RICE UNIVERSITY

Design, Synthesis, and Testing of Novel Organic Oligomers for Use as Molecular-Scale Electronic Devices

by

Austen Kyle Flatt

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

APPROVED, THESIS COMMITTEE:

James M. Tour,
Chao Professor of Chemistry, Chair

W. Edward Billups,
Professor of Chemistry

Michael S. Wong,
Assistant Professor of Chemical Engineering

HOUSTON, TEXAS

JUNE, 2005
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Volume I of II
For my wife
ABSTRACT

Design, Synthesis, and Testing of Novel Oligomers for use as Molecular-Scale Electronic Devices

By

Austen K. Flatt

Based on rational design principles, diverse arrays of small organic oligomers containing unique electronics structures and redox functionalities have been synthesized for use in molecular-scale electronic device architectures. Thiol terminated oligoanilines were found to exhibit reproducible bistable switching behavior with an on-off ratio of > 10:1 at room temperature when biased between metal electrodes. The synthesis of orthogonally functionalized oligomers has resulted in compounds containing functionalities on one end known to form ordered self-assembled monolayers on metal surfaces while at the other end an intact thioacetate is present whereby self-assembly may again occur after an in situ deprotection for use in NanoCell electronic memories. The NanoCell devices were found to exhibit switching behavior when biased, with a two state memory; however the switching proved to be metallic in nature. Additionally, orthogonally functionalized oligomers allow for the covalent attachment of carbon nanotubes to silicon surfaces for possible uses in sensor and electronic device embodiments. This technique relies on the ability to graft aryldiazonium salts onto a silicon hydride passivated surface followed by diazotization of the terminal aniline. Organic aryltriazenes have been shown to assemble on hydride passivated silicon surfaces by using an in situ diazotization protocol in dilute HF solution. Film thicknesses range from a monolayer to 200 nm depending on conditions. Novel U-shape oligomers have been synthesized to aid in the elucidation of
molecular switching behavior and monolayer film formation using advanced surface characterization techniques. These conformationally restricted oligomers are designed to be of use in studies utilizing scanning probe microscopy techniques to elucidate switching mechanisms and negative differential resistance behavior thought to be based on molecular conformational changes.
Acknowledgements

It is with great anticipation that I begin to compose my Ph.D. thesis, a culmination of the many years I have spent building the foundation upon which to start my professional career. I find it best to catalogue my list of thanks by starting at the beginning. I want to thank the living Lord and my savior Jesus Christ for bestowing the many blessings upon my life which made attaining this degree possible. I thank my parents whose support financially and emotionally would not have permitted me to reach this level of education. I thank my mother for the years she took off work to raise a family, nurture her sons, and introduce me to the world of science. I thank my father for the endless hours of helping me with my math homework at the dining room table when there were certainly more entertaining ways to occupy his time. To my brother, who was my best friend and best competition; you shaped my life like no other. I was so fortunate to share my childhood with you.

My research began at the University of Miami under the watchful eye of professor Nita Lewis, whose time spent teaching me the basics was by far my most valuable asset when I embarked on my graduate career. For two years she explained, re-explained and instilled enough confidence in me to enter the Ph.D. program at Rice under the tutelage of Jim Tour. I thank Mrs. Sofia Medrano-Correra for going the extra mile to make me feel welcome during my initial visit to the Rice chemistry department. Her hospitality and kindness were unmatched at every other institution I visited.

The individual who influenced me the most as an incoming graduate student was Shawn M. Dirk. I am forever indebted to him and the only way I can express my gratitude is by passing on his teaching and encouragement to other first-year graduate
students. I am extremely grateful to have Jacob Ciszek as a friend and teacher as well as to break up the monotony of graduate school with interesting bets on the Astros and college football. I thank Francisco Maya for the scientific discussions and challenges we faced as collaborators and friends. I would like to thank Jared Hudson and Jason Stephenson for the enjoyable conversations, political banter, and computer help. I thank Yasuhiro Shirai and Takashi Sasaki for their friendship and laughter. I thank Michael Stewart and Bo Chen for their work on the surface analysis of many of my compounds. I thank the many collaborators at Penn State, including Dave Allara, Theresa Mayer, Christine McGuiness, Hjalti Skulason, andLintao Cai for their work on the oligoanilines.

I am especially grateful to Professor Tour for his encouragement and confidence in me as a graduate student. His words challenged me to tackle new projects and investigate science beyond my comfort zone. More importantly however, I thank him for the fine example he sets as a Christian, the boldness of his faith, and for re-introducing me to the life of salvation. I thank Christopher J. Gintz for the many heartfelt discussions and business advice. Chris, you took time to nurture my business curiosity, believed in me, and helped me realize my vision of bringing Super C to market.

Finally, I thank my wife Casey. Without her constant love and support I would not have survived my first week as a graduate student. She has made me want to be a better husband, friend, confidant, student, and teacher. I am so fortunate to have you by my side. As we transition from students to married working professionals there is no one else I would rather share my life with.
# Table of Contents

## Volume I

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Title Page</td>
<td>i</td>
</tr>
<tr>
<td>Dedication</td>
<td>iii</td>
</tr>
<tr>
<td>Abstract</td>
<td>iv</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>vi</td>
</tr>
<tr>
<td>Table of Contents</td>
<td>viii</td>
</tr>
<tr>
<td>List of symbols and abbreviations</td>
<td>x</td>
</tr>
<tr>
<td>Preface</td>
<td>xiv</td>
</tr>
</tbody>
</table>

**Chapter 1. Synthesis and Testing of End-Functionalized**

- Oligoanilines for Molecular Electronic Device Candidates 1
- Introduction, Synthesis and Testing, and Summary 2
- Experimental Section 16
- References 43

**Chapter 2. Synthesis and Self-Assembly of Orthogonally**

- Functionalized Oligomers for Molecular Electronics and NanoCell Architectures 46
- Introduction, Synthesis, and Summary 47
- Experimental Section 59
- References 75

**Chapter 3. Synthesis, Self-Assembly, and Monolayer Analysis**

- of Novel Conformationally Restricted U-Shape Oligomers 78
- Introduction, Results, and Summary 79
Experimental Section

References

Chapter 4. Design and Synthesis of Azobenzene Oligo
(Phenylene Ethynylene)s for Potential Molecular Electronic Devices

Introduction, Synthesis, and Summary
Experimental Section
References

Chapter 5. Fabrication of Carbon Nanotube-Molecule-Silicon
Junctions and Molecular Grafting to Silicon Surfaces
in Air Using Organic Triazines as Stable Diazonium Sources and HF as a Constant Hydride-Passivation Source

Introduction, Results, and Conclusions
Experimental Section
References

Volume II
Chapter 1 Spectral Data
Chapter 2 Spectral Data
Chapter 3 Spectral Data
Chapter 4 Spectral Data
Chapter 5 Spectral Data
List of Symbols and Abbreviations

Å       angstrom
Ac      acetyl
Ac₂O    acetic anhydride
AcOH    acetic Acid
AFM     atomic force microscopy
BF₃·OEt₂ boron trifluoride diethyl etherate
BINAP   2,2'-bis-(diphenylphosphino)-1,1'-binaphthyl
Boc     tert-butoxycarbonyl
bp      boiling point
t-BuONO tert-butyl nitrite
°C      degrees Celsius
CaH₂    calcium hydride
calcd   calculated
CH₂Cl₂  dichloromethane
CH₃CN   acetonitrile
cm      centimeter(s)
cm⁻¹    inverse centimeter(s)
CMOS    complementary metal-oxide semiconductor
CV      cyclic voltammetry
CuI     copper(I) iodide
δ       chemical shift in parts per million from tetramethysilane
d       day(s); doublet (spectral)
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>decomp</td>
<td>decomposition</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>equiv</td>
<td>equivalent</td>
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<tr>
<td>Et₂O</td>
<td>diethyl ether</td>
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<tr>
<td>EtOAc</td>
<td>ethyl acetate</td>
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<td>EtOH</td>
<td>ethanol</td>
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<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
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<tr>
<td>g</td>
<td>gram(s)</td>
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<tr>
<td>h</td>
<td>hour(s)</td>
</tr>
<tr>
<td>HBF₄</td>
<td>fluoroboric acid</td>
</tr>
<tr>
<td>HCl</td>
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</tr>
<tr>
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<td>hydrofluoric acid</td>
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<td>H₂SO₄</td>
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<td>HOMO</td>
<td>highest occupied molecular orbital</td>
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<td>high-resolution mass spectrometry</td>
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<td>i-PrOH</td>
<td>2-propanol</td>
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<tr>
<td>IETS</td>
<td>inelastic electron tunneling spectroscopy</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
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<tr>
<td>J</td>
<td>coupling constant (spectral)</td>
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<td>K₂CO₃</td>
<td>potassium carbonate</td>
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<td>Symbol</td>
<td>Definition</td>
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<tr>
<td>KOH</td>
<td>potassium hydroxide</td>
</tr>
<tr>
<td>λ</td>
<td>wavelength</td>
</tr>
<tr>
<td>L</td>
<td>liter(s)</td>
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<tr>
<td>LHMDS</td>
<td>lithium hexamethyldisilazide</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>μ</td>
<td>micro</td>
</tr>
<tr>
<td>m</td>
<td>meter(s); multiplet(spectral)</td>
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<tr>
<td>M</td>
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<td>MHz</td>
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<td>mp</td>
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<td>NaI</td>
<td>sodium iodide</td>
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<tr>
<td>NaOH</td>
<td>sodium hydroxide</td>
</tr>
<tr>
<td>NDR</td>
<td>negative differential resistance</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>ammonium chloride</td>
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<tr>
<td>NH₄F</td>
<td>ammonium fluoride</td>
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<tr>
<td>NH₄OH</td>
<td>ammonium hydroxide</td>
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<tr>
<td>nm</td>
<td>nanometer</td>
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<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Name</td>
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<tr>
<td>--------------</td>
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</tr>
<tr>
<td>OPE</td>
<td>oligo(phenylene ethynylene)</td>
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<td>Pd(dba)$_2$</td>
<td>bis(dibenzylideneacetone)palladium(0)</td>
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<td>PdCl$_2$(PPh$_3$)$_2$</td>
<td>palladium(II)dichloride bis(triphenylphosphine)</td>
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<td>toluene</td>
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<tr>
<td>PPh$_3$</td>
<td>triphenylphosphine</td>
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<td>ppm</td>
<td>parts per million (spectral)</td>
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<tr>
<td>rac</td>
<td>racemic</td>
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<tr>
<td>s</td>
<td>second(s); singlet (spectral)</td>
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<tr>
<td>SAM</td>
<td>self-assembled monolayer</td>
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<tr>
<td>SCE</td>
<td>saturated calomel reference electrode</td>
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<tr>
<td>SDS</td>
<td>sodium dodecylsulfate</td>
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<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
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<tr>
<td>SWE</td>
<td>single wavelength ellipsometry</td>
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<tr>
<td>SWNT</td>
<td>single wall carbon nanotube</td>
</tr>
<tr>
<td>t</td>
<td>triplet (spectral)</td>
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<tr>
<td>TBAF</td>
<td>tetrabutylammonium fluoride</td>
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<td>THF</td>
<td>tetrahydrofuran</td>
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<td>TLC</td>
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<td>TMSA</td>
<td>trimethylsilylacetylene</td>
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<tr>
<td>TMS</td>
<td>trimethylsilyl; tetramethylsilane</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>V</td>
<td>volt</td>
</tr>
<tr>
<td>XPS</td>
<td>x-ray photoelectron spectroscopy</td>
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</tbody>
</table>
Preface

Design, Synthesis, and Testing of Novel Oligomers for use as Molecular-Scale Electronic Devices

By

Austen K. Flatt

Intel co-founder Gordon Moore is credited with the observation that the number of processors on an integrated circuit chip doubles every one and a half years.\(^1\) This statement, commonly referred to as “Moore’s Law” has become commonplace within the electronics industry. As the miniaturization of solid-state silicon circuitry continues in order to increase speed, capacity, and power, a point will be reached at which processors can no longer be made smaller, faster, and cheaper. As a result, the nascent field of molecular electronics is poised to capitalize on the physical and monetary limitations of CMOS technology which prevent the continuation of this trend.\(^2\)

Molecular electronics is seen as a platform technology which uses single organic molecules to mimic the on-off behavior of silicon transistors. The use of organic molecules as electronic devices was first proposed over 30 years ago by Aviram and Ratner,\(^3\) however only recently has molecular electronics been widely accepted among the scientific community by being named “Breakthrough of the Year” in 2001.\(^4\) This acclaim was due, in part, by work done in our group and by our collaborators, on functionalized thioacetate derivatized OPE molecules (Figure 1).
**Figure 1.** Nitro (1) and nitroaniline (2) functionalized OPE derivatives shown to exhibit NDR behavior.

Both the nitro (1) and nitroaniline (2) functionalized OPEs were found to exhibit NDR behavior when positioned between two gold electrodes in Mark Reed's nanopore\textsuperscript{5} solid state test bed (Figure 2).\textsuperscript{6,7} The nanopore devices consist of a 30-50 nm metallic surface where a self-assembled monolayer can form and a top contact metal can be evaporated. The $I(V)$ trace for the nitroaniline OPE (2) at 60 K is shown in Figure 2D. As the device is biased from 0 to 1.7 V, current remains at \~1 pA. However, once the voltage is increased above 1.7 V current rises to over 1 nA. When the voltage is swept past 2.2 V, the current drops to 1 pA resulting in a peak-to-valley ratio of over 1000:1.
Figure 2. Schematics of the nanopore device. (A) Cross section of a silicon wafer with a nanopore etched through a silicon nitride membrane. (B) Au-SAM-Au junction in the pore area. (C) Enlarged view of B with an OPE in the junction. (D) Typical $I(V)$ curve if 2 in the junction.

The proposed mechanism for the observed switching behavior is thought to be due to the nitro functionality in the OPE (Figure 3). As the voltage approaches 1.7 V the molecule was thought to undergo a one-electron reduction and as voltage is swept past 2.2 V a second electron is injected into the molecule. The observed NDR behavior was absent in control studies where unfunctionalized OPE molecules were used. The two
terminal NDR devices here may have several target applications including high
frequency oscillators, mixers, multipliers, and logic devices.

![Diagram]

**Figure 3.** Proposed mechanism for the NDR effect. (A) Ground state of the molecule.
(B) Molecule becomes conductive following a one-electron reduction. (C) Molecule
becomes non-conductive following a second-electron reduction.

