Somsakul Watcharinyaon

Structure of Self-Assembled Monolayers on Gold Studied by NEXAFS and Photoelectron Spectroscopy
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DISSERTATION

Karlstad University Studies 2008:40
ISSN 1403-8099
ISBN 978-91-7063-200-6

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Distribution:
Faculty of Technology and Science
Physics
651 88 Karlstad
054-700 10 00

www.kau.se

Printed at: Universitetstryckeriet, Karlstad 2008
To my mother
Kanya Watcharinyanon
Abstract

Self-assembled monolayers (SAMs) provide well-defined and ordered films of molecules spontaneously chemisorbed on a surface. By designing molecules with desired functionalities, such molecular films can be interesting for a range of applications from molecular electronics to catalysis. Important parameters for SAM applications are the film structure and quality, which are dependent on the structure of molecular constituents, the substrate, and the self-assembly process. In this work, SAMs on Au(111) of a variety of functionalized molecules, with thiol and silane headgroups, have been studied using high-resolution X-ray photoelectron spectroscopy (HRXPS), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, Infrared reflection absorption spectroscopy (IRRAS), contact angle measurements, and Kelvin probe measurements. In particular, the effects of varying the size of the backbone, varying the headgroup, inclusion of a porphyrin tailgroup, deprotection method of the headgroups, and formation process of mixed molecular layers have been investigated.

The first part of this thesis work is focused on SAMs of oligo(phenyleneethynylene) (OPE) derivatives, where first the effect of the extent of the conjugated system on the structure of SAM was investigated. As the lateral π-system in the OPE backbone increases, molecular surface densities become lower and molecular inclinations larger. Subsequently, a bulky porphyrin tailgroup was added onto the OPE molecule. Porphyrin-functionalized OPE with several headgroups were compared and the thioacetyl anchor group was found to form a high quality SAM.

In the second part of the work, the molecular orientation in thiol-derivatized tetraphenylporphyrin layers was studied. The geometry of the molecular layer and the number of linkers that bind to the gold surface were found to depend strongly on preparation schemes, i.e. whether or not the acetyl protection groups on the thiols were removed before adsorption.

Finally, mixed SAMs of a ferrocene-terminated alkanethiol and an unfunctionalized alkanethiol were studied. By diluting the ferrocene-functionalized molecules in a matrix of unfunctionalized alkanethiols, the orientational order and the packing density improved. The geometrical structure and the fraction of the ferrocene-terminated molecules can be tuned by controlling the parameters in the preparation scheme.
Preface

This thesis presents a summary of the work that was carried out in Materials Physics group at Karlstad University, Sweden, during the years 2002 to 2008. The thesis comprises of an introduction to the molecular layers fabricated by self-assembly process. In particular, the work put emphasis on the characterization techniques that were utilized to investigate a structure of these layers. The scientific papers related to the work are also included.

During these years, I have had a great pleasure of working, not only with research, but also with teaching which I have gained a lot of experiences from. All the work in this thesis would not be completed without the helps from numerous people who I want to take this opportunity to thank them here. First of all, I am indebted to my supervisors, Lars Johansson and Ellen Moons, for their great advices and supports. I am very grateful to their patience and kindnesses. Michael Zharnikov and Andrey Shaporenko are gratefully acknowledged for their collaboration and assistance at Max-lab. I have learned greatly about XPS and NEXAFS from them. I would like to thank Jerker Mårtensson and Daniel Nilsson for the chemical synthesis and great inputs on my work in paper I and II. I am very thankful to Carla Puglia and Emmanuelle Góthelid for their collaboration in the work on metal porphyrin. I am very impressed by their generous advices and a power of women in physics. Special thanks go to Kerstin Moatti for taking a great care of everyone in Physics department, to Daniel Johansson for his technical supports, and to the members of Physics department for creating a pleasant working place.

In particular, A big thank go to Pon, P, and Rodrigo for our everlasting friendship and weekend trips which help me refreshing my brain, to P’ Ek for wakeup calls and his encouragement and to my dear friend, Cecilia for making my working day during the past years more enjoyable.

I would never have made it without my family. I would like to thank my mother who has always been there for me, my father for his love and a great support until the end of his life and my brothers for their loves and cares. Finally, I sincerely wish to thank Tue and Matilda for their endless loves, laughs, and smiles that really delight me during a hectic time.

Somsakul

Karlstad, September 2008
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CHAPTER 1

Introduction

Controlling the properties of solid surfaces is a challenge that has attracted wide scientific, as well as technological, interest. In applications, such as, in wetting, lubrication, and corrosion control, in catalysis, and in electronic and optical devices, the surface and interfaces are crucial. One way to achieve surfaces with controlled and tunable properties is by modifying them with well-defined molecular films. Self-assembly is a method that has attracted significant interest in physics, chemistry, and biology, because it provides a convenient and simple way of creating a highly ordered thin molecular film with tailored chemical and electrical properties. In a self-assembly process, an ultra-thin molecular layer is formed by the adsorption of molecules from solution onto a solid surface [1]. Then the adsorbates spontaneously arrange themselves until finally a completely ordered molecular monolayer is formed, a so-called self-assembled monolayer (SAM).

The SAM constituents can be designed and tailor-made by chemical synthesis. Their physical properties are determined by their chemical structure. Thus, an assembly of SAMs can produce a well-defined molecular layer with alterable chemical functionalities at the surface. Nowadays, a great deal of research focuses on the application of SAMs in molecular electronics [2, 3]. As further downscaling of electronic devices that are fabricated based on silicon technology, will soon meet physical and economic limitations, molecular electronics is one of the promising alternative technologies. The concept of molecular electronics is the use of single molecules or arrays of molecules for the fabrication of electronic components such as wires, switches, and storage elements [3]. There are several classes of molecules that exhibit such electronic properties. For example, diarylethenes [4] and rotaxanes [5] exhibit a switch property by using light to trigger. This class of molecules could be used as
storage elements. Due to the difficulties in contacting and manipulating single molecules, the research on molecular electronics in the first period was focused on the electronic properties of the molecules in solution. Later on, the development of scanning probe techniques has allowed the operation and manipulation on a level of a single molecule. The electrical properties of various molecules have been studied by these techniques [3, 6, 7]. However, the devices based on single molecules are still highly challenging, therefore most of the recent research have focused on single monolayer films for the first effort.

In this work, oligo(phenyleneethynylene) (OPE) derivatives, thiolated porphyrins, and ferrocene-terminated alkanethiol (FcCn), which exhibit electrical conductivity and redox properties, were used to form SAMs. OPE derivatives are fully conjugated molecules which makes them beneficial for electron transport. This makes the molecule interesting as molecular wire in molecular electronic devices [8, 9]. Moreover, in single-molecule studies it was found that an unfunctionalized OPE molecule behaves as a molecular rectifier [6], whereas when functionalized with nitro, amino, or fluoro groups, it exhibits negative differential resistance [10-12]. By adding a photoactive functional group, such as porphyrin, on the OPE the molecule becomes even more interesting. Porphyrins are well known to exhibit electron-accepting or donating (redox) properties. Two porphyrins covalently linked by OPE-based molecules are one example of donor-bridge-acceptor systems, for which photoinduced energy and electron transfer have been studied in solution [13-15]. As an extension of these studies in solution, it is interesting to investigate the electron-transfer properties of similar systems when they are bound to surfaces. There have been a number of previous studies on energy and electron transfer in porphyrins immobilized on the surface, particularly as model systems for photosynthesis [13, 15, 16]. Also ferrocenethiol-decorated surfaces are interesting for electron transfer studies. Such studies have been done mostly in solution [17, 18]. SAMs of ferrocene-terminated thiols were found to exhibit a negative differential resistance [19], and photon-induced switching [20]. These properties provide a basis for the construction of interfacial devices, such as sensors and transducers that utilize electron-transfer reactions. Molecules with redox properties can be used in sensor applications [21, 22], [17]. Furthermore, SAMs can also be utilized in heterogeneous catalysis. By immobilizing the catalyst on a surface, by means of self-assembly, catalytic activity is improved [23] because this solution overcomes a problem found in homogeneous
catalysis, in which the product and the catalyst need to be separated after the process.

In order to study the properties of surfaces that are modified by SAMs, it is required to understand the molecular structure, orientation and packing density in the layer. To successfully access the functional properties of a single or a group of molecules, a well-defined and stable layer is needed. For this purpose, we study the influence of a number of parameters, such as the structure of molecular constituents and the preparation schemes, on the structure and quality of SAMs. The tools for investigating the SAMs are also an important factor to develop the technology. In this work, various techniques were employed to characterize the SAMs. High-Resolution X-ray Photoelectron Spectroscopy (HRXPS), Near-Edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy, and Infrared Reflection Absorption Spectroscopy (IRRAS) were used to evaluate surface composition, molecular orientation, packing density, and coverage. Contact angles are measured to obtain information on the surface order and density from the wetting behavior. In addition, Kelvin probe measurements were employed to obtain the influence of the SAMs on the work function of the modified surface.

In this work, I have collaborated with scientists of the Organic Chemistry group at the Department of Chemistry and Bioscience, and with the Department of Applied Semiconductor Physics at Chalmers University of Technology, as well as the Department of Physics and Materials Science at Uppsala University. The overall purpose of the collaborations has been to develop new functional molecular materials, and characterize and understand the structure and functional properties of molecular layers. My contribution to this collaboration has been the structural characterization of molecular layers that were fabricated by the self-assembly process as described in this thesis. Information obtained from this study on the structure of molecular layers forms a basis for further studies on the function of these layers in the future.
CHAPTER 2

Self-Assembled Monolayers (SAMs)

Research in the field of thin organic films began about 200 years ago. Franklin observed the calming effect of an oil film on water surfaces in 1774 [24]. At the end of the 19th century, amphiphilic monolayers at air-water interfaces were prepared and studied by Pockels [25]. Later in 1917, Irving Langmuir published a systematic study of monolayers of amphiphilic molecules on a water surface [26]. This monolayer system was named after Langmuir. In 1935, Blodgett [27] carried out a study on the transfer of fatty acids onto a solid substrate from a film on the air-water interface. Such films are called Langmuir-Blodgett films. A systematic study related to self-assembled monolayers (SAM) was performed later by Bigelow in 1946 [28]. He published a method for the preparation of monolayers by adsorption of molecules from solution onto a clean metal substrate. Kuhn used this method to form a monolayer of chlorosilane derivatives on glass [29]. Later on, Nuzzo and Allara discovered that SAMs of thiolate on gold can be prepared by adsorption of bifunctional organic disulfide from a dilute solution [30].

SAMs were found to provide a convenient and simple way to tailor the interfacial properties of metals, metal oxides, and semiconductors [1]. In the beginning, SAMs were studied for the purpose of controlling the wetting properties of the metal surfaces [31]. Recently, SAM studies are motivated by the potential applications in biological sensors, catalysis and molecular electronics [1, 3, 32]. SAM systems that have been investigated extensively include:

- organosilanes (R-SiCl₃, R-SiH₃, R-Si(OCH₃)₃) on hydroxylated surfaces (SiO₂, Al₂O₃, glass, etc.) [33-35],
- dialkyl sulfides (RSR') and disulfides (RS-SR') on gold [30, 36],
- carboxylic acids on aluminum oxide and silver [37, 38],
Self-Assembled Monolayers (SAMs)

- organothiol (R-SH) on gold, silver, copper and GaAs [39-44],
- organoselenol (R-SeH) on gold and silver [45, 46].

2.1 Concept of Self-Assembly

Self-assembled monolayers (SAMs) are molecular assemblies formed spontaneously by the adsorption of molecular constituents from solution or from the gas phase onto the surface of solids [1]. SAMs formed from solution are the focus of this work. Figure 2.1 shows the common preparation scheme and the constituents of a SAM. SAMs are prepared by immersion of a substrate into a solution of organic molecules.

![Figure 2.1. Schematic of SAM preparation and the constituents of a SAM-molecule (headgroup, spacer and tailgroup) [2].](image)

Molecules that form SAMs typically consist of three units:

1. A **headgroup** that binds to the substrate. The molecules are immobilized on the surfaces via an interaction between the headgroup and the substrate and form a chemical bond. There are a number of headgroups that bind to specific metals, metal oxides, and semiconductors. For example, organosilanes bind to hydroxylated surfaces via a Si-O bond, thiols bind to gold via a S-Au bond, and carboxylic acids bind to silver via an ionic COO⁻-Ag⁺ bond.
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2. A **spacer or backbone** that connects headgroup and tailgroup. This part affects the intermolecular interaction and molecular orientation. Furthermore, the spacer can provide a well-defined thickness, and influence the electronic conductivity.

3. A **tailgroup** that constitutes the outer surface of the film. SAMs with different surface properties can be achieved by combining the spacer with a functional tailgroup such as carboxyl, hydroxyl, porphyrin, or ferrocene, etc.

The understanding of the self-assembly process is important in order to construct a well-designed SAM. The self-assembly process has been investigated most intensively for SAMs of alkanethiols on gold [47-50] (See the review by Schreiber for a detailed description [50]). To a first approximation, the growth of the molecular layer follows a Langmuir growth curve, with an exponential uptake (with respect to time) up to saturation coverage. Detailed studies have revealed deviations from this curve and have shown that there are different stages in the growth process, with different time scales and phases. Generally, the process is divided in two distinct stages. In the first stage, which takes a few minutes, the molecules adsorb and form bonds between the headgroup and the substrate. A molecular adsorption results in that about 80% of the surface is covered by alkanethiols on gold [47]. Although it is difficult to observe the assembly process in the solution, Yamada [51] and Sylvain [52] observed an ordered assembly of the alkanethiol molecules lying flat on the surface (striped phase) in this stage by using in-situ scanning probe microscopy. The same structure was observed in similar SAMs prepared in the gas phase at low coverage [49]. As the surface coverage increases, islands are formed at the domain boundary of the striped structure. These islands arise from a transformation of the molecules to a standing-up configuration, caused by the lateral pressure. In the second stage, which lasts several hours, the islands grow until the surface reaches saturation. At this stage, the molecules organize themselves to reach equilibrium and form an ordered film. The organization of the molecules on the surface results from optimizing the lateral interaction among the molecular moieties (intermolecular van der Waals interaction). The final structure, however, involves the balance between the headgroup-substrate interaction which forms at the first stage and the intermolecular interaction which arise at the final stage.
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The headgroup-substrate interaction is the strongest of all interactions [53]. It is the primary driving force for the self-assembly process. A very strong headgroup-substrate interaction results in an immobilization of the molecules on specific sites on the surface. For alkanethiol SAMs on gold, the energy associated with the S-Au interaction is about 160-190 kJ/mol [54]. As a result of the very strong interaction, the molecules try to occupy every available site on the surface, thus pushing together molecules that are already bound. For higher surface coverage, the intermolecular interaction becomes more and more important. It drives the self-assembly after the molecules have been pinned on the surface. This interaction is caused by the van der Waals forces between the spacers. The energy associated with the intermolecular interaction is in the order of tens of kJ/mol (but lower than 42 kJ/mol) [53]. This interaction plays a crucial role in the molecular packing on the surface. The tailgroup can also influence the SAM formation. For methyl terminated molecules, the tailgroup-tailgroup interaction is not very strong, but for other terminations, such as ferrocene, it can play a significant role for a final structure of the SAMs.

The self-assembly technique provides us the possibility to obtain well-defined molecular layers with tailored properties. The first self-assembled monolayers of organosilicon, octadecyltrichlorosilane (OTS) \( \text{C}_{18}\text{H}_{37}\text{SiCl}_3 \), on hydroxylated surface were reported by Sagiv [33]. For this system, the Si headgroup loses all the Cl atoms upon reaction with the OH groups on the surface and forms a Si–O bond to the substrate and a network of Si–O–Si bonds between the molecules. This makes the molecules connected to the surface and to each other as shown in Figure 2.2a. This type of SAM can be used to construct a multilayer. By modifying the tailgroups of the SAM constituents into hydroxyl groups which provide a hydroxylated surface, another layer of OTS can be formed (Figure 2.2b). Such multilayers were proposed for the use in molecular electronics [55]. As shown in Figure 2.2b, a multilayer that consists of electron donor and acceptor groups separated by a well-defined distance from each other may allow the charge transfer. However, the quality of these SAMs is very sensitive to the preparation conditions (water contained in solution, immersion time, temperature) [1, 56-58]. Moreover, the substrates (SiO\(_2\), Al\(_2\)O\(_3\), glass, etc.) used in these SAMs formation are not atomically smooth. Hence, high quality SAMs of organosilicons are not simple to obtain.
The most extensively studied class of SAMs is based on the adsorption of thiol (-SH) molecules on metal surfaces. The thiol headgroup is one of the functionalities that form a strong interaction with noble metals [40, 59]. It is therefore possible to utilize the thiol molecules to generate well-defined SAMs on gold and silver surfaces [32]. Apart from thiol, selenol (-SeH) can be used as an alternative since the chemical properties of sulfur and selenium are quite similar. Selenol compounds were found to form SAMs on gold and silver substrates [45, 46, 60]. The molecular orientation, degree of order and packing density of alkaneselenolate SAMs on Au(111) were found to be similar to those of alkanethiols [45] but alkaneselenates have a high toxicity [61]. Tellurium is another element that has been used in the headgroup for a SAMs [62, 63]. SAMs formed from tellurium-containing compounds are not stable under ambient conditions. They were found to oxidize easily after the film formation [62, 63].

In this study, thiols were chosen as the main headgroup for the SAM formation. There are a number of substrates that support the formation of thiol-derived SAMs. The most common substrate is a thin gold film on mica or silicon. Apart from gold, other noble metals such as silver and copper can be used to form well-defined SAMs [41]. Alkane and aromatic thiol-based SAMs on silver exhibit a higher packing density and a smaller molecular inclination.
than the same molecules on gold [41]. However, silver and copper can easily form a surface oxide which can complicate the SAMs formation [32, 64]. Especially for copper, surface pretreatment is needed in order to obtain an oriented monolayer [64]. Due to its chemical inertness compared to other metals, gold has been chosen as the preferred substrate in this work. Nevertheless, CO$_2$, O$_2$, H$_2$O and hydrocarbons in the ambient air can contaminate a gold surface. To minimize this oxidation it could be stored in an argon atmosphere before the monolayer adsorption. In the following section, an overview of SAMs formed by adsorption of thiol compounds on gold is given. In particular, the structure and mechanism of SAM formation are presented.

2.2 SAMs of Thiolates on Gold

A thiol is a compound that contains a hydrogen-sulfur (-SH) group. Thiols are also referred to as mercaptans. This family of compounds is widely used for self-assembly on gold. The thiol immobilizes on the gold surface via a S-Au bond. However, the nature of the S-Au bond and the arrangement of the sulfur groups on the underlying surface are still not completely understood. It is assumed that the formation of the S-Au bond requires the loss of the hydrogen from the S-H groups [65] and that the thiolate (R-S-) is bound to the gold surface by a covalent bond [53]. The most common procedure for preparing SAMs of thiolates on gold is immersion of a clean gold substrate into a thiol solution for several hours or a day.

It is known that the formation of SAMs involves the interplay of headgroup-substrate and intermolecular interactions [1]. In the case of thiol-derived SAMs on gold, these two interactions are governed by the substrate template and the molecular constituents. The arrangement of the sulfur moieties on the gold surface defines the free space available for the molecules, who will organize themselves to optimize the intermolecular interactions within their geometric constraints. The structure of the monolayer is thus highly depended on these factors [1, 44, 66, 67].

Most structural investigations have been carried out on SAMs of alkanethiols (CH$_3$(CH$_2$)$_n$SH) on Au(111) surfaces. Strong and Whitesides were the first who studied the structure of the SAMs of alkanethiol on Au(111) by using electron
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Figure 2.3. Schematic diagram depicting the arrangement of a monolayer formed by alkanethiols on a Au(111) surface. A \( (\sqrt{3} \times \sqrt{3})R30^\circ \) overlayer structure where the sulfur atoms (dark gray circles) are positioned in the three-fold hollow sites of the gold lattice (white circles), \( a = 2.88 \) Å. The light gray circles with the dash lines is the approximate projected surface area occupied by each alkane chain [32].

diffraction [39]. They observed a \( (\sqrt{3} \times \sqrt{3})R30^\circ \) structure of adsorbed molecules on the Au(111) surface with an intermolecular spacing of 4.97 Å and calculated an area per molecule of 21.4 Å². Later, Porter et al. observed the same structure based on scanning tunneling microscopy studies [68]. A theoretical study of structure and binding of alkanethiol SAMs suggested that the molecules preferably adsorb at a three-fold hollow site of the Au(111) surface [66]. Considering the possible binding sites on Au(111), the three-fold hollow site is the most stable binding site, with lowest surface energy, compared to the bridge and on-top positions [66, 69]. This chemisorption arrangement agreed well with the experimental results obtained by Strong, Whitesides and Porter et al. The proposed structure of a monolayer formed by alkanethiols on a Au(111) surface is shown in Figure 2.3. The bonding between the sulfur and Au(111) surface in the three-fold hollow site has both \( \sigma \) and \( \pi \)-character [1]. The \( \sigma \)-bonding is accomplished by the sulfur p-orbitals and the gold 6s-orbitals, with contributions from the gold p- and d-orbitals. The \( \pi \)-bonding involves the sulfur and gold p-orbitals. It appears that the \( \pi \)-bonding significantly contributes to the S-Au bond and that it gives rise to the linear structure of the Au-S-C at the hollow site [66]. However, the alkyl chains in the SAMs were found to be tilted instead of standing upright on the surface [41, 70]. Taking into account the Van der Waals interaction between the molecular spacers, the
Figure 2.4. Schematic visualisation of the orientation of alkanethiol SAMs. The alkyl chains tilt with an angle $\phi$ with respect to the surface normal.

alkyl chains in the SAMs are tilted in order to optimize the intermolecular interaction and balance the headgroup-substrate interaction, thus minimizing the surface energy. As shown in Figure 2.4, the alkanethiol molecules in the SAMs are oriented with an average tilt angle of $\sim27^\circ-35^\circ$ with respect to the surface normal [41, 71-73]. The recent studies on alkanethiol SAMs on coinage metal surfaces using normal incidence X-ray standing waves by Woodruff et al. reported that the interaction of the thiols with Au(111) surface leads to a reconstruction of the outermost gold surface layer [74, 75]. In particular, the self-assembly involves the organization of Au-adatom-thiolate moieties, and not simply thiolate species [74, 75].

Some studies of thiol SAMs on differently oriented gold surfaces are available. The alkanethiol SAMs on Au(100) exhibit a simple square structure with a c(2×2) periodicity [39, 76]. The intermolecular spacing observed in this SAMs is 4.54 Å and calculated area per molecule is 20.6 Å$^2$ [39]. Based on this result, it was proposed that the molecules are adsorbed on both on-top and hollow sites [66].

The structure of the monolayers is determined by the interplay of the headgroup-substrate and intermolecular interactions [1, 44, 66, 67]. The roles and relative importance of each of these two interactions were studied by Zharnikov using NEXAFS and photoelectron spectroscopy for aliphatic and aromatic thiol-derived SAMs [44]. It was found that the headgroup-substrate interaction plays a dominant role for the structure and packing density in alkanethiol SAMs. In contrast, in the thioaromatic SAMs, these parameters are mainly determined by the intermolecular interactions [44].
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In thioaromatic SAMs, the role of the molecular spacer can be addressed. The intermolecular forces between aromatic moieties are stronger than the van der Waals forces between the alkyl chains in the aliphatic systems [77]. By extending the length of the aromatic moieties, which increases the intermolecular interaction, the SAMs become more densely packed and well-ordered [78-81]. Instead, for aliphatic SAMs, the coverage and packing density do not exhibit a pronounced chain length dependence [44]. The structural investigations on aromatic thiol SAMs showed that compounds such as biphenylthiols, terphenylthiol, and oligo(phenylene-ethynylene) thiols orient on Au(111) with a slightly smaller tilt than alkanethiols [43, 82, 83]. However, the structural arrangement of these SAMs on Au(111) surfaces exhibits the \( (\sqrt{3} \times \sqrt{3})R30^\circ \) structure as found in SAMs of alkanethiol [82, 83]. This implies that these molecules bind at the same sites as alkanethiols. Considering the cross-sectional area of the phenyl ring (21.1 Å\(^2\)) is close to the area per molecule in the \( (\sqrt{3} \times \sqrt{3})R30^\circ \) structure (21.4 Å\(^2\)) of alkanethiol SAMs on Au(111), this type of thioaromatic molecules is well suited to form SAMs with a dense packing.

By introducing functional tailgroups on the thiol-derived compounds, the molecules become more attractive because of the ability to customize the surface properties. A Teflon-like or hydrophobic surface can be produced by using the alkanethiol with the CF\(_3\) tailgroup. On the other hand, a hydrophilic surface can be achieved using the OH or COOH tailgroups. A surface with redox property can be obtained using thiol-derived compounds with a porphyrin tailgroup. These type of systems can be used in applications such as sensor [21, 22] and catalysis [23]. Moreover, thiol-derivatized porphyrins are often utilized in the study of energy and electron transfer particularly as models for photosynthesis [13, 15, 16]. However, the substitution of the functional group can also influence the molecular packing. The alkanethiols with functional groups, such as OH or NH\(_2\), which are not bulky, form SAMs with the ordered \( (\sqrt{3} \times \sqrt{5})R30^\circ \) structure [84]. This SAM shows a high packing density as found in unfunctionalized alkanethiol SAMs [85]. On the other hand, more bulky tailgroups on alkanethiols, such as azobenzene, were reported to interrupt the orientational order in the SAMs [86].

It is possible to form a monolayer that comprises of a mixture of different thiol-derived molecules. Such a monolayer with a well-defined structure is
Self-Assembled Monolayers (SAMs)

called “mixed SAM”. By coadsorption of thiols with different functionalities, the surface properties can be designed via the control of surface chemical functionalities. Mixed SAMs provide the possibility to improve the quality of the monolayer that comprises molecules whose physical dimension precludes a well-organized assembly. An example is the formation of SAMs of ferrocene alkanethiol. By diluting the ferrocene alkanethiol in unfunctionalized alkanethiols, the packing density and the orientational order are improved as reported in Paper IV. Moreover, mixed SAMs are useful for controlling the molecular composition on the surface. They can also form a pattern on the surfaces using a technique called microcontact printing [87-89]. This technique uses an elastomeric stamp and alkanethiol ink to form patterned SAMs on a gold surface. Then another SAM can be formed in the bare region of the gold surface by immersion of the substrate in a solution containing another thiol. The patterned SAMs are useful for microfabrication [87, 89].

In this work, several thiol-derived compounds which contain aliphatic and aromatic spacers, and functional tailgroups are used to form SAMs on Au(111). In addition, apart from thiol, another headgroup, trimethylsilane (TMS), \( \text{R} \equiv \text{Si}((\text{CH}_3)_3) \), that was proposed to form SAMs on gold was also studied. The properties, structure and binding mechanism of these compounds are presented in the next chapter.
CHAPTER 3

The Studied Molecules

3.1 Oligo(phenyleneethynylene) (OPE)

Oligo(phenyleneethynylene) (OPE) derivatives are molecules which consist of phenyl rings connected with triple bonds, Figure 3.1. They are fully conjugated molecules. Conjugated bonds play an important role in electron conduction because $\pi$-electrons are delocalized over a distance, called the conjugation length. Because of their large delocalized $\pi$-system and their linear structure OPE derivatives are sometimes regarded as a molecular wire. In order to be able to electrically connect the functional molecules to an electrode, the molecular wire is equipped with a headgroup (e.g. thiol) that can bind to the electrode. A functional tailgroup (e.g. switches, redox-centers) can then be attached to the other end of the molecule.

In this work, various OPE-derivatives with different headgroups (sulfur- and silicon-based), spacers, and functional tailgroups were used to form SAMs on
The studied molecules Au(111) surfaces. The resulting molecular layers were studied in terms of their structure and molecular orientation.

3.1.1 Thiolated OPE

The thiolated OPE molecules under study are presented in Figure 3.2. The thiolates are commonly protected with an acetyl group \((R=S\text{COCH}_3)\) to prevent oxidation, disulfide formation and side reactions during synthesis [61, 78]. This moiety is often referred to as a thioacetyl group. The acetyl protection groups are expected to be removed during the self assembly process allowing the formation of thiolate-gold bond \((S^-\text{Au})\).

Figure 3.2. Chemical structures of thiolated OPE molecules with an acetyl protection group. OPE molecules with 1) benzene, 2) naphthalene, and 3) anthracene as the central moiety of the aromatic spacer. 4) OPE with a methylene linker between thioacetyl and aromatic moieties.

The balance between the intermolecular interaction and the interaction between the thiolate and the gold surface results in a tilt of the aromatic chain. To investigate this effect, the thiolated OPE was modified. The OPEs with 1) benzene, 2) naphthalene, and 3) anthracene as the central aromatic moiety in Figure 3.2 were investigated to see the effect of the molecular structure on the orientation of SAMs.

The methylene linker between the thiolate and OPE moiety was inserted with the intention to alter the tilt of the OPE chain (Figure 3.3). We intended to achieve an improvement of orientational order and increase of the packing density with the methylene, as occurs in oligophenyl-substituted alkanethiols on gold [90-92]. A more upright orientation of the oligophenyl moieties and consequently a denser molecular packing was observed for an insertion of a methylene linker between the sulfur and oligophenyl moiety [90-92].
3.1.2 Trimethylsilane OPE

While silane are usually used for adsorption to hydroxylated surfaces such as SiO$_2$, Al2O3, etc., it is here proposed as a binding group to a gold surface. Trimethylsilane (TMS), $R$-Si(CH$_3$)$_3$, is another candidate headgroup for binding to gold and driving the self-assembly. Due to the high reactivity displayed by the acetyl in the thioacetyl group, the syntheses of complex molecules can be complicated or even impossible. A more stable group, that is suitable for the SAM formation, would therefore be essential for construction of functionalized molecules of the complexity necessary for future applications. Such a group might be the TMS. It is a well established protective group in organic synthesis with a desirable reactivity pattern. The scanning tunneling microscopy study by the group of Fichou showed that TMS-ethynylene, $R$-≡Si(CH$_3$)$_3$, is suitable for the formation of SAMs when attached to alkynes [94, 95]. However, the interaction of the TMS with the gold surface is still unknown. The hypothesis presented by these authors is that Si being directly connected to an electron-withdrawing group, such as the C≡C triple bond, interacts with an electron-donating atom such as gold, which leads to pentacoordinated silicon as illustrated in Figure 3.4 [94-97].
The Studied Molecules

Figure 3.4. Suggested binding configuration for TMS-ethynylene showing a pentacoordination on the gold surface [95].

To investigate this hypothesis, that the unsaturated bond was involved in the attachment of the molecule to the gold surfaces, OPE systems with different unsaturated bonds (ethynylene, vinylene and phenylene) next to the trimethylsilane were used to prepare SAMs and characterized. The structure of these systems is shown in Figure 3.5.

Figure 3.5. Three different trimethylsilane systems.

3.2 Porphyrin-Functionalized OPE

A porphyrin is a planar aromatic molecule that consists of four pyrrole rings linked together with methylene bridges. The porphyrin with two hydrogen atoms at the core are referred to as free-base porphyrin, Figure 3.6 (1). The core of the porphyrin can also be ligated with a metal, forming so called metalloporphyrin, Figure 3.6 (2). The porphyrins contain 22 π-electrons. They are well known to exhibit electron-accepting or electron-donating properties. Moreover, photoinduced electron transfer was observed in porphyrin complex systems [13, 16, 98]. Because of these properties, porphyrins are utilized in many applications, for example, sensors [21, 22, 99], catalysis [100], solar cells [98], or other optoelectronic devices [101-104].
By introducing a porphyrin as the tailgroup of the OPE moiety, one can create a wire-like molecule with optical and donor-acceptor properties. By attaching these molecules to an electrode using the self-assembly process, the charge can be transported between the functional tailgroup and the electrode and thus the function of the porphyrins can be accessed and controlled. In order to conduct fundamental studies of these properties and obtain a good functionality in technological applications, a good knowledge of the molecular orientation and packing density for the SAM formed from these porphyrin functionalized OPEs is needed. In this work, the free-base porphyrins connected by the OPE bridge to different anchor groups were used to form SAMs. The structure of these molecules are shown in Figure 3.7.

![Chemical structure of porphyrin functionalized OPE molecules with three different anchor groups.](image-url)
3.3 Thiol-Derivatized Tetraphenylporphyrin

Thiol-derivatized tetraporphyrins were designed and synthesized for the use in catalysis applications [100]. Tetraphenylporphyrin is a porphyrin with phenyl rings substituted at four \textit{meso}-positions. By decorating the inner core with metal, the molecules have attracted attention as catalysts in oxidation reactions [100]. For many years, metalloporphyrins have been used as homogeneous catalysts in which the catalysts are presented in the same phase as the reactants. There are several drawbacks in these catalytic systems such as the low solubility of the metalloporphyrin in most organic solvents, the degradation of this catalyst in an acidic media and the need to separate the product from the catalyst. To overcome these limitations, the metalloporphyrins were immobilized on the surface and used as a heterogeneous catalyst. The heterogeneous catalysts are present in a different phase than the phase of the reactants. They are mostly solid and functioning in a liquid or gaseous reaction. Moreover, the immobilized porphyrins even showed an increased activity in the reaction [105, 106]. Recently, the impact of molecular order in the immobilized porphyrin layer on the catalysis has been investigated [107].

![Chemical structure of thiol-derivatized porphyrin](image)

**Figure 3.8.** Chemical structure of thiol-derivatized porphyrin [100].

Porphyrsins can bind to the surface such as gold [108, 109], and silicon [110], via the linkers that contain an anchor group. In this work, free-base and cobalt-tetraphenylporphyrins bearing four linkers with thioacetyl-functionalized carbon chains (Figure 3.8) were immobilized on the gold surfaces. With this molecular structure, we expected to produce an ordered layer with a coplanar porphyrin ring on the gold surfaces.
3.4 Ferrocene-Terminated Alkanethiol

Ferrocene (Fc), Fe(C5H5)2, is an aromatic compound that consists of an iron atom in a +2 oxidation state, sandwiched between two cyclopentadiene rings, each bearing a negative charge, thus resulting in a neutral molecule. Each cyclopentadiene ring contains six π-electrons making them conjugated. The cyclopentadiene rings are separated about 3.32 Å from each other. The ferrocene is well known to easily exhibit reduction-oxidation (redox). This property was well characterized by electrochemical methods [111]. Moreover, the change of the oxidation state of the iron in the core allows a switching property [20, 112, 113].

![Chemical structure of ferrocene substituted alkanethiol.](image)

Figure 3.9. Chemical structure of ferrocene substituted alkanethiol.

In order to access these properties of the ferrocene, it should be attached to the electrode surface. In this case, the ferrocene was modified by substituting an alkanethiol to one of the rings, Figure 3.9. To measure the charge transfer between an electrode and ferrocene, a well-defined and stable system is required [111]. Thus, the ferrocene-substituted alkanethiol was diluted in a highly ordered alkanethiol SAMs on gold. The coadsorption of these two molecules was shown to improve the structural order of the monolayer [114]. These layers are stable and can be oxidized and reduced without changing the properties [111]. In this work, we investigate the structure of mixed ferrocene-substituted alkanethiol and alkanethiol SAMs in order to develop a functional monolayer and to understand the role of the structure on the charge transfer process. By varying the SAM preparation methods, the structure and the fraction of the ferrocene on the surface can be controlled.
CHAPTER 4

Preparation of SAMs

4.1 Gold Substrate

Polycrystalline gold has been used as a substrate for the SAMs under study. Gold has been chosen because it forms a strong bond with thiol that we used as the headgroup in most of the molecules in the study. Also, gold is a considerably inert metal compared to other metals, such as silver or copper [32]. This property makes it useful for handling and manipulating samples in ambient air instead of in ultra high vacuum (UHV).

![AFM image](image-url)

**Figure 4.1.** AFM image (10 μm × 10 μm) of a 300 nm thick gold film on mica.

In this study, the gold substrates were purchased from Georg Albert PVD-Beschichtungen (Heidelberg, Germany). They were prepared by thermal evaporation of 300 nm of gold onto mica and then flame-annealed in air. These
Preparation of SAMs

films were previously shown to be polycrystalline with a predominant (111) orientation [115]. The grain sizes of these films are about 1000 nm with flat (111) terraces of about 50-100 nm in width. They are widely used for structure characterization of SAMs by scanning probe microscopy techniques because of their flat surface. The substrates were stored under argon before monolayer adsorption. An atomic force microscopy (AFM) image of the gold substrate is shown in Figure 4.1.

4.2 SAMs Preparation

SAMs can be formed on substrates by either adsorption from solution or evaporation. In this study, we employed the solution method due to its convenience. The common procedure for preparing SAMs is immersion of a clean substrate in a dilute (0.5-1 mM) ethanol solution of the target molecule for ~20h at room temperature. However, there are several factors in the preparation scheme that affect the structure of the resulting SAMs, for example, solvent, immersion time, concentration of the adsorbate, and cleanliness of the substrate. In particular, for the molecules with a protective group at the anchor, the deprotection method also influences the structure of the layer.

A widely used solvent for self-assembly is ethanol. Other alternatives are tetrahydrofuran (THF), dimethylformamide (DMF), and toluene. The choice of solvent for SAM formation depends on the solubility of the studied molecules. Alkanethiol SAMs formed from 1 mM solution in ethanol (immersion time for 20h) show a saturated and well-ordered monolayer. The minimum concentration for forming a dense SAM is 1 μM but it requires a long immersion time [47, 116]. The immersion time for SAM formation at normal concentration is 12-20h, where the first process to attach the adsorbates on the gold surface takes a few minute and the second process to organize the adsorbates and form an ordered layer takes several hours. The coverage of the surface increases with extending immersion time.

Even though the thiols can displace the adventitious materials on the gold surface, exposing the substrate to the ambient conditions for a long time seems to reduce the quality of the SAMs. Thus, it is crucial to keep the clean substrates in an inert atmosphere before SAM preparation. In practice, it is also important to maintain the inert environment over the solution during the SAMs formation and reduce the concentration of the oxygen in the solution in order
to avoid oxidation of the thiols to sulfinate and sulfonate [117]. SAMs are degraded under UV light, especially in combination with oxygen. Therefore, they should be placed under the inert atmosphere in the dark as soon as possible after completing preparation.

For an adsorbate with the thioacetyl group, there are several routes for removal of the acetyl group. A small amount of NH₄OH, NaOH or HCl is commonly added to the solution of thioacetyl to hydrolyze the acetyl protective group and allow the thiol to bind to the gold surface. Moreover, the acetyl group could be deprotected in situ upon direct exposure to the gold surface [78]. A previous study revealed that the different routes for the removal of the protective acetyl group do not influence the molecular structure of the SAMs [78]. However, we have found that the choice of deprotection method affects the electronic and structural properties of the thiol-derived porphyrin layers on gold surface as reported in Paper III.

Self-assembled monolayers can be comprised of a mixture of two or more adsorbates, so called “mixed SAMs”. Several methods of making mixed SAMs have been reported [59, 118], including: (1) Coadsorption from solution containing mixtures of the desired adsorbates. (2) Subsequent adsorption of the adsorbates one at a time. In this case, the adsorbates were diluted in the matrix SAM of another adsorbate by subsequent immersion. (3) Adsorption of asymmetric disulfides that contain two different moieties (RS-SR’ ) in which the disulfide will break and form bonds to gold surface. In this work, the first two methods were employed. The structure and relative contribution of the two adsorbates on the surface can be controlled by varying the preparation schemes as reported in Paper IV.

We present below the preparation schemes of the specific SAMs that were used in this study.

### 4.2.1 OPE derivatives and porphyrin-functionalized OPE SAMs

The organic compounds, OPE derivatives and porphyrin functionalized OPE were synthesized at the Department of Organic Chemistry, Chalmers University of Technology [61]. Tetrahydrofuran (THF) was used as a solvent. THF is a standard solvent used in SAM formation for acetyl protected OPE-thiols [12, 78, 119, 120]. It was dried by distillation from sodium/benzophenone under
Preparation of SAMs

The preparations of SAMs were carried out in an argon atmosphere to avoid undesired pollutants (e.g., CO₂, O₂) from the ambient air. The desired molecule was dissolved in dried THF to give a 1 mM solution. Then the gold substrates were placed into the solution under argon atmosphere in a closed vial. An excess (2-4 drops) of a 1% ammonium hydroxide solution in THF (prepared from ammonium hydroxide, 25-30% NH₃) was added to the reaction vessel to hydrolyze the acetyl-protecting group. The samples were kept in the solution for 20h at room temperature in the absence of light. When removed from the solution, the samples were thoroughly rinsed with THF, then blown dry with nitrogen and stored under argon.

In the case of OPE derivatives and porphyrin functionalized OPE with the TMS headgroup, the same procedure was applied, except no additional activation for the acetyl deprotection was needed.

4.2.2 Thiol-derivatized tetraphenylporphyrin layers

The thiol-derivatized porphyrins were synthesized at the Department of Organic Chemistry, Stockholm University [100]. DMF was chosen as the solvent for SAM formation. Porphyrin monolayers on Au surfaces were prepared employing two preparation schemes.

1.) Protected scheme: the porphyrins with the protective thioacetyl groups were dissolved in DMF to give a 0.5 mM solution. The gold substrate was then immersed in this solution under argon atmosphere in a closed vial. The samples were kept in the solution at room temperature in the absence of light for 20h. Then, to remove the remaining physisorbed molecules on the surface, the sample was rinsed with DMF, soaked for 10-20 min in DMF, rinsed again with DMF and afterwards rinsed with deionized water. Finally, the sample was blown dry with argon.

2.) Deprotected scheme: in this case the acetyl protective groups were removed in the solution before the monolayer formation. The molecules were dissolved in DMF to obtain a 0.5 mM solution. Then, an excess of 0.5 M NaOH in methanol was added in the porphyrin solution to hydrolyze the acetyl protective groups. The final concentration of NaOH solution in the porphyrin solution was 4% (v/v). After 1h reaction, the gold substrate was immersed in this solution and left in the absence of light for 1h. Then the sample was rinsed...
with the same rinsing procedure as for the protected scheme and finally blow dried with argon.

4.2.3 Mixed ferrocene-terminated and unsubstituted alkanethiol SAMs

The 11-ferrocene-1-undecanethiol (here abbreviated FeC\textsubscript{11}) molecules were purchased from Probior, Germany. Decanethiol (here abbreviated C\textsubscript{10}) molecules was purchased from Sigma-Aldrich. Ethanol (purity grade 99.5\%) was used as a solvent. The mixed C\textsubscript{10}/FeC\textsubscript{11} SAMs were prepared by using two different schemes.

1.) Mixed solution, the gold substrates were immersed in a solution containing 0.5 mM C\textsubscript{10} and 0.5 mM FeC\textsubscript{11} in ethanol for 24 h.

2.) Subsequent immersion, the gold substrates were immersed into 1 mM solution of C\textsubscript{10} in ethanol (the time was varied from 3, 30 to 150 min). Then, the samples were removed from C\textsubscript{10} solution and rinsed with ethanol. After that, they were immersed in a 1 mM solution of FeC\textsubscript{11} in ethanol for 24 h.

These two types of mixed SAMs were prepared at room temperature. After immersion, the samples were thoroughly rinsed with ethanol, blow dried with and stored under argon.

For comparison, the homogenous FeC\textsubscript{11} and C\textsubscript{10} SAMs were prepared by immersion of gold substrates in a 1 mM solution of the respective compound in ethanol and kept in solution at room temperature in the absence of light for 24 h. The samples were rinsed and dried with the same procedure described above.
CHAPTER 5

Characterization of SAMs

Several techniques have been utilized to study the characteristics of SAMs. The complementary techniques that were used in all the paper included in this thesis are high-resolution X-ray Photoelectron Spectroscopy (HRXPS) and Near-edge X-Ray Absorption Fine Structure (NEXAFS) Spectroscopy. These two techniques provide information on the electronic and geometric structure of the SAMs. Moreover, Infrared Reflection Absorption Spectroscopy (IRRAS) and contact angle measurements were also employed to characterize the structure of the SAMs. Finally, the work function of the SAMs compared to the substrate was monitored by using Kelvin probe measurements.

5.1 X-Ray Photoelectron Spectroscopy (XPS)

5.1.1 Principles

X-ray Photoelectron Spectroscopy (XPS) is a surface analysis technique that provides information about the chemical state and concentration of the elements comprising the outermost surface layer of a solid. XPS is also called electron spectroscopy for chemical analysis (ESCA) and the two acronyms can be used interchangeably. In this thesis work, XPS is employed to study core levels in adsorbates by ionizing the core electron and measuring their kinetic energy distribution. When a sample is irradiated with a flux of X-ray photons, photoelectrons are emitted from the sample after direct transfer of the energy of the photon to the core-level electron. This is known as the “photoionization process”. These emitted electrons are subsequently separated according to their kinetic energy and counted. The energy of the photoelectrons is related to the atomic and molecular environment from which they originated. The number of electron emitted is related to the concentration of the emitting atoms in the
Characterization of SAMs

sample. The conservation of energy is required in the photoionization process, simply stated

\[ E_i^N + h\nu = E_f^{N-1} + E_k \]  

(5.1)

where \( E_i^N \) is the initial state energy of the system with \( N \) electrons, \( h\nu \) is the photon energy, \( E_f^{N-1} \) is the final state energy of the ionized system with \( N-1 \) electron and \( E_k \) is the kinetic energy of the emitted photoelectron. The binding energy of the photoelectron, \( E_b \), can be expressed by the initial and final state configurations,

\[ E_b = E_f^{N-1} - E_i^N \]  

(5.2)

From Eq. 5.1 and 5.2, if the photon energy, \( h\nu \), is well defined, the binding energy of the electron in the atom, \( E_b \), can be expressed by [121, 122]

\[ E_b = h\nu - E_k \]  

(5.3)

In the discussion so far the energy reference has been the vacuum level of the sample. The vacuum level is defined as the energy of the electron at rest just outside the surface of the solid [122, 123]. In practice, the kinetic energy of the emitted photoelectrons is measured with reference to a vacuum level of the spectrometer, which does not have to coincide with that of the sample. Figure 5.1 shows a core-level photoionization and the energy alignment between the sample and spectrometer. In order to establish the binding energies of the photoelectrons, a common reference level between sample and detector is needed. By grounding both the sample and the spectrometer, the Fermi level, \( E_F \), of both systems are at the same energy level. Thus the Fermi level is chosen as the reference. The photoelectron is emitted from the sample surface with a kinetic energy, \( E_k \). When the photoelectrons move to the entrance slit of the spectrometer, they are either accelerated or retarded by an amount equal to the difference between the work function of the sample, \( e\phi_s \), and the work function of the spectrometer, \( e\phi_w \).
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Figure 5.1. The energy level diagram showing a core-level photoionization process and the energy alignment between the sample and the spectrometer.

The kinetic energy of the photoelectron at the spectrometer, $E'_k$, related to the kinetic energy of the photoelectron at the sample, $E_k$, and the work functions by

$$E'_k = E_k - (e\phi_s - e\phi_p) \quad (5.4)$$

From Figure 5.1, the kinetic energy of photoelectron at the sample related to the binding energy $E_B^f$ (with reference to the Fermi level) and the photon energy by

$$E_k = h\nu - e\phi_p - E_B^f \quad (5.5)$$

From Eq. 5.4 and Eq. 5.5, the binding energy with reference to the Fermi level, can be related to the measured kinetic energy by

$$E_B^f = h\nu - E'_k - e\phi_p \quad (5.6)$$

Therefore, with the known photon energy $h\nu$, $E_B^f$ can be determined by measuring $E'_k$ and $e\phi_p$. The work function of the spectrometer, $e\phi_s$, is
obtained upon calibration of the spectrometer where a sample with a well known binding energy is studied. The calibration can be done by placing a clean Au standard in the spectrometer and adjusting the instrumental setting such that the known $E_B$ values for the Au are obtained (e.g., $E_B = 0$ eV, Au 4f7/2 = 83.95 eV). The linearity of the $E_B$ scale is then calibrated by adjusting the energy difference between two widely spaced lines of the sample to their known values. Once the spectrometer energy scale has been calibrated, it is assumed to remain constant.

### 5.1.2 Chemical shift and final state effects in core spectra features

Siegahn and co-workers [124] (who pioneered the technique of XPS) showed that XPS is a probe of the chemical environment. The binding energy of the core levels of an atom will depend critically on the species to which it is bonded. Even though the core electrons are not involved in the chemical bonding, they are sensitive to chemical environment, for example, neighboring atoms, molecules or surfaces. The formation of chemical bonds via the valence electrons causes a change in the distribution and density of electrons in the atom resulting in a change in the core level binding energy, a so called “chemical shift”. The atom that binds to another atom with higher electronegativity will have less electron density resulting in a shift to a higher binding energy of the core electron, as shown in the example in Figure 5.2. The chemical shifts in XPS spectra can be used as a fingerprint to locate certain atoms in a molecule or adsorbed atoms on the substrate.

![Figure 5.2: XPS spectrum of C 1s obtained from the molecule ethyltrifluoroacetate showing binding energy differences due to four different chemical environments of carbon atoms [124].](image-url)
Characterization of SAMs

The measured binding energy corresponds to the energy difference between the system in its initial ground state and its final excited state as seen in Eq. 5.2. The initial state effects contribute to the binding energy if the energy of the atom at its ground state is changed, for example, by formation of chemical bonds as mentioned above. So-called final state effects can also have an impact on the measured binding energy. The removal of the core electron causes a large perturbation of the electronic structure due to the excited ionized state leading to significant rearrangement of the remaining electrons in order to screen the core hole. In molecular layers, there are two types of mechanisms of screening the core hole created by photoionization process, intermolecular and intramolecular relaxation. These relaxations can cause a binding energy shift in the XPS spectra. The intermolecular relaxation is caused by electronic polarization of the surrounding molecules, which will give rise to the shift by approximately 1-2 eV in the measured binding energy [125]. The intramolecular relaxation is caused by the rearrangement of outer shell electrons or nuclei within a molecule. The time period for these relaxation events is about 10-100 femtoseconds.

![Diagram](image-url)

Figure 5.3. Schematic representation of different excitation events occur during and after the photoionization process [126].

The intramolecular relaxation processes give rise to emitted electrons with a distribution of energies, corresponding to different excited states. This results in new features in the spectrum. Figure 5.3 shows some different excitation events that might occur during and after photoionization namely: shake-up, shake-off and Auger emission. A shake-up peak arises from the outgoing photoelectron losing part of its kinetic energy to excite a valence electron into an unoccupied orbital (e.g., $\pi \rightarrow \pi^*$ transition). If the photoelectron transfers sufficient energy
into the valence electron to ionize it into the continuum, the process is called shake-off. The Auger decay occurs after ionization of the core level and then the de-excitation takes place by an electron filling the place at the core level. The liberated energy excites another electron to the continuum. The features in the photoelectron spectra that arise from these events appear at higher binding energies than the main line.

5.1.3 Quantitative analysis

XPS is very useful for quantitative analysis. The intensity of photoemission peaks in the XPS spectra are related to the amount of each element presented in the sample. However, for quantitative analysis, two of the parameters, a photoionization cross section $\sigma$ and an attenuation length $\lambda$, must be taken into consideration in order to obtain good quantitative results. The photoionization cross-section is the probability that the incident X-ray photon will create a photoelectron. It is dependent on the incident photon polarization and energy. The attenuation length is the average distance normal to the surface at which an electron can escape without energy loss due to inelastic collisions. It is strongly dependent on the kinetic energy of the photoelectrons.

In XPS experiments, we are concerned only with the intensity of the emitted photoelectrons that have lost no energy. If an electron suffers energy loss, but still has sufficient energy to escape from the surface, it will contribute to the background signal, but not to the photoemission peak. The intensity of the photoelectrons that have suffered no energy loss traveling through matter, is given by [127]

$$I = \sigma j k \int n(x) \exp \left( -\frac{x}{\lambda \cos \theta} \right) dx$$

(5.7)

where $I$ is the intensity, $\sigma$ is the photoionization cross-section for a particular transition, $j$ is the flux of X-ray photons, $k$ is an instrument factor, $n(x)$ is the concentration of the element of interest at a distance $x$ below the surface while $\lambda$ is the attenuation length, $\theta$ is the angle between the surface normal and the ejected electron and $x$ is the distance from the sample surface. In this work, the atomic photoionization cross-section values are obtained from the calculated values by Yeh and Lindau [128]. The $\lambda$ values are obtained from the expression
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derived by Lamont [129] for alkanethiol SAMs, which valid in the range of 300-1000 eV, as expressed by

\[ \lambda = 0.3E^{0.64} \]  
(5.8)

If the sample comprises of a thin overlayer of thickness \( d \) on the bulk substrate, the total intensity of the surface layer \( (I_s) \) and bulk \( (I_b) \) will be

\[
I_s = \sigma j k n \lambda_s \cos \theta \left[ 1 - \exp \left( -\frac{d}{\lambda_s \cos \theta} \right) \right] 
\]  
(5.9)

\[
I_b = \sigma j k n \lambda_b \cos \theta \exp \left( -\frac{d}{\lambda_b \cos \theta} \right) 
\]  
(5.10)

where \( \lambda_s \) and \( \lambda_b \) are the attenuation length of the surface layer and the bulk, respectively.

Thus, with the formulas above, the thickness of the overlayer can be derived from the intensity ratio between the surface and bulk components.

5.1.4 Instrumentation

For photoemission experiments, a monochromatic light source which is tunable over a wide energy range, has high intensity, and is polarized is desired. Synchrotron radiation from a storage ring can provide these desirable properties. Synchrotron radiation is created when charged particles travel in a storage ring with a speed close to that of light. The change in direction of the charged particles by the magnetic field from a bending magnet cause light emission. The light is emitted over a wide spectral range, has a high intensity of photons, and is linearly polarized in the plane of the storage ring. Even higher photon intensities, as well as different polarization, can be achieved by inserting periodic magnet structures in straight section of the ring, so called wiggles and undulators.

In order to utilize this radiation a system of focusing mirrors and monochromators is typically needed. This system is called the beamline and is designed to provide monochromatic light into an end station in which the actual experiment is carried out. For photoemission studies the end station is
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equipped with an electron analyzer to detect and record the energy distribution of the electrons emitted from the sample. Normally the end station also contains various other types of equipment for surface preparation and characterizations, all of these are in ultra high vacuum (UHV).

In my work, the XPS measurements were carried out at the synchrotron storage ring MAX II at MAX-lab in Lund, Sweden, using the D1011 beamline (Figure 5.4).

![Figure 5.4. Beamline D1011 at the synchrotron storage ring MAX II at MAX-lab in Lund, Sweden.](image)

The beamline covers a photon energy range from 30 to 1500 eV. It is equipped with a modified SX-700 monochromator [130] and a two-chamber ultrahigh vacuum experiment station with a hemispherical Scienta electron analyzer [131]. The spectra were acquired in normal emission geometry.

The analyzer system (Figure 5.5) consists of a lens system, an energy analyzer and a detector. The lens system is used to collect photoelectrons and to focus these electrons onto the entrance slit of the analyzer. In addition, the lens system also retards the kinetic energy of photoelectrons down to the chosen kinetic energy (the pass energy) of the analyzer. The energy analyzer, hemispherical type, consists of two electrically isolated concentric hemispheres with a potential difference between them. The electric field separates electrons by allowing only electrons with the chosen pass energy go through the exit slit and hit the detector. Electrons of kinetic energy lower or higher than the pass energy are attracted by the inner positive or outer negative hemispheres, respectively, and are neutralized.
Thus, the energy resolution, $\Delta E$, of the hemispherical analyzer can be defined as [122]

$$\frac{\Delta E}{E} = \frac{x_1 + x_2}{2r} + \alpha^2, \quad r = \frac{a + b}{2}$$

(5.11)

where $E$ is the energy of the electron, $x_1$ and $x_2$ are the width of the entrance and the exit slits, $a$ and $b$ are the radius of the inner and outer hemisphere electrodes, and $\alpha$ is the maximum angular deviation of the electron trajectories at the entrance slit with respect to the center line.

In modern electron analyzers like the Sciena, the exit slit is replaced by a large-area position-sensitive detector, consisting of a multi-channel plate detector and a sensitive CCD-camera. Thereby, electrons in a wide energy range around the pass energy can be counted simultaneously. The exit slit is set by choosing the energy step across the detector.

In these experiments, the pass energy, energy step, and the width of the entrance slit of the analyzer were set to obtain the energy resolution about 0.1 eV. The acceptance angle of the analyzer system is 16º.
5.2 Near-Edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy

5.2.1 Principles

Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy is a technique to characterize surfaces by evaluation of unoccupied electronic states. NEXAFS provides information on chemical and structural properties of adsorbates in the film. In NEXAFS, the X-ray photon energy is scanned over a core-level absorption edge, and the absorbed X-ray intensity is measured by probing the excitation of the core electron to unoccupied states. This method requires a tunable monochromatic light source with smooth characteristics in the energy regions of interest, as well as high intensity and energy resolution. Synchrotron radiation sources are therefore well suited for NEXAFS spectroscopy. NEXAFS refers to the absorption fine structure close to an absorption edge about the first 30 eV above the actual edge. This region usually shows the largest variations in the X-ray absorption coefficient and is often dominated by intense narrow resonances.

This technique relies on a two-step process. In the first step the photon excites a core electron to the unoccupied state, hence creating a core hole, and in the second step the recombination process of the core hole takes place. There are many possible channels for the core hole recombination process (Figure 5.6): the radiative type, producing the emission of photons (fluorescence), or the non-radiative type (Auger-like transitions), producing the emission of electrons, which can be collected from the surface with suitable detectors [132]. In our experiment, the latter type was measured.

There are two kinds of the Auger-like transitions in this case: participator decay in which the excited electron participates in the core-hole decay process and spectator decay in which the excited electron remains in the normally unoccupied level and two valence electrons are removed. The number of generated Auger electrons is directly proportional to X-ray absorption cross section [133].
Several techniques can be chosen to detect the absorption. The most common method is an electron yield measurement which measures the emitted electrons that are created by the absorbed X-ray. There are several ways to perform electron yield measurements: Total electron yield (TEY), Partial electron yield (PEY) or Auger electron yield (AEY). In the TEY method, all Auger electrons and photoelectrons are measured. This results in a high signal rate but a very small signal-to-noise ratio. In the PEY method, by placing a retarding voltage in front of the electron detector, a fraction of Auger electrons are measured. Because of the flexibility in choosing the retarding voltage, one can avoid the interference from the low kinetic energy electron, increasing signal-to-noise ratio. In the third method, the AEY method, Auger electrons are measured by setting the energy analyzer at a specific Auger transition energy. This method offers the largest signal-to-noise ratio of all electron-yield techniques, but the smallest signal rate. Another technique to measure the X-ray absorption spectra is a transmission measurement. This can be done by measuring the current to the sample after photons are transmitted through it. This technique requires a thin sample while the electron yield technique can be used for conventional samples. In this work, the PEY method was employed.

5.2.2 X-ray absorption rate [133]

NEXAFS concerns the electronic transition form atomic core levels to unoccupied states. The X-ray absorption rate or cross section, $\sigma_x$, is defined as
the number of electrons excited per unit time divided by the number of the incident photons per unit time per unit area [133]. The absorption rate can be calculated by using Fermi’s Golden Rule for the transition from the initial state, \( \phi_i \), to the final state, \( \phi_f \), and the dipole approximation as

\[
\sigma = \frac{4\pi^2}{m^2} \frac{e^2}{\hbar c \omega} \left| \langle \phi_f | \hat{p} \cdot \hat{E} | \phi_i \rangle \right|^2 \zeta(E)
\]  

(5.12)

where \( \hbar \omega \) is the incident photon energy, \( e \) and \( m \) are the charge and mass of electron respectively, \( \zeta(E) \) the density of final states and \( \langle \phi_f | \hat{p} \cdot \hat{E} | \phi_i \rangle \) the dipole matrix which shows the scalar product of the interaction between the linear momentum operator of electron, \( \hat{p} \), and a unit vector of electric field of a polarized incident light, \( \hat{E} \). The dipole matrix can be used to determine the orientation of molecule on the surface due to the basis of the polarization dependence of NEXAFS spectra which will be discussed in the next section.

Another form of the dipole matrix element can be obtained by using the total linear momentum operator

\[
\hat{p} = m \hat{v} = -i\hbar \nabla = \frac{im(E_f - E_i)}{\hbar} \hat{r}
\]  

(5.13)

where \( \nabla \) and \( \hat{r} \) are the sum of the electron velocities and positions. Then the matrix term can be expressed as

\[
\left| \langle \phi_f | \hat{p} \cdot \hat{E} | \phi_i \rangle \right|^2 \propto \zeta(E) \left| \hat{E} \cdot \hat{r} \phi_i \right|^2
\]  

(5.14)

\( \langle \phi_f | \hat{p} \cdot \hat{E} | \phi_i \rangle \) is defined as the transition dipole moment (TDM) associated with a transition between the initial and the final state. The TDM is directly related to molecular orbitals involved in the excitation, and thereby to the molecular geometry. Importantly, the transition of the electron must obey the dipole selection rules. Thus only transitions with the change of angular momentum quantum number \( \Delta l = \pm 1 \) are allowed and contribute to the spectra. The absorption rate is also directly proportional to the density of final states which represents the numbers of the unoccupied states in the molecule.
5.2.3 Angular dependence of NEXAFS resonance intensity

Upon the photoelectron excitation, the amplitude and direction of the unoccupied state on the excited atom can be probed by NEXAFS spectroscopy. In this section, the determination of molecular orientations of the adsorbrates on the surfaces from analysis of the angular dependence of the resonance intensities in K-shell ($1s$) NEXAFS spectra is presented. In particular, the angular dependence of the so-called $\sigma$ and $\pi$ resonances which, in a molecular-orbital picture, correspond to transitions from the $1s$ initial state to the empty $\sigma^*$ and $\pi^*$ final states are discussed. The well defined symmetry of the initial ($1s$) and final ($\sigma^*$ and $\pi^*$) states involved in the electronic dipole transitions and the linearly polarized nature of synchrotron radiation are responsible for the strong angular dependence of the NEXAFS resonance intensities. Because the $\sigma^*$ and $\pi^*$ orbitals are defined relative to the molecular symmetry axis or plane, the angular dependence of the $\sigma$ and $\pi$' resonance intensities directly reflects the orientation of the molecule on the surface.

For the discussion of the angular dependence of NEXAFS resonances, it is convenient to classify the molecules into general groups as shown in Figure 5.7. The classification consists of diatomic molecules containing single, double and triple bonds and a benzene ring. The orientation of $\sigma^*$ and $\pi^*$ orbitals of these molecules are illustrated in the figure. These concepts of the bonding in diatomic molecules and benzene ring can serve as the basis for all other cases.

Figure 5.7 shows that single-bonded molecule is characterized by a $\sigma^*$ orbital along molecular axis, double-bonded molecule by a $\sigma^*$ and an orthogonal $\pi^*$ orbital, and triple-bonded molecule by a $\sigma^*$ and two orthogonal $\pi^*$ orbitals. In general, a single orbital is represented by a vector and two orthogonal orbitals by a plane. In the case of aromatic ring, the atoms are arranged in a plane, thus the $\sigma^*$ system is characterized by a plane. The $\pi^*$ orbitals can be represented by a vector perpendicular to the plane. Thus we need to consider the angular dependence of the NEXAFS resonance for two cases: vector-type and plane-type orbital. The vector-type orbital is chosen for the calculation below, an analogous calculation for the plane type orbital can be found in reference [133].

Considering the angular dependence of specific resonances, the intensity of the transitions can be derived from Eq. 5.12, which links the resonance intensity, $I$, to the matrix element by
Figure 5.7. Schematic illustration of orientation of $\sigma^*$ and $\pi^*$ orbitals in four important groups of molecules [133].

\[
I \propto |\langle \phi_f | \vec{e} \cdot \vec{p} | \phi_i \rangle|^2 \tag{5.15}
\]

where $\vec{e}$ is a unit vector of the electric field vector $\vec{E}$, $\vec{p}$ is the momentum operator, $|\phi_i\rangle$ is the $1s$ initial state and $|\phi_f\rangle$ is the molecular orbital final state of the transition.

For polarized synchrotron light, the electric field vector is composed of two components, a component parallel to the orbit plane of the storage ring, $\vec{E}^{\parallel}$, and a component that is perpendicular, $\vec{E}^{\perp}$. The degree of linear polarization or polarization factor $P$ can be expressed by

\[
P = \frac{|\vec{E}^{\parallel}|^2}{|\vec{E}^{\parallel}|^2 + |\vec{E}^{\perp}|^2} \tag{5.16}
\]
Characterization of SAMs

In the case of linearly polarized light, $|\vec{E}_\parallel| = 0$ or $P = 1$, and for circularly polarized light, $|\vec{E}_\perp| = |\vec{E}|$ or $P = 0.5$. From Eq. 5.15 and the above definition of $P$, the total resonance intensity is given by

$$I \propto P \left| \frac{\varphi}{\vec{e}_\parallel \cdot \vec{p} \varphi_\parallel} \right|^2 + (1-P) \left| \frac{\varphi}{\vec{e}_\perp \cdot \vec{p} \varphi_\perp} \right|^2$$

(5.17)

where $\vec{e}_\parallel$ and $\vec{e}_\perp$ are unit vector of the in-plane and perpendicular electric field components, respectively. The total intensity can be rewritten with the contribution of the resonance intensity associated with $\vec{E}_\parallel$ components, $I^\parallel$, and the resonance intensity associated with $\vec{E}_\perp$ components, $I^\perp$, as

$$I \propto [P I^\parallel + (1-P) I^\perp]$$

(5.18)

The intensity $I^\parallel$ and $I^\perp$ can be derived from the coordinate system in Figure 5.8.

As shown in the Figure 5.8, the TDM, $\tilde{O}$, is characterized by a polar angle $\alpha$ and an azimuthal angle $\phi$. The X-rays are incident in the $(x, z)$ plane with an angle $\theta$ respect to the surface plane. They contain two electric field components $\vec{E}_\parallel$ and $\vec{E}_\perp$. $\vec{E}_\parallel$ is tilted from the surface normal by the angle $\theta$ which is equal to the X-ray incidence angle. $\vec{E}_\perp$ lies in the surface plane, along the $y$-axis. For a 1s initial state and a $\pi^\ast$ or $\sigma^\ast$ vector final state orbital, the matrix element points in the direction of the TDM, $\tilde{O}$, and the intensity can be derived to be
where $A$ is the angle-integrated cross section and $\delta$ is the angle between the electric field vector $\vec{E}$ and the direction of the TDM, $\vec{O}$. From Eq. 5.19, we obtain the angular dependence of the resonance intensity associated with the $\vec{E}$ and $\vec{E}^\perp$ component as

$$I^\parallel = A(\cos^2 \theta \cos^2 \alpha + \sin \theta \sin^2 \alpha \cos^2 \phi + 2 \sin \alpha \cos \alpha \sin \theta \cos \theta \cos \phi)$$  \hspace{1cm} (5.20)

$$I^\perp = A(\sin^2 \alpha)$$  \hspace{1cm} (5.21)

For molecular adsorption geometry on substrates with three-fold or higher symmetry as we assumed for the attachment of the thiol at the three-fold hollow site of the Au(111) substrate, the $\cos^2 \phi$ term averages to 1/2 and the Eq. 5.20 and 5.21 simplify to

$$I^\parallel = A\left(\frac{1}{2} \left(3 \cos^2 \theta - 1 \right) \left(3 \cos^2 \alpha - 1 \right) \right)$$  \hspace{1cm} (5.22)

$$I^\perp = A\frac{\sin^2 \alpha}{2}$$  \hspace{1cm} (5.23)

Hence, the total intensity $I$ can be derived using Eq. 5.18 to be:

$$I = A \left[ \frac{P}{3} \left(1 + \frac{1}{2} \left(1 \cos^2 \theta - 1 \right) \left(3 \cos^2 \alpha - 1 \right) \right) + (1 - P) \frac{1}{2} \sin^2 \alpha \right]$$  \hspace{1cm} (5.24)

To determine molecular orientation, the intensity ratios are used instead of the absolute intensity, thus the constant $A$ can be neglected. If $P$ and $\theta$ are known, the intensity obtained from the measurement, the average tilt angle $\alpha$ of the TDM of the molecules on the surface can be determined.

### 5.2.4 Instrumentation

The NEXAFS measurements were carried out at the synchrotron storage ring MAX II at MAX-lab in Lund, Sweden, using the D1011 beamline. The details
of the beamline are previously described in the XPS section. The NEXAFS spectra were measured using a Multi Channel Plate (MCP) detector in a partial electron yield mode. The spectra were acquired at the C 1s, N 1s and Fe 2p absorption edge with retarding voltage -150, -300 and -450 eV, respectively. The incident angle of the light was varied from 90° (E-vector in the surface plane) to 20° (E-vector near the surface normal) to examine the molecular orientation. The raw NEXAFS spectra were normalized to the incident photon flux by dividing the spectrum by a spectrum of a clean, freshly sputtered gold substrate.

5.3 Infrared Reflection Absorption Spectroscopy (IRRAS)

5.3.1 Principles

Infrared Reflection Absorption Spectroscopy (IRRAS) is a powerful tool for characterization of the presence and structure of adsorbed molecular layers on metal surfaces. The molecular orientation can be studied by probing the vibration of the bond established between atoms in molecules. The spectral region can be presented in terms of wavelength as meters or wavenumber in cm\(^{-1}\). The latter unit is widely used in infrared spectroscopy.

In order to study the structure and the orientation of molecular adsorbates on metal surfaces, the IR radiation is incident on the surface at grazing angle, which maximizes surface sensitivity. In the reflection process, it is useful to consider the s- and p-polarized components of the radiation where p refers to parallel polarized radiation and s to perpendicular polarized radiation with respect to the surface normal. As shown in Figure 5.9, at the point of contact with the surface, the p-polarized radiation has a net combined amplitude that is almost twice that of the incident radiation via the summation of the incident electric vector, \(E_p\), and the reflected electric vector, \(E_{p'}\). However, for the s-polarized radiation, the incident and reflected electric vector \(E_s\) and \(E_{s'}\) undergo a 180 degrees phase difference to each other and so the net amplitude of the IR radiation with polarization parallel to the surface plane is zero. Thus only the p-component of the IR radiation may result a finite interaction with the surface and hence the only active vibrations that may be observed in IR spectra must have a component of the transition dipole moment (TDM) in the direction normal to the surface plane, this is referred to as the so called “surface selection rule” as expressed by
Figure 5.9. Schematic representation of the electric vector of the s- and p-polarized components of radiation incident on a metal surface. Primed and unprimed vectors refer to reflected and incident radiation, respectively.

\[ M = \frac{d\mu}{dR} \neq 0 \]  

(5.25)

where \( M \) is the transition dipole moment of the infrared active bond that has the dipole moment, \( \mu \), changes with the vibrational coordinate, \( R \).

The spectral intensity varies as a function of the square of the amplitude of the electric field vector, \( E \), and the transition dipole moment, \( M \), as expressed by

\[ I \propto |M \cdot E|^2 = |M|^2 \cdot |E|^2 \cdot \cos \alpha \]  

(5.26)

where \( \alpha \) is the angle between the electric field and the transition dipole moment. The maximum intensity is obtained when the \( M \) and \( E \) are parallel to each other.

In this thesis work, an isotropic sample was used as a reference system. In that sample, the molecules are pressed in KBr pellets. They are oriented randomly, thus the entire possible vibrational mode can be observed. The spectra obtained from this sample revealed the presence of chemical bonds contained in the molecules. For the sample with molecular adsorbates on the substrate, only vibrations of the bonds with TDM perpendicular to the surface show pronounced feature in the IR spectra. By measuring these two systems, information on the types of bonds and molecular orientation (relative to the surface) of the adsorbate layer can be obtained.
5.3.2 Instrumentation

The infrared absorption spectra were recorded using a Bruker IFS 66v/S spectrometer equipped with a wide-band liquid nitrogen cooled mercury cadmium telluride (MCT) detector and with the optics and sample compartment evacuated to 3 mbar. For measurements of the SAM spectra, incident polarized light at 80º (with respect to the surface normal) was used, so called “grazing angle incidence”. For each sample and reference a single beam spectrum, comprising of an average of 10000 scans, was recorded, and the absorption spectra were calculated as: \( A = -\log\left(\frac{I}{I_{ref}}\right) \). Clean gold samples were mainly used as references, but also gold samples with SAMs of alkanethiol (dodecane) and deuterated alkanethiol. The resulting spectra were manipulated by the interactive baseline correction utility in the OPUS software to remove large baseline fluctuations caused by interference and differences in reflectivity from sample to sample.

5.4 Contact Angle Measurements

5.4.1 Principles

Measurement of a contact angle of a liquid on a solid surface can be used to detect the presence of a molecular film and estimate the density of the molecular adsorbates on the surface. The contact angle can be observed by dropping a liquid, often water, onto a solid surface. When the drop spreads, the area of the liquid-vapor interface increases, the area of solid-vapor decreases and the area of solid-liquid interface also increases. In principle, the drop comes to rest when the energies that contribute to these changes in areas are balanced.

![Figure 5.10. A liquid drop on a solid surface.](image)

At equilibrium, the angle between the tangent on the surface of the drop in a point where the liquid-vapor interface meets the solid surface (see Figure 5.10),
the so called contact angle, $\theta$, is measured. The relationship between the contact angle and the free energy at the three interfaces (liquid-vapor, solid-vapor, and solid-liquid) is described by Young’s equation as follows

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL}$$  \hspace{1cm} (5.27)

where $\gamma_{LV}$, $\gamma_{SV}$, and $\gamma_{SL}$ are the liquid-vapor, solid-vapor, and solid-liquid surface free energy, respectively.

The interpretation of contact angle results relies on comparisons of values obtained from several systems rather than interpretation of absolute value obtained from only one system. By comparing the contact angle between a sample and a clean substrate, the difference in values can indicate the formation of the film. The packing density can be determined by comparison of the contact angle values with those for standard samples published in the literature. For example, a surface composed of methyl (CH$_3$) endgroups exhibit higher contact angles for water than those exposing methylene (CH$_2$) groups [47]. In a monolayer of alkanethiol, as the methyl groups at the outermost surface become less close packed, the number of exposed methylene groups increases. Consequently, the contact angle value is lower compared to densely packed layers which expose a high density of methyl groups at the surface.

### 5.4.2 Instrumentation

Static contact angle was measured with a Ramé-Hart 100 instrument using deionized water. The contact angle instrument consists of a sample stage to hold the substrate, a syringe to apply a droplet of liquid, a light source to illuminate the droplet, and a set of optics for magnifying the image on the screen. In this work, contact angles were measured by the following method. A drop of water with a fixed size is formed at the end of a needle and lowered to the surface. When the needle is raised, the drop falls from the tip to the surface.
5.5 Kelvin Probe Measurements

5.5.1 Principles

Kelvin probe is a technique that provides information on the work function of materials and the changes induced by surface modifications or treatments. The work function is the energy required to release the electron from the highest occupied level (Fermi level) to the vacuum. Note that the work function, $\phi$, is normally defined as a voltage. In the energy term, it becomes $e\phi$. A change in work function can be induced by the adsorption of the molecules on the surface and is associated with changes in the surface dipole layer or by charges on the surface (trapped for instance in surface states). Thus, the measurement yields information on the degree of charge reorganization upon adsorption which can in turn give evidence of coverage and orientation of adsorbates.

The principle of Kelvin probe is based on the measurement of the contact potential difference (CPD) between two materials as shown in Figure 5.11. When the surfaces of two materials with different work function are brought into electrical contact, electrons in the material with a lower work function will flow to the one with a higher work function until the Fermi levels align to each other (see Figure 5.11b). The two surfaces become equally and oppositely charged and a contact potential, $V_c$, is generated. The contact potential is equal to the work function difference of these two samples. It can be measured by applying the external backing voltage, $V_b$, to both samples until the surface charges disappear as illustrated in Figure 5.11c. At this point the external backing voltage potential equals the contact potential, with opposite sign.

In practice, the two materials form a parallel plate capacitor where a reference plate (or a tip) is vibrating above a sample plate. As a tip vibrates, a varying capacitance is produced as expressed by

$$C = \frac{Q}{V} = \varepsilon \frac{A}{d} \quad (5.28)$$

where $C$ is the capacitance, $Q$ is the charge, $V$ is the potential across capacitor which is equal to $V_b + V_c$, $\varepsilon$ the permittivity of the dielectric between the plates.
Characterization of SAMs

(usually air), $A$ the surface area of the capacitor plates (or, in practice, the area of the reference probe, since the sample is larger) and $d$ is the spacing between the plates which varies with time as

$$d = d_0 + d_1 \sin(\omega t)$$  \hspace{1cm} (5.29)

where $\omega$ is the angular frequency of the generated vibration.

![Figure 5.11. Schematic representation of energy diagram for a Kelvin probe measurement. a.) Two conducting materials with different work functions, b.) The two materials are brought into electrical contact, and c.) The backing potential, $V_b$, is applied to compensate the surface charges and measure the contact potential, $V_c$.](image)

The current that is generated by the vibration is then given by

$$I = \frac{dQ}{dt} = -eAV - \frac{d_1 \omega \cos(\omega t)}{\left[d_0 + d_1 \sin(\omega t)\right]^2}$$  \hspace{1cm} (5.30)

It can be seen from Eq. 5.30 that the current vanishes when the total potential, $V = V_b + V_c$, goes to zero. This occurs when the applied backing voltage is equal to the contact potential between the tip and the sample.

The change in work function, $e\Delta\phi$, is then related to the measured contact potential by

$$e\Delta\phi = e\phi^{\text{ref}} - e\phi^{\text{ads}}$$  \hspace{1cm} (5.31)

where $e\phi^{\text{ref}}$ and $e\phi^{\text{ads}}$ are the work function of the reference and the sample with the adsorbates, respectively. Since the measurement determines the
contact potential which is related to the work function of the probe tip, an external reference, usually a bare substrate must be used to determine the work function change due to the surface modification with the adsorption. Just like for contact angle measurement, this method is usually not used to determine absolute values but to evaluate the difference relative to a standard sample.

For a surface with adsorbed molecules, the change in work function arises from a dipole layer at the surface. The dipole layer may be modelled as a parallel plate capacitor. The change in work function is related to the surface dipole moment, \( \mu \), by

\[
e\Delta \phi = \frac{e \Delta \mu}{\varepsilon_0 A}
\]

where \( A \) is surface area per adsorbed molecule, \( e \) is an electron charge, \( \varepsilon_0 \) is the permittivity of free space, and \( \Delta \mu \) is the component of the dipole moment normal to the surface. Consider the change in work function of the gold surface upon the adsorption of alkanethiols as shown in Figure 5.12, assuming alkanethiols are oriented nearly perpendicular to the surface.

\[\text{Figure 5.12. Schematic diagram of the two layer model for alkanethiol SAM on gold.}\]

The contribution to the work function changes can be considered to comprise of two dipole moments: First, an induced dipole moment, \( \mu_1 \), which arise from a charge transfer between the metal surface and the molecule, occurring upon the chemisorption of the SAMs (e.g. the formation of the \( \text{S-Au} \) bond). Second, the intrinsic dipole moment of the molecule, \( \mu_2 \), (e.g. the dipole moment of a hydrocarbon chain). The change in work function is simply given by

\[
e\Delta \phi = \frac{e}{\varepsilon_0 A} \left[ \mu_1 + \mu_2 \right]
\]
The interaction between thiolate and gold induces a positive dipole in which the dipole moment point from the Au to the S atom [134, 135]. On the other hand, the intrinsic dipole moment of hydrocarbon chain is negative and point from the CH₃ tailgroup at the surface to S atom. Sita and Ulman observed the work function change induced by alkanethiol SAMs on Au(111) about -300 mV (hexadecanethiol) and -600 mV (dodecanethiol), respectively. The experimental results show a negative change in work function of the gold surface upon the adsorption of alkanethiol indicating that the second dipole layer formed from hydrocarbon chains has a dominant contribution to the total dipole moment on the surface [136, 137]. Thus the adsorption of alkanethiol decreases the work function of the gold surface.
CHAPTER 6

Summary of the Papers

Self-assembly process has become a widely used technique for fabricating a well-defined and ordered molecular layer. The layers that formed by this process, so-called self-assembled monolayers (SAMs) are built up from molecular scale by chemisorption of the molecules on a solid surface. The molecules can be tailor-made with desired functionalities. Thus, the layer properties are tunable by the structure of the molecules. A dense and stable film as provided by self-assembly is attractive for applications in corrosion protection, lubrication, wetting control, catalysis, molecular electronics, etc. A high molecular order in SAMs makes them an interesting as components in novel electronic devices.

The structure and quality of the SAMs are strongly dependent on the structure of the molecular constituents, the substrate and the self-assembly process. In this work, the influences of the molecular constituents and the preparation methods on their structure have been investigated using high-resolution X-ray photoemission spectroscopy (HRXPS), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, Infrared reflection absorption spectroscopy (IRRAS), contact angle measurements and Kelvin probe measurements. Important questions in this work have been: (a) which molecules with a specific, desired functionality, can form a well-ordered SAM and (b) how does the various constituents (headgroup, backbone and tailgroup) and different preparation schemes influence the growth and the structure. Consequently, the effects of varying the size of the backbone, varying the headgroup, inclusion of a bulky tail group, different protection of the headgroups and mixed molecular layers have been investigated.
In paper I, II and IV, several SAM systems that were formed from molecules that could be used as a new material in molecular electronic devices, such as oligo(phenyleneethynylene) (OPE) derivatives, porphyrin-functionalized OPEs, and ferrocene-terminated alkanethiol (FeC_{11}), were studied. Self-assembled monolayers of tetraphenylporphyrins were studied in paper III. Such SAMs are interesting for catalysis applications. Information about geometrical and electronic structure of the SAMs obtained from these studies is intended to form a basis for developing new types of functionalized monolayers.

**Paper I**

**Characterization of Self-Assembled Monolayers of Oligo(phenyleneethynylene) Derivatives of Varying Shapes on Gold : Effect of Laterally Extended π-Systems**

A series of three oligo(phenyleneethynylene), OPE, derivatives 1, 2, and 3 (see figure below) were synthesized and self-assembled monolayers (SAMs) of these molecules were prepared on Au(111) surfaces.

![Chemical structures](image)

The effect of the molecular structure on the binding/adsorption, orientation and packing density of these three SAMs was studied by infrared reflection spectroscopy, spectroscopic ellipsometry, contact angle measurements, high resolution X-ray photoelectron spectroscopy (HRXPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. The NEXAFS spectroscopy results revealed that the increasing π-system of the middle aryl moiety, from benzene to naphthalene to anthracene resulted in lower packing density and larger inclination. SAM 1 showed a well-ordered and densely packed layer with almost upright standing molecules. This was deduced from thickness,
IR spectra, HRXPS results and angular dependence of NEXAFS resonances. The structure of the SAMs formed from 2 and 3 is affected by the intermolecular interaction and the structure template provided by the substrate, which can not provide a commensurate \((\sqrt{3} \times \sqrt{3})R30^\circ\) packing as in SAM 1. The average tilt angles of the molecular axis derived from NEXAFS data were estimated to be about 30°, 40° and 42° relative to the surface normal for SAM 1-3, respectively. However, the information obtained from NEXAFS spectroscopy at molecular tilt angles close to 43º (TDM tilted ~55º) is limited. Therefore, from the present results, the conclusion whether molecules 2 and 3 are oriented with a large inclination in a well-ordered SAM or with a random arrangement in a poorly defined monolayer can not be drawn.

Paper II

A Spectroscopic Study of Self-Assembled Monolayers of Porphyrin-Functionalized Oligo(phenyleneethynylene) on Gold: the Influence of the Anchor Moiety

Porphyrin-functionalized OPEs with different anchor groups: (1) an acetyl-protected thiol \((-S-COCH_3)\), (2) an acetyl-protected thiol with methylene linker \((-CH_2-S-COCH_3)\), and (3) a trimethylsilylene-thynyl-group \((-C≡C-Si(CH_3)_3)\) were synthesized and corresponding molecular layers were prepared on Au(111) surfaces. HRXPS and NEXAFS were utilized to investigate the chemical, structural and packing properties of these layers. The combined results show that the properties of the respective molecular layers are strongly affected by the nature of the anchor group. The adsorbate 1 (the anchor does not contain the methylene linker between the sulfur and the OPE moiety) forms a high-quality SAM. SAM 1 shows a well-ordered and densely packed structure with an almost upright orientation of the molecules. The methylene linker, which is inserted between the sulfur and the OPE moiety in adsorbate 2, affects the molecular orientation of the molecular layer. Earlier studies have been shown that the methylene linker improved the layer structure in oligophenyl SAMs, adsorbate 2 was expected to form also a highly ordered and densely packed SAMs. Instead, adsorbate 2 forms a film of highly inclined molecules and low packing density even though the molecules bind to the Au surface with a similar S-Au bond as found in SAM 1. Finally, adsorbate 3, with trimethylsilane anchor, was found to bind to the gold surface but the resulting molecular layer has poor quality. The film comprises of strongly inclined
molecules and significant disorder. These results suggest that the anchor group plays an important role on the quality of OPE-based molecular layers.

**Paper III**

**Molecular Orientation of Thiol-Derivatized Tetraphenylporphyrin on Gold Studied by XPS and NEXAFS**

Tetraphenylporphyrins with four thioacetyl linkers were immobilized on a gold surface via thiolate-gold bonds. Two different preparation routes were investigated and the choice was found to affect the molecular structure of the tetraphenylporphyrin layer. In the first preparation route, the protected scheme, the molecule with thioacetyl groups was used directly for adsorption on the Au(111) surface. The acetyl protective groups were expected to be removed during adsorption and the released thiolate (S-) binds to the gold surface. In the second route, the deprotected scheme, the acetyl groups in the linkers were removed in order to form thiols (SH) before molecular adsorption took place. The resulting films from both preparation methods were investigated by XPS and NEXAFS. XPS revealed that the porphyrins in the film that was prepared by the protected scheme bind to the gold surface via two thiolate-gold bonds per molecule, whereas porphyrin in the film prepared by the deprotected scheme formed three thiolate-gold bonds to the surface. Angle-resolved XPS results indicate that the unbound linkers in both systems are most likely pointing outward, away from the surface. The orientation of the porphyrin ring on the surface was studied by NEXAFS. The results imply that, for the protected system, the porphyrin rings are oriented with their normal axis tilted ~50º with respect to surface normal. For the deprotected systems, the porphyrin ring is oriented more parallel to the surface with the normal axis tilted ~38º with respect to surface normal. Moreover, the deprotected systems have a higher order than the protected systems, as indicated by the more pronounced angular dependence in the NEXAFS spectra. The effect of the metal core in the porphyrin on the molecular orientation was also studied. By comparing XPS and NEXAFS results of the metallo- and free-base porphyrin, we could observe that the core metal has a very small influence on the molecular orientation of the film. The results from this fundamental study can be used as a basis for application in catalysis: the efficiency of catalysts can be enhanced if the structure and geometry of the molecules on the surface can be controlled.
Paper IV

Structure Investigation of Mixed Self-Assembled Monolayer of Ferrocene-Terminated and Unsubstituted Alkanethiols on Gold

Mixed SAMs of ferrocene-terminated and unsubstituted alkanethiols (FcC_{11} and C_{10}, respectively) were prepared on gold surfaces. The structure and electronic properties of these SAMs was then characterized by HRXPS, NEXAFS and Kelvin probe. The results show that the orientation and degree of order of the SAM constituents are significantly dependent on the preparation scheme. Moreover, the fraction of the FcC_{11} molecules in the mixed SAMs can be controlled. The mixed FcC_{11} and C_{10} SAMs were prepared from mixed solution (FcC_{11} + C_{10}) and by subsequent immersion (first in C_{10} solution with variable time from 3, 30 to 150 min, then in FcC_{11} solution for 24 h). The SAMs prepared from mixed solution exhibits a high quality and a phase separation between the FcC_{11} and C_{10} species. The fraction of FcC_{11} molecules in the SAM was found to be 62%, suggesting favorable adsorption kinetics of the FcC_{11} molecule. The ferrocene moieties are oriented more upright than the aliphatic chains, caused by the interaction between the ferrocene moieties. For the SAMs prepared by subsequent immersion schemes, the FcC_{11} molecules were diluted into the C_{10} matrix. The HRXPS results suggest that the FcC_{11} molecules in these SAMs are distributed in the C_{10} matrix, which is different from the case of SAM prepared from mixed solution. The portion of FcC_{11} molecules in these mixed SAMs increases with decreasing the immersion time in C_{10}. The values vary from 35-55%. The degree of order in the SAMs increases with increasing the immersion time in C_{10} solution. In particular, the orientation of the ferrocene moieties is tilted with an average angle close to that of the aliphatic chains.

The effect of these SAMs on the work function of the gold surface was studied by Kelvin probe. The adsorption of C_{10} was found to decrease the work function of the gold surface while the adsorption of FcC_{11} increases this value. The work function of the gold surface increases with increasing the fraction of FcC_{11} in the mixed SAMs. Hence, it is possible to fine-tune the work function of the gold surface by varying the fraction of the adsorbate molecules. In this study, the work function of the gold surface could be varied over the range of 400 mV by varying the fraction of the FcC_{11} in the mixed SAMs.
Supplementary Results

7.1 Studies of Trimethylsilane as an Anchor Group for SAM Formation of OPE Derivatives on Gold

Trimethylsilane (TMS) was chosen as an alternative anchor group apart from thiol for the SAM formation of OPE derivatives on Au(111). Silanes are usually used to form SAMs on hydroxylated surfaces, such as SiO$_2$ [33]. The previous studies by Fichou and co-workers reported that the silane anchor group can be used to form SAMs of unsaturated carbon chain on gold [94, 95]. They proposed that it required the ethynylene group next to the TMS in order to form a Si-Au bond where the molecular moiety is standing upright on a pentacoordinated Si atom [94, 95] as illustrated in Figure 3.4. The hypothesis presented by these authors is that Si being directly connected to an electron-withdrawing group, such as the C≡C triple bond, interacts with an electron-donating atom such as gold, which lead to pentacoordinated silicon [94-97]. The OPE with thiol anchor group was found to form a SAM on Au(111) with a slight cant and high order [138]. With the alternative TMS anchor group, we expected

![Figure 7.1](image)

**Figure 7.1.** Drawing of the OPE SAMs with the anchors 1) ethynylene-TMS, 2) vinylene-TMS, and 3) phenylene-TMS.
to form SAMs with an upright orientation of the OPE moieties in accordance to the pentavalent structure of the Si-Au bond. Therefore, OPEs with the TMS anchor group were synthesized and used to prepare SAMs on Au(111). In particular, we investigated the influence of the unsaturated ethynylene group next to the TMS on the binding by exchanging this group with vinylene and by removing it and making direct bond to the phenylene of OPE. In Figure 7.1, the three different motifs that were used as the anchors in this study are shown: 1) ethynylene-TMS, 2) vinylene-TMS, and 3) phenylene-TMS.

![HRXPS spectra](image)

Figure 7.2. Si 2p HRXPS spectra for layers of molecules 1-3 acquired at the photon energy 160 eV.

SAMs of OPE attached to a gold surface via the TMS anchor groups were prepared by the immersion of the Au(111) substrates into a 1 mM solution of the desired molecule in dry THF. The SAMs were kept at the room temperature in the absence of light for 20 h. After that, they were thoroughly rinsed with THF, dried with nitrogen and stored in argon. After a day, they were characterized by HRXPS and NEXAFS.

SAMs formed from molecules 1-3 on Au(111) surfaces were characterized by HRXPS to probe the bonding nature of the different TMS anchor groups to the substrate. The Si 2p spectra are presented in Figure 7.2. The spectrum of the layer formed from OPEs with ethynylene-TMS anchor group (1) shows a
strong Si 2p signal. The emission peak of this sample consists of a spin-orbit split doublet (0.6 eV) with a Si 2p\(3/2\) binding energy of 101.27 eV and fwhm of 1.03 eV. The splitting cannot be resolved due to the large fwhm. The peak at this position is assigned to the Si-C bonds in the TMS group [139, 140]. For layers formed from OPE with vinylene- and phenylene-TMS, 2 and 3 respectively, very broad and weak Si 2p signals were observed, indicating very small amounts of Si on the surfaces.

The following conclusion can be drawn from these results: the Si 2p peaks observed from layer 1 originate from the corresponding molecules bound to the surface. The peak position at 101.27 eV, which corresponds to the Si-C bonds in the TMS anchor group, indicates that the Si-CH\(3\) bonds are not broken during the adsorption. If any of the Si-CH\(3\) bonds were broken, the Si 2p spectra should have a contribution at lower binding energy. A Si 2p peak at \(\sim\)100 eV was observed in the alkylsilane (C\(_n\)H\(_{2n-1}\)SiH\(_3\)) SAMs on Au, in which all three Si-H bonds are broken during the SAM formation and then Si atoms form covalent bonds to the gold surface [141, 142]. No peak at \(\sim\)100 eV is observed in our spectra. The large fwhm that observed in this layer could be a result of a structural inhomogeneity of the molecules on the surface.

Apart from the investigation of the Si 2p core level, the interaction of the anchor group with the Au surface can also be examined by probing the Au 4f core level. The Au 4f\(7/2\) spectra from a clean Au substrate and from 1-3 on Au(111) are shown in Figure 7.3. In this Figure, the Au 4f\(7/2\) spectrum for the clean Au surface is deconvoluted into a bulk and a surface component. The binding energies of these two components are 83.95 eV and 83.62 eV, respectively, and the fwhm is 0.40 eV for both components. Upon the interaction of the molecules with the substrate, the electrons from the Au surface have to participate in the bonding that results in the shift of the Au surface peak to a higher binding energy. The shift is observed in the Au 4f spectra of 1 and 2, which show one emission peak at a binding energy of about 83.95 eV and a slight increase in the fwhm by about 0.02-0.03 eV, compared to that for the clean Au. The slightly larger fwhm values may be caused by a partial overlap of the shifted surface-component with the bulk component. A larger fwhm value was observed in the spectrum of 3 (0.48 eV) which could mean that the substrate is presumably covered by contaminants but not the intended molecules. The different intensities of the Au 4f line for the different layers are consistent with the Si 2p analysis above. The low intensity of the Au 4f emission
for 1 is caused by the attenuation of the photoelectron by the molecular overlayer, while the higher Au 4f intensities for 2 and 3 indicate less dense, or absence of overlayer. This shows that molecule 1 forms the most dense overlayer.

![HRXPS spectra](image.png)

**Figure 7.3.** Au 4f\(_{7/2}\) HRXPS spectra of a clean Au surface and molecules 1-3 acquired at the photon energy 350 eV. The binding energies of the bulk and surface components of the clean Au sample and the fwhm of all the peaks are indicated.

The C 1s spectra of 1-3 are shown in Figure 7.4. For 1, the spectrum exhibits main peaks at binding energies 284.76 eV. This peak is assigned to the aromatic backbone. In addition, a minor peak at higher binding energy of about 286 eV is observed in the spectrum. This shoulder has previously been observed for aromatic thiolate SAMs and was assigned to a shake-up process [43, 138]. By comparing the C 1s intensities for 1, 2, and 3, which all have the same molecular moiety but different anchor group, the highest intensity was observed for 1. The higher intensity of the C 1s emission, the Si 2p peak, and the lower intensity of the Au 4f emission for 1 indicate that a film of higher packing density was obtained from the molecule with an anchor group composed of ethylene-TMS group compared to the other two molecules.
Figure 7.4. C 1s HRXPS spectra of layer 1-3 acquired at the photon energy 350 eV.

The C K-edge NEXAFS spectra of SAMs formed from molecules 1-3 are shown in Figure 7.5. The spectra were acquired at an incidence angle of 55°. At this particular angle, the measured resonance intensity is independent of the molecular orientation [133]. The NEXAFS spectrum of 1 shows the characteristic absorption resonances of phenyleneethynylene moieties as observed in the NEXAFS spectrum of OPE with thiol-derived anchor [138]. The dominant peak at ~285 eV corresponds to a transition from C 1s to the lowest unoccupied antibonding π* orbital, the π* resonance. This peak is accompanied by a similar transition to higher antibonding π* orbitals, the weaker π*, at ~288.7 eV. The broad features at ~293 and 302 eV are associated with σ* resonances, i.e. excitation of C 1s electrons into unoccupied antibonding σ* orbitals. Characteristic features of the phenyleneethynylene moieties are also observed in the spectrum of the SAM formed from molecule 2. But this film contains some contamination as indicated by the peak at about 288 eV which is assigned to the π* resonance of C=O. No characteristic absorption resonance of phenyleneethynylene moieties can be discerned in the spectrum of 3. Thus, the molecule 3 does not bind to any appreciable extent to the Au surface. The surfaces of sample 3 are likely to be passivated by other organic compounds, such as solvent residues, and carbon monoxide. In conclusion, strong absorption with the characteristic features shown by OPEs
was observed for 1. The strength of these features is lower for 2. Further, none of these features can be discerned in the spectra of 3. This suggests that 1 forms a layer of much higher packing density than the other systems.

![NEXAFS: C1s Spectra at 55°](image)

**Figure 7.5.** C K-edge NEXAFS spectra acquired at an incidence angle of 55° for SAMs formed from molecules 1-3.

The structure of system 1 was also studied by angular dependent NEXAFS. The dependence of the absorption resonance intensity on the X-ray incidence angle, i.e. linear dichroism, could be used to estimate the orientation and ordering of the film. The differences spectrum between a spectrum with the light incident at 90 and at 20° is shown in Figure 7.6.
Figure 7.6. The difference of the NEXAFS spectra of SAMs 1 taken at the incidence angles 90° and 20°. The dashed line corresponds to zero difference. The intensity scale is the same as Figure 7.5.

The difference spectrum exhibits a weaker angular dependence compared to the OPE with thiol anchor group [138]. In particular the spectrum shows a negative signal at π* resonances. Such a feature observed for 1 can be interpreted in either of two ways: (a) the molecules on the surface are inclined with the molecular axis strongly tilted from the surface normal with the tilt angle of the transition dipole moment (TDM) close to 55° (considering equation 5.24 in Chapter 5, if the tilt angle of the TDM is close to the magic angle ~55°, the resonance intensity has a small dependence on the X-ray incidence angle θ), or (b) the molecules have low orientational order. The derived value for the average tilt angle of the π* TDM for 1 is 53° which is very close to the magic angle. Therefore, it is not possible to distinguish between a well-ordered or disordered film for 1 by using NEXAFS. Nevertheless, if the film is well oriented, the molecules are not in the upright orientation as we expected, because in that case the difference spectra should show a positive signal for the π* resonance.

When comparing the different proposed anchor groups all the analytical methods hint at the same conclusion. The ethynylene-TMS anchor (molecule 1) gives the best interaction and forms a bond to the gold surface. The vinylene-TMS anchor (molecule 2) might bind to the surface, but less strongly than 1. The NEXAFS spectra of 2 also show the resonance feature of the OPE, but the coverage of the molecules on the surface is very low. This indicates that the molecule-substrate interaction for 2 is not as strong as for 1. The signal is almost not observable in the Si 2p HRXPS spectra for 3. Neither is the characteristic feature of the OPE moiety observed in the NEXAFS spectra. The very small amount of Si may come from traces of physisorbed molecules.
Supplementary Results

on the surface. Thus, the phenylene-TMS structure does not support bonding to Au(111) surfaces.

The HRXPS results support the assumption from the previous publications [94, 95] that the ethynylene group next to TMS anchor is involved in the binding of the molecule to the Au(111) surfaces. But NEXAFS results show that the geometry of the molecule on the surface is contrary to their proposal. If the molecules were standing upright on a pentacoordinated Si atom, one would expect to see the evidence of this in the NEXAFS measurements, which we do not. Perhaps the configuration of the silicon is different for our OPE compared to the mostly aliphatic molecules studied earlier. The larger flexibility of the aliphatic molecules studied by Fichou and co-workers might allow them to compensate for the tilt induced by the anchor group and thereby form less tilted SAMs. For the bonding, we speculate that the ethynylene-TMS group binds more strongly than the vinylene-TMS group because the ethynyl group is more electron withdrawing, causing a stronger interaction with the electron donating gold surface.

In conclusion, OPE based adsorbates have for the first time been attached to a Au(111) surface by the ethynylene-TMS anchor group. Two additional TMS-based motifs for attachment to Au(111) substrates have been evaluated with respect to their SAM-forming abilities. Of these three, the ethynylene-TMS group is the only one that forms a Si-Au bond, as evidenced by HRXPS, and NEXAFS analysis. Also the vinylene-TMS group interacts with the gold surface and binds the adsorbates to it, but most probably only support formation of films of low density and with a low degree of order. This cannot be considered a SAM. The third group, the phenylene-TMS where the TMS group was directly attached to the aromatic molecular wire backbone, did not attach to the surface at all.
Bibliography


Structure of Self-Assembled Monolayers on Gold Studied by NEXAFS and Photoelectron Spectroscopy

Self-assembled monolayers (SAMs) provide well-defined and ordered films of molecules spontaneously chemisorbed on a surface. By designing molecules with desired functionalities, such molecular films can be interesting for a range of applications from molecular electronics to catalysis. Important parameters for SAM applications are the film structure and quality, which are dependent on the structure of molecular constituents, the substrate, and the self-assembly process. In this work, SAMs on Au(111) of a variety of functionalized molecules, with thiol and silane headgroups, have been studied using high-resolution X-ray photoelectron spectroscopy (HRXPS), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, Infrared reflection absorption spectroscopy (IRRAS), contact angle measurements, and Kelvin probe measurements. In particular, the effects of varying the size of the backbone, varying the headgroup, inclusion of a porphyrin tailgroup, deprotection method of the headgroups, and formation process of mixed molecular layers have been investigated.