table 3.3. These studies demonstrate that energy transfer is not the main reason for the decrease in the lifetime of the donor molecule upon incorporation of an acceptor layer. The incorporation of optically inactive spacer layers into these multilayer assemblies did not have an effect on the lifetime of the MDA. This finding led us to believe that there were other phenomena occurring in the layers that required further exploration.

Although there were no significant changes in the absorbance spectra with respect to the solution spectra, which would indicate aggregate formation, the donor fluorescence lifetime senses changes in the local environment within the layers. To test if the structure-dependent variation in donor lifetime is due simply to changes in local

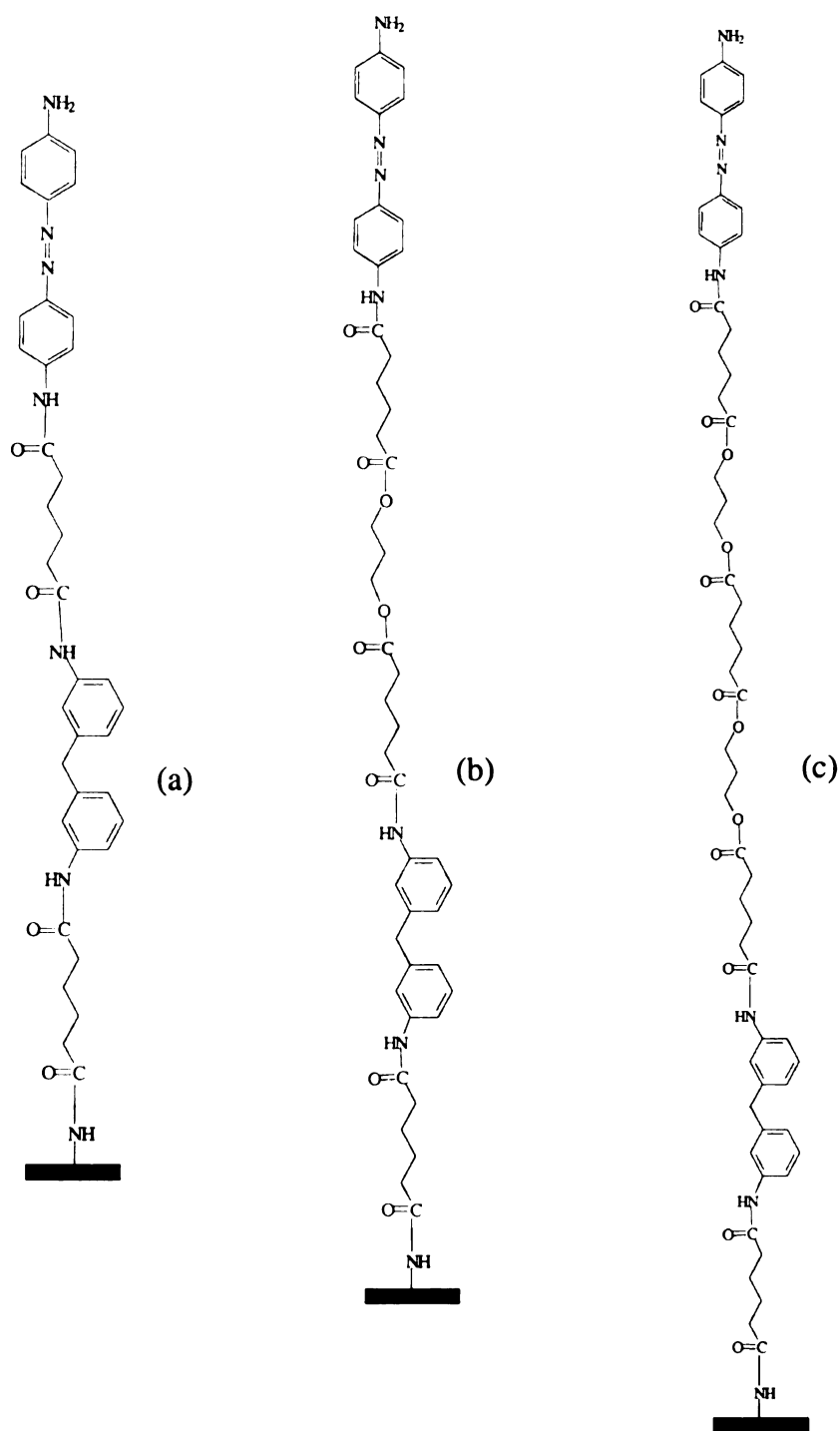


Figure 3.7 Different multilayer structures constructed for the energy transfer studies: (a) MDA + azobenzene, no spacer; (b) 1 spacer, (c) 2 spacers. Note that the spacer layer used in these studies was 1,3-propanediol.

dielectric response with the addition of an overlayer, we built a multilayer that consisted of an MDA (donor) layer, then a hydrolyzed adipoyl chloride layer, but without the azobenzene acceptor layer. We recovered a short lifetime component for the MDA of 442 ± 22 ps, and a longer time component of 3047 ± 226 ps. The short lifetime is the same within the uncertainty as the uncapped MDA monolayer (434 ± 15 ps). The longer time components are similar (but not equal) for the two samples (MDA alone = 2648 ± 143 ps).