The continued advance of molecular electronics is limited primarily by the
inability to individually address billions of tiny molecules in a micron-sized area.
Recently, however, attempts have been made to overcome this difficulty by using
disordered arrays of organic molecules and nanorods. It has been shown theroretically\(^8\)
and experminetally\(^9\) that this approach, termed a NanoCell, is noteworthy. The research
presented in this thesis showcases advances made in the emerging field of molecular
electronics. As we continue to gain a better perspective of how organic molecules
behave when biased, as organic chemists we can tailor our syntheses to reflect this understanding.

Chapter 1 presents the synthesis of end-functionalized oligoanilines for use as molecular electronic devices. These compounds were synthesized to mimic the unique ability of polyaniline to switch between conductive and non-conductive states. The thiol and diazonium salt functionalities allow for a selective method of surface attachment for incorporation into nano-electronic architectures containing metal or semiconductor electrodes. When positioned in a metal-molecule-metal junction, thiol terminated oligoanilines exhibit reproducible bistable switching behavior with an on-off ratio of > 10:1 at room temperature. IETS of the molecular junction demonstrates changes in the vibrational modes of the oligoaniline dimers when the device switches from the low-current state to the high current state at 10 K. Such nanoscale molecular switches are hoped to be embedded into high-density molecular electronic circuits and memory units.

Chapter 2 contains the synthesis and self-assembly data of orthogonally functionalized oligomers for molecular electronics and NanoCell architectures. These compounds are terminated with complementary thiol protecting groups to allow for selective self-assembly. The target compounds contain functionalities on one end known to form ordered self-assembled monolayers on metal surfaces while at the other end an intact thioacetate is present whereby self-assembly may again occur after an in situ deprotection. Self-assembly data is reported for selected compounds to assess efficacy in surface adhesion. This chapter also describes the incorporation of these molecules into
NanoCell molecular electronic architectures⁹ and the resultant electronic switching behavior of these devices.

Chapter 3 describes the synthesis and surface attachment of conformationally restricted U-shape oligomers.¹⁴ The target compounds were synthesized with a 1,8-functionalized anthracenyl or terphenyl head groups to inhibit molecular rotation when biased on a surface using “alligator clips” to promote surface adhesion. The resulting monolayers were studied, and the integrity of the molecule-surface attachment was corroborated by SWE, CV, and XPS. Additionally, the kinetics of SAM formation on a gold electrode was probed by CV, while a clear signal corresponding to the thiol-gold bond was detected by XPS. These conformationally restricted oligomers are designed to be of use in studies utilizing scanning probe microscopy techniques to elucidate switching mechanisms and NDR behavior thought to be based on molecular conformational changes.

Chapter 4 contains the synthesis of azobenzene derivatized OPEs.¹⁵ It has been shown that OPEs containing a redox active aromatic nitro functionality exhibit NDR at various temperatures.⁷ The proposed mechanism is that the redox center contributes to the switching behavior of the molecule.¹⁶ By incorporating an azo functionality into an OPE, an additional redox center is created where switching behavior is likely to be observed. In addition to the redox active site, azobenzenes are known to isomerize between the E and Z conformers when irradiated with light,¹⁷ giving rise to other probable switching mechanisms currently being investigated by other research groups.¹⁸

Chapter 5 presents a hybridization strategy for the covalent attachment of SWNTs to hydride passivated silicon surfaces using an orthogonal bis-diazonium
functionalization protocol. This silicon-nanotube assembly strategy could provide the union of easily patterned silicon with the often hard-to-affix nanotubes thereby providing the basis for directing SWNTs to precise junctions in electronic, optical and sensor arrays. To our knowledge this is the first report of a procedure to covalently attach SWNTs to a silicon surface that does not require a CVD growth process. Also presented is an in situ film assembly procedure using organic triazenes for the formation of Si-molecule assemblies under ambient conditions. Dilute aqueous HF serves as the reagent for the organic conversion (triazene to diazonium) and concomitantly acts as an in situ etchant for Si-O to Si-H conversion, thereby making the reactions possible in air. Most of the triazenes formed thin films, with several forming layers up to 200 nm thick if desired.

References


18. Weiss *et. al.* unpublished results.


Chapter 1

Synthesis and Testing of End-Functionalized Oligoanilines for
Molecular Electronic Device Candidates
1. Introduction

Over the past few decades the semiconductor industry has been able to reduce transistor dimensions according to Moore's law\(^1\) resulting in extremely powerful processors. However, due to the physical imitations of elemental silicon and heat dissipation problems in exceedingly dense processors, barriers to continued miniaturization are being encountered.\(^2\) It was proposed over 30 years ago that single organic molecules several nanometers in length may serve as the next generation of switching and memory devices.\(^3\) Since then, a substantial amount of work in the field of molecular electronics has been performed by our group and others\(^4,\,5,\,6,\,7\) resulting in compounds that function as viable molecular rectifiers, diodes, and even switches that give rise to NDR behavior.\(^9\) This chapter describes the design, synthesis, and testing of oligoaniline-based molecules as a new class of switching and memory type devices designed to mimic the redox behavior of polyaniline.

Polyaniline is known to switch reversibly between numerous redox-active states resulting in dramatic changes in conductivity in a controlled fashion.\(^10\) namely between the conductive emeraldine salt and the three other non-conductive states shown in Figure 1. This reversible oxidative switching behavior has been probed in oligoanilines via solution based electrochemical studies\(^11\) and more recently by Lindsay and co-workers\(^12\) using a hepta-aniline thioacetate functionalized oligomer attached to gold electrodes held under potential control in an electrolyte solution. However this behavior has yet to be corroborated in solid-state devices and exploited for use in higher order molecular electronic devices. It is hoped that these oligoanilines, which are end-functionalized for contacting metal or semiconductor electrodes, will exhibit behavior in the solid phase
similar to that of the bulk polymer giving rise to a potential on-off 'memory-like' effect.\textsuperscript{13}

![Redox schematic of polyaniline.]

**Figure 1.** Redox schematic of polyaniline.

2. Synthesis and Testing

Extensive research on couplings of aryl halides with anilines by Buchwald and Hartwig\textsuperscript{14,15} has facilitated the synthesis of oligoanilines. The present work introduces a new series of oligoanilines for use as potential molecular electronic devices by incorporating a sulfur moiety into the molecule, which allows contact between the molecule and a metal electrode. The target oligomers were synthesized with various groups attached to the nitrogen atoms to help ensure oxidation to the highly conductive emeraldine salt and not to the non-conductive emeraldine base or leuco salt, provided pH is controlled.\textsuperscript{16} Additionally, each nitrogen atom is capable of losing one electron, therefore the structures here could offer multiple independent electronic states. The structures of the thiol derivatized oligoaniline targets 1-5 are shown in Figure 2.
The synthesis of oligomer 1 is shown in Scheme 1. Employing Buchwald's conditions,\textsuperscript{14} \textit{N}-phenyl-\textit{p}-phenylenediamine was coupled to 2-(trimethylsilyl)ethyl-\textit{p}′-bromophenyl sulfide (6),\textsuperscript{17} to afford 7. Due to the harsh coupling conditions, the robust ethyltrimethylsilyl protecting group was employed rather than the more labile thioacetate. Deprotection of the ethyltrimethylsilyl group using tetrabutylammonium fluoride\textsuperscript{17} and quenching with excess 1 M HCl afforded 1 as the free thiol.

\textbf{Scheme 1.} Synthesis of monothiol oligoaniline dimer 1.
The synthesis of oligoaniline 2 (Scheme 2) began by coupling \textit{p}-phenylenediamine to 2-(trimethylsilyl)ethyl-4'-bromophenyl sulfide (6)\textsuperscript{17} to afford the dicoupled product 8. Deprotection of 8 using tetrabutylammonium fluoride followed by quenching with acetyl chloride afforded the dithioacetate oligoaniline dimer 2. Attempts to quench the dithiolate with HCl in order to isolate the dithiol resulted in the formation of a poly(disulfide) mixture. However, quenching with acetyl chloride affords the dithioacetate which can be deprotected in situ and assembled on gold in a manner similar to that used for an aromatic thiol\textsuperscript{18}. Therefore, the thioacetate moieties provide a convenient handle for isolation, particularly when the targets are \(\alpha,\omega\)-difunctionalized, since the aromatic thiols are so prone to oxidative dimerization.

\[ \text{Scheme 2. Synthesis of the dithioacetate oligoaniline dimer 2.} \]

Our attempts to synthesize 3 via deprotection of an ethyltrimethylsilyl protecting group proved ineffective, therefore we used an alternative route as shown in Scheme 3. Coupling \(N\)-phenyl-\(p\)-phenylenediamine with \(p\)-dibromobenzene afforded the desired product 9. Treating 9 with methylithium at \(-78^\circ\text{C}\) followed by the addition of methyl
iodide at $-60 \, ^\circ\text{C}$ afforded intermediate $11$ in excellent yield. Reacting $11$ with tert-butyllithium followed by the addition of sulfur and quenching with acetyl chloride$^{19}$ afforded the thioacetate $13$. Deprotection of the thioacetate under acid conditions afforded the target compound as the free thiol $3$ in excellent yield. We also synthesized the unfunctionalized oligoaniline dimer $10^{20}$ by coupling $N$-phenyl-$p$-phenylenediamine with bromobenzene, as well as the unfunctionalized $N$-methyl dimer $12^{21}$ by treating $10$ with methyllithium and quenching with methyl iodide. $10$ and $12$ were needed for subsequent electrochemical characterization (not shown) as models for surface-bound $3$.

Scheme 3. Synthesis of $N$-methyl oligoaniline dimers.

The $N,N'$-dimethyl dithioacetate dimer $4$ was synthesized in a similar fashion. As shown in Scheme 4, $p$-phenylenediamine was coupled to $p$-dibromobenzene to afford the dicoupled product $14^{22}$. Treating $14$ with methyllithium followed by methyl iodide afforded the dibromo species $15$. Reacting $15$ with tert-butyllithium at $-78 \, ^\circ\text{C}$ followed
by the addition of sulfur and quenching with acetyl chloride gave the dithioacetate 16. Deprotection to the dithiol under acidic condition afforded the target 4 in excellent yield.


The synthesis of the tetramer 5 (Scheme 5) was accomplished by coupling the dibromide 15 with \( N \)-phenyl-\( p \)-phenylenediamine which afforded the monocoupled intermediate. Reacting immediately (to avoid air oxidation to the diiminoquinone) with methyllithium followed by methyl iodide, yielded the monobromo tetramer 17. Treating 17 with tert-butyllithium, then sulfur and acetyl chloride afforded the thioacetate protected compound 5. For electrochemical characterization, the unfunctionalized \( N \)-methyl tetramer 18 was also synthesized by coupling 11 with \( N \)-phenyl-\( p \)-phenylenediamine, followed by treatment with methyllithium and methyl iodide.
Scheme 5. Synthesis of the monothioacetate tetramer 5 and the unfunctionalized tetramer 18.

With the synthesis of the free thiol oligoaniline compounds completed, we sent the molecules to our collaborators at Penn State University (Dave Allara, Theresa Mayer and Thomas Mallouk) for electrical testing. A single molecular monolayer of the \textit{N}-methylated oligoaniline dithiol dimer (4) was integrated into a sub-40 nm diameter metal wire to form an in-wire molecular device. These devices were found to exhibit stable, robust, reversible switching behavior and showed temperature-independent coherent tunneling electron transport through the molecular device. Further, IETS of the molecular junction revealed changes in the vibrational modes of the oligoaniline dimers when the device switched from the low-current state to the high current state at 10 K, allowing us
to conclude that a change in oxidation state of the oligoaniline occurred thus confirming our rationale for synthesizing these systems. On:off ratios were found to be >10:1 at room temperature with device yields over 70%.

Figure 3 shows the Au-SAM(4)-Pd nanowire positioned in the electrical measurement circuit. The nanoscale metal-molecular junctions were fabricated by the template replication of nanowires at a polycarbonate track-etched membrane following a chemical self-assembly of active molecules and a "seeding" procedure with metal nanoparticles for the second metal electrodeposition. The whole process produces approximately $10^{11}$ nanowires with sub-40 nm diameter, similar to previously reported methods.\textsuperscript{24,25} Integration of the nanowires into the circuit was achieved by AC electrofluidic assembly, which aligned and positioned individual nanowires to 100 pairs of Au electrodes defined lithographically on an oxidized silicon wafer.

![Figure 3. Schematic of a Au-SAM(4)-Pd nanowire positioned in the electrical measurement circuit.](image)

Figure 4 shows a typical $I(V)$ curve of a Au-SAM(4)-Pd device exhibiting a reversible and stable switching behavior at room temperature. Starting from 0 V to 1 V, the current shows a stable and nonlinear change with bias (1). When the junction is scanned to a higher voltage, the currents suddenly jump up to higher values once the threshold voltage is reached (2). As the bias returns to 0 V, the device remains in the high
conductivity state (3), and does not drop down to its initial low-current state even if the bias scans again to positive voltage. To restore the molecule to its original state, the bias is swept to more negative values until it reaches the threshold voltage (4). Here, the current suddenly drops to lower values (5). As the bias returns to 0V, the molecule remains in its low-current state (6).

![Figure 4](image)

**Figure 4.** The typical $I(V)$ curves for an Au-SAM(4)-Pd nanowire molecular junction exhibiting a reversible switching behavior. Arrows show voltage sweep directions.

In light of the testing results confirming molecular switching behavior in thiol functionalized oligoanilines, we sought to synthesize diazonium salt functionalized oligoanilines for assembly onto hydride passivated silicon surfaces in an attempt to exploit the electronic switching properties of the organic molecules in silicon based devices. We rationalize that aryldiazonium salt functionalized organic molecules, previously shown to assemble on Si (hydride passivated single crystal or poly Si; $<111>$
or <100>, p-doped, n-doped or intrinsic), GaAs, and Pd surfaces, hold promise as a way to hybridize electronically active organic molecules with the current silicon technology.

The target diazonium salt oligoanilines (19-24) are shown in Figure 5. Compounds 20-24 are electron deficient and the nitrogen atoms are protected with Boc protecting groups to prevent against N-nitroso formation of secondary nitrogen atoms in the presence of a nitrosating agent such as NOBF₄ or t-BuONO. The Boc protecting group is also convenient because of the ability to be thermally removed following film assembly. This will result in the assembled oligoaniline film becoming more similar in structure to polyaniline, having secondary nitrogen atoms along the backbone instead of tertiary. Additionally, during the course of our synthesis, we found electron poor oligoanilines significantly more stable than electron rich oligoanilines which tended to decompose during the diazotization step or decompose upon exposure to oxygen, thus making the Boc protecting group even more useful.

![Figure 5. Diazonium salt functionalized oligoanilines 19-24.](image-url)
The one-step synthesis of the two-ring oligoaniline compound 19 is shown in Scheme 6. Commercially available N-phenyl-p-phenylenediamine was treated with one equivalent of t-BuONO in BF$_3$·OEt$_2$ to give a mixture of the N-nitroso adduct and the desired product which was selectively precipitated to afford 19.


The synthesis of the Boc-protected two-ring oligoaniline diazonium salt 20 is shown in Scheme 7. Aniline was coupled with 1,4-dibromobenzene by employing conditions of Buchwald$^{14}$ to give the monocoupled product 25$^{28}$ which was treated with methyllithium followed by the addition of Boc$_2$O to afford 26. The aryl bromide 26 was then converted to the aniline by reacting 27 with LHMDS$^{29,30}$ followed by removal of the silicon group using TBAF to give 27 which was then diazotized using NOBF$_4$ in acetonitrile to give the target 20.

Scheme 7. Synthesis of compound 20.
Compound 21, containing a nitro group in the 4' position, was synthesized as shown in Scheme 8. The installation of the nitro group provides an additional functionality that can be probed using XPS to further evaluate monolayer formation. 4-Nitroaniline was coupled to 1,4-dibromobenzene to give 28 followed by installation of the Boc protecting group to give 29. Compound 29 was reacted with LHMDS followed by TBAF to give the aniline 30, which was diazotized using t-BuONO in BF₃·OEt₂ to give the desired diazonium salt 21.


With several two-ring oligoaniline diazonium salts in hand, we sought to synthesize longer three-ring systems. Attempts to synthesize these systems with secondary nitrogen atoms (N-hydrogen) were unsuccessful due to the inability to separate multiple N-nitroso side products from the desired compounds. Thus the Boc protecting group was again employed in the synthesis of compound 22 as shown in Scheme 9. Compound 9 was treated with methyllithium followed by Boc₂O to afford 31. Compound 31 was then reacted with LHMDS followed by TBAF to give the aniline 32, which was diazotized using t-BuONO in BF₃·OEt₂ to give the desired diazonium salt 22.

A three-ring oligoaniline diazonium salt with a fluorine atom in the 4' position (23) was synthesized as shown in Scheme 10. 4-Fluoro-1-bromobenzene was coupled to p-phenylenediamine to afford 33 which was further coupled to 1,4-dibromobenzene to give compound 34. Compound 34 was then treated with methyllithium followed by Boc₂O to afford 35. Compound 35 was then reacted with LHMDS followed by TBAF to give the aniline 36, which was diazotized using t-BuONO in BF₃·OEt₂ to give the desired diazonium salt 23.

Scheme 10. Synthesis of diazonium salt 23.
We desired to synthesize a bis-diazonium salt oligoaniline for comparison to the monodiazonium salts. The synthesis of the bis-diazonium salt 24 is shown in Scheme 11. Compound 14 was treated with methyllithium followed by Boc₂O to afford 37. Compound 37 was then reacted with LHMDS followed by TBAF to give the aniline 38, which was diazotized using t-BuONO in BF₃·OEt₂ to give the desired bis-diazonium salt 24.


3. Summary

This chapter presents the synthesis and testing data of end-functionalized oligoanilines. These compounds were designed and synthesized based on the redox behavior of polyaniline to reversibly change between differing conductivity states. When positioned between metal electrodes, thiol terminated oligoanilines give rise to reproducible switching behavior with on-off ratios > 10:1. Diazonium salt functionalized oligoanilines have also been synthesized as a complement to the thiols whereby the protecting groups can be thermally removed following covalent self-assembly on silicon.
surfaces. The diazonium salt oligomers are intended to provide a more convenient and effective way to hybridize molecular electronics to existing silicon technology.

4. Experimental

4.1. Materials and General Procedures. Unless stated otherwise, reactions were performed in oven-dried glassware under a nitrogen atmosphere using freshly distilled solvents. Reagent grade Et<sub>2</sub>O and THF were distilled from sodium benzophenone ketyl. PhMe and TEA were distilled from calcium hydride. Reagent grade n-hexanes, CH<sub>2</sub>Cl<sub>2</sub>, MeOH, EtOH, and EtOAc were used without further distillation. TMSA was donated by FAR Research Inc. All other commercially available reagents were used as received. Unless otherwise noted, reactions were magnetically stirred and monitored by TLC using E. Merck silica gel 60 F<sub>254</sub> precoated plates (0.25-mm). Flash chromatography was performed with the indicated solvent systems using silica gel grade 60 (230-400 mesh). <sup>1</sup>H and <sup>13</sup>C NMR spectra were observed at 400 and 100 MHz, respectively, on a Bruker Avance 400 spectrometer. NMR chemical shifts values for deuterated solvents were followed as reported. FTIR spectra were obtained on a Nicolet Avatar 360 IR. Mass spectroscopy was performed at the Rice University Mass Spectroscopy Laboratory. Melting point values are uncorrected. All new compounds were named using the Beilstein AutoNom application of Beilstein Commander 2000 software.

4.2. General Amination Procedure for the Cross-Coupling of an Aryl Halide and an Aromatic Amine. To an oven dried round bottom flask containing a magnetic stir bar was added the aryl halide, sodium tert-butoxide (1.5 equiv. based on aryl halide), rac-BINAP (4.5 mol %), and Pd(dba)<sub>2</sub> (3 mol %). A rubber septum was affixed and the reaction vessel was evacuated and backfilled with nitrogen (3×). The aniline (if liquid)
and toluene were then added. The reaction was heated at 100 °C until the aryli halide was consumed as determined by TLC. The reaction was allowed to cool to room temperature, absorbed onto silica gel, and purified by flash chromatography.

4.3. 4-(4-Phenylamino-phenylamino)-benzenethiol (1). To a 250 mL round bottom flask containing a magnetic stir bar was added 7 (1.53 g, 3.90mmol) followed by tetrabutylammonium fluoride (39.90 mL of a 1 M solution in THF). The reaction was allowed to stir at room temperature overnight followed by heating to 55 °C for 3 h. The reaction was allowed to cool to room temperature and 50 mL of a 1 M HCl solution was added and allowed to stir for 1 h. The reaction was poured into water, extracted with CH₂Cl₂ (3×), dried with anhydrous MgSO₄, and the solvent was removed in vacuo. Flash chromatography, silica gel (CH₂Cl₂) afforded the product as a white crystalline solid (0.82 g, 72%). mp: 151-160 °C. FTIR (KBr) 3398, 3019, 2400, 1597, 1515, 1425, 1216 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.28 (m, 4H), 7.05 (m, 6H), 6.90 (m, 3H), 5.63 (s, 1H), 5.59 (s, 1H), 3.41 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 144.7, 143.9, 138.0, 137.0, 133.0, 129.8, 121.7, 121.1, 120.6, 118.7, 117.3, 117.0. HRMS calcd for C₁₉H₁₆N₂S: 292.1034. Found: 292.1033.

4.4. Thioacetic acid S-{4-[4-(4-acetysulfanyl-phenylamino)-phenylamino]-phenyl} ester (2). To a 500 mL round bottom flask containing a magnetic stir bar was added 8
(0.43 g, 0.83 mmol). Tetrabutylammonium fluoride (16.5 mL of a 1 M solution in THF) was added and the reaction allowed to stir at room temperature overnight. The next day the reaction was warmed to 55 °C for 3 h. The reaction was cooled to room temperature, acetyl chloride (2.36 mL, 33.01 mmol) was added and allowed to stir for 1 h. The reaction was poured through a silica gel plug and washed with CH₂Cl₂. The solvent was removed in vacuo and flash chromatography, silica gel (CH₂Cl₂) afforded 2 as a yellow solid (0.118 g, 35%). mp: 198-200 °C. FTIR (KBr) 3429, 3019, 2400, 1699, 1595, 1514, 1424, 1215 cm⁻¹. ¹H NMR (400 MHz, (CD₃)₂CO) δ 7.59 (s, 2H), 7.22 (d, J = 8.3 Hz, 4H), 7.20 (s, 4H), 7.07 (d, J = 8.3 Hz, 4H), 2.35 (s, 6H). ¹³C NMR (100 MHz, (CD₃)₂CO) δ 195.4, 147.5, 137.7, 136.8, 122.2, 116.9, 116.2, 29.8. HRMS calcd for C₂₂H₂₀N₂O₂S₂: 408.0966. Found: 408.0961.

4.5. 4-{Methyl-[4-(methyl-phenyl-amino)-phenyl]-amino}-benzenethiol (3). To a 500 mL round bottom flask containing a magnetic stir bar was added 13 (0.40 g, 1.10 mmol). CH₂Cl₂ (20 mL) was added followed by MeOH (20 mL). H₂SO₄ (0.3 mL) was added dropwise and the reaction was allowed to stir at room temperature overnight. The next day the reaction was poured into water, extracted with CH₂Cl₂ (3×), dried with anhydrous MgSO₄ and the solvent was removed in vacuo to afford the title compound as a white crystalline solid (0.34 g, 96%). mp: 102-104 °C. FTIR (KBr) 1593, 1509, 1492, 1340, 1255, 1136 cm⁻¹. ¹H NMR (400 MHz, (CD₃)₂CO) δ 7.22 (m, 4H), 7.03 (s, 4H), 6.95 (m, 2H), 6.83 (m, 3H), 4.01 (s, 1H), 3.29 (s, 3H), 3.26 (s, 3H). ¹³C NMR (100 MHz,
(CD$_3$)$_2$CO) $\delta$ 150.3, 148.8, 145.2, 144.4, 132.2, 129.9, 124.5, 123.8, 120.9, 120.2, 119.5, 119.4, 40.7, 40.6. HRMS calcd for C$_{20}$H$_{20}$N$_2$S: 320.1347. Found: 320.1357.

4.6. $N,N'$-dimethyl-1,4-diamine-benzenethiol (4). To a 500 mL round bottom flask containing a magnetic stir bar was added 16 (0.19 g, 0.43 mmol). CH$_2$Cl$_2$ (20 mL) was added followed by MeOH (10 mL). H$_2$SO$_4$ (0.15 mL) was added dropwise and the reaction was allowed to stir at room temperature overnight. The next day the reaction was poured into water, extracted with CH$_2$Cl$_2$ (3 x), dried with anhydrous MgSO$_4$ and the solvent was removed in vacuo to afford the title compound as a yellow crystalline solid (0.14 g, 92%). mp: 150-153 °C. FTIR (KBr) 1591, 1509, 1492, 1338, 1255, 1137 cm$^{-1}$. $^1$H NMR (500 MHz, (CD$_3$)$_2$CO) $\delta$ 7.22 (d, $J = 8.7$ Hz, 4H), 7.03 (s, 4H), 6.85 (d, $J = 8.7$ Hz, 4H), 4.03 (s, 2H), 3.26 (s, 6H). $^{13}$C NMR (125 MHz, (CD$_3$)$_2$CO) $\delta$ 148.7, 144.7, 132.1, 124.1, 120.6, 119.8, 40.7. HRMS calcd for C$_{20}$H$_{20}$N$_2$S$_2$: 352.1068. Found: 352.1061.

4.7. $N$-(4-thioacetic acid-phenyl)-$N,N'$-Bis[4-methylphenylamino)phenyl]-$N,N'$-dimethyl-1,4-benzenediamine (5). To a 100 mL round bottom flask containing a magnetic stir bar was added 17 (0.23 g, 0.40 mmol). THF (10 mL) was added and the reaction was cooled to -78 °C. tert-Butyllithium (0.47 mL of a 1.7 M solution in
pentane) was added dropwise and the reaction was allowed to stir at -78 °C for 1 h. With a strong back pressure of nitrogen the septum was removed, sulfur powder (0.014 g, 0.44 mmol) was quickly added and the septum replaced. The reaction was warmed to 0 °C and allowed to stir for 15 min. The reaction was recooled to -78 °C and acetyl chloride (0.034 mL, 0.48 mmol) was added and allowed to warm to room temperature overnight. The next day water (50 mL) was added and the organics extracted with CH₂Cl₂ (3×). The organic layer was dried using anhydrous MgSO₄ and the solvent was removed in vacuo. Flash chromatography, silica gel (CH₂Cl₂) afforded 5 as a white solid (0.038 g, 17%). mp: 148-152 °C. FTIR (KBr) 3019, 2400, 1694, 1593, 1499, 1424, 1333, 1216, 1133 cm⁻¹. ¹H NMR (400 MHz, (CD₃)₂CO) δ 7.19 (m, 4H), 7.05 (m, 10H), 6.93 (d, J = 8.7 Hz, 2H), 6.89 (m, 2H), 6.8 (t, J = 6.9 Hz, 1H), 6.75 (d, J = 8.7 Hz, 2H), 3.30 (m, 6H), 3.28 (s, 3H), 3.27 (s, 3H), 2.33 (s, 3H). ¹³C NMR (100 MHz, THF-d₈) δ 194.6, 151.7, 150.7, 148.3, 146.1, 145.8, 144.0, 143.5, 140.7, 136.2, 129.6, 127.7, 125.0, 124.8, 122.3, 121.8, 120.0, 119.1, 118.3, 115.9, 115.4, 40.8, 40.6, 40.6, 29.5. HRMS calcd for C₃₆H₃₆N₄OS: 572.2610. Found: 572.2600.

![](image)

4.8. 2-(Trimethylsilyl)ethyl-4'-bromophenyl sulfide (6). To a screw cap tube was added 4-bromo thiophenol (10.00 g, 52.89 mmol), vinyltrimethylsilane (9.80 mL, 63.47 mmol), and tert-butyl peroxide (1.46 mL, 7.93 mmol) and allowed to stir at 100 °C overnight. The next day the reaction was poured into hexane, washed with water, then 5% NaOH, dried with anhydrous MgSO₄ and the solvent was removed in vacuo. The product was distilled at 0.3 mm Hg at 110-130 °C to afford the title compound as a clear
viscous oil (011.5 g, 75%). $^1$H NMR (400 MHz, (CDCl$_3$) $\delta$ 7.40 (d, $J = 8.6$ Hz, 2H), 7.18 (d, $J = 8.6$ Hz, 2H), 2.94 (m, 2H), 0.93 (m, 2H), 0.05 (s, 9H).

4.9. $N$-Phenyl-$N'$-[4-(2-trimethylsilylanyl-ethylsulfanyl)-phenyl]-benzene-1,4-diamine (7). $N$-Phenyl-$p$-phenylenediamine (1.91 g, 10.37 mmol) was coupled to 6 (3.00 g, 10.37 mmol) following the general amination procedure. The reaction was stirred at 100 °C for 24 h until the starting material was consumed as determined by TLC. Flash chromatography, silica gel (2:1 CH$_2$Cl$_2$/hexanes) afforded 7 as a white solid (3.42 g, 84%). mp: 61-63 °C. FTIR (KBr) 3426, 3018, 2955, 2915, 2400, 1597, 1511, 1492, 1440, 1386, 1302, 1249, 1217, 1179, 1162, 1012 cm$^{-1}$. $^1$H NMR (400 MHz, (CD$_3$)$_2$CO) $\delta$ 7.25 (m, 6H), 7.12 (s, 4H), 7.05 (m, 2H) 7.00 (d, $J = 8.2$ Hz, 2H), 6.79 (t, $J = 6.8$ Hz, 1H), 2.89 (m, 2H), 0.90 (m, 2H), 0.06 (s, 9H). $^{13}$C NMR (100 MHz, (CD$_3$)$_2$CO) $\delta$ 145.5, 145.0, 138.1, 136.9, 133.5, 129.4, 124.8, 121.2, 120.4, 119.5, 116.2, 116.2, 31.8, 17.4, - 2.1. HRMS calcd for C$_{23}$H$_{28}$N$_2$SSi: 392.1742. Found: 392.1741.

4.10. $N,N'$-Bis-[4-(2-trimethylsilylanyl-ethylsulfanyl)-phenyl]-benzene-1,4-diamine (8). $p$-Phenylenediamine (0.34 g, 3.459 mmol) was coupled to 6 (2.00 g, 6.917 mmol) according to the general amination procedure. The reaction mixture was stirred at 100 °C for 24 h until the aryl bromide was consumed as determined by TLC. Flash chromatography, silica gel (2:1 CH$_2$Cl$_2$/hexanes) afforded the dicoupled product as a pink
crystalline solid (1.55 g, 85%). mp: 79-81 °C. FTIR (KBr) 3427, 3019, 2955, 2400, 1595, 1513, 1493, 1422, 1301, 1250, 1215 1180, 1162, 1012 cm⁻¹. ¹H NMR (400 MHz, CD₃CN) δ 7.27 (d, J = 8.2, 4H), 7.07 (s, 4H), 6.95 (d, J = 8.2, 4H), 6.58 (s, 2H), 2.89 (m, 4H), 0.87 (m, 2H), 0.04 (s, 18H). ¹³C NMR (100 MHz, CDCl₃) δ 143.9, 137.4, 133.5, 126.4, 121.5, 117.0, 32.3, 17.7, -1.3. HRMS calcd for C₂₉H₄₀N₂S₂Si₂: 524.2172. Found: 524.2169.

4.11. **N-(4-Bromo-phenyl)-N'-phenyl-benzene-1,4-diamine (9).** *N*-Phenyl-*p*-phenylenediamine (5.00 g, 27.14 mmol) was coupled to *p*-dibromobenzene (6.40 g, 27.14 mmol) according to the general coupling procedure. The reaction mixture was heated at 100 °C for 24 h. Flash chromatography, silica gel (CH₂Cl₂) afforded the desired compound as a white solid (6.52 g, 71%). mp: 119-120 °C. FTIR (KBr) 3427, 3019, 2400, 1596, 1515, 1494, 1303, 1216, 1177, 1074 cm⁻¹. ¹H NMR (400 MHz, (CD₃)₂CO) δ 7.32 (s, 1H), 7.30 (d, J = 8.9 Hz, 2H), 7.23 (s, 1H), 7.20 (m, 2H), 7.10 (m, 4H), 7.04 (m, 2H), 6.96 (d, J = 8.9 Hz, 2H), 6.78 (t, J = 8.9 Hz, 1H). ¹³C NMR (100 MHz, (CD₃)₂CO) δ 146.3, 146.2, 139.4, 137.3, 133.1, 130.4, 122.5, 121.1, 120.5, 118.1, 117.2, 110.7. HRMS calcd for C₁₈H₁₅BrN₂: 338.0419. Found: 338.0417.

4.12. **N,N'-Diphenyl-1,4-phenylenediamine (10).**²⁰ *N*-Phenyl-*p*-phenylenediamine (2.00 g, 10.86 mmol) was coupled to bromobenzene (1.70 g, 10.86 mmol) according to
the general amination procedure. The reaction mixture was stirred at 100 °C for 24 h until the starting material was consumed as determined by TLC. Flash chromatography (silica gel, CH₂Cl₂) afforded the desired compound as a white solid (1.89 g, 67%). \(^1\)H NMR (400 MHz, (CD₃)₂CO) δ 7.18 (m, 4H), 7.14 (s, 2H), 7.10 (s, 4H), 7.02 (m, 4H), 6.76 (t, \(J = 6.8\) Hz, 2H).

![Molecule structure](image)

4.13. \(N\)-(4-Bromo-phenyl)-\(N, N'\)-dimethyl-\(N'\)-phenyl-benzene-1,4-diamine (11). To a 250 mL round bottom flask containing a magnetic stir bar was added 9 (1.50 g, 4.42 mmol). THF (20 mL) was added and the reaction cooled to -78 °C. Methyllithium (11.05 mL of a 1.4 M solution in diethyl ether) was added dropwise and the mixture was allowed to stir at -78 °C for 1 h. The reaction was warmed to -60 °C and methyl iodide (4.11 mL, 66.3 mmol) was added. The mixture was then allowed to warm to room temperature overnight. The next day water (100 mL) was added followed by extraction with CH₂Cl₂ (3x). The organics were dried using anhydrous MgSO₄ and the solvent was removed in vacuo. Flash chromatography (silica gel, 1:1 CH₂Cl₂/hexanes) afforded 11 as a white solid (1.54 g, 95%). mp: 96-97 °C. FTIR (KBr) 3017, 2947, 2882, 2814, 2400, 1594, 1494, 1337, 1255, 1216, 1134, 1118 cm\(^{-1}\). \(^1\)H NMR (400 MHz, (CD₃)₂CO) δ 7.30 (m, 4H), 7.05 (m, 6H), 6.93 (t, \(J = 7.1\) Hz, 1H), 6.80 (d, \(J = 8.9\) Hz, 2H), 3.32 (s, 3H), 3.28 (s, 3H). \(^13\)C NMR (100 MHz, (CD₃)₂CO) δ 149.68, 149.30, 145.91, 142.85, 131.95, 129.51, 125.58, 122.50, 121.15, 119.96, 118.39, 110.43, 40.18, 40.14. HRMS calcd for C₂₀H₁₉N₂Br: 366.0732. Found: 366.0731.
4.14. *N,N'-Dimethyl-N,N'-diphenyl-1,4-benzenediamine* (12).\(^{21}\) To a 500 mL round bottom flask containing a stir bar was added 10 (1.08 g, 4.15 mmol). THF (50 mL) was added and the reaction cooled to -78 °C. Methylithium (10.38 mL of a 1.4 M solution in diethyl ether) was added dropwise and the mixture was allowed to stir at -78 °C for 1 h. The reaction was warmed to -60 °C and methyl iodide (3.86 mL, 62.25 mmol) was added. The mixture was then allowed to warm to room temperature overnight. The next day water (100 mL) was added followed by extraction with CH\(_2\)Cl\(_2\) (3×). The organics were dried using anhydrous MgSO\(_4\) and the solvent was removed in vacuo. Flash chromatography (silica gel, 1:1 CH\(_2\)Cl\(_2/\)hexanes) afforded 12 as a white solid (1.12 g, 94%). \(^1\)H NMR (400 MHz, (CD\(_3\))CN) δ 7.27 (m, 4H), 7.05 (s, 4H), 6.95 (m, 4H), 6.89 (t, \(J = 7.4\) Hz, 2H), 3.28 (s, 6H).

4.15. *Thioacetic acid S-(4-{methyl-[4-(methyl-phenyl-amino)-phenyl]-amino}-phenyl) ester* (13). To an oven dried round bottom flask containing a magnetic stir bar was added 11 (0.80 g, 2.18 mmol). THF (20 mL) was added and the reaction was cooled to -78 °C. *tert*-Butyllithium (2.56 mL of a 1.7 M solution in pentane) was added dropwise and the reaction was allowed to stir at -78 °C for 1 h. With a strong back pressure of nitrogen the septum was removed, sulfur powder (0.014 g, 0.44 mmol) was quickly added, and the septum replaced. The reaction was warmed to 0 °C and allowed
to stir for 15 min. The reaction was recooled to -78 °C and acetyl chloride (0.034 mL, 0.48 mmol) was added. The reaction was allowed to warm to room temperature overnight. The next day water (100 mL) was added and the organics extracted with CH₂Cl₂ (3×). The organic layer was dried using anhydrous MgSO₄ and the solvent was removed in vacuo. Flash chromatography, silica gel (CH₂Cl₂) afforded 13 as a white crystalline solid (0.50 g, 63%). mp: 104-106 °C. FTIR (KBr) 3018, 2943, 2883, 2816, 2400, 1696, 1593, 1497, 1339, 1255, 1216, 1190, 1132 cm⁻¹. \(^1\)H NMR (400 MHz, (CD₃)₂CO) δ 7.29 (m, 2H), 7.19 (d, J = 9.1 Hz, 2H), 7.14 (d, J = 9.1 Hz, 2H), 7.06 (m, 4H), 6.95 (t, J = 7.1 Hz, 1H), 6.81 (d, J = 9.1 Hz, 2H), 3.33 (s, 3H), 3.31 (s, 3H), 2.33 (s, 3H). \(^{13}\)C NMR (100 MHz, (CD₃)₂CO) δ 196.6, 150.8, 149.4, 146.5, 141.8, 135.9, 129.7, 127.0, 121.9, 121.8, 120.8, 115.8, 115.1, 40.8, 40.7, 30.3. HRMS calcd for C₂₂H₂₂N₂O₂S: 362.1454. Found: 362.1453.

\[ \text{\begin{center} \includegraphics[width=0.1\textwidth]{brbb.png} \end{center}} \]

4.16. \( \text{N,N'-Bis-(4-bromo-phenyl)-benzene-1,4-diamine (14).}^{22} \) \( p \)-Phenylenediamine (2.00 g, 18.50 mmol) was coupled to \( p \)-dibromobenzene (8.72 g, 37.00 mmol) following the general coupling procedure. The reaction was stirred at 100 °C for 3 d, cooled to room temperature and filtered through a silica gel plug. The filtrate was collected and the solvent was removed in vacuo. A minimum of CH₂Cl₂ was added to dissolve the remaining solid followed by the addition of hexanes (100 mL). Care was taken to remove only the CH₂Cl₂ in vacuo to afford a gray precipitate which was filtered and washed with hexanes to afford 14 (4.35 g, 56%). \(^1\)H NMR (400 MHz, (CD₃)₂CO) δ 7.38 (s, 2H), 7.31 (d, J = 8.8 Hz, 4H), 7.11 (s, 4H), 6.96 (d, J = 8.8 Hz, 4H).
4.17. *N,N*-Bis-(4-bromo-phenyl)-*N,N*-dimethyl-benzene-1,4-diamine (15). To a 250 mL round bottom flask containing a magnetic stir bar was added 14 (1.84 g, 4.39 mmol). THF (30 mL) was added and the reaction cooled to -78 °C. Methyl lithium (11.0 mL of a 1.4 M solution in diethyl ether) was added dropwise and the mixture was allowed to stir at -78 °C for 1 h. The reaction was warmed to -60 °C and methyl iodide (4.08 mL, 65.85 mmol) was added. The mixture was then allowed to warm to room temperature overnight. The next day water (100 mL) was added followed by extraction with CH₂Cl₂ (3×). The organics were dried using anhydrous MgSO₄ and the solvent was removed in vacuo. The residue was dissolved in a minimum amount of CH₂Cl₂ followed by the addition of hexanes (100 mL). Care was taken to remove the hexanes only in vacuo. The flask was put on ice to precipitate out the product. Filtration followed by washing with hexanes afforded 15 as a gray powder (1.48 g, 75%). mp: 158-160 °C. FTIR (KBr) 3019, 2400, 1588, 1509, 1490, 1335, 1216, 1135 1081 cm⁻¹. ¹H NMR (400 MHz, (CD₃)₂CO) δ 7.35 (d, J = 8.6 Hz, 4H), 7.13 (s, 4H), 6.86 (d, J = 8.6 Hz, 4H), 3.30 (s, 6H). ¹³C NMR (100 MHz, (CD₃)₂CO) δ 149.0, 144.5, 132.1, 124.8, 119.5, 111.3, 40.2. HRMS calcd for C₂₀H₁₈N₂Br₂: 443.9837. Found: 443.9832.

4.18. Thioacetic acid *S*-([4-([4-acetyl sulfanyl-phenyl]-methyl-amino)-phenyl]-methyl-amino)-phenyl] ester (16). To a 100 mL round bottom flask containing a
magnetic stir bar was added 15 (0.50 g, 1.12 mmol). THF (20 mL) was added and the reaction was cooled to -78 °C. tert-Butyllithium (2.63 mL of a 1.7 M solution in pentane) was added dropwise and the reaction was allowed to stir at -78 °C for 1 h. With a strong back pressure of nitrogen the septum was removed, sulfur powder (0.075 g, 2.35 mmol) was quickly added and the septum replaced. The reaction was warmed to 0 °C and allowed to stir for 15 min. The reaction was recooled to -78 °C and acetyl chloride (0.19 mL, 2.68 mmol) was added. The reaction was allowed to warm to room temperature overnight. The next day water (100 mL) was added and the organics extracted with CH₂Cl₂ (3x). The organic layer was dried using anhydrous MgSO₄ and the solvent was removed in vacuo. Flash chromatography, silica gel (CH₂Cl₂) afforded 16 as a pale solid (0.20 g, 41%). mp: 168-170 °C. FTIR (KBr) 3018, 2884, 2817, 2400, 1887, 1694, 1591, 1556, 1495, 1454, 1423, 1337, 1255, 1216, 1191, 1120, 1075 cm⁻¹. ¹H NMR (400 MHz, (CD₃)₂CO) δ 7.23 (m, 8H), 6.92 (d, J=8.9 Hz, 4H), 3.36 (s, 6H), 2.35 (s, 6H). ¹³C NMR (100 MHz, (CD₃)₂CO) δ 194.7, 150.6, 144.8, 136.0, 126.1, 116.8, 116.7, 40.1, 29.3. HRMS calcd for C₂₄H₂₄N₂O₂S₂: 436.1279. Found: 436.1275.

![Chemical Structure](image)

4.19. N-(4-bromophenyl)-N,N'-Bis[4-methylphenylamino]phenyl]-N,N'-dimethyl-1,4-benzenediamine (17). N-Phenyl-p-phenylenediamine (0.23 g, 1.34 mmol) was coupled to 15 (0.46 g, 1.03 mmol) according to the general coupling procedure. The reaction mixture was stirred at 100 °C for 24 h until the aryl bromide was consumed as determined by TLC. The reaction was cooled to room temperature and flash
chromatography (silica gel, 4:1 CH$_2$Cl$_2$/hexanes) afforded the coupled product. Immediately the solid was dissolved in THF (15 mL) and cooled to -78 °C. Methyl lithium (1.17 mL of a 1.4 M solution in diethyl ether) was added dropwise and the mixture was allowed to stir at -78 °C for 1 h. The reaction was warmed to -60 °C and methyl iodide (0.51 mL, 8.19 mmol) was added. The mixture was then allowed to warm to room temperature overnight. The next day water (50 mL) was added followed by extraction with CH$_2$Cl$_2$ (3×). The organics were dried using anhydrous MgSO$_4$ and the solvent was removed in vacuo. The residue was dissolved in a minimum amount of CH$_2$Cl$_2$ followed by the addition of hexanes (100 mL). Care was taken to remove the CH$_2$Cl$_2$ only in vacuo. Filtration followed by washing with hexanes afforded 17 as a white solid (0.244 g, 41%). mp: 173-176 °C. FTIR (KBr) 3019, 2400, 1595, 1504, 1426, 1333, 1216, 1134 cm$^{-1}$. $^1$H NMR (400 MHz, (CD$_3$)$_2$CO) $\delta$ 7.28 (d, $J = 8.6$ Hz, 2H), 7.21 (m, 2H), 7.03 (m, 10H), 6.93 (m, 2H), 6.88 (m, 2H), 6.81 (m, 1H), 6.71 (d, $J = 8.6$ Hz, 2H), 3.28 (m, 12H). $^{13}$C NMR (100 MHz, THF-d$_8$) $\delta$ 148.2, 147.6, 145.2, 143.4, 143.3, 141.3, 141.3, 139.0, 129.8, 127.1, 124.3, 122.5, 122.0, 119.6, 119.5, 117.5, 117.2, 115.7, 115.3, 108.0, 38.3, 38.0, 38.2, 38.1. HRMS calcd for C$_{34}$H$_{35}$BrN$_4$: 576.1889. Found: 576.1887.

4.20. $N,N'$-Bis[4-methylphenylamino]phenyl-$N,N'$-dimethyl-1,4-benzenediamine (18). $N$-Phenyl-$p$-phenylenediamine (0.276 g, 1.50 mmol) was coupled to 11 (0.50 g, 1.36 mmol) according to the general coupling procedure. The reaction mixture was
stirred at 100 °C for 30 h until the aryl bromide was consumed as determined by TLC. The reaction was cooled to room temperature and flash chromatography (silica gel, 4:1 CH₂Cl₂/hexanes) afforded the coupled product. Immediately the solid was dissolved in THF (25 mL) and the solution was cooled to -78 °C. Methyllithium (2.66 mL of a 1.4 M solution in diethyl ether) was added dropwise and the mixture was allowed to stir at -78°C for 1 h. The reaction was warmed to -60 °C and methyl iodide (0.99 mL, 15.94 mmol) was added. The mixture was then allowed to warm to room temperature overnight. The next day water (50 mL) was added followed by extraction with CH₂Cl₂ (3×). The organics were dried using anhydrous MgSO₄ and the solvent was removed in vacuo. The residue was dissolved in a minimum amount of CH₂Cl₂ followed by the addition of hexanes (100 mL). Care was taken to remove the hexanes only in vacuo. Filtration followed by washing with hexanes afforded 18 as a white solid (0.40 g, 62%). mp: 208-210 °C. FTIR (KBr) 3019, 2400, 1597, 1504, 1333, 1216, 1134 cm⁻¹. ¹H NMR (500 MHz, THF-d₈) δ 7.12 (t, J = 9.9 Hz, 4H), 6.96 (m, 8H), 6.89 (d, J = 9.9 Hz, 4H), 6.81 (d, J = 9.9 Hz, 4H), 6.72 (t, J = 9.9 Hz, 2H), 3.25 (s, 6H), 3.23 (s, 6H). ¹³C NMR (100 MHz, THF-d₈) δ 148.3, 143.9, 142.3, 140.7, 127.1, 122.8, 120.5, 118.5, 117.1, 115.2, 38.4, 38.1. HRMS calcd for C₃₄H₃₄N₄: 498.2783. Found: 498.2791.

![Image](image_url)

4.21. 4-Phenylamino-benzenediazonium tetrafluoroborate (19). To a 250 mL round bottom flask was added N-phenyl-p-phenylenediamine (1.00 g, 5.43 mmol). THF (30 mL) was added and cooled to -50 °C. BF₃•OEt₂ (2.75 mL, 21.72 mmol) was added dropwise followed by the dropwise addition of t-BuONO (0.86 mL, 6.52 mmol) in THF
(5 mL). The reaction was allowed to warm to \(-10 \, ^\circ C\) at which point \(\text{Et}_2\text{O} (150 \, \text{mL})\) was added. The suspension was allowed to stir for 10 min. The precipitated solid was collected by vacuum filtration to afford a mixture of 19 and the \(N\)-nitroso adduct. The collected solid was dissolved in a minimum of \(\text{CH}_3\text{CN} (10 \, \text{mL})\) and \(\text{Et}_2\text{O} (150 \, \text{mL})\) was added. The green solid was collected by vacuum filtration to afford the title compound as a light green solid (0.31 g, 20%). FTIR (KBr) 2244, 2186, 1603, 1579, 1531, 1493, 1366, 1323, 1112 cm\(^{-1}\). \(^1\)H NMR (400 MHz, \((\text{CD}_3\text{CN})\) \(\delta\) 8.80 (s, 1H), 8.06 (d, \(J = 9.5 \, \text{Hz}, 2\text{H}), 7.50 \, (m, 2\text{H}), 7.35 \, (m, 3\text{H}), 7.10 \, (d, \(J = 9.5 \, \text{Hz}, 2\text{H}). \(^{13}\)C NMR (100 MHz, \((\text{CD}_3\text{CN})\) \(\delta\) 156.5, 137.3, 135.3, 130.5, 127.8, 124.5, 116.2, 92.6.

\[ \text{Boc} \quad \begin{array}{c} \text{N} \\ \text{Ph} \end{array} \quad \begin{array}{c} \text{N} \\ \text{Ph} \quad \text{BF}_4^- \end{array} \]

4.22. \textit{4-}-(\textit{tert-}Butyloxycarbonyl-phenyl-amino)-benzenediazonium tetrafluoroborate (20). To a 100 mL round bottom was added NOBF\(_4\) (0.07 mL, 0.55 mmol) in a nitrogen filled glove box. A septum was added and the flask was removed from the glove box. \(\text{CH}_3\text{CN} (5 \, \text{mL})\) was added and cooled to \(-40 \, ^\circ C\). Compound 27 (0.15 g, 0.53 mmol) was added to a small vial under nitrogen atmosphere and dissolved in \(\text{CH}_3\text{CN} (5 \, \text{mL})\). The aniline was added dropwise to the NOBF\(_4\) solution. Following addition, the solution was stirred at \(-40 \, ^\circ C\) for 20 minutes, then allowed to warm to room temperature. \(\text{Et}_2\text{O} (50 \, \text{mL})\) was added to precipitate the diazonium salt. The solid was collected by vacuum filtration to afford the desired product as a shiny white solid (0.09 g, 46%). FTIR (KBr) 2982, 2267, 1723, 1577, 1494, 1370, 1327, 1309, 1278, 1253, 1167, 1101, 1057 cm\(^{-1}\). \(^1\)H NMR (400 MHz, \((\text{CD}_3)_2\text{CO})\) \(\delta\) 8.68 (d, \(J = 9.5 \, \text{Hz}, 2\text{H}), 7.80 \, (d, \(J = 9.5 \, \text{Hz}, 2\text{H}, 7.56
(m, 2H), 7.51 (m, 1H), 7.40 (m, 2H), 1.49 (s, 9H). $^{13}$C NMR (100 MHz, (CD$_3$)$_2$CO) δ 155.4, 153.0, 141.3, 134.9, 131.0, 129.54, 129.47, 124.7, 105.7, 84.4, 28.0.

4.23. 4-[ tert-Butoxycarbonyl-(4-nitro-phenyl)-amino]-benzenediazonium tetrafluoroborate (21). To a 250 mL round bottom was added BF$_3$·OEt$_2$ (0.10 mL, 0.82 mmol) and cooled to −40 °C. Compound 30 (0.09 g, 0.27 mmol) dissolved in THF (3.0 mL) was added dropwise. Following addition, t-BuONO (0.06 mL, 0.54 mmol) was added dropwise to the reaction mixture and allowed to warm to room temperature. Et$_2$O (100 mL) was added to precipitate the diazonium salt. The solid was collected by vacuum filtration to afford the desired product as pale solid (0.09 g, 78%). FTIR (KBr) 2262, 1735, 1574, 1523, 1344, 1315, 1275, 1252, 1153, 1085 cm$^{-1}$. $^1$H NMR (500 MHz, (CD$_3$)$_2$CO) δ 8.75 (d, $J = 9.5$ Hz, 2H), 8.41 (d, $J = 9.1$ Hz, 2H), 7.89 (d, $J = 9.5$ Hz, 2H), 7.75 (d, $J = 9.1$ Hz, 2H), 1.47 (s, 9H). $^{13}$C NMR (125 MHz, (CD$_3$)$_2$CO) δ 154.5, 152.2, 148.1, 147.2, 135.0, 130.8, 126.14, 126.07, 107.7, 85.3, 27.9.

4.24. 4-[ tert-Butoxycarbonyl-[4-( tert-Butoxycarbonyl-phenyl-amino)-phenyl]-amino]-benzenediazonium tetrafluoroborate (22). To a 250 mL round bottom flask was added BF$_3$·OEt$_2$ (0.10 mL, 0.76 mmol) and cooled to −40 °C. 33 (0.12 g, 0.25 mmol) in THF (5 mL) was added dropwise. t-BuONO (0.06 mL, 0.51 mmol) was added dropwise to the reaction mixture and allowed to warm to room temperature. Et$_2$O (150
mL) was added to precipitate the diazonium salt. The solid was collected by vacuum filtration to afford the desired compound as a white solid (0.03 g, 21%). FTIR (KBr) 2978, 2280, 1737, 1716, 1579, 1509, 1371, 1338, 1322, 1271, 1252, 1164, 1085, 1055 cm\(^{-1}\). \(^1\)H NMR (500 MHz, (CD\(_3\))\(_2\)CO) \(\delta\) 8.69 (d, \(J = 9.5\) Hz, 2H), 7.84 (d, \(J = 9.5\) Hz, 2H), 7.39 (m, 6H), 7.29 (m, 2H), 1.44 (s, 18H). \(^13\)C NMR (125 MHz, (CD\(_3\))\(_2\)CO) \(\delta\) 155.4, 153.9, 152.9, 144.5, 143.8, 138.0, 135.0, 129.8, 129.7, 128.8, 128.3, 127.0, 124.8, 105.7, 84.5, 81.6, 28.3, 28.0.

![Structure](image)

4.25. \(4\)-(tert-Butyloxycarbonyl-\{4-(tert-Butyloxycarbonyl-(4-fluoro-phenyl)-amino)-(phenyl)-amino\}-benzenediazonium tetrafluoroborate (23). To a 250 mL round bottom flask was added BF\(_3\)OEt\(_2\) (0.05 mL, 0.37 mmol) and cooled to \(-40^\circ\)C. 37 (0.06 g, 0.12 mmol) in THF (5 mL) was added dropwise. \(t\)-BuONO (0.03 mL, 0.24 mmol) was added dropwise to the reaction mixture and allowed to warm to room temperature. Et\(_2\)O (200 mL) was added to precipitate the diazonium salt. The solid was collected by vacuum filtration to afford the desired compound as a light green solid (0.06 g, 84%). FTIR (KBr) 2901, 1615, 1506, 1430, 1372, 1318, 1163, 1113, 1059, 1033 cm\(^{-1}\). \(^1\)H NMR (500 MHz, (CD\(_3\))\(_2\)CO) \(\delta\) 8.68 (d, \(J = 9.5\) Hz, 2H), 7.83 (d, \(J = 9.5\) Hz. 2H), 7.44 (d, \(J = 8.8\) Hz, 2H), 7.35 (m, 4H), 7.17 (m, 2H), 1.44 (s, 18H). \(^13\)C NMR (125 MHz, (CD\(_3\))\(_2\)CO) \(\delta\) 155.4, 153.8, 152.9, 144.3, 140.0, 138.1, 134.9, 130.4, 130.3, 129.7, 128.6, 124.8, 116.5, 116.4, 105.8, 84.5, 81.8, 28.3, 28.0.
4.26. [4-(tert-Butyloxycarbonyl-phenyl-amino)-phenyl]-phenyl-carbamic acid-4,4′-tert-buty1 ester benzenediazonium tetrafluoroborate (24). In a nitrogen filled glove box was added NOBF₄ (0.04 g, 0.34 mmol). A septum was added and the flask was removed. CH₃CN (9 mL) and sulfolane (1 mL) were added and cooled to −30 °C. To a separate 100 mL round bottom was added 28 (0.08 g, 0.16 mmol) dissolved in sulfolane (16 mL) and CH₃CN (2 mL). The aniline solution was added dropwise to the NOBF₄ dropwise and allowed to stir at −30 °C for 30 minutes. The reaction was warmed to 0 °C and Et₂O (25 mL) was added. The formed precipitate was collected by vacuum filtration to afford the desired product as an orange/brown solid (0.07 g, 63%). FTIR (KBr) 2977, 2274, 2224, 2166, 1729, 1578, 1508, 1370, 1313, 1109 cm⁻¹. ¹H NMR (400 MHz, (CD₃)₂CO) δ 8.69 (d, J = 9.6 Hz, 4H), 7.93 (d, J = 9.6 Hz. 4H), 7.62 (s, 4H), 1.48 (s, 18H). Attempts to acquire ¹³C NMR spectral information were unsuccessful due to the instability of compound 24 in solution for extended time periods.

4.27. (4-Bromo-phenyl)-phenyl-amine (25).²⁸ Aniline (7.00 g, 75.16 mmol) was coupled to bromobenzene (19.51 g, 82.68 mmol) according to the general amination procedure. The reaction mixture was stirred at 100 °C for 24 h until the starting material was consumed as determined by TLC. Flash chromatography, silica gel hexane/CH₂Cl₂ (1:1) afforded the desired compound as a white solid (13.47 g, 72%). ¹H NMR (400
MHz, (CD$_3$)$_2$CO) δ 7.51 (s, 1H), 7.36 (d, $J = 9.0$ Hz, 2H), 7.25 (m, 2H), 7.12 (m, 2H), 7.06 (m, 2H), 7.90 (m, 1H).

4.28. (4-Bromo-phenyl)-phenyl-carbamic acid tert-butyl ester (26). To a 250 mL round bottom flask containing a magnetic stir bar was added 25 (10.00 g, 40.14 mmol). THF (100 mL) was added and the reaction cooled to -78 °C. Methylthium (34.41 mL of a 1.4 M solution in diethyl ether) was added dropwise and the mixture was allowed to stir at -78 °C for 45 min. Boc$_2$O (13.14 g, 60.21 mmol) was added dissolved in THF (10 mL). The mixture was allowed to warm to room temperature. Water (100 mL) was added followed by extraction with CH$_2$Cl$_2$ (3×). The organics were dried using anhydrous MgSO$_4$ and the solvent was removed in vacuo. Column chromatography, silica gel CH$_2$Cl$_2$/hexanes (3:2) was attempted several times to remove excess Boc$_2$O from the product without success. Kugelrohr distillation at 0.2 mm Hg at 80 °C was used to remove additional Boc$_2$O. Complete Boc$_2$O removal (~80% pure) was not possible and the material was used without further purification (13.00 g, 93%). An analytical sample was prepared for characterization. mp: 82-84 °C. FTIR (KBr) 2978, 1711, 1491, 1369, 1338, 1316, 1292, 1279, 1254, 1162 cm$^{-1}$. $^1$H NMR (400 MHz, (CD$_3$)$_2$CO) δ 7.51 (d, $J = 8.9$ Hz, 2H), 7.36 (m, 2H), 7.24 (m, 3H), 7.20 (d, $J = 8.9$ Hz, 2H), 1.42 (s, 9H), 7.90. $^{13}$C NMR (100 MHz, (CD$_3$)$_2$CO) δ 153.8, 143.8, 143.7, 132.5, 129.7, 129.6, 128.2, 126.9, 119.0, 81.5, 28.3. HRMS calcd for C$_{17}$H$_{18}$BrNO$_2$: 347.0521. Found: 347.0523.
4.29. (4-Amino-phenyl)-phenyl-carbamic acid tert-butyl ester (27). To a 100 mL round bottom flask was added 26 (2.00 g, 5.74 mmol), P(t-Bu)₃ (0.06 g, 0.29 mmol), Pd(dba)₂ (0.17 g, 0.29 mmol), LHMDS (6.89 mL of a 1 M solution in THF) and toluene (5 mL). The reaction was stirred at room temperature overnight. The next day TBAF (6.89 mL of a 1 M solution in THF) was added to the reaction and allowed to stir 24 h. The reaction was poured into water, extracted with CH₂Cl₂, dried using MgSO₄, filtered, and concentrated. Column chromatography, silica gel, EtOAc/hexane (1:1) afforded the product as a white solid (1.00 g, 61%). mp: 144-149 °C. FTIR (KBr) 3444, 3356, 2982, 1685, 1628, 1595, 1518, 1491, 1358, 1307, 1163, 1057 cm⁻¹. ¹H NMR (400 MHz, (CD₃)₂CO) δ 7.25 (m, 4H), 7.11 (m, 1H), 6.91 (d, J = 8.6 Hz, 2H), 6.63 (d, J = 8.6 Hz, 2H), 4.66 (s, 2H), 1.40 (s, 9H). ¹³C NMR (100 MHz, (CD₃)₂CO) δ 154.1, 147.2, 144.6, 133.1, 128.8, 128.6, 126.5, 125.0, 114.6, 79.9, 27.9. HRMS calcd for C₁₇H₂₀N₂O₂: 284.1525. Found: 284.1522.

4.30. (4-Bromo-phenyl)-(4-nitro-phenyl)-amine (28). Following the general amination procedure 4-nitroaniline (2.00 g, 14.5 mmol) was coupled to p-dibromobenzene (5.12 g, 21.7 mmol) using K₂PO₄ (6.15 g, 29.0 mmol), rac-BINAP (0.45 g, 0.7 mmol), Pd(dba)₂ (0.42 g, 0.7 mmol) and toluene (50 mL). Column chromatography, silica gel (CH₂Cl₂) afforded the desired product as an orange powder (2.00 g, 47%). mp: 153-156 °C. FTIR
(KBr) 3314, 1606, 1580, 1530, 1484, 1331, 1291, 1110 cm\(^{-1}\). ¹H NMR (400 MHz, (CD\(_3\))\(_2\)CO) δ 8.48 (s, 1H), 8.13 (d, \(J = 9.3\) Hz, 2H), 7.54 (d, \(J = 9.3\) Hz, 2H), 7.27 (d, \(J = 6.8\) Hz, 2H), 7.16 (d, \(J = 6.8\) Hz, 2H). ¹³C NMR (100 MHz, (CD\(_3\))\(_2\)CO) δ 150.5, 140.3, 139.9, 132.7, 126.1, 122.9, 115.5, 114.4. HRMS calcd for C\(_{12}\)H\(_9\)BrN\(_2\)O\(_2\): 291.9848. Found: 291.9844.

4.31. (4-Bromo-phenyl)-(4-nitro-phenyl)-carbamic acid tert-butyl ester (29). To a 250 mL round bottom flask was added 28 (0.65 g, 2.20 mmol), KO-t-Bu (1.04 g, 9.24 mmol), Boc\(_2\)O (4.35 g, 19.94 mmol) and THF (100 mL). A reflux condenser was added and heated to reflux for 4 h. The reaction was cooled to room temperature, poured into H\(_2\)O and extracted with CH\(_2\)Cl\(_2\) (3×). The organics were combined, dried using Mg SO\(_4\) and concentrated. Column chromatography, silica gel CH\(_2\)Cl\(_2\) followed by a second column, silica gel CH\(_2\)Cl\(_2\)/hexane (1:1) gave the desired product as a yellow oil (0.55 g, 64%). FTIR (KBr) 1719, 1594, 1518, 1489, 1343, 1315, 1290, 1254, 1156 cm\(^{-1}\). ¹H NMR (400 MHz, (CD\(_3\))\(_2\)CO) δ 8.20 (d, \(J = 9.1\) Hz, 2H), 7.61 (d, \(J = 8.5\) Hz, 2H), 7.49 (d, \(J = 9.1\) Hz, 2H), 7.27 (d, \(J = 8.5\) Hz, 2H), 1.45 (s, 9H). ¹³C NMR (100 MHz, (CD\(_3\))\(_2\)CO) δ 152.7, 149.2, 144.6, 141.9, 132.7, 130.5, 126.2, 124.4, 120.4, 82.4, 27.7. HRMS calcd for C\(_{17}\)H\(_{17}\)BrN\(_2\)O\(_4\): 392.0372. Found: 392.0379.

4.32. N-Methyl-N-(4-nitro-phenyl)-benzene-1,4-diamine (30). To a 250 mL round
bottom flask was added 29 (0.53 g, 1.35 mmol), P(\text{-Bu})_3 (0.01 g, 0.07 mmol), Pd(dba)_2 (0.04 g, 0.07 mmol), LHMDS (1.62 mL of a 1 M solution in THF) and toluene (10 mL). The reaction was stirred at room temperature overnight. The next day TBAF (2.70 mL of a 1 M solution in THF) was added to the reaction and allowed to stir 24 h. The reaction was poured into water, extracted with CH_2Cl_2, dried using MgSO_4, and concentrated. Column chromatography, silica gel, CH_2Cl_2 afforded the product as a yellow oil (0.33 g, 74%). mp: 55-58 °C. FTIR (KBr) 3369, 1708, 1592, 1514, 1305, 1253, 1155 cm\(^{-1}\). \(^1\)H NMR (500 MHz, (CD_3)_2CO) \(\delta\) 8.15 (d, \(J = 9.4\) Hz, 2H), 7.48 (d, \(J = 9.4\) Hz, 2H), 6.94 (d, \(J = 8.6\) Hz, 2H), 6.72 (d, \(J = 8.6\) Hz, 2H), 4.86 (s, 2H), 1.43 (s, 9H). \(^{13}\)C NMR (125 MHz, (CD_3)_2CO) \(\delta\) 153.6, 150.5, 148.3, 143.5, 131.2, 129.4, 124.5, 124.1, 115.0, 81.4, 27.8. HRMS calcd for C_{17}H_{19}N_3O_4: 329.1376. Found: 329.1383.

![Chemical Structure](image)

4.33. \{4-[(4-Bromo-phenyl)-tert-butoxycarbonyl-amino]-phenyl\}-phenyl-carbamic acid tert-butyl ester (31). To a 500 mL round bottom flask containing a magnetic stir bar was added 9 (1.33 g, 3.92 mmol). THF (50 mL) was added and the reaction cooled to -7 8°C. Methylthiium (9.80 mL of a 1.4 M solution in diethyl ether) was added dropwise and the mixture was allowed to stir at -78 °C for 45 min. Boc_2O (5.13 g, 23.52 mmol) was added dissolved in THF (10 mL). The mixture was allowed to warm to room temperature. Water (100 mL) was added followed by extraction with CH_2Cl_2 (3×). The organics were dried using anhydrous MgSO_4 and the solvent was removed in vacuo. Column chromatography, silica gel CH_2Cl_2 afforded the product as a white crystalline solid (1.62 g, 77%). mp: 138-140 °C. FTIR (KBr) 2969, 1712, 1512, 1491, 1369, 1327,
1304, 1287, 1256, 1159, 1074, 1056, 1011 cm⁻¹. ¹H NMR (500 MHz, (CD₃)₂CO) δ 7.48 (d, J = 8.8 Hz, 2H), 7.32 (m, 2H), 7.20 (m, 9H), 1.41 (s, 18H). ¹³C NMR (125 MHz, (CD₃)₂CO) δ 153.9, 153.7, 144.0, 143.5, 141.9, 140.9, 132.5, 129.6, 128.1, 128.03, 127.98, 126.6, 81.6, 81.3, 28.4, 28.3. HRMS calcd for C₂₈H₃₁BrN₂O₄: 538.1467. Found: 538.1475.

4.34. [(4-Amino-phenyl)-tert-butoxycarbonyl-amino-phenyl]-phenyl-carbamic acid tert-butyl ester (32). To a 250 mL round bottom flask was added 31 (0.75 g, 1.39 mmol), P(t-Bu)₃ (0.01 g, 0.07 mmol), Pd(dba)₂ (0.04 g, 0.07 mmol), LHMDS (1.67 mL of a 1 M solution in THF) and toluene (10 mL). The reaction was stirred at room temperature overnight. The next day TBAF (3.06 mL of a 1 M solution in THF) was added to the reaction and allowed to stir 24 h. The reaction was poured into water, extracted with CH₂Cl₂, dried using MgSO₄, and concentrated. Column chromatography, silica gel, CH₂Cl₂/EtOAc (5:1) afforded the product as a white crystalline solid (0.51 g, 77%). mp: 190-191 °C. FTIR (KBr) 3442, 3358, 2974, 1690, 1626, 1511. 1368, 1340, 1286, 1160, 1060 cm⁻¹. ¹H NMR (500 MHz, (CD₃)₂CO) δ 7.32 (m, 2H), 7.22 (m, 5H), 7.14 (d, J = 8.9 Hz, 2H), 6.92 (d, J = 8.6 Hz, 2H), 6.64 (d, J = 8.6 Hz, 2H), 4.69 (s, 2H), 1.41 (s, 18H). ¹³C NMR (125 MHz, (CD₃)₂CO) δ 154.6, 154.1, 147.9, 144.4, 142.5, 140.7, 133.4, 129.6, 129.4, 128.0, 127.8, 127.0, 126.5, 115.2, 81.2, 80.6, 28.5, 28.4. HRMS calcd for C₂₈H₃₃N₃O₄: 475.2471. Found: 475.2477.
4.35. \textit{N-(4-Fluoro-phenyl)-benzene-1,4-diamine} (33). Following the general amination procedure 4-fluoro-1-bromobenzene (5.00 g, 28.57 mmol) was coupled to \textit{p}-phenylenediamine (4.63 g, 42.86 mmol) using NaO-\textit{t}-Bu (5.49 g, 57.14 mmol), \textit{rac}-BINAP (0.20 g, 0.36 mmol), Pd(dba)$_2$ (0.33 g, 0.57 mmol) and toluene (50 mL). Column chromatography, silica gel CH$_2$Cl$_2$ afforded the desired product as an orange solid (3.79 g, 66%). mp: 66-68 °C. FTIR (KBr) 3371, 1515, 1320, 1271, 1215 cm$^{-1}$. $^1$H NMR (400 MHz, (CD$_3$)$_2$CO) $\delta$ 6.87 (m, 6H), 6.72 (s, 1H), 6.64 (d, $J$ = 8.7 Hz, 2H), 4.39 (s, 2H). $^{13}$C NMR (100 MHz, (CD$_3$)$_2$CO) $\delta$ 157.4, 144.3, 144.0, 134.5, 123.1, 123.0, 115.9, 115.8, 115.7, 115.6, 115.5. HRMS calcd for C$_{12}$H$_{11}$FN$_2$: 202.0906. Found: 202.0908.

4.36. \textit{N-(4-Bromo-phenyl)-N'-(4-fluoro-phenyl)-benzene-1,4-diamine} (34).

Following the general amination procedure 33 (3.79 g, 18.74 mmol) was coupled to 1,4-dibromobenzene (6.63 g, 28.11 mmol) using NaO-\textit{t}-Bu (3.68 g, 37.48 mmol), \textit{rac}-BINAP (0.23 g, 0.37 mmol), Pd(dba)$_2$ (0.22 g, 0.37 mmol) and toluene (50 mL). Column chromatography, silica gel CH$_2$Cl$_2$/hexane (1:1) afforded the desired product as a yellow solid (1.48 g, 22%). mp: 101-104 °C. FTIR (KBr) 3385, 1589, 1522, 1508, 1486, 1307, 1292, 1221, 1074 cm$^{-1}$. $^1$H NMR (400 MHz, (CD$_3$)$_2$CO) $\delta$ 7.28 (m, 3H), 7.16 (s, 1H), 7.06 (m, 6H), 6.99 (m, 2H), 6.92 (d, $J$ = 8.9 Hz, 2H). $^{13}$C NMR (100 MHz, (CD$_3$)$_2$CO) $\delta$ 158.4, 156.0, 145.5, 141.6, 139.2, 136.3, 132.2, 121.8, 119.5, 118.4, 118.3, 117.2, 116.0,
4.37. (4-Bromo-phenyl)-{4-[tert-butoxycarbonyl](4-fluoro-phenyl)-amino]-phenyl}-carbamic acid tert-butyl ester (35). To a 500 mL round bottom flask containing a magnetic stir bar was added 34 (1.48 g, 4.14 mmol). THF (30 mL) was added and the reaction cooled to -78 °C. Methyllithium (6.07 mL of a 1.4 M solution in diethyl ether) was added dropwise and the mixture was allowed to stir at -78 °C for 45 min. Boc₂O (1.90 g, 8.69 mmol) was added dissolved in THF (10 ml). The mixture was allowed to warm to room temperature. Water (100 mL) was added followed by extraction with CH₂Cl₂ (3×). The organics were dried using anhydrous MgSO₄ and the solvent was removed in vacuo. Column chromatography, silica gel CH₂Cl₂ afforded the product as a white crystalline solid (0.94 g, 41%). mp: 163-170°C. FTIR (KBr) 2974, 1708, 1509, 1368, 1334, 1288, 1229, 1163, 1059 cm⁻¹. ¹H NMR (400 MHz, (CD₃)₂CO) δ 7.49 (d, J = 8.7 Hz, 2H), 7.30 (m, 2H), 7.20 (m, 6H), 7.11 (m, 2H), 1.41 (s, 18H). ¹³C NMR (100 MHz, (CD₃)₂CO) δ 162.1, 159.7, 153.5, 153.2, 143.0, 141.3, 140.6, 139.83, 139.80, 132.1, 129.7, 129.6, 129.2, 127.7, 127.4, 118.7, 115.7, 81.2, 81.0, 27.85, 27.83. HRMS calcd for C₂₈H₂₆BrFN₂O₄: 556.1373. Found: 556.1370.

4.38. {4-[(4-Amino-phenyl)-tert-butoxycarbonyl-amino]-phenyl}-(4-fluoro-phenyl)-carbamic acid tert-butyl ester (36). To a 100 mL round bottom flask was added 35
(0.94 g, 1.69 mmol), P(\(t\)-Bu)\(_3\) (0.02 g, 0.08 mmol), Pd(dba)\(_2\) (0.05 g, 0.08 mmol), LHMDS (2.02 mL of a 1 M solution in THF) and toluene (10 mL). The reaction was stirred at room temperature overnight. The next day TBAF (2.02 mL of a 1 M solution in THF) was added to the reaction and allowed to stir 24 h. The reaction was poured into water, extracted with CH\(_2\)Cl\(_2\), dried using MgSO\(_4\), and concentrated. Column chromatography, silica gel, CH\(_2\)Cl\(_2\)/EtOAc (7:2) afforded the product as a white crystalline solid (0.53 g, 64%). mp: 212-214 °C. FTIR (KBr) 3443, 3359, 2974, 1693, 1627, 1509, 1368, 1340, 1287, 1230, 1160, 1061 cm\(^{-1}\). \(^1\)H NMR (400 MHz, (CD\(_3\))\(_2\)CO) \(\delta\) 7.28 (m, 2H), 7.20 (d, \(J = 9.1\) Hz, 2H), 7.15 (d, \(J = 9.1\) Hz, 2H), 7.11 (m, 2H), 6.91 (d, \(J = 8.7\) Hz, 2H), 6.64 (d, \(J = 8.7\) Hz, 2H), 4.68 (s, 2H), 1.41 (s, 18H). \(^{13}\)C NMR (100 MHz, (CD\(_3\))\(_2\)CO) \(\delta\) 154.5, 154.0, 147.8, 142.6, 140.5, 133.3, 130.0, 129.9, 129.4, 127.6, 126.9, 116.3, 116.0, 115.1, 81.3, 80.6, 28.4, 28.3. HRMS calcd for C\(_{28}\)H\(_{32}\)F\(_2\)N\(_3\)O\(_4\): 493.2377. Found: 493.2374.

4.39 (4-Bromo-phenyl)\{-4-\{(4-bromo-phenyl)-\textit{tert}-butoxycarbonyl-amino\}-phenyl\}-carbamic acid \textit{tert}-butyl ester (37). To a 500 mL round bottom flask containing a magnetic stir bar was added 14 (1.74 g, 4.16 mmol). THF (20 mL) was added and the reaction cooled to -78 °C. Methyllithium (7.43 mL of a 1.4 M solution in diethyl ether) was added dropwise and the mixture was allowed to stir at -78 °C for 45 min. Boc\(_2\)O (1.98 g, 9.07 mmol) was added dissolved in THF (10 ml). The mixture was allowed to warm to room temperature. Water (100 mL) was added followed by extraction with
CH₂Cl₂ (3×). The organics were dried using anhydrous MgSO₄ and the solvent was removed in vacuo to afford the product as a white crystalline solid (2.49 g, 97%). mp: 187-190 °C. FTIR (KBr) 1708, 1510, 1489, 1368, 1328, 1304, 1286, 1159, 1056 cm⁻¹. 

¹H NMR (400 MHz, (CD₃)₂CO) δ 7.53 (d, J = 8.9 Hz, 4H), 7.24 (s, 4H), 7.21 (d, J = 8.9 Hz, 4H), 1.42 (s, 18H). 

¹³C NMR (100 MHz, (CD₃)₂CO) δ 153.7, 143.5, 141.4, 132.6, 129.7, 128.3, 119.2, 81.7, 28.3. HRMS calcd for C₂₈H₃₀Br₂N₂O₄: 618.0555. Found: 618.0548.

4.40. (4-Amino-phenyl)-(4-{(4-amino-phenyl)-tert-butoxycarbonyl-amino}-phenyl)-carbamic acid tert-butyl ester (38). To a 100 mL round bottom flask was added 37 (1.25 g, 2.02 mmol), P(t-Bu)₃ (0.02 g, 0.10 mmol), Pd(dba)₂ (0.06 g, 0.10 mmol), LHMDS (4.45 mL of a 1 M solution in THF) and toluene (15 mL). The reaction was stirred at room temperature for 3 d. TBAF (6.06 mL of a 1 M solution in THF) was added to the reaction and allowed to stir 24 h. The reaction was poured into water, extracted with CH₂Cl₂, dried using MgSO₄, and concentrated. The residue was dissolved in a minimum of CH₂Cl₂ followed by the addition of hexane. Care was taken to remove only the CH₂Cl₂ on the rotovap. The precipitated solid was filtered and washed with hexanes to afford the product as a tan solid (0.56 g, 57%). mp: 223-225 °C. FTIR (KBr) 3369, 1708, 1686, 1508, 1369, 1327, 1292, 1159, 1058 cm⁻¹. 

¹H NMR (400 MHz, (CD₃)₂CO) δ 7.14 (s, 4H), 6.90 (d, J = 8.7 Hz, 4H), 6.62 (d, J = 8.7 Hz, 4H), 4.63 (s, 4H), 1.40 (s, 18H). 

¹³C NMR (100 MHz, (CD₃)₂CO) δ 154.6, 147.6, 141.6, 133.5, 129.3,
126.7, 115.1, 80.4, 28.4. HRMS calcd for C_{28}H_{34}N_{4}O_{4}: 490.2580. Found: 490.2574.

5. References


Chapter 2

Synthesis and Self-Assembly of Orthogonally Functionalized Oligomers

for Molecular Electronics and NanoCell Architectures
1. Introduction

Molecular electronics seeks to exploit the switching properties of organic oligomers in device architectures for memory and logic applications. Current drawbacks to product development and commercialization abound, however, there may be none more daunting than the difficulty of addressing billions of switches at the molecular level. Further, the feasibility of positioning individual molecules in a given location or orientation is not known. As a result of these drawbacks, our group has developed the NanoCell architecture for molecular computing. The NanoCell consists of a disordered array of metallic islands connected to nanostructures (metallic nanorods, nanoparticles or carbon nanotubes) using orthogonally functionalized OPEs that are known to exhibit NDR behavior when biased. Lithographically defined leads allow contact between the NanoCell and the microscopic environment. This approach offers tremendous default tolerance compared to silicon computing devices and is much less complex that other molecular electronic architectures.

The metal-molecule-nanostructure architecture within the NanoCell is dependent on organic molecules that allow for the selective self-assembly onto nanostructures, followed by assembly on a discontinuous metallic film. This chapter describes the synthesis of such molecules terminated with complementary “alligator clips,” by which the molecule can covalently attach to the desired surface. The target compounds contain functionalities on one end known to form self-assembled monolayers on metal surfaces or carbon nanotubes while at the other end a protected aromatic thiol is present whereby self-assembly may again occur after an in situ deprotection. Self-assembly data is also reported for selected compounds to assess their efficacy in surface adhesion. This
chapter will also briefly report of the incorporation of several molecules into NanoCell devices and subsequent electronic behavior.

2. Synthesis

The structures of the target orthogonal compounds (1-7) are shown in Figure 1. Compounds (1-6) have been designed to allow for self-assembly onto metallic nanorods via the free thiol\textsuperscript{8,9} nitrile\textsuperscript{10} while protecting the other sulfur atom as a thioacetate to ensure molecular directionality and to inhibit crosslinking if self-assembled monolayer (SAM) assembly on nanorods is desired. Following initial assembly, the acetate can be removed with NH\textsubscript{4}OH or acid to afford the thiolate or thiol, respectively, which can be assembled onto another metallic material.\textsuperscript{11} For the mononitro compounds, this affords a monolayer with all the nitro groups oriented in the same direction, a result made possible only by the orthogonal protection scheme outlined here.\textsuperscript{1}

Compound 7 is designed to be reacted with carbon nanotubes via the diazonium salt.\textsuperscript{12} The tert-butoxycarbonyl group can then be removed\textsuperscript{13} and subsequently assembled on a metallic surface.

\textbf{Figure 1.} Structures of the orthogonally functionalized targets 1-7.
To exploit the orthogonally functionalized approach, the syntheses were accomplished via the use of a Boc-protected sulfur atom that could be deprotected using trifluoroacetic acid (TFA) to afford the free thiol,\(^{13}\) leaving the thioacetate moiety on the other end intact.

The synthesis of the S-Boc protected intermediate 8 is shown in Scheme 1. Treatment of \(p\)-diiodobenzene with \(\text{tert-}\)butyllithium at \(-78\, ^\circ\text{C}\), followed by the addition of sulfur,\(^{14}\) and quenching with \(\text{di(tert-}\)butyl)dicarbonate afforded the desired compound 8 in moderate yield.

![Scheme 1. Synthesis of the S-Boc intermediate 8.](image)

The synthesis of the mononitro compound 1 is shown in Scheme 2. Diazotization of 4-bromo-2-nitroaniline\(^ {15}\) followed by iodination afforded the desired aryl iodide 9, which was selectively coupled with TMSA to give 10\(^9\) in high yield. Compound 10 was coupled with 1-ethynyl-4-thioacetylbenzene\(^ {14}\) to afford 11. Deprotection of the alkyne using TBAF\(^ {14}\) afforded the terminal alkyne 12, which was coupled with 8 to give the orthogonally protected 13 in moderate yield. Chemoselective cleavage of the Boc group using TFA in anisole and \(\text{CH}_2\text{Cl}_2\), yielded the target molecule 1 with the nitro group exclusively at the 3'-position oriented towards the thiol.
Scheme 2. Synthesis of the mononitro compound 1.

To examine the effects of the nitro group on the electrical characteristics of the series of molecules, the unfunctionalized compound 2 was synthesized. The synthesis of 2 is shown in Scheme 3 and began by coupling 14 with 1-ethynyl-4-thioacetylbenzene to afford the desired product 15. The alkyne was then deprotected to afford 16. Without the addition of AcOH and Ac₂O, the acetate was also lost. Compound 16 was then coupled with 8 to give 17. Treatment of 17 with TFA afforded the target molecule 2 in fair yield. Also shown in Scheme 3 is the synthesis of the more soluble diethyl-derivatized compound 3, accomplished by coupling 1-ethynyl-4-thioacetylbenzene with 18 to give 19. Compound 19 was then deprotected to give the alkyne 20, which was coupled
with 8 to give 21. Chemoselective deprotection of 21 using TFA afforded the target compound 3.

Scheme 3. Synthesis of compounds 2 and 3.

With several OPEs synthesized, we focused on making the aliphatic thiol-thioacetate derivatized molecule 417 as shown in Scheme 4. Although the synthesis did not require the use of a Boc protected intermediate, this compound was needed as a control for electrical testing in the NanoCell. Commercially available 1,12-dibromododecane was converted to the dithioacetate using potassium thioacetate in DMF18 to afford 22.19 The dithioacetate was deprotected using NaOH in acetone to give
the dithiol 23. The dithiol was then mono-protected using 1 equivalent of acetic anhydride in pyridine and CH₂Cl₂ to afford the target molecule 4.

![Chemical structure](image)

**Scheme 4.** Synthesis of the aliphatic compound 4.

In an effort to synthesize similar molecules with alternative metal bonding groups, we turned our focus to synthesizing 5 (Scheme 5). Compound 5 allows for self-assembly via the thiolate (after deprotection) with the resulting SAM terminated with amino groups that could then form coordination compounds with metallic nanorods and nanoparticles. Alkyne 24 was coupled with 10 to afford the desired compound 25. 25 was then deprotected to give 26 and coupled with 1-iodo-4-thioacetylbenzene to afford the target compound 5 in fair yield.

Also shown in Scheme 5 is the synthesis of the nitrile terminated OPE 6, produced in order to take advantage of the known bonding interactions between nitriles and metals. The alkyne 27 was coupled with 10 to give 28, followed by deprotection to afford the alkyne 29. Compound 29 was then coupled with 4-iodothioacetylbenzene to yield the target compound 6.
Scheme 5. Synthesis of the amine (5) and nitrile (6) orthogonally functionalized thioacetate compounds.

With the completed thiol derivatized molecules in hand, we carried out SAM formation on gold for compounds 1, 2, and 4. Using ellipsometry, we compared the observed and theoretical thicknesses (Table 1) to assess monolayer formation. Immersion times were limited to 40 min, due to the rapid assembly of thiols on gold compared to thioacetates. Assembly data for all three compounds are close to the predicted values. Self-assembly data obtained corroborate with our previous published data.
Table 1. Chemical self-assembly data for compounds 1, 2, and 4 in THF for 40 min. 

*Value measured by ellipsometry with ca. ± 0.2 nm error in the measurement. †The theoretical thickness calculated by molecular mechanics including the Au-S bond and a tilt angle of 20° for the OPEs and 33° for the alkane.""""""""24

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Once several thiol-thioacetate derivatives were synthesized for use attaching metallic nanorods to the discontinuous gold film in the NanoCell, attention was turned to synthesizing a molecule that would permit attachment of single walled carbon nanotubes (SWNTs) to the discontinuous gold film (compounds 7).

The synthesis of compound 7 is shown in Scheme 6. The aryl iodide 1416 was coupled to 4-ethynylaniline21 followed by deprotection of the alkyne to give the desired compound 30.25 The alkyne was coupled with 8 to give 31 which was then treated with boron trifluoride etherate and t-BuONO to afford the desired aryl diazonium salt 7.

With compounds 1-7 synthesized, several oligomers were incorporated into the NanoCell nanoelectronic device. Nanoelectronic architectures could prove to be a complement to traditional solid-state devices. Most proposed architectures are dependent upon precise order and on building devices with exact arrays of nanostructures (i.e., molecule-embedded cross-bars) painstakingly interfaced with microstructure. Conversely, the NanoCell approach is not dependent on placing molecules or nanosized metallic components in precise orientations or location. The internal portions are, for the most part, disordered and there is no need to precisely locate any of the switching elements. The nanosized switches are added in abundance between the micrometer-sized input/output electrodes, and only a small percentage of them need to assemble in an orientation suitable for switching. The result of the NanoCell architecture is that patterning challenges of the input/output structures become far less exacting since micrometer-scale lithography can afford the needed address system. Also, fault tolerance
is enormous. However, programming is significantly more challenging than when ordered ensembles are used.

The NanoCells used for these experiments consist of a two-dimensional unit of juxtaposed electrodes fabricated atop a Si/SiO₂ substrate with a discontinuous gold film vapor-deposited onto the SiO₂ in the central region. An SEM image of a NanoCell assembled with compound 1 is shown in Figure 2.

![SEM image of NanoCell](image_url)

**Figure 2.** SEM image of the NanoCell after assembly of the Au nanowires and 1. The top image shows the five juxtaposed pairs of fabricated leads across the NanoCell, and some Au nanowires are barely visible on the internal rectangle of the discontinuous Au film. The lower image is a higher magnification of the NanoCell's central portion showing the disordered discontinuous Au film with an attached Au nanowire, which is affixed via the OPE-dithiol (not observable) derived from 1.
The assembly of molecules and nanowires in the central portion of the NanoCell was carried out to provide a current pathway across the NanoCell. Compounds similar to the mononitro OPE, 1, have been shown previously to exhibit switching and memory storage effects when fixed between proximal Au probes. The target compounds utilized for the NanoCell experiments contain thiol functionalities on one end which form a self-assembled monolayer on the gold nanorods while at the other end a protected aromatic thiol is present whereby self-assembly on the discontinuous gold film may occur after an in situ deprotection (Figure 3).
Figure 3. Schematic representation of the molecule/nanowire assembly on the discontinuous gold film.

The assembled NanoCells show two stable and reproducible switching peaks observed in a bias range of -10 and +10 V as shown in Figure 4. The devices showed no degradation to >2000 scans over a 22 h period of continuous sweeping. Also, after testing, an assembled NanoCell was stored in a capped vial (air) for 2 months with little, if any, signal variations relative to the readings recorded at the initial testing.

Figure 2. $I(V)$ characteristics of the NanoCell at 297 K. Curves a, b, and c are the first, second, and third sweeps, respectively (~40 s/scan). The black arrow indicates the sweep direction of negative to positive.

The NanoCell exhibits reproducible switching behavior and two types of memory effects, one being a destructive read and the second a nondestructive read. Both types of memories are stable for over a week at room temperature and probably much longer.
Data suggest that nanofilamentary metal formation is the likely mode of current transport, however molecule incorporation into the NanoCell devices is imperative for stable and reproducible switching behavior. With the present size embodiments, write/erase speeds, and the lack of isolation and fanout, the NanoCell is not a harbinger for DRAM, flash, or MRAM replacements. However, it demonstrates the first fabrication of a disordered nanoscale ensemble for high-yielding switching and memory while mitigating the painstaking task of nanoscale lithography or patterning, thereby furthering the promise of disordered programmable arrays for complex device functionality.

3. Summary

This chapter presents the synthesis, assembly data, and incorporation of orthogonally functionalized oligo(phenylene ethynylene)s into NanoCell architectures. The target compounds were designed and synthesized to give control during the self assembly process using complementary thiol-thioacetate protecting groups. When compound 1 was assembled in the NanoCell, the system showed stabilized switching and memory type behavior. Subsequent control experiments found the NanoCell switching mechanism to be based most likely on metal filaments breaking and forming due to electromigration of the discontinuous gold film and gold nanowires. The NanoCell demonstrates the first fabrication of a disordered nanoscale ensemble for high-yielding switching and memory while mitigating the painstaking task of nanoscale lithography or patterning, thereby furthering the promise of disordered programmable arrays for complex device functionality.

4. Experimental
4.1. **Materials and General Procedures.** Unless stated otherwise, reactions were performed in oven-dried glassware under a nitrogen atmosphere using freshly distilled solvents. Reagent grade Et$_2$O and THF were distilled from sodium benzophenone ketyl. PhMe and TEA were distilled from calcium hydride. Reagent grade n-hexanes, CH$_2$Cl$_2$, MeOH, EtOH, and EtOAc were used without further distillation. TMSA was donated by FAR Research Inc. All other commercially available reagents were used as received. Unless otherwise noted, reactions were magnetically stirred and monitored by TLC using E. Merck silica gel 60 F$_{254}$ precoated plates (0.25-mm). In general, the chromatography guidelines reported by Still were followed. Flash chromatography was performed with the indicated solvent systems using silica gel grade 60 (230-400 mesh). $^1$H and $^{13}$C NMR spectra were observed at 400 and 100 MHz, respectively, on a Bruker Avance 400 spectrometer. NMR chemical shifts values for deuterated solvents were followed as reported. FTIR spectra were obtained on a Nicolet Avatar 360 FTIR. Mass spectroscopy was performed at the Rice University Mass Spectroscopy Laboratory. Melting point values are uncorrected. All new compounds were named using the Beilstein AutoNom application of Beilstein Commander 2000 software.

4.2. **General procedure for coupling a terminal alkyne with an aryl halide (Castro-Stephens/Sonogashira protocol).** To an oven dried flask containing a magnetic stir bar was added the aryl halide, PdCl$_2$(PPh$_3$)$_2$ (5 mol % based on aryl halide), and CuI (10 mol % based on aryl halide). Alternatively, Pd(dba)$_2$ (5 mol % based on aryl halide), PPh$_3$ (20 mol %), and CuI (10 mol %) was used. The vessel was then sealed with a rubber septum, evacuated and backfilled with N$_2$ (3×). A cosolvent of THF was added followed by the amine base. The terminal alkyne was added and the reaction was heated,
if necessary, until the aryl halide was consumed as judged by TLC. The reaction vessel was cooled to room temperature and quenched with water. The organic layer was diluted with CH₂Cl₂ and washed with a saturated solution of NH₄Cl. The organic layer was dried using anhydrous MgSO₄ and the solvent was removed in vacuo. The crude product was then purified by flash chromatography (silica gel).

4.3. **General procedure for the formation of self-assembled monolayers (SAMs).**

The gold substrate was evaporated and cleaned according to established procedures.³⁵,³⁶

The compound (2 mg) was added to a 20 mL vial followed by 10 mL of freshly distilled THF. The gold substrate was added and allowed to incubate in the dark for 40 min at room temperature. The substrate was removed, rinsed with anhydrous EtOH, and dried with N₂. Monolayer thickness was determined on a Gaertner-LSE ellipsometer. Measurements were performed immediately before and immediately after monolayer formation. Thicknesses were calculated based on the refractive index \( n_r = 1.5 \) for compound 4 and \( n_r = 1.55 \) for compounds 1 and 2 (\( k_r = 0 \) for all compounds).

![Chemical structure](image)

4.4. **Thioacetic acid S-{4-[4-(4-mercapto-phenylethynyl)-3-nitro-phenylethynyl]-phenyl} ester (1).** To a 50 mL round bottom flask containing a stir bar was added 13 (0.25 g, 0.47 mmol), CH₂Cl₂ (6.0 mL), anisole (0.5 mL) and TFA (1.0 mL). The reaction was allowed to stir at room temperature for 4 h. EtOAc (25 mL) was then added and washed with water (3×). The organic layer was dried using anhydrous MgSO₄ and the solvent was removed in vacuo. The residue was dissolved in a minimum amount of
CH$_2$Cl$_2$ and hexanes were then added. Care was taken to evaporate only the CH$_2$Cl$_2$ on the rotary evaporator. The solid was filtered, washed with hexanes, and purified by flash chromatography, silica gel (CH$_2$Cl$_2$) to afford the product as an orange solid (0.125 g, 70%). mp: 105-108 °C. FTIR (KBr) 2564, 2209, 1709, 1587, 1539, 1503, 1398, 1343, 1270, 1119, 1094, 1014, 953 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.23 (d, $J = 1.5$ Hz, 1H), 7.71 (dd, $J = 8.1$, 1.5 Hz, 1H), 7.67 (d, $J = 8.1$ Hz, 1H), 7.58 (d, $J = 8.5$ Hz, 2H), 7.47 (d, $J = 8.6$ Hz, 2H), 7.44 (d, $J = 8.6$ Hz, 2H), 7.27 (d, $J = 8.5$ Hz, 2H), 3.58 (s, 1H), 2.46 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 193.4, 149.6, 135.5, 134.6, 134.5, 134.0, 132.8, 132.5, 129.5, 129.0, 127.9, 123.9, 123.4, 119.4, 118.5, 98.9, 92.9, 88.6, 85.5, 30.6. HRMS calcd for C$_{24}$H$_{19}$NO$_3$S$_2$: 429.0493. Found: 429.0496.

4.5. Thioacetic acid S-{4-[4-(4-mercapto-phenylethynyl)-phenylethynyl]-phenyl} ester (2). To a 100 mL round bottom flask containing a stir bar was added 17 (0.56 g, 1.16 mmol), CH$_2$Cl$_2$ (18 mL), anisole (1.5 mL) and TFA (3.0 mL). The reaction was allowed to stir at room temperature for 4 h upon which time an orange precipitate had formed. Hexanes (50 mL) was added and the solid was filtered, washed with hexanes and purified by flash chromatography, silica gel (3:1 CH$_2$Cl$_2$/hexanes) to afford the product as a white solid (0.29 g, 65%). mp: decomposes at 190 °C. FTIR (KBr) 2567, 2209, 1920, 1709, 1689, 1584, 1512, 1479, 1403, 1351, 1304, 1267, 1118, 1094, 1014 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.56 (d, $J = 8.6$ Hz, 2H), 7.50 (m, 4H), 7.40 (d, $J = 8.6$ Hz, 2H), 7.39 (d, $J = 8.5$ Hz, 2H), 7.24 (d, $J = 8.5$ Hz, 2H), 3.54 (s, 1H), 2.45 (s, 3H). $^{13}$C NMR (100Hz, CDCl$_3$) $\delta$ 193.7, 134.5, 132.39, 132.38, 131.8, 131.7, 129.1, 128.5,
124.5, 123.5, 122.9, 120.3, 91.1, 90.9, 90.7, 89.7, 30.5. HRMS calcd for C\textsubscript{24}H\textsubscript{16}OS\textsubscript{2}: 384.0643. Found: 384.0636. Anal. Calcd: C, 74.97; H, 4.19. Found: C, 74.68; H, 4.12.

4.7. **Thioacetic acid S-\{12-mercaptopo-dodecyl\} ester (4).**\textsuperscript{17} To a 50 mL round bottom flask containing a stir bar was added 23 (0.20 g, 0.85 mmol), CH\textsubscript{2}Cl\textsubscript{2} (5.0 mL), pyridine (5.0 mL), and acetic anhydride (0.08 mL). The reaction was allowed to stir at room temperature overnight. The next day the reaction was concentrated in vacuo. The residue was dissolved in CH\textsubscript{2}Cl\textsubscript{2} and purified by flash chromatography, silica gel (CH\textsubscript{2}Cl\textsubscript{2}) to afford the product as a white solid (0.10 g, 41%). mp: 32-34 °C. FTIR (KBr) 2919, 2851, 1697, 1471, 1435, 1355, 1135, 1114 cm\textsuperscript{-1}. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 2.85 (t, J = 8.3 Hz, 2H), 2.51 (quart, J = 8.3, 7.2 Hz, 2H), 2.31 (s, 3H), 1.60 (m, 4H), 1.34-1.25 (m, 17H). \textsuperscript{13}C NMR (100Hz, CDCl\textsubscript{3}) δ 196.5, 34.5, 31.1, 29.93, 29.90, 29.85, 29.6, 29.51, 29.47, 29.2, 28.8, 25.1. HRMS calcd for C\textsubscript{14}H\textsubscript{28}OS\textsubscript{2}: 276.1582. Found: 276.1587. Anal. Calcd: C, 60.81; H, 10.21. Found: C, 61.01; H, 10.30.

4.8. **Thioacetic acid S-\{4-[4-(4-amino-phenylethynyl)-2-nitro-phenylethynyl]-phenyl\} ester (5).** See the general coupling procedure. Used were 26 (0.78 g, 2.97 mmol), 1-iodo-4-thioacetylbenzene (0.91 g, 3.27 mmol), Pd(db)\textsubscript{2} (0.09 g, 0.15 mmol), PPh\textsubscript{3} (0.16 g, 0.60 mmol), CuI (0.06 g, 0.30 mmol), THF (20 mL) and \textit{i}-Pr\textsubscript{2}NEt (2 mL, 12 mmol). The reaction was stirred at room temperature for 15 h. The mixture was then poured into water and extracted with EtO\textsubscript{Ac} (2×). The combined organics were washed with brine (2×) and dried over anhydrous MgSO\textsubscript{4}. The crude materials were purified by
flash chromatography, silica gel (12:24:1 hexane/CH$_2$Cl$_2$/EtOAc). The collected fractions were concentrated to about 5 mL and then diluted with hexanes; the formed precipitates were filtered to give 5 as orange crystals (0.67 g, 55%). mp: 181-183 °C. FTIR (KBr) 3447, 3366, 2214, 2194, 1710, 1626, 1600, 1534, 1518, 1477, 1399, 1348, 1289, 1268, