Investigations of Structure / Property Interrelationships of Organic Thin Films Using Scanning Probe Microscopy and Nanolithography

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INVESTIGATIONS OF STRUCTURE / PROPERTY INTERRELATIONSHIPS OF ORGANIC THIN FILMS USING SCANNING PROBE MICROSCOPY AND NANOLITHOGRAPHY

A Dissertation
Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Chemistry

by
Zorabel Mallorca LeJeune
B.S., University of the Philippines Los Banos, 1999

December 2010
DEDICATION

I want to dedicate this work to my parents, Jessie and Remedios Mallorca for instilling the value of education in the family; my brother, Franco Lambatin for his assistance and sacrifices for my education; and my husband, Jason Paul LeJeune, for believing in me and for his undying patience and support.
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<th>Full Form</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>CAD</td>
<td>Computer Assisted Design</td>
</tr>
<tr>
<td>CMPS</td>
<td>Chloromethylphenyl Trichlorosilane</td>
</tr>
<tr>
<td>CPMD</td>
<td>Car-Parrinello Molecular Dynamics</td>
</tr>
<tr>
<td>CSAFM</td>
<td>Current-Sensing Atomic Force Microscopy</td>
</tr>
<tr>
<td>CP-AFM</td>
<td>Conductive Probe Atomic Force Microscopy</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>DNA</td>
<td>Deoxyribonucleic Acid</td>
</tr>
<tr>
<td>DPN</td>
<td>Dip Pen Nanolithography</td>
</tr>
<tr>
<td>DPP</td>
<td>5,10-diphenyl-15,20-di-pyridin-4-yl-porphyrin</td>
</tr>
<tr>
<td>DSU</td>
<td>Dithiobis(Succinimidyl Undecanoate)</td>
</tr>
<tr>
<td>EDC</td>
<td>1-Ethyl-3-(3-Dimethylaminopropyl) Carbodiimide Hydrochloride</td>
</tr>
<tr>
<td>FACSS</td>
<td>Federation of Analytical Chemistry &amp; Spectroscopy Societies</td>
</tr>
<tr>
<td>F-OPE</td>
<td>Monofluoro-Substituted Oligo(Phenylene-Ethylenylene)</td>
</tr>
<tr>
<td>GIXD</td>
<td>Grazing Incidence X-Ray Diffraction</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric Acid</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>HOPG</td>
<td>Highly Oriented Pyrolytic Graphite</td>
</tr>
<tr>
<td>IR</td>
<td>Infra Red</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium-Tin-Oxide</td>
</tr>
<tr>
<td>I-V</td>
<td>Current – Voltage</td>
</tr>
<tr>
<td>LON</td>
<td>Local Oxidation Nanolithography</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>MHA</td>
<td>16-Mercaptohexadecanoic Acid</td>
</tr>
<tr>
<td>MUA</td>
<td>11-Mercaptoundecanoic Acid</td>
</tr>
<tr>
<td>MUD</td>
<td>11-Mercaptoundecanol</td>
</tr>
<tr>
<td>NEXAFS</td>
<td>Near-Edge X-Ray Absorption Fine Structure</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>NPRW</td>
<td>NanoPen Reader and Writer</td>
</tr>
<tr>
<td>NSOM</td>
<td>Near-Field Scanning Optical Microscopy</td>
</tr>
<tr>
<td>ODT</td>
<td>Octadecanethiol</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic Light Emitting Diodes</td>
</tr>
<tr>
<td>OPA</td>
<td>Octadecylphosphonic Acid</td>
</tr>
<tr>
<td>OTE</td>
<td>Octadecyltriethoxysilane</td>
</tr>
<tr>
<td>OTS</td>
<td>n-Octadecyltrichlorosilane</td>
</tr>
<tr>
<td>PDMS</td>
<td>Poly(Dimethylsiloxane)</td>
</tr>
<tr>
<td>SAS</td>
<td>Society for Applied Spectroscopy</td>
</tr>
<tr>
<td>SAM</td>
<td>Self-Assembled Monolayer</td>
</tr>
<tr>
<td>SNP</td>
<td>Scanning Near-Field Photolithography</td>
</tr>
<tr>
<td>SPIE</td>
<td>Society of Photo Optical Instrumentation Engineers</td>
</tr>
<tr>
<td>SPM</td>
<td>Scanning Probe Microscopy</td>
</tr>
<tr>
<td>SPL</td>
<td>Scanning Probe Lithography</td>
</tr>
<tr>
<td>ssDNA</td>
<td>single-stranded DNA</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Tunneling Microscopy</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------------</td>
</tr>
<tr>
<td>TLC</td>
<td>Thin Layer Chromatography</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra High Vacuum</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra Violet</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultra Violet-Visible</td>
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</table>
ABSTRACT

Studies of the surface assembly and molecular organization of organic thin films were studied using scanning probe microscopy (SPM) and scanning probe lithography (SPL). Systems of organic thin films such as \(n\)-alkanethiols and pyridyl functionalized porphyrins were characterized at the molecular level, and measurements of the conductive properties of polythiophenes containing in-chain cobaltabisdicarbollides were accomplished. Understanding the self-organization and mechanisms of self-assembly of organic molecules provides fundamental insight for structure/property interrelationships. Investigations of the surface assembly of 5,10-diphenyl-15,20-di-pyridin-4-yl-porphyrin (DPP) on Au(111) were done using SPL methods of nanoshaving and nanografting. Automated computer designs were developed for nanofabrication to provide local characterizations of the thickness of DPP films and nanostructures. Nanolithography was accomplished using DPP films as either matrix self-assembled monolayers (SAMs) or as molecules for nanofabrication. Results presented in this dissertation demonstrate that DPP forms compact layers on Au(111), which can be used for inscribing nanopatterns of \(n\)-alkanethiols. Arrays of DPP nanopatterns with precise geometries and alignment were fabricated within \(n\)-alkanethiols by nanografting, demonstrating nanoscale lithography with pyridyl porphyrins can be accomplished to produce an upright surface orientation on Au(111) mediated by nitrogen-gold chemisorption. Beyond research investigations, the applicability of atomic force microscopy (AFM) and advancements with automated SPL were applied for teaching undergraduate chemistry laboratories to introduce the fundamentals of surface chemistry and molecular manipulation. New classroom activities were developed for the Chemistry 3493 Physical Chemistry laboratory to give students “hands-on” training with AFM. Undergraduates were trained to prepare nanopatterns of \(n\)-alkanethiols using software to control the position, force and speed of the AFM tip for nanolithography.
experiments. The sensitivity and nanoscale resolution of current sensing AFM was applied for studies of the conductive properties of electropolymerized thin films of polythiophenes with cobaltabis(dicarbollide) moieties. Images acquired with AFM furnished views of the morphology of different polymers prepared on gold surfaces. Surface maps of the conductivity of electropolymerized films were acquired with AFM current images. These studies provide new insight of the effects of the bound cobaltabis(dicarbollide) moiety and coordinated metal centers for the electronic properties of the resulting conducting materials.
CHAPTER 1. INTRODUCTION

The exquisite resolution and precision obtainable with scanning probe microscopy (SPM) enables studies of molecular organization, self-assembly and chemical binding processes on surfaces. The associated physical properties of samples can be investigated at the nanometer scale because of the unprecedented sensitivity of SPM. The main objectives of this dissertation were to develop strategies to investigate the surface assembly of n-alkanethiols and pyridyl-functionalized porphyrins; and measure the conductive properties of specific systems, such as organic thins of polythiophenes with cobaltabisdicarbollide moieties and electopolymerized carboranyldithiophenes using SPM. Methods of scanning probe microscopy (SPM) and nanolithography were the tools applied in this dissertation to investigate chemical reactions, surface structures and properties of nanomaterials and organic thin films. Our goals were to achieve new fundamental insight of structure-property relationships for surface reactions. Investigations of surface properties and processes at the molecular level will help advance the field of molecular electronics towards new discoveries for sensing and energy applications.

1.1 AFM Based Nanofabrication with Self-assembled Monolayers

Scanning probe lithography (SPL) is one of the nanofabrication techniques which can be applied for writing nanometer-sized surface patterns of designed chemistry. Combined with computer automation, SPL can be used to create surface patterns ranging from nanometer to micrometer sizes with precise alignment, spacing and arrangement on surfaces. A contemporary review of SPL methods in Chapter 2 highlights the exquisite resolution and precision that can be achieved with SPM-based lithography with self-assembled monolayers(SAMs).\textsuperscript{1} Scanning probe instruments used for nanofabrication of SAMs include scanning tunneling microscopy (STM), atomic force microscopy (AFM) and near-field scanning optical microscopy (NSOM). Scanning probe microscopes have progressed beyond basic use as an imaging tool, to become a primary
technique for physical measurements of material properties, as well as a tool for manipulation of atoms and molecules at the nanoscale. Approaches for SPL with self-assembled monolayers (SAMs) are reviewed and summarized from research with methods of nanoshaving, nanografting, Dip-Pen Nanolithography (DPN), NanoPen Reader and Writer (NPRW), bias-induced lithography, catalytic probe lithography, and NSOM lithography.

1.2 Automated Scanning Probe Lithography with n-Alkanethiol Self Assembled Monolayers on Au(111): Application for Teaching Undergraduate Laboratories

Controllers for scanning probe instruments can be programmed for automated lithography to generate desired surface arrangements of nanopatterns of organic thin films, such as n-alkanethiol self-assembled monolayers (SAMs). In Chapter 3, atomic force microscopy (AFM) methods of lithography known as nanoshaving and nanografting were used to write nanopatterns within organic thin films. Commercial instruments provide software to control the length, direction, speed, and applied force of the scanning motion of the tip. For nanoshaving, higher forces are applied to an AFM tip to selectively remove regions of the matrix monolayer, exposing bare areas of the gold substrate. Nanografting is accomplished by force-induced displacement of molecules of a matrix SAM, followed immediately by the surface self-assembly of n-alkanethiol molecules from solution.

Advancements in AFM automation enable rapid protocols for nanolithography, which can be accomplished within the tight time restraints of undergraduate laboratories. Example experiments with scanning probe lithography (SPL) are described in Chapter 3 that were accomplished by undergraduate students during laboratory course activities and research internships in the chemistry department of Louisiana State University. Students were introduced to principles of surface analysis and gained “hands-on” experience with nanoscale chemistry. For this report, reproduced by permission from the Journal of the Association for Laboratory
Automation, works from three undergraduate researchers were showcased as examples of the capabilities of SPL for student laboratories and research activities. One of the LSU students mentored, Ms. Treva T. Brown received a prestigious 2009 ALA Young Scientist Award from the Analytical Systems Digital Library under my direction. In this chapter, work is consolidated and summarized from several years of effort in directing and mentoring undergraduate research projects based on SPL and high resolution imaging with SPM.

1.3 Surface Assembly of Pyridyl-Substituted Porphyrins on Au(111) Investigated In Situ Using Scanning Probe Lithography

A new direction progressing beyond studies with $n$-alkanethiols as a model molecular system was established for this dissertation. Applications of nanografting have been limited to creating patterns with thiol-based chemistries on gold substrates through sulfur-gold chemisorption. Chapter 4 demonstrates that pyridyl-functionalized porphyrins are potentially a new class of self-assembled monolayers which can be grafted directly onto surfaces of Au(111), most likely mediated through nitrogen-gold chemisorption. Our practical goals were to use SPM for studying a more complex and robust system of conjugated molecules such as porphyrins which have valuable technological applications due to inherent photoemissive and photoconductive properties. Our goals were to develop new AFM-based protocols for in situ studies in solution, whereas most studies of these systems have been accomplished either in air or UHV environments using STM. Scanning probe characterizations of porphyrin patterns prepared by nanografting in liquid media were accomplished, which provide insight for the molecular orientation and surface assembly of porphyrins bearing pyridyl and phenyl substituents. In-situ AFM provides highly local views of the assembly of pyridyl-substituted porphyrins on surfaces of Au(111). Matrix self-assembled monolayers (SAMs) of $n$-alkanethiols were used as a molecular ruler for gauging height measurements. Nanografting was used as an
in situ tool for local measurements of the thickness of porphyrin films providing side-by-side comparisons against the heights of \( n \)-alkanethiol nanopatterns. As previously shown for \( n \)-alkanethiols on Au(111), nanografting alters the assembly pathway through a mechanism of spatial confinement.\(^6\) When nanografted, pyridyl porphyrins were shown to assemble onto gold directly into an upright configuration rather than adopting a coplanar arrangement. The studies presented in Chapter 4 provide further corroborative evidence that steps of surface self-assembly can be altered when nanografting by spatial confinement; thus nanografting provides a tool for controlling molecular orientation.

1.4 Assembly of 5,10,15,20-di-pyridin-4-yl-porphyrin on Au(111) from Mixed Solvents

The mechanism of the surface assembly of porphyrins from solution results from complex intermolecular interactions and the affinity for surface binding. The binding interactions between peripheral groups and the surface as well as the influence of pi-pi stacking between macrocycles dictate the resulting configuration and organization for structures that form. In Chapter 5, high resolution AFM imaging combined with scanning probe lithography was used for investigations of the surface structures that form by natural solution-based assembly and compared to artificial nanostructures prepared by the spatially confined assembly mechanism of nanografting for 5,10-diphenyl-15,20-di-pyridin-4-yl-porphyrin (DPP).\(^7\) Our goals were to understand the mechanisms of solution-based assembly of pyridyl-functionalized porphyrins and to develop new molecular test platforms for measurements of surface properties. By comparing porphyrins with different molecular designs, experiments with SPM and SPL were used to gain insight for structure-property relationships. In situ AFM experiments disclosed that for spontaneous self-assembly processes, monolayers of DPP from ethanol/dichloromethane solutions form mixed monolayers with two distinct configurations on Au(111), exhibiting phase segregated domains. Nanoshaving and nanografting provide an in situ tool for local
measurements of the thickness of DPP films with angstrom precision. High resolution AFM images of DPP reveal that two distinct phase segregated domains of different heights were formed over time. One phase corresponds to the height of a lying-down arrangement of DPP with the macrocycle adapting a coplanar orientation. The thickness of the second phase corresponds precisely to the theoretical height of a 90 degree perpendicular orientation of the molecules (an upright, standing configuration), with two pyridyl groups attached to the surface. The surface coverage of the upright domains increased over time to near saturation. However, for structures of DPP nanografted within a matrix monolayer of alkanethiol SAMs under the conditions of spatial confinement, the heights of nanopatterns correspond to an upright orientation. Complicated designs and geometries of DPP patterns were successfully created by nanografting DPP within matrix SAMs of \(n\)-alkanethiols of different chain lengths (decanethiol, dodecanethiol, octadecanethiol). In collaborative work with Professor Bin Chen, models with energy minimized structures of pyridyl-substituted porphyrins on Au(111) were computed using Car-Parrinello Molecular Dynamics (CPMD) that corroborate results with AFM.

Results of this research project were disclosed in presentations and garnered the best poster awards at conferences both at Pittcon 2010 in Orlando Florida; and at the Society for Applied Spectroscopy (SAS) symposium during the 34\textsuperscript{th} National Meeting, Federation of Analytical Chemistry & Spectroscopy Societies (FACSS 2007) in Memphis, TN. Also, this research was recognized as one of the finalists for the best poster awards for Material Systems and Processes for Three-Dimensional Micro- and Nanoscale Fabrication and Lithography symposium in 2009 Materials Research Society Spring Meeting in San Francisco, CA.

1.5 Polythiophenes Containing In-Chain Cobaltabis(dicarbollide) Center

New cobalt(III) bis(dicarbollide) complexes covalently linked to two 2-oligothienyl units were synthesized and electropolymerized to produce the corresponding polythiophene films
containing in-chain metallic centers. The incorporation of the metal center in the conjugated chain is expected to improve electronic conductivity and magnetic and optical properties of metallopolymers. The goal of this project was to establish a new unprecedented conducting metallopolymers using metalla-bisdicarbolide complexes. My role was to furnish molecular details of AFM surface studies and conducting probe measurements of charge transport for these novel systems. Detailed characterizations using electrochemistry, UV-Vis spectroscopy and scanning probe microscopy (tapping mode and conducting probe AFM) are presented in Chapter 6, towards understanding how the bound cobaltabisdicarbollide moiety influences the electronic properties of the resulting conducting materials. The polymer films that were electrogogenerated from the bithienyl and terthienyl derivatives display redox processes, yielding conducting polymer deposits on the electrode surface. In contrast, the electrochemical oxidation of thienyl units resulted in the gradual passivation of the electrode surface, with no conductive polymers observed. Analysis with UV-Vis spectroscopy demonstrated that the polymer incorporating the sexithienyl segments is more conjugated than that with the quaterthienyl segments. Conducting probe AFM characterizations indicate that polymers with bithienyl and terthienyl behave like heavily doped semiconductors rather than pure semiconductors. The current-voltage (I-V) profile for poly-thienyl exhibits no measurable current over the range of applied voltage which is consistent with the insulating character of the film. Substantial differences for the morphologies of the polymer films were apparent for comparisons with tapping mode AFM. The studies reported in Chapters 6 result from an international collaboration with Professor Bruno Fabre of the Université de Rennes, who is an expert in the area of electrochemistry. Professor M. Graca H. Vicente of the LSU chemistry department contributed expertise in organic synthesis, for accomplishing research overall with a broad interdisciplinary focus.

Conjugated polymers have promising applications in the semiconductor industry for
microelectronics, photovoltaics, organic light emitting diodes (OLED), organic field effect transistors, electrochemical switching, and chemical and physical sensing. Structure-property relationships are important in advancing the design and synthesis of conjugated polymers for molecular electronic applications.9-10
CHAPTER 2. AFM-BASED NANOFABRICATION WITH SELF-ASSEMBLED MONOLAYERS*

2.1 Introduction

Scanning probe lithography (SPL) is an emerging family of techniques which can be applied for writing nanometer-sized surface patterns of designed chemistry. One of the main advantages in comparison to other nanoscale lithographies is that the versatile approaches of SPL not only enable nanofabrication with designed size and geometry, but also provide precise control of the chemistry on surfaces, as determined by the choice of molecules for writing. The exquisite resolution and precision of scanning probe microscopy (SPM) has brought an evolution of new methods and experimental configurations which can be valuable for multiple disciplines. One can easily predict that SPL will advance new discoveries for future science. This chapter will focus on the scanning probe based lithographies which have been applied to write nanostructures of self-assembled monolayers (SAMs). The chemistry of SAMs has been used previously to tailor the selectivity of surfaces as pattern transfer molds,^{11-12} etch resists^{13-14} and for microcontact printing.^{15-17} To evolve to the next generation of miniaturization at the nanoscale, the immediate benefits of SPL are to enable researchers to probe the fundamental limits of measuring molecular properties and to contribute to the fundamental knowledge of chemical binding, surface organization and self-assembly.

An overview of the various lithography methods according to the type of SPM instrument is presented in Figure 2.1. Scanning probe techniques applied for nanofabrication of SAMs include scanning tunneling microscopy (STM), atomic force microscopy (AFM) and near-field scanning optical microscopy (NSOM). Note that bias-induced lithography can be accomplished using either scanning tunneling microscopy (STM) or conductive-probe AFM. Scanning probe

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microscopes furnish tools for visualization, physical measurements and precise manipulation of atoms and molecules at the nanometer scale. The additional tools attainable with AFM for nanoscale lithography are accessible to investigators across a broad range of disciplines and do not require expensive instrument modification. In fact, most SPM manufacturers have developed software to give operators complete control of SPL parameters such as the speed, bias, force, direction and residence time of the scanning probe. To progress to the smallest sizes, SPL can be applied to define surface patterns at either nanometer or micrometer scales. With computer automation, the arrangement, alignment and spacing of patterns can be defined precisely at the scale of nanometers.

Figure 2.1 Overview of the most commonly used scanning probe lithography methods for nanofabrication of self-assembled monolayers.
There are several key differences when comparing SPL methods beyond the choice of instrument, such as the mechanism of writing, the type of chemical changes that can be achieved, and whether characterization of nanopatterns can be accomplished in situ. The writing mechanisms and changes in surface chemistry will be detailed in succeeding sections of this chapter. Lithography methods which enable in situ characterization of surface changes use the same SPM probe for writing and subsequent interrogation of the nanostructures that were written. Often, the various steps to modify the surface chemistry of nanopatterns can be accomplished without removing the sample or tip, provided that the tip is not damaged or altered by the fabrication process. There are a few SPL methods such as Dip-Pen Nanolithography (DPN) and catalytic probe lithography which require the use of different probes for the steps of writing and characterizing surface patterns, and these have been categorized as ex situ methods. Combined with the capabilities for high-resolution imaging and characterization, SPM enables a molecular-level approach for visualizing changes that occur on surfaces after successive steps of chemical reactions. In essence, SPL furnishes a new variable for experiments by providing a means to manipulate or alter the chemistry of local regions of surfaces. Very small areas of designed chemistry can be inscribed on surfaces with defined reactivity for binding nanoparticles, proteins and other molecules. After the nanopatterned surface is subjected to various chemical treatments, changes in the morphology and thickness of the nanopatterns can assist in the interpretation of surface kinetics and reaction mechanisms.6,18-19

Detailed information about the operating principles of SPM instruments can be found in previous publications for AFM,20-24 STM 25-29 and NSOM.30-32 The SPM methods for writing patterns are based on an operating platform which uses electronic controllers for piezoelectric positioning of a surface probe. The feedback loop for tip-positioning and mechanisms of surface characterization are quite different for AFM, STM and NSOM; and likewise provide a range of
approaches for nanofabrication. The probe for an STM instrument is a conductive metal wire brought within tunneling range of the surface. The imaging and fabrication accomplished with STM are obtained at a proximal distance from the surface, within tunneling range of < 1 nm. Lithography using NSOM is also accomplished in non-contact operation, within the optical near-field regime. For NSOM lithography, a specially constructed aluminum-clad fiber optic probe transmitting light is scanned at a certain distance from the sample. In contrast, AFM-based lithography and imaging usually involve direct contact of the scanning probe with the surface.

The primary consideration for choosing an SPL method is the desired surface chemistry and environment for imaging. A useful analogy is to consider the SPM tip as a ‘pen’ which writes molecular ‘ink’ on various surfaces or ‘paper.’ A comparison of SPL methods using this simple analogy is presented in Table 2.1. The summary focuses on the most widely applied methods for writing nanopatterns of SAMs; there are other specialized SPL methods reported for different surfaces and systems of molecules and nanomaterials which are beyond the scope of this chapter. The table presents a brief synopsis of SPL methods, comparing the mechanism of writing, the environment (ambient air or liquids) as well as the outcome of the chemical or physical changes to the surface. The detailed steps for writing nanopatterns and recent research which apply these methods for the fabrication of SAMs will be presented in later sections. The chapter will begin with a general discussion of the chemistry of SAMs, followed successively by details of force-induced lithography methods of nanoshaving and nanografting. Further sections will describe “Dip-Pen” methods of nanolithography (DPN), NanoPen Reader and Writer (NPRW), and catalytic probe lithography with SAMs. Recent developments in SPL that are evolving with bias-induced lithography methods and NSOM photooxidation of SAMs will also be presented. The chapter concludes with a prospectus of future directions in automated SPL.
Table 2.1 Mechanisms for writing SAM nanopatterns.

<table>
<thead>
<tr>
<th>SPL method</th>
<th>pen</th>
<th>paper</th>
<th>environment</th>
<th>protocol</th>
<th>writing mechanism</th>
<th>surface chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>nanoshaving</td>
<td>bare AFM tip</td>
<td>SAMs including silanes, thiol</td>
<td>air or liquid</td>
<td>in situ</td>
<td>force &amp; sweeping tip motion</td>
<td>uncovered areas of substrate</td>
</tr>
<tr>
<td>nanografting</td>
<td>bare AFM tip in a SAM solution</td>
<td>thiol</td>
<td>liquid</td>
<td>in situ</td>
<td>force &amp; solution replacement</td>
<td>diverse functional groups of SAMs</td>
</tr>
<tr>
<td>Dip-Pen Nanolithography (DPN)</td>
<td>coated AFM tip</td>
<td>clean, uncoated surfaces</td>
<td>air</td>
<td>ex situ</td>
<td>meniscus liquid transfer</td>
<td>diverse functional groups of SAMs &amp; other materials</td>
</tr>
<tr>
<td>electrochemical DPN</td>
<td>thiol-coated AFM tip</td>
<td>clean, uncoated surfaces</td>
<td>air</td>
<td>in situ</td>
<td>Local surface oxidation</td>
<td>electrochemistry</td>
</tr>
<tr>
<td>thermal DPN</td>
<td>thiol-coated AFM tip</td>
<td>clean, uncoated surfaces</td>
<td>air</td>
<td>in situ</td>
<td>heating of tip for deposition of polymer inks</td>
<td>heating</td>
</tr>
<tr>
<td>NanoPen Reader and Writer (NPRW)</td>
<td>thiol-coated AFM tip</td>
<td>thiol SAMs/Au</td>
<td>air or water</td>
<td>in situ</td>
<td>force &amp; molecular replacement</td>
<td>diverse functional groups of SAMs</td>
</tr>
<tr>
<td>catalytic probe lithography</td>
<td>AFM tip coated with a catalyst</td>
<td>SAM surface groups</td>
<td>air or liquid</td>
<td>ex situ</td>
<td>local tip-induced hydrolysis</td>
<td>patterns written by localized catalysis</td>
</tr>
<tr>
<td>bias-induced oxidation</td>
<td>biased STM or AFM tip in air</td>
<td>conductive or semi-conductive substrates</td>
<td>air</td>
<td>in situ</td>
<td>surface oxidation via electrochemistry in the water meniscus between the tip and surface</td>
<td>oxidized SAMs</td>
</tr>
<tr>
<td>bias-induced replacement</td>
<td>biased STM or AFM tip in a SAM solution</td>
<td>conductive or semi-conductive substrates</td>
<td>liquid</td>
<td>in situ</td>
<td>displacement of SAMs under elevated bias &amp; successive replacement</td>
<td>diverse functional groups of SAMs</td>
</tr>
<tr>
<td>NSOM photooxidation</td>
<td>NSOM probe</td>
<td>SAMs</td>
<td>air</td>
<td>in situ</td>
<td>photooxidation of irradiated areas of the SAM</td>
<td>photooxidized SAMs</td>
</tr>
<tr>
<td>NSOM photoconversion</td>
<td>NSOM probe</td>
<td>SAMs</td>
<td>air</td>
<td>in situ</td>
<td>photoconversion of terminal groups irradiated by the probe</td>
<td>photochemistry</td>
</tr>
</tbody>
</table>
2.2 Surface Chemistry of Self-Assembled Monolayers

Self-assembled monolayers of alkanethiols and alkylsilanes have been applied for surface modification, \(^{15,33-35}\) corrosion inhibition, \(^{36-38}\) biosensor design, \(^{39-42}\) and molecular device fabrication. \(^{43-44}\) The synthetic flexibility of SAMs provide advantages for designing the chemistry of surfaces with desired spacer lengths and functional groups. \(^{45-46}\) The surface properties such as wettability, acidity and adhesion can be controlled by choosing the functional headgroups of SAMs. For example, to design the wettability properties of surfaces, SAMs terminated with methyl groups are hydrophobic, whereas SAMs terminated with carboxyl, hydroxyl, or amine groups (moieties that can hydrogen-bond to a polar surface) are hydrophilic. \(^{47-48}\)

It is well documented that SAMs of \(n\)-alkanethiols form densely packed, well-ordered monolayers on coinage metal surfaces such as gold or silver. \(^{49-52}\) The packing density of SAMs is shown to change depending on the alkane chain length or terminal chemistry of the molecule. \(^{46}\) The basic structure of an \(n\)-alkanethiol SAM consists of three parts: the tail, the carbon backbone, and the headgroup (Figure 2.2). The tail is composed of thiol molecules for chemisorptive attachment to surfaces. The thiol is bonded directly to a saturated 2 to 18-carbon chain; this carbon backbone forms a spacer for tuning the vertical thickness of SAM nanopatterns. The carbon chain is capped with a headgroup which determines the surface properties. A variety of functional groups (esters, alkyls, hydroxyls, carboxylates, amides, etc.) are commercially available, depending on the desired application. Readers are directed to previous reports for details regarding synthesis, preparation, and characterization of SAMs. \(^{36,46,52-53}\)

To prepare SAMs of \(n\)-alkanethiols, Au(111) substrates are submerged in dilute solutions of alkanethiols dissolved in solvents such as ethanol or 2-butanol for various time intervals. As
examples, the wide range of conditions used to form SAMs of methyl terminated $n$-alkanethiols and alkysilanes on various surfaces is summarized in Table 2.2. The concentration and the amount of time the substrate remains in solution will vary depending on the solubility of the molecule in the chosen solvent, and the nature of the SAM headgroups. Controlling variables such as the
solution concentration and intervals of immersion may prohibit the formation of double layers and ensures sufficient surface coverage to produce mature, densely-packed SAMs. It has also been reported that minimizing exposure to light serves to prevent oxidation of thiols. For UHV studies, vapor deposition has also been used to prepare SAMs.

Table 2.2 Protocols for preparing SAMs.

<table>
<thead>
<tr>
<th>SAM</th>
<th>Substrate</th>
<th>Concentration (mM)</th>
<th>Time (hr)</th>
<th>Temperature (°C)</th>
<th>Solvent</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>hexanethiol, octanethiol,</td>
<td>Au(111)</td>
<td>0.001-1 mM</td>
<td>24 h</td>
<td>RT</td>
<td>ethanol</td>
<td>58</td>
</tr>
<tr>
<td>decanethiol, dodecanethiol,</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>benzenethiol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dodecanethiol</td>
<td>Au(111)</td>
<td>1 mM</td>
<td>24-36 h</td>
<td>RT</td>
<td>ethanol</td>
<td>59</td>
</tr>
<tr>
<td>hexadecanethiol</td>
<td>Au(111)</td>
<td>0.0002 mM</td>
<td>&lt; 1 h</td>
<td>21</td>
<td>ethanol</td>
<td>60</td>
</tr>
<tr>
<td>octadecanethiol</td>
<td>Au(111)</td>
<td>0.0001 mM</td>
<td>&lt; 1 h</td>
<td>21</td>
<td>ethanol</td>
<td>61</td>
</tr>
<tr>
<td>octadecyltriethoxysilane</td>
<td>mica</td>
<td>1 mM</td>
<td>&lt; 1 h</td>
<td>RT</td>
<td>mixed solvents, water, tetrahydrofuran, hydrochloric acid, cyclohexane</td>
<td>62</td>
</tr>
<tr>
<td>octadecyltrichlorosilane</td>
<td>silica</td>
<td>5 mM</td>
<td>30 s</td>
<td>RT</td>
<td>bicyclohexyl</td>
<td>63</td>
</tr>
</tbody>
</table>

According to studies conducted using IR, near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, and grazing incidence X-ray diffraction (GIXD), the alkyl chains of \( n \)-alkanethiol SAMs are tilted approximately 30° with respect to the surface normal. Thiol atoms of SAMs bind to triple hollow sites of a Au(111) lattice by chemisorption. The solution self-assembly of \( n \)-alkanethiol SAMs on bare gold surfaces is reported to occur in two phases. The stripe phase forms when thiol molecules initially make contact with the surface, in which the backbone of the molecules are oriented parallel to the substrate in a lying-down configuration. However, over time the \( n \)-alkanethiol molecules rearrange into a standing
position with the molecular backbone tilted \( \sim 30^\circ \) from surface normal.\textsuperscript{70} The mature crystalline phase forms an enthalpy favorable, close-packed commensurate \((\sqrt{3} \times \sqrt{3})R30^\circ\) configuration with respect to the plane of the Au(111) lattice.\textsuperscript{51,71-73} The exquisite details of the surface structure and long range ordering of \( n \)-alkanethiol SAMs has been revealed with STM and AFM to enable a direct view of defect sites such as etch pits, steps and dislocations within films.\textsuperscript{51-53} Etch pits are small depressions observed in high resolution images that result from the displacement of atoms of the Au(111) substrate, caused by reconstruction when thiols of the SAM endgroups bind to a gold surface.

A representative AFM topographic image of a naturally-formed \( n \)-alkanethiol SAM/Au(111) acquired in liquid is presented in Figure 2.3. High-resolution images obtained with AFM disclose substrates that are not truly smooth and flat; rather, from the atomic perspective, surfaces contain defects such as pinholes, missing atoms, and scars. When SPM images reveal these natural defects then true molecular or atomic resolution has been achieved. Looking at the AFM images, the surface may appear rather rough and irregular. However, the surface is actually very flat from an atomic perspective. The height of gold steps is only 0.25 nm and thus the overall surface roughness of the underlying gold substrates for these samples is less than 1 nm. The topography images in Figure 2.3 display height changes according to color contrast from dark to light, analogous to a height map of the surface terrain. The dark colors indicate shallow features whereas brighter areas are taller. In the wide view image (500 \( \times \) 500 nm\(^2\)) of an octadecanethiol (ODT) SAM in Figure 2.3A, the terrace domains of the underlying gold surface are clearly observed. The AFM image captures a detailed view of a concentric spiral arrangement of overlapping gold steps, which are often observed for surfaces of epitaxially grown gold thin films. The step edges of the terraces are not smooth; rather the uneven and angular profiles at edges reflect the true surface morphology. The ODT-covered surface is
decorated with tiny holes called etch pits, which are 0.2 nm deep, corresponding to the depth of one atomic layer of gold. Etch pits or gold vacancy islands are defect sites resulting from the reconstruction of Au(111) during the chemisorption of thiol molecules. A close-up view (200 × 200 nm$^2$) of a terrace area is displayed in Figure 2.3B which begins to reveal the ordered molecular domains between areas of etch pits. The size and density of etch pits varies widely for various samples, according to sample preparation conditions such as age and oxidation. Details of the surface morphology of $n$-alkanethiol SAMs on Au(111) substrates has also been investigated with STM.

![Figure 2.3](image)

**Figure 2.3** Views of a self-assembled monolayer of octadecanethiol on gold. [A] Topograph of a 500 x 500 nm$^2$ area; [B] zoom-in view of a single terrace.

The properties of alkylsilane SAMs are quite different from alkanethiol SAMs. A key difference is that alkylsilanes can be covalently formed on a wide variety of surfaces, such as oxide surfaces (silicon, aluminum, and germanium), mica, glass, zinc, quartz, and selenide. Alkylchlorosilanes, alkylalkoxysilanes and alkylaminosilanes require hydroxyl groups on surfaces to form polysiloxane, which connect to surfaces via a network of Si-O-Si bridges (Figure 2.2B). Alkylsilane monolayers typically consist of domains separated by
boundaries of mica. Within these domains, silane molecules form structures without long-range order or periodicity. The anchoring groups of silane SAMs form a cross-linked network on surfaces, and the chains tilt approximately 15° from surface normal.

The self-assembly of thiol and silane SAMs supply a convenient and efficient means for designing surface chemistry. Depending on the mechanism of molecular writing, SAMs furnish a practical and effective “ink” for writing nanostructures with molecular dimensions using SPL.

2.3 Fabrication of SAMs Using Nanoshaving

Nanoshaving can be accomplished by applying mechanical force to the probe during scans; essentially small areas of the SAM are “shaved” away by the action of a scanning AFM tip. Nanoshaving is used to uncover selected regions of surfaces which are surrounded by a passivating matrix SAM; these uncovered regions are then available for deposition of new molecules and materials. Information about the thickness of molecular layers on surfaces can be derived by using the nanoshaved areas as a baseline for cursor measurements. Nanoshaving was introduced in 1994 for a SAM of octadecyltriethoxysilane (OTE); changes in the observed lattice were used to confirm that molecules were displaced from the surface.

The process of nanoshaving is achieved by scanning several times over a small local area of a surface with an AFM tip, while applying a higher force than that used for imaging (Figure 2.4). After molecules are removed, the AFM probe can still be used to image the surface by returning to low force. In nanoshaving, a high local pressure is applied by an AFM tip to the area of contact. This pressure causes high shear forces, and thus displaces SAM adsorbates as the tip is scanned back and forth across the surface. As a result, the bare substrate is exposed. By carefully controlling the amount of force applied, the AFM tip is not damaged during fabrication. The three basic steps of nanoshaving are shown in Figure 2.4. The first step uses an AFM tip under minimal force (less than 1 nN). The surface is characterized at low force to
locate an area for writing. A flat plateau area of the surface with few scars and defects is desirable for shaving patterns. Next, a higher force is applied (ranging from 2-20 nN depending on the monolayer adsorption properties) which causes the AFM tip to push through the matrix SAM to make contact with the surface. The molecules directly under the tip are shaved away, to uncover areas of the surface. Sufficient force is applied to the AFM probe to ensure that matrix SAM molecules are removed, without disturbing the underlying gold substrate.\textsuperscript{34} In the final step, the newly fabricated areas of the surface are characterized with the same AFM tip using a reduced force (less than 1 nN). Thus, nanoshaving enables \textit{in situ} fabrication of SAMs.

\textbf{Figure 2.4} Steps of nanoshaving. Areas of a matrix self-assembled monolayer are “shaved” away under high force by a scanning AFM tip.

It is critical to optimize the amount of force applied to the AFM tip for nanoshaving SAMs. Of course, if too much force is applied the sharp apex of the tip can be broken; therefore it is important to find a minimum force to remove molecular layers without damaging the tip. Atomic force microscope controllers provide precise control of the force applied to AFM tips using electronic feedback. The threshold force is determined for each experiment by successively incrementing the amount of force applied during scans. As the force is increased the tip is pushed though the matrix SAM to contact the underlying substrate. The tip is then rastered several times to sweep molecules from the surface, since the actual area of contact is very small between the tip and surface. If too much force is applied, the torsion on the cantilever
will cause the tip to twist and produce non-linear movements. At the optimized minimum force threshold, the desired square, linear or circular geometries will be produced.

The imaging media and the nature of the molecule influence the success of nanoshaving. When imaging in air, displaced SAM molecules often pile up at the sides of the trenches or holes that are uncovered; whereas in liquid media the molecules dissolve in the surrounding solvents. Nanoshaving has not been accomplished for \(n\)-alkanethiols with fewer than ten carbons because holes or trenches refill with short-chain molecules. Immediately after the molecules have been removed by the scanning AFM tip, molecules of short-chain thiol SAMs backfill into the uncovered areas. In contrast, SAMs of any chainlength of \(n\)-alkylsilanes are irreversibly displaced by nanoshaving in either liquid or ambient environments.\(^{82-83}\)

An example array of nanoshaved patterns produced within an octadecanethiol (ODT) SAM is presented in Figure 2.5. The topographic image displays twelve dark squares written into an ODT matrix in ethanol. The squares correspond to uncovered areas of Au(111). The areas of brighter contrast indicate taller features whereas the dark areas are shallower. Even when writing with an open-loop AFM scanner, there is very precise alignment of the rows and columns of the array and well-defined square geometries for nanoshaved patterns. The high-resolution image of Figure 2.5A was acquired after nanoshaving and evidences that after writing under force the tip has not become blunt or damaged. The \textit{in situ} topograph clearly exhibits the indicators of a high-resolution image, such as circular gold terraces, concentric circular steps and line scars. The friction image (Figure 2.5B) provides a spatial map of the changes in chemistry for nanoshaved patterns. The matrix areas of ODT show uniform contrast, which is clearly distinguishable from the brighter nanoshaved areas. Within the nanoshaved squares the homogeneous color evidences clean removal of the matrix SAM. A cursor profile along the bottom row of nanoshaved patterns reveals the height difference between the ODT SAM and the
underlying surface measures 2.0 ± 0.2 nm. This value agrees closely with the expected thickness (2.1 nm) for an ODT SAM.

![Figure 2.5](image)

**Figure 2.5** Nanoshaved array of 100 x 100 nm² squares in an octadecanethiol matrix. [A] topography; [B] frictional force image; [C] corresponding cursor profile along the bottom row of nanopatterns.

The thickness of the films can be measured from cursor profiles across the film and uncovered substrates. Nanoshaving can be applied to determine the thickness of thin films with angstrom precision by referencing the substrate as a baseline for cursor measurements. In addition to alkanethiol SAMs, nanoshaving has been used for characterizations of molecularly thin films of porphyrins, alkylsilanes, sexithiophene, dimercaptobiphenyl multilayers, and DNA. After local areas of the surface have been uncovered by nanoshaving, new molecules or nanomaterials can then be selectively deposited on the exposed areas to form nanopatterns.

### 2.4 Nanografting of n-Alkanethiol SAMs

Nanografting was introduced in 1997 by Xu and Liu. A useful analogy for describing AFM-based lithography is to consider the AFM tip as a pen, a matrix SAM on gold as the paper, and fresh n-alkanethiols in solution as the “ink” for writing patterns. Nanografting basically uses the same procedure as nanoshaving, except that the steps are accomplished while the tip and the sample are immersed in a dilute solution of new thiol molecules chosen for writing (Figure 2.6). The matrix SAM is first characterized in liquid media by applying a low force, less than 1 nN.
Imaging in liquids enables one to achieve high resolution with low, nondestructive forces. After choosing an area for writing, a greater force (1-10 nN) is applied to the AFM tip (pen) to shave the matrix molecules from the gold substrate. The SAM molecules which are removed from the surface (paper) are either deposited at the edges of the nanopatterns, or are dissolved in the surrounding solvent. New thiol molecules from solution immediately self-assemble onto the shaved areas following the scanning track of AFM tip. The written patterns can then be characterized in situ without changing tips by returning to low force.

For nanografting, it is critical to control the amount of force to ensure that the tip remains sharp after writing nanopatterns. Unfortunately, the microfabrication processes used to manufacture tips have not yet achieved nanoscale reproducibility for the shape and spring constants for each lever, thus, an in situ approach is useful to derive the optimized threshold force for each AFM tip. To optimize the writing force, a simple computer script can be used to write several patterns at incrementally increasing force. The lowest force at which a complete pattern is observed is then chosen as the optimized force for nanografting. When too much force is applied to the AFM probe while scanning, it is possible to scratch away the underlying surface or to break the apex of the probe. If the selected threshold force is too great, the torsion on the cantilever will cause the tip to write irregular shapes and produce stray lines and marks around the patterns. When a minimum force is used for nanografting, hundreds of patterns can be written with the same AFM tip without sacrificing topographic resolution. In fact, often the resolution of AFM imaging is improved by the sharpening process or cleaning of the tip by scratching the surface.

Depending on the choice of molecules, nanografting can generate patterns that are taller or shorter than the SAM matrix. For example, A cross-shaped pattern of 11-mercaptoundecanol (MUD) was written into matrix of ODT in Figure 2.7A. The simultaneously acquired frictional
force image exhibits dark contrast for the MUD areas of the cross, which are terminated with hydroxyl groups. The surrounding methyl-terminated matrix areas of ODT exhibit lighter frictional contrast, clearly distinguishing the differences in surface chemistry after nanografting. The line profile of Figure 2.7C indicates the nanostructure is 0.7 ± 0.3 nm shorter than the matrix SAM, in close agreement with the theoretical differences in thickness, (ODT measures 2.1 nm, MUD is 1.5 nm). The measurements of film thicknesses with nanografting are highly dependent on the flatness of the surface; in this example the error term for the nanografted domains take into consideration the roughness of gold step edges (± 0.25 nm).

An example is presented for a positive height pattern of 16-mercaptohexadecanoic acid (MHA) in Figure 2.7D. The square nanopattern (200 x 200 nm²) was written within a dodecanethiol matrix and is well-centered on a terrace step of Au(111). The friction images provide additional information about the chemical changes on the surface which take place after writing new molecules. The corresponding friction image shows bright contrast for the carboxylic acid areas of the square pattern, whereas the surrounding methyl-terminated matrix
Figure 2.7 Nanografted patterns of self-assembled monolayers. [A] Cross-shaped pattern of 11-mercaptooundecanol fabricated within a matrix of octadecanethiol; [B] corresponding frictional force image; [C] cursor profile for the white line in A. [D] Mercaptohexadecanoic acid forms a taller pattern within a dodecanethiol matrix, the square has bright contrast; [E] friction image; [F] cursor profile across the nanopattern in D.

has dark contrast. There is adhesion between the tip and surface of the square nanopattern, which caused linespikes only on the patterned area along the horizontal direction of the scanning AFM tip. The line artifacts are clearly visible in the friction image. In contrast, the methyl-terminated areas do not exhibit the stick-slip adhesion because the methyl groups do not interact as strongly with the tip. The expected thickness for MHA is 1.9 nm, and for dodecanethiol is 1.5 nm. A representative cursor profile (Figure 2.7F) indicates that the pattern is $0.4 \pm 0.2$ nm taller than the molecules of the matrix, in close agreement with the theoretical height difference. An attribute of the nanografting process with thiol SAMs demonstrated with these examples is the remarkable angstrom to nanometer precision for edge resolution, even when using open-loop feedback for electronics. Such well-formed regular geometries at the square edges and corners of patterns are routinely achievable with AFM, because the piezocontrollers enable exquisite
control of small forces applied to the tip.

Arrays of patterns can also be produced with automation software when nanografting. An array of squares of 11-mercaptoundecanoic acid (MUA) was fabricated within a matrix of ODT in Figure 2.8. The sides of the square elements measure 100 ± 10 nm, and each pattern is separated vertically and horizontally at intervals of 60 ± 10 nm. Depending on the number of line scans used to write the patterns, it took approximately 30 seconds to write each pattern in Figure 2.8A. The patterns were inscribed using 50 linesweeps per square, advancing 2 nm after each line was scanned while the AFM tip was rastered in continuous contact with the surface. The corresponding friction image clearly displays the changes in surface chemistry after the patterns were written. The nanografted squares of carboxyl-terminated MUA exhibit bright frictional contrast against the darker background of the methyl-terminated ODT SAM. The expected thickness difference is 0.7 nm, in good agreement with the experimental measurement of the cursor profile in Figure 2.8C which averages 0.6 ± 0.3 nm.

Multiple patterns with various shapes and components can be quickly created and modified with nanografting, and all of the steps of nanofabrication and characterization are accomplished in situ.34,93 Nanografting enables precise control of the size, geometry, chemical functionality and location of structures on the surface. A spatial precision of 1 nm and edge-
resolution better than 2 nm have been demonstrated using nanografting.\textsuperscript{80} Patterns written by nanografting consist of well-ordered, close-packed thiol molecules with selected functionalities and chain lengths.\textsuperscript{80,93-94} Nanopatterns of thiolated molecules with different chain lengths and terminal groups have been written.\textsuperscript{93} A positive or negative height of patterns can be achieved (with reference to the matrix SAM) depending on the chain length of the grafted molecules. For $n$-alkanethiol SAMs, chain lengths ranging from 2 to 37 carbons have been grafted successfully on Au(111) and within the nanopatterns the molecules display a periodic arrangement.\textsuperscript{70,80} In a multiple ink experiment, nanopatterns of different composition were nanografted; parallel arrangements of nanopatterns of octadecanethiol and docosanethiol were nanografted side-by-side to provide molecularly-resolved views of close-packed SAMs.\textsuperscript{34}

A key element of nanografting is that $n$-alkanethiols chemisorb spontaneously to surfaces in an upright arrangement to form a crystalline phase, due to a mechanism of spatial confinement.\textsuperscript{6} When $n$-alkanethiols assemble naturally, there is a phase transition from a side-on orientation with the backbone of the molecule oriented along the surface, to a standing orientation in which the molecules adopt a tilted orientation as in Figure 2.\textsuperscript{2,52,57,70} When nanografting, it is thought that the molecules bypass the lying-down phase and assemble immediately into a standing configuration because there is not sufficient space for the molecules to assemble on the surface in a horizontal direction.\textsuperscript{6} A kinetic Monte Carlo model of natural and nanografted deposition of alkanethiols on gold surfaces was developed by Ryu and Schatz, which reproduces experimental observations for the variation of SAM heterogeneity with AFM tip writing speed.\textsuperscript{95} The speed of the AFM tip influences the composition of the monolayers formed along the writing track.

After nanografting a pattern, new molecules or nanomaterials can be attached to the reactive sites of the fabricated area by selective adsorption. For example, mercaptoundecanoic
acid was grafted into an octadecanethiol matrix, and then the nanopatterns were further reacted with octadecyltricholorosilane for positive and negative pattern transfer. The hydroxyl terminal groups reacted with trichlorosilane headgroups of molecules in solution to form a new layer of molecules on the surfaces. The nanografted patterns provide spatial selectivity for anchoring molecular assemblies with desired spacer lengths and terminal functionalities.

Metal nanostructures were produced on nanografted SAM patterns using electroless deposition of copper onto carboxylic acid terminal groups. Selectivity for adsorption on acid-terminated nanopatterns was accomplished by writing within a resistive matrix of hydroxyl-terminated SAMs. Combining automated AFM-based nanografting with electroless metal deposition enables high-resolution investigation of metal deposition processes at the nanoscale. First, a series of nanopatterns with a programmed gradient of densities was written within a resistive hydroxyl-terminated SAM matrix. Next, copper deposition was accomplished in situ from an alkaline copper plating solution. The lateral dimensions of the metal deposits were defined by the nanografted areas of the nanopatterns. The vertical dimensions of the patterns could be controlled with parameters of the surface density of reactive acid groups, and by the concentration of reactants in the plating solution. This approach offers promise for preparation of metal-molecule-metal junctions for fundamental investigations of electron transport in nanoscale junctions.

Structures of thiolated single-stranded DNA (ssDNA) were written by nanografting. The sulfur headgroup of thiolated oligonucleotides adsorbed to uncovered areas of gold surfaces to adopt a standing orientation. Line patterns as small as 10 nm were written by nanografting. In situ AFM investigations revealed surface changes for ssDNA nanopatterns after adding solutions of enzyme to the liquid cell. The nonrestriction endonuclease (DNase I) cleaves ssDNA randomly to cause a decrease in the heights of the ssDNA patterns, and the free fragments were
released into the surrounding buffer solution. Label-free hybridization of ssDNA nanostructures was also accomplished for nanografted ssDNA patterns using complementary segments of designed sequences. These investigations provide fundamental information about the specificity and selectivity of surface-bound ssDNA towards the complementary strands, which is important for constructing DNA-based devices and surface assays.

Micropatterning of proteins has already been applied for biosensors and biochips. In fact, patterning is essential for the integration of biological molecules into miniature bioelectric and sensing devices since the sensing element consists of a layer of biomolecules for capture of target molecules and analytes. Protein patterning has been accomplished at the micrometer level using microcontact printing, photolithography, and microfluidic channels. Thus, capabilities for micrometer scale methods offer valuable research capabilities at a size scale of hundreds of nanometers or larger. One may predict that nanoscale studies will advance the development of approaches for immobilization and bioconjugation chemistries, particularly with regard to understanding the parameters which influence protein activity, structural integrity and function. Precisely engineered surfaces can be used for the exploration of biochemical reactions in controlled environments and provide insight on the mechanisms of surface adsorption and molecular recognition.

Spatially well-defined regions of surfaces can be constructed with reactive or adhesive terminal groups for the attachment of biomolecules. In biochips and biosensors, SAMs with certain functional groups such as carboxylate and aldehyde have been used as linkers for the immobilization of proteins and other biomolecules on surfaces. Researchers have begun to apply nanografting to study proteins and biomolecular reactions on surfaces, towards resolving reactions with single molecules.

Thiolated proteins can be written directly on gold surfaces using nanografting. De novo
proteins that were designed to contain a single cysteine thiol at the C-terminus were nanografted within a matrix layer of octadecanethiol. Both a 3-helix metalloprotein and 4-helix bundle protein were successfully patterned and imaged using AFM. Measurements of the heights of protein nanopatterns matched the predicted dimensions, thus nanografting was demonstrated to enable coupling of the protein to the gold surface while preserving the tertiary structure of the protein.

Nanografted patterns of SAMs can be applied to immobilize proteins for in situ nanoscale surface assays. The dimensions of the apex of AFM tips are on the order of tens of nanometers, however, depending on the applied force and the geometry of asperities on the tip apex, the actual physical area of contact between the tip and surface is much smaller. The smallest feature yet produced by nanografting is a \(2 \times 4 \text{ nm}^2\) dot pattern which would accommodate approximately 32 thiol molecules. Patterns written by nanografting provide an ideal size for defining the placement of proteins on surfaces, since the dimensions of proteins are on the order of tens to hundreds of nanometers. The terminal moieties of SAM nanopatterns mediate the mechanism for binding proteins, such as through covalent, electrostatic, specific interactions or molecular recognition. Lithography writing parameters can be used to precisely control the arrangement and density of SAM binding sites at the nanometer level.

A key advantage of using nanografting for protein assays is the ability to conduct experiments in situ. The successive changes in surface topography after the steps of nanopatterning SAMs, rinsing, and introducing buffers or protein solutions can be viewed with high resolution AFM imaging after each reaction step. Protein patterns are not dried or exposed to air, rather the in situ steps enable immersion of proteins in a controlled buffered environment. Nanoscale studies with AFM offer new approaches to refine essential parameters used to link and organize proteins on surfaces of biochips and biosensors. The orientation, reactivity and
stability of protein molecules adsorbed on nanostructures of SAMs can be monitored with successive time-lapse images in near-physiological conditions. These investigations provide molecular-level information through the visualization of biomolecular reactions on surfaces for advancing biotechnology towards the nanoscale.

Adsorption of proteins such as lysozyme, rabbit IgG and BSA onto nanografted SAM patterns was first accomplished in 1999 by Wadu-Mesthrige et al.\textsuperscript{114} The general steps for \textit{in situ} protein immobilization investigations with nanografting are (1) to write nanopatterns of SAMs which are adhesive for proteins within a resistive matrix monolayer; (2) accomplish selective protein adsorption on nanografted patterns by adding buffered protein solutions to the liquid cell; (3) to achieve further reactions of the proteins with antibodies or small molecules without the use of radiolabels or fluorescent tags. Electrostatic binding of proteins such as IgG and lysozyme was demonstrated for nanografted patterns with carboxylic acid terminal groups, and covalent binding was accomplished by forming imine bonds to lysine residues of IgG and lysozyme.\textsuperscript{114} The methyl-terminal groups of alkanethiol SAMs furnished a resistive matrix to ensure that proteins attached selectively to either carboxylate or aldehyde nanopatterns. Each of the reaction steps for IgG nanostructures was captured \textit{in situ} with AFM images when patterns were reacted with anti-IgG.\textsuperscript{116} The electrostatic immobilization of proteins (lysozyme, rabbit IgG and carbonic anhydrase) was investigated by Zhou et al. for nanografted patterns at varied pH conditions to reveal changes in surface coverage of proteins with differences in surface charge.\textsuperscript{124} A side-by-side comparison of nanografted patterns with three different surface functionalities was accomplished in a single experimental platform, within a resistive matrix of hexa(ethylene glycol) SAM. Proteins can be anchored on reactive SAM patterns using robust covalent binding strategies. The surface moieties of nanografted SAM patterns were reacted with coupling reagents such as 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) and
dithiobis(succinimidyl undecanoate) (DSU) to mediate covalent linkages with proteins. By reacting 11-mercaptoundecanoic acid with EDC and DSU for chemical activation, Kenseth et al. demonstrated covalent immobilization of IgG onto nanografted patterns within a glycol-terminated monolayer.\textsuperscript{125} Nanografting and AFM characterizations provide valuable new tools for exploring binding strategies for proteins with unprecedented nanoscale views of surface changes after biochemical reactions.

2.5 Fabrication of SAMs Using Dip Pen Nanolithography

Dip Pen Nanolithography (DPN) is an AFM-based method for writing molecules on surfaces developed by Professor Chad Mirkin and coworkers in 1999.\textsuperscript{126} The AFM tip (pen) is coated with the molecules or nanomaterials to be written (ink), and a clean substrate serves as the paper. The molecular ink must have an affinity for both the AFM tip and for the substrate. For example, \textit{n}-alkanethiols attach to silicon nitride AFM tips through physisorption (physical adsorption) however, molecules bind through chemisorption to surfaces of coinage metals. For DPN writing, molecules are transported to the surface via capillary diffusion through the nanoscopic water meniscus formed between the tip and sample in an ambient environment (Figure 9A). The transfer of the ink has been found to depend on the relative humidity, which affects the size of the water meniscus formed between the tip and the surface. Writing with DPN does not require applying additional force to the AFM tip, instead the tip is held in contact with the surface for certain time intervals. For DPN, the naturally formed water meniscus in ambient environments enables capillary transport of inks to the surface. The duration of contact and the nature of the ink molecules affect the size of written nanostructures, as shown for the examples in Figure 2.9. Individual dots, lines, and grid patterns of alkanethiols can be written by DPN. Examples of octadecanethiol and mercaptohexadecanoic acid nanopatterns written with DPN are shown with lateral force AFM images (Figure 2.9). The duration of contact between the tip and
surface, the humidity and the nature of the ink influence the size of the dot patterns as evident in Figures 2.9B and 2.9C. To reproducibly generate an array of dot patterns the tip motion and contact intervals were programmed, (Figure 2.9D) to precisely translate the tip and maintain contact with the surface for 20 seconds. By scanning the tip along a defined design (Figure 2.9E), line patterns can be generated as shown for a grid pattern of 100 nm width lines. Each line of the grid was written in 90 seconds using octadecanethiol ink.

The resolution of DPN depends on several parameters, such as the geometry of the AFM tip, the humidity of the ambient environment, as well as by the duration in which the inked tip is placed in contact with the surface – typically for 1 to 10 seconds. With typical cantilevers, DPN routinely generates feature sizes down to 15 nm. The resolution for writing nanostructures using DPN also depends on factors such as the grain size of the substrate, the scan rate and relative humidity.\textsuperscript{126-127, 128} Coating an AFM tip is accomplished by dipping the probe into a drop of ink molecules, or immersion of tips in a liquid containing molecules to be written. The surfaces of AFM tips are highly suitable for writing thiol molecules, because the sulfur groups have a strong affinity for silicon and silicon nitride surfaces. Since molecules coat the AFM tips through physisorption, a liquid meniscus enables the flow of molecular ink to chemisorb to clean surfaces.

The transfer of ink during DPN has been found to depend on the relative humidity, which affects the size of the water meniscus formed between the tip and surface. Several researchers have investigated the transport mechanism for writing nanopatterns with DPN.\textsuperscript{128-136} The smallest size of patterns written with DPN is on the order of 10-20 nm, with an ultrasharp probe.\textsuperscript{137} Dip-pen nanolithography has begun to emerge as an important and versatile method for producing multicomponent arrays of SAM nanopatterns, as well as other molecules and nanomaterials. Readers are directed to previous reviews of experimental work applying DPN for
further examples and applications.\textsuperscript{138-140}

**Figure 2.9** Principle of Dip Pen Nanolithography (DPN) and example nanopatterns. [A] Schematic representation of DPN writing. [B] Lateral force microscopy images of dots of octadecanethiol after 2, 4, 16 seconds contact with the substrate. [C] Lateral force microscopy images of mercaptohexadecanoic acid after 10, 20, 40 seconds contact with the surface. [D] Array of octadecanethiol dots generated with 20 second contact intervals. [E] A grid written with octadecanethiol. (Reprinted with permission from Ref.\textsuperscript{126}, R. D. Piner et.al *Science* **283**, 661 (1999) Copyright\textregistered American Association for the Advancement of Science.

Dip Pen nanolithography is not limited to thiols as ink and has been applied successfully for other molecules. A wide range of molecules and nanomaterials have been nanopatterned on various surfaces using DPN. For ambient DPN, the choice of ink must be compatible with water
for transfer of molecules through a water meniscus to deposit on surfaces, and the molecules should not be susceptible to hydrolysis reactions. The most commonly used inks reported for DPN are octadecanethiol and mercaptohexadecanoic acid (MHA).\textsuperscript{126-131,136,141-147} Higher molecular weight compounds such as octadecylphosphonic acid (OPA), 2-mercaptobenzothiazole, 4-amino-5-hydrazino-1,2,4-triazо-3-thiol, 4-mercaptopyridine, and 2-mercaptoimidazole were used successfully as inks for writing nanopatterns with DPN, by increasing the humidity as high as 85\%.\textsuperscript{148} Other molecules and nanomaterials used for inks include silanes on semiconductive substrates;\textsuperscript{137,149-150} peptides on GaAs substrates;\textsuperscript{151} dendrimers,\textsuperscript{152} dyes,\textsuperscript{153-155} proteins,\textsuperscript{156-157} and DNA\textsuperscript{158-159} on gold or silicon surfaces; metal salts on silicon substrates;\textsuperscript{160-165} and certain polymers on silicon.\textsuperscript{166-169} In addition to direct writing of proteins, protocols have been developed for attaching proteins\textsuperscript{123,170-175} or viruses\textsuperscript{176-177} to nanopatterns written by DPN.

An approach for inking an AFM tip for DPN was developed using a poly(dimethylsiloxane) (PDMS) coating for ink transfer.\textsuperscript{178} This approach is a hybrid of microcontact printing and DPN, and was successfully demonstrated for ink molecules of 16-mercaptohexadecanoic acid, 1-octadecanethiol, PAMAM dendrimers and cystamine. The polymer coating provides a reservoir which adsorbs various inks, and the tip can be used for imaging nanostructures after writing patterns due to differences in diffusion rates of inks from PDMS coatings.

Ink solutions for DPN are not limited to molecules at ambient temperatures. A method of thermal DPN was developed using a heated AFM cantilever and tip, to deposit solid inks.\textsuperscript{179-182} An advantage of this approach is that the ink-coated cantilever can be used for fabrication as well as for \textit{in situ} imaging of the nanostructures that were written, by changing the temperature of the tip. At cold or ambient temperatures, the ink molecules remain attached to the tip, and the tip
can thus be used for imaging without unintended deposition of ink molecules during AFM characterizations. When the cantilever is heated near the melting temperature of the solid ink, the molecules are transferred to the substrate following the scanning path of the AFM tip. The melted liquid flows from the heated tip to the surface. Ink molecules that have been used successfully with thermal DPN include octadecylphosphonic acid at 122°C, a conductive polymer of poly(3-dodecylthiophene) at 134°C, a mixed polymer film of diazide-diyn at 170°C, and nanosoldering of indium at 500°C. Thus, thermal DPN enables writing with molecular inks that have poor solubility in water.

2.6 Writing Patterns of \(n\)-Alkanethiol SAMs Using NanoPen Reader and Writer, NPRW

An SPL method of “NanoPen Reader and Writer” (NPRW) was invented in 1999 by Amro et al. For NPRW, the paper is a resistive methyl-terminated surface of a SAM. As with DPN, an AFM tip is inked with thiol molecules and writing is accomplished in air. At low force, molecules stay on the tip and provide high-resolution images of surface topography. Tip coatings provide a lubricant to minimize the stick-slip adhesion that is often present with ambient AFM imaging. When the force is increased, the thiol-coated tip pushes through the matrix SAM to deposit molecules from the tip onto the underlying gold substrate. The thiols within the nanopatterns were demonstrated to be well-ordered and close-packed with the evidence of molecularly resolved images acquired with a coated AFM tip. Patterns can be written in air or in certain solvent media that are immiscible with the ink molecules. The NPRW approach combines the advantages of nanografting and Dip-Pen Nanolithography so that the same ink-coated AFM tip can be used for both writing and characterizing (reading) inscribed nanopatterns. The resolution of NPRW depends on the sharpness of the tips used for writing and the capabilities of the AFM scanner.
The *in situ* steps for NPRW are illustrated in Figure 2.10. Under low imaging force, the ink molecules remain attached to the AFM tip and do not deposit on the surface of a methyl-terminated *n*-alkanethiol SAM matrix or ‘*paper*’ (Figure 2.10A). Thiolated molecules readily physisorb to the surfaces of silicon or silicon nitride AFM tips, but are not chemically bonded. Thus, when the force is increased to a certain threshold, the tip is pushed through the resist layer of the matrix SAM to make contact with the underlying gold substrate for writing nanopatterns (Figure 2.10B). Simultaneous with the shaving action of the AFM tip operating under high force, surface molecules are displaced and scraped away and fresh ink molecules from the tip chemisorb to the uncovered gold surface. By returning to low force, the same tip can be operated to “read” or characterize the patterns that were written (Figure 2.10C). An advantage of NPRW in comparison to DPN is that ink can be deposited only when higher forces are applied to the AFM tip, to enable selectivity for writing. At low forces the ink molecules do not transfer to methyl-terminated SAMs of the ‘*paper*.’ An intrinsic capability of AFM scanners is to provide exquisite control of the vertical forces applied to the tips, even in the range of piconewtons. For NPRW, the SAM-coated gold ‘*paper*’ resists nonspecific deposition of thiol inks throughout areas of the surface, because the coating remains on the tip while scanning at low force. The ink also serves as a lubricant to facilitate high-resolution imaging in air. It has previously been
established that coating AFM tips with organic molecules can substantially improve resolution by minimizing stick-slip adhesion.\(^{185-187}\)

![Figure 2.11 Circle patterns of mercaptohexadecanoic acid written in a dodecanethiol matrix using NanoPen Reader and Writer (NPRW). (A) Topograph of four sets of concentric circle patterns; (B) Corresponding frictional force image; (C) Cursor profile for the line in A. (D) Map of the lithography design.](image)

The key difference between DPN and NPRW is the mechanism of writing. For DPN, ink is transferred through a narrow water meniscus, and the size of the written patterns largely depends on the length of time the tip is held in contact with the surface, according to the diffusion rate of the ink molecules used for writing. For NPRW, an increased force on the AFM tip is required for writing nanopatterns; the writing mechanism provides removal of a matrix SAM followed by rapid replacement with new molecules from the tip via sulfur-gold chemisorption.

An example set of nanopatterns written in air using NPRW is displayed in Figure 2.11 using hexadecanethiol ink and a matrix SAM of hexanethiol. An Agilent 5500 AFM/SPM system with Picoscan v5.3.3 and Picolith beta version 0.4.5 software was used to write and
characterize the nanopatterns. An oxide-sharpened silicon nitride probe with an average force constant of 0.5 N/m (Veeco ProbeStore, Santa Barbara, CA) was used for writing nanopatterns of SAMs. The tip was immersed in a neat solution of hexadecanethiol for 15 minutes and dried in air under ambient conditions. By applying an increased load on the AFM tip, the shorter molecules of the hexanethiol matrix were replaced by ink molecules of hexadecanethiol following the scanning track of the probe. The speed used for writing via NPRW was 0.05 µm/s.

Circular nanopatterns of hexadecanethiol SAM were written within a hexanethiol matrix using NPRW (Figure 2.11). Four sets of patterns were written within a 1 x 1 µm\(^2\) area, as viewed in the AFM topograph of Figure 2.11A. The gold contains a dark line scar which traverses the top, side and bottom of the image. The depth of this natural defect limits the attenuation of the color scale for clearly resolving the contours of the nanopatterns for topography, however, the corresponding friction image in Figure 2.11B clearly distinguishes the outlines of the circular patterns. The patterns were written by outlining concentric rings, and thus the composition of the patterns contains a mixture of the matrix and ink molecules. Writing for all four patterns was completed in 2 minutes using NPRW. The sets of patterns consist of five concentric rings which were outlined once. The cursor profile across one of the patterns exhibits a thickness difference of 1.0 ± 0.3 nm in close agreement with the 0.9 nm theoretical difference in thickness between hexadecanethiol (1.9 nm) and hexanethiol (0.8 nm).

User-friendly software with a graphical user interface for designing nanopatterns has been developed by Agilent Technologies, as displayed in Figure 2.11D. The shapes of the patterns can be sketched using different colored outlines, and the attributes of the patterns (bias, speed, force) can be assigned by choosing the pattern colors that are drawn on the computer. In this example, four sets of concentric circles were designed; the execution of the drawing parameters is viewed in Figures 2.11A and 2.11B. By changing colors and assigning a range of
variables the nanopatterning protocols can be systematically tested. Thus, automation of AFM-based lithography with improvements in controller software enables the experimentalist to rapidly optimize the writing parameters such as speed and force for different surfaces and ink molecules.

Nanopatterns of thiol-modified gold nanoparticles were written within a decanethiol SAM/Au(111) using NPRW (Figure 2.12). The probe was inked with gold nanoparticles by inverting the AFM tip and placing a droplet of nanoparticle solution onto the tip. An example rectangular nanopattern of thiol-encapsulated gold nanoparticles written by NPRW within a C_{10}S SAM matrix is presented in Figure 2.12. The shapes of individual nanoparticles can be resolved within the nanostructure, and only a single layer of nanoparticles formed on the gold surface. For NPRW with nanoparticle ink, the decanethiol matrix was replaced with gold nanoparticles following the shaving track of the tip for particle sizes between 1.2 - 8.2 nm. The methyl-terminated matrix SAM was an effective resist layer and prevented the non-specific adsorption of nanoparticles when imaging at low force. When higher force was applied, the nanoparticle “ink” could be precisely written on surfaces as defined by positioning the AFM tip. After writing, the nanoparticle patterns could be characterized in situ using the same AFM tip under low force.

Nanoscale characterization of the thickness of monofluoro-substituted oligo(phenylene-ethynylene) (F-OPE) thiolated SAMs on gold was accomplished by combining AFM characterizations and nanofabrication. Topographic images provide high resolution views of the surface morphology, and lithography enables measurements of the thickness of organic films at the level of angstroms. Nanopatterns of dodecanethiol and octadecanethiol were written within a matrix of F-OPE using NPRW, to measure the thickness of the films. Since the heights of \textit{n}-alkanethiols are well established, the nanopatterned SAM molecules provide an internal height
A reference or molecular ruler for nanoscale measurements. Frictional force images were also acquired using a coated AFM tip, to pinpoint the locations of inscribed nanopatterns.

Figure 2.12 Nanopattern of gold nanoparticles written with NPRW. The surface of the nanoparticles were modified with a mixture of alkanethiols and written within a decanethiol monolayer. (Reprinted with permission from Ref. 90, J. C. Garno et al., Nano Lett. 3, 389 (2003). Copyright @ American Chemical Society.

2.7 Catalytic Probe Lithography

Catalytic probe lithography is a recently developed and promising strategy for chemical modification of surfaces with nanoscale resolution. For catalytic probe lithography, an AFM tip
is coated with molecules or metals that will catalyze a chemical reaction on the sample surface. The catalysis reaction occurs in areas where the coated tip makes contact with the surface (Figure 2.13). For example, the terminal chemistry of SAMs can be changed to a different functional group. As the catalytic probe is scanned in contact with the surface, nanopatterns are generated following the scanning track of the AFM tip to produce designed nanopattern geometries. The linewidth resolution of patterns written by catalytic SPL corresponds to the size of the contact area between the tip and sample. Depending on the nature of the catalysis reaction, the same tip can be used to image the nanopattern by changing certain experimental parameters, or optical microscopy has also been applied to view nanopatterns after site selective surface reactions.

Figure 2.13 Principle of catalytic probe lithography.

Unlike DPN or NPRW lithographies, the transfer of ‘ink’ from the tip to the surface is not part of the process for writing patterns with catalytic probe lithography. The catalytic coating on the AFM probe is not the product or reactant, the role of the catalyst is to either initiate or accelerate the rate of a chemical reaction. The catalyst is not consumed by the reaction
and is not deposited on the surface to create patterns. The length of contact time and the amount of force applied to the tip affect the resolution of writing and these parameters are reaction specific. Tip coatings used for catalytic probe lithography include platinum,\textsuperscript{190} palladium\textsuperscript{191-192} and gold films with molecular coatings.\textsuperscript{193-194}

The earliest report of localized catalysis with an AFM probe was reported in 1995 by Müller et al.\textsuperscript{190} Chemical modification of the terminal azide group of SAMs was achieved with a platinum-coated AFM tip as the catalyst to produce amine-terminated patterns. After writing patterns, the samples were reacted with aldehyde-modified latex or fluorescent tags which attached selectively to the SAM patterns. The fluorescent patterns were then imaged using optical microscopy.

A palladium-coated AFM tip was used to catalyze the chemical conversion of azide, carbamate, and alkene terminal groups of organosiloxane SAMs on glass substrates.\textsuperscript{192} Three reaction schemes were demonstrated for palladium-catalyzed addition and transfer reactions to produce amine-terminated patterns. To demonstrate that the reactions occurred, the patterns were labeled with fluorescent probes and also with biotin, which selectively binds streptavidin-functionalized gold nanoparticles. The labeled nanopatterns were imaged by tapping-mode AFM with an uncoated probe and also by confocal microscopy.

A Suzuki coupling reaction was accomplished by catalytic probe lithography using a palladium-coated AFM tip.\textsuperscript{195} A gold surface was coated with an aryl bromide monolayer, and the palladium-coated probe and surface were immersed in a boronic acid reagent solution. Nanopatterned areas could be resolved by frictional force images in the absence of the reagent media. Further reactions were demonstrated for the nanopatterns with amine-specific fluorophores and aldehyde-functionalized nanospheres, which were viewed using optical microscopy.
Catalytic probe lithography was accomplished with a gold AFM tip that was further coated with an acidic SAM.\textsuperscript{193} When brought into contact with the surface, the acid groups on the tip induced hydrolysis of the silyl ether groups of a reactive SAM, bis-(ω-tert-butyldimethyl-siloxyundecyl)disulfide (Figure 2.14). The tip was scanned across the SAM layer to produce well-defined patterns of different sizes and the shapes. Patterns were imaged by frictional force AFM using the functionalized AFM tip. A written resolution of 25 nm linewidths was achieved for these experiments, comparable to the area of contact between the coated AFM probe and the surface.

\textbf{Figure 2.14} Patterns with well defined sizes and geometry can be produced using catalytic probelithography. [A] Friction image of line structures written on bis(ω-tert-butyldimethyl-siloxyundecyl)disulfide (TPDMS) monolayer using a tip functionalized with 2-mercapto-5-benzoimidazole sulfonic acid. [B] Example of a grid pattern written by selective hydrolysis of TBDMS. (Reprinted with permission from Ref. \textsuperscript{193}, 184, M. Peter \textit{et al.}, \textit{J. Am. Chem. Soc.} \textbf{126}, 11684 (2004). Copyright@American Chemical Society.

\textbf{2.8 Biased-induced Lithography of SAMs}

When an electric field is applied between a conductive SPM tip and sample, at certain bias voltages the area beneath the tip undergoes chemical or physical changes. Such surface
changes provide a mechanism for local fabrication of surfaces at elevated bias. Both STM and AFM have been used for bias-induced lithography, in which voltages between a conductive tip and sample are controlled to selectively alter the surface chemistry of local areas scanned by the probe. Scanning probe based oxidation using STM was discovered in 1990 by Dagata et al.\textsuperscript{196-197} A hydrogen-terminated silicon surface was locally oxidized when an elevated bias voltage was applied between an STM tip and the surface. It was later demonstrated in 1993 that local oxidation of surfaces could also be achieved using AFM, oxide lines were written on silicon surfaces using a metal-coated AFM tip.\textsuperscript{198}

The general concept for surface fabrication using AFM for bias-induced lithography is depicted in Figure 2.15. For nanofabrication of SAMs, bias-induced lithography is accomplished by generating an electric field between the tip and the sample, either to oxidize or to replace surface molecules. As the AFM or STM tip is rastered over the surface at elevated bias, a pattern is generated for the areas scanned by the conductive probe. Typically, short (microsecond to millisecond) pulses of tunneling current or bias voltage are applied between a conductive tip and sample, in the range of 10-30 volts. The current generated during nanofabrication is very small, in the range of picoamperes or less. To accomplish bias-induced lithography, the tip must be conductive and the substrate must also be conductive or semi-conductive. Conductive AFM tips are prepared by sputtering a thin film of metal onto a tip. Conductive probes for bias-induced lithography are available commercially with coatings of cobalt, diamond-like carbon, doped diamond, platinum, platinum/iridium, tungsten carbide, titanium nitride, and nickel. The substrates that have been used are flat metal films (titanium tantalum aluminum, molybdenum, nickel, niobium) and compound III-V semiconductors.\textsuperscript{197,199}

There are several mechanisms that have been proposed for nanofabrication using bias-induced lithography, depending on the nature of the environment and surfaces. The factors that
determine the size of features are the duration of the applied bias, the magnitude of the applied electric field, humidity and also the dimensions of the SPM tip. With bias-induced oxidation, the changes produced by an electric field often do not induce changes in molecular heights, and thus cannot be detected by topographic images. However, other AFM or STM imaging modes, such as lateral force imaging, force modulation and current imaging can be used to clearly resolve differences for oxidized areas. Tip proximity is a key difference for using AFM versus STM. For STM, the tip is brought very close, within tunneling distance (< 1 nm), but remains out-of-contact with the surface. For AFM, the tip is brought into direct contact with the sample during bias-induced lithography. Thus, the mechanisms for surface modification are quite different for STM versus AFM. In a UHV environment with STM where water is essentially removed, the surface changes are a consequence of Ohmic heating, which induces evaporation or desorption of surface layers. In ambient conditions, when the tip is in contact with the surface, changes result from electrochemistry reactions at either the tip or sample which are caused by electric field effects. There are advantages for using AFM rather than STM for bias-induced nanofabrication, because of differences in the positional feedback for STM. With STM, the
tunneling current depends on the physical distance or gap between the tip and sample, which varies exponentially with distance. Thus nanofabrication with STM is accomplished without physical contact between the tip and surface. In contrast, for AFM the tip touches the surface directly with well-controlled force, and voltage can be applied directly to the tip-surface contact. Direct contact with the surface intrinsically enables better control of the voltages applied for surface modification.

For the mechanism of local surface oxidation of surfaces using bias-induced lithography in ambient environments, the tip functions as a cathode, the substrate acts as the anode, and the water meniscus formed between tip and surface serves as the electrolyte. The applied bias induces an electric field between the tip and surface, ionizing the water molecules of the meniscus to effect electrochemical reactions on the surface.\(^{202-203}\) The narrow capillary meniscus formed in ambient environments is essentially an ultra miniaturized electrochemical cell. This process is generally known as bias-induced nanolithography; however other terms used to describe this method of writing are local oxidation nanolithography (LON), scanning probe oxidation, nano-oxidation or local anodic oxidation.\(^{197,204}\)

Considerable work has been published for bias-induced lithography of metals,\(^{197,203,205-207}\) and semiconductor surfaces such as gallium arsenide,\(^{208}\) silicon nitride\(^{209}\) or silicon.\(^{198,210-219}\) Examples which follow will present results applying bias-induced lithography for writing nanopatterns with SAM surfaces, such as silane SAMs on silicon or alkanethiol SAMs on gold surfaces. A summary of the SAM surfaces and fabrication conditions is presented in Table 2.3. Parameters such as the amount of bias voltage applied and speed of writing vary according to the nature of the surface to be patterned. Voltages reported for bias-induced lithography with surfaces of SAMs range from -7 V to +17 V. When writing SAMs on silicon, patterns with a positive height with respect to the surface are formed at negative bias, whereas at positive
### Table 2.3 Examples of bias-induced lithography.

<table>
<thead>
<tr>
<th>SAM/Surface</th>
<th>Lateral resolution of nanopatterns</th>
<th>Volts applied</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>octadecyltrichlorosilane/silicon surface methyl groups oxidized to carboxylate</td>
<td>10-40 nm</td>
<td>+ 8.5-8.7 V</td>
<td>220-222</td>
</tr>
<tr>
<td>thiol-functionalized silane monolayer/silicon defined sites for electrodeposition of silver</td>
<td>30 nm</td>
<td>+ 5-8 V</td>
<td>223</td>
</tr>
<tr>
<td>octadecyltrichlorosilane/silicon surface methyl groups oxidized to carboxylate</td>
<td>60-300 nm dots</td>
<td>+7-10 V</td>
<td>224</td>
</tr>
<tr>
<td>trimethylsilyl SAM prepared on silicon patterns were chemically etched</td>
<td>80 nm grooves</td>
<td>+5 V</td>
<td>202,225</td>
</tr>
<tr>
<td>18-nonadecynyltrichlorosilane/silicon surface vinyl groups oxidized</td>
<td>9 nm lines</td>
<td>-8.0-9.5 V</td>
<td>226</td>
</tr>
<tr>
<td>oligo-(ethylene glycol)-terminated SAM/silicon bias-induced desorption</td>
<td>90 nm holes</td>
<td>+ 17 V</td>
<td>122</td>
</tr>
<tr>
<td>octadecyltrichlorosilane/silicon patterns were used for grafting of polymers, or for adsorption of gold nanoparticles</td>
<td>40 nm</td>
<td>- 8-10 V</td>
<td>227</td>
</tr>
<tr>
<td>octadecylyphosphonic acid monolayer on silicon molecules desorbed at positive bias; oxides formed at negative bias</td>
<td>50-80 nm</td>
<td>± 6-7 V</td>
<td>228</td>
</tr>
<tr>
<td>octadecanethiol SAM on Au(111) bias-induced replacement with decanethiol ink</td>
<td>50 nm</td>
<td>+ 4-5 V</td>
<td>229</td>
</tr>
<tr>
<td>dodecanethiol SAM on Au(111) bias-induced replacement</td>
<td>10-15 nm lines</td>
<td>+2.7-3.8 V</td>
<td>230-231</td>
</tr>
<tr>
<td>octanethiol, dodecanethiol, dodecanethiol and tetradecanethiol SAMs on Au(111) bias-induced replacement</td>
<td>12 nm lines</td>
<td>+1.9-3.3 V</td>
<td>200</td>
</tr>
<tr>
<td>palmitic acid monolayer on silicon positive height patterns formed at negative bias; desorption observed at positive bias</td>
<td>60-80 nm</td>
<td>± 10 V</td>
<td>213</td>
</tr>
<tr>
<td>n-octadecyl mercaptan SAM/Au(111)</td>
<td>10-50 nm</td>
<td>+3 V, -3 V</td>
<td>232-233</td>
</tr>
</tbody>
</table>
voltage the molecules desorb to form trenches or holes in the surface layer. Also, depending on
the nature of the surface headgroups, at certain positive bias thresholds, the endgroups can be
oxidized without evidencing a change in height.\textsuperscript{223}

Bias-induced lithography can convert the endgroups of SAMs via oxidation reactions. Local oxidation of methyl terminal groups of an \textit{n}-octadecyltricholorosilane (OTS) monolayer on silicon was accomplished by Liu et al. to produce carboxylate nanopatterns.\textsuperscript{220} Topography and simultaneously acquired frictional images of the nanopatterns produced within an OTS monolayer are shown in Figure 2.16. The ultrasmall dot patterns (40 ± 4 nm) are vaguely distinguishable in the topographic view; however the changes in surface chemistry are clearly evident in the friction image. The 9 x 9 array of dot patterns was written using contact mode AFM by applying 8.8 volt pulses for 3.0 ms/point in ambient humidity of 60%. Patterns written in OTS monolayers with bias-induced oxidation were found to be stable for months under ambient conditions in air. Various methods of constructive nanolithography have been developed by Sagiv et al. to build complex assemblies with additional steps of chemical derivatization and adsorption of nanoparticles.\textsuperscript{220-223} The bottom-up approaches combining bias-induced lithography with chemical processing have potential for preparing components of nanodevices.

Desorption of silane molecules to form nanosized holes was accomplished for oligo-(ethylene glycol) terminated monolayers on silicon substrates at +17 V bias.\textsuperscript{122} Biomolecular arrays were formed by attachment of proteins in further steps using avidin and biotinylated BSA. The glycol-terminated SAM provided an effective resist layer to prevent non-specific adsorption of proteins on the non-patterned areas. This approach offers promise for producing high-density arrays of protein patterns for biosensing platforms.
Figure 2.16 Nanopatterns within \textit{n}-octadecyltrichlorosilane were generated by bias-induced lithography (+8.8 V) to oxidize methyl headgroups. Patterned dots in the simultaneously acquired [A] topography and [B] friction image have carboxylic acid terminal groups. (Reprinted with permission from Ref. \textsuperscript{220}, S. T. Liu \textit{et al.}, 	extit{Nano Lett.} \textbf{4}, 845 (2004). Copyright@American Chemical Society.

Oxidative desorption of \textit{n}-alkanethiol SAMs on gold surfaces can be applied for an STM-based replacement lithography as developed by Gorman et al.\textsuperscript{231} Writing nanopatterns of thiol SAMs was accomplished \textit{in situ} by increasing the STM bias in a nonpolar solvent containing new molecules to be written. At elevated bias, the molecules under the STM tip desorb and are replaced by thiol molecules in solution. Returning to nondestructive imaging conditions, the nanopatterns can be characterized. The newly written patterns display height differences corresponding to the thickness of the \textit{ink} molecules from solution. Bias replacement lithography was used to selectively desorb areas of a dodecanethiol SAM on gold and replaced with
ferrocenyl-undecanethioacetate molecules (Figure 2.17). Thiol desorption was accomplished at +3.0 V bias voltage. Gradient patterns were fabricated by adjusting the replacement bias, tip scan rate and the relative humidity. The resolution of the line patterns measured 10 to 15 nm. The structure and electrochemical desorption properties of the surface monolayer determines the bias conditions for lithography; for example, SAMs composed of longer-chain molecules require higher bias.

Approaches have been developed which combine bias-induced lithography with various coatings on AFM tips. A method of electrochemical Dip-Pen Nanolithography was demonstrated using a silicon cantilever coated with platinum salts (H₂PtCl₆). When the tip was scanned in a humid environment across a P-type Si(100) surface at positive DC bias (+1 to +4 V), platinum metal was generated at the cathodic surface.

In another example, SPM-induced cathodic electrografting was accomplished with different alkyne molecules. Molecular inks of 1-octadecyne, 1-dodecyne or 1,4-diethynylbenzene were loaded onto silicon cantilevers for writing with bias-induced lithography. A negative bias (-1.0 to -2.2 V) was applied to the tip for writing. The alkyne molecules were shown to bind covalently to the surface forming patterns with heights corresponding to the thickness of a monolayer.

Electro Pen Nanolithography uses a tip coated with ‘ink’ molecules for writing, and requires that a bias pulses (+9 V) be applied to a conductive AFM tip. Trialkoxysilanes were used as inks (mercaptopropyltrimethoxysilane, 3-aminopropyltrimethoxysilane, octadecyltrimethoxysilane) to write patterns on an OTS-coated silicon wafer. The width of the lines increased with humidity, achieving linewidth resolution of 50 nm. The ink does not transfer to the surface unless a bias is applied, therefore the coated AFM tip can be used interchangeably for imaging and writing patterns by changing the voltage.
Figure 2.17 Bias-induced replacement lithography was used to write a nanopattern of ferrocenyl undecanethioacetate within a dodecanethiol SAM. (Reprinted with permission from Ref. 230, R. Fuierer et al., Adv. Mater. 14,154 (2002). Copyright © John Wiley & Sons, Inc.

2.9 NSOM Lithography with SAMs

Photolithography with SAMs has become a practical tool for constructing biosensor arrays,235 fabricating microfluidic channels236-237 and for development of microelectronic devices/components.238-239 Chemical reactions of photolithography are accomplished by irradiating selected small areas of a surface, while masking other areas to prevent photodegradation. By irradiating SAMs with certain wavelengths of light the molecules become oxidized and detach from the surface. The exposed areas of the surface can then be etched to produce 3D structures. Depending on the choice of molecules, photolithography can be used to change the surface chemistry of photoreactive monolayers,240-242 or can be applied for oxidation/degradation of SAMs.243-246 Photolithography is the primary tool used for preparing computer memory chips and the manufacture of photoresists has become a multimillion dollar
industry.\textsuperscript{247} The resolution for conventional photolithography is limited by optical diffraction; structures that are smaller than the wavelength of incident light cannot be produced. Near-Field Scanning Optical Microscopy (NSOM or SNOM) combines the technology of scanning probe instruments with optical spectroscopy in the near field regime.\textsuperscript{32} The resolution of NSOM surpasses the diffraction limit, and is determined by the size of aperture and the gap distance between the probe and sample.\textsuperscript{32} Lithography with NSOM does not require a photomask, since only selected areas are irradiated by the NSOM probe. The point light source of the probe is scanned above the sample surface to enable selective irradiation of well-defined nanosize regions to accomplish photochemical conversion or oxidation reactions.

In NSOM lithography, nanopatterns are created by exposing an area of the surface to a light source from a fiber optic probe. Instruments for NSOM are operated in noncontact mode and use an illuminated aperture as a light source. A tapered optical fiber coated with metal provides a conduit for light, with a nanoscopic aperture at the end of the sharp probe. The typical distance of the probe to the sample is in the range of 10 nm and the size of aperture is smaller (<200 nm) than the wavelength of light used for imaging.\textsuperscript{31}

Scanning near-field photolithography (SNP) uses an intense collimated light source, such as a laser coupled to an NSOM.\textsuperscript{248} Patterns as small as tens of nanometers have been fabricated with SNP.\textsuperscript{249} Scanning near field lithography has been applied to create patterns on sol-gel films,\textsuperscript{250} silicon,\textsuperscript{251-254} azobenzene polyester,\textsuperscript{252} triglycine sulfate ferroelectric surfaces,\textsuperscript{255} polymers,\textsuperscript{256} chloromethylphenylsiloxanes,\textsuperscript{257} oligo(ethylene glycol) SAMs\textsuperscript{258} and alkanethiol SAMs.\textsuperscript{249,259} For SNP with SAMs, a metal-clad fiber optic probe (aperture size ~50nm) that is coupled to a laser is scanned at a distance of 5-10 nm from the surface. Either photooxidation\textsuperscript{249,260} or photochemical conversion\textsuperscript{257} occur selectively on the areas of the surface that are irradiated when the NSOM probe is scanned above the SAM. An example of SNP by
photooxidation of decanethiol SAMs is presented in Figure 2.18. The line patterns were formed by irradiation of selected regions of the surface with an argon laser (254 nm), to form alkanesulfonates by photooxidation (Figure 2.18). The oxidized SAMs of exposed areas are readily displaced from the surface.\(^\text{259}\) Nanopatterns of different molecules can be created by immersing the sample into a second thiol solution. Alternatively, the sample can be placed in an etchant solution for selective etching of the photooxidized areas of the surface.\(^\text{259,261}\) The size of patterns generated by SNP is not limited by the size of the probe aperture, patterns as small as 20 nm have been written for hexadecanethiol SAMs.\(^\text{249}\) Examples of nanoscale patterns of SAMs fabricated using SNP are shown with friction images in Figure 2.18.\(^\text{260}\)

Line patterns of dodecanethiol were successfully written within mercaptoundecanoic acid (11-MUA) as evident by the color contrast of the images. In the patterned regions, 11-MUA was oxidized. Molecules within the oxidized areas were displaced when the sample was
immersed in a dodecanethiol solution. The reverse protocol using a SAM of dodecanethiol as the matrix was accomplished in Figure 2.18B. The changes in frictional contrast are caused by differences in tip-surface adhesion between methyl and carboxyl headgroups. 260

Nanopatterns produced with SNP are not limited to photooxidation reactions of thiolate molecules. Scanning near-field photolithography can also be accomplished for monolayers with photoactive terminal groups. As regions are scanned by the NSOM probe, exposure to light causes the photoconversion of headgroups to different functionalities. 257 Spatially defined chemical reactions can be achieved by photoconversion of certain terminal groups using SNP. For example, the terminal groups of monolayers of chloromethylphenyl trichlorosilane (CMPS) monolayers on silicon oxide surfaces were converted to carboxylic acid moieties by irradiation with a 244 nm laser source. 257 The patterns were reacted with further chemical steps to anchor nanoparticles and DNA molecules.

2.10 Automated Scanning Probe Lithography

Computer automation can precisely and accurately control the tip position, speed, bias voltage, and fabrication force. All of the SPL strategies presented in Table 2.1 can be coupled with computer automation to enable fabrication of complex patterns. Automated nanografting of SAMs was accomplished with computer assisted design (CAD) software using an open-loop AFM scanner. However, nanoscale imperfections in writing were introduced by creep and drift of the piezoscanner electronics. Also, artifacts may be introduced by the twisting motion of the cantilever under force. Closed-loop AFM controllers which incorporate a secondary sensor to correct for scanner non-linearities provide better alignment and precision for patterning larger sized areas (micron) of surfaces. Writing individual patterns is not practical as a strategy for manufacturing devices, in which millions of structures may be needed for a single memory chip or circuit design. The serial nature of SPL is problematic for future applications, which will
require high throughput and speed. This problem has been addressed by creating arrays of multiple probes for parallel writing and by increasing the speed of writing processes.\textsuperscript{262}

Parallel writing using DPN has been accomplished with 2-D arrays of cantilevers. Probe arrays with 2,\textsuperscript{263} 8,\textsuperscript{264} 10,\textsuperscript{265-268} 26,\textsuperscript{141} 32,\textsuperscript{264} and 55,000\textsuperscript{269} AFM tips have been successfully applied for DPN. The individual probes of the arrays are spaced at intervals ranging from 30 to 310 microns. For the 2-D arrays, all of the tips can be moved in unison to draw identical patterns, while only one of the probes is used for positional feedback by the AFM controller. Alternatively, 2-D arrays have been designed to activate each of the individual probes through various strategies for positional feedback. Probe arrays which use electrostatic actuation,\textsuperscript{268} conductivity-based sensing of surface contact\textsuperscript{265} and thermal bimorph actuation\textsuperscript{266-267} have been developed for parallel writing with DPN. An optical micrograph of a probe array of cantilevers is presented in Figure 2.19. For this example, the tips touch the surface through gravity-driven alignment under the weight of the whole array.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure219.png}
\caption{Section of a 55,000 probe array used for parallel DPN. (Reprinted with permission from Ref.\textsuperscript{269}, K. Salaita \textit{et al.}, \textit{Angew. Chem. Int. Ed.} \textbf{45}, 7220 (2007). Copyright\textsuperscript{©} John Wiley \& Sons, Inc.)}
\end{figure}
Several design strategies have been tested for AFM imaging which provide activation of individual probes within the 2-D arrays. Parallel imaging was demonstrated with a microfabricated 4 × 4 array of cantilevers with integrated piezoresistive sensors.\textsuperscript{270} High speed (4 mm/s) imaging was achieved with an array of 50 cantilevers spaced at 200 µm pitch.\textsuperscript{262} The design integrated a piezoresistive sensor and zinc oxide actuator for each cantilever to enable individual control of the set point, gain and feedback for imaging.\textsuperscript{271} Thermal actuation of individual cantilevers was demonstrated with an array of 128 probes for parallel AFM imaging.\textsuperscript{272} The cantilevers were driven to vibrate by thermal actuation at the probe resonance frequency, and the magnitude of the current established the cantilever deflection.

A 32 × 32 “Millipede” array with 1024 AFM tips was constructed by IBM corporation, and is envisioned for applications for data storage media.\textsuperscript{273} The platform design uses thermal sensing for read/write operations of the array. The 2-D array of probes has an approximate size of 3 x 3 mm and was fabricated entirely of silicon. The Millipede concept does not enable individual control of each cantilever, rather feedback is provided by three sensors for the entire chip.

2.11 Summary and Future Prospectus

The examples of SPL described in this chapter are based on writing mechanisms using force, elevated bias, electrochemistry, diffusion and surface adsorption, catalytic reactions and photochemistry with SAMs. Depending on the nature of the molecules chosen for nanolithography, we predict that further innovations for writing strategies will be advanced in future research. Besides the commercial goals of nanotechnology, SPL methods are becoming an indispensable approach for fundamental investigations of the interrelations between chemical structure and properties. Surface structures of SAMs furnish test platforms for size-dependent studies of physical properties. Writing with SAMs provides a way to tune the properties of
surfaces for specific applications, e.g. hydrophobicity, surface pKa, reactivity, etc. Surfaces can be designed to anchor materials such as DNA, proteins, polymers, metals, organic molecules and polymers for bottom-up assembly of nanomaterials.

Scanning probe lithography provides an efficient and versatile tool for fabrication or local modification of SAMs on surfaces and enables precise spatial control over chemical functionality, shape, dimension and spacing at the level of nanometers. Combining molecular self-assembly and scanning probe lithography is a viable route towards nanotechnology. Although perhaps SPL is not yet practical for high-throughput manufacturing, substantial progress has been advanced. One can anticipate that there will be future significant contributions for biotechnology, molecular electronics, engineered materials, and chemical/biochemical sensors.
CHAPTER 3. AUTOMATED SCANNING PROBE LITHOGRAPHY WITH n-ALKANETHIOL SELF ASSEMBLED MONOLAYERS ON Au(111): APPLICATION FOR TEACHING UNDERGRADUATE LABORATORIES*

3.1 Introduction

Since the invention of atomic force microscopy (AFM) in 1986, \(^{274-275}\) scanning probe methods for imaging and nanolithography have become increasingly valuable as tools for basic and applied research. Advances in computer software and hardware, as well as continued improvements of instrument designs have progressively improved the ease-of-use for scanning probe microscopes (SPM). Scanning probe instruments can be operated in a range of environments (UHV, air, liquids) and can measure current, magnetic forces, surface charge, friction, electrostatic forces, etc. with nanoscale sensitivity. The imaging and measurement capabilities of scanning probe microscope have been introduced for undergraduate laboratories in several disciplines including chemistry laboratories. However, the capabilities of SPM for nanolithography have not been as widely applied for undergraduate teaching. New trends in software and improvements in the automation of SPM instruments hold promise for bringing nanoscale experiments into the undergraduate curriculum, and eventually may even be integrated into high school science labs. Optical microscopes have become common in educational labs for a wide range of science disciplines, and the next generation of young scientists will benefit from gaining skills with SPM instruments. To advance beyond the resolution limits of optical microscopes, SPM enables direct views, measurements and manipulation of nanoscale phenomena.

A diverse range of experiments can be planned for educational lab exercises using SPM instruments, which have dozens of different measurement modes and instrument configurations integrated within a single instrument platform. The instruments are inherently a multidisciplinary

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toolkit because nanoscience measurements extend across all of the science disciplines of physics, chemistry, materials science, biology, medicine, and engineering. For example, college laboratory exercises have been developed to illustrate principles of nanoscale measurements for magnetic, electronic, adhesive or frictional forces. A basic example would be to illustrate force-displacement profiles and calculations to demonstrate molecular bond rupture events by developing experiments using AFM probes with molecular coatings. Other lab exercises could illustrate the imaging capabilities of AFM or scanning tunneling microscopy (STM), particularly for resolving atomic or molecular lattices. Educational lab exercises with SPM have been reported for imaging surface changes caused by chemical reactions, nanopatterning, and studies with biomolecules. Student experiments with SPM provide 2D and 3D surface maps for illustrating the analysis of data such as height histograms, roughness measurements and digital image processing. Students obtain hands-on experience with molecules and nanoscience, and there are also intangible benefits of the “wow” factor for stimulating intellectual curiosity and enthusiasm for scientific discovery. Examples of SPM systems designed for college laboratories include instruments from NanoInk such as the NanoProfessor, and the model 5400 system from Agilent. These systems were designed with intuitive software and ease-of-use for installing probes and samples. Most of the laboratory time is occupied with the use of software interfaces, which minimizes possible damage to the scanners. Meanwhile, SPM probes are relatively inexpensive to replace, as a consumable item. Students can learn to tune in “slow TV” as the images are gradually generated on the computer monitor to reveal exquisite details of molecularly-resolved surface landscapes.

Along with the unprecedented advantages for imaging and measurements of surfaces, a further compelling attribute of SPM instruments for educational activities are the capabilities for nanoscale manipulation of molecules and nanomaterials using scanning probe lithography (SPL),
as described in this report. Significant advances in instrument automation to provide intuitive, user-friendly software offers exciting new possibilities for integrating cutting-edge technologies into the undergraduate laboratory curriculum.

3.2 Basic Operating Principle of AFM

The most common set-up for positional feedback with AFM is the deflection-type configuration illustrated in Figure 3.1. An AFM tip is attached directly to a piezoceramic scanner for directing tip movement in the x, y or z direction. The piezoceramic material of the scanner tube expands and contracts upon the application of small voltages causing movement at the level of angstroms. An electronic feedback circuit is used to control the amount of force applied between the tip and sample by adjusting the voltages sent to the scanner tube, to maintain a constant deflection of the cantilever.\(^{21}\) The light of a diode laser is reflected off the back of the cantilever and detected by a position sensitive quadrant photodetector, as shown with the red lines of Figure 3.1. The amount of light impinging on the four photodetector elements changes as the tip is scanned across the surface, and the signals are used for positional feedback. As the AFM tip is scanned in a raster pattern, the up-down and left-right motion of the tip is profiled by the photodetector changes, and this signal is amplified and converted into digital images of topography and lateral force. Topographic images are maps of the surface morphology and are represented by an arbitrary color scale. Lateral force images

![Basic instrument configuration for AFM imaging and nanolithography.](image)

**Figure 3.1** Basic instrument configuration for AFM imaging and nanolithography.
indicate variations in the chemical nature of the molecules on the surface, which result from changes in the attractive and repulsive forces experienced by the tip. Topographic and lateral force images are acquired simultaneously. Most importantly, the force applied to an AFM tip can be precisely controlled at the level of nano- to pico- Newtons. Low forces are used when characterizing surfaces to prevent unintentional damage to the sample, whereas higher forces are used for steps of nanofabrication for nanoshaving and nanografting of organic thin films.

A typical set-up for “contact-mode” AFM is presented in Figure 3.1, in which the tip is scanned in continuous contact with the surface. Other protocols can be accomplished by lifting the tip from the surface at a controlled distance for modes of “non-contact” imaging. A further imaging mode known as “intermittent-contact” mode is accomplished with a vibrating tip which intermittently taps the surface, also known as “tapping” mode. Readers are directed to previous publications for further details of SPM imaging modes. Images presented in this article were acquired using continuous contact mode AFM imaging.

3.3 Approaches for AFM-based Nanolithography

Mechanisms for SPM-based nanolithography

As methods for imaging and measurements with SPM were developed, researchers observed that under certain experimental conditions small areas of the surface could be accidentally altered or damaged. For example, when too much force was applied to the probe, the surface could be scratched or rearranged. Contaminants on the surface could be picked up by the tip and redeposited in other locations. Nanoscale lithography methods came to be developed by carefully controlling the changes that were made to surfaces, to selectively and intentionally change the chemistry of small areas under the tip. Bias-induced nanolithography, dip-pen nanolithography (DPN), catalytic-probe lithography, nanoshaving, nanografting and NanoPen Reader and Writer (NPRW) are examples of SPL which have different mechanisms for writing
nanopatterns. The nature of the desired changes in surface chemistry will help determine which nanolithography methods are most suitable and convenient for experiments.

A summary of different techniques for writing nanopatterns using SPM-based lithography is presented in Table 3.1. Very little modification of AFM instruments are needed to accomplish nanolithography. Methods of nanoshaving, nanografting and NPRW require controlling the force applied to an AFM probe to inscribe patterns within self-assembled monolayers (SAMs). For DPN, the tip is coated with molecules or nanomaterials to be written. The writing of molecules on surfaces is accomplished by transfer from the tip through a liquid meniscus to a clean substrate. For catalytic probe lithography, an AFM tip is coated with catalyst molecules or metals. The coating is not transferred to the surface, instead the catalyst coating of the probe is used to catalyze a chemical reaction and selectively alter the chemistry of areas where the tip is placed in contact with the surface. The catalytic reaction only occurs at areas touched by the tip. Bias-induced lithography is achieved using a conductive tip with a conductive or semi-conductive substrate, in which an electric field is generated between the tip and the sample. As the AFM tip is scanned in contact with the surface at elevated

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bias, molecules are either oxidized, desorbed or replaced to create nanopatterns. \textsuperscript{122,198,200} Details of strategies and mechanisms for patterning with SPL have previously been reviewed. \textsuperscript{34,138,197,203,300,302,305-307}

3.4 Experimental Approach

3.4.1 Materials and Chemicals

Reagent grade dodecanethiol, octadecanethiol, 11-mercaptoundecanol (MUD), and 16-mercaptohexadecanoic acid (MHA) were obtained from Sigma Aldrich (St. Louis, MO, USA) and used without further purification. Ethanol (200 proof) was purchased from AAper Alcohol and Chemical Co. (Shelbyville, KY, USA). Flame-annealed ultra flat films of Au(111) prepared on mica substrates were obtained from Agilent Technologies, Inc. (Tempe, Arizona, USA).

3.4.2 Preparation of Self-assembled Monolayers (SAMs)

Because of the ease of preparation, stability and reproducibility for preparing well-ordered surface structures, SAMs of \textit{n}-alkanethiols are good models for nanolithography experiments. Monolayer films of defined thickness and designed properties can be generated by changing the functional (head) groups of the alkyl chain; these functional groups can also be used for further chemical reactions in later chemical steps. The preparation, characterization, and properties of SAMs have been described and reviewed previously.\textsuperscript{36,46,52-53} Samples of matrix monolayer films were prepared by immersing gold substrates in 0.01 mM ethanolic solutions of the chosen \textit{n}-alkanethiols for at least 12 hours. The samples were then removed from the thiol solution, rinsed copiously with fresh ethanol and placed into a liquid cell holder for AFM imaging and lithography. Ethanol solutions of MHA (10\textsuperscript{-9} M) and MUD (10\textsuperscript{-6} M) were freshly prepared for nanografting protocols.

3.4.3 Scanning Probe Microscopy (SPM)

Experiments were accomplished in solution using either an Agilent 5500 SPM system or
an RHK system interfaced with a PicoSPM scan head. The Agilent system was equipped with PicoScan version 5.3.3 software and PicoLITH beta v.0.6.0 for nanolithography. Images were acquired at a scan rate of 3.0 nm/s using 512 lines/frame. The RHK system was operated with XPMPPro v1.1.0.9 software using SPM100 controllers. Oxide sharpened V-shaped silicon nitride probes from Veeco Probes (MSCT-AUHW, Santa Barbara, CA) were used for imaging and nanofabrication. The probes have an average force constant of 0.5 N/m. Image processing was accomplished using either Gwyddion software, version 2.5, which is freely available for download and is supported by Czech Metrology Institute or with PicoScan version 5.3.3 from Agilent.

3.5 Results and Discussions

3.5.1 Creating Patterns Within a SAM Matrix Using Nanoshaving

Nanoshaving describes AFM-based methods of nanofabrication in which the tip is operated under force to uncover or scratch away selected regions of substrates that are covered with a matrix layer of an organic thin film. Nanoshaving can be accomplished in air or in liquid media. In air, the molecules that are displaced tend to accumulate at the edges of nanopatterns, whereas in liquid the displaced molecules can be dissolved in the surrounding solvent. Imaging in liquids has the advantage of improving resolution, since strong shear forces and tip-surface attraction caused by capillary forces in air are greatly decreased when imaging in liquids. Nanoshaving is accomplished by applying a high mechanical force to an AFM tip as it is raster scanned across the surface to sweep away molecules of the surface layer as shown in Figure 3.2.

The process of nanoshaving is completed in three basic steps. First, a flat area of the surface is identified and imaged under low force (Figure 3.2A). For the characterization step, typically forces less than 1 nN are applied to the probe to enable high resolution characterization of the topography without damaging the sample surface. An area with few defects is chosen for
Figure 3.2 Basic steps for nanoshaving with an AFM tip operated under different forces. [A] Characterization under low force. [B] Nanoshaving is accomplished when the force is increased. [C] Returning to low force, the nanoshaved patterns can be imaged.

inscribing patterns, preferentially a flat gold plateau which is wide enough to write the desired pattern sizes. Next, a greater force ranging from 1–10 nN is applied to the AFM tip to shave away the matrix molecules from the substrate as it is scanned with a pattern design (Figure 3.2B). A sufficient amount of force is needed to ensure complete removal of the matrix SAMs without damaging the underlying gold substrate. After molecules are shaved away, the same AFM probe is used for imaging the newly fabricated patterns by returning to a low force (Figure 3.2C). With careful control of the forces applied to the tip, hundreds of patterns can be fabricated within a few hours of an experiment. The uncovered regions created from nanoshaving are then available for deposition of new molecules and materials. Nanoshaving has also been used to provide information about the thickness of molecular layers on surfaces. The uncovered areas of the substrate provide a baseline for thickness measurements of SAMs with angstrom precision.

3.5.2 Automated Nanolithography Using Designs Created with Picolith Software

Computer automation of scanning probe instruments enables the rapid fabrication of complex patterns with intricate designs and arrangements at the nanoscale to be a relatively routine accomplishment. Patterns with nanometer dimensions can be readily achieved with
precision and accuracy using software that controls the position, force, bias and speed of the probe. Example designs used for creating nanopatterns are shown in Figure 3.3 using PicoLITH software from Agilent. Automated nanoshaving is more complicated than producing images for a computer printer, since the user must consider where the tip is picked up or placed down on the surface. When the tip is picked up and placed down this can lead to gaps or stray marks for designs. Better fidelity is achieved when the tip is moved continuously across the surface without removing the tip. The analyst will need to experiment with different designs to determine how many times to outline the features to observe which scanning paths work best for sweeping material from the surface. Sketches of the desired patterns are outlined with PicoLITH scripts using a computer mouse or pen stylus to draw the patterns. For the examples in Figure 3.3, arrows indicate the writing direction for translating the AFM tip. The overall size of the patterns is defined by the size of the view window selected within the data acquisition window of the PicoSPM operating software, e.g. 1×1 μm². Patterns can be outlined once or traced several times. The colored squares at the bottom of the PicoLITH design (Figure 3.3) are the scientific pallets that can be used to assign specific parameters for operating the probe. For example, experimental parameters for the speed, amount of force or bias voltage applied to an AFM tip are assigned by choosing a color and assigning values. Automated lithography with an RHK SPM is accomplished with a computer controlled vector scan module as previously described by Cruchon-Dupeyrat, et al.⁴ Computer statements to control the motion of the probe are written and compiled into lithography scripts to designate the writing speed, length, direction and force applied for inscribing nanopatterns.

3.5.3 Writing Patterns of Self-assembled Monolayers with Nanoshaving

Patterns for the designs of Figure 3.3 with different shapes and geometries written are shown in Figure 3.4, for nanoshaving within a matrix SAM of n-octadecanethiol.
Octadecanethiol has 18 carbons aligned in a chain as the backbone of the molecule, and is anchored to the surface by a single gold-sulfur bond. The headgroups at the surface of the molecular layer are methyl groups (CH$_3$), and the overall thickness of the SAM film is approximately 2.1 nanometers. Topography images acquired with AFM are displayed by a selected color scale; in this report the shorter features are dark and taller structures are brighter in color. Nanoshaving was accomplished in ethanol by applying a high force to the AFM tip as it was scanned, to sweep away and remove selected areas of the matrix monolayer from the gold surface following the outline of the designs shown in Figure 3.3. After writing patterns, the same AFM probe was used to immediately characterize the patterns in situ. The images in Figure 3.4 reveal intricate details of the surface morphology of octadecanethiol as directly viewed by nanosize defects such as scratches, scars, pinholes and etch pits. Overlapping terrace steps and the outlines of the gold substrates underlying the SAM are also visible in the images. Although the surface may appear somewhat rough, the terrace steps are only 0.25 nm in height and are characteristic landmarks of a high-resolution image of a SAM. At the nanoscale, even very small features such as etch pits, which are only 0.2 nm deep can be resolved using AFM. The small
Figure 3.4 Nanoshaved patterns created with the designs of Figure 3 within a matrix monolayer of octadecanethiol on a gold substrate. [A] AFM topography view of six stick figures and the corresponding trace and retrace lateral force images (from left-to-right). [B] Topography and lateral force images of the cat cartoon patterns produced with nanoshaving. [C] Topography and lateral force images of an array of ring nanopatterns.

Holes scattered over the surface are commonly called etch pits, (also known as molecular vacancy islands) which are produced by surface reconstruction. The fine details of the irregular contours of the edges of the gold terraces can only be observed with a sharp tip. Such high-
resolution images can be routinely acquired by using AFM in liquid environments.

Figure 3.4A displays images of six stick people inscribed within octadecanethiol using nanoshaving. The images and nanopatterns were produced by undergraduate students during a 3 hour laboratory session of Physical Chemistry (Chem 3493). The trace and retrace lateral force images do not show height information; rather the changes in tip-surface friction are mapped to disclose variations in surface chemistry for the areas of the nanopatterns. Lateral force images are acquired simultaneously with contact mode topography images and provide additional chemical information of the sample nature. For these examples, the tip-surface adhesion between the AFM tip is markedly different for the uncovered gold substrate of the nanopatterns compared side-by-side with the methyl-terminated molecules of the SAM matrix areas. The patterns of stick people were written using a single pass of the AFM probe to outline the design and were completed in one minute. The linewidth measures approximately 10 nm, and varies according to the sharpness of the AFM probe.

A more sophisticated pattern was nanoshaved (Figure 3.4B) to outline a cartoon of a cat design. This example was accomplished within 3 minutes using a writing speed of 0.1 μm/s and an applied force of 2 nN. The speeds used for nanoshaving are comparable to the optimized speeds for acquiring images; of course if the tip is rastered too quickly it can break contact with the surface to produce discontinuous patterns. One might be concerned that operating an AFM tip under force might cause it to become dull or break the apex of the probe, however this example exhibits superb resolution for resolving etch pits, pin hole defects and the lacey contours of step edges, despite having used the tip under force for nanoshaving. We have found that silicon nitride probes are quite robust within the typical operating range of 2–10 nN of force used for SPL. Often the tip becomes sharper and resolution improves over time when nanoshaving. The patterns of Figure 3.4B were traced once and measure 7 nm in linewidth.
Using nanoshaving, 25 ring patterns were inscribed within an octadecanethiol SAM (Figure 3.4C), however for this example the designs were outlined four times. A force of 2 nN was applied for nanoshaving to produce rings measuring 80 nm in diameter with widths of 18 nm. Scanner hysteresis and drift can produce small changes in the nanoscale registry of the pattern arrangements, as viewed for the misalignment along the x direction. This is likely caused by using too much force to write the patterns, leading to a slight drift in probe motion across the array of ring designs. However, the precision for writing rows of patterns in the y direction is near perfect, with uniform 100 nm spacing between each ring in the x and y directions.

3.5.4 Automated SPL Using Computer Scripts

Examples of sixteen nanoshaved patterns of interconnected circles created within octadecanethiol are presented in Figure 3.5, generated with an in-house designed computer script with an RHK controller. The exquisite reproducibility for controlling nanoscale lithography is evidenced by the precise, regular shapes and interpattern spacing and alignment at the nanoscale. The topography frame of Figure 3.5A shows a 1.2 × 1.2 μm² view of the nanopatterns and the corresponding design is sketched in Figure 3.5B. The design of each pattern was produced by outlining four circles with a common focal point. The rings are shallower than the surrounding monolayer of octadecanethiol. Each individual ring measures 60 nm in diameter, with the smallest line width measuring approximately 10 nm. A few stray marks are apparent above the patterns, which results from up-down translation of the tip when it is picked up or placed at locations for writing. For this example, the scars of the underlying gold film influence the brightness of the image color scale, since the nanoshaved patterns are shallower in depth (2.1 nm) than the defects of the substrate (10 nm). However, the fidelity of nanoshaving for writing precise nanoscale designs can still be sufficiently well resolved at this size scale.
**Figure 3.5** Example nanopatterns produced by nanoshaving selected regions of octadecanethiol using an SPM instrument from RHK Technologies. [A] Contact mode topograph; [B] sketch for the corresponding patterns in A.

### 3.5.5 Using Nanografting to Write Designed Patterns of *n*-Alkanethiols

Nanografting is likewise accomplished by increasing the force applied to an AFM probe;
however, instead of operating the tip in clean solvent, the imaging media was replaced with a freshly prepared, dilute solution of \( n \)-alkanethiols to be patterned. Nanografting was developed in 1999 by Xu, et al. and since then has been used for writing a range of molecules with thiol groups.\(^{93,302}\) Similar to nanoshaving, there are three basic steps for nanografting as outlined in Figure 3.6. In the first characterization step, a flat area that has few defects is selected for inscribing patterns by imaging under low force, typically less than 1 nN (Figure 3.6A). Next, the force is increased to push through the surface monolayer to make contact with the gold surface underneath. As the tip is scanned under force, the matrix molecules underneath the tip are shaved away and immediately replaced with new molecules from the surrounding solution (Figure 3.6B). Following the scanning path of the AFM tip, molecules assemble and bind to the areas of gold that were uncovered by the probe to produce designed patterns. Returning to low force (Figure 3.6C) the same probe is used to characterize the nanopatterns that were fabricated. When the tip is operated under low force the surface is not disturbed and no patterns are formed. Patterns are produced only when the force has been increased.

![Figure 3.6](image)

**Figure 3.6** Steps for nanografting are accomplished by scanning with a tip under high force, while the tip is immersed in a solution containing molecules to be written. [A] Surface characterization is accomplished under low force while imaging in a solution containing thiol molecules. [B] Nanografting is accomplished by increasing the force applied to the AFM tip; fresh molecules from solution assemble following the path of the scanning probe. [C] Returning to low force, the nanografted patterns can be imaged.
When designing nanografting protocols, the analyst can choose from a range of commercially available thiol molecules with different lengths and head group chemistries. Examples are shown in Figure 3.7 of nanografted patterns with heights that are shorter than the matrix monolayer. The topography and corresponding lateral force images of the design for an AFM instrument schematic are presented in Figures 3.7A and 3.7B, respectively. The instrument components were described previously in Figure 3.1. Characteristics of the general morphology of an $n$-alkanethiol SAM are apparent in the topography frame, such as etch pits and terrace steps. The lateral force image more prominently reveals the pattern design, because the
Figure 3.8 Nanografted patterns of 16-mercaptohexadecanoic acid written within a SAM of dodecanethiol. [A] Topography image (1.2×1.2 µm²) of an array of ring patterns; [B] corresponding lateral force image; [C] height profile for the line in A; [D] topograph of a rectangular pattern (2.5×2.5 µm²); [E] lateral force image for D; [F] line profile across the pattern in D; [G] height model for the nanografted pattern of A; [H] model of the double-layer pattern of D.

headgroups of the pattern areas are chemically different than the matrix SAM which provides frictional contrast. The areas surrounding the pattern are methyl-terminated octadecanethiol and the patterns were written with hydroxyl-terminated 11-mercaptoundecanol, which is 0.6 nm shorter than the matrix SAM. A model of the molecular heights is shown in Figure 3.7C. The
script used to outline the nanopatterns is shown in Figure 3.7D, with excellent correspondence between the design and resulting nanografted patterns for such small size scales. The smallest linewidth achieved for this pattern was accomplished with a single sweep for the vertical line between the backside of the cantilever and the diode laser, measuring 13 nm in width. With an ultra sharp AFM probe, the smallest feature produced with nanografting is an island of a 2×4 nm² dot pattern, which is an area that would accommodate approximately 32 thiol molecules. Examples of nanografted patterns with heights that are taller than the matrix monolayer are shown in Figure 3.8. Interestingly, the same molecules were used for Figures 3.8A and 3.8D, however the concentration of the imaging media was increased for Figure 3.8D. The topography and corresponding lateral force images of an array of ring patterns shown for the design of Figure 3.3 are presented in Figures 3.8A and 3.8B, respectively. At low concentration, (10⁻⁹ M) 16-mercaptophexadecanoic acid (MHA) forms patterns with heights corresponding to a monolayer.

For these examples, the matrix monolayer is dodecanethiol, which has 12 carbons in the hydrocarbon backbone chain. Dodecanethiol is ~0.5 nm shorter than MHA, which is consistent with the height measured for a line profile across one of the nanopatterns (Figure 3.8C). When the concentration of the imaging media of MHA was increased to 10⁻⁶ M, molecules with carboxylic acid-terminated headgroups form dimers and assemble to generate double layers (Figure 3.8D). Dimers of MHA are produced in solution by coupling of the acid headgroups. Height models of the MHA nanopatterns are shown in Figures 3.8G and 3.8H for the single and double layer patterns, respectively. The acid headgroups of the nanopatterns exhibit strong tip-surface adhesion, producing line spike artifacts in the topography frames. The differences in surface chemistry between the nanografted patterns (carboxylic acid headgroups) and the dodecanethiol matrix SAM (methyl headgroups) provide excellent contrast for the lateral
force image of Figure 3.8B. However, for the lateral force image of Figure 3.8E, the headgroups of the rectangular pattern are most likely terminated with a thiol endgroup.

These examples of nanografted patterns illustrate the inherent capabilities of SPL for 3-dimensional control of nanostructures by selecting the molecular length, headgroups, and pattern geometries. Nanoscale characterizations and lithography are valuable tools for directly studying surface chemical reactions at the nanoscale within a well-controlled, liquid environment. After producing nanopatterns with nanoshaving or nanografting, further chemical reaction steps can be accomplished by exchanging the imaging media, for example by introducing solutions of new molecules,\textsuperscript{19} copper salts\textsuperscript{96} or proteins\textsuperscript{116,312} to build complicated architectures from the bottom-up.

3.6 Applications of Scanning Probe Nanolithography

Scanning probe lithography approaches such as nanoshaving and nanografting with organic thin films extend beyond simple fabrication of nanopatterns to enable control of surface composition and reactivity at the nanoscale. Methods to precisely arrange molecules on surfaces already contribute to discoveries that are advancing future technologies in molecular electronics, nanomedicine and surface chemistry. Automation of SPL will likely have a significant role for implementing nanotechnology in commercial products.

3.6.1 Impact of SPL for Advancements in Molecular Electronics

Writing individual patterns of organic films one at a time will not be a practical strategy for manufacturing devices in which billions of structures are needed, such as for designs of computer memory chips and circuits. Future nanotechnology applications will require much higher throughput and speed for generating patterns. This problem is being addressed by the development of arrays of multiple probes for parallel writing.\textsuperscript{269,273} For semiconductor-based technologies, organosilane thin films are widely used as resist layers for microfabrication of
circuits, wires, transistors and memory chips. As the size of components achieves ever smaller dimensions, the inherent advantages for miniaturizing to the nanometer level will be the benefits of higher information density and faster processing time. Nanotechnology holds promise for advantages of smaller, cheaper and more energy efficient electronic devices. To achieve smaller elements will require molecular-level precision such as the capabilities provided by automated SPL.

3.6.2 Application of SPL for Nanomedicine

Nanoscale assays provide intriguing possibilities for the direct detection and \textit{in situ} visualization of the binding of small molecules, DNA, antibodies or proteins to nanopatterns, while enabling surface changes to be monitored with time-lapse AFM images.\textsuperscript{301-302} Nanostructures of SAMs written by SPL provide highly controllable test environments for exquisite images of surface changes during biochemical reactions.\textsuperscript{313} Although electron microscopies can be used for high-resolution 2D imaging of biomolecules that have been freeze-dried and sputter-coated with conductive films, reactions conducted in aqueous (physiological) media or buffers cannot be accomplished in the UHV environments of electron microscope chambers. Approaches with SPM provide 3D images of fragile biomolecule systems and cells with minimal sample preparation. Tools of SPL extend the capabilities of high-resolution scanning probe imaging to enable experimentalists to control surface arrangements of biomolecules at the molecular level. Examples of fundamental studies incorporating tools of SPL for investigations of biomolecules include the regulation and control of multiplexing, reactivity, and polyvalent interactions; nanoscale assays with oligonucleotides\textsuperscript{98} or receptors for sensing or bioassays;\textsuperscript{314-315} as well as construction of DNA\textsuperscript{97,316-318} and protein\textsuperscript{116,312} nanostructures.

3.6.3 Role of SPL for Fundamental Investigations of Surface Chemistry

Intuitively, binding between molecules is a nanometer-sized phenomenon, thus a close-up
view of molecules on surfaces can provide a fresh perspective for mechanisms of how reactions occur. Nanografted patterns can be incubated with desired nanomaterials or molecules, and time-lapse AFM provides direct views to monitor the successive changes in height and surface morphology as reactions proceed over time. The reaction sites are spatially constrained to nanosized areas defined by the headgroups of nanografted/nanoshaved patterns, providing exquisite control of reaction parameters at the nanoscale. Such studies provide insight about surface reaction mechanisms and kinetics. For example, in situ investigations with nanografting have been reported for adsorption of proteins\textsuperscript{114,118,124-125} electroless deposition of copper on nanografted SAMs,\textsuperscript{96} templated growth of ionic self-assembled multilayers,\textsuperscript{319} and pattern transfer reactions with polymers.\textsuperscript{19}

3.7 Underlying Themes for Undergraduate Instruction

The take-home message from a scanning probe lab exercise would perhaps be that we “looked at molecules” and learned how to write nanopatterns on surfaces. The existence of atoms or molecules in materials is a critical concept for understanding chemistry and physics, along with calculations of the size and number of molecules/atoms that are present. Many students have difficulties in understanding concepts of atomic and molecular scale phenomena, and the challenge of visualizing the shapes and arrangements of atoms and molecules has been implicated as a core issue.\textsuperscript{287} Scanning probe experiments offer premiere opportunities for students to learn interactively to visualize surfaces, measure properties and to manipulate surface chemistry at resolutions down to molecular and atomic length scales. Advancements in software and automation have made scanning probe instruments relatively easy to operate, and the new capabilities are ideally suited for undergraduate laboratories. As the field of nanoscience research has evolved, SPM methods have mostly been limited to professional researchers and graduate students; however, there is increasing interest for advancing nanoscience education at the
undergraduate level. Our practical strategy at LSU has been to accomplish undergraduate teaching activities using our research instruments, with the slight expense of a few broken probes.

The background information to be presented for SPM laboratories will depend on the timeframe and type of experiments that are designed. A complete grasp of nanoscale concepts most likely exceeds the scope of an undergraduate course. However, a basic introduction and illustration of selected topics of nanoscience can certainly be accomplished to provide a spark for future student interest. During the past four years at LSU, we have successfully integrated SPM modules into the third-year undergraduate physical chemistry lab course. During each semester, 12–16 students are given an opportunity for hands-on experiments with AFM/STM instruments. One session is devoted to an introduction of the basic principles of nanoscale imaging and instrument operation, and a second session is used for nanolithography experiments. As an indicator of the level of student enthusiasm, the afternoon class is scheduled for 3 hours duration, but usually several students persist late into the evening to capture additional frames and to experiment with designs for writing nanopatterns (Figure 3.9). From these classroom groups, 30

![Figure 3.9](image)

**Figure 3.9** Undergraduate students from an LSU physical chemistry laboratory engaged in learning new skills with an AFM instrument.

undergraduates have further elected to take additional hours of supervised research credit, choosing to work with projects using SPM. The undergraduates have all made contributions as
co-authors of research posters and/or journal articles, and have participated in fundamental studies with systems of nanoparticles, proteins or self-assembled monolayers.

3.8 Future Prospectus

Impressive accomplishments have been attained by manufacturers of scanning probe instruments for the automation of SPL and for providing user-friendly software for routinely imaging at the nanoscale, as evidenced by the nanofabrication examples of this report. One can easily predict that such capabilities will become ever more widely applied in education, research and technology in the near future. There is an emerging need for workers with scanning probe skills, since methods of SPM and SPL are becoming indispensable for fundamental investigations related to nanotechnology. Data published on the National Nanotechnology website (www.nni.gov) estimates that 20,000 researchers are currently working in nanotechnology worldwide, and the National Science Foundation has estimated that 2 million workers will be needed to support nanotechnology industries globally within 15 years.321

A skilled scientific workforce will be an essential requirement for implementing nanoscience discoveries in future manufacturing or technology applications. Knowledge and experience in modern methods of surface measurements and analysis will be pivotal to the rapid transfer of nanotechnology into commercial products. At present, scanning probe microscopes and scanning probe-based lithography are primarily used for laboratory research investigations rather than as tools for manufacturing. The transfer of new technologies developed in academic research labs to the public sector will require dissemination of skills and information from cutting-edge nanoscience research to the undergraduate curriculum across scientific disciplines. The latest advances in automation of SPM instruments enable new possibilities for educational modules using SPL, providing opportunities for designing diverse and compelling student activities to teach the concepts of chemistry and nanoscience, showcased at the molecular level.
CHAPTER 4. SURFACE ASSEMBLY OF PYRIDYL-SUBSTITUTED PORPHYRINS ON Au(111) INVESTIGATED IN SITU USING SCANNING PROBE LITHOGRAPHY*

4.1 Introduction

Porphyrin and metalloporphyrin systems are excellent materials for molecular electronics due to their diverse structural motifs, associated electrical, optical and chemical properties, and thermal stability.\textsuperscript{322} Structures of porphyrins have been proposed as components for molecule-based information-storage devices,\textsuperscript{323-324} photovoltaic cells,\textsuperscript{325-326} organic light-emitting diodes,\textsuperscript{327-328} and molecular wires.\textsuperscript{329} The function and efficiency of porphyrins in devices is largely attributable to how the molecules are organized on surfaces.\textsuperscript{43,330-331} The surface assembly of porphyrins is influenced by complex intermolecular interactions between the macrocycles as well as by the binding interactions between the surface and peripheral groups. There is a problem with processability for producing monolayer films of porphyrins on surfaces, because at high concentrations the pi-pi interactions between macrocycles tend to produce aggregate structures in solution such as nanocrystals or stacked arrangements. In previous reports, porphyrins have been shown to form a coplanar arrangement on surfaces, usually exhibiting low-density, incomplete surface coverage.\textsuperscript{332-338} The conditions which produce liquid crystals of porphyrins are not well-suited for producing monolayer films on surfaces. A problem of solubility in certain solvents is posed for nanofabrication protocols, which can be addressed by using mixed solvent systems.

In this report, nanografting was applied for patterning pyridyl-functionalized porphyrins. A model porphyrin functionalized with two pyridyl and two phenyl groups was chosen for nanofabrication studies. Patterns of 5,10-diphenyl-15,20-di-pyridin-4-y1-porphyrin (DPP) were nanografted within \textit{n}-alkanethiol self-assembled monolayers (SAMs) on gold substrates. Our

\*Reproduced with permission from Society of Photo Optical Instrumentation Engineers (SPIE).
goal was to direct the surface orientation of DPP to generate single layer nanostructures with an upright configuration. We hypothesized that the mechanism of spatial confinement that occurs when nanografting in ethanolic solutions would generate an upright configuration of DPP, rather than produce stacks of multilayered structures with coplanar arrangements. Pyridyl groups provide a means to attach porphyrins to the substrate mediated by nitrogen-gold chemisorption. Nanostructures of DPP fabricated using nanografting can be compared side-by-side with the well-known dimensions of $n$-alkanethiol SAMs to gain molecular-level views of the surface orientation of DPP. The well known heights of $n$-alkanethiol SAMs as a surface matrix layer provide a molecular ruler for local measurements of the thickness of DPP nanopatterns.

Nanografting was introduced in 1997 by Xu and Liu for fabricating patterns of thiolated molecules on gold surfaces. With nanografting, a mechanical force is applied to the tip of an atomic force microscope (AFM) to write thiolated molecules directly in an upright orientation, and surface attachment occurs through sulfur-gold chemisorption. Nanografting is accomplished in dilute solutions of molecules selected for patterning and has been used with a broad range of thiolated molecules such as alkanethiols and alkanedithiols. Nanostructures of SAMs produced using nanografting can then be used as a foundation for bottom-up assembly of complex nanostructures of polymers, metals, and proteins. Nanografting was also used to study the assembly mechanism of $n$-alkanethiol SAMs in a spatially confined environment. Significant advantages for in situ investigations have been achieved with nanografting since the steps of characterization and writing are accomplished in liquid media without exchanging AFM tips. Since experiments are conducted in liquid media, tremendous resolution can be achieved for AFM images because the strong capillary interactions between the AFM probe and sample that are present in ambient air are reduced or eliminated when imaging in a liquid environment. Details of the successive changes in morphology of the surface can be
viewed with high resolution AFM after successive steps of characterization and nanopatterning. With in situ writing, the nanopatterns remain in a carefully controlled environment and solutions within the liquid cell can be exchanged to introduce new reagents for further chemical reactions.

**Figure 4.1.** Structure and possible configurations of 5,10-diphenyl-15,20-di-pyridin-4-yl-porphyrin (DPP) on Au(111).

Diphenyl dipyriddyl porphyrins could form either upright or co-planar orientations, with one or more surface linkages to the surface. Possible configurations of 5,10,15,20-di-pyridin-4-ylporphyrin(DPP) on Au(111) are presented in Figure 4.1. An upright configuration with linkages through two pyridyl rings anchored on the surface is shown in Figure 4.1A, measuring 1.1 nm in height if the molecule is oriented perpendicular to the substrate. If the linkage is through a single pyridyl group, the fully extended molecular height would measure 1.6 nm for a perpendicular orientation (Figure 4.1B). A coplanar orientation would have a height measuring 0.6 nm with the plane of the macrocycle aligned parallel to the surface (Figure 4.1C). The peripheral substituents of phenyl or pyridyl rings are oriented 90 degrees relative to the plane of the porphyrin macrocycle for all three structures.

4.2 Experimental Approach

4.2.1 Materials and Reagents

Matrix thiols such as octadecanethiol (ODT) and decanethiol were obtained from Sigma Aldrich (St. Louis, MO) and used without further purification. Ethanol (200 proof) was obtained from AAper Alcohol and Chemical Co. (Shelbyville, KY) and dichloromethane was purchased
from EMD Chemicals (Gibbstown, NJ). The substrates used for nanolithography were flame-annealed Au(111) film of 150 nm thickness, supported on mica (Agilent Technologies, Phoenix, AZ). Self-assembled monolayers (SAMs) of n-alkanethiols were prepared by immersing gold substrates in a 0.01 mM ethanolic solution of n-alkanethiols for at least 12 h. The SAMs on Au(111) were then copiously rinsed with fresh ethanol and placed in the AFM liquid cell. Stock solutions of porphyrins were prepared by dissolving 5,10-diphenyl-15,20-di-pyridin-4-yl-porphyrin (DPP) in dichloromethane. To prepare a nanografting solution of DPP, the dichloromethane solution was further diluted with absolute ethanol to $10^{-6}$ M.

4.2.2 Atomic Force Microscopy

An Agilent 5500 AFM/SPM system operated in contact-mode was used for AFM characterizations and lithography (Agilent Technologies, Chandler, AZ). Images were acquired at a scan rate of 3.0 nm/s with 512 lines/frame using Picoscan v5.3.3 software. Oxide-sharpened silicon nitride probes (MSCTAUHW) from Veeco (Santa Barbara, CA) were used for AFM experiments. The probes have V-shaped cantilevers and force constant, $k_{avg} = 0.5$ N/m. The same probes were used for both imaging and nanofabrication. Picolith v2.2 was used to design and write patterns for nanografting.

4.2.3 Procedure for Nanografting

Nanografting of DPP was accomplished by applying a local mechanical force to an AFM tip to replace matrix alkanethiols on the gold surface with DPP molecules from solution, following the scanning track of the AFM tip. Nanografting is accomplished \textit{in situ} while the tip and the sample are immersed in a dilute solution of new molecules chosen for writing, with three basic steps as shown in Figure 4.2. In the first step, the surface of a SAM was characterized with minimal force to select a relatively flat area with few defects. A small nondestructive force, typically less than 1 nN was used for the characterization step with contact mode AFM imaging.
Next, the force was increased to 2-5 nN to push the tip through the matrix layer to touch the underlying gold surface. As the tip was raster scanned across the surface under high force, molecules from the substrate were shaved away to leave areas of the gold surface uncovered. Immediately following the path of the tip, DPP molecules from solution attach to the uncovered areas. The area of contact between the AFM tip and substrate is quite small, producing a spatially confined area for surface assembly. In the final step, the force was reduced for AFM imaging to characterize the nanopatterns of DPP \textit{in situ}. For nanografting, the amount of force applied to the tip must be carefully controlled to preserve the sharpness of the AFM probe. The optimized minimal force to successfully write a complete pattern was chosen by writing a series of patterns at different force settings and choosing the minimal force setting which successfully produced a pattern.

4.3 Results and Discussions

The liquid media used for imaging and nanofabrication was a solution of mixed solvents, 1% dichloromethane in ethanol with $10^{-6}$ M DPP. Solvents which evaporate quickly such as dichloromethane or toluene are not suitable for AFM experiments; however solutions of ethanol, sec-butanol and water work well for AFM imaging in liquids. Unfortunately, porphyrins are mostly insoluble in alcohols or aqueous solvents so a two-step protocol was developed with mixed-solvents in which the porphyrin was first dissolved in a chlorinated solvent, then the stock
solutions was subsequently diluted further in ethanol to prepare the liquid media for nanografting.

4.3.1 Nanografting of DPP Within a Decanethiol SAM

Example nanopatterns of DPP produced by nanografting in a decanethiol matrix SAM are shown in Figure 4.3 before and after nanografting. For the AFM topographs, (Figures 4.3A and 4.3D) the heights are displayed with a relative color scale, where taller structures have brighter contrast and shallow features appear darker. As revealed in high resolution images, surfaces are not truly flat and uniform at the nanoscale; rather there are defects such as scratches, scars and pinholes. A selected area of the surface shown in Figures 4.3A and 4.3B shows a staircase arrangement of overlapping terrace steps of a decanethiol covered gold substrate.

![Figure 4.3 Nanografted patterns of DPP produced within a SAM of decanethiol/Au.](image)

- [A] Contact mode AFM topograph of the SAM before nanografting; [B] corresponding lateral force image for A; [C] cursor profile for the line in A. [D] Nanografted line patterns of DPP written in the same area; [E] lateral force image for D; [F] cursor profile for D.
The surface morphology of the SAM exhibits the characteristic features of molecular vacancy islands or etch pits, measuring approximately 0.2 nm in depth. Etch pits result from the displacement of gold atoms during surface reconstruction upon chemisorption of \( n \)-alkanethiols to gold.\textsuperscript{46} Eight overlapping terraces of the gold surface are visible in the selected area. The heights of the terrace steps provide an internal reference for Z calibration with AFM measurements. The simultaneously acquired lateral force image (Figure 4.3B) also defines the edges of overlapping gold steps. A line spike in the middle of the image results from the tip sticking to the surface during the scan. A representative cursor line profile is shown in Figure 4.3C across several gold steps. After nanografting with DPP, topography and lateral force images of the surface are presented in Figures 4.3D and 4.3E, respectively for the same area that was shown in Figure 4.3A. Five vertical line patterns were written within the decanethiol matrix, by programming the direction, force and motion of the AFM tip. The dark lines in Figure 4.3D correspond to areas where DPP molecules were nanografted, revealing a shorter height than the surrounding matrix areas of decanethiol. A force of 2.3 nN was used for nanografting; however the sharpness of AFM probe was retained after writing under force, as evidenced by views of high resolution features characteristic of gold steps and etch pits. The lateral force image (Figure 4.3E) shows brighter contrast for the patterned areas compared to the surrounding matrix indicating that the surface chemistry of the fabricated areas has changed. The expected height of the decanethiol matrix is 1.4 nm. The thickness of DPP patterns are 0.4 ± 0.2 nm shorter than the surrounding decanethiol SAM which indicates that DPP adopts a standing up configuration with two pyridyl linkages to the surface, corresponding to the model of Figure 4.1A.

A map of the path programmed for the AFM tip is shown in Figure 4.4. The patterns were written with automated software using a single pass of the AFM tip across the surface following the direction of the arrows. The array of lines was completed within 1 minute. The
line resolution and pattern fidelity are remarkable, considering that an open loop AFM scanner was used for writing nanopatterns. The line patterns have progressively wider lateral dimensions of 20, 33, 50, 60, and 66 nm (from left to right), with a uniform vertical length of 400 nm.

**Figure 4.4** Computer design used for nanografting line patterns of DPP within a decanethiol matrix

### 4.3.2 Nanografting of DPP Within an Octadecanethiol SAM

Further experiments were accomplished for nanografting DPP in mixed solvent media with a taller matrix SAM of n-octadecanethiol (ODT). A circular pattern filled with DPP was successfully nanografted within an ODT matrix as shown in Figure 4.5. The pattern was written in 2 min using a force of 3.4 nN. The diameter of the filled circle measured 300 nm and the design of the pattern was achieved by outlining 50 concentric rings of successively increasing sizes. The filled circle is mostly sited on a single terrace area of Au(111) except for a small area at the top left corner where it is situated on the next gold step. The trace and retrace lateral force images disclose the pattern edges and changes in surface chemistry for the area patterned with DPP. Bands at the sides of the pattern were introduced artificially during image processing and
are not true changes in heights or frictional force. The expected thickness of an ODT SAM is 2.1 nm, and the DPP nanopattern is approximately $1.0 \pm 0.3$ nm shorter than the ODT matrix (Figure 4.5D). The height closely corresponds to a standing configuration for the nanografted patterns with two pyridyl linkages, as shown in Figure 4.5E.

![Figure 4.5](image)

**Figure 4.5** Circular nanopattern of DPP written within an ODT SAM. [A] contact mode topograph; corresponding [B] trace and [C] retrace lateral force images of the nanopattern; [D] corresponding line profile for A. [E] Height model for patterns of DPP nanografted within an ODT matrix.

During nanografting, the surface assembly of DPP porphyrins most likely follows a similar reaction pathway previously described for alkanethiol SAMs due to spatial confinement. Unlike the zig-zag backbone of alkanethiol molecules, porphyrins have wider overall dimensions which are bulkier for surface assembly within a confined space. It is interesting to note that the heights of nanografted patterns of DPP match closely with the height expected for a perpendicular configuration with respect to the surface. It is likely that the
rotated orientation of the phenyl and pyridyl groups relative to the macrocycle provides a block-like geometry which stabilizes the upright orientation and serves to prevent a tilted arrangement. Under conditions of nanografting the transient reaction environment confined between the scanning AFM tip and surrounding matrix SAM is sufficiently small to prevent DPP molecules from assembling in a coplanar, lying-down orientation. When nanografting, a small local area of freshly exposed gold substrate is produced by scanning the AFM tip under high force. The transient bare area of the surface is confined between the AFM probe and thiol matrix molecules with dimensions less than the molecular length of the DPP molecules, therefore nanografted molecules assembling on the surface do not have sufficient space to assemble in a lying-down configuration. According to the height measurements, DPP molecules assemble directly onto gold with a standing configuration when nanografted.

4.4 Conclusions

Nanopatterns of pyridyl porphyrins (DPP) were successfully produced by nanografting within different $n$-alkanethiol matrices, revealing that pyridyl porphyrins can directly assemble on Au(111) into an upright configuration. Nanografting in liquid media was accomplished by using a mixed solvent system, to solve the problem of solubility with porphyrins. Matrix monolayers of decanethiol and octadecanethiol were used as a molecular ruler to evaluate the thickness and surface orientation of nanografted patterns of DPP. These investigations suggest that a mechanism of spatially-confined self-assembly occurs when writing patterns of dipyridyl porphyrins during nanografting, and it is likely that surface linkages of DPP are formed through nitrogen-gold chemisorption. Nanografting enables surface assembly in a dilute regime with mixed solvent systems, e.g. dichloromethane/ethanol. With nanografting, DPP molecules assemble directly onto gold with a standing-up configuration due to spatially constrained self-assembly.
CHAPTER 5. ASSEMBLY OF 5,10,15,20-DI-PYRIDIN-4-YL-PORPHYRIN ON Au(111)
FROM MIXED SOLVENTS

5.1 Introduction

Porphyrins and metalloporphyrins are useful materials for devices because of photoelectric, catalytic and electronic properties. For surface and structural characterizations, porphyrins have been deposited on surfaces of Ag,\textsuperscript{340} Au,\textsuperscript{341-343} HOPG,\textsuperscript{344-345} Si,\textsuperscript{346-347} and sapphire.\textsuperscript{344} The properties and surface morphology are largely determined by the length, composition, nature and position of the peripheral groups attached to the macrocycle.\textsuperscript{84,348-349} For example, the electrical conductance of linear dithiolated porphyrin arrays was found to be influenced by molecular length.\textsuperscript{350} Porphyrins have applications for molecular electronics,\textsuperscript{351-353} switching devices,\textsuperscript{354} sensors,\textsuperscript{355-357} photonic devices,\textsuperscript{358} photovoltaic cells,\textsuperscript{348} and photoelectrochemical cells for light-harvesting applications.\textsuperscript{359-361} The organization of molecules on surfaces determines the function and efficiency of devices.\textsuperscript{330-331,362} Understanding the self-organization and assembly of porphyrins is important for optimizing the function of these molecules for potential device applications.

The assembly of porphyrins on surfaces is a complex process resulting from the interplay of interactions between porphyrin macrocycles, attached substituents and the nature of the surface chemistry. Unlike thiol\textsuperscript{363-365} and organosilane\textsuperscript{366} molecules that have been extensively investigated, the solution phase assembly of porphyrins has not been widely studied. The ability of linear molecules with thiol and silane moieties to form ordered monolayers on surfaces results from interactions between the alkane chains of the individual molecules as well as endgroup chemistry.\textsuperscript{367} In contrast, the planar macrocycles of porphyrins have a fully conjugated $\pi$ electron system which enables intermolecular interactions between planar rings, which tends to result in self-aggregation to form crystals. Complex intermolecular interactions, such as pi-pi stacking
between macrocycles or binding interactions between peripheral groups and surfaces dictate the overall assembly processes of porphyrins from solution.\textsuperscript{368-369}

Porphyrins have been reported to adopt a coplanar arrangement with surfaces, forming stacks and clusters on surfaces because of strong pi-pi interactions.\textsuperscript{332-338} Deposition methods and the nature of organic solvents have also been found to influence the formation of porphyrin clusters on surfaces.\textsuperscript{370-371} Different structures can be observed on the surface depending on methods of sample deposition, the nature of the solvent that was used and the overall molecular architecture. At high concentration, samples of porphyrins often spontaneously form crystals.\textsuperscript{372-373} Porphyrins have limited solubility in certain solvents, and are often immiscible in water or alcohol which limits the processing ability for producing organic thin films for surface studies.

In this report, high resolution imaging combined with scanning probe lithography were used to investigate the surface assembly of 5,10,15,20-di-pyridin-4-yl-porphyrin (DPP) on Au(111) from mixed solvent solutions. Details of changes in the surface morphology of pyridyl-functionalized porphyrins were captured over time using atomic force microscopy (AFM) imaging. Scanning probe lithography (SPL) approaches of nanografting and nanoshaving were used make local measurements of the thickness of porphyrin nanostructures. Nanoshaving has previously been used to characterize films of \textit{n}-alkanethiol SAMs,\textsuperscript{3,88} organosilane SAMs,\textsuperscript{85,374} polymers,\textsuperscript{375-376} DNA\textsuperscript{377-378} and molecular micelles.\textsuperscript{379} Selective patterning of molecules has been accomplished with nanografting to write patterns of different thiolated molecules such as \textit{n}-alkanethiols,\textsuperscript{2,34} alpha,omega alkanedithiols,\textsuperscript{380} thiolated proteins,\textsuperscript{118,381} nanoparticles,\textsuperscript{90} and thiolated DNA.\textsuperscript{382} Nanografting is known to alter the assembly of \textit{n}-alkanethiols through a mechanism of surface confinement.\textsuperscript{6} By designing the arrangement of pyridyl and phenyl substituents linked to the macrocycle our goal was to gain molecular level insight for controlling the orientation of porphyrins on Au(111) surfaces, to prepare a densely packed monolayer of
defined thickness. We hypothesized that the assembly of porphyrins which typically assemble in a coplanar orientation on surfaces could likewise be disrupted by spatially confined self-assembly with nanografting to form an upright orientation on Au(111), mediated by nitrogen-gold surface linkages of pyridyl groups.

5.2 Materials and Methods

5.2.1 Materials and Reagents

Silica gel from Sorbent Technologies 32-63 µm was used for flash column chromatography. $^1$H- and $^{13}$C-NMR were obtained on a ARX-300 Bruker spectrometer. Electronic absorption spectra were measured on a Perkin Elmer Lambda 35 UV-Vis spectrophotometer and fluorescence spectra were measured on a Perkin Elmer LS55 spectrometer. Mass spectra were obtained with an Applied Biosystems QSTAR XL. All solvents used for synthesis were purchased from Fisher Scientific (HPLC grade) and used without further purification.

Reagents such as ethanol (Aaper, Shelbyville, KY), dichloromethane (EMD Chemicals, Gibbstown, NJ), sulfuric acid (EMD Chemicals, Gibbstown, NJ), hydrogen peroxide (Fisher Chemical, Fairlawn, NJ) were used without further purification. Flame annealed gold-coated mica substrates (150 nm thickness) were acquired from Agilent Technologies, Inc. (Chandler, AZ). Highly ordered pyrolytic graphite (MikroMasch, Wilsonville, OR) and polished silicon wafers (Virginia Semiconductor, Inc. Fredericksburg, VA) were also used as substrates for AFM samples. Alkanethiols such as octadecanethiol, dodecanethiol and decanethiol were purchased from Sigma Aldrich (St. Louis, MO, USA) and used without further purification.

5.2.2 Synthesis of Bis(pyridyl)bis(phenyl)porphyrin

The bis(pyridyl)bis(phenyl)porphyrin was prepared via a mixed porphyrin condensation in refluxing propionic acid, as previously reported.$^{383-385}$ This procedure is known as the Adler
and Longo methodology\textsuperscript{386} and afforded all six porphyrins in yields varying from 0.5 to 5%. To a refluxing solution of benzaldehyde (7.0 mL, 138 mmol) and pyridine-4-carboxaldehyde (3.0 mL, 63.0 mmol) in propionic acid (250 mL) was added pyrrole (6.25 mL, 180 mmol), dropwise. This caused the solution to rapidly change from yellow to black in color. The solution was stirred and refluxed for 1.5 h. To the cooled reaction solution diethylene glycol (175 mL) was added and the solution was refrigerated overnight. The precipitate formed was isolated by vacuum filtration and washed with methanol. The crude product was loaded on a silica gel column and eluted with CH\textsubscript{2}Cl\textsubscript{2} to remove any tetraphenylporphyrin in the mixture. A second silica gel column was loaded with the remaining compound and eluted with 1-5\% methanol/CH\textsubscript{2}Cl\textsubscript{2} mixture, slowly increasing the polarity of the eluent to obtain separation of the five pyridylporphyrins. The compounds eluted in the following order: 5,10,15,20-tetraphenylporphyrin, 5-(4’-pyridyl)-10,15,20-tri(phenyl)porphyrin, \textit{cis}-5,10-bis(4’-pyridyl)-15,20-bis(phenyl)porphyrin, \textit{trans}-5,15-bis(4’-pyridyl)-10,20 bis(phenyl) porphyrin, 5,10,15-tri(4’-pyridyl)-20-(phenyl)porphyrin and 5,10,15,20-tetra(4’-pyridyl) porphyrin. The \textit{cis}-5,10-bis(4’-pyridyl)-15,20-bis(phenyl)porphyrin was obtained in 1 \% yield (0.0620 g), and its spectroscopic characterization agreed with the reported values.\textsuperscript{383-385}

\textbf{5.2.3 Preparation of Substrates}

Prior to sample deposition, pieces of HOPG were freshly cleaved with a piece of adhesive scotch tape to expose a clean surface. Silicon wafers were first immersed in solution of concentrated sulfuric acid and hydrogen peroxide (3:1) for 1 h, then copiously rinsed with deionized water, followed with ethanol and sonicated for 30 min in 99\% ethanol. The acid cleaned silica pieces were then exposed to UV light (Spectroline, Westbury, NY), 254 nm for 15 min prior to use. Gold substrates were used without further treatment.

\textbf{5.2.4 Preparation of Dried Samples}
Stock solutions of porphyrins were prepared by dissolving 5,10-diphenyl-15,20-di-pyridin-4-yl-porphyrin (DPP) in dichloromethane (DCM). The solution was further diluted with absolute ethanol to the desired concentration \((10^{-3} \text{ – } 10^{-6} \text{ M})\). A single 10 µL drop of porphyrin solution was placed onto the substrates and dried at room temperature for at least 24 h.

5.2.5 In Situ Investigations of the Assembly of Porphyrin Films

The self-assembly of 5,10-diphenyl-15,20-di-pyridin-4-yl-porphyrin (DPP) in real time was investigated by first imaging Au(111) in ethanol using contact mode AFM to select a flat area with few defects. A solution of 0.01 mM DPP in ethanol/DCM was then injected into the AFM liquid cell. Surface morphology changes were monitored for three hours, with images taken at 5 min intervals. The surface layer of DPP that formed was then further characterized by nanoshaving and nanografting.

5.2.6 Preparation of \(n\)-Alkanethiol Self-Assembled Monolayers (SAMs)

Freshly prepared octadecanethiols \((10^{-9} \text{ M})\) dissolved in absolute ethanol were used as nanografting solutions for \textit{in situ} characterizations of the pyridyl porphyrin film. Matrix alkanethiols such as octadecanethiol, dodecanethiol and decanethiol for writing pyridyl porphyrins were prepared by immersing flame-annealed ultra flat films of Au(111) prepared on mica substrates in a \((10^{-3}\text{ M})\) solution of chosen alkanethiol in ethanol for at least 12 h. The SAMs on Au(111) were then removed from the thiol solution, copiously rinsed with fresh ethanol and immediately placed into a liquid cell holder for AFM imaging and lithography to minimize surface oxidation.

5.2.7 Atomic Force Microscopy (AFM)

Samples prepared by the drying method were imaged using tapping mode in air with a model 5500 SPM (Agilent Technologies, Inc. Chandler, AZ). Probes with resonant frequencies ranging from 265-400 kHz were used for tapping-mode imaging (MikroMasch Wilsonville, OR).
Scan rates of 3.0 μm/s and 256 line frame per second were used for acquiring images. For in situ investigations, AFM images were acquired in contact mode using a hybrid system, a PicoSPM scanner from Agilent (Chandler, AZ) was interfaced with electronic controllers and software (XPM Pro v.1.2.1.0) from RHK Technology (Troy, MI). Silicon nitride cantilevers with force constants ranging from 0.1 to 0.5 Nm\(^{-1}\) were used for imaging in liquids (Veeco Probes, Santa Barbara, CA). Digital images were processed with Gwyddion (version 2.5) open source software which is freely available on the Internet and supported by the Czech Metrology Institute.\(^{387}\)

5.3 Results and Discussions

The DPP molecule chosen for these studies is a free-base porphyrin with two adjacent phenyl and two adjacent pyridine rings as peripheral groups (Figure 5A). Possible configurations of 5,10,15,20-di-pyridin-4-yl-porphyrin(DPP) on Au(111) are shown in Figures 5.1B-5.1C with energy minimized structural models. Different configurations of DPP are possible on Au(111), depending on whether there is one, two or four linkages to the surface. In these models, DPP will

![Figure 5.1](image)

**Figure 5.1.** Structural formula and possible configurations of 5,10-diphenyl-15,20-di-pyridin-4-yl-porphyrin (DPP) with the corresponding heights on Au(111). [A] Molecular structure of DPP; [B] upright configuration of DPP with two pyridyl rings anchored to surface; [C] perpendicular orientation of DPP with one pyridyl anchoring group; [D] coplanar configuration of DPP on Au(111).
adapt an upright orientation if one (Figure 5.1B) or two (Figure 1C) pyridyl rings attach to the surface. For a coplanar orientation, the ring bends towards the surface with the macrocycle ring oriented as shown in Figure 5.1D.

5.3.1 Assembly of Pyridyl Porphyrins to Form “Stacks” on Surfaces

Surface assemblies of “stacks” of porphyrins often are formed that are oriented in a coplanar arrangement with respect to the surface plane when liquid samples of porphyrins are dried on flat surfaces. Depending on the drying conditions, the nature of the solvent and the concentration of the porphyrin in the parent solution, different heights and surface coverage of stacks are produced. Initial investigations of the assembly of 5,10-diphenyl-15,20-di-pyridin-4-yl-porphyrin (DPP) prepared either by methods of drying or immersion of various substrates in porphyrin solutions were found to spontaneously produce stacks when prepared in ambient environments, as shown in Figure 5.2. Dried samples of DPP that were prepared on surfaces of Au(111), HOPG and Si(111) were characterized using tapping mode AFM in air.

Representative AFM topographs of each surface (3×3 um² scan) are displayed, which reveal structures of small white islands or stacks distributed throughout the sample areas. (Figure 2). The stacks of DPP formed on Au(111) tend to be located at edges or corners of the irregularly shaped terraces(Figure 5.2A), and range in height from 1 to 10 nm. Analysis of the heights from several images (n = 100) show that 70% of the measurements range from 2 – 4 nm, corresponding to 4-8 porphyrin layers per stack, oriented in a planar configuration. The surface of HOPG shows preferential deposition at the step edges of graphite (Figure 5.2B). Size analysis reveals that stacks range in height from 0.3 - 5.0 nm, 52% of which measure ~1.0 nm, indicating two layers of DPP. On polished silicon wafers (Figure 5.2C), the distribution of porphyrin stacks throughout the surface areas was more random, with taller overall dimensions, compared to gold
and graphite surfaces. Most of the stacks measured 4 – 8 nm in height, which corresponds to thicknesses of 7 to 13 layers of DPP.

Figure 5.2. Stack structures of DPP formed on surfaces of [A] Au(111); [B] HOPG; [C] Si(111); with corresponding height distributions for stack sizes.

Droplet samples of porphyrins dried in ambient conditions produce stacks regardless of the surface, as viewed in Figure 5.2 for samples which were prepared side-by-side using similar conditions of concentration and solvent. The strong pi-pi interactions between the macrocycles
predominate to form columnar discotic phases (stacks) when solutions of porphyrins are dried. As the solvent evaporates during the drying step, the capillary forces of the evaporating liquid pulls DPP molecules closer together. The heights of the stacks are influenced by the wettability and resulting surface energy of the substrates. The preferential formation of stacks on step boundaries of gold and HOPG can be attributed to the active sites in terrace edges, as previously reported.\textsuperscript{389-391} Density functional theory (DFT) has shown that step edges of gold substrates have a greater concentration of electron density thereby allowing a maximum overlap between molecular orbitals.\textsuperscript{389} The same conformational feature has been observed with 5-(4-methylthiophenyl)-10,15,20-tris(3,5-di-t-butylphenyl)porphyrin (MSTBPP) deposited on Au(111).\textsuperscript{392} Aggregates of 1-10 nm were formed on polished silicon substrates indicating that the intermolecular attraction between porphyrin molecules was greater than the molecule-substrate interaction. After evaluating a range of different substrates, solvent media, immersion and drying conditions, the predominant outcome of surface morphologies observed for DPP were stack structures. Further experiments were designed for viewing surface assembly processes in situ, without a drying step, as described in the next sections.

\textbf{5.3.2 Assembly of Pyridyl Porphyrins on Au(111) from Solutions of Mixed Solvents}

A requirement for liquid AFM imaging is to use a solvent that does not evaporate rapidly in ambient conditions; common imaging solvents that are suitable for liquid cell imaging are 2-butanol, ethanol or water. However, DPP is nearly insoluble in these solvents so an approach with mixed media was developed, similar to experiments that were previously described for studies of \textit{n}-alkanethiols in water-based media.\textsuperscript{393} The media used for studies with DPP was a mixture of ethanol and dichloromethane (DCM). The porphyrin was first dissolved in DCM to prepare a parent solution, and this solution was further diluted in ethanol to approximately 1 vol\% DCM.
After imaging a clean surface of Au(111) in ethanol, a solution of 0.01 mM DPP was injected into the AFM liquid cell and the surface morphology was monitored for several hours. Molecular views of the spontaneous self-assembly of pyridyl-porphyrins from mixed solvent solutions were captured in situ using contact mode AFM as shown in Figure 5.3. A few minutes after injection of DPP, small islands of porphyrins of various heights begin to appear. The initial changes of the surface morphology are shown in Figure 5.3A after 3 h of immersion, with the appearance of adsorbates, covering 15% of the surface area and a few bright island features. The bright white globular structures observed were about 80 spots/µm$^2$ area. The simultaneously acquired lateral force image (Figure 5.3B) shows no distinct features.

In the next step of the liquid AFM experiment, a rectangular area (200 × 300 nm$^2$) was shaved as shown in the topography and lateral force frames of Figure 5.3D and 5.3E. Nanoshaving is an SPL method in which local areas of a surface are scraped or shaved away by the action of a sweeping AFM tip to remove adsorbates.$^{34}$ The uncovered substrate provides a baseline for measuring the thickness of the film. The outline of the edges of the nanoshaved area is distinct both in topography and lateral force image frames. The angular boundaries of step edges of the underlying gold substrate are resolved in the lower corners of the topography image (Figure 5.3D). The clean removal of DPP is also apparent in the lateral force image (Figure 5.3E), showing a uniformly dark contrast for the nanoshaved hole. A cursor line profile was chosen across a central area of the hole without step features, as shown in Figure 5.3F. The height of the DPP film measured ~ 0.6 nm, which matches the expected thickness for a coplanar orientation. The assembly process was continued for 48 h, and then the sample was removed from the DPP solution, rinsed with ethanol and immediately imaged in ethanol. Further changes in surface morphology for the self-assembly process were captured by imaging in ethanol using very low forces to prevent damage to the sample, as shown in Figure 5.4.
Figure 5.3. Films of DPP on Au(111) after 3 h immersion in mixed solvent media. [A] Topograph of DPP film before nanoshaving; [B] lateral force image of A; [C] corresponding cursor profile for the line in A. [D] topograph showing the nanoshaved pattern of the DPP film; [E] lateral force image of D; [F] corresponding cursor profile for the line in D.

Segregated domains of different thicknesses of DPP were observed to form on Au(111) after longer immersion. Distinct areas of brighter islands surrounded by a film with shorter heights are evident in Figure 5.4A. The left side of the image shows a predominance of taller islands of DPP, whereas the left area exhibits very few bright islands, with saturation coverage of the shorter phase. Approximately 65% of the surface for the area framed has shorter heights, corresponding to the coplanar arrangement. The irregular fractal shapes of the bright islands of DPP in Figure 5.4B cover approximately 53% of surface in Figure 5.4A. A magnified view in Figure 5.4C reveals the detailed domain structures of the mixed phases of coplanar and upright DPP, exhibiting 69% surface coverage for the taller structures. The width between upright domains measures 5-15 nm. The height difference between the taller and shorter phases of Figure 5.4D measures between 0.2 nm-0.4 nm.
Figure 5.4. Domains of mixed heights of DPP on Au(111) observed under conditions of natural self-assembly. [A] Contact-mode topograph showing taller and shorter DPP molecules on the surface; [B] topograph image of an area with greater coverage of the taller phase of DPP [C] zoom in topographic view of the mixed phases of DPP; [D] cursor profile for the line in C.

The thickness of the DPP film of Figure 5.4 was measured by nanoshaving (Figure 5.5) in ethanol. A 100 × 100 nm² hole was neatly shaved within the DPP film, as shown in Figure 5.5A. The thickness of the layer measured 1.1 ± 0.3 nm corresponding to an upright orientation of DPP with two pyridyl groups attached to gold. Nitrogen-gold chemisorption has been
previously reported for SAMs terminated with cyano and nitrile end groups.\textsuperscript{394} Thus, for the natural self-assembly process of dipyridyl diphenyl porphyrins, mixed domains of both co-planar (lying-down) and upright orientations are observed, with a predominance of the brighter domains of upright DPP increasing as time progressed. Height measurements from Figure 5.4B indicate that coplanar domains of DPP persist in the boundary areas between the bright islands.

![Figure 5.5. Nanoshaved hole within a DPP film formed after 48 hours of immersion. [A] Contact mode AFM topograph of a 100 x 100 nm$^2$ shaved area within the film; [B] cursor profile for the line in A. Scan size is 260 nm.](image)

From liquid AFM experiments captured at 3 h and 48 h time points, the surface assembly of DPP begins with a coplanar orientation on Au(111) and transitions over time to produce an upright configuration as the surface coverage increases. For studies of the assembly of
porphyrins in liquid media without a drying step, round domains of stack structure were not observed. Instead, liquid cell experiments reveal that a continuous monolayer is formed throughout the surface (Figures 5.3 and 5.4). Further studies were conducted with nanografted structures of \( n \)-alkanethiols/Au as a molecular ruler, to verify the thicknesses obtained with nanoshaving experiments, as described in the next section.

### 5.3.3 Molecular Rulers: Nanografting of \( n \)-Octadecanethiol Within a Porphyrin Film

Films of DPP porphyrins formed on Au(111) are sufficiently densely packed that patterns of \( n \)-alkanethiols can be inscribed within porphyrin films via nanografting. Nanografting can be described as mechanical removal of SAMs under a high force followed with \textit{in situ} replacement of another molecule following the scanning track of the tip. A cross-shaped pattern of 0.001 mM octadecanethiol (ODT), was written into the porphyrin film as evidenced by the topograph and lateral force images (Figure 5.6). A cross pattern of taller molecules of ODT surrounded by DPP film are clearly visible in the topograph (Figure 5.6A). The lateral force image in Figure 5.6B shows darker contrast for the methyl-terminated areas of the nanografted pattern of ODT, which is further evidence that a new molecule was successfully inscribed within the monolayer. The thickness of the porphyrin film on Au(111) was evaluated by comparison with the well-known height of ODT. Since the height of ODT is known to be 2.1 nm, ODT serve as a molecular ruler to determine the exact thickness of the porphyrin monolayer with angstrom precision. Both nanografting as well as nanoshaving results reveal that the thickness of the shorter phase of DPP porphyrin films formed \textit{in situ} on Au(111) measures \( \sim0.6 \) nm, in agreement with a co-planar orientation of a single layer, whereas the taller domains correspond to an upright orientation that is nearly perpendicular to the surface, measuring \( \sim1.2 \) nm in thickness.
Figure 5.6. Nanografted cross pattern of octadecanethiol placed within a matrix of DPP. [A] Contact mode AFM topograph; [B] corresponding lateral force image; [C] cursor profile for the line in A; [D] molecular model showing heights of DPP and octadecanethiol.

The thickness of the upright phase also corresponds to the dimensions a multilayer structure of two macrocycles in a coplanar arrangement; however we would expect to observe a distribution of multiple heights for the nanostructures if stacking assembly takes place rather than a consistent bilayer dimension. It is unlikely that only bilayer structures would form if a coplanar assembly mechanism were followed. Also, the strong interaction between nitrogen and gold chemisorption is more favorable and would tend to produce a rearrangement into an upright orientation.

5.3.4 Nanografted Structures of DPP Formed Under Conditions of Spatial Confinement

During nanografting, assembly of pyridyl porphyrins follows a different reaction pathway due to a spatial confinement, which has been reported previously for $n$-alkanethiol SAMs.395-396
Under conditions of local confinement produced during nanografting, the transient reaction environment is sufficiently small to prevent the molecules from assembling in a lying-down position. When nanografting, very small areas of freshly exposed gold are produced by scanning with a high force applied to the AFM tip. The bare area on the surface is confined between the AFM probe and thiol matrix molecules. The confined area uncovered by the AFM tip has dimensions less than the molecular length of the molecules, therefore \( n \)-alkanethiol molecules from solution do not have sufficient room on the surface to assemble in a lying-down configuration. Thus, the initial physisorbed phase is bypassed and molecules assemble directly onto gold with the favored standing-up configuration.

Nanopatterns of pyridyl porphyrins were successfully prepared by nanografting in mixed solvent media, using different \( n \)-alkanethiol matrices. Example arrays of nanopatterns of pyridyl porphyrins produced by nanografting while scanning in a solution containing a mixture of solvents (1% dichloromethane in ethanol) and pyridyl porphyrins are presented in Figure 5.7. Automated nanografting enables direct control of parameters such as the size, arrangement, geometry and spacing of pyridyl porphyrins at the nanoscale. The heights of the DPP nanopatterns shown in first column of Figure 5.7 are shorter than the selected alkanethiol SAMs as evidenced by the darker contrast for the patterns in the topography images. The lateral force images shown on the second column of Figure 5.7 exhibit contrast differences with chemistry present on the surface. Since the thickness of \( n \)-alkanethiol SAMs has been well-established, the matrix SAMs can be used as a molecular ruler to evaluate the orientation of new molecules. Side-by-side comparisons of the dimensions of nanostructures formed on gold surfaces enable precise measurements of the thickness of pyridyl porphyrin patterns.

Rings patterns of pyridyl porphyrins with decreasing diameter ranging from 20-60 nm were nanografted within decanethiol matrix (Figure 5.7A). The theoretical height of the matrix
decanethiol is 1.4 nm. The cursor indicates a height difference of 0.3 ± 0.2 nm, which likely corresponds to an upright conformation (1.1 nm) in which both of the pyridyl groups are attached to the surface. To test the reproducibility of nanografting pyridyl porphyrins, ring patterns of the same size (75 nm diameter) were fabricated within dodecanethiol (DDT) matrix as shown in Figure 5.7B. High resolution topograph was captured after nanografting as evidenced by the etch pits and the lacey contours of the step edges on areas covered with dodecanethiol SAMs. The height difference between the DDT and pyridyl porphyrins as indicated in the cursor profile is 0.5 nm ± 0.2 corresponding to the expected thickness between DDT and pyridyl porphyrins if pyridyl porphyrins have an upright orientation on Au(111).

An array of nine filled circles of pyridyl porphyrins (Figure 5.7C) inscribed within the octadecanethiol matrix displayed differences in height and surface chemistry of the pyridyl porphyrin patterns positioned on gold terraces. The diameter of the circular pattern is about 200 nm. The height difference between the matrix ODT and porphyrin patterns measures 1.0 ± 0.3 nm as indicated in the representative line profile in Figure 5.7C corresponding to the expected difference of 1.1 nm. The sizes of the desired patterns can be produced depending on number of line sweeps executed by the AFM probe. With nanografting, the width of the pattern is limited by the size of the AFM probe and the density of the pattern.

5.3.5 Computer Simulation of DPP Structure on Au(111)

The configurations and electronic structures of DPP on Au(111) were tested using Car-Parrinello molecular dynamics ver. 3.11. First, DPP was optimized in the gas phase to remove any potential bad contacts and to create a good starting configuration for the surface studies. Vanderbilt Ultra-Soft pseudopotentials were employed with a kinetic energy cutoff of 35 Ry with a electron density cutoff threshold of 10⁻⁶. The gold slab had three layers, containing 150
Figure 5.7. Nanopatterns of DPP nanografted within various SAM matrices. AFM topograph; corresponding lateral force image and line profile (from left-to-right) of DPP patterns written within [A] decanethiol; [B] dodecanethiol; [C] octadecanethiol matrices.

Atoms fixed to their crystal lattice position to save computational expense. Periodic boundary conditions in the x and y directions were used. The starting configurations of the porphyrin was placed 3.5 angstroms away from the gold surface. A combined geometry and electronic structure optimization was used to initially relax this new configuration. Then a short 200 step CPMD simulation was conducted to refine the structure. The time step used here was 0.14 fs. The coplanar orientation of DPP has two possible flat orientations on Au(111). Both configurations had a slight twist in the porphyrin.
**Figure 5.8.** Different configurations and electronic structures of DPP on Au(111). [A] Flat-Carbon ring; [B] Flat N-ring; [C] 1-Nitrogen; [D] 2-Nitrogen

The outer 6-membered was brought closer to the surface with and without the nitrogen. For flat C-ring (Figure 5.8A), the ring bends towards the surface with the macrocycle five-membered ring. The hydrogen atom provides a density overlap bridge to the gold surface. The flat N-ring conformation exhibited similar overall configuration to Flat-C (Figure 5.8B) as the macrocycle 5-membered ring is also drawn towards the surface. The nitrogen’s density is more localized and competes with the pi bonds in the ring which brings a hydrogen closer to the surface ~2.4Å. For porphyrin anchored on the surface with one pyridyl ring as a leg (Figure
5.8C), the 6-membered ring was adjusted by various angles with respect to the surface to find the lowest energy structure. Results show that the nitrogen density is drawn towards the surface. Interestingly, the hydrogen orientates towards an interstitial site on the surface. The overall density of DPP has increased when 2 pyridine rings are anchored to the surface (Figure 5.8D). Both pyridine rings twist so that the pi system and nitrogens can both become closer to the surface. The 5-membered macrocycle is forced to the surface and the electron density overlaps with the hydrogens.

5.4 Conclusions

Scanning probe-based fabrication of nanostructures of porphyrins has been problematic, due to the insolubility of porphyrins in solvents that are typically used as liquid imaging media. In this report, studies of the surface self-assembly of pyridyl-functionalized porphyrins was accomplished using a mixture of solvents. Unconstrained assembly of pyridyl-functionalized porphyrins from solution produced compact monolayers with two distinct configurations on the surface, exhibited by a mixture of upright and co-planar islands. Nanografted patterns of n-alkanethiols were used as a molecular ruler to evaluate the orientations of the porphyrins on Au(111) through side-by-side comparisons of the dimensions of the molecules. Computer simulation correlates with AFM results disclosing that solution phase assembly of pyridyl-functionalized porphyrins adapts different configurations on the surface. However with nanografting, DPP molecules assemble directly onto gold with a standing-up configuration due to a mechanism of spatially constrained self-assembly. Nanografting results demonstrated for the first time that pyridyl porphyrins in a dilute mixed solvent solution can assemble directly on Au(111) in an upright orientation. Understanding the self-organization and assembly of designed porphyrins will contribute to rational designs for applications in electronic and photonic devices.
CHAPTER 6. POLYTHIOPHENES CONTAINING IN-CHAIN COBALTABISDICARBOLIDE CENTER*

6.1 Introduction

Carboranes, in both neutral and anionic forms, are boron clusters with delocalized electrons and unique properties, including high hydrophobic character, low nucleophilicity, electron-withdrawing nature, and exceptional chemical, thermal, and optical stabilities as a result of their three-dimensional aromatic character. Furthermore, complexation of the anionic open cage carborane derivatives with a variety of metal ions (e.g., Fe, Ni, and Co) leads to highly stable sandwich-type metalla-bis(dicarbollide) compounds. Depending upon the valence of the metal these compounds can be neutral or charged, usually with one or two negative charges. These metal complexes have received much interest because of their prominent role in the extraction of radionuclides from nuclear wastes, in molecular recognition, in biomedicine, and in the construction of redox-switched molecular rotors. For example, Hawthorne and co-workers have reported that nickel bisdicarbollide has a rotation barrier of 6 kcal/mol and that it rotates depending on the valence of the metal, when actuated by electrical or light energy. Several carborane-containing organic molecules have been synthesized in the last decades and some of these are currently finding applications in medicine and in materials science. Furthermore, their incorporation within organic materials has been demonstrated to be valuable to confer novel properties upon the host matrix, such as high thermal and chemical stability, unique optoelectronic characteristics and an ordered structure. Several polymers containing carborane groups, usually linked to the host molecule by aromatic spacers, have been synthesized and characterized. These macromolecular systems showed extreme resistance to combustion and a two-dimensional grid-shaped structure using the

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boron cage as a molecular connector. However, such materials were usually synthesized in several steps and did not show peculiar electronic conducting properties, which preclude them from certain applications, such as electrochromic and charge storage devices, and electroresponsive sensors. Some years ago, Teixidor’s group and ourselves prepared novel electroconductive polypyrroles and polythiophenes functionalized with various neutral and anionic carboranes, either via side-chain modification or direct incorporation into the polymer backbone. These materials, which were electrochemically generated in one step, exhibited a strong enhancement of their electrochemical stability and overoxidation resistance compared with unsubstituted parent conducting polymers. Recently, carborane-substituted polyfluorenes were prepared which showed advantageous luminescent properties for light-emitting diodes.

Within the attractive class of boron clusters, the metalla-bisdicarbollide complexes offer novel opportunities to prepare unprecedented conducting metallopolymers. Toward this goal, we report herein the synthesis and characterization of cobalt(III) bisdicarbollide derivatives covalently linked to electropolymerizable 2-oligothienyl units (Scheme 6.1). It was expected that oxidative coupling of the aromatic rings would lead to polythiophene films with the metal complexes incorporated in the main polymer chain. Metal-containing polymers have been the focus of intense investigations because of their potential applications in catalyses and in ion or small molecule binding. A central issue in the development of conducting metallopolymers is the control of the interactions between metal centers and the conducting organic polymer backbone. Compared with other conducting polymers bearing a metal center, either through a spacer arm or by electrostatic entrapment, the presence of the metal center in the conjugated chain of the polymer is expected to significantly impact on the electronic conductivity and the magnetic and optical properties of such materials. Moreover, in addition to these interesting
effects, the presence of in-chain metalla-bisdicarbollide complex may also confer improved thermal and electrochemical stabilities to the host conducting material, as previously demonstrated for other carborane-functionalized polypyrroles \(^{421,423,425,427,429}\) and polythiophenes.\(^ {428-429}\) The new conducting polymers resulting from electropolymerization of the substituted cobaltabisdicarbollides have been characterized by electrochemistry, UV–vis spectroscopy and conducting probe atomic force microscopy in order to provide significant insights on the effects of the bound cobaltabisdicarbollide moiety on the electronic properties of the resulting conducting materials. Such metallopolymers were used for the electrocatalytic reduction of H\(^+\) and the efficiency of the electrocatalytic process was found to be highly dependent on the thickness of the metallopolymer film.

**Scheme 6.1** Synthesis of Oligothiophene-Disubstituted Cobaltabisdicarbollide Compounds

### 6.2 Experimental Section

Synthesis of Oligothiophene-Disubstituted Cobaltabisdi-carbollide Compounds. General

All reactions were monitored by thin layer chromatography (TLC) using 0.25 mm silica gel plates with or without UV indicator (60F-254). The carborane clusters were detected by emerging into a solution of PdCl\(_2\) in aqueous HCl (1 g PdCl\(_2\) in 80 mL water and 20 mL concentrated HCl) and heated until black spot(s) was/were seen on TLC. Silica gel from Sorbent Technologies 32–63 μm was used for flash column chromatography. \(^1\)H and \(^{13}\)C NMR were obtained on either a DPX-250 or a ARX-300 Bruker spectrometer. Chemical shifts (δ) are given in ppm relative to CDCl\(_3\) (7.26 ppm, \(^1\)H; 77.2 ppm, \(^{13}\)C), CD\(_2\)Cl\(_2\) (5.32 ppm, \(^1\)H; 77.2 ppm, \(^{13}\)C) or acetone-d\(_6\) (2.05 ppm, \(^1\)H; 54.0 ppm, \(^{13}\)C). MALDI-TOF mass spectra were obtained on a
Bruker ProFLEX III MALDI-TOF mass spectrometer using positive mode and dithranol as the matrix. High-resolution mass spectra were obtained by using ESI-TOF with the negative mode on an Applied Biosystems QSTAR XL quadrupole time-of-flight mass spectrometer. The isotope peaks were matched with the calculated patterns; only the most abundant peaks for each compound are listed. All solvents were obtained from Fisher Scientific (HPLC grade) and used without further purification. Toluene was dried over sodium metal and distilled. Decaborane was obtained from Katchem, Inc. (Czech Republic) and all other reagents were obtained from Sigma-Aldrich and used without further purification.

**Compound 2a, Thiophene-2-o-carborane.** Diethylsulfide (4 g, 44 mmol) was added under N₂ to decaborane (2.44 g, 20 mmol) in 30 mL of dry toluene. The mixture was stirred at 40 °C for 3 h and then at 60 °C for another 2 h. A solution of commercially available 2-ethynylthiophene 1a (2.16 g, 20 mmol) in 30 mL of dry toluene was added and the final reaction mixture was refluxed for 2 days. The reaction was cooled to room temperature and the solvent was evaporated. Methanol (50 mL) was added and the reaction mixture was stirred for 30 min. After evaporation under reduced pressure, the resulting residue was purified by silica gel chromatography, using 20% dichloromethane in hexane as the eluent. The first major fraction was collected and dried under a vacuum, giving white crystals of 2a (2.31 g) in 53 % yield. ¹H NMR (CDCl₃, 250 MHz) δ 7.25–7.27 (1H, m, ArH), 7.20–7.21 (1H, m, ArH), 6.90–6.92 (1H, m, ArH), 3.86 (1H, s, CH), 1.50–3.50 (br, 10H, BH). ¹³C NMR (CDCl₃, 63 MHz) 137.2, 130.4, 128.3, 127.7, 72.4, 63.7. ¹¹B NMR (CDCl₃, 128 MHz, BF₃.OEt₂) δ −3.3 (d, ¹J(B,H) = 146 Hz, 1B) −6.6 (d, ¹J(B,H) = 147 Hz, 1B), −10.0 to −16.0 (br m, 8B). MALDI-TOF [M + H]⁺ 226.3. HRMS(ESI) m/z calcd for C₆H₁₃B₁₀S, 225.1739; found, 225.1746.

**Compound 2b, 2,2′-Bithiophene-5-o-carborane.** To a 100 mL reaction flask was added decaborane (0.61 g, 5 mmol), 2-ethynylthiophene 1b (0.57 g, 3 mmol), dry CH₃CN (4 mL),
and dry toluene (16 mL). The reaction mixture was stirred under N₂ at 80 °C for 24 h. After it was cooled to room temperature, methanol (10 mL) was added to the reaction mixture and stirred for 30 min. After removal of the solvents under vacuum, the residue was purified by silica gel chromatography, using 10% dichloromethane in hexane as the eluent. The first major fraction was collected and dried under vacuum, giving a light brown solid (0.70 g) in 76 % yield. ¹H NMR (CDCl₃, 250 MHz) δ 7.27 (1H, d, J = 5.10 Hz, ArH), 7.18 (1H, d, J = 3.00 Hz, ArH), 7.09 (1H, d, J = 3.73 Hz, ArH), 7.03 (1H, t, J = 4.48 Hz, ArH), 6.94 (1H, d, J = 3.71 Hz, ArH), 3.86 (1H, s, CH), 1.50−3.50 (br, 10H, BH). ¹³C NMR (CDCl₃, 63 MHz) 140.4, 136.0, 135.2, 131.1, 128.5, 126.2, 125.3, 123.8, 72.4, 63.8. ¹¹B NMR (CDCl₃, 128 MHz, BF₃.OEt₂) δ −3.4 (d, ¹J(B,H) = 145 Hz, 1B), −6.5 (d, ¹J(B,H) = 141 Hz, 1B), −10.0 to −16.0 (br m, 8B). MALDI-TOF [M + H]⁺ 309.5. HRMS (ESI) m/z calcd for C₁₀H₁₅B₁₀S₂, 307.1630; found, 307.1623.

**Compound 2c, 2,2′,5′,2′′-Terthiophene-5-o-carborane.** This compound was prepared and isolated as described above for the synthesis of 2b, starting from 1c (0.25 g, 0.92 mmol) and decaborane (0.20 g, 1.62 mmol). The result was a light yellow solid (0.19 g) in 53% yield. ¹H NMR (CD₂Cl₂, 300 MHz) δ 7.28 (1H, br s, ArH), 7.20 (1H, br s, ArH), 7.05−7.10 (4H, m, ArH), 6.95 (1H, br s, ArH), 6.95 (1H, s, CH), 1.50−3.50 (br, 10H, BH). ¹³C NMR (CD₂Cl₂, 63 MHz) 139.9, 138.0, 136.9, 134.9, 134.5, 131.2, 128.4, 125.9, 125.5, 124.8, 124.6, 123.6, 72.5, 64.0. ¹¹B NMR (CDCl₃, 128 MHz, BF₃.OEt₂) δ −3.2 (d, ¹J(B,H) = 143 Hz, 1B), −6.4 (d, ¹J(B,H) = 148 Hz, 1B), −10.0 to −16.0 (br m, 8B). MALDI-TOF [M + H]⁺ 391.3. HRMS (ESI) m/z calcd for C₁₄H₁₇B₁₀S₃, 390.1468; found, 390.1475.

**Compound 3a, tetrabutylammonium Thiophene-2-o-nido-carborane.** To a solution of compound 2a (1.13 g, 5.0 mmol) in 50 mL THF was added 10 mL of n-Bu₄NF solution (1.0 M in THF). The reaction mixture was stirred at 60 °C for 2 h, until no starting material was visible by TLC, and then poured into 50 mL of water and extracted with ethylacetate (3 × 50 mL). The
organic layers were dried over anhydrous Na₂SO₄ and concentrated under vacuum. The resulting residue was purified by passing through a pad of silica gel, using ethylacetate for elution. The title compound was obtained as a white power (2.14 g) in 94% yield. \(^1\)H NMR (acetone-d₆, 250 MHz) δ 6.95–6.96 (1H, m, ArH), 6.74–6.76 (1H, m, ArH), 6.65–6.67 (1H, m, ArH), 3.37–3.39 (8H, m, CH₂), 3.35 (1H, br, CH), 1.75–1.77 (8H, m, CH₂), 1.50–3.50 (br, 9H, BH), 1.37–1.45 (8H, m, CH₂), 0.91–1.01 (12H, m, CH₃), −2.03–2.50 (1H, br, BH). \(^{13}\)C NMR (CDCl₃, 100 MHz) 150.9, 126.3, 121.9, 121.5, 60.3, 59.0, 24.0, 21.0, 19.7, 13.6. \(^{11}\)B NMR (CDCl₃, 128 MHz, BF₃.OEt₂) δ −10.0 to −16.0 (br m, 3B), −18.0 to −20.0 (br m, 3B), −24.6 (d, \(^1\)J(B,H) = 149 Hz, 1B), −34.7 (dd, \(^1\)J(B,H) = 43.8 Hz, \(^1\)J(B,H) = 43.7 Hz, 1B), −37.6 (d, \(^1\)J(B,H) = 138 Hz, 1B). HRMS (ESI) [M-NBu₄]⁻ m/z calcd for C₆H₁₄B₉S, 214.1657; found, 214.1664.

**Compound 3b, Tetrabutylammonium 2,2'-Bithiophene-5-o-nido-carborane.** This compound was prepared as described above for the preparation of 3a, from 2b (0.62 g, 2.0 mmol) and 4.0 mL of nBu₄NF 1.0 M solution in 20 mL of THF, in 95% yield (1.02 g). \(^1\)H NMR (acetone-d₆, 250 MHz) δ 7.27 (1H, dd, \(J = 1.11\) Hz, \(J = 4.02\) Hz, ArH), 7.08 (1H, dd, \(J = 1.07\) Hz, \(J = 2.50\) Hz, ArH), 6.98 (1H, dd, \(J = 5.04\) Hz, \(J = 1.43\) Hz, ArH), 6.88 (1H, d, \(J = 3.69\) Hz, ArH), 6.58 (1H, d, \(J = 3.73\) Hz, ArH), 3.36–3.43 (8H, m, CH₂), 2.87 (1H, br s, CH), 1.73–1.83 (8H, m, CH₂), 1.50–3.50 (br, 9H, BH), 1.35–1.46 (8H, m, CH₂), 0.91–1.00 (12H, m, CH₃), −2.51 (br, 1H, BH). \(^{13}\)C NMR (acetone-d₆, 63 MHz) 152.1, 138.8, 133.5, 128.6, 124.3, 123.7, 123.2, 122.9, 80.5, 77.1, 59.2, 24.3, 20.3, 13.8. \(^{11}\)B NMR (CDCl₃, 128 MHz, BF₃.OEt₂) δ −10.0 to −16.0 (br m, 3B), −18.0 to −20.0 (br m, 3B), −24.6 (d, \(^1\)J(B,H) = 149 Hz, 1B), −34.7 (dd, \(^1\)J(B,H) = 43.8 Hz, \(^1\)J(B,H) = 43.7 Hz, 1B), −37.6 (d, \(^1\)J(B,H) = 138 Hz, 1B). HRMS (ESI) [M-NBu₄]⁻ m/z calcd for C₁₀H₁₆B₉S₂, 298.1582; found, 298.1586.

**Compound 3c, Tetrabutylammonium 2,2',5',2''-Terthio-phene-5-o-nido-carborane.** This compound was prepared as described above for the preparation of 3a, from 2c (0.18 g, 0.46
mmol) and 1.0 mL of $n$Bu$_4$NF 1.0 M solution in 5 mL of THF, in 85% yield (0.25 g). $^1$H NMR (acetone-$d_6$, 250 MHz) $\delta$ 7.43 (1H, d, $J = 4.91$ Hz, ArH), 7.25 (1H, d, $J = 3.41$ Hz, ArH), 7.16 (1H, d, $J = 3.71$ Hz, ArH), 7.05–7.08 (2H, m, ArH), 6.95 (1H, d, $J = 3.61$ Hz, ArH), 6.59 (1H, d, $J = 3.64$ Hz, ArH), 3.40–3.47 (8H, m, CH$_2$), 3.02 (1H, br s, CH), 1.75–1.8 (8H, m, CH$_2$), 1.50–3.50 (br, 9H, BH), 1.36–1.44 (8H, m, CH$_2$), 0.93–0.99 (12H, m, CH$_3$), −2.40 (br, 1H, BH). $^{13}$C NMR (acetone-$d_6$, 63 MHz) 152.1, 137.2, 137.1, 135.2, 132.6, 128.6, 125.3, 124.9, 124.1, 123.7, 123.6, 122.8, 80.8, 67.7, 59.0, 24.2, 20.0, 13.6. $^{11}$B NMR (CDCl$_3$,128 MHz, BF$_3$·OEt$_2$) $\delta$ −10.0 to −16.0 (br m, 3B), −18.0 to −20.0 (br m, 3B), −24.6 (d, $^1J(B,H) = 149$ Hz, 1B), −34.7 (dd, $^1J(B,H) = 43.8$ Hz, $^1J(B,H) = 43.7$ Hz, 1B), −37.6 (d, $^1J(B,H) = 138$ Hz, 1B).

HRMS (ESI) [M-$n$Bu$_4$N$^-$] $m/z$ calcd for C$_{14}$H$_{18}$B$_9$S$_3$, 380.1462; found, 380.1466.

**Compound 4a, Tetrabutylammonium Cobalt(III) Bis-(thiophene-2-o-nido-carborane).**

Compound 3a (458 mg, 1 mmol), tBuOK (1.12 g, 10 mmol), and anhydrous CoCl$_2$ (1.35 g, 10 mmol) were mixed in a 50 mL Schlenk reaction tube and 10 mL of anhydrous dimethoxyethane (DME) was added via syringe. The reaction was refluxed for 30 h under nitrogen, and then cooled to room temperature and filtered to remove the inorganic salt. The filtrate was partitioned between dichloromethane and $n$-Bu$_4$NHSO$_4$ aqueous solution, dried under a vacuum, and purified by silica gel chromatography using dichloromethane as the eluent. The first major fraction was collected and dried under a vacuum, giving a yellow powder (251 mg) in 70% yield. $^1$H NMR (acetone-$d_6$, 250 MHz) $\delta$ 7.22–7.24 (1H, m, ArH), 7.13–7.15 (1H, m, ArH), 6.89–6.91 (2H, m, ArH), 6.75–6.78 (1H, m, ArH), 6.63–6.64 (1H, m, ArH), 4.27 (1H, s, CH), 3.41–3.47 (8H, m, CH$_2$), 3.22 (1H, s, CH), 1.76–1.78 (8H, m, CH$_2$), 1.50–3.50 (18H, br, BH), 1.37–1.51 (8H, m, CH$_2$), 0.95–1.01 (12H, m, CH$_3$). $^{13}$C NMR (CDCl$_3$, 100 MHz) 125.7, 125.8, 123.2, 59.1, 30.9, 24.1, 19.7, 13.7. $^{11}$B NMR (CDCl$_3$, 128 MHz, BF$_3$·OEt$_2$) $\delta$ 9.0–30.0 (br m,
max at 5.9, −0.5, −8.8 and −30.8, 18B) ppm. HRMS (ESI) [M-NBu_4]^− m/z calcd for C_{12}H_{26}B_{18}S_{2}Co, 488.26; found, 488.2628.

**Compound 4b, Tetrabutylammonium Cobalt(III) Bis(2,2′-bithiophene-5-o-nido-carborane).** This compound was prepared as described above for the synthesis of 4a, from 3b (541 mg, 1 mmol), tBuOK (1.12 g, 10 mmol), and anhydrous CoCl_2 (1.35 g, 10 mmol), and was obtained (0.28 g) in 63% yield as a dark yellow solid. ^1^H NMR (acetone-d_6, 250 MHz) δ 7.19–7.28 (3H, m, ArH), 7.06–7.09 (2H, m, ArH), 6.98–7.04 (2H, m, ArH), 6.79 (2H, br s, ArH), 6.41 (1H, br s, ArH), 4.17 (1H, br s, CH), 3.32 (1H, br s, CH), 3.07–3.11 (8H, m, CH_2), 1.60–1.62 (8H, m, CH_2), 1.50–3.50 (18H, br, BH), 1.37–1.46 (8H, m, CH_2), 1.00–1.06 (12H, m, CH_3). ^13^C NMR (CDCl_3, 100 MHz) 127.6, 127.4, 124.7, 123.5, 123.2, 122.8, 59.2, 43.0, 24.0, 19.8, 13.7. ^11^B NMR (CDCl_3, 128 MHz, BF_3.OEt_2) δ 9.0–30.0 (br m, max at 5.9, −0.5, −8.8 and −30.8, 18B) ppm. HRMS (ESI) [M-NBu_4]^− m/z calcd for C_{20}H_{30}B_{18}S_{2}Co, 652.2346; found, 652.2362.

**Compound 4c, Tetrabutylammonium Cobalt(III) Bis-(2,2′,5′,2″-terthiophene-5-o-nido-carborane).** This compound was prepared as described above for the synthesis of 4a, from 3c (0.22 mg, 0.35 mmol), tBuOK (0.23 g, 2 mmol), and anhydrous CoCl_2 (0.27 g, 2 mmol), and was obtained (0.108 g) in 61% yield as a dark yellow solid. ^1^H NMR (acetone-d_6, 250 MHz) δ 7.40–7.43 (2H, m. ArH), 7.25–7.27 (2H, m, ArH), 7.16–7.18 (2H, m, ArH), 7.05–7.08 (4H, m, ArH), 6.81–6.97 (2H, m, ArH), 6.50–6.61 (2H, m, ArH), 3.60 (1H, br s, CH), 3.40–3.47 (8H, m, CH_2), 3.10 (1H, br s, CH), 1.73–1.81 (8H, m, CH_2), 1.50–3.50 (18H, br, BH), 1.37–1.45 (8H, m, CH_2), 0.95–1.00 (12H, m, CH_3). ^13^C NMR (CDCl_3, 100 MHz) 138.1, 137.9, 135.1, 132.5, 127.5, 126.2, 124.8, 123.9, 123.5, 122.7, 68.7, 58.9, 42.6, 24.2, 20.0, 13.6. ^11^B NMR (CDCl_3, 128 MHz, BF_3.OEt_2) δ 9.0–30.0 (br m, max at 5.9, −0.5, −8.8 and −30.8, 18B) ppm. HRMS (ESI) [M-NBu_4]^− m/z calcd for C_{28}H_{34}B_{18}S_{6}Co, 816.2129; found, 816.2115.
6.2.1 Electrochemical Characterizations

Linear potential sweep cyclic voltammetry experiments were performed with an Autolab PGSTAT 20 potentiostat from Eco Chemie B.V., equipped with General Purpose Electrochemical System GPES software (version 4.5 for Windows). The working electrode was a 1 mm diameter platinum or glassy carbon disk (area: \(8 \times 10^{-3} \text{ cm}^2\)) and the counter electrode was a glassy carbon rod. Potentials were relative to the system \(1 \times 10^{-2} \text{ M Ag}^+ | \text{Ag}\) in acetonitrile used as the reference electrode (\(+0.29 \text{ V vs aqueous SCE}\)). All reported potentials are referred to SCE (± 0.01 V). Tetra-\(n\)-butylammonium hexafluorophosphate \(\text{Bu}_4\text{NPF}_6\) was purchased from Fluka (puriss, electrochemical grade) and was used at 0.1 mol L\(^{-1}\) as supporting electrolyte in acetonitrile (anhydrous, analytical grade from SDS). The (CH\(_3\)CN + 0.1 M \(\text{Bu}_4\text{NPF}_6\)) electrolytic medium was dried over activated, neutral alumina (Merck) for 30 min, under stirring, and under argon. Alumina was previously activated at 450 °C under a vacuum for several hours. About 7 mL of this solution was transferred with a syringe into the electrochemical cell prior to experiments. All electrochemical measurements were carried out inside a homemade Faraday cage at room temperature (20 ± 2°C) and under a constant flow of argon.

6.2.2 UV−Visible Spectroelectrochemistry

UV−visible absorption spectra were recorded on a Shimadzu Multispec-1501 spectrophotometer (190–1100 nm scan range) interfaced with a microcomputer for data acquisition and using quartz SUPRASIL cells from Hellma (1 cm pathlength). The polymer films were grown on an indium tin oxide (ITO)-coated glass slide electrode.

6.2.3 Computational Details

Geometry optimizations of \(4a–c\) models in a cisoid conformation were carried out with density functional theory (DFT)\(^{433-434}\) calculations and performed with the hybrid Becke three-parameter exchange functional \(^{435-437}\) and the Lee–Yang–Parr nonlocal correlation functional \(^{438}\).
(B3LYP) implemented in the Gaussian 03 (Revision D.02) program suite using the LanL2DZ basis set and the default convergence criteria implemented in the program. The figures were generated with MOLEKEL 4.3.

6.2.4 Conducting Probe Atomic Force Microscopy (AFM)

Samples of doped and undoped cobaltabisdicarbollide-functionalized polythiophene films were prepared on gold surfaces on glass (EMF Corporation, Ithaca, NY) using controlled potential electropolymerization. The electropolymerization potentials were previously optimized using cyclic voltammetry experiments with millimetric platinum electrodes. The substrates have a gold coating (1000 Å) on a 50 Å layer of Cr formed on glass. Surface characterizations were accomplished in ambient conditions using a model 5500 scanning probe microscope (SPM) equipped with Picoscan v5.3.3 software (Agilent Technologies, Inc., Chandler, AZ). Characterizations of the surface morphology were accomplished using intermittent or tapping mode atomic force microscopy (AFM). Tapping mode AFM images were acquired at a scan rate of 3.0 nm s⁻¹ rastered for 512 lines per frame. Monolithic silicon probes (PPP-NCL) from Nanosensors (Neuchtel, Switzerland) were used for tapping mode experiments, with an average force constant of 48 N m⁻¹ and resonant frequency of 172 kHz. A multipurpose SPM scanner with a scanning area of 11 × 11 μm² was used for imaging, with interchangeable nose cones for either tapping mode or conductive probe AFM experiments. For tapping-mode, the nose cone contains a small piezoceramic chip for tip actuation. For current imaging and $I-V$ measurements, a preamp is integrated within the nose cone. Conductive probe AFM experiments were accomplished using a V-shaped conductive AFM tip (CSC11/Ti-Pt, Micromasch, San Jose, CA) coated with 10 nm Pt layer on a sublayer of 20 nm Ti. All AFM images were processed with free and open source software for data visualization and analysis, Gwyddion (version 2.5) supported by the Czech Metrology Institute (http://gwyddion.net/). Gwyddion is a modular program for
SPM data visualization and analysis. Estimates of surface coverage were obtained with UTHSCA Image Tool. The AFM current images were converted to grayscale bitmaps and a threshold value was selected visually for conversion to black and white pixels. The percentage of colored pixels provided a relative estimate of surface coverage.

6.3 Results and Discussions

6.3.1 Synthesis of Oligothiophene-Disubstituted Cobaltabisdicarbollide Compounds

As shown in Scheme 6.1, compounds 2a–c were synthesized in 53–76% yield from decaborane, ethyl sulfide and the terminal thiynylacetylenes 1a–c. Deboronation of the ortho-carborane cages of 2a–c using nBu₄NF gave the corresponding nido-carborane derivatives 3a–c as the nBu₄N⁺ salts, in almost quantitative yields. The cobalt(III) complexes 4a–c were synthesized in a two-step/one-pot procedure, by mixing tBuOK and Co(OAc)₂ in dimethoxyethane, followed by air oxidation in 61–70% overall yields. The target complexes 4a–c were characterized by NMR and HRMS, which gave the expected isotope pattern distributions.

6.3.2 Electrochemical Characterization of Oligothiophene-Disubstituted Cobaltabisdicarbollides and Corresponding Conducting Polymer Films

Within the investigated potential range −2.0/2.3 V vs SCE, all compounds show redox activity in CH₃CN medium both due to the reversible reduction of Co(III) to Co(II) and to the oxidation of the thiophene rings (Figure 6.1 and Table 6.1). This assignment is consistent with the results of DFT calculations (Figure 6.2) that show a significant metal character in the LUMOs and a major oligothiophene character in the HOMOs of 4a–c. First, the reversible one-electron reduction of Co(III) to Co(II) occurs between −1.2 and −1.0 V vs SCE for the three complexes and unexpectedly gives rise to two closely spaced systems for 4a and 4b and a single broad system for 4c. The values of the formal potential $E^{\circ}$ corresponding to each system are
listed in Table 6.1 and the cyclic voltammogram of 4a is shown in Figure 6.1 as a representative example. The separation between the two formal potentials $\Delta E^{\circ'}$ is found to decrease with increasing the number of thiophene rings linked to the cobaltabis(dicarbollide) moiety. It is obvious that the second system cannot be assigned to the reduction of Co(II) to Co(I), as this process is observed at much more negative potentials, below $-2.0$ V vs SCE. Moreover, the Co(III)/Co(II) process of the unsubstituted cobaltabis(dicarbollide) is characterized by a single reversible wave at $E^{\circ'} = -1.34$ V vs SCE.\textsuperscript{407,449} In the case of our study, the presence of two closely spaced systems is directly connected to the presence of the 2-oligothienyl substituents. Based on our electrochemical data, it can be proposed that the reduction of oligothiénylcobaltabis(dicarbollide) complexes involves two redox conformers, both the relative stability and the proportion of which are strongly dependent on the number of bound thiophene rings (Scheme 6.2). Indeed, from Scheme 6.2, the parameter $\Delta E^{\circ'}$ can be written as a function of the equilibrium constants (eq 1).

$$\text{eq. 1} \quad \Delta E^{\circ'} = \frac{2.3RT}{F} \log \left( \frac{K_{\text{Co(II)}}}{K_{\text{Co(III)}}} \right)$$

Although rotational conformers of nickel-\textsuperscript{408-409,450} and cobalt-bis(dicarbollide) complexes \textsuperscript{451} have been demonstrated by Hawthorne and Teixidor et al. respectively, electrochemical evidence of such systems has not been reported so far, to the best of our knowledge. Further investigations are required in order to define the structure of the redox conformers involved in the reduction of these oligothiénylcobaltabis(dicarbollide) complexes. The LUMOs of 4a–c have an antibonding character between the $d_{xz}$ or $d_{yz}$-type metal atomic orbital and the $p \pi$-type orbitals of the carbon atoms in the two dicarbollide cages. Populating this orbital may then trigger the relative rotation of the cages around the metal towards a more stable redox conformer. In addition, as the length of the oligothiophene substituents increases in 4a–c, the calculated nature of the LUMO becomes
less centered on the metallabisdicarbollide and more delocalized on the oligothiophene substituents. We note that this correlates well with the observed decrease in $\Delta E^{\circ'}$ values in 4a–c, Table 6.1.

![Cyclic (solid line) and differential pulse (dotted line) voltammograms of 4a at 1 × 10$^{-2}$ M in CH$_3$CN + 10$^{-1}$ M Bu$_4$NPF$_6$ (0.1 V s$^{-1}$).](image)

**Figure 6.1** Cyclic (solid line) and differential pulse (dotted line) voltammograms of 4a at 1 × 10$^{-2}$ M in CH$_3$CN + 10$^{-1}$ M Bu$_4$NPF$_6$ (0.1 V s$^{-1}$).

**Table 6.1** Cyclic Voltammetry Data of Oligothienylcobaltabisdicarbollide Complexes at 1 × 10$^{-2}$ M (except for 4c, 5 × 10$^{-3}$ M) in CH$_3$CN + 10$^{-1}$ M Bu$_4$NPF$_6$; Potential Scan Rate = 0.1 V s$^{-1}$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reduction</th>
<th>Oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E^{\circ'}$ / V vs SCE $^a$</td>
<td>$E_{pa}$ / V vs SCE $^b$</td>
</tr>
<tr>
<td>4a</td>
<td>-1.06 (78); -1.19 (83)</td>
<td>1.60 $^5$</td>
</tr>
<tr>
<td>4b</td>
<td>-1.03 (60); -1.12 (60)</td>
<td>1.21 (sh); 1.37; 1.58 (sh); 1.85 (sh); 2.18</td>
</tr>
<tr>
<td>c</td>
<td>-1.07 (114)</td>
<td>0.88; 0.98; 1.24; 1.49; 1.75 (sh)</td>
</tr>
</tbody>
</table>
Average of anodic and cathodic peak potentials; the peak-to-peak separation in mV is indicated between brackets.

Irreversible processes; sh = shoulder.

Figure 6.2 HOMOs and LUMOs of 4a−c from DFT calculations.

Scheme 6.2 Square Scheme Depicting the Different Species Involved in the Reduction of Oligothienylcobaltabisdicarbollide Complexes. \( ^{a} E^{\circ \prime}_{a} \) and \( E^{\circ \prime}_{b} \) are the formal potentials corresponding to the Co(III)/Co(II) couple of the two conformers denoted “a” and “b”, respectively. \( K_{\text{Co(III)}} \) and \( K_{\text{Co(II)}} \) are the related equilibrium constants between the two conformers for the Co(III) and Co(II) forms.
Now, oxidation of these compounds is characterized by a single irreversible peak at ca. 1.6 V vs SCE for 4a (Figure 6.1) and multiple irreversible peaks in the range 1.2–2.2 V and 0.9–1.75 V for 4b and 4c respectively (Figure 6.3A,B). The irreversible nature of anodic electron transfer steps at all investigated potential scan rates (0.02–1 V s\(^{-1}\)) is consistent with the multielectronic oxidation of the 2-oligothienyl rings into reactive radical cation species. Furthermore, the oxidation potentials of these systems are found to decrease in the order 4a > 4b > 4c, in agreement with the lengthening of the linked π-conjugated segment and with the result of DFT calculations (Table 6.1 and Figure 6.2). The electrochemical oxidation of 4b and 4c leads to the formation of conducting polymer deposits on the electrode surface. Such films could be electrogenerated either potentiodynamically or potentiostatically with no significant effect of the electropolymerization method on their respective electrochemical responses.

Representative cyclic voltammograms corresponding to the potentiodynamical electropolymerization of 4b and 4c are shown in Figure 6.3C, D. These are characterized by the regular growth of a new system at less positive potentials. In contrast to the facile electropolymerization of 4b and 4c, 4a does not yield a conducting polymer deposit regardless of the tested experimental conditions (by changing the monomer concentration, the oxidation potential or the solvent). Instead, a poorly electroactive film is electrogenerated, yielding the gradual passivation of the electrode surface. Such a situation has already been encountered in the case of the anodic electrochemistry of other redox-active metallic systems incorporating 2-thienyl units\(^ {452-453}\) and can be explained by the high reactivity of the thiophene radical cation in close proximity of the cobaltabisdicarbollide unit which undergoes a rapid decomposition. DFT calculations indicate that the HOMO of 4a has a mixed and balanced character between a typical organic thiophene contribution, consistent with a possible electropolymerisation, and a bonding
contribution between a $d_{xz}$ or $d_{yz}$-type metal atomic orbital and the $p\pi$-type orbitals of the carbon atoms in the two dicarbollide cages (Figure 6.2)

![Graphs showing cyclic voltammetry](image)

**Figure 6.3** Oxidative cyclic voltammograms of (A) 4b at $1 \times 10^{-2}$ M and (B) 4c at $5 \times 10^{-3}$ M in CH$_3$CN + 0.1 M Bu$_4$NPF$_6$. Potentiodynamical growth of (C) poly(4b) and (D) poly(4c). Potential scan rate: 0.1 V s$^{-1}$.

Removing an electron from such an orbital may explain the decomposition of the cobaltabisdicarbollide bridges in the resulting polymer deposit. Hence, the theoretical data are consistent with the experimental passivation of the electrode with an insulating material after anodic oxidation of 4a. As the length of the oligothiophene substituents increases, in 4b and 4c, the metallic and dicarbollide cage carbon atoms contributions in the HOMO decrease dramatically so that the highest occupied frontier orbitals of 4b and 4c can be considered as almost purely oligothiophene-based. This corroborates the observed electropolymerisation of these oligothiophenes and the stability (through the robustness of the cobaltabisdicarbollide bridges) and conductivity of the resulting polymers based on 4b and 4c.
**Figure 6.4** Electrochemical response of the electrognerated poly(4b) in CH$_3$CN + 0.1 M Bu$_4$NPF$_6$ at 0.1 V s$^{-1}$. The consumed electropolymerization charge is 12.5 (A) and 64 mC cm$^{-2}$ (B). (C) Corresponding $I_{pc}$ vs $v$ plots for the Co(III)/Co(II) process as a function of the film electropolymerization charge. (D) Corresponding log$I_{pa}$ vs log$v$ for the p-doping/undoping process of poly(4b) as a function of the film electropolymerization charge.

Following their electrosynthesis, the electroactive poly(4b) and poly(4c) films are examined in a monomer-free electrolytic medium. First, the electrochemical response of poly(4b) in oxidation is characterized by a broad reversible system at $E^{\circ'} = 0.80$–0.85 V vs SCE corresponding to the p-doping/undoping of the expected quaterthienyl segments (Figure 6.4). The oxidation of sexithienyl segments in poly(4c) is characterized by two quasi-reversible redox
processes at 0.72 and 1.00 V vs SCE (Figure 6.5). To evaluate the mechanism that controls the charge transport in poly(4b) and poly(4c), the anodic peak current intensities $I_{pa}$ corresponding to the p-doping process were plotted as a function of the potential scan rate, $v$, in a logarithmic form. Representative plots are shown in Figure 6.4D for poly(4b) but quite similar plots are also obtained for poly(4c). The values of the slope for thin films are ca. 1.0, as expected for surface-immobilized electroactive species. A decrease in the slope from 1.0 to ca. 0.8 is observed upon increasing the film thickness. Ideally, a slope of 0.5 is obtained for semiinfinite diffusion-controlled process. These results indicate that for thick films the charge transport mechanism in poly(4b) and poly(4c) becomes controlled by the diffusion of electrolyte counterions across the polymer film to ensure the electroneutrality of the material. The doping level $\delta$ of poly(4b) and poly(4c) is estimated respectively at 0.30–0.35 and 0.20–0.25 positive charge per monomer (i.e., quaterthienyl and sexithienyl respectively) unit and is somewhat independent on the film thickness. Compared with unsubstituted polythiophene, the oxidation level of both polymers is much lower, which demonstrates the prominent role of the incorporated cobaltabisdicarbollide center on the ion transport in these films. On the basis of these values of $\delta$, the oxidation/reduction of such polymers is expected to involve the transport of electrolyte cations (in our case, Bu$_4$N$^+$) to neutralize the negative charge of the metallic center, as opposed to the transport of counteranions as commonly observed for the doping of polythiophenes.

Now, we shall turn towards the electrochemical behavior of these polymers when the potential is scanned towards negative potentials. As shown in Figure 6.4A for poly(4b), a perfectly reversible system is observed in reduction at −1.08 V corresponding to the Co(III)/Co(II) couple. For thin films, the peak-to-peak separation and the full width at half-maximum (fwhm) measured at low scan rates (typically 0.05 V s$^{-1}$) are less than 20 mV and ca. 130 mV, respectively.
Figure 6.5 Electrochemical response of the electrogenerated poly(4c) in CH₃CN + 0.1 M Bu₄NPF₆ at 0.1 V s⁻¹. The consumed electropolymerization charge is 25 mC cm⁻².

These values are very close to the theoretically predicted values as a zero peak-to-peak separation and a fwhm of 90 mV are expected for a surface-confined monoelectronic redox center. Consistent with that, the peak currents are found to vary linearly with the potential scan rate \( v \) (Figure 6.4C). Interestingly, upon increasing the film thickness, the system assigned to Co(III)/Co(II) becomes less and less visible and the variation of the electrochemical parameters are all consistent with a decrease in the electron-transfer rate. Indeed, the peak-to-peak separation and the fwhm increase to 130 and >270 mV respectively, and a deviation from linearity is observed in the peak currents vs \( v \) plots. Similar effects of the film thickness on the Co(III)/Co(II) response are obtained for poly(4c). Nevertheless, even in thin films, the Co(III)/Co(II) system is much less reversible than that observed for poly(4b). Indeed, the cathodic step ascribed to the Co(III) reduction is more intense than its related anodic component.
Such intriguing effects of the film thickness on the electroactivity of the surface-confined Co(III)/Co(II) couple have already been reported by others with cobalt salen-based polymers.\textsuperscript{455-456}

It must be kept in mind that the cobalt-centered redox process occurs within a potential range where the oligothienyl units are in their neutral reduced state, i.e., in their electronically insulating state. Consequently, the reduction of Co(III) to Co(II) is expected to occur by electron hopping between cobalt centers down to the electrode surface and involves cation migration through the film in order to ensure the electroneutrality of the material. For thick films, a large amount of cobalt centers within the film are not electrochemically addressable because electrolyte cations cannot migrate up to them. Such mass transport constraints can be explained by the more compact and less rough structure of the reduced polymer compared with the polymer in its oxidized state, as evidenced by their AFM analysis (vide infra).

6.3.3 UV−Visible Spectroscopy Analysis of Polymers

To gain further insight into the electronic properties of cobaltabisdicarbollide-substituted polythiophenes, a UV-vis spectroscopic analysis was performed focusing on the electroactive polymers electrogenerated from 4b and 4c. First, the UV-vis spectrum of compounds 4a–c in CH\textsubscript{2}Cl\textsubscript{2} consists of four absorption bands within 230–500 nm. The two bands at 260–280 nm and 460–500 nm can be ascribed to the cobaltabisdicarbollide center,\textsuperscript{401,405,457} the second less intense one being due to the d–d transition in the Co metal. The bands observed at 250, 325, and 373 nm in the spectra of 4a, 4b, and 4c respectively are assigned to the π−π* transition in the aromatic substituents. However, compared with the unsubstituted parent oligothiophenes,\textsuperscript{458} these bands are red-shifted by ca. 15–25 nm in the metallic complexes. Such features indicate a weak electronic delocalization through through the cobaltabisdicarbollide center. The
electroactive polymers in their neutral form show an absorption maximum for the interband $\pi-\pi^*$ transition at 410 and 448 nm for poly(4b) and poly(4c), respectively (Figure 6.6).

![Figure 6.6](image)

**Figure 6.6** Solid-state UV−vis spectra of (A) poly(4b) and (B) poly(4c) in their doped (solid line) and reduced (dotted line) states.

Expectedly, the polymer incorporating the sexithiophene segments is more conjugated than that with the quaterthiophene segments. Furthermore, poly(4b) and poly(4c) display a more extended degree of conjugation than the parent oligothiophenes as quaterthiophene and sexithiophene show an absorption maximum at 388 and 432 nm, respectively. The magnitude of the red-shift is similar to that observed with the monomers (ca. 20 nm), which accounts for the same electronic influence of the cobaltabisdicarbollide on the conjugated aromatic chain of the polymer. It must be stressed that the presence of the cobaltabisdicarbollide center in the polymer films cannot be evidenced from their optical spectra essentially because of the strong absorbance below 350 nm of the used optically transparent electrode and the very weak intensity of the band at 460–500 nm attributed to the cobalt complex. The as-grown oxidatively doped poly(4b) and poly(4c) films display several new doping-induced bands with maxima at 425, 664, and 738 nm for poly(4b) and 465, 669, 739, and 852 nm for poly(4c) (Figure 6.6). A further broad band attributed to the formation of the so-called “free carrier tail” is also visible in the near IR region above 1100 nm. Similarly to the neutral forms, the bands of p-doped poly(4b) and poly(4c) are red-shifted to approximately the same extent with respect to those of oxidized
quaterthienyl and sexithienyl moieties. 459 The position of these doping-induced bands and the lowly doped character of the as-grown polymers indicate the formation of polaronic charge states along the polymer chain.

6.3.4 Conducting Probe AFM Characterization of the Cobaltabisdicarbollide-Functionalized Polymers

Nanoscale Comparison of Surface Morphologies

Samples of electropolymerized poly(4a–c) films in their doped and undoped forms were characterized using tapping-mode AFM in an ambient environment. Substantial differences are apparent for views of the surface morphology of the polymer films, as presented in Figures 6.7 and 6.8. The surface structures of electropolymerized films and subsequently undoped by electrochemical reduction are shown in Figure 6.7. Undoped poly(4a) exhibits irregular island domains with angular features having lateral dimensions ranging from 0.45 to 2.8 μm. The height of the domains ranges from 100 to 390 nm. The angular domains cover 66% of the surface and the root-mean-square (rms) surface roughness is estimated at 81 nm. A closer view (5 × 5 μm²) reveals that the larger domains are made of segments that are tightly packed to form larger assemblies (Figure 6.7A). Interesting features are observed in the corresponding phase image (Figure 6.7B), in which the groove areas are displayed with a bright yellow color due to saturation. Although results for distinguishing differences in surface chemistry are not conclusive, the phase image is still useful for identifying edges of surface features. The surface of the undoped poly(4b) exhibits isolated globular structures of different sizes (Figure 6.7C). The smooth round domains range from 0.5 to 2.0 μm in lateral dimension and the heights range from 23 to 180 nm. The smooth globular domains cover 23% of the surface and the local surface roughness measures 19 nm. The simultaneously acquired phase image (Figure 6.7D) displays a relatively homogeneous color for the globular domains and flatter areas of the film, which
Figure 6.7 (A, C, E) Tapping-mode AFM topographs and (B, D, F) corresponding phase topographs of (A, B) neutral undoped poly(4a), (C, D) poly(4b), and (E, F) poly(4c). The scan size for all topographs is $5 \times 5 \, \mu\text{m}^2$. 
Figure 6.8 (A, C, E) Tapping-mode AFM topographs and (B, D, F) corresponding phase topographs of as-grown p-doped (A, B) poly(4a), (C, D) poly(4b), and (E, F) poly(4c). The scan size for all topographs is $5 \times 5 \ \mu m^2$. 
indicates a uniform surface composition for the film. The faint dark shadows which outline the round features can be attributed to edge effects as the tapping tip is scanned across the sample. Distinct changes in surface features are evident for the undoped poly(4c) (Figures 6.7E) as compared to the previous samples. The surface is composed of small clusters packed tightly into irregular domains. There are valleys or channels between taller clusters, which range from 120 to 260 nm in depth, with a rms roughness of 71 nm. The diameter of the grains comprising the clusters measures $164 \pm 66$ nm. The phase image exhibits relatively consistent color throughout areas of the surface, except at a few boundary areas of the deeper grooves (Figure 6.7F). Changes in surface composition are not apparent for this phase frame.

A comparison of the surfaces of as-grown p-doped films is shown in Figure 6.8. Irregular islands are evident for poly(4a) (Figure 6.8A) ranging from 0.4 to 2.8 μm in lateral dimensions. The heights of the angular domains range from 100 to 540 nm, with an rms roughness of 91 nm which is not significantly different from that of the undoped sample. For the most part, the surface features of the undoped versus doped poly(4a) samples are indistinguishable. This is not really surprising because of the nonelectroactive character of this polymer in both reduced and oxidized forms, as demonstrated by cyclic voltammetry experiments. Even the phase frames exhibit markedly similar color contrast. The surface features of the doped and undoped films of poly(4b) are found to be slightly different at the nanoscale. Smooth round structures are apparent for doped poly(4b), which range from 0.1 to 1.8 μm in lateral dimensions (Figure 6.8C). The globular domains range from 29 to 320 nm in height, and the rms roughness is more than two times higher than that estimated for the undoped sample, namely 50 nm against 19 nm. At a local level, the round globular areas cover approximately 18% of the surface. More significant morphology changes are evident when comparing the doped and undoped poly(4c) films. The sizes of the nanoclusters and assembled domains have larger dimensions for the doped sample.
(Figure 6.8E). The depth of the channels between taller aggregate domains measures from 68 to 430 nm. The nanoclusters that pack tightly into surface aggregates are slightly larger and have an oval shape which is more elongated for the doped sample. As for poly(4b), the rms surface roughness of doped poly(4c) is also two times higher than that estimated for the undoped sample, namely 170 nm against ca. 70 nm. The phase image (Figure 6.8F) reveals more clearly the arrangement and packing of the round nanoclusters, which are more irregularly shaped and polydisperse in size. The undoped samples exhibit very small, regular shaped features, whereas the domains of the doped sample contain more random sizes and shapes for the nanoclusters. Globally, the AFM analysis of poly(4b) and poly(4c) films shows a more compact and less rough structure of insulating undoped samples compared with conducting doped samples, which is in agreement with electrochemical data of these polymers (vide supra).

**Conducting Probe AFM Characterizations**

For our study, the local conductive properties of the doped cobaltabisdicarbollide-functionalized films were evaluated using conductive probe AFM by measuring the current $I$ flowing through the polymer/gold surface junction in ambient conditions, as a function of the applied voltage $V$. The $I$−$V$ profiles were generated by measuring the current as the voltage was incrementally swept from −3 to +3 V. A comparison of $I$−$V$ profiles plotted for the as-grown doped films is shown in Figure 6.9. Each curve is an average of 12 data sets acquired at different locations of the surface. The differences in the current measured for each polymer can be confidently related to the differences in their conductivity properties because the thickness of the studied polymer films was almost similar (close to 4.0 ± 0.5 μm) and the same contact force was applied to each sample. The $I$−$V$ profile for poly(4a) exhibits no measurable current over the range of applied voltage (±3 V), which is consistent with the insulating character of this film. The profiles for poly(4b) and poly(4c) demonstrate that poly(4c) is more conducting than
poly(4b), which is consistent with the more conjugated character of poly(4c) as determined from optical data. From corresponding semilog plots, it can be evidenced the almost symmetrical character of conduction profiles. Indeed, the rectification factors measured at ±2.0 V are 0.7 and 0.6 for poly(4b) and poly(4c), respectively. The non asymmetry of these curves suggests that poly(4b) and poly(4c) behave like heavily doped semiconductors rather than pure semiconductors for which asymmetrical current responses are usually observed. The mean conductivity of these films was estimated using eq 2

\[ \sigma = \frac{d}{(A_t R)} \]  

where \( \sigma \) is the electron conductivity, \( d \) is the polymer film thickness, and \( R \) is the resistance of the polymer sample, which is equal to the inverse of the slope of the \( I-V \) curve. Because the \( I-V \) curve is not linear, the slope was estimated from the linear fit of the curve. \( A_t \) is the area of the AFM tip in contact with the surface computed as \( A_t = \pi r^2 \), with \( r \approx 35 \) nm, as the contact radius between tip and sample. An average conductivity of \( 1.4 \times 10^{-4} \) S cm\(^{-1}\) and \( 7.5 \times 10^{-4} \) S cm\(^{-1}\) were calculated for poly(4b) and poly(4c), respectively. Such conductivity values well-match those usually reported for other conducting metallopolymers.

Figure 6.9 (A) Current–voltage curves and (B) corresponding semilog plots for as-grown doped poly(4a), poly(4b), and poly(4c), acquired under ambient conditions.
6.4 Electrocatalytic Reduction of Protons at Cobaltabisdicarbollide-Functionalized Polymers

Redox-active metal centers, such as cobalt(III) bisdicarbollide, can provide efficient sites for electrocatalytic experiments at modified electrodes. As a proof-of-concept, we demonstrate that the reduction of protons to dihydrogen can be efficiently electrocatalyzed by the cobalt(II) form of the metal center incorporated in the host polythiophene matrix. As illustrated for the case of poly(4b), the electrochemical response of the bound Co(III)/Co(II) system is dramatically changed upon the addition of H\(^+\) in the electrolytic medium (Figure 6.10A). An increase in the reduction wave of Co(III) to Co(II) is observed, the intensity of which is found to vary linearly with the proton concentration. A simple electrocatalytic mechanism consistent with our data can be written as follows.

**Figure 6.10** (A) Cyclic voltammograms at 0.1 V s\(^{-1}\) of a poly(4b)-coated glassy carbon (1 mm diameter) electrode in CH\(_3\)CN + 0.1 M Bu\(_4\)NPF\(_6\) in the absence (dashed line) and in the presence of 1, 2, 5, 10, 15, and 20 mM HBF\(_4\) (solid lines). The consumed electropolymerization charge is 64 mC cm\(^{-2}\). (Inset) Corresponding \(I_{\text{cat}}\) vs H\(^+\) concentration plot with \(I_{\text{cat}}\), the electrocatalytic current (difference between the reduction currents observed in the presence and in the absence of H\(^+\)) determined at −1.15 V vs SCE. (B) Effect of the poly(4b) thickness on the electrocatalytic reduction of H\(^+\) at 20 mM. The consumed electropolymerization charge is 25 (red), 50 (black), 64 (blue), and 255 mC cm\(^{-2}\) (purple). The dotted line corresponds to the cyclic voltammetry curve obtained at the bare glassy carbon electrode.

Compared with the cyclic voltammogram obtained for the direct reduction of H\(^+\) at the bare glassy carbon electrode, the electrocatalytic effect of the immobilized metal center is evident and leads to a significant shift of the cyclic voltammogram towards less negative
potentials (Figure 6.10B). As commonly observed for catalysis at redox polymer coated electrodes,\textsuperscript{468} the electrocatalytic activity of cobaltabisdicarbollide-functionalized polythiophene films is strongly dependent on the film thickness. For the thinnest films, the increase in the film thickness produces the expected increase of the catalytic current as a result of an increase in the surface coverage of cobalt catalyst. The catalytic effect is maximum for a film electrogenerated with a ca. 50 mC cm\(^{-2}\) charge and decreases dramatically for thicker films. For the latter situation, the catalysis becomes kinetically controlled by the transport of charge and/or the diffusion of the substrate through the film,\textsuperscript{468} which is entirely consistent with the thickness-dependent Co(III)/Co(II) electrochemical response (vide supra).

Analysis of the data reported on Figure 6.10B for the optimum polymer thickness (black curve, 50 mC cm\(^{-2}\) electropolymerization charge) shows that the overpotential for hydrogen evolution is significantly decreased by ca. 230 mV with respect to that obtained with the bare glassy carbon electrode (measured for a current density of 1.4 mA cm\(^{-2}\) in the presence of 20 mM HBF\(_4\)). Despite the improved performance of the optimized modified electrode for proton reduction, the absolute potential for catalysis remains fairly negative (ca. −0.85 V vs. SCE at 1.4 mA cm\(^{-2}\), black curve Figure 6.10B). We note, however, that this potential compares well with
the potential range where most of the synthetic metal complexes hydrogenase mimics that have been reported so far operate (in similar organic electrolytes).\textsuperscript{469}

### 6.5 Concluding Remarks

The electrochemical oxidation of bis(bithienyl) and bis(terthienyl) cobalt(III)bis(dicarbollide) complexes yielded conducting metallopolymers with quaterthienyl and sexithienyl segments, respectively. The electrochemical response of such polymers showed two reversible well-separated redox processes attributed to the Co(III)/Co(II) couple and the $p$-doping of the organic polymer backbone. Although the metal-based process was totally reversible for thin films, a decrease in the rate of electron hopping between the metal centers was observed upon increasing the film thickness. This was consistent with an electron transfer controlled by the diffusion of electrolyte countercations through the film to ensure the electroneutrality. Moreover, the optical data indicated a weak electronic communication between the oligothienyl segments through the cobaltabisdicarbollide bridge. However, the presence of the metallic complex accounted for the lowly doped character of the polymer film and the measured conductivity values below $1 \times 10^{-3}$ S cm$^{-1}$, which are much lower than those commonly found for doped polythiophene films. The electrocatalytic results suggest that conducting polymers containing in chain metallabis(dicarbollide) could find interesting applications as robust and efficient catalysts for the activation of small molecules, and especially for the important $\text{H}^+$/H$_2$ inter-conversion.\textsuperscript{470} So far, little attention has been paid to the catalytic potential of metallabis(dicarbollides), as most catalysis studies have involved the metal dicarbollide fragment as a substitute/alternative to a piano-stool metalloocene framework.\textsuperscript{471} We believe that the present work opens the way for refining this promising new type of electrocatalytic material in terms of the nature of the conducting polymer, length of monomer, nature of the metal, and thickness of polymer. Toward the challenging goal of preparing highly
conducting carborane-based metallopolymers with versatile electrocatalytic properties, other electropolymerizable metallabisdicarbollides with metal cations, such as Fe, Ni, and Cu, will be investigated in order to obtain different overlaps of the electrochemical responses for the metal and the polymer backbone.
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APPENDIX A. LABORATORY PROTOCOL FOR PREPARING ORGANOSILANE NANOPORES ON POLISHED SILICA USING PARTICLE LITHOGRAPHY COMBINED WITH TEMPLATE IMMERSION

Cleaning of silica mesoparticle template

1. Standard dry form Angstromsphere silica powder (Fiber Optic Center, New Bedford, MA) need to be redispersed in solution prior to use as templates for particle lithography.
   a. Measure 10 ml of absolute ethanol using a graduated cylinder.
   b. Transfer into a glass bottle with cover.
   c. Add the previously weighed 0.1 g Silica particles. Cover.
   d. Sonicate for 30 min or longer until all the powder is completely redispersed in solution.
2. The first step is not needed if Silica particles are already suspended in solution, e.g. silica spheres from Thermo scientific.
3. Measure 400 uL of silica particles using a micropipette.
4. Transfer into a plastic centrifuge tube.
5. Add deionized water to about 1 mL.
6. Vortex mix for 2 min or until particles are completely suspended in solution.
7. Centrifuge for 10 min at 20000 rpm. Longer time may be needed for smaller particles.
8. Carefully remove the liquid portion with a Pasteur pipette and discard the liquid.
9. Repeat steps 5-8 twice for complete cleaning of the particles.
10. After the third rinse, measure about 200 uL of ethanol using a micropipette.
11. Add the measured ethanol to the solids left in centrifuge tube. This will be the particle template.
12. Vortex mix. Make sure all particles are uniformly dispersed in the solution.
**Cleaning Si wafer**

It is important that silica substrates must be properly cleaned prior to use. Cleaning with acidic piranha removes any organic residues and facilitates the formation of oxide layer on the surface. Proceed with caution when preparing piranha solution. A solution of piranha is highly energetic and may cause explosion. Use glass, pyrex containers for preparing the solution as piranha will melt plastics. All work must be performed inside the hood and proper protective measures such as gloves and eye goggles must be used. Glasswares must be properly cleaned and dried before use.

1. Cut pieces of silica into 1 x 1 cm$^2$.
2. Clean silica pieces with copious amount of ethanol. Let dry at ambient.
3. Measure 9 mL of sulfuric acid using graduated cylinder and transfer acid into a clean beaker.
4. Using a pipet, measure 3 mL of 30% hydrogen peroxide.
5. Add the measured amount of hydrogen peroxide to the beaker containing sulfuric acid. REMEMBER: Add slowly to avoid violent reaction.
6. Swirl mixture to mix completely.
7. Heat the solution in a hot water bath, keep the water bath temp at around 70$^\circ$C, do not boil the piranha solution.
8. Slowly and individually immerse silica pieces for 30 min. A longer immersion time promotes surface roughening. Make sure silica pieces are separated from each other in the beaker to prevent scratching and for uniform cleaning of substrates.
9. Using a tweezers, remove silica pieces and immediately rinse with copious amount of water.
10. Dry silica using a stream of Argon or Nitrogen gas. Use the substrates immediately. Do not let cleaned silica be exposed to ambient air for a long time since adventitious carbon can immediately deposit on the surface.

Deposition of template particles

1. Measure 20 uL of diluted particle template using a micropipette.
2. Deposit slowly to the center of cleaned silica wafer.
3. Let sample dry in ambient conditions for approximately 2 min.
4. Heat sample in oven for 20 min at 100 ºC.
5. Expose to ambient environment for 20 min. Record the humidity using a humidity meter.

Preparation of alkylsilane solution for immersion

Glasswares used for preparing silane solution need to be completely dried. Even minute amount of water present in the glasswares can make silane polymerized. The polymerized solution appears to have a milky color. The most common solvent used for silane is anhydrous toluene; however, bicyclohexyl also works well.

1. To preserve the integrity of the anhydrous toluene, use a syringe for drawing the solvent out of sure seal bottle by following the outlined steps.
   a. Fill syringe with Nitrogen gas. The volume of the Nitrogen gas should be approximately the same as the needed amount of solvent.
   b. Insert needle into the septum inlet making sure that the needle is above the surface of the liquid.
   c. Push the plunger of syringe to release gas inside the bottle.
2. Using the same syringe, slowly pull back plunger to draw about 5 mL of solvent back into the syringe.
3. Prepare 1% silane solution in anhydrous toluene (5µl silane/5ml solvent).
4. Swirl the solution slowly to ensure complete mixing.
5. Immerse the template into the silane solution for 8h. Cover.

**Rinsing of sample**

1. Using tweezers, carefully remove sample from the solution of silane.
2. Individually rinse each sample with copious amount of deionized water, followed by ethanol.
3. Place the sample in a glass bottle with about 10 mL toluene. Do not crowd the bottle with samples to avoid scratches of samples. Cover the bottle.
4. Sonicate for 30 minutes. Do not let the water in the sonicator get hot. Place ice in the sonicator if water gets warm.
5. Rinse with ethanol, followed by toluene.
6. Sonicate again in fresh toluene for another 30 min or until the template is no longer visible.
7. Rinse with ethanol followed with water.
8. Sample should look like very clean silica. If not, continue sonicating in fresh toluene, and followed by sonication in clean ethanol.
APPENDIX B. LABORATORY PROTOCOL FOR PREPARING NANOGLOBULES OF OCTADECYLTRICHLOROSILANE ON POLISHED SILICA USING PARTICLE LITHOGRAPHY COMBINED WITH TEMPLATE IMMERSION

Cleaning of polystyrene latex mesospheres template

1. Measure 400 uL of polystyrene latex spheres using a micropipette.
2. Transfer into a plastic centrifuge tube.
3. Add deionized water to about 1 mL.
4. Mix sample using a vortex mixer for 2 min or until particles are completely suspended in solution.
5. Centrifuge for 15 min at 20000 rpm. Longer centrifugation time may be needed for smaller particles.
6. Carefully remove the liquid portion with a Pasteur pipette and discard the liquid.
7. Repeat steps 3-6 twice for complete cleaning of the particles.
8. After the third rinse, measure about 100 uL of absolute ethanol water using a micropipette.
9. Add the measured absolute ethanol to the solids left in centrifuge tube. This will be the particle template.
10. Vortex mix. Make sure all particles are uniformly dispersed in the solution.

Cleaning Si wafer

Refer to appendix A for preparation of silica substrates

Deposition of template particles

1. Measure 20 uL of diluted particle template using a micropipette.
2. Deposit slowly to the center of cleaned silica wafer.
3. Expose sample in ambient conditions until dry, approximately 2 min.
4. Heat sample in oven for 30 min at 75 °C.
5. Expose to ambient environment for 30 min. Record the humidity using a humidity meter.

**Preparation of alkylsilane solution for immersion**

Glasswares used for preparing silane solution need to be completely dried. Even minute amount of water present in the glasswares can make silane polymerized. The polymerized solution appears to have a milky color.

1. Prepare 1% octadecyltrichlorosilane (OTS) solution in bicyclohexyl (5µl OTS/5ml solvent).
2. Swirl the solution slowly to ensure complete mixing.
3. Immerse the template into the silane solution for 8h. Cover.

**Rinsing of sample**

Refer to appendix A for rinsing of samples.
APPENDIX C. PROTOCOLS FOR BACKFILLING NANOPORES OF OCTADECYLTRICHLOROSILANE (OTS) FILM WITH CHLOROMETHYLPHENYLTRICHLOROSILANE (CMPS)

1. Clean all glasswares thoroughly.

2. Dry glasswares using a vacuum oven at 120°C to remove all traces of water.

3. Add 5 µL of Chloromethylphenyltrichlorosilane (CMPS) to 5 mL of anhydrous toluene.
   Refer to Appendix A. PREPARATION OF ALKYLSILANE SOLUTION FOR IMMERSION for details.

4. Immerse the sample into the CPS solution for desired time (30 min-24 h).

5. After the immersion step, individually rinse the sample with acetone.

6. Sonicate the sample in chloroform for 2 min four times.

7. Dry in Nitrogen or Argon gas.

8. Store in a close container.
APPENDIX D. VACUUM LINE OPERATION

Make sure the oil on the vacuum pump is on appropriate level before usage.

Preparation of sample for vacuum line deposition

1. Place about 20 μL of the sample for deposition on a quartz glass.
2. Let sample dry at ambient conditions.

Vacuum line operation

1. Open all the valves.
2. Purge the whole vacuum line through the gas inlet with nitrogen gas for about 3 min.
3. The valves are numbered and at the start of the operation should be:
   1 open
   2 close
   3 open
   4 close
   5 close
4. Fill Nitrogen dewar with liquid nitrogen slowly until it is three quarters full.
5. Turn on the vacuum pump.
6. Let the pump run for 15 min.
7. Place the substrate for deposition on the metal plate attached to the sample holder.
8. Cover with quartz glass, side with sample film facing the substrate.
9. Move up the substrate holder by turning the knob slowly so that the substrate is very close but not touching the quartz glass.
10. Open vacuum line to the sample by slowly opening valve 4. The whole system should be in vacuum now.
11. Turn on the digital pressure read out. Drop in pressure should be observed.

12. Place the UV lamp directly on top of quartz glass. Secure the UV lamp with clamps.

13. Cover the areas of the UV lamp that are not in contact with aluminum foil.

14. Monitor the pressure.

15. Refill liquid nitrogen in the dewar when the liquid level drops.

16. Time required for deposition is dependent on the type of sample.
Figure D. 2 UV lamp is placed directly on top of the sample, secured tightly and covered with aluminum foil.

After sample deposition

1. Turn off UV lamp.
2. Remove UV lamp.
4. Slowly fill the vacuum line with Nitrogen while supporting the quartz glass. It will pop out if not handled correctly.
5. Turn off vacuum pump.
APPENDIX E: STANDARD OPERATING PROCEDURE FOR CURRENT SENSING AFM

Current sensing AFM (CS-AFM) or Conductive Probe AFM (CP-AFM) is an advance imaging mode which is use to characterize conductive materials on the surface. The probes used for CSAFM must be coated with a thin film of conducting metal; typical coatings are Platinum, Iridium, Gold. The conductivity of the sample as well as topography and lateral force images are mapped with CSAFM. Consequently, current voltage (IV) plots at a specific location on the sample can be generated with CSAFM. A bias voltage is applied to the sample while the cantilever is kept grounded. A current flow, which is used to map the conductivity of the sample is generated when an applied voltage is applied between the sample and the conductive probe. The CSAFM is operated in contact mode while keeping the force applied to the AFM tip constant.

Figure E.1 Scanner and nose cone assembly for current sensing AFM. The nose cone for current sensing has four pins.

When imaging using CSAFM, surface contamination should be avoided at all times. The presence of water layer on the surface of sample can greatly affect the resolution. It is recommended that CSAFM be performed in a low humidity environment. The environmental
chamber should be kept dry at all times and be closed tightly prior to imaging. A petri dish of drierite is recommended to be placed inside the environmental chamber to help remove moisture.

The nose cone for CSAFM must be properly inserted to the Agilent Multipurpose scanner. The nose cone assembly has a pre-amp that is color coded for sensitivity. Verify the color of the wire on the pre-amp prior to imaging. The existing pre-amp for CSAFM nosecone in the laboratory is green which has a sensitivity of 1 nA/V, bandwidth of 6.3 kHz and resistor of 1 GΩ.

1. Insert a conducting AFM tip and focus the laser.

2. Prepare the sample for mounting on the sample plate. A microscope glass must be placed in between the sample plate and the sample. It is important that the sample must be electrically isolated from the sample plate.

3. Attach a copper wire as an electrode connecting the sample and the sample. Insert the copper wire under the spring loaded electrode clip.

![Diagram of sample plate set-up of current sensing AFM](image)

**Figure E.2** Sample plate set-up of current sensing AFM.
4. Check that the copper wire touches the sample.

5. Check the continuity of the electrical connection by using a conductivity meter.

6. Plug the 3-pin socket of the sample plate to the 3-pin EC connector of the AC/MAC cable.

7. Mount the sample on the AFM microscope.

8. In the PicoScan, choose mode: CSAFM.

9. In the Buffer assignment window, activate topography, friction, deflection and AUX in BNC. The current channel is displayed in AUX in BNC.

10. The operation of CSAFM is the same as the contact mode such as setting set point, I/P gains, scan speed in the servo control window.

11. Approach the sample.

12. After approaching, in the servo control AFM window, enter the bias voltage. The applied bias depends on the conductivity of the sample. (Start with a small voltage first, then increase if no signal is achieved.)

13. The current signal shown in the image channel is a positive which is viewed as high features when a negative bias is applied to the sample.
To acquire current-voltage (I-V) profiles:

1. Pick a certain location in the sample.

2. In the AC Mode Control Window, click sweep.

3. The AFM IV Spectroscopy should appear. If not, go to mode, choose AFM IV Spectroscopy.

4. Select voltage to use by using the slider.

5. Click START.

6. Save the spectra.
7. Multiple spectra can be acquired at several locations on the sample by following the same steps in acquiring the spectra.
APPENDIX F. PICO PLUS TAPPING MODE OPERATING PROCEDURE

A. Mounting the sample and AFM tip.

1. Mount the sample on the Pico Plus sample holder.

2. Inspect that the right nose cone for tapping mode is inserted in the scanner.
   The oscillation of the cantilever is driven by the piezo-electric transducer in the nosecone.
   The nosecone assembly has two contact pins for the signal to be routed to the transducer.

3. Insert nosecone assembly to the scanner using a nose cone removal tool. Do not use a
tweezer to prevent damage to the nose cone.

4. Insert a tapping mode tip on the tip holder.

5. Load the scanner in the system.

6. Load the sample plate.

7. Adjust its distance by pressing open and close in the black head electronics box. Close
   brings the sample closer to the scanner.
6. Make sure that the laser is on by turning the **On** button on the laser box controller.

7. On the desktop, open **UltraTV** so you can view the AFM tip.

8. Focus the laser on the tip of the AFM probe.

9. Adjust the Deflection and LFM so that both values are ‘0’.

**B. AC Mode Software Controls**

1. Open the Picoplus software in the desktop by clicking the PicoScan icon.

2. Under the **Mode** on the main menu, select AC AFM.
3. Under the View on the main menu, select AC Mode Controls, then

4. Check drive on.

5. Enter 5 for the drive %

6. Set the Gain to 1x.

7. Click the Sweep button. The AFM AC mode frequency plot will appear.
8. A full scale scan of the cantilever frequency should be performed.
   
   a. Drag the top frequency slider completely to the right and the bottom frequency slider to the left.
   
   b. Click the **start** button.

The peak obtained corresponds to the resonant frequency of the cantilever.
c. Narrow the resonance peak frequency by adjusting the frequency slider until the resonance peak is centered on the plot.

![Image of a resonance plot]

d. Click the **Start** button for another frequency sweep.

e. Repeat steps 8b-8d until the frequency range is less than 10 kHz and the amplitude is between 3-7.

f. Check the Active check box in the Frequency plot window.

![Image of a frequency plot with Active box checked]

g. Left click on the left side of the peak maximum to get the exact resonance frequency.

h. Adjust the drive frequency to 5 ± 1 Volts.
i. Set the Proportional (P) gain to 0.5 and the integral (I) gain % to 1.000 in the Servo tab of the Servo Control window.

![Servo Control Window](image)

Make sure the Servo Range is set to its maximum value.

9. Ready to approach.

The approach speed should be around 10.

The scan speed should be around 1.0-3.0.

10. Click Approach button. When it has engaged, this message will appear.
11. Adjust the amplitude setpoint below the initial amplitude.

12. Optimize imaging resolution by changing speed, I/P gains and set point.
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Zorabel Escondida Mallorca LeJeune was born in Pigcawayan, North Cotabato, Philippines, to Jessie and Remedios Mallorca. She graduated valedictorian from both Midsayap Pilot Elementary School and Notre Dame of Midsayap for Girls. Zorabel received her Bachelor of Science degree in agricultural chemistry from University of the Philippines Los Baños in 1999. Upon graduation, she joined the Quality Assurance and Chemistry Division of United Laboratories, Inc. In fall 2004, she enrolled in the doctoral program for analytical chemistry at Louisiana State University where she joined the research group of Dr. Jayne C. Garno.

During her graduate years, the LSU Department of Chemistry has given her several recognitions, including the Colgate-Palmolive and Departmental Teaching Scholar Award (2006) and the Outstanding Teaching Award in Analytical Chemistry (2007). For excellence in research, she was awarded the LSU Department of Chemistry Research Scholar in 2008 and Procter and Gamble Research Award in 2009. Her final year at LSU was culminated with James Traynham Distinguished Graduate Student Award.

Zorabel has participated in regional, national and international meetings presenting her research in contributed and invited talks, and poster presentations. To finance her attendance in conferences, she received multiple travel awards including Coates Graduate Award (2009), LSU graduate travel stipend (2006 and 2009), and National Science Foundation (DMR-0630575) Student Travel Award (2006). Her research projects along with her presentation skills garnered best poster awards at conferences both at Pittcon 2010 in Orlando Florida; and at the Society for Applied Spectroscopy (SAS) symposium during the 34th National Meeting, Federation of Analytical Chemistry & Spectroscopy Societies (FACSS 2007) in Memphis, Tennessee.

The degree of Doctor of Philosophy will be conferred to Zorabel at the Fall 2010 Commencement at Louisiana State University, Baton Rouge, Louisiana.