Somsakul Watcharinyanon

Characterization of Self-Assembled Monolayers of Oligo(phenyleneethynylene) Derivatives on Gold

Karlstad University Studies
2007:18
Characterization of Self-Assembled Monolayers of Oligo(phenyleneethynylene) Derivatives on Gold
Somsakul Watcharinyanon. *Characterization of Self-Assembled Monolayers of Oligo(phenyleneethynylene) Derivatives on Gold*

Licentiate thesis

Karlstad University Studies 2007:18
ISSN 1403-8099
ISBN 978-91-7063-121-4

© The author

Distribution:
Karlstad University
Faculty of Technology and Science
Physics
SE-651 88 Karlstad
SWEDEN
Phone +46 54 700 10 00

www.kau.se

Printed at: Universitetstryckeriet, Karlstad 2007
Abstract

Oligo(phenyleneethynylene) (OPE) molecules are a class of fully conjugated aromatic molecules, that attract attention for their application as “molecular wires” in molecular electronic devices. In this thesis work, self-assembled monolayers (SAMs) formed from a variety of OPE derivatives have been studied. The chemical properties, structure, and packing density of the SAMs have been characterized utilizing techniques such as high-resolution X-ray photoemission spectroscopy (HRXPS), near-edge X-ray absorption fine structure spectroscopy (NEXAFS), Infrared reflection absorption spectroscopy (IRRAS), contact angle measurements, and atomic force microscopy (AFM).

In a first study, three OPE-derivatives, with benzene, naphthalene and anthracene, respectively, inserted into the backbone, and an acetyl-protected thiophenol binding group were found to form SAMs on Au(111) substrates with lower molecular surface densities and larger molecular inclination as the lateral π-system increases.

In a second study, porphyrin was introduced as the endgroup to the wire-like OPE molecule. The purpose was to obtain well-organized and functionalized surfaces with optical and redox properties. Three porphyrin-functionalized OPEs with different binding groups, an acetyl-protected thiophenol, a benzylic thiol, and a trimethylsilylethynylene group, were found to form molecular layers on gold surfaces with differences in structure and degree of order. The molecules with the acetyl-protected thiophenol binding group were found to form a high quality SAM, contrary to the other two. This SAM exhibits a well-ordered and densely packed layer.

This study gives rise to a better understanding of SAM formation of OPE derivatives, and will form a base for further investigations of charge transport properties of these molecular films, which is of interest for applications in molecular electronic devices.
Acknowledgements

I would like to express my gratitude to my supervisors Lars Johansson and Ellen Moons for their advice, support and guidance from the early stage of this research work. I am very grateful to their patience and kind assistance.

I would like to thank Michael Zharnikov and Andrey Shaporenko for collaborating in the experiments at Max-lab and sharing their valuable knowledge with me.

I would also like to thank Daniel Nilsson, Jerker Mårtensson, Bo Albinsson and Mattias Eng for the chemical synthesis, FTIR measurements and fruitful discussion in the chemistry point of view.

I wish to thank my friends, Rodrigo and Pon for a good and an enjoyable time both in a scientific and a realistic word.

A very special thank to my colleagues at the department, especially my roommate, Cecilia for all the helps and practicing my Swedish.

Most importantly, I would like to thank my family, my parents and my lovely brothers for their love and always support.

Last, but not least, I would like to thank Tue and Matilda for their love and making my life fulfilled.

Somsakul
Karlstad, April 2007
List of publications

The thesis is based on the following papers

Paper I  *Characterization of Self-Assembled Monolayers of Oligo(phenyleneethynylene) Derivatives of Varying Shapes on Gold: the Effect of Laterally Extended π-Systems*
Accepted for publication in *Langmuir*

Paper II  *HRXPS and NEXAFS Study of Self-Assembled Monolayers of Porphyrin-Functionalized Oligo(phenyleneethynylene) on Gold: the Influence of the Binding Group*
Manuscript

Related paper not included in this thesis

Paper III  *Characterization of Self-Assembled Monolayers of Oligo(phenyleneethynylene) Molecular Wire Attached to Gold via a Trimethylsilylamine Anchor Group*
Manuscript
Contents

Abstract i
Acknowledgements iii
List of publications v
Chapter 1: Introduction ................................................................. 1
Chapter 2: Self-Assembled Monolayers (SAMs) on Gold ................. 4
  2.1 Concept of Self-Assembly ....................................................... 5
  2.2 SAMs of Thiolates on Gold .................................................... 6
  2.3 Oligo(phenyleneethynylene) (OPE) ....................................... 9
    2.3.1 The sulfur headgroup .................................................. 10
    2.3.2 The silane headgroup .................................................. 11
  2.4 The Porphyrin Functionalized OPE ....................................... 12
Chapter 3: Experimental Methods ................................................ 14
  3.1 Sample Preparation ............................................................ 14
  3.2 Characterization Techniques ............................................... 15
    3.2.1 X-ray Photoelectron Spectroscopy (XPS) ......................... 15
      • Principles ........................................................................... 15
      • Chemical shift, molecular relaxation and other core spectra ... 18
      • Spectral Quantification .................................................... 20
      • Instrumentation ............................................................. 22
    3.2.2 Near-Edge X-ray Absorption Fine Structure (NEXAFS) ....... 23
      • Principles ........................................................................... 23
      • Theory ............................................................................... 25
      • Angular Dependence of NEXAFS resonance intensity ......... 27
      • Instrumentation ............................................................. 31
    3.2.3 Infrared Reflection Absorption Spectroscopy (IRRAS) ...... 32
      • Principles ........................................................................... 32
      • Instrumentation ............................................................. 34
    3.2.4 Contact angle measurement ............................................ 34
    3.2.5 Atomic Force Microscopy (AFM) ..................................... 36
Chapter 4: Summary of Papers ..................................................... 39
Chapter 5: Future Plans ................................................................. 42
Bibliography .............................................................................. 44
Paper I
Paper II
Chapter 1

Introduction

The electrical properties of organic molecules have attracted much attention due to the continuous search for new approaches for further miniaturization of electronic devices. According to Moore’s law, the number of transistors on an integrated circuit is doubling every two years [1]. If this trend is to continue, the size of the transistor will soon reach the scale of atoms or molecules. Consequently, the silicon-based technology will suffer because of physical and economic limitations. Molecular electronic is one of the promising technologies which would be an alternative. The concept of molecular electronics is the use of single molecules or arrays, or layers of molecules for the fabrication of electronic components such as wires, switches, and storage elements. The molecules can be designed and tailor-made by chemical synthesis. Their physical properties are tunable by their structure. In particular, a very small size of the molecules makes them ideal to fabricate a high-density electronic device.

In 1974, Aviram and Ratner proposed that functionalized aromatic molecules could be used as new materials for electronic devices [2]. Over two decades later, the first prototypes of the respective devices have been demonstrated [3-6]. Reed and co-workers reported on measurements of the conductance of a single molecule [3]. Since then, this field has grown rapidly. Several functionalized molecules that exhibit the electronic properties have been synthesized and widely studied in recent years [7-9]. For example, by using light, or electricity to trigger and switch the properties, such as a conductance, of the molecule a molecular switch was formed [10-13]. If the difference in conductance between the two states is sufficiently high and stable, this type of molecule could be used as storage element. Dithienylcyclopentenes [10] and rotaxanes [11, 14] are examples of molecules in this class. The basic electronic function is a wire. Transferred to a molecular scale, a molecule with a rod-like structure that transports electrons from one end to the other [15] is of particular interest. Oligo(phenyleneethynylene) (OPE) derivatives are fully
conjugated molecules. The benzenes and alkynes in the OPE molecule contain delocalized states in the form of π-bonds [16] which are beneficial for electron transport. This particular type of molecule has recently attracted much attention because of the high electron conductivity of the phenyleneethynylene backbone, which makes the molecule applicable as molecular wire in molecular electronic devices. In addition, OPE molecules with nitro, amino, or fluoro groups added on the central ring exhibit negative differential resistance. [4, 5, 12, 13, 17]

The function of the molecules can be accessed by attaching the molecules to an electrode. To contact and manipulate a single molecule is still a challenge, therefore the research was focused on single monolayer films for the first efforts. To immobilize molecules on an electrode, can be achieved by using the self-assembly process. In this process, the molecules spontaneously arrange themselves on a surface until finally a completely ordered monolayer is formed, a so-called self-assembled monolayer (SAM). Herein we focus on the SAM of OPE molecular wire systems. The OPE derivatives attach to the electrode, in this case, a gold surface, at an available binding site via an anchor group. In this work, the effects of the anchor group and the structure of the OPE derivatives on the SAM formation were investigated. In addition, SAMs formation of a functionalized OPE molecule with an optical probe, such as porphyrin, was also studied. Such a monolayer is of interest for applications in optoelectronic devices, such as solar cells [18] or sensors [19-21].

This research work is part of a collaboration between The Materials Physics group at Karlstad University, Organic Chemistry at the Department of Chemistry and Bioscience and Department of Applied Semiconductor Physics at Chalmers University of Technology. The purpose is to develop new functional organic molecular materials, characterize and understand the structure and electronic properties of molecular layers. In particular, the characterization of SAMs has been described in this thesis. We have investigated the monolayers formed from different derivatives of OPE on gold (111) surfaces. In order to understand how the electrons are transported through the monolayer, it is necessary to have a firm knowledge of the molecular structure, orientation and packing density in the SAMs. Thereby, a set of complementary experimental techniques such as High-Resolution X-ray Photoelectron Spectroscopy (HRXPS), Near-Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS), Infrared Reflection Absorption
Spectroscopy (IRRAS), contact angle and Atomic Force Microscopy (AFM) are used. An overview of the self-assembly process and the molecules used in the work is given in Chapter 2. Chapter 3 describes the experimental techniques. The summary of the work is found in Chapter 4, while Chapter 5 discusses the future plans relevant to this research.
Chapter 2

Self-Assembled Monolayers on Gold

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 [22]. At the end of the 19th century, monolayers of insoluble liquid at air-water interfaces were prepared and studied by Pockels [23-25], followed by the work of Rayleigh [26], Hardy [27], and Devaux [28]. Later in 1917, Langmuir published a systematic study of monolayers of amphiphilic molecules on a water surface [29]. This monolayer system was named after Langmuir. In 1935, Blodgett [30] carried out a study on the deposition of fatty acids onto a solid substrate from a film existing on the air-water interface. Such films are called Langmuir-Blodgett film. A systematic study related to self-assembled monolayers (SAM) was performed later by Bigelow in 1946 [31]. He published the preparation of monolayers by adsorption of molecules from solution onto a clean metal substrate. Kuhn used this method to form a monolayer of a chlorosilane derivatives on glass [32]. Later on, Nuzzo and Allara discovered that SAMs of alkanethiolates on gold can be prepared by adsorption of dialkyl disulfide from a dilute solution [33]. Several SAMs systems have been investigated so far. These include:

- organosilane (R-SiCl₃, R-SiH₃, R-Si(OCH₃)₃) on hydroxylated surfaces (SiO₂, Al₂O₃, glass, etc.) [34-36],
- alkanethiol (R-SH) on gold, silver, copper and GaAs [37-40],
- dialkyl sulfides (RSR) and disulfides (RS-SR) on gold [33, 41],
- carboxylic acids on aluminum oxide and silver [42, 43].
2.1 Concept of Self-Assembly

Self-assembled monolayers (SAMs) are molecular assemblies that are formed spontaneously by the adsorption of molecular constituents from solution or from the gas phase onto the surface of solids [44, 45]. SAMs are prepared by immersion of a substrate into a solution of an organic molecule. The molecules that form SAMs, also called surfactants, consist of three units: a headgroup which binds to the substrate, an endgroup (tail group) that constitutes the outer surface of the film, and a backbone or bridge that connects headgroup and endgroup and affects the intermolecular separation and molecular orientation [46]. Figure 2.1 shows a scheme, including the preparation method and the constituents of a SAM.

There are a number of headgroups that bind to specific metals, metal oxides, and semiconductors as mentioned earlier. The most extensively studied class of SAMs is derived from the adsorption of thiol (-SH) molecules on noble metals and semiconductor surfaces. The thiol headgroup is one of the rather rare functionalities which form a strong interaction with noble metals [38, 48]. Therefore, it is possible to utilize the thiol molecules to generate well-defined organic surfaces with alterable chemical functionalities displayed at the outer surface [45].
2.2 SAMs of Thiolates on Gold

In 1983, Nuzzo and Allara showed that dialkyl disulfides (RS-SR) form oriented monolayers on gold surface [33]. Monolayers of dialkyl disulfides were spontaneously assembled on the gold surface through the breaking of the S-S bridges, and formation of a covalent bond of the sulfur to the gold surface. Later, it was found that sulfur compounds would bind strongly to gold, silver, copper, and platinum surfaces [44, 45]. However, gold surfaces are studied most intensively, mainly because they are chemically relatively inert compared to other metals such as silver or copper [45]. Nevertheless, CO, O₂, H₂O and hydrocarbons can contaminate the gold surface. Therefore, it should be stored in argon atmosphere before the monolayer adsorption.

A thiol is a compound that contains a hydrogen-sulfur (-SH) group. Thiols are also referred to as mercaptans. This family of compounds is the most widely used for self-assembly on gold. However, the nature of the sulfur-gold bond and the arrangement of the sulfur groups on the underlying surface are still not completely understood. It is assumed that the formation of S-Au bond requires the loss of the hydrogen from the S-H groups [49] and that the thiolate (R-S⁻) is bound to the gold surface by a covalent bond [50]. 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. There are two distinct stages in the monolayer formation: first a fast process, which takes a few minutes, when the thiol is adsorbed and interacts with the gold surface and then a relatively slow process, which lasts several hours, when the molecules organize to reach equilibrium and form an ordered film.

The structure of the monolayers will be determined by both the intermolecular and headgroup-substrate interactions. The balance between these two interactions determines the lateral density and the structure of SAMs [44, 51-53]. Most structural investigations have been carried out on SAMs of alkanethiols (CH₃(CH₂)ₓSH) on Au (111) surfaces. The structure of the high-coverage SAMs of alkanethiol on Au(111) were first observed by Strong and Whitesides [37]. It is generally accepted to be based on a \( \sqrt{3} \times \sqrt{3} \)R30° overlayer (Figure 2.2) where the sulfur atoms are positioned in the 3-fold hollow sites of the Au(111) surface [37, 54-56]. An average tilt angle of \( \sim 27°-35° \) was observed for alkanethiol molecules in SAMs on Au(111) [39, 57-59]. The recent study, using X-ray standing wave experiments, showed that
the thiolate actually bonds to gold adatoms and the R-S-Au moieties can mobile on the surface [60].

The bonding of the thiol to the substrate and the structure of the thiol SAMs can be examined using the photoelectron spectroscopy techniques. The X-ray photoelectron spectroscopy (XPS) is used to probe the sulfur headgroup by exciting electron from the S 2p core level.

![Schematic diagram depicting the arrangement of a monolayer formed by alkanethiols on a Au(111) surface](image)

**Figure 2.2.** 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 3-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 [45].

![S 2p HRXPS spectra of alkanethiol SAMs on gold and silver surfaces](image)

**Figure 2.3.** S 2p HRXPS spectra of alkanethiol SAMs on gold and silver surfaces [61].
Synchrotron-based high-resolution XPS (HRXPS) was for the first time used to study SAMs by Heister, Zharnikov, Johansson, et al. [61, 62], allowing the resolution of the S 2p doublet. The HRXPS S 2p spectra of alkanethiol SAMs on gold and silver are shown in Figure 2.3. The spectra exhibit the S 2p doublet (S 2p3/2, 1/2) with spin-orbit splitting of ~1.2 eV. The binding energy of the S 2p3/2 peak is ~161.9 eV which indicate the formation of a sulfur-metal bond. This peak is different from unbound thiol (S-H bond) by about 1.5 eV [61]. The structure and orientation of SAMs can also be provided using X-ray absorption spectroscopy. The near edge X-ray absorption fine structure (NEXAFS) spectra of alkanethiol and terphenylthiol SAMs on gold are presented in Figure 2.4. These two molecules are oriented almost in an upright position on the surfaces. The pronounced linear dichroism of the NEXAFS spectra, i.e. their dependence on the angle of light incidence, implied well-ordered and densely packed layers [63].

![Figure 2.4. C K-edge NEXAFS spectra at different incidence angle for C16 alkanethiol [64] (left) and terphenylthiol [65] (right) SAMs on gold surface.](image)

Various other thiols have been investigated. By functionalizing alkanethiol with CF3 [66, 67], OH, COOH, NH2, [68-71] tetraphenylporphyrin [72, 73], ferrocenylazobenzene [74], etc; SAMs with different surface properties can be achieved. A Teflon-like or hydrophobic surface can be produced by using the alkanethiol with the CF3 endgroup. On the other hand, a hydrophilic surface can be achieved using OH and COOH endgroups. Furthermore, the OH and COOH and NH2 endgroups can be utilized to prepare a multilayer film [68].
Beside the aliphatic SAMs, the thiolaromatic SAMs which formed from the molecules such as oligo(phenylene)thiol [61, 65, 75, 76] and oligo(phenyleneethynylene)thiol [12, 13, 77, 78] also attract much attention due to their electrical properties.

The headgroup-substrate interaction plays a dominant role for the structure and packing in alkanethiol SAMs. Whereas in the thioaromatic SAMs these parameters are mainly determined by the intermolecular interaction [46]. For the SAMs of the simplest thioaromatic molecule, thiophenol (C₆H₅SH), on Au(111), a strongly inclined [79, 80] adsorption geometry of the phenyl rings has been reported. With increasing number of the phenyl rings in the aromatic chain, the monolayers become more densely packed and well-ordered [79-84], which can be related to the increasing intermolecular interaction. The average tilt angle reported for the well-oriented biphenylthiol and terphenylthiol SAMs on Au are about 23° and 20° from the surface normal as obtained from NEXAFS measurements [65]. For biphenylthiol SAMs on Au, the X-ray diffraction data imply a commensurate \( \sqrt{3} \times \sqrt{3} \)R30° surface lattice [85].

In this work, the thioaromatic SAMs which formed from the thiolated oligo (phenyleneethynylene) (OPE) molecules are studied.

2.3 Oligo(phenyleneethynylene) (OPE)

Oligo(phenyleneethynylene) (OPE) derivatives are molecules which consist of phenyl rings connected with triple bonds. They are fully conjugated molecules. Conjugated bonds play an important role in electron conduction because π-electrons are delocalized over a distance, called the length of conjugation. Because of their large delocalized π-system and their simple linear structure OPE derivatives are sometimes regarded as a molecular wire. A wire is a basic electronic function that allows the transport of charges from one end to the other [15]. In this work, SAMs on gold surfaces from various OPE-derivatives with different binding group (sulfur and silicon), backbones, and functional endgroups are formed and studied in terms of their structure and molecular orientation. The molecules are presented in Figures 2.5 and 2.8.
2.3.1 The sulfur headgroups

The thiolated OPE molecules under study are derivatives of 1-acetylthio-[4-(4′-phenylethynyl-phenylethynyl)]benzene and are presented in Figure 2.5. The acetate (-COCH₃) is used as a protection group because it is stable in the reaction conditions used during the synthesis [86]. It is removed during the self-assembly process to provide the thiolate group which binds to the gold surface.

As a result from the balance between the intermolecular interaction (e.g. van der Waals force) and the interaction of sulfur and the gold surface, the aromatic chain tilts away from the surface normal. To investigate this effect, the 1-Acetylthio-[4-(4′-phenylethynyl-phenylethynyl)]benzene was modified and studied. The OPEs with benzene (1), naphthalene (2), and anthracene (3) as the central moiety of the aromatic backbone, and (4) with a methylene linker.

![Chemical structures of OPE molecules with a sulfur headgroup and acetate protection group. OPE molecules with (1) benzene, (2) naphthalene, and (3) anthracene as the central moiety of the aromatic backbone, and (4) with a methylene linker.](image)

Figure 2.5. Chemical structures of OPE molecules with a sulfur headgroup and acetate protection group. OPE molecules with (1) benzene, (2) naphthalene, and (3) anthracene as the central moiety of the aromatic backbone, and (4) with a methylene linker.

As a result from the balance between the intermolecular interaction (e.g. van der Waals force) and the interaction of sulfur and the gold surface, the aromatic chain tilts away from the surface normal. To investigate this effect, the 1-Acetylthio-[4-(4′-phenylethynyl-phenylethynyl)]benzene was modified and studied. The OPEs with benzene (1), naphthalene (2), and anthracene (3) as the central aromatic moiety were investigated to see the effect of the molecular structure on the orientation of SAMs. By adding a methylene group between the sulfur and OPE moiety (4), the tilt of the chain might also be altered (Figure 2.6). It has been reported before that the terphenyl-substituted alkanethiols on gold with methylene linkers were found to be well-defined, densely packed and
oriented more perpendicular to the surface plane than the terphenylthiolated SAMs without methylene linker.[46, 75, 87]

Figure 2.6. Schematic picture of a possible orientation for the OPE thiolates without and with a methylene linker [86].

2.3.2 The silane headgroup

Besides the formation of a covalent bond between the sulfur and the gold surface, SAMs could be obtained from weak non-covalent, molecule-substrate and molecule-molecule van der Waals interactions. If a higher molecular complexity is demanded, the sulfur based molecule may make synthesis more difficult because of the high reactivity displayed by the acetyl protection group [86]. A new binding group for SAM formation on gold would be an alternative. We have chosen trimethylsilylethylene (TMS- ethylene) which consists of a trimethylsilyl group and a triple bond (R−C≡C−Si(CH₃)₃), terminated with the OPE molecule, for a new SAM system. This headgroup were used in the SAM formation of a porphyrin-functionalized OPE for comparison with the sulfur headgroup. The binding interaction of the TMS-ethylene group with the gold surface is still an essential question. In particular, it has been reported that TMS-ethylene system can form SAM via the Si and Au bond [88, 89]. The hypothesis of this mechanism is that Si directly connected to an electron-withdrawing group, such as the C≡C triple bond (and CH₃ group), is activated. When it interacts with an electron-donating atom such as gold, it becomes pentacoordinated as illustrated in Figure 2.7 [88-91]. Then one would expect
the methyl groups to be in the surface plane and the aromatic moiety standing upright above the pentacoordinated Si atom [88].

![Figure 2.7. Binding configuration for TMS-ethynylene showing a pentacoordinated on the gold surface [88].](image)

In related studies, several OPE systems with TMS groups have been designed, synthesized and characterized. These results are not included in the thesis.

### 2.4 The Porphyrin Functionalized OPE

By introducing a porphyrin as the endgroup (tailgroup) of the OPE moiety, one can create a wire-like molecule with optical and redox properties. This molecule can be utilized to fabricate a well-organized organic surface which may be used for application in solar cells [18], sensors [19-21] or other optoelectronic devices [92-95]. In this work, the free-base porphyrins connected by the OPE bridge to different binding groups were used to form SAMs. The molecular structures of these molecules are shown in Figure 2.8.

A porphyrin is a heteroaromatic molecule that consists of four pyrrole rings linked together in a cyclic arrangement. The porphyrin structure can be modified by varying the side-chain on the pyrrole rings or at the meso-positions between the two nitrogens. The core of the porphyrin can also be ligated with a metal ion, hence affecting the electron-accepting or -donating properties of the molecule. The photoinduced electron transfer in molecular donor-bridge-acceptor (D-B-A) systems, which are composed of two different porphyrin systems as a donor (e.g. Zinc porphyrin) and an acceptor (e.g. gold(III) porphyrin or free-base porphyrin) covalently linked by a variety of the OPE based bridges, have been studied in solution [96-98]. It has been demonstrated
that the electron transfer process in this porphyrin-based D-B-A system depends on the structure of the OPE bridge [96-98].

Consequently, it is interesting to investigate the electron transfer process of the porphyrin functionalized OPE and some other OPE derivatives when bound to an electrode surface and compare to the results obtained in the solution. However, the molecules self-assembled at the surface of a material experience a different environment than those in solution [99], hence, a good knowledge of the molecular orientation and packing density for the SAM formed from these OPE molecules is needed before fundamental studies of electron transport through the SAMs can be conducted.
Chapter 3

Experimental Methods

3.1 Sample Preparation

Polycrystalline gold has been used as a substrate for the SAMs under study. The gold substrates were purchased from Georg Albert PVD-Beschichtungen (Heidelberg, Germany) and were prepared by thermal evaporation of 300 nm of gold onto mica and then flame-annealed in air. These films were previously shown to be polycrystalline with a predominant (111) orientation [100]. The substrates were stored under argon before monolayer adsorption and used without further cleaning.

The organic compounds 1-7 were synthesized at the Department of Organic Chemistry, Chalmers University of Technology [101]. Tetrahydrofuran (THF) was dried by distillation from sodium/benzophenone under nitrogen. THF is a standard solvent used in SAM formation for acetyl protected OPE-thiols [5, 82, 102, 103]. The preparations of SAMs were carried out in an argon atmosphere to avoid undesired pollutants (e.g. CO, O) 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. 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 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.
3.2 Characterization Techniques

Several techniques have been utilized to monitor the following characteristics of SAMs: chemical composition, binding energy of core level electron, molecular orientation and packing density. The techniques used in this work are high-resolution X-ray Photoelectron Spectroscopy (XPS), Near-edge X-Ray Absorption Fine Structure Spectroscopy (NEXAFS), Infrared Reflection Absorption Spectroscopy (IRRAS), Contact angle measurement and Atomic Force Microscopy (AFM).

3.2.1 X-Ray Photoelectron Spectroscopy (XPS)

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 of known energy, photoelectrons are emitted from the sample after direct transfer of the energy from 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 sample.

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

\[ E_i^N + h\nu = E_{\text{ion}}^{N-1} + E_k \]  \hspace{1cm} (3.1)

where \( E_i^N \) is the total energy of the system with \( N \) electrons in its ground state (initial state), \( h\nu \) is the photon energy, \( E_{\text{ion}}^{N-1} \) is the total energy of the ionized
system with \( N \)-1 electron (final state) and \( E_i \) is the kinetic energy of the emitted photoelectron. The binding energy of the photoelectron, \( E_b \), can be defined by the initial- and final-state configurations,

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

(3.2)

From Eq. 3.1 and 3.2, if the photon energy, \( h\nu \), is well defined, the binding energy of the electron in the atom, \( E_b \), can be expressed by [104]:

\[
E_b = h\nu - E_i
\]  

(3.3)

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 solid [105]. In order to measure the kinetic energy of the emitted photoelectrons, a spectrometer is used. The spectrometer measures the kinetic energy with reference to its own vacuum level, which does not have to coincide with that of the sample. The XPS process is illustrated in Figure 3.1 which shows a core-level photoionization in the diatomic molecule and the energy alignment between the sample and spectrometer.

![Figure 3.1](image_url)

**Figure 3.1.** The energy level diagram showing a core-level photoionization process and the energy alignment between the sample and the spectrometer [106].
In order to measure the absolute binding energies of the electrons in the sample, a calibrated spectrometer and suitably energy reference is required. Conducting samples are placed in electrical contact with the spectrometer, typically by grounding both the sample and the spectrometer. This puts the Fermi level \((E_F)\) of both the sample and spectrometer, at the same energy level. 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, \(\phi_s\), and the work function of the spectrometer, \(\phi_p\). 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:

\[
E'_k = E_k - (\phi_p - \phi_s)
\]

In the case of metal and adsorbates, the binding energy is related to the Fermi level \(E_F\), which is the highest occupied energy level and has a separation \(\phi_s\) from the vacuum level, \(E_{vac}\). The photoelectron emitted from the core level with the binding energy of \(E'_b\) (with reference to the Fermi level) has kinetic energy equal to:

\[
E_k = h\nu - \phi_s - E'_b
\]

From Eq. 3.4 and Eq. 3.5, the measured kinetic energy can be related to the binding energy with reference to the Fermi level, \(E'_b\), as:

\[
E'_k = h\nu - E'_b - \phi_p
\]

Therefore, \(E'_b\) can be determined by measuring \(E'_k\) and \(\phi_p\). For conducting samples it is the work function of the spectrometer (\(\phi_p\)) that is important. This can be calibrated 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., \(E_F = 0\) eV, Au 4f/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.

**Chemical shift, molecular relaxation and other core spectra features**

Siegbahn and co-workers [107] (who pioneered the technique of XPS) showed that XPS is a probe of the chemical environment. The precise binding energy of the core levels of an atom will depend critically on the species to which it is bonded. 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. 3.2. The initial state is the ground state of the atom prior to the photoemission process. If the energy of the atom’s initial state changed, for example, by formation of chemical bonds with other atoms, then the binding energy of electrons in that atom will change. The change in binding energy is called the chemical shift. As an example in Figure 3.2, XPS can be used as a fingerprint technique to locate certain atoms in a molecule by using their chemical shifts. This is the same in the case of adsorbed atoms on the substrate.

![Figure 3.2. XPS spectrum of C 1s obtained from the molecule ethyltrifluoroacetate showing four different chemical environments of carbon atoms [107].](image)

The measured binding energy can also be affected by the final state effect. The removal of the core electron causes a large perturbation of the electronic structure where the relaxation of the remaining electrons might end up in an excited ionized state. There are two types of mechanisms of screening the hole created by photoemission process, intermolecular and intramolecular relaxation. These relaxations can cause a binding energy shift in the photoelectron...
Chapter 3: Experimental Methods

spectrum. The intermolecular relaxation (screening) 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 [108]. The intramolecular relaxation is caused by the electrons or nuclei within a molecule.

![Diagram](image)

**Figure 3.3.** Schematic representation of different excitation events occur during and after the photoionization process [106].

These relaxation events are very fast processes, occurring at about 10-100 femtoseconds. Several different 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 3.3 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, 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.

In this report, the S (2p<sub>3/2</sub>) peak of a bound thiol molecule to gold is found at binding energy 162.03 eV and compared to the S (2p<sub>3/2</sub>) peak of an unbound molecule at about 163.30 eV as shown in Figure 3.4. This difference stems from the formation of the sulfur-gold bond and the screening of the S 2p core hole by the substrate electrons [109].
Spectral Quantification

While X-rays can readily travel through solids, electrons exhibit significantly less ability to do so. In fact, for X-rays of 1 keV, the X-rays will penetrate 1000 nm or more into matter while electrons of this energy will only penetrate approximately 10 nm. Because of this difference, XPS, in which only emitted electrons are measured, is surface sensitive.

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 decrease in the number of the photoemitted electrons that have suffered no energy loss traveling through matter, is described by

\[ dl = n j \sigma k \exp \left( -\frac{x}{\lambda \cos \theta} \right) dx \]

(3.7)
where \( I \) is the intensity, \( n \) is the number of the atoms per unit area of the element of interest, \( j \) is the flux of X-ray photons, \( \sigma \) is the photoionization cross-section for a particular transition and \( k \) is a factor characteristic to the instrument performance, while \( \lambda \) is the inelastic mean free path (IMFP), \( \theta \) is the angle between the surface normal and the ejected electron and \( x \) is the distance from the sample surface. The IMFP is defined as the average distance that an electron with a given energy travels between inelastic collisions.

For samples with a thin overlayer of thickness \( d \), the total intensity of the surface layer (\( s \)) and bulk (\( b \)) can be determined by evaluating the integral of Eq. 3.7 from 0 to \( d \) and from \( d \) to infinity, respectively, resulting to:

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

(3.8)

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

(3.9)

where \( \lambda_s \) and \( \lambda_b \) are the IMFP of the surface layer and the bulk, respectively. The thickness of the overlayer can be calculated by using the intensity ratios of the above equations, so the energy-independent parts \((jk\cos \theta)\) can be neglected.

![Figure 3.5. Mean free path of electron as a function of kinetic energy [110].](image-url)
Chapter 3: Experimental Methods

For quantitative analysis, two of the parameters, $\sigma$ and $\lambda$, are the most important in order to obtain good quantitative results. The photoionization cross-sections, $\sigma$, is the probability that the incident X-ray will create a photoelectron. It is dependent on the incident photon polarization and energy. The inelastic mean free path, $\lambda$, is strongly dependent on the kinetic energy of the photoelectrons as may be inferred from Figure 3.5. This general features are similar for all elements. The curve is commonly called the “universal curve” [110, 111]. The reason for this universality is that the inelastic scattering of electrons in this energy range mostly involves excitations of valence band electrons, which have nearly the same density for most materials [110]. Consequently, a Golden rule calculation of the inelastic mean free path of electrons in a solid (of this density) gives a result as shown in Figure 3.5. Therefore electrons with kinetic energies in the appropriate range that escape from a solid without subsequent energy loss must originate from the surface region.

Instrumentation

A monochromatic light source which is tunable over a wide energy range, has high intensity, and is polarized is what one wishes to have access to the photoemission experiments. Synchrotron radiation from a storage ring can provide these desirable properties. Synchrotron radiation is created when the momentum of a charged particle, traveling in a storage ring at a speed close to that of light, is changed by the magnetic field from a bending magnet or in an insertion device. The radiation is emitted over a wide spectral range, has a high intensity of photons, and is linearly polarized in the plane of the storage ring. 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 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 characterization, all of these are in the ultra high vacuum conditions (UHV).
In my presented work the XPS measurements are carried out at the synchrotron storage ring MAX II at MAX-lab in Lund, Sweden, using the D1011 beamline (Figure 3.6).

Figure 3.6. Beamline D1011 at the synchrotron storage ring MAX II at MAX-lab in Lund, Sweden [112].

The beamline covers an photon energy range from 30 to 1500 eV. The beamline is equipped with a modified SX-700 monochromator[113] and a two-chamber ultrahigh vacuum experiment station with a SCIENTA type analyzer. To study the S 2p, C 1s and Au 4f core levels, the excitation energies 350 and 580 eV were used. The photon energy for a particular spectrum was based on the optimization of the photoionization cross section for the corresponding core level. The spectra were acquired in normal emission geometry. The resolution was better than 0.1 eV.

3.2.2 Near-Edge X-ray Absorption Fine Structure

Principles

Near-Edge X-ray Absorption Fine Structure, NEXAFS, spectroscopy is a technique to characterize surfaces by evaluation of unoccupied electronic states. It is also a core level spectroscopy technique. As opposed to the XPS technique, where the photon energy is fixed and the electron intensity is measured as a function of electron kinetic energy, in NEXAFS the X-ray energy is scanned and the absorbed X-ray intensity is measured. This simply requires a tunable monochromatic light source so that NEXAFS measurement can be performed at synchrotron radiation facilities. NEXAFS spectroscopy 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. NEXAFS is also called X-ray Absorption Near Edge Structure, XANES. Now, the term XANES is typically used for hard X-ray absorption spectra, with the X-ray region from 1250 eV to several thousands eV, and NEXAFS for soft X-ray spectra, i.e. in the region from 50 eV to 1250 eV.

These techniques rely on a two-step process. In the first step the photon excites a core electron, hence creating a core hole-photoelectron pair, 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 3.7): the radiative type, producing the emission of photons (fluorescence), or the non-radiative type (Auger transitions), with emission of electrons or ions, which can be collected from the surface with suitable detectors [114].

**Figure 3.7.** Schematic diagram of photoexcitation and recombination processes. The photo-generated core hole is filled by an electron in a higher shell either radiatively by emission of a photon, or non-radiatively by emission of an Auger electron.

Only a sufficient photon energy enables the photoexcitation of a core level electron beyond the vacuum level. The ionized atom may relax by occupation of the core hole with an electron from the valence band, while the generated energy will normally not be used for the emission of the photon but will be absorbed for the emission of an Auger electron. In case of a non-sufficient energy for the emission of the primary electron, this electron may excite into an unoccupied level, so similar relaxation processes become possible. There are
two kinds of the Auger transitions: participator decay in which the excited electron participate in the Auger process and spectator decay in which the excited electron stay in the excited unoccupied level. The number of generated Auger electrons is therefore directly proportional to X-ray absorption cross section [115].

Several techniques can be chosen to detect the absorption. The most common method is an electron yield measurement which measures the photoelectrons that are created by the absorbed X-ray. Electron yield measurements can be carried out in three ways: Total electron yield (TEY), Partial electron yield (PEY) or Auger electron yield (AEY) The methods differ in their sensitivity to surface and bulk composition. The TEY method measures the yield of all photoelectrons and Auger electrons. The TEY signal is dominated by low energy electrons with kinetic energy below about 20 eV [115]. These low energy electrons have large mean free paths making the method more bulk sensitive. The PEY method collects a fraction of a low-energy secondary electron by placing a retarding electric field in front of the electron detector. A typical bias voltage applied is in the order of 100 eV, which repels the bulk sensitive, low energy electrons, thus, making the method more surface sensitive. The AEY method measures Auger electrons by setting the energy analyzer at a specific Auger transition energy. This method is highly surface sensitive and offers the largest signal to background 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 is employed.

Theory

NEXAFS concerns the electronic transition form atomic core levels to unoccupied states. In classical quantum theory, the X-ray absorption cross section, $\sigma_x$, describes the probability of the X-ray photon in exciting an electron from the initial state, $\phi_i$, to the final state, $\phi_f$. It 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 [63]. The cross section can be calculated by using Fermi’s Golden Rule and the dipole approximation.
Chapter 3: Experimental Methods

\begin{equation}
\sigma_s = \frac{4\pi^2 \hbar^2}{m^2} \frac{e^2}{\hbar c \hbar \omega} \left| \langle \phi_f | \vec{e} \cdot \vec{p} | \phi_i \rangle \right|^2 \zeta(E)
\end{equation}

where \(\hbar \omega\) is the incident photon energy, \(e\) and \(m\) are the charge and mass of electron respectively, \(\zeta(E)\) the energy density of final states and \(\langle \phi_f | \vec{e} \cdot \vec{p} | \phi_i \rangle\) the dipole matrix.

The absorption cross section, \(\sigma_s\), is proportional to the energy density of final states \(\zeta(E)\), which qualitatively explains the direct correlation between a NEXAFS spectrum and the nature of unoccupied states. The dipole matrix term, \(\langle \phi_f | \vec{e} \cdot \vec{p} | \phi_i \rangle\), shows the scalar product of the interaction between the linear momentum operator of electron, \(\vec{p}\), and a unit vector in the direction of electric field of a linearly polarized incident X-ray photon, \(\vec{e}\). The dipole matrix term is the theoretical basis of the polarization dependence of NEXAFS measurements, employed in the determination of the orientation of molecular adsorbates.

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

\begin{equation}
\vec{p} = m \vec{v} = -\hbar \nabla = \frac{im(E_f - E_i)}{\hbar} \vec{r}
\end{equation}

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

\begin{equation}
\left| \langle \phi_f | \vec{e} \cdot \vec{p} | \phi_i \rangle \right|^2 \propto \left| \vec{e} \cdot \langle \phi_f | \vec{r} | \phi_i \rangle \right|^2
\end{equation}

It is convenient to express the intensity of a resonance transition as a dimensionless quantity, the optical oscillator strength, \(f\), which is related to the X-ray absorption cross section according to

\begin{equation}
\sigma_s(E) = C \frac{df}{dE}
\end{equation}
where $C = \frac{2\pi^2 e^2 \hbar}{mc}$. Since $f$ is the energy integral of the cross section, the oscillator strength is a measure of the intensity of the resonance and the intensities of bound state transition are typically quoted as

$$f = \frac{2}{m\hbar^2} |\langle \phi_f | \hat{e} \cdot \hat{p} | \phi_i \rangle|^2. \quad (3.14)$$

**Angular Dependence of NEXAFS resonance intensity**

Upon the photoelectron excitation, the amplitude and directionality of an unoccupied electronic state on the excited atom can be probed by NEXAFS spectroscopy. In this section the determination of molecular orientations on surfaces from analysis of the angle-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 nearly 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.

The orientation of $\sigma^*$ and $\pi^*$ orbitals of diatomic molecules containing single, double and triple bonds and a benzene ring are illustrated in Figure 3.8. These concepts of the bonding in diatomic molecules and benzene ring can serve as the basis for all other cases.
Molecules can be divided into two classes depending on whether the $\sigma^*$ and $\pi^*$ orbitals point in a specific direction (vector type) or span a plane (plane type). Only the orientation of the orbital, i.e. the direction of maximum orbital amplitude, determines the angular dependence of the K-shell spectra. Therefore a single orbital can be represented by a vector and two orthogonal orbitals by a plane.

Considering the angular dependence of specific resonances, the change in resonance intensity will be proportional to the change in oscillator strength as well as the change in X-ray absorption cross section, by use of Eq. 3.10 or 3.14 we can write

$$I \propto \left| \langle \phi | \mathbf{d} \cdot \mathbf{p} | \phi \rangle \right|^2 \propto \frac{1}{|E|^2} \left| \langle \phi | \mathbf{E} \cdot \mathbf{p} | \phi \rangle \right|^2 \propto \left| \mathbf{E} \langle \phi | \mathbf{p} | \phi \rangle \right|^2$$  \hspace{1cm} (3.15)
where \( \mathbf{e} \) is a unit vector in the direction of the electric field vector \( \mathbf{E} \), \( \mathbf{p} \) is the momentum operator, \( |\varphi_1\rangle \) is the 1s initial state and \( |\varphi_f\rangle \) is the molecular orbital final state of the transition. According to Maxwell’s equation, the electric field vector is always perpendicular to its propagation direction. For polarized synchrotron light, the electric field vector is composed of two components, a component parallel to the orbit plane of the storage ring, \( \mathbf{E}^\perp \), and a component that is perpendicular, \( \mathbf{E}^\parallel \). These two components of the electric field are related to each other via the degree of linear polarization or polarization factor \( P \) by

\[
P = \frac{|\mathbf{E}^\parallel|^2}{|\mathbf{E}^\parallel|^2 + |\mathbf{E}^\perp|^2}
\]

(3.16)

\( P \) is determined by the X-ray energy and the X-ray optics of the beam line. In the case of linearly polarized light, \( |\mathbf{E}^\perp| = 0 \) or \( P = 1 \). With the above definition of \( P \), the total resonance intensity is given by

\[
I \propto P|\langle \varphi_f | \mathbf{e}^\perp \cdot \mathbf{p} | \varphi_1 \rangle |^2 + (1 - P)|\langle \varphi_f | \mathbf{e}^\parallel \cdot \mathbf{p} | \varphi_1 \rangle |^2
\]

(3.17)

where \( \mathbf{e}^\perp \) and \( \mathbf{e}^\parallel \) are unit vector of the in-plane and perpendicular electric field components, respectively. The total measured intensity will have \( I^\perp \) and \( I^\parallel \) contributions with some factors determined by \( |\mathbf{E}^\parallel|^2 \) and \( |\mathbf{E}^\perp|^2 \), respectively. Eq. 3.15 can be written as

\[
I = C\left[P I^\perp + (1 - P) I^\parallel\right]
\]

(3.18)

where \( C \) is a constant.
As shown in the Figure 3.9, the orientation of the orbital, i.e., of the vector $\bar{O}$, is characterized by a polar angle $\alpha$ and an azimuthal angle $\phi$. The X-ray are incident in the $(x, z)$ orbital and contains the major electric field vector component $\overrightarrow{E}^\|$. The X-ray incidence angle $\theta$, which is also the polar angle of $\overrightarrow{E}^\|$, is changed by rotating the crystal about the $y$-axis. The weaker component $\overrightarrow{E}^\perp$ lies in the surface plane, along the $y$-axis. The $z$-axis is the surface normal and $[115]$. For a 1s initial state and a $\pi^*$ or $\sigma^*$ vector final state orbital, the matrix element points in the direction of the final state orbital $\bar{O}$, and Eq. 3.15 can be derived to

$$I = A \cos^2 \delta$$

where $A$ is constant which describe the absolute angle-integrated cross section and $\delta$ is the angle between the electric field vector $\overrightarrow{E}$ and the direction of the final state orbital $\bar{O}$. From Eq. 3.19, we obtain the angular dependence of the resonance intensity associated with the $\overrightarrow{E}^\|$ and $\overrightarrow{E}^\perp$ component. The intensity can be expressed for in-plane, $I^\|$ and perpendicular component, $I^\perp$ as

$$I^\| = \cos^2 \theta \cos^2 \alpha + \sin^2 \theta \sin^2 \alpha \cos^2 \phi + 2 \sin \alpha \cos \alpha \sin \theta \cos \theta \cos \phi$$

$$I^\perp = \sin^2 \alpha \sin^2 \phi$$
For any molecular chemisorption geometry on substrates with threefold or higher symmetry, the $\cos^2 \phi$ term averages to $1/2$ and the above expression simplifies to

$$I^+ = \cos^2 \theta \cos^2 \alpha + \frac{1}{2} \sin^2 \theta \sin^2 \alpha = \frac{1}{3} \left[ 1 + \frac{1}{2} (3 \cos^2 \theta - 1) (3 \cos^2 \alpha - 1) \right]$$ (3.22)

$$I^+ = \frac{1}{2} \sin^2 \alpha$$ (3.23)

After simplification, intensity $I$ can be derived using Eq. 3.18:

$$I = C \left[ \frac{P}{3} \left( 1 + \frac{1}{2} (3 \cos^2 \theta - 1) (3 \cos^2 \alpha - 1) \right) + \left( 1 - P \right) \frac{1}{2} \sin^2 \alpha \right]$$ (3.24)

In this work the molecules are assumed to be attached to the threefold hollow sites of the Au(111) surface. The calculation of the average tilt angle of molecular orbitals was performed for vector-type orbitals.

**Instrumentation**

The NEXAFS measurements were carried out at synchrotron laboratory MAX-lab in Lund, Sweden using D1011 beamline. The details of the beamline are previously described in the XPS section. The NEXAFS partial electron yield mode is measured using a Multi Channel Plate (MCP) with retarding voltage -150 eV. The spectra were acquired at the C 1s absorption edge. A linear polarized synchrotron light with a polarization factor, $P$, of $\sim 100 \%$ was used. The incident angle of the light was varied from $90^\circ$ (E-vector in the surface plane) to $20^\circ$ (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.
3.2.3 Infrared Reflection Absorption Spectroscopy (IRRAS)

Principles

This technique has proven to be a powerful tool for the study of adsorbed molecular layers on metal surfaces. IRRAS can be used to identify molecules since functional groups and backbone structures have characteristic vibrational frequencies. The molecular orientation can also be probed due to the vibration of the bond established between atoms in molecules. The spectra region can be presented in the term of wavelength as meters or wavenumber in cm\(^{-1}\). The latter unit is widely used in infrared spectroscopy. The most common wavenumber range for IR spectroscopy of molecules is 800 to 4000 cm\(^{-1}\).

When the infrared light illuminates the molecules, they may be excited to higher vibrational modes if the energy of the incident photons matches the excitation energy. The vibration of a molecular bond is infrared active, if the dipole moment, \(\mu\), of the bond changes with the vibrational coordinate, \(R\). An infrared active transition dipole moment, \(M\), can be express as \[M = \frac{d\mu}{dR} \neq 0\] (3.25)

The intensity of an absorption band in an infrared spectrum is proportional to the square of the scalar product of the transition dipole moment, \(\vec{M}\), and the electric field, \(\vec{E}\):

\[I_j \propto |\vec{M}_j \bullet \vec{E}|^2 = |\vec{M}_j|^2 \cdot |\vec{E}|^2 \cdot \cos \phi_{(\vec{M}, \vec{E})}\] (3.26)

where \(\phi_{(\vec{M}, \vec{E})}\) is the angle between the transition dipole moment and the electric field. It can be seen form Eq. 3.26 that IR absorption will occur when the transition dipole moment of the vibrational mode parallel to the electric field.

In this thesis work two types of IR set-ups were used: transmission IR spectroscopy and reflection absorption IR spectroscopy (IRRAS). The first type is used to measure isotropic samples. Molecules measured in this mode are normally pressed in KBr pellet. They are oriented randomly, thus the entire possible vibrational mode can be observed. The spectra obtained from this
transmission mode revealed the presence of chemical bonds contained in the molecules which can be used as fingerprint for the sample. On the other hand, the latter type is suited for the study of adsorbed layers on metal surfaces.

In order to study the structure and the orientation of molecular adsorbates on the metal surfaces, the incidence radiation is used 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 [117]. As shown in Figure 3.10, 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 vector summation of the incidence 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 degree phase-shift with respect to each other and so the net amplitude of the IR radiation with polarization parallel to the surface plane is zero.

![Surface normal](image)

**Figure 3.10.** Schematic representation of the electric vector of the s- and p-polarized components of radiation incident on metal surface. Primed and unprimed vectors refer to reflected and incidence radiation, respectively.

Thus only radiation having a $p$-component 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 in the direction normal to the surface plane. This is a statement of the so called “surface selection rule”.

The selection rule can be used to obtain information about bond orientation relative to the surface by comparing the relative intensities of the bands in the
Chapter 3: Experimental Methods

IR spectrum of SAM and the transmission spectrum of the randomly oriented molecules in KBr.

Instrumentation

The infrared absorption spectra were recorded using a Bruker IFS 66v/S spectrometer equipped with a wide-band liquid nitrogen cooled MCT detector and with the optics and sample compartment evacuated to 3 mbar. For measurements of the SAM spectra a grazing angle reflectance cell (Bruker A513) and $p$-polarized light at 80° (to the surface normal) of incidence were used. For each sample and reference a single beam spectrum, comprising of the average of 10000 scans, was recorded, and the absorption spectra was calculated as: $A = -\log(I/I_{ref})$. 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 in 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.

3.2.4 Contact angle measurement

Contact angle measurement can be used to detect the presence of a molecular film. The contact angle ($\theta$) can be observed by dropping liquid onto a solid surface. Contact angles depend on the liquid used for examination. When a droplet of liquid rests on the surface, the angle between the tangent line and the solid surface is measured as illustrated in Figure 3.11. Comparison with the contact angle for a clean gold substrate gives some indication on how well the surface is covered with molecules.

![Figure 3.11. A liquid drop on a solid surface.](image-url)
The quality of monolayer films can be estimated from the results of contact angle measurements. This is due to the fact that the shape of a liquid drop on a surface is affected by the free energy of this surface. The equation describes the relationship between the free energy of the surface and a contact angle, $\theta$, is called Young’s equation, written as

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL}$$

(3.27)

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

In general, a surface composed of methyl (CH$_3$) groups exhibit higher contact angles for water than those exposing methylene (CH$_2$) groups [118]. In a monolayer of alkanethiol, as the methyl groups at the interface (solid-liquid) become less close packed, the number of exposed methylene groups increases. Consequently, the surface free energy increases, and the contact angle decreases.

We note that a surface rarely exhibits a true, thermodynamic equilibrium contact angle [44]. In this case, a different contact angle is measured when the drop has advanced ($\theta_a$) or receded ($\theta_r$) on the surface, for which we define the difference in contact angle as the hysteresis, simply expressed by:

$$\Delta \theta = \theta_a - \theta_r$$

(3.28)

In previous studies, this hysteresis has been found to be greatest for polar, heterogeneous, or rough surfaces [118]. This value is associated with the quality of SAMs in which a small hysteresis imply a homogenous and a well-ordered layer. In this work we have employed static contact angle measurements. A drop of a fixed size is formed on the end of a needle and lowered to the surface. When the needle is raised, the drop falls from the tip to the surface. This method is believed to obtain a lower contact angle [44] but has the advantage of a slightly greater reproducibility.
Chapter 3: Experimental Methods

Instrumentation

Static contact angle is 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.

3.2.5 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is a surface characterization technique that measures the topography of a surface. Measurements are done by scanning a very sharp tip over the sample surface. The principle of operation of AFM is illustrated in Figure 3.12. A tip, typically constructed from silicon nitride, with diameter between 6 and 20 nm, is mounted on a cantilever. It is important that the cantilever is insensitive to vibrational noise from the laboratory. As the resonance frequency ($\nu$) is given by

$$\nu = \frac{1}{2\pi} \sqrt{\frac{K}{m}}$$ \hspace{1cm} (3.29)

where $K$ is the cantilever force constant and $m$ is its mass.

![Experimental configuration of the AFM.](image)

There are two main scanning modes: contact mode and non-contact mode (also called tapping mode).
Contact mode. The AFM tip, when brought into contact with a surface experiences a very small force (of the order of nanoNewtons) as a result of interaction with the surface atoms. This leads to the cantilever being either attracted or repelled as it is scanned across the surface. The deflection of the cantilever may be monitored by an optical technique such as that shown in Figure 3.12 in which a laser beam is reflected from the back of the cantilever onto a segmented photodetector. As the sample is scanned with respect to the tip, the deflections in the beam arise from changes in local surface topography. To probe the molecular layer, the applied force during the AFM imaging is minimized by adjusting the set point to the lower limit, which corresponds to setting the height of the cantilever as far from the surface as possible.

Non-contact mode. In this case the tip is not in contact with the surface. In order to enhance the sensitivity of the technique the tip is forced to vibrate close to its resonance frequency. Variations in the sample-tip forces will alter the resonant frequency of the tip, and this frequency shift is used to give a measure of the magnitude of the forces in action. Obviously, for a surface protrusion, the forces acting on the tip will be large so topographic images of surface force versus lateral position on the surface are possible even with non-conducting samples.

In this work AFM contact mode was used to study the surface structure of the organic molecular film. There are, of course, problems created by the tip-surface interaction and worries concerning the possibility of tip-induced movement of molecules across the sample surface. Atomic resolution images of the topical molecules have not been obtained. However, some observations on other SAM systems such as fluorinated alkanethiol have been made. The atomic resolution image of the fluorinated alkanethiol SAM is shown in Figure 3.13.
Figure 3.13. AFM image of fluorinated alkanethiol (CF3(CF2)9(CH2)11SH) SAM on Au(111).
Chapter 4

Summary of Papers

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.

The effect of the molecular structure on the binding/adsorption, orientation and packing density of these three SAMs was characterized by infrared reflection spectroscopy, spectroscopic ellipsometry, contact angle measurements, high resolution X-ray photoelectron spectroscopy (HRXPS) and near-edge X-ray absorption fine structure spectroscopy (NEXAFS). The NEXAFS spectroscopy results reveal 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 shows a well-ordered and densely packed 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° 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 is limited at angles close to the magic angle (~55°). 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. Nevertheless, a recent STM study on SAMs of a molecule similar in structure to 3 reported a well-ordered structure [119].

Paper II: HRXPS and NEXAFS study of Self-Assembled Monolayers of Porphyrin-Functionalized Oligo(phenyleneethynylene) on Gold: the Influence of the Binding Group

Porphyrin-functionalized OPEs with different binding groups: (1) an acetyl-protected thiophenol (R-S-COCH₃), (2) a acetyl-protected benzylic thiol (R-CH₂-S-COCH₃) and (3) a trimethylsilylethynyl-group (R-C≡C-Si(CH₃)₃) were synthesized and corresponding molecular layers were prepared on Au(111) surfaces. High-resolution X-ray photoemission spectroscopy (HRXPS) and near-edge X-ray absorption fine structure spectroscopy (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 binding group. The adsorbate 1 forms a high-quality self-assembled monolayer (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 S and the OPE moiety in adsorbate 2, affects the molecular orientation of the molecular layer. 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 was found to form a molecular layer on the Au surface with highly inclined molecules or molecules with random orientation. Two N 1s peaks were observed in the HRXPS spectra of SAM 1, corresponding to the two different nitrogen species in the free-base
porphyrin functional group (protonated and unprotonated nitrogen). Only a single nitrogen peak was observed in the HRXPS spectra for molecular layer 2 and 3. This is typically observed for metal-coordinated porphyrin [120-122]. We interpret this result as an indication that the porphyrins in the adsorbates in molecular layers 2 and 3, which are oriented almost flat to the surface, are metal-coordinated, perhaps through interaction with the Au surface.
Chapter 5

Future Plans

The organization and packing of OPE derivatives in SAMs is different depending on the molecular structure and the binding group. SAMs of OPE-derivatives and porphyrin-functionalized OPE-derivatives with an acetyl-protected thiophenol headgroup were found to form highly oriented and densely packed films. We plan to further investigate the electrical properties of these SAMs. To investigate charge transport through the molecules, we will use scanning tunneling spectroscopy (STS). With this technique current-voltage (I-V) curves are obtained that can be used to determine conductivity and the density of electronic states of the SAMs. The work function of SAM-modified surfaces will be measured by Kelvin probe. Changes in work function upon adsorption of molecules have been studied extensively for various types of SAMs and can indicate the formation of surface dipoles. Combined with estimated values for the molecular dipole, this could yield another way of verifying SAM orientation and packing.

From the earlier work, the orientation and ordering of a SAM system such as the extended π-systems OPE (with anthracene as the central aryl moiety) are not clearly determined. In order to obtain direct structural information for this SAM, we plan to use scanning tunneling microscopy (STM).

Beside gold we plan to use silicon as a substrate. We will study SAMs of OPE derivatives on silicon with suitable binding groups.

The donor-bridge-acceptor (D-B-A) system, which is created from two different porphyrins (free-base, zinc, gold(III), etc.) covalently linked by a “bridge” of OPE exhibits charge-transfer characteristics in solution. It is interesting to investigate charge transfer in D-bridge-surface or A-bridge-surface systems. We plan to study free-base and metallated porphyrin-functionalized OPE attached to a gold surface and compare the electronic properties of the modified surfaces by STS and Kelvin probe. HRXPS and
NEXAFS will be used to investigate the chemical and structural properties of these molecular layers. The presence of a central metal atom in the porphyrin allows core level spectroscopy of another characteristic element. In addition, the optical properties of porphyrin are of interest. Therefore, we plan to investigate the possibility of using emission spectroscopy (fluorescence) on surfaces modified with porphyrin-functionalized OPE to indirectly study the photo-induced electron transfer of these SAMs.
Bibliography


[22] Franklin, B. *Phil. Trans. R. Soc.* 1774, 64, 445.


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

Daniel Nilsson,‡ Somsakul Watcharinyanon,† Mattias Eng,‡ Liqian Li,‡ Ellen Moons,‡

Lars S. O. Johansson,† Michael Zharnikov,§ Andrey Shaporenko,§

Bo Albinsson,‡ Jerker Mårtensson*‡

Department of Chemical and Biological Engineering, Chalmers University of Technology, S-41296 Göteborg, Sweden

Department of Physics, Karlstad University, S-65188 Karlstad, Sweden, and

Angewandte Physikalische Chemie, Universität Heidelberg, Im Neuenheimer Feld 253, D69120, Heidelberg, Germany

* Corresponding author. E-mail: jerker@chalmers.se

‡ Chalmers University of Technology

† Karlstad University.

§ Universität Heidelberg
ABSTRACT

Fully conjugated organic molecules, such as the oligo(phenyleneethynylene) (OPE) systems are of growing interest within the field of molecular electronics, as is the self-assembly of well-defined molecular thin films with predefined functions. The structure and function of such films are intimately related and governed by the structures of their molecular constituents, through the intermolecular interactions, and the interactions between the molecules and the substrate, onto which the film is assembled. Here we report on the synthesis of a series of three OPE-derivatives, with the general structure phenylethynylene-aryl-ethynlenephenylene-headgroup, and the structural investigation of the self-assembled monolayers (SAMs) formed from them on Au(111) surfaces. The SAMs were characterized by infrared reflection absorption spectroscopy, spectroscopic ellipsometry, high-resolution X-ray photoemission spectroscopy, and near-edge X-ray absorption fine structure spectroscopy. The effective thickness of the SAMs was observed to decrease as the π-system of the aryl moiety of the OPE adsorbate was extended perpendicular to its molecular long axis. Changing the aryl moiety from benzene to naphthalene to anthracene resulted in lower molecular surface densities and larger molecular inclination. The average tilt angles for the benzene, naphthalene, and anthracene SAMs were found to be about 30º, 40º, and 42º from the surface normal, respectively. For the largest adsorbate, the anthracene derivative, there are spectroscopic evidence suggesting the existence of non-equivalent binding sites. The differences observed between the SAMs are rationalized in terms of the shape of the adsorbates and the strength of the π-π interactions between them.

1. Introduction

The development toward increasingly smaller sized electronics has turned interest toward organic molecules as potential circuit elements/components, such as conductors, rectifiers, transistors, and logic gates. Fundamental to the operation of electronics is the flow of electrons; consequently, electron transport through organic molecules is likely to be an essential issue in future electronics and has become a field of intense research. In this regard, molecules with extended π-conjugation have received special attention, because these are expected to show relatively facile charge transport and have been
considered as potential molecular wires. Oligo(phenyleneethynylene) (OPE) derivatives are a class of fully conjugated molecules with several aromatic moieties that has been studied extensively with respect to electron conductivity. The necessary electrical contact between the molecular scale systems and the macroscopic world is presently most often brought about by attaching the molecular systems to the surfaces of metals, oxides or semiconductors by reversible bonding between the head group of the molecule and the surface. In this way molecular layers can organise spontaneously on a surface and form so-called self-assembled monolayers (SAMs). Such monolayers formed on gold surfaces from different derivatives of the OPE-type of molecule 4-[[4-(phenylethynyl)phenyl]ethynyl]benzenethiol have shown particularly interesting electrical properties. They have enhanced electrical conductivity compared to SAMs of alkanethiols of comparable thickness, and their electrical properties can be varied significantly by relatively minor chemical modifications. In particular, an unfunctionalized OPE-type molecule behaves as a molecular rectifier, whereas functionalized with nitro, amino or fluoro groups it shows negative differential resistance.

Given a particular substrate, the structure of a SAM is governed by the molecular structure of the adsorbates, through their interaction with each other and the substrate. The properties, e.g. electrical conductivity, of a SAM are determined by a combination of the molecular and the SAM structure. Although numerous studies of SAMs comprised of aromatic thiols on gold have been reported, in general, there is still a need for information on both their structure and properties of the SAMs formed from them. The orientation of entirely aromatic thiol adsorbates in monolayers on gold has been reported to vary from vertical to partially tilted. This orientation and the packing density of a SAM are a result of the interplay between the sulfur-gold and the intermolecular lateral interactions between the SAM constituents. It has been reported that the packing of the organic groups can be improved by stacking interactions between the aromatic rings in the adjacent adsorbates, thus increasing the packing density. However, the packing density reported for OPE SAMs is lower than that for aliphatic SAMs.
In previous efforts made by two of the authors to delineate how the chemical structure of the medium between electron donors and acceptors affects the electron transport, a series of donor-acceptor (D-A) systems covalently linked by a variety of OPE-based bridges were prepared and studied in solution. As a natural consequence, an investigation of the electron transport properties of some of these OPE bridge structures when bound to electrode surfaces is planned. It is expected that comparisons of the results obtained for the D-A systems in solution with those obtained for arrays of the same OPE structures on surfaces can provide valuable information to gain a better understanding of the relationships between the molecular structure and the electrical properties of SAMs. However, as molecules at the surface of a material experience a different environment than those in solution, a firm knowledge of the packing geometries and densities for the SAMs formed from these OPE adsorbates is needed before fundamental studies of electron transport through the SAMs can be conducted.

The OPE systems studied are bound to the surface via a thiophenolate unit that will position the adsorbate at available binding sites on the Au(111) surface. Although difficult to predict, the OPE moieties respond to the positioning by tilting and twisting to achieve a close-packed structure; guided by the shape of the adsorbates and the intermolecular interaction between them and their π-systems. In this paper, we report structural information for SAMs formed on gold from three different OPE type adsorbates obtained by Infrared Reflection Absorption Spectroscopy (IRRAS), contact angle goniometry, Spectroscopic Ellipsometry (SE), High-Resolution X-ray Photoemission Spectroscopy (HRXPS), and Near-Edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy. By studying three different adsorbates with systematic structural variation, we hope to contribute to the understanding of the relationships between the molecular structure of target aromatic adsorbates and the resulting SAM structure.

2. Experimental Section
Figure 1. OPE’s with benzene (1), naphthalene (2), and anthracene (3) as the central aromatic moiety combined with the coordinate system used for the molecules.
Scheme 1. (i) Phenylacetylene, Pd$_2$dba$_3$, PPh$_3$, CuI, TEA, toluene, 38%; (ii) TIPS-acetylene, Pd$_2$dba$_3$, PPh$_3$, CuI, TEA, toluene, 66%; (iii) TBAF, THF; (iv) 1-acetylthio-4-iodobenzene, Pd$_2$dba$_3$, PPh$_3$, CuI, Hünig base, toluene, 88%; (v) TIPS-acetylene, Pd$_2$dba$_3$, PPh$_3$, CuI, TEA, toluene, 46%; (vi) Phenylacetylene, Pd$_2$dba$_3$, PPh$_3$, CuI, TEA, toluene, 88%; (vii) TBAF, THF; (viii) 1-acetylthio-4-iodobenzene, Pd$_2$dba$_3$, PPh$_3$, CuI, Hünig base, toluene, 76%

Materials and methods. 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. The substrates were stored under argon before monolayer adsorption and used without further cleaning.

Triethylamine (TEA) was dried by distillation from calcium hydride under nitrogen. Toluene and tetrahydrofuran (THF) were dried by distillation from sodium/benzophenone under nitrogen. All dried
solvents were used immediately after distillation. Other commercially available reagents were purchased from Aldrich, Acros or Lancaster and used without further purification.

Column chromatography and flash chromatography was performed on silica gel (Matrex, normal phase, LC60Å/35-70 µm). Proton (400 MHz) NMR spectroscopy was performed on a Varian UNITY-400 NMR spectrometer at ambient temperature in CDCl₃. Tetramethylsilane was used as reference for the chemical shifts (δH=0 ppm). An inert atmosphere was applied by three repetitive vacuum-argon cycles using a high vacuum pump. The reactions were then carried out under argon. The solvents were removed using a rotary evaporator at reduced pressure unless stated otherwise.

**Synthesis**

1-bromo-4-phenylethynynaphtalene (4). 1,4-Dibromonaphtalene (2.53 g, 8.86 mmol), Pd₂dba₃ (48 mg, 53 µmol), PPh₃ (83 mg, 0.32 mmol), and CuI (43 mg, 0.23 mmol) were added to a dry 250 ml flask under argon atmosphere. To the solids, toluene (60 ml), TEA (20 ml), and phenylacetylene (1.25 ml, 3.0 mmol) were added and the solution was stirred over night at 65 °C. The solution was then filtered and concentrated to give a black solid. The solid was triturated twice with warm hexane and filtered to remove insoluble byproducts. The hexane solution was concentrated to give a red-brown oil, which was purified using flash chromatography (hexane) to give the desired product as a white solid (1.02 g, 3.32 mmol, 38 %); ¹H –NMR (CDCl₃) δ 7.38-7.44 (m, 3H), 7.60 (d, 1H), 7.62-7.68 (m, 4H), 7.78 (d, 1H), 8.25-8.31 (m, 1H), 8.43-8.49 (m, 1H) Elemental analysis (%) calc. C₁₈H₁₁Br C: 70.38 H: 3.61 found C: 70.43 H: 3.68

1-phenylethynyl-4-triisopropylsilylethynynaphtalene (5). Compound (4) (344 mg, 1.12 mmol), Pd₂dba₃ (11 mg, 12 µmol), PPh₃ (18 mg, 68 µmol), and CuI (12 mg, 64 µmol) were added to a dry 100 ml flask under argon atmosphere. To the solids toluene (20 ml), TEA (5 ml), and triisopropylsilylacetylene (0.30 ml, 1.3 mmol) were added and the solution was stirred over night at 60 °C. The solution was then filtered and concentrated to give a solid. The solid was triturated with warm hexane and filtered to remove insoluble byproducts. The hexane solution was concentrated and the residual oil was purified using flash chromatography (hexane) to give the desired product as a colorless,
highly viscous, oil (300 mg, 0.735 mmol, 66 %); $^1$H –NMR (CDCl$_3$) δ 7.38-7.44 (m, 3H), 7.60 (d, 1H), 7.62-7.68 (m, 4H), 7.78 (d, 1H), 8.25-8.31 (m, 1H), 8.43-8.49 (m, 1H) Elemental analysis (%) calc. C$_{29}$H$_{32}$Si C: 85.23 H: 7.89 found C: 85.15 H: 7.82

1-phenylethynyl-4-acetylenenaphthalene (6). Compound (5) (81 mg, 0.20 mmol) was dissolved in THF (30 ml) and tetrabutylammoniumfluoride (0.24 ml, 0.24 mmol) was added. After 1h the reaction mixture was added to toluene (30 ml), washed with water (4x20 ml), dried over MgSO$_4$, and concentrated to give a brown oil, which solidified and was used without further purification.

1-phenylethynyl-4-ethynyl-(4´-acetylthiophenyl)naphthalene (2). Compound (5) (44 mg, 0.18 mmol), 1-acetylthio-4-iodobenzene (49 mg, 0.18 mmol), Pd$_2$dba$_3$ (4.8 mg, 5.2 µmol), PPh$_3$ (8.9 mg, 34 µmol) and CuI (2.1 mg, 11 µmol) were added to a dry 100 ml flask under argon atmosphere. To the solids, toluene (10 ml) and diisopropylethylamine (1 ml) were added, and the solution was stirred at ambient temperature overnight, filtrated, and concentrated to give a solid. The solid was purified by flash chromatography (hexane/DCM, 2:3) to give the desired product as a white solid (62 mg, 0.15 mmol, 88 %); $^1$H –NMR (CDCl$_3$) δ 2.46 (s, 3H), 7.38-7.49 (m, 5H), 7.64-7.71 (m, 6H), 7.75 (s, 2H), 8.42-8.51 (m, 2H) Elemental analysis (%) calc. C$_{28}$H$_{18}$OS C: 83.55 H: 4.51 found C: 83.38 H: 4.64

9-bromo-10-triisopropylsilylethynylanthracene (7). Dibromoantracene (2.0 g, 5.9 mmol), Pd$_2$dba$_3$ (33 mg, 32 µmol), PPh$_3$ (46 mg, 0.18 mmol), and CuI (31 mg, 0.16 mmol) were added to a dry 250 ml flask under argon atmosphere. To the solids, toluene (40 ml), TEA (10 ml), and triisopropylsilylacetylene (0.67 ml, 3.0 mmol) were added and the solution was stirred over night at 65 °C. The solution was then filtered and concentrated to give an orange solid, which was recrystallized (toluene:isooctane; 1:2) to remove excess dibromoantracene. The filtrate was concentrated to give a solid that was recrystallized (neat isooctane) to remove trace amounts of dibromoantracene. The filtrate was concentrated and the ensuing solid was recrystallized (neat ethanol) to give orange needleshaped crystals of 9,10-ditriisopropylsilyl ethynylanthracene. The filtrate was concentrated and purified by flash chromatography three times (hexane) to afford 7 as an orange solid (0.60 g, 1.4 mmol, 46 %); $^1$H –
NMR (CDCl₃) δ 1.22-1.31 (m, 21H), 7.60-7.66 (m, 4H), 8.56 (d, 2H), 8.67 (d, 2H) Elemental analysis (%): calc. C₂₅H₂₉BrSi C: 68.63 H: 6.68 found C: 68.45 H: 6.59

9-phenylethynyl-10-triisopropylsilylethynlanthracene (8). Compound (7) (0.33 g, 0.75 mmol), Pd₂dba₃ (15 mg, 15 µmol), PPh₃ (23 mg, 88 µmol), and CuI (9.5 mg, 50 µmol) were added to a dry 100 ml flask under argon atmosphere. To the solids, toluene (15 ml), TEA (2 ml), and phenylacetylene (0.10 ml, 0.90 mmol) were added and the solution was stirred for 36h at 65 °C. The solution was then filtered and concentrated to give a black oil/solid mixture, which was diluted with neat isooctane. This mixture was filtered and the filtrate was concentrated to give a black oil. The oil was purified by flash chromatography (hexane/DCM, 6:1) to give a yellow oil (0.30 g, 0.65 mmol, 88 %); ¹H –NMR (CDCl₃) δ 1.24-1.29 (m, 21H), 7.42-7.47 (m, 3H), 7.60-7.65 (m, 4H), 7.78 (d, 2H), 8.63-8.70 (m, 4H) Elemental analysis (%): calc. C₃₃H₃₄Si C: 86.41 H: 7.47 found C: 86.55 H: 7.42

9-phenylethynyl-10-acetyleneanthracene (9). Compound (8) (65 mg, 0.14 mmol) was dissolved in THF (40 ml) and tetrabutylammoniumfluoride (0.15 ml, 0.15 mmol) was added. After 1h the reaction mixture was added to toluene (30 ml), washed with water (6x40 ml), dried over MgSO₄, and concentrated to give a brown oil, which was used without further purification.

9-phenylethynyl-10-ethynyl-(4´-acetylthiophenyl)anthracene (3). The compound (9) (37 mg, 0.12 mmol), 1-acetylthio-4-iodobenzene (32 mg, 0.12 mmol), Pd₂dba₃ (6.0 mg, 5.8 µmol), PPh₃ (8.5 mg, 32 µmol), and CuI (2.5 mg, 13 µmol) were added to a dry 100 ml flask under argon atmosphere. To the solids, toluene (10 ml) and diisopropylethylamine (2 ml) were added, and the solution was stirred at ambient temperature overnight, filtrated, and concentrated to give a solid. The solid was purified by flash chromatography (hexane/DCM, 2:3) to give the desired product as an orange solid (42 mg, 92 µmol, 76 %); ¹H –NMR (CDCl₃) δ 2.48 (s, 3H), 7.42-7.53 (m, 5H), 7.63-7.68 (m, 4H), 7.77-7.83 (m, 4H), 8.64-8.73 (m, 4H) Elemental analysis (%): calc. C₃₂H₂₀OS C: 84.93 H: 4.45 found C: 84.88 H: 4.38

SAM-preparation. The following procedure was used to form SAMs from 1, 2 and 3 (see Figure 1): The desired molecule was dissolved in THF to give a 1 mM solution. The gold substrate was then immersed in 1-2 ml of this solution under argon and an excess (2 to 4 drops) of 1% ammonium...
hydroxide (NH₄OH (aq)) was added to hydrolyze the acetyl protecting group. The SAMs were formed at room temperature in the absence of light over 20h and then rinsed with THF three times, dried with nitrogen, and stored under argon.

Grazing incidence reflection absorption Fourier transform infrared spectroscopy (IRRAS). The infrared absorption spectra were recorded using a Bruker IFS 66v/S spectrometer equipped with a wide-band liquid nitrogen cooled MCi detector and with the optics and sample compartment evacuated to 3 mbar. For measurements of the SAM spectra, a grazing angle reflectance cell (Bruker A513) and p-polarized light at 80° incidence (relative to the surface normal) were used. For each sample and reference, a single beam spectrum, comprising 10000 scans, was recorded, and the absorption spectra were calculated as: $A = -\log(I/I_{\text{ref}})$. Clean gold samples were mainly used as references, but also SAMs of alkanethiol (dodecane) and deuterated alkanethiol. The resulting spectra were corrected by the interactive baseline correction utility of the OPUS software to remove large baseline fluctuations caused by interference and differences in reflectivity from sample to sample.

The IR spectra of the molecules in the gas phase were calculated using the Gaussian 03 program suite. Geometry optimizations and frequency calculations were performed without symmetry constraints using the B3LYP-functional with the 6-311+G(d,p) basis set.

Contact angle goniometry. Static water contact angles were measured with a Ramé-Hart 100 instrument using deionized water. Each measurement was performed three times and then averaged.

Spectroscopic Ellipsometry (SE). Spectroscopic ellipsometry measurements were performed over a wavelength range of 245-1000 nm using a J.A. Woollam M2000 ellipsometer. Three different angles of incidence with respect to the surface normal were used, 65, 70, and 75°. A clean gold surface was the reference for the bulk material in the model used to fit the experimental data. The analysis of these data was performed using the WVASE32 software, supplied with the instrument, and a Cauchy model was applied in the fitting procedure. The refractive index, $n$, was determined as 1.46 for SAM 1 using the data from the wavelength interval ($\lambda>$350nm) at which the molecule does not absorb, i.e. where the extinction coefficient $k$ was zero. The latter parameter $k$ was then modeled over the entire
wavelength range (245<λ<1000 nm), thereby verifying the proposed $n$-value. This $n$-value was used as an approximation for all systems; it also complies well with earlier published data.\textsuperscript{34} The quality of the fit was evaluated by the $\chi^2$ criterion and by visual inspection of how well the $n$ and $k$ values reproduced the solution absorption spectrum for the particular molecule.

**High-Resolution X-ray Photoelectron Spectroscopy (HRXPS).** The high-resolution XPS measurements were performed at the synchrotron storage ring MAX II at MAX-lab in Lund (Sweden) using the D1011 beamline. The beamline is equipped with a Zeiss SX-700 plane-grating monochromator and a two-chamber ultrahigh vacuum experiment station with a SCIENTA type analyzer. To probe the S 2p, C 1s, and Au 4f core levels, the excitation energies 344, 350 and 580 eV were used. The photon energy choice for a particular spectrum was based on the optimization of the photoionization cross section for the corresponding core level. The spectra were acquired in normal emission geometry, and the resolution was better than 0.1 eV.

HRXPS spectra were used to determine the electron binding energies of the relevant core levels of the different molecular components. Samples of dodecanethiol and hexadecanethiol SAMs on Au, attached to the same sample holder as the probed sample, were used as a reference for the energy scale and thickness. The binding energy scale of every spectrum was individually calibrated using the Au 4f$^{7/2}$ emission line at 83.95 eV of the dodecanethiol-covered Au substrate; this energy is given by the latest ISO standard.\textsuperscript{35} The spectra were fitted by a symmetric Voigt function with a variable Lorenz-Gauss ratio,\textsuperscript{36} and a Shirley background was applied.\textsuperscript{37} The S 2p$^{3/2,1/2}$ doublet was fitted by using the same full width at half-maximum (fwhm) for both components, a spin-orbit splitting of 1.18 eV, and a branching ratio (S2p$^{3/2}$/S2p$^{1/2}$) of 2. If there were several different species in a particular spectrum, the same fwhm was used for all individual emission bands. From the HRXPS data, the film thicknesses were derived using the intensity ratio of the C 1s and Au 4f emissions.\textsuperscript{15, 38}

**Near-Edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy.** The NEXAFS measurements were carried out at the HE-SGM beamline of the synchrotron storage ring BESSY II in Berlin (Germany) and also at the D1011 beamline at MAX-lab in Lund (Sweden) using the partial
electron yield mode. The results from both facilities were consistent. Here, the data set from BESSY II is presented. The spectra were acquired at the C K-edge with a retarding voltage of -150 eV. The incident angle of the linearly polarized synchrotron light was varied from 90° (E-vector in the surface plane) to 20° (E-vector near surface normal) to examine the molecular orientation. The raw NEXAFS spectra were normalized to the incident photon flux by dividing the SAM spectrum by a spectrum of a clean, freshly sputtered gold substrate. The spectra were normalized to the height of the absorption edge after setting the pre-edge range to zero.

3. Results and Discussion

**Synthesis.** The synthesis of 1 was performed as reported elsewhere. The syntheses of the two OPE adsorbates 2 and 3 (Scheme 1), in which the central benzene ring is replaced by naphthalene or anthracene introduces a synthetic problem, because suitable, unsymmetrical starting materials are unavailable. The syntheses of unsymmetrical OPEs usually begins from a starting material with two different halogenatoms, i.e. bromine and iodine. The construction of the systems is then simplified due to the difference in reactivity between iodine and bromine in the applied palladium-catalyzed Sonogashira cross-coupling. Because this type of building block is presently unavailable, a statistical approach is necessary. The sequence with which the phenylacetylene and triisopropylsilylacetylene (TIPS-acetylene) moieties were attached in the syntheses has been optimised. For the synthesis of the naphthalene analogue, attaching the TIPS-ethylene first results in a mixture, in which the desired product is very difficult to separate from the disubstituted by-product, thereby necessitating the addition of phenylacetylene first. On the other hand, attaching the phenylethylene moiety to the anthracene core first results in an insoluble solid intermixed with by-products. Fortunately, coupling TIPS-acetylene to the anthracene core first gives a solid that can be purified using conventional chromatography.

Thus, the synthesis of the naphthalene analogue commenced with the coupling of 1,4-dibromonaphthalene with one equivalent of the phenylacetylene in the presence of a palladium catalyst. The monoalkynylated product was then separated from the statistical mixture of products and starting material and coupled with the triisopropylsilylacetylene. Subsequent removal of the triisopropylsilyl
followed by the final cross-coupling with 1-acetylthio-4-iodobenzene afforded the target compound 2 in
acceptable yield. The anthracene analogue was also obtained in acceptable yield by a similar route, although the sequence of attachment of the phenylacetylene and triisopropylsilylacetylene was reversed.

Because the reactions consist of two subsequent Sonogashira couplings a one pot reaction, allowing the core arene to react first with one equivalent of the appropriate acetylene and then with an excess of the other one might seem tempting. Although seemingly reducing the number of work-up steps, attempts towards this route ensued in a plethora of by-products and intermediates making purification difficult and the approach too cumbersome.

The SAMs were grown under standard conditions for acetyl protected OPE-thiols. The gold substrate was immersed into a THF-solution of the OPE-derivate of interest, which was deprotected by addition of excess aqueous ammonium hydroxide, therefore; rather concentrated THF-solutions of adsorbates (1 mM) were used. The surfaces were immersed into the THF-solutions for 20 h. Saturated monolayers of both aliphatic and aromatic thiols have been shown to form within a couple of hours of immersion into considerable less concentrated solutions than the ones used here. Of particular relevance, at a tenth of the concentration we use, immersion for 21 h was reported to be the optimum time for film growth of an adsorbate similar to 1. Further, STM studies of adsorbates of identical lateral bulk as for 3 have been reported that show images of well-ordered SAMs after 24 h growth from solution of substantially lower concentrations (50 µM) than ours. Accordingly, under the above conditions, a possible influence of kinetic effects can usually be excluded, and the fabricated SAMs should correspond to the thermodynamically equilibrium state. The SAMs were protected from ambient air during and after the monolayer formation to prevent the oxidation of the thiolate groups. To remove weakly bound adsorbate molecules, which could be present at the SAM-ambient interface, the films were thoroughly rinsed with THF. Sonication of the SAMs during washing caused the gold film to flake off, and was therefore not used.

**Wetting properties.** The static water contact angles obtained for the SAMs 1, 2, and 3 were 74 (±3), 83 (±1), and 85° (±1), respectively. These values can be expected for this type of aromatic film;
they differ significantly from the contact angles that are observed for either a clean gold surface or non-
substituted aliphatic films.\textsuperscript{17} This finding shows that there are macroscopic films of the OPE-derivatives
on the substrates.

\textbf{Grazing incidence reflection absorption Fourier transform infrared spectroscopy (IRRAS).}
Infrared spectroscopy has proven to be a very powerful technique to characterize SAM films on metal
substrates.\textsuperscript{18} Different surface sensitive IR-based techniques have been used and varying degrees of
sophistication in the subsequent analysis have been employed in order to gain information on the film
thickness, packing density, and average tilt angle of the chemisorbed molecules.\textsuperscript{20, 34} For the SAMs of
this study, we decided to use grazing incidence (80° to the surface normal) reflection absorption FTIR
spectroscopy, combined with isotropic FTIR spectroscopy of the acetyl protected precursor molecules
in KBr pellets. The interpretation of the experimental data was supported by quantum mechanical
calculations of the frequencies, intensities, and polarizations for the vibrational normal modes using the
double harmonic approximation. From the dipole selection rules for molecules adsorbed on conducting
substrates, it follows that transitions with a dipole parallel to the surface normal are allowed and those
perpendicular to the surface normal (parallel to the conducting surface) are forbidden.\textsuperscript{49} The measured
intensity of an IR band can thus be related to the orientation of the corresponding transition dipole
moment and, therefore, information about the molecular orientation can be obtained from polarized
IRRAS spectra.
Figure 2. IRRAS spectrum of SAM 1 (top), calculated spectrum of 1 as the free thiol (middle), and IR spectrum of 1 in a pressed KBr pellet (bottom). The polarizations of the peaks in the calculated spectrum are indicated and related to the axis convention shown in Figure 1.
Figure 3. IRRAS spectrum of SAM 2 (top), calculated spectrum of 2 as the free thiol (middle), and IR spectrum of 2 in a pressed KBr pellet (bottom).
Figures 2-4 show the IRRAS spectra of the SAMs 1-3 and the bulk spectra of the respective compounds, taken as references. The quality of the spectra is quite good considering the very low absorbances ($A < 3 \cdot 10^{-4}$) of these monolayers. In addition to the presented IR region (1650-600 cm$^{-1}$), the samples show weak bands in the CH-stretching range (3200-3000 cm$^{-1}$) and very weak bands in the C≡C-stretching region (2200-2000 cm$^{-1}$). When compared to the KBr spectra of the acetyl-protected precursors, the relative intensities of several peaks are found to be quite different, which is interpreted with the help of the surface-selection rules. Apart from the obvious difference that stems from the difference in molecular structure (the adsorbed molecules does not have any acetyl group, which has a
very strong C=O stretching vibration at 1700 cm⁻¹, outside the displayed region), the relative intensities of the characteristic peaks are quite different. This difference is most obvious for the spectra of SAM 1 (Figure 2), if the low energy region (900-600 cm⁻¹) is compared to the high-energy region (1650-1350 cm⁻¹). In the KBr spectrum, the strongest bands are found in the low-energy region (~800 cm⁻¹), which is dominated by out-of-plane short-axis polarized CCH deformations (x-polarized, see Figure 1), while the long-axis polarized transitions (z-polarized) at high energy are much weaker. In the SAM spectrum, the intensities in these two regions are almost equal. This behaviour is a qualitative indication of the orientational order and an upright molecular orientation in the SAM film, in which the long-axis polarized transitions should have a larger relative magnitude compared to the x/y-polarized transitions if the molecules are oriented with their long axes preferentially along the surface normal. The fact that the short-axis transitions are nevertheless visible is a further indication that the molecules are not exactly aligned along this normal, but are inclined to some extent. In principle, it is possible to extract quantitative information about the inclination angle from comparison of the SAM spectra with the isotropic bulk spectra but, due to the very large uncertainties in such treatment, we refrain from this analysis here. Note only that the spectra of SAMs 2 and 3 (Figures 3 and 4) show similar features as the spectrum of SAM 1, but the difference in the relative magnitudes of the high and low-energy bands compared to the KBr spectra are less pronounced.

**Spectroscopic ellipsometry (SE).** Based on the measurements of several different samples for each type of SAM, the average layer thicknesses were estimated at 1.9 (±0.1), 1.6 (±0.1), and 1.4 (±0.1) nm for SAMs 1, 2, and 3, respectively. The absolute values of the SAM thicknesses are dependent on the $n$-value assumed, which explains the relatively large error margins. The data fit in itself gives a tenfold smaller margin for error, which confirms the validity of the model used.

**HRXPS measurements.** The C 1s and S 2p HRXPS spectra are shown in Figures 5 and 6, respectively. The peak position, fwhm and the relative intensity of the different peak components for these spectra are presented in Table 1.
As seen in Figure 5, C 1s spectra of SAMs 1, 2 and 3 exhibit the main emission peak at a binding energy of ~284.2-284.6 eV (see table 1 for details). This peak is assigned to the aromatic backbone. In addition, a low-intensity shoulder at higher binding energy is observed for all SAMs, with an intensity that is slightly different for each SAM. This shoulder has previously been observed for aromatic SAMs and assigned to the carbon atom bound to the sulfur headgroup or to a shake-up process. The latter assignment was supported by an earlier HRXPS study on biphenyl-substituted alkanethiol SAMs, while the former assignment is most consistent with the most recent data for a series of SAMs with an oligophenylene backbone. The fwhm of the main C 1s peak varies from 0.99 eV for SAM 1, to 1.10 eV for SAM 2, and 1.29 eV for SAM 3 (see Table 1). The values for SAMs 1 and 2 are slightly higher, and for SAM 3 significantly higher, than the analogous values reported for biphenyl and terphenyl thiol SAMs (~ 0.8 eV) on Au(111) as measured by HRXPS using the same experimental setup. The higher fwhm values for the SAMs of this study may have several causes. First, charge redistribution within the more extended π-systems of SAMs 2 and 3 will lead to slightly different binding energies for the C 1s electrons for the non-equivalent C atoms. The slight asymmetry of the C 1s peak for SAM 2 is a further indication for multiple components in the spectrum. Second, a structural inhomogeneity related to a complex molecular arrangement or lower degree of structural order for the larger molecules may also cause a larger fwhm.
XPS is a useful technique to determine the thickness of SAMs because the signal intensity correlates to the degree of coverage or density of molecules at the surface. Film thicknesses were estimated from the HRXPS data using the intensity ratio of C 1s and Au 4f photoelectron signals which were acquired at a photon energy of 580 eV (spectra not shown), standard attenuation lengths, and spectra for the hexadecanethiol film measured as a reference system during the same experiment.

The thickness was calculated using eq.1,

\[
\frac{I_C}{I_{Au}} = k \left[ 1 - \exp \left( \frac{-d_{eff} - d_S}{\lambda_C} \right) \right] \exp \left( \frac{-d_{eff}}{\lambda_{Au}} \right)
\]

where \( I_C \) and \( I_{Au} \) are the integrated intensities of the C 1s and Au 4f signals, \( \lambda_C \) and \( \lambda_{Au} \) are the attenuation lengths for the C 1s and Au 4f photoelectrons at the given kinetic energy, respectively, \( k \) is an instrument-specific constant, \( d_S \) is a spacing for the S-Au unit (1.8 Å), and \( d_{eff} \) is the effective thickness of the molecular film. Values for \( \lambda_C \) and \( \lambda_{Au} \) were estimated using the expression
$\lambda = 0.3 E_{\text{iso}}^{0.64}$ obtained for alkanethiol SAMs.\textsuperscript{54} The $k$ value was determined using the reference system (hexadecanethiol SAM on Au). The resulting effective thicknesses are 1.8 nm for SAM 1 and 1.7 nm for SAMs 2 and 3, respectively. The uncertainty in these values is estimated to ± 0.1 nm.

![HRXPS spectra](image)

**Figure 6.** The S 2p HRXPS spectra of SAMs 1-3 on Au (111) substrates.

HRXPS is also a powerful tool to investigate the identity of the headgroup-substrate interface. For this purpose, S 2p HRXPS spectra were recorded for all the investigated SAMs. Representative spectra are presented in Figure 6. The relatively low signal-to-noise ratio of these spectra is related to the attenuation of the signal by the aromatic overlayer. All S 2p spectra show a S 2p doublet ($S 2p_{3/2}$, $S 2p_{1/2}$) with the $S 2p_{3/2}$ maximum at ~162 eV, which is assigned to the thiolate species bound to the metal surface.\textsuperscript{56-60} This doublet is accompanied by a less intense doublet with the $S 2p_{3/2}$ peak at ~163.5 eV (slightly lower binding energy for SAM 1), see Table 1, which might originate from residual physisorbed molecules at the SAM-ambient interface,\textsuperscript{61} since this peak is usually assigned to unbound thiols or disulfides.\textsuperscript{62} In addition, a doublet at about 161 eV ($S 2p_{1/2}$) was observed in the spectra of SAMs 2 and 3. Peaks at this binding energy have previously been assigned to atomic sulfur or
differently bound SAM constituents.\textsuperscript{12, 53, 63-65} We believe that the latter assignment is true for SAMs 2 and 3.

**Table 1.** Binding energy position, fwhm and the relative intensity ratio of the individual features in the C 1 s and S 2p HRXPS spectra of SAM 1-3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C 1s</th>
<th>S 2p</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Position (eV)</td>
<td>fwhm (eV)</td>
</tr>
<tr>
<td>SAM 1</td>
<td>284.50</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>285.37</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>284.33</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>285.38</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SAM 2</td>
<td>284.46</td>
<td>1.29</td>
</tr>
<tr>
<td></td>
<td>285.59</td>
<td>1.29</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The relative contributions of the different species could be estimated from the ratio between the respective peak area and the total area (integrated intensity) for the S 2p signal (see the right column in Table 1). Assuming that the peak at ~163.5 eV originates from physisorbed species at the SAM-ambient interface, its intensity has to be scaled down to correct for the lack of attenuation of the S 2p signal from such species. For this correction, we used the film thicknesses obtained above and the attenuation length given by Lamont \textit{et al.}\textsuperscript{54} Thus, the relative contributions of the three different species (differently bound, thiolate-bound, and physisorbed adsorbates) corresponding to the S 2p\textsubscript{3/2,1/2} doublets at 161, 162, and 163.5 eV (S 2p\textsubscript{3/2}) were estimated as 0, 97, and 3\% for SAM 1; 10, 89, and 1\% for SAM 2; and 22, 73, and 5\% for SAM 3, respectively. The relatively small fraction of the physisorbed molecules (S 2p ~163.5 eV) is in accordance with the monolayer-range film thicknesses found for the SAMs by the ellipsometry and HRXPS measurements.
NEXAFS Measurements. The NEXAFS spectra of SAMs 1-3 were acquired at the C K-edge with the incidence angle of the linearly polarized synchrotron light varied from 90 to 20° and are shown in Figure 7. These spectra provide information about the electronic structure and average orientation of the molecules 1-3 in the respective films. The dominant spectral feature is the $\pi^*$ resonance at $\sim$284.9 eV (see Table 2 for the exact values) related to the aromatic $\pi$-system of the OPE moieties (a transition of the C 1s electrons into an antibonding $\pi^*$ orbital). This peak is accompanied by a weaker $\pi_2^*$ resonance at $\sim$289 eV.

![Figure 7: C K-edge NEXAFS spectra of SAMs 1-3 on Au(111) acquired at different angles of X-ray incidence (top panels) and the differences of the spectra collected at X-ray incident angles of 90 and 20° (bottom panels). The dash lines represent the zero level of the difference spectra.](image)

The spectra of SAMs 2 and 3 exhibit a more complex $\pi^*$ resonance structure than those for SAM 1. There is a pronounced splitting of the $\pi^*$ resonance into the several individual resonances, which can be
related to the chemical shift of the symmetry independent carbon atoms of naphthalene and anthracene units in the molecules 2 and 3 with strong influence of excitonic effects; similar splitting is observed in the NEXAFS spectra of polyacenes. The broad resonances at about 293.5 and 303 eV can be assigned to an excitation of the C 1s electrons into the $\sigma^*$ orbitals. The assignments and positions of the resonances are given in Table 2.

Table 2. Assignments and energy positions of the C K-edge NEXAFS resonances for SAMs 1-3 on Au(111).

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Resonance position (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\pi_1^*$</td>
<td>284.92</td>
</tr>
<tr>
<td></td>
<td>$\pi_{1a}^*$ 284.91</td>
</tr>
<tr>
<td></td>
<td>$\pi_{1b}^*$ 285.61</td>
</tr>
<tr>
<td>$\pi_2^*$</td>
<td>288.63</td>
</tr>
<tr>
<td></td>
<td>288.73</td>
</tr>
<tr>
<td>$\sigma_1^*$</td>
<td>293.51</td>
</tr>
<tr>
<td></td>
<td>293.53</td>
</tr>
<tr>
<td>$\sigma_2^*$</td>
<td>$\approx$ 303</td>
</tr>
</tbody>
</table>

The incidence angle of the linearly polarized light was varied from 90 to 20°. The intensity of the NEXAFS resonance depends on the orientation of the transition dipole moment (TDM) of the probed molecules relative to the polarization of the incoming light. The intensity is at a maximum if the direction of the electric field of the incidence light ($E$ vector) and the TDM are parallel to each other. Inversely, when the two are orthogonal, the excitation does not occur. As illustrated in Figure 7, the NEXAFS spectra of SAM 1 shows a pronounced linear dichroism, i.e. dependence of the resonance intensity on the angle of X–ray incidence, implying a well-ordered layer. The $\pi_1^*$ and $\pi_2^*$ resonance intensities are higher and the $\sigma^*$ resonance intensities are lower at the normal incidence than at the grazing incidence. The TDMs of the $\pi_1^*$ and $\pi_2^*$ resonances are perpendicular to the molecular plane ($x$ polarized, see Figure 1), while those of the $\sigma^*$ resonances are oriented within the molecular plane,
mostly along the long molecular axis (z polarized). Considering this orientation, the observed linear dichroism implies an upright orientation of the SAM constituents in SAM 1. The spectra of SAM 2 and 3 show a smaller dichroism than those of SAM 1. The relatively small angular dependence of the resonance intensity can be interpreted in several ways. It indicates a relatively strong inclination of the molecules, with effective average orientation of their TDM almost at the magic angle (\( \alpha \approx 54.7^\circ \)) relative to the surface normale (vide infra), and/or low orientational order. It is principally not possible to distinguish between these two possibilities based on NEXAFS data.

The average tilt angle of the SAM constituents was obtained by a quantitative analysis of the angular dependence of the NEXAFS resonance intensities and the evaluation was based on the standard procedure. For this analysis, the intensity of the \( \pi_1^* \) resonance (splitted for SAMs 2 and 3) was selected, since it is the most intense and well-resolved absorption peak in the spectra. For the topical molecules, the intensity \( I \) of the \( \pi_1^* \) resonance is related to the average tilt angle \( \alpha \) of the corresponding TDM with respect to the surface normal and the incidence angle \( \theta \) by

\[
I(\theta, \alpha) \propto 1 + \frac{1}{2} (3 \cos^2 \theta - 1)(3 \cos^2 \alpha - 1)
\]

(2)

The angles are defined in Figure 8. The term \( \cos^2 \alpha \) can be expressed through the twist angle \( \vartheta \) of the aromatic rings with respect to the plane spanned by the surface normal and the molecular axis and through the average tilt angle \( \phi \) of the molecular axis with respect to the surface normal by

\[
\cos \alpha = \cos \vartheta \sin \phi
\]

(3)

Consequently, the intensity expressed in the average tilt angle \( \phi \) of the molecular axis and the twist angle \( \vartheta \) is given by

\[
I(\theta, \vartheta, \phi) \propto 1 + \frac{1}{2} (3 \cos^2 \theta - 1)(3 \cos^2 \vartheta \sin^2 \phi - 1)
\]

(4)
The intensity ratios $I(\theta)/I(20^\circ)$ were used instead of the absolute intensity to avoid normalization problems. From the experiment, the average tilt angles ($\alpha$) of the TDM were determined to be 65, 57, and 56° for SAM 1, 2, and 3, respectively. The molecular orientation is estimated by the relation between the three angles, $\alpha$, $\varphi$, and $\vartheta$ as expressed in equation 3. In the calculations of the tilt angle ($\varphi$) of the molecular axis, the value of the twist angle $\vartheta$ was taken as 32°, which is the twist angle for the herringbone arrangement of bulk biphenyl ($\pm 32^\circ$).\textsuperscript{16} It is also supported by the calculated 2D molecular arrangements for biphenyl and naphthalene mercaptan on Au,\textsuperscript{15} and the observation of a herringbone arrangement for a series of oligo(phenylethynyl)benzenethiols.\textsuperscript{13} However, while the chosen twist angle is well motivated for SAM 1, it is most likely not the same for all three SAMs. Assuming this twist angle, the critical tilt angle at which the TDM is slanted away from the surface normal by the magic angle is 43° according to equation 4. The average tilt angles calculated for SAMs 1-3 are ~30, 40 and 42° for SAM 1, 2 and 3, respectively. However, if present as suggested by the HRXPS measurements (vide supra), the physisorbed species, presumably orientated parallel to the surface, should to some
extent influence our IRRAS and NEXAFS results, thereby causing an over-estimation of the tilt angle and underestimation of the order of the adsorbates.

Figure 9. Angular dependencies of the $\pi_1^*$ intensity ratios for SAMs 1 (■), 2 (●), and 3 (▼). For comparison, the theoretical dependencies for different tilt angles of the aromatic backbone are added as dotted lines.

NEXAFS data can be used to estimate the film thickness based on the derived average tilt angles. Taking a theoretical length of the aromatic chain $d_{\text{theo}}$ and a spacing $d_s = 1.8$ Å for the S-Au unit,$^{70, 71}$ we can calculate the effective thickness $d_{\text{eff}}$ of the thioaromatic molecules from the NEXAFS-derived average tilt angle $\phi$ by

$$d_{\text{eff}} = d_{\text{theo}} \cos \phi + d_s$$

(5)

The resulting NEXAFS-derived thicknesses are 1.8 nm for SAM 1, 1.6 nm for SAM 2, and 1.5 nm for SAM 3, which is in agreement with the thicknesses obtained by SE (Table 3). In contrast, the HPXPS-derived data give higher values for the layer thicknesses of SAMs 2 and 3 and, thus, a much less pronounced decrease in layer thickness going from SAMs 1 to 3. This behavior might be explained by
the fact that the model used for the thickness calculations from the HRXPS data does not take into account the structural differences between the various aromatic systems. In addition, the reference used in the thickness determinations is an alkylthiol, not an aromatic system. However, the important trend of decreasing thickness with increasing OPE bulk is the same for all measurements. It should be noted that the good agreement for the thicknesses obtained by NEXAFS and SE, justifies the choice of twist angle in the NEXAFS analysis for SAMs 2 and 3.

**Table 3.** Comparison of the thickness and average tilt angles for SAMs 1-3 obtained by SE, HRXPS, and NEXAFS measurements.

<table>
<thead>
<tr>
<th>Methods</th>
<th>SAM 1</th>
<th>SAM 2</th>
<th>SAM 3</th>
<th>SAM 1</th>
<th>SAM 2</th>
<th>SAM 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>SE</td>
<td>1.9</td>
<td>1.6</td>
<td>1.4</td>
<td>25</td>
<td>42</td>
<td>49</td>
</tr>
<tr>
<td>HRXPS</td>
<td>1.8</td>
<td>1.7</td>
<td>1.7</td>
<td>31</td>
<td>38</td>
<td>38</td>
</tr>
<tr>
<td>NEXAFS</td>
<td>1.8</td>
<td>1.6</td>
<td>1.6</td>
<td>30</td>
<td>40</td>
<td>42</td>
</tr>
</tbody>
</table>

* For each experimental technique, the values in italic are derived from the values in bold, according to eq. 5 and the necessary assumptions (see above).

**Structural evaluation.** No specific molecular arrangement can be assigned to the SAMs because neither of the techniques used in this study gives conclusive information on this point. Nevertheless, several conclusions regarding the SAM structure can be drawn from the analysis of the presented spectroscopic data. The spectroscopy results imply that all molecules formed ordered SAMs on the Au(111) substrate, with some differences in structure and degree of order. IRRAS and NEXAFS results indicate that SAM 1 is well-ordered and densely packed with almost upright standing molecules. The high quality of the film is further supported by the HRXPS data; The S 2p spectrum shows a dominant single peak from the thiolate bond, and the fwhm values of S 2p and C 1s are small. The experimental data for SAM 2 are in several aspects similar to SAM 1. However, the NEXAFS data indicate a significantly larger molecular inclination (40° compared to 30° for SAM 1). This is also qualitatively
implied by the IRRAS data, with a smaller difference observed for SAMs 2 and 3 in the relative magnitude of the high and low-energy bands in the IRRAS spectrum compared to the KBr spectrum than the difference observed for SAM 1 (Figure 2-4). The layer thickness was found to be smaller for SAM 2 than for SAM 1 (see Table 3) both by ellipsometry and HRXPS measurements, thereby indicating that the molecules have a stronger inclination in the former than in the latter one, which confirms the NEXAFS results.

For SAM 3, the NEXAFS spectra show only a weak variation in the absorption resonance intensity with a varying incidence angle of the polarized light. Such a result can be interpreted in either of two ways: First, it might indicate that SAM 3 is a layer of well-ordered but strongly inclined molecules with an inclination close to the magic tilt angle or, second, it might indicate a poorly defined monolayer that consists of randomly oriented molecules. In analogy with the observations of well-ordered SAMs reported for systems similar to our anthracene system 3,46 we believe it is reasonable to assume that SAM 3 is a well-ordered and close-packed SAM of highly inclined adsorbates. Within this model, the tilt angle for SAM 3 was found to be about 42° (from NEXAFS measurements), which is substantially larger than that for SAM 1.

Comparing the HRXPS data for the three SAMs, we note that the main C 1s peak shows different fwhm’s in these three systems – the fwhm value for SAM 1 is slightly smaller than that for SAM 2 and noticeably smaller than that for SAM 3 (see Table 1). Presumably these differences in the fwhm can be a result of a higher structural inhomogeneity in SAMs 2 and 3 (especially) as compared to 1.50 Further, the fwhm of the S 2p\(_{3/2,1/2}\) peaks behave in a similar way - they are 0.51, 0.52, and 0.69 eV for SAMs 1, 2 and 3, respectively. Compared to the S 2p\(_{3/2,1/2}\) fwhm of 0.50 eV obtained in previous HRXPS measurements on high-quality bphenylthiol72 and bphenyl-substituted alkanethiol73 films on Au(111) with the assumed fully commensurate (\(\sqrt{3} \times \sqrt{3}\))R30° surface lattice structures, SAMs 1 and 2 would be expected to have an arrangement of the sulfur headgroups, which is close to a commensurate one. However, presumably the (\(\sqrt{3} \times \sqrt{3}\))R30° structure is not accessible by 2 because its cross-section is too large, see discussion below. The larger fwhm found for SAM 3 possibly implies a higher inhomogeneity
of the adsorption sites for the thiolate-bound molecules on the substrate. Note also that there is noticeable spectral weight of the 161 eV (S 2p_{3/2}) doublet in the S 2p HRXPS spectrum of SAM 3, which suggests that a part of the molecules 3 is bound to the substrate in a different way than in archetypical SAMs of thiolates. The inhomogeneity may be caused by the relatively strong intermolecular interaction between the adsorbate molecules. The π-π interactions could force the adsorbates to shift to some extent from equivalent adsorption sites or even distribute between non-equivalent adsorption sites, overcoming the headgroup-substrate interaction.

The observed structural differences between the SAMs formed by molecules 1-3 can be understood by considering the constraints imposed on the SAM formation by the adsorption “template” (i.e., surface structure) provided by the substrate, the size of the molecules, and sterical effects. The exact geometry of the adsorption site for thiolates is still under discussion. In the early work, a preferential attachment at a three-hollow site of the Au(111) substrate has been suggested, however, more recently the atop position has been favoured. Irrespective of the identity of the adsorption site, if only equivalent positions are occupied, small sized adsorbates on Au(111) are expected to give a fully commensurate ($\sqrt{3} \times \sqrt{3}$)R30° surface-lattice structures. The van der Waals cross-section (22 Å²) of benzene perpendicular to the ring plane is in nearly perfect agreement with the available area per binding site (21.6 Å²) in a theoretical ($\sqrt{3} \times \sqrt{3}$)R30° structure of thiolates on an Au(111) surface. SAM 1 should therefore be relatively easily accommodated by the Au(111) surface, close-packed in a herringbone structure with the molecular backbones having relatively small tilt angles. Such a structure for SAM 1 has been as suggested by J. J. Stapelton et al. who reported that 1 forms a well-ordered SAM with an average tilt angle of ~33° from the surface normal. This value is in good agreement with the 30° tilt angle obtained in our NEXAFS measurements of SAM 1. It should be noted that, while the adsorption positions are expected to form a ($\sqrt{3} \times \sqrt{3}$)R30° 2D lattice, the herringbone arrangement of the molecules leads to a doubled 2D unit cell, (2$\sqrt{3} \times \sqrt{3}$)R30°, for the molecular layer, with two molecules per unit cell.
The cross-sections of naphthalene (31 Å²) and anthracene (39 Å²) perpendicular to the ring planes and along the long axes of these structural motifs are both considerably larger than the available binding area in a SAM of a (√3 × √3)R30° structure. Therefore, the larger molecules 2 and 3 are expected to form a different, more extended and less dense lattice. Indeed, it was recently reported that, instead of a herringbone structure stabilized mainly by an edge-to-face σ-π interaction, anthracene adsorbates with structural features similar to the topical systems form well-ordered SAMs governed mainly by parallel-displaced face-to-face π-π stacking interactions that align the molecules in wavelike rows in the π-π interaction direction. The area per molecule in the SAMs of the two adsorbates with the most structural similarity to ours are about 53-56 Å², which is considerably larger than the cross-section of interest for anthracene. The larger area occupied by each molecule indicates that these molecules should be more inclined than the adsorbates in SAMs of benzene analogues, such as 1. Presumably, the mismatch between the size and shape of the molecule and the alignment of the favorable binding sites at the surface directs them into a different, more expanded arrangement than the (√3 × √3)R30° structure. The intermolecular distances between the adsorbed headgroups, given by the substrate “template”, are presumably much larger than the effective lateral van der Waals dimensions. In consequence, the molecules respond by tilting to fill the void space and to give the most favourable intermolecular interactions possible for the given surface lattice. This is consistent with the results of the present study. As stated above, several independent spectroscopic methods indicate a larger molecular inclination for SAMs 2 and 3 compared to SAM 1.

If oriented perpendicular to the surface, the anthracene adsorbate 3 should theoretically cover 1.8 binding sites per molecule (available area per binding site in an commensurate (√3 × √3)R30° structure divided by the anthracene cross-section). Analogously, each naphthalene adsorbate 2 should occupy and shield 1.5 binding sites, a slightly smaller number of sites than covered by 3, but still a larger number than the single site occupied by 1. Thus, the surface density of molecules in SAM 2 is expected to be lower than in SAM 1 but is likely to be higher than in SAM 3. This behavior is consistent with the data obtained from all our measurements. The thickness of SAM 2 falls in between that obtained for SAMs 1
and 3 as measured by SE (1.6 nm). As measured by HRXPS, the thickness for SAM 2 is the same for both SAMs 2 and 3 (1.7 nm). The tilt angle of 40° observed for the molecules in SAM 2 is in between that observed for the adsorbates in SAMs 1 and 3. This angle suggests that the molecules in SAM 2 are bound farther apart than theoretically necessary but are, relatively speaking, not forced apart as much as the molecules in SAM 3 to achieve the optimum packing geometry.

4. Conclusions

Herein, we have studied the effect of the molecular structure on the organization and packing of OPE-based molecules in SAM films. For this purpose, two new molecules have been synthesized and compared to the known system 1. Contact angle and IRRAS measurements show that SAMs were formed in all the cases, which was further verified by SE, HRXPS, and NEXAFS experiments. In agreement with previous reports, our results indicate that SAM 1 is highly oriented and densely packed, with the SAM-constituents being only slightly inclined. Based on the same set of measurements, our conclusion is that both adsorbates 2 and 3 form SAMs, albeit with an increasing tilt angle and decreasing surface density of molecules going from SAM 1 to SAM 2 and further to SAM 3. Because of the intrinsic limitations of NEXAFS spectroscopy, we cannot make an ultimate conclusion whether the large average tilt angles in SAMs 2 and 3 correspond to a large molecular inclination in the well-ordered SAMs or to a decreasing degree of molecular order in the SAMs. The comparison between the fwhm’s of the C 1s and S 2p emissions (HRXPS) for all three SAMs favours the former model for SAM 2 and the latter model for SAM 3. However, in view of the SAM structures reported for the adsorbates with similar molecular structure as 3, a well-ordered structure for SAM 3 cannot be excluded. Further, features in the HRXPS spectrum indicate that non-equivalent binding sites are occupied in SAM 3, which emphasize the importance of the intramolecular interactions in determining the SAM structure. Irrespectively of the actual structure, we assume that the structure of SAMs 2 and 3 result from the interplay between the structural template provided by the substrate and the intermolecular interaction, affected by the introduction of the naphthalene and anthracene moieties into the oligo(phenyleneethynylene) backbone. Due to the sterical constraints provided by these moieties, a
quasi-commensurate ($\sqrt{3} \times \sqrt{3}$)R30$^\circ$ packing of the adsorbates 2 and 3 is not possible, so that these molecules are forced to a looser lateral packing compensated for by a large molecular tilt.

Acknowledgment. This work is supported by grants from the National Graduate School in Materials Science (NFSM), the Swedish Research Council (VR), the German Research Foundation (grant ZH 63/9-2), and the European Community (Access to Research Infrastructure action of the Improving Human Potential Programme). M.Z. and A.S. would like to thank M. Grunze for the support, Ch. Wöll for the technical cooperation at BESSY II, and the MAX-lab and BESSY II staffs for assistance during the synchrotron-based experiment.

References


(35) Surface chemical analysis-X-ray photoelectron spectrometers-Calibration of the energy scales. ISO 15472, 2001


The area covered is calculated from the reported dimensions of the unit cells and the number of adsorbates in them.
For Table of Contents Use Only

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

Nilsson, Daniel; Watcharinyanon, Somsakul; Eng, Mattias; Moons, Ellen; Johansson, Lars; Zharnikov, Michael; Shaporenko, Andrey; Albinsson, Bo; Mårtensson, Jerker

Increased adsorbate size and inclination

Au(111)
Paper II
HRXPS and NEXAFS Study of Self-Assembled Monolayer of Porphyrin-Functionalized Oligo(phenyleneethynylene) on Gold: The Influence of the Binding Group.

Somsakul Watcharinyanon,† Daniel Nilsson,‡ Ellen Moons,†
Michael Zharnikov,§ Andrey Shaporenko,§ Bo Albinsson,‡
Jerker Mårtensson,‡ Lars S. O. Johansson†

Department of Physics, Karlstad University, S-65188 Karlstad, Sweden,
Department of Chemical and Biological Engineering, Chalmers University of Technology, S-41296 Göteborg, Sweden, and
Angewandte Physikalische Chemie, Universität Heidelberg, Im Neuenheimer Feld 253, D69120, Heidelberg, Germany

† Karlstad University.
‡ Chalmers University of Technology
§ Universität Heidelberg
Abstract

The porphyrin-functionalized oligo(phenyleneethynylene)s (OPE) are promising molecules for molecular electronics application. Three porphyrin-functionalized OPEs with different binding groups: (1) an acetyl protected thiophenol (R-S-COCH$_3$), (2) an benzylic thiol (R-CH$_2$-S-COCH$_3$), and (3) a trimethylsilylethynyl-group (R-C≡C-Si(CH$_3$)$_3$) have been synthesized and the corresponding molecular layers on Au(111) surfaces have been prepared. The chemical and packing properties of the molecular layers were characterized by X-ray photoelectron spectroscopy and near-edge X-ray absorption fine structure spectroscopy. The results reveal that layers formed from 1 have a high orientational order with an upright orientation and dense packing indicating a good quality self-assembled monolayer (SAM). On the other hand molecule 2 formed disordered molecular layers even though the molecule-surface bond is similar to the S-Au bond in 1. This suggests that the methylene linker in molecule 2 affects the molecular orientation so that a well-ordered, upright oriented SAM can not be formed. The silane system, 3, is also able to bind to the gold surface but the molecules are on the average inclined or have a poorly defined orientation. The packing of the respective molecular layers are strongly affected by the nature of the binding group.

Introduction

Molecular electronics arrays have recently received much attention in connection with the ongoing feature size reduction of electronic devices. In order to operate this electronics, the electron transport through the molecular layer is essential. Oligo(phenyleneethynylene) (OPE) derivatives have attracted our interest due to their large delocalized $\pi$-conjugated systems. 1-9 By introducing a porphyrin as the end group in OPE molecules, a wire-like molecule with optical and redox properties can be created, of interest for application in solar cells, 10, 11, sensors, 12-14 or other optoelectronic devices. 15-18 The immobilization of the molecules on the electrode, in this case, gold, can be achieved by self-assembly, in which molecules can organize themselves on the surface, 19 in so-called self-assembled monolayers (SAMs). In recent years, a number of studies of functionalized porphyrin SAMs
have been reported.\textsuperscript{20-29} In many cases, thiolate (S-) is used as an anchor which chemically binds to the gold surface. The high affinity of sulfur for the surfaces of noble metals makes it possible to create a well-defined organic surface with useful and alterable chemical functionalities displayed at the outer surface.\textsuperscript{30}

To achieve a high quality SAMs, an important aspect is to use an appropriate anchor or headgroup for attaching molecules to a substrate. For this purpose, we have synthesized free-base porphyrin-functionalized OPE with three different headgroups: (1) an acetyl-protected thiphenol ($R-\text{S-COCH}_3$), (2) an acetyl-protected benzylic thiol ($R-\text{CH}_2-\text{S-COCH}_3$), and (3) a trimethylsilylthynyl ($R-\text{C}≡\text{C-Si(CH}_3)_3$) group, where $R =$ porphyrin-functionalized OPE. For the first two groups, the acetyl groups are removed upon the adsorption, leaving the unprotected sulfur bound to the gold surface. By inserting a methylene linker in between S and the phenyl ring, one would expect a more upright orientation and more densely packed film as reported earlier for the terphenyl-substituted alkanethiol SAMs on gold.\textsuperscript{31-33} Adsorbates with an odd number of the methylene group in between the binding group and the terphenyl moiety were found to be more well-defined, more densely packed and orientated more perpendicular to the surface plane than the terphenylthiol SAMs itself.\textsuperscript{31-33} If a higher molecular complexity is demanded, then the high reactivity displayed by the acetyl group in the thiophenolesters may render the synthesis of such elaborate systems impossible. A less labile group, still supporting SAM formation, would therefore be of vital importance for successful construction of functionalized molecules of the complexity necessary for future applications. One such group might be the trimethylsilyl (TMS) group, a well established protective group in organic synthesis with a desirable reactivity pattern, which has been shown to support the formation of SAMs when attached to alkynes. However the interaction of the trimethylsilyl with the gold surface is still unknown. For that reason, we have chosen to explore the trimethylsilylethynyl group ($R-\text{C}≡\text{C-Si(CH}_3)_3$) as the binding/anchoring group. Our recent studies on a series of unfunctionalized OPE with the different TMS based anchors showed that the TMS-ethynyl group supports the formation of SAMs on Au(111) while the TMS-vinyl group produces a low quality thin film, and the TMS-phenyl group, in which the TMS connected directly
to the OPE moiety, does not attached the adsorbates to the surfaces at all. In particular, it has been reported that the chemical reaction between Si and the gold surface could occur in the formation of SAMs of alkanes with TMS-ethynyl anchor group and derivatives on Au.

To investigate the headgroup-substrate interaction, we performed High Resolution X-ray Photoelectron Spectroscopy (HRXPS) on the respective molecular layers. The HRXPS was also used to determine the composition and thickness of the film. The chemical and structural information of the molecules on the surface are provided by the Near-Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS). The structure, packing density and the orientation of these porphyrin-functionalized OPE system are interpreted by mean of these results in comparison with the unfunctionalized OPE SAM system. In the following section the experimental procedure and techniques are described. Thereafter, the results are presented and discussed. A conclusion of the work is given in the last section.
Experimental Section

Synthesis

Scheme 1. (i) Pd₂(dba)₃, triphenylphosphine, diisopropylethylamine, THF; (ii) Pd₂(dba)₃, triphenylarsine, TEA, CH₂Cl₂, MeOH.

5-(3,5-di-tert-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-{4-[4-(4-acetylthiophenylethynyl)phenylethynyl]phenyl}porphyrin (1). To 1-Acetylthio-4(4'-ethynyl)phenylethynylbenzene (9.0 mg, 33 μmol), 5-(3,5-di-tert-
butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-para-iodophenylporphyrin (21 mg, 24 μmol) and triphenylphosphine (15 mg, 55 μmol) put under an argon atmosphere and dry toluene (10 ml) and diisopropylethylamine (2 ml) were added followed by bubbling with argon for 20 min. Pd₂(dba)₃ (9.9 mg, 9.6 μmol) was added and the reaction mixture was stirred at 40°C for 12h and then concentrated to give a red solid. The solid was dissolved in CH₂Cl₂ and added to a short silica pad, washed with CH₂Cl₂, followed by elution with diethylether. Evaporation of the solvent gave a red solid which was purified with column chromatography (pentane/diethylether, 10:1 followed by pentane/diethylether, 1:1) followed by SEC (toluene) to give 1 as a red solid (7 mg, 6.9 μmol, 29%); °H-NMR (CDCl₃) δ -2.44 (br s, 2H), 1.50 (s, 18H), 1.77 (m, 12H), 2.45 (m, 9H), 2.55 (s, 6H), 3.97-4.06 (m, 8H), 7.43 (d, 2H), 7.58-7.62 (m, 4H), 7.69 (d, 2H), 7.80 (m, 1H), 7.90 (d, 2H), 7.93 (d, 2H), 8.10 (d, 2H), 10.23 (s, 2H); HRMS (FAB) calculated for [C₇₀H₇₃N₄OS]+ 1017.5506, found 1017.5504.

5-(3,5-di-tert-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-{4-[4-(4-acetylthiomethylphenylethynyl)phenylethynyl]phenyl}porphyrin (2). Using the same reaction conditions as for 1, with the exception that the quota toluene/diisopropylethylamine was 10:3, 5-(3,5-di-tert-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-para-iodophenylporphyrin (21 mg, 24 μmol) and 1-acetylthiomethyl(-4-(4-ethyl)-phenylethynyl)benzene (10 mg, 33 μmol) was coupled and purified to give 2 as a red solid (18 mg, 17 μmol, 61%); °H-NMR (CDCl₃) δ -2.43 (br s, 2H), 1.51 (s, 18H), 1.78 (m, 12H), 2.39 (s, 3H), 2.46 (s, 6H), 2.55 (s, 6H), 3.98-4.06 (m, 8H), 4.15 (s, 2H), 7.31 (d, 2H), 7.50 (d, 2H), 7.60 (d, 2H), 7.68 (d, 2H), 7.81 (m, 1H), 7.90-7.96 (m, 4H), 8.11 (d, 2H), 10.24 (s, 2H); HRMS (FAB) calculated for [C₇₁H₇₅N₄OS]+ 1031.5662, found 1031.5675.

5-(3,5-di-tert-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-{4-[4-(4-trimethylsilylethynylphenylethynyl)phenylethynyl]phenyl}porphyrin (3). 1-iodo(-4(4´-trimethylsilylethynyl)phenylethynyl)benzene (3.5 mg, 8.7 μmol), Pd₂(dba)₃ (0.74 mg, 0.71 μmol) and triphenylarsine (1.3 mg, 4.2 μmol) were put under an argon atmosphere. To the mixture, a solution of 2 (0.67 ml, 10 μmol) in CH₂Cl₂ and CH₂Cl₂ (2.33 ml) was added, followed by addition of MeOH (3 ml)
and TEA (80 μl). The reaction mixture was stirred at ambient temperature over night and then concentrated affording a brownish solid. The solid was dissolved in CH₂Cl₂ and added to a silica pad, washed with CH₂Cl₂, followed by elution with diethylether. Subsequent evaporation and SEC (toluene) gave 3 as a red solid (4.7 mg, 4.5 μmol, 52%); ¹H-NMR (CDCl₃) δ -2.43 (br s, 2H), 0.26 (s, 9H), 1.50 (s, 18H), 1.78 (m, 12H), 2.46 (m, 6H), 2.56 (s, 6H), 3.97-4.07 (m, 8H), 7.46-7.53 (m, 4H), 7.60 (d, 2H), 7.69 (d, 2H), 7.81 (m, 1H), 7.91 (d, 2H), 7.94 (d, 2H), 8.11 (d, 2H), 10.24 (s, 2H) HRMS (FAB) calculated for [C₇₃H₇₉N₄Si]+ 1039.6075, found 1039.6061.

Materials. Reagents and solvents were purchased from Acros and Aldrich and used without further purification. Tetramethylsilane was used as reference for the chemical shifts (δH=0 ppm). Solvents were dried by distillation under nitrogen, triethylamine (TEA) from calcium hydride and toluene and tetrahydrofurane (THF) from sodium/benzophenone. Inert argon atmosphere was applied by three repetitive vacuum-argon cycles that replaced the atmosphere above the reactants. Solvents were removed using a rotary evaporator at reduced pressure unless stated otherwise.

Gold substrates were purchased from Georg Albert PVD-Beschichtungen (Heidelberg Germany). They were prepared by thermal evaporation of 300 nm of gold onto mica. Then the gold films were flame-annealed in air, resulting in a polycrystalline film. The substrates were stored under argon before monolayer adsorption and used without further cleaning.

Methods. Column chromatography was performed on silica gel (Matrex, normal phase, LC60Å/35-70 μm). The porphyrin systems were purified using size exclusion chromatography (SEC) (Bio-Rad, Bio-beads S-X3, 200-400 mesh). Proton (400 MHz) NMR spectroscopy was performed on a Varian UNITY-400 NMR spectrometer, while carbon (100.6 MHz) NMR were performed on a JEOL Eclipse 400, both at ambient temperature in CDCl₃.
**SAM preparation.** The appropriate compound was dissolved in THF to give a 1 mM solution. The gold substrate was immersed into 1-2 ml of this solution and an excess (2-3 drops) of a 1% ammonium hydroxide solution in THF (prepared from ammonium hydroxide, 25-30% NH₃) was added to the reaction vessels containing compounds 1 and 2 to remove the acetyl protective group. For the silane, 3, no additional activation was needed. The gold substrates were allowed to stand in the solution under argon, at room temperature, and in the dark for 20h. The samples were then thoroughly rinsed with THF, dried with nitrogen and stored under argon, in the absence of light. Keeping the samples free from air and light is needed to avoid oxidation and photoinduced degradation. Additional cleaning of the samples using sonication was not possible, due to flaking of the gold substrate. As discussed below, it is uncertain whether all three molecular layers can be regarded as true SAMs. However, for simplicity, we use the notation SAM 1, SAM 2 and SAM 3 for molecular layer formed from compound 1, 2, and 3, respectively.

**High-Resolution X-ray Photoelectron Spectroscopy (HRXPS).** The SAMs were characterized by synchrotron-based HRXPS. The measurements were carried out at the synchrotron storage ring MAX II at MAX-lab in Lund, Sweden, using the beamline D1011. The beamline is equipped with a Zeiss SX-700 plane-grating monochromator and a two-chamber ultrahigh vacuum experiment station with a SCIENTA type analyzer. The spectra were acquired in a normal emission geometry at photon energies of 350 and 580 eV for Au 4f and C 1s. The photon energies of 350 and 160 eV were used to probe the S 2p and Si 2p core level regions, respectively. The N 1s region was also monitored with photon energy 580 eV. The binding energy scale of every spectrum was calibrated using the Au 4f⁷/₂ emission line of a dodecanethiol SAM on an Au substrate at 83.95 eV. The energy resolution of the spectrometer was better than 0.1 eV. The HRXPS spectra were fitted by a symmetric Voigt function with a variable Lorentz-Gauss ratio and a Shirley background was subtracted. The S 2p₃/₂,₁/₂ doublet were fitted by using a 1.2 eV spin-orbit splitting and a branching ratio (S 2p₃/₂/S 2p₁/₂) of 2. The Si 2p₃/₂,₁/₂ doublet were fitted by using a 0.6 eV spin-orbit splitting and the same branching ratio. The spin-orbit splitting components were fitted with the same full width at half-maximum (fwhm). If there were several different species in a
particular spectrum, the fwhm was used for all individual emissions. The film thicknesses were estimated using the intensity ratio and attenuation lengths of C 1s and Au 4f emissions. 42

Near-Edge X-ray absorption Fine Structure Spectroscopy (NEXAFS). This technique can give information about chemical and structural properties of molecules in the SAMs by probing electron transitions from core-levels to unoccupied molecular orbital which are characteristic for specific bonds or functional groups.43 The X-ray photon energy is scanned and the absorbed X-ray intensity is measured. The average orientation can be determined by observing the intensity modulation of resonance peaks in the spectra when X-ray incidence angles are varied. The NEXAFS measurements were performed at the beamline D1011 at MAX-lab. The spectra were acquired at the C K-edge in the partial electron yield mode with a retarding voltage of -150 eV. The incidence angle of the light was varied from 90° (E-vector in the surface plane) to 20° (E-vector near surface normal) to monitor 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. The NEXAFS spectra were then normalized to the height of the absorption edge.

Results

Synthesis. Three free-base porphyrin systems were synthesized (Scheme 1.), with different nature of the headgroup responsible for the attachment of the SAM-constituent to the gold substrate, i.e. either an acetyl protected thiophenol or benzylic thiol or a TMS-acetylene group. Syntheses of the OPE building blocks 1B, 2B and 3B (see Scheme 1) and the porphyrins P1 and P2 have been reported elsewhere.44-46 Terminal alkynes and aryl halides are normally cross-coupled by palladium catalysis in the presence of cuprous salts. However, because copper readily can be inserted into the porphyrin cavity, copper-free conditions had to be used in the preparation of compounds 1-3. Compound 3 was prepared in a satisfactory yield by a cross-coupling of the acetylene functionalized porphyrine P2 with the bridge building block 3B using the conditions optimized for couplings of
Due to the high reactivity of the acetyl protective group towards nucleophiles, other coupling conditions was necessary in the preparation of compounds 1 and 2. The sterically hindered and less nucleophilic diisopropylethylamine had to be used as the base instead of more favourable bases with higher nucleophilicity. Also triphenylarsine, a preferred ligand under copper-free conditions, interfered with the acetyl protective group and the less efficient triphenylphosphine had to be used. The substantial difference in obtained yield of compound 1 and 2 reflects the difference in stability of the two different acetyl protected thiols towards nucleophiles. In contrast to the high lability of the acetyl protected thiols, the TMS-acetylene group is stable under a large variety of reaction condition. This would make it an attractive attachment group if it supports the formation or high-quality SAMs.

**HRXPS measurements.** The S 2p, Si 2p and Au 4f core level spectra were examined to characterize the binding motif of the molecules to the Au surface. The S 2p spectra of both thiol-derived porphyrin SAMs are shown in Figure 1. The spectra show a poor signal which results from the attenuation of the photoelectron by a thick overlayer of large molecules. The intensity of the S 2p signal is expected to be lower than the Si 2p signal by a factor of 3 due to the photoionization cross section for the different photon energies and core levels.

After the curve fitting, two doublets were distinguished in the spectra obtained from both SAM 1 and SAM 2. The S 2p3/2 peak of the doublet at the lowest binding energy in each spectrum is found at ~162 eV was observed in both SAMs. This peak is commonly assigned to the thiolate-type sulfur bound to a metal surface indicating that the molecules 1 and 2 bind to the gold surface through the sulfur atoms. The other doublet at ~163-163.5 eV has previously been assigned to unbound sulfur which might indicate the existens of residual physisorbed molecules on the SAM-surface. The relative contributions of the two species were estimated from the ratio between the respective peak area and the total area for the S 2p signal. However, for the physisorbed species, the molecules were assumed to reside at the SAM-ambient interface. Therefore the intensity of the peak related to physisorbed molecules has to be scaled down to correct for the lack of attenuation.
of the S 2p signal. For this correction, the film thicknesses obtained from the intensity ratio of C 1s and Au 4f (described below) and the attenuation length given by Lamont et al.\textsuperscript{58} were used. After the attenuation correction of the S 2p signal, the ratio between bound and unbound sulfur was estimated to be 98:2 for SAM 1 and 91:9 for SAM 2. Although the signal to noise ratio makes the exact values uncertain, this indicates that most of the sulfur atoms in the films are present in the thiolate-gold bond configurations. The fwhm of both components of S 2p peaks in SAM 1 obtained by the fitting procedure is 0.56 eV while the value for SAM 2 is larger by 0.1 eV. The S 2p intensity signal of SAM 2 is slightly lower than SAM 1.

![HRXPS spectra of thiol-derivatived porphyrin SAMs](image)

**Figure 1.** S 2p HRXPS spectra of thiol-derivatived porphyrin SAMs, a) SAM 1 and b) SAM 2. The binding energy and fwhm of the S 2p\textsubscript{3/2} peaks are indicated.

The Au 4f\textsubscript{7/2} spectra of a clean gold substrate and for SAM 1, 2, and 3, which were acquired with a photon energy of 350 eV are presented in Figure 2.
Figure 2. Au 4f HRXPS spectra of clean Au and SAM 1, 2, and 3. The binding energy and fwhm of the Au 4f$_{7/2}$ peaks are indicated.

The spectrum of the clean gold substrate shows two components at binding energies 83.95 and 83.62 eV (fwhm of 0.40 eV). They are assigned to gold atoms in the bulk and in the surface layer, respectively. On the other hand, the spectrum of SAM 1, 2, and 3 exhibit a single peak. We interpret this peak as the result of a shift of the Au 4f surface component to higher binding energy upon adsorption, so that it overlaps with the bulk component. The low intensity of the Au 4f for SAM 1 is related to the attenuation of the photoelectron by the molecular overlayer. The higher Au 4f intensities for SAM 2 and 3 indicate a thinner or less dense overlayer. The Au 4f peak positions for SAM 2 (83.80 eV) and 3 (83.81) are almost equal whereas SAM 1 exhibits a peak at a slightly higher binding energy 83.85 eV.
Figure 3. Si 2p HRXPS spectra of SAM 3. The binding energy and fwhm of the Si 2p$_{3/2}$ peaks are indicated.

For SAM 3, the interaction of TMS-acetylene (R−C≡C−Si(CH$_3$)$_3$) with the gold surface was investigated by probing the Si 2p core levels. Figure 3 shows the Si 2p spectrum of SAM 3, with the TMS-ethynyl anchor. The binding energy of the emission peak is 101.85 eV, which was assigned to the Si-C bond in the TMS group. The fwhm of the peak is 1.24 eV. In recent studies on the alkylsilane (C$_n$H$_{2n+1}$SiH$_3$) SAMs on Au, the Si doublet (Si 2p$_{3/2, 1/2}$) peaks were observed at a binding energy of 99.8 eV and fwhm of 0.4 eV. It was supposed that the three Si-H bonds are broken during the SAM formation and then Si atoms form the three covalent bonds to the gold surface. In our case, TMS-ethynyl system, the observed binding energy of the Si 2p peak at 101.85 eV indicates that the Si-CH$_3$ bonds are not broken during the formation of the film (at least not all of them). This suggests that the binding configuration for molecules 3 to the Au surface is different from the alkylsilane system. The Si 2p signal from our TMS-ethynyl system is quite intense which would not be the case if molecule 3 did not bind to the Au surface, since any physisorbed molecules should be removed when the samples were thoroughly rinsed during the SAM preparation.
The C 1s spectra of all SAMs are shown in Figure 4. The spectra were acquired at a photon energy of 350 eV. The main emission peaks were observed at binding energies of 284.73, 284.38 and 284.33 eV for SAM 1, 2 and 3, respectively. These peaks are composed of the C 1s signals from the OPE moieties and additional C 1s signals from the porphyrin group. However, these different contributions are not possible to resolve by curve fitting but are reflected as an increased fwhm. Consequently, a larger fwhm was obtained for the porphyrin system SAMs (~1.24-1.35 eV) compared to our previous results on the OPE system (0.86 eV)\textsuperscript{65}. For SAM 2, the main peak is accompanied by a small shoulder at a higher binding energy 285.96 eV. Such a shoulder has previously been observed for different aromatic SAMs and were assigned to the carbon atom bound to the sulfur headgroup or to a shake-up process.\textsuperscript{66-69} This shoulder cannot be fitted in the
spectrum of SAM 1. For SAM 3, a minor peak was observed at a similar binding energy 285.65 eV. The total intensities dramatically decrease from SAM 1 to 2 and 3, respectively.

![HRXPS spectra of SAM 1, 2, and 3](image)

**Figure 5.** N 1s HRXPS spectra of a) SAM 1 taking at BE range 393-402 eV, b) SAM 2 and c) SAM 3 taking at the BE range 396-402 eV. Peak positions and fwhm are indicated.

In Figure 5, N 1s HRXPS spectra for SAM 1, 2, and 3 are presented. Two N 1s emission peaks were observed for SAM 1. The binding energies of the peaks are at 396.69 and 398.71 eV, which correspond to the two chemically different nitrogen present in the free-base porphyrin, i.e. N and NH, respectively. The observed N 1s binding energies for SAM 1 are lower by ~1.0 eV compared to what have been observed previously in XPS measurements of free-base octaethylporphyrins. The slightly different binding energy of N 1s peaks is caused by the substituent effect in porphyrin. The N 1s core-level electrons in a central porphyrin are very sensitive to the perturbation to a macrocycle. The porphyrin system 1, a macrocycle is substituted with a methyl and ethyl group at the edge of the four
pyrole rings, further more, one meso-position connected with a phenyl ring and another one at the opposite side connected with the OPE moiety. It can be seen that the nitrogen would have attended an additional electron density from the alkyl and phenyl substituents and especially the OPE moiety which make the binding energy slightly shifted. The relative intensity of these two peaks (N:NH, 43:57) is roughly equivalent to the 1:1 of N:NH stoichiometric value of the molecule. The two peaks are separated by 2.02 eV which is corresponding well to the values typically observed in the free-base porphyrin (2.1 ± 0.1 eV).\textsuperscript{71, 73, 74} Both peaks have a fwhm of 0.99 eV.

The N 1s emission was observed also in SAM 2 and 3. However, the spectra show only a single peak at 398.68 eV (fwhm of 1.03 eV) and 398.55 eV (fwhm of 1.04 eV) for SAM 2 and 3, respectively. This result suggests that the central nitrogens are symmetrically coordinated. The single N 1s peak is commonly observed in the metalloporphyrins in which the four nitrogens become equivalent.\textsuperscript{72, 75} Yasseri et al. observed a single N 1s peak at binding energy 398.2 ± 0.1 eV in the SAM of zinc porphyrins bearing the OPE bridge and the same binding group as 2.\textsuperscript{22} However, the observed single N 1s peak for the free-base porphyrin for SAM 2 and 3 is still not interpreted. NEXAFS results show that SAM 2 and 3 oriented almost parallel to the surface (see below). It may be possible that SAM 2 and SAM 3 are metal-coordinated, perhaps by interaction with the Au surface.

The thickness of the films was estimated by using the intensity ratio between the Au 4f and the C 1s XPS signals and the standard attenuation lengths for Au 4f and C 1s emission\textsuperscript{42} acquired at a photon energy of 580 eV.

\[
\frac{I_C}{I_{Au}} = k \left[ 1 - \exp\left( -\frac{d_{off} - d_{off(0)}}{\lambda_C} \right) \right] \exp\left( -\frac{d_{off}}{\lambda_{Au}} \right) \tag{1}
\]

where \(I_C\) and \(I_{Au}\) are the integrated intensity of C 1s and Au 4f signal, respectively, \(k\) is an instrument specific constant for a given photon energy, \(\lambda_C\) and \(\lambda_{Au}\) are the attenuation lengths for C 1s and Au 4f photoelectrons at the given kinetic energy,
\( d_{S\text{Au}} \) is the S-Au or Si-Au distances, both assumed to be 1.8 Å, and \( d_{\text{eff}} \) is the effective thickness of the film. The \( k \) value was determined from the reference system (hexadecanethiol SAM on Au). \( \lambda_C \) and \( \lambda_{Au} \) were obtained using the expression \( \lambda = 0.3E_{\text{kin}}^{0.64} \) for alkanethiol SAMs. 58

The effective thickness values obtained for SAM 1-3 are 2.9, 1.2 and 1.1 nm, respectively.

**NEXAFS measurements.** The C K-edge NEXAFS spectra of SAM 1-3, which were acquired at X-ray incidence angle of 55°, are shown in Figure 6. At this particular angle, the measured intensity distribution is independent of the molecular orientation.43 The assignments of the absorption resonances in comparison with the free-base porphyrin molecule and unfunctionalized OPE SAM (same as 1, but without the porphyrin endgroup) are presented in Table 1.

The spectrum of unfunctionalized OPE SAM (top curve) exhibits the dominant peak at 284.6 eV which associated to the \( \pi_1^* \) resonance from the phenyl rings in OPE moiety, having a transition from C 1s to C=C \( \pi^* \) state. This peak is accompanied by a weaker \( \pi_2^* \) resonance at 288.1 eV and broad \( \sigma^* \) resonances at higher photon energies about 293 and 302 eV. The C K-edge NEXAFS spectrum of free-base porphyrin according to ref. 75 exhibits the peak at ~285 and 287.3 eV correspond to \( \pi^* \) resonance for C=C in the porphyrin ring and \( \sigma^* \) resonance for the C-H in the alkyl groups surrounding the porphyrin76, respectively. The \( \pi^* \) resonance for C=N was expected to be observed at about 286.5 eV but it was not distinguished in the spectrum. The broad \( \sigma^* \) resonances at about 293 and 303 eV were also observed in this spectrum.
Figure 6. The C K-edge NEXAFS spectra of SAM 1, 2 and 3 on Au(111) in comparison with unfunctionalized OPE SAM (same as 1, but without the porphyrin endgroup) acquired at X-ray incidence of 55°.

The spectra features of SAM 1-3 are similar to the C K-edge NEXAFS spectra which have been reported for free-based porphyrin. By comparing to the NEXAFS spectrum of the unfunctionalized OPE SAM, the spectra of SAM 1-3 look slightly different. The first absorption resonance intensities of SAM 1-3 are lower than the OPE SAM which is caused by the larger π-system of the porphyrin and therefore stronger delocalization than in OPE molecules. The second resonance peaks for SAM 1 and 2 are broader than the OPE SAM which resulted from the combination of the OPE and porphyrin building block spectra of the molecules.
Table 1. Resonance positions and assignments of the C K-edge NEXAFS resonances for SAMs 1-3, unfunctionalized OPE SAM (same as 1, but without the porphyrin endgroup) on Au(111) and free-base porphyrin molecule.

<table>
<thead>
<tr>
<th>Resonance position</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAM 1</td>
<td>SAM 2</td>
</tr>
<tr>
<td>284.6</td>
<td>284.6</td>
</tr>
<tr>
<td>284.9</td>
<td>287.6</td>
</tr>
<tr>
<td>288.1</td>
<td>288.4</td>
</tr>
<tr>
<td>292</td>
<td>292</td>
</tr>
<tr>
<td>~302</td>
<td>~302</td>
</tr>
<tr>
<td>~302</td>
<td>~302</td>
</tr>
</tbody>
</table>

For our porphyrin SAM systems, the peak at about 285 eV is associated with the π\(^*\) resonances from the phenyl rings and the porphyrin groups, having a transition from C 1s to C=C π\(^*\) state. For SAM 1 and 2, the second resonance peaks are dominated by the σ\(^*\) resonance from C-H bond in the alkyl chain around the porphyrin at 287.6 eV and the π\(^*\) resonances from the phenyl rings at 288.10 eV. For SAM 3, surprisingly the second resonance peak was found at 288.4 eV with only a weak shoulder at 287.6 eV. This may indicate a contamination, with the peak at 288.4 eV related to a π\(^*\) C=O resonance. However, in the HRXPS spectra for SAM 3, no clear indication of contamination was found. The broad features at about 292 and 302 eV observed for all the SAMs are contributions from the excitation of C 1s electrons into σ\(^*\) states.
Figure 7. The C K-edge NEXAFS spectra of SAM 1, 2 and 3 on Au(111) acquired at X-ray incidence of 90°, 55°, and 20°, along with the difference between the 90° and 20° spectra. The dashed line corresponds to zero.

The C K-edge NEXAFS spectra of SAM 1-3 at X-ray incidence angle of 20°, 55°, 90°, and the difference between 90° and 20° spectra are shown in Figure 7. Comparing the NEXAFS spectra acquired at the selected X-ray incidence angles 20°, 55° and 90°, the average orientation of the molecules can be estimated. The intensity of NEXAFS resonance depends on the orientation of the polarization of incidence light with respect to the probed transition dipole moment (TDM) of the probed molecular orbital. The intensity is maximum if the direction of the electric field of the incidence light (E-vector) and the TDM are parallel to each other. Conversely, when the E-vector is orthogonal to the direction of the TDM, the resonance is greatly attenuated. The dependence of the resonance intensity on the angle of light incidence (linear dichroism) can give information on the packing density and ordering of the film. A pronounced linear dichroism in the NEXAFS spectra implies well-ordered and densely packed layers.
In the C K-edge spectra of SAM 1, the $\pi^*$ resonances are more intense at normal incidence than at grazing incidence. On the other hand, the $\sigma^*$ resonances are more intense at grazing than normal incidence. The spectra show a significant linear dichroism. For the studied molecules, the TDM of the C 1s $\rightarrow \pi^*$ and the C 1s $\rightarrow \sigma^*$ transitions are oriented perpendicular to and along the molecular axis, respectively. This indicates that molecules 1 on the average are oriented in an upright position on the substrate in a well-ordered and densely packed SAM. On the other hand, for SAM 2, the intensity of $\pi^*$ resonances decreases with increasing X-ray incidence angle, i.e. SAM 2 shows a negative linear dichroism. Thus, on the average, these molecules are oriented parallel to the surface. Finally, the NEXAFS spectra of SAM 3 exhibit almost no linear dichroism. This can be interpreted in either of two ways: First, it may indicate that molecules are strongly inclined with the average tilt angle of their TDM almost at the magic angle $\alpha = 54.7^\circ$ or second, it may indicate a low orientational order.

The values of the average tilt angle of the molecules can be determined from the angular dependence of the NEXAFS resonance intensity. The evaluations are based on the procedure developed by Stöhr. The $\pi^*$ resonance at photon energy ~285 eV has been selected as the most intense absorption feature in the spectra. The average tilt angle $\alpha$ of the respective TDM with respect to the surface normal is given by

$$I(\theta, \alpha) \propto 1 + \frac{1}{2}(3\cos^2 \theta - 1)(3\cos^2 \alpha - 1)$$

(2)

where $\theta$ is the X-ray incidence angle and $\gamma$ is the twist angle of the molecule with respect to the plane spanned by the surface normal and the molecular axis.

The intensity ratios $I(\theta)/I(20^\circ)$ were used instead of the absolute intensity to avoid normalization problems. The average tilt angles $\alpha$ of the $\pi^*$ TDM were determined to be $61^\circ$, $49^\circ$, and $55^\circ$ for 1, 2 and 3, respectively. The estimated tilt angle $\alpha$ for SAM 3 corresponds to the small linear dichroism observed in the NEXAFS spectra. The TDM tilt angle $\alpha$ is related to the average tilt angle of the molecular axis $\varphi$ and the twist angle $\gamma$ of the molecule with respect to the plane spanned by the surface normal by
\[ \cos \alpha = \cos \gamma \sin \varphi \]  

(3)

Assuming the twist angle to be 32°, as found from the prior experimental results of thioaromatic SAMs (e.g. oligo(phenyleneethynylene)), the average tilt angles of the molecular axis \( \varphi \) are estimated to be \( \sim 35°, 50° \) and \( 42° \) for SAM 1, 2 and 3, respectively. However, it is likely that the OPE moieties and porphyrin are not in-plane, but rotated by 90° around the molecular axis. This makes the estimated values uncertain because the assumed twist angle for the porphyrin-functionalized molecule is not likely to be the same as for the non-functionalized OPE.

**Discussion**

Ultra thin molecular layers were prepared from the porphyrin decorated oligo(phenyleneethynylene) molecules with three different binding groups. The XPS and NEXAFS results reveal that all the molecules form molecular layers on the Au substrate but with different average orientation, structural order and packing density. The C K-edge NEXAFS spectra for all molecular layers show the absorption resonance features which are characteristic for the porphyrin functional group.

Molecule 1 and 2 are both bound to the Au surface via a thiolate bond as evident by the characteristic thiolate S 2p doublet in the XPS spectra. The molecule without the methylene linker between the OPE moiety and the sulfur (molecule 1) was found to form a higher quality SAM compared to the one with the linker (molecule 2). This conclusion can be drawn from the observation of the small fwhm value of the S 2p XPS signal for SAMs 1 (0.56 eV), indicating a good homogeneity of the bonding configurations. Thus, the relatively larger fwhm value for SAM 2 (0.66 eV) can be a result of a higher structural inhomogeneity (e.g., different adsorption sites). The packing density of the film can also be implied from the shift of the C 1s main peak in the HRXPS spectra. Comparing the C 1s HRXPS spectra for the SAM 1 and SAM 2, we note that the main C 1s peak shows a decreasing binding energy, going from SAM 1 to SAM 2 (see Figure 4). This can be the result of a
decreased lateral packing density, a change in molecular arrangement, or both.\textsuperscript{33} The lower intensities of the S 2p and C 1s signals for SAM 2 compared to SAM 1 also indicate a lower packing density. The HRXPS-derived thicknesses for SAM 1 and SAM 2 are significantly different. The thickness of SAM 1 is 2.9 nm while the thickness of SAM 2 is only 1.2 nm. In addition, the C K-edge NEXAFS spectra indicate that SAM 1 is well-ordered with the molecules/adsorbates standing almost upright (35° from the surface normal), whereas the adsorbates in SAM 2 are significantly inclined (50° from surface normal) as suggested by the pronounced negative linear dichroism. This result corresponds well to the film thickness obtained from HRXPS.

Furthermore, N 1s HRXPS spectrum for SAM 1 exhibits two emission peaks, which indicate the two different nitrogen species (N and NH) in the free-base porphyrin, while the N 1s spectrum for SAM 2 shows a single emission peak. This single peak for SAM 2 shows that the porphyrin is significantly disturbed in the film. Possibly, the single peak may be caused by metal coordination, probably with the Au surface. Considering the inclination of the adsorbates 2 in the molecular layer, there is a possibility that the porphyrin would lie close to the Au surface. This result is in accordance with the slightly shift of the Au 4f peak positions for SAM 2 to the lower binding energy compared to SAM 1.

For molecule 2, the methylene group was inserted in between the sulfur and OPE moiety with the purpose of enabling the molecule to orient more upright on the surface and thereby improve the packing density in the molecular layer. Surprisingly, SAM 2 exhibits the opposite features with strongly inclined molecules, low packing density and low film thickness, indicating poorly defined layer. The result for SAM 2 is remarkably different from the XPS and the NEXAFS studies on oligo(phenylene)-substitued alkanethiol SAMs on Au, in which well-ordered and upright standing molecules were observed in the films formed from the molecules with the methylene linked systems.\textsuperscript{31, 32, 67, 78, 81}

For SAM 3, adsorbates 3 are likely to adsorb on the Au surface as indicated by an intense Si 2p doublet and the shift of the surface component of the Au 4f signal.
(compared to the clean Au substrate) in the XPS spectra. The Si 2p signal at binding energy of 101.85 eV suggests that the Si-CH₃ bonds are not broken upon the adsorption. This is in accordance with recently reported studies that show that molecules with the same binding group, (R=C≡Si(CH₃)₃), form SAMs on Au surfaces. The reported STM results showed a densely packed arrangement with a distance between molecules equal to the diameter of the trimethylsilyl (Si-(CH₃)₃) group (5.0 Å). However, the nature of bonding between the trimethylsilyl group and the Au surface is still not understood. It has been proposed that Si becomes pentavalent and binds to the Au surface in an axial position. Further, it is hypothesized that the Si directly connect to an electron-withdrawing group, such as the C≡C triple bond and CH₃ group, it is activated and then becomes pentacoordinated when it interacts with an electron-donating atom such as gold. The activated Si should have a higher binding energy compared to a clean Si sample (99.3 eV). The observed Si 2p peak at 101.85 eV in our XPS results is consistent with this model. The NEXAFS average tilt angle α of the π* TDM was derived to a value of 55° which is very close to a magic angle (54.7°). This corresponds to a very small linear dichroism observed in the NEXAFS spectra which can be a result either from strongly inclined and well-ordered film or a poorly defined monolayer consisting of randomly oriented molecules. It is reasonable to assume that the interaction between the trimethylsilyl and Au is not strong enough to support the large molecule, as our porphyrin system, and make it inclined or oriented randomly on the surface. This results in a loosely packed film which caused the NEXAFS spectra of this SAM to show a weak linear dichroism and the thickness obtained from HRXPS data of is small ~1.1 nm.

Conclusion

Porphyrrins-functionalized OPEs with three different binding groups were synthesized and used in the preparation of molecular layers on Au surfaces. The effects of the binding group: the thiphenolate, the thiolate, and trimethylsilylethynyl group, on the adsorbate-surface binding interaction and the packing were investigated using HRXPS and NEXAFS. We have demonstrated that the molecule 1, the thiophenolate structure, without any methylene groups in-
between the sulfur and the OPE moiety, forms the best quality SAM of all three molecules. The NEXAFS results of SAM 1 clearly show an orientational order with a slightly inclined (35°) orientation of the adsorbates. In contrast, molecule 2, with the methylene group between the sulfur and the OPE moiety, which was expected to form a highly ordered and densely packed SAM with an upright orientation on the substrate shows the opposite result. It binds to the gold surface through the sulfur atoms similarly to SAM 1 but it forms a highly inclined and low packing density film. The trimethylsilylthynyl group gives an inclined or a randomly oriented molecular layer. The HRXPS results suggest that the Si could bind to the gold surface with an extra bond, besides the usual four covalent bonds, in which Si-CH₃ bonds are not broken.

Reference
(51) Yeh, J. J.; Lindau, I., Atomic Data and Nuclear Data Tables 1985, 32, (1), 1-155.
Oligo(phenyleneethynylene) (OPE) molecules are a class of fully conjugated aromatic molecules, that attract attention for their application as “molecular wires” in molecular electronic devices. In this thesis work, self-assembled monolayers (SAMs) formed from a variety of OPE derivatives have been studied. The chemical properties, structure, and packing density of the SAMs have been characterized utilizing techniques such as high-resolution X-ray photoemission spectroscopy (HRXPS), near-edge X-ray absorption fine structure spectroscopy (NEXAFS), Infrared reflection absorption spectroscopy (IRRAS), contact angle measurements, and atomic force microscopy (AFM).

In a first study, three OPE-derivatives, with benzene, naphthalene and anthracene, respectively, inserted into the backbone, and an acetyl-protected thiophenol binding group were found to form SAMs on Au(111) substrates with lower molecular surface densities and larger molecular inclination as the lateral π-system increases.

In a second study, porphyrin was introduced as the end group to the wire-like OPE molecule. The purpose was to obtain well-organized and functionalized surfaces with optical and redox properties. Three porphyrin-functionalized OPEs with different binding groups, an acetyl-protected thiophenol, a benzylic thiol, and a trimethylsilylethynylene group, were found to form SAMs on gold surfaces with differences in structure and degree of order. The molecules with the acetyl-protected thiophenol binding group were found to form a high quality SAM, contrary to the other two. This SAM exhibits a well-ordered and densely packed layer.

This study gives rise to a better understanding of SAM formation of OPE derivatives, and will form a base for further investigations of charge transport properties of these molecular films, which is of interest for applications in molecular electronic devices.