The addition of an adipoyl chloride overlayer has little or no effect on the lifetime of the MDA molecule. We propose that the addition of the azobenzene molecule results in a more ordered multilayer structure, and hence the decrease in the lifetime of the donor. The azobenzene molecule is planar, and will attempt to remain planar in a multilayer structure, allowing for substantial intermolecular interactions between acceptors. An MDA monolayer, and a monolayer with an overlayer of adipoyl chloride yield the same lifetime. Once the azobenzene molecule is incorporated into the assembly, the lifetime of the MDA becomes shorter. The addition of optically inactive spacer layers (1,3-propanediol) results in the same shorter lifetime. Each assembly that yields a shorter lifetime is capped with an azobenzene, which proves that the azobenzene must be the reason for the change in the lifetime of the donor. We rule out excitation transport based on the donor-acceptor distance independence of the lifetimes.

We propose that the ordering of the assembly occurs in the following manner. The first monolayer of MDA is organized to some extent on the surface. The addition of the azobenzene forces the entire assembly into a more ordered arrangement. The new order within the multilayer assembly alters the structure of the aggregates in this

environment. The radiative monomers are now in closer proximity to a medium with a larger dielectric constant than before. It has been shown in the literature^{20,21} that the result of decreasing the distance between a dipole and a dielectric is to shorten the lifetime of the dipole, in this case, a radiative monomer.

From these studies, it does not appear that interlayer energy transfer plays a major role in the relaxation dynamics of the chromophores that we have studied in this work. We saw no change in the donor lifetime of the 2,7-diaminofluorene/azobenzene pair, even though energy transfer should be favorable in this system. Although we see a decrease in MDA lifetime with the second donor-acceptor pair, this is most likely due to ordering within the layers initiated by the planar azobenzene molecule.

Horne and Blanchard also probed the ZP multilayers for the possibility of interlayer energy transfer.²² In this work, they calculated that, based on the orientation of the chromophores within a layer, that interlayer energy transfer should be twice as efficient as intralayer energy transfer. They found no dependence of the donor lifetime on the presence of acceptor, indicating that efficient interlayer energy transfer was not occurring. They thought that the donor lifetime in those studies was dominated by same molecule ($D_1^* + D_2 \rightarrow D_1 + D_2^*$) energy transfer. Another underlying assumption of the Förster model is that the dielectric medium is spatially uniform between the donor and acceptor. Due to the ZP functionality present between the two molecules, this requirement is not necessarily fulfilled. They concluded that interlayer energy transfer was mediated by the presence of the polarizable ZP moieties, which shielded the donor and acceptor transition dipole moments.

There are no polarizable linkages between layers in our covalent assemblies, so the exact reason for the lack of energy transfer is unsure. Work in the literature involving assemblies such as LB⁷⁻⁹ and polyelectrolyte^{10,11} films demonstrate that energy transfer can proceed efficiently in these multilayer assemblies. Evans *et al.* studied energy transfer from excited aggregates to monomers in LB films, and found it to be very efficient.²³ In these experiments they showed that in a system with primarily aggregates, (<0.5% monomer) the monomer dominated the emission spectrum.²³ This fact was true even when the system was excited at the absorbance maximum of the aggregate, and not the monomer. They concluded that the aggregate is a dark state, and only relaxes non-radiatively, and any emission must be from a transfer of energy to the monomer. Under this assumption, the lifetime that we see must be due only to the monomer, and not to both the monomer and the aggregate. This also supports Horne and Blanchard's conclusion that the double exponential decay seen on the surface in their studies was due to the monomer in two different environments.

One other point of interest is the effect of the primer layer on the resulting assembly. Horne and Blanchard also looked at the effect of priming on the dynamics of their system. The normal priming method used in our studies was 3-aminopropyltrimethoxysilane (APDMES), which is known to be less stable than another type of primer used by Horne *et al.*, 3-aminopropyltriethoxysilane (APTES). APTES is known to polymerize²⁴, producing a cross-linked structure due to three reactive ethoxy groups, compared to the one ethoxy group present in APDMES. In AFM studies, they demonstrated the differences in the surface topology with the two different primers.²² In contrast to the results found by Horne *et al.*, when we primed a substrate

with APTES, and then added a monolayer of MDA to this surface, we recovered a lifetime which was longer than MDA on a surface primed with APDMES. The short and long time components of MDA on this APTES primed surface were 544 ± 18 ps and 2787 ± 410 ps, respectively. This difference in lifetime can be attributed to the different types of bonding present in each system. In ZP systems, the bonding is primarily ionic, while in our systems the bonding is covalent. The polymerized primer is also a covalent network, and will therefore contribute to the covalent bonding that occurs in subsequent layers. This change in the lifetime of MDA demonstrates very effectively the sensitivity of this technique, and why the information gained is so valuable.

3.4 Conclusions

In this work we constructed multilayer assemblies using optically active chromophores. The steady state and time-resolved dynamics of these chromophores both in solution and within multilayers were studied. The first donor-acceptor pair measured consisted of 2,7-diaminofluorene and 4,4'-diaminoazobenzene. The fluorescence lifetime of the donor in this pair, 2,7-diaminofluorene, was studied both in a homogeneous monolayer, and in multilayers that also contained azobenzene. No change in the donor lifetime was recovered in the presence of the acceptor molecule. Another donor-acceptor pair, MDA and 4,4'-diaminoazobenzene was then considered. Once again the fluorescence lifetime of the donor, in this case MDA, was studied both in a homogeneous monolayer and in the presence of the acceptor. Unlike the first donor-acceptor pair, in this instance, a decrease in the donor lifetime was seen, which could be indicative of energy transfer within the assembly. Studies were performed which incorporated both one and two spacer layers into this assembly, and no change was seen

between these results and the donor and acceptor directly next to one another. We therefore concluded that energy transfer was not occurring as previously thought, and that the presence of the azobenzene was ordering the assembly, thereby decreasing the lifetime of the donor molecule. Based on the double exponential decay that was recovered for the lifetime of both donor molecules we believe that the chromophores are aggregating on the surface and perhaps impeding interlayer energy transfer. An upper bound for the size of an aggregate island was estimated based on an exciton hopping model. From this model, we found that while we could not determine the exact island sizes, we could place an upper bound of $50 \times 50 \text{ \AA}$ on their area. Although interlayer energy transfer should compete effectively with intralayer transfer between aggregates and monomers, this was not seen in these assemblies. Further studies which probe the intralayer energy transfer within these assemblies will give a clearer picture of the exact behavior in these systems.

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Chapter 4

Conclusions

This thesis has focused on the synthesis and characterization of novel multilayer systems. Multilayer assemblies have been built using both coordinate chemistry through the chelation of EDTA with Zr^{4+} ions, and covalent linking chemistry, which utilized urea, urethane, ester and amide bonds. The covalent linkage studies were of importance because of the possibility of probing energy transfer within these layered systems. Horne and Blanchard studied energy transfer in ZP multilayer systems and found that interlayer energy transfer was not the dominant means of relaxation in these systems. This result motivated us to replace the ZP functionality with something less polarizable, and focus on the resulting covalent assemblies, in the hope that energy transfer could be mediated structurally in these systems.

We have shown that the synthesis of multilayers containing urea, urethane, amide and ester linkages proceeds in a controlled manner. Fundamental characterization of these systems using techniques such as ellipsometry, FTIR, UV-visible spectrometry and XPS was performed. All of these techniques show the expected trend of a linear increase in response with an increasing number of layers. The incorporation of optically active chromophores into the covalent assemblies utilizing amide bonds was also accomplished. The growth of bilayers containing functionalized chromophores was also shown to proceed in a controlled manner.

Using these covalent multilayer systems we hoped to better understand the role of energy transfer in the relaxation dynamics of these molecules. It was discovered that a

donor-acceptor pair containing the molecules 2,7-diaminofluorene and 4,4'-diaminoazobenzene exhibited no decrease in the lifetime of the donor molecule, indicating a lack of energy transfer. Another donor-acceptor pair was also studied, incorporating the same acceptor molecule, but using a different donor, MDA. In this system a decrease was seen in the lifetime of the donor in the presence of the acceptor. Subsequent experiments that separated the donor and acceptor with optically inactive layers showed no change in the lifetime of the donor with increasing donor-acceptor separation, and we concluded that the decrease in lifetime was not due to Förster energy transfer.

One possibility for this decrease in lifetime is that the azobenzene molecule is forcing order upon the system upon its addition to the multilayer. This explanation seems reasonable since a more ordered assembly should exhibit a shorter lifetime due to structural mediation of the local dielectric response. There are several reasons that interlayer energy transfer is not occurring efficiently, even in situations where it should be favorable. The first reason stems from aggregation of the chromophores on the surface. Evans *et al.* studied the aggregation of chromophores in LB films, and found that Förster energy transfer from the aggregate to the monomer was the prevalent means of relaxation for these chromophores.¹ Horne and Blanchard also reported on the significance of aggregates in their work.² In their studies of both intralayer and interlayer energy transfer, they discovered that the chromophores were aggregated into islands that were separated by distances greater than the Förster critical radius. As a result, even though it should have been efficient, no transfer of energy was seen between different chromophores in these assemblies. In this instance the result was believed to be due to

the ZP moiety separating the donor and acceptor molecules. In our work, as shown in Chapter 3, we studied the dynamics of a multilayer assembly that did not contain this polarizable ZP functionality. We discovered that interlayer energy transfer was not an efficient means of relaxation in these covalent systems. This result is surely because of chromophore aggregation on the surface.

Chromophore aggregation is seen in numerous multilayer assemblies³⁻⁵ in the literature, and there does not appear to be any simple way to eliminate this problem. The priming step is an area of great concern. AFM studies performed by Horne *et al.* demonstrated that while the addition of a primer to the surface fills grooves or depressions in the surface, the silanes react in areas with dense active silanol sites, forming island-like structures.⁶ These island-like structures inhibit the formation of a uniformly smooth surface. As shown in Chapter 3, different primers had an influence on the resulting donor lifetime. The triethoxy silane primer is known to polymerize on the surface, and the initial layer is therefore harder to control.⁷ The dimethylethoxy silane primer may be easier to control, but the resulting structure is less stable due to the lack of cross-linking, which is seen when using the triethoxy silane primer. The difference in donor lifetimes for monolayers made with the two primers demonstrates that the priming step can have a profound effect on the structure of the resulting layers.

It will be very important in future work to devise a priming method that will result in a more uniform initial layer. There is current work in our laboratory that will make use of a polymer templating layer to remove the functional group density and distribution of the surface. A dramatic change should be seen in the surface morphology of the resulting

layers if the initial layer is more uniform. Excitation transport measurements will be critical in the evaluation of this “remapping” chemistry.

The issue of aggregation must be studied in greater detail in these assemblies. It would be helpful to utilize AFM surface images and combine them with results from intralayer energy transfer studies. In our lab we are in the process of devising a second harmonic generation (SHG) imaging system, which could provide a wealth of information about the groups on the surface of a substrate. This combination could provide more useful information about the exact aggregate island sizes and spacing between aggregates. This SHG imaging system may also prove to be another technique that could be used to gather topological information. The only drawback to this technique may be the resolution, which will be on the micron scale. This may not be a small enough scale for us to look at island formation. However the studies are performed, the intralayer population dynamics of these assemblies must be studied in greater detail.

In Chapter 2, the rotational freedom of the acceptor molecule, 4,4'-diaminoazobenzene was questioned. Although the energy barrier for the isomerization of azobenzenes is estimated as ~50 kcal/mol, it would be interesting to perform isomerization and anisotropy studies on these covalent systems. These rotational dynamics will be pertinent to the optical information storage work currently underway in our laboratory. The read/write function of chromophores in multilayers will be mediated by a *cis-trans* isomerization. It will also be very important to determine if the molecules have motional freedom while in a multilayer structure. These results may also help

explain the lower thicknesses that were seen in the ellipsometric studies of the azobenzene molecule.

It would be interesting to perform solution phase studies on analogs of the surface bound species. This would be a useful set of studies for several reasons. First, it would be helpful to note if the shifts in the absorbance spectra of the chromophores are due primarily to changes in their electronic structures, aggregation of the molecules, binding them to a surface or combinations of these factors. By forming amide bonds in solution, the chromophore's characteristics in this environment can be measured and shifts in the absorbance and emission spectra can be noted. The second reason that solution phase studies could be important is for energy transfer studies in solution. These solution phase energy transfer studies would provide a controlled reference experiment with which to compare the surface studies, and may or may not demonstrate efficient energy transfer. Whatever the results of these studies, they would provide a wealth of information that is not currently accessible.

There is still much work to be done in the area of covalent multilayers. We have shown that the deposition of layers occurs in a seemingly controlled manner. The use of a more sensitive technique, fluorescence lifetimes, has demonstrated that this may not be the case. There is obviously aggregation of the chromophores on the surface and we need to understand this mechanism better. As long as aggregation occurs, the potential of covalent systems is very limited. The incorporation of different chromophores may alleviate the problem, but this is doubtful considering the number of studies that have been performed, which demonstrate aggregate formation.

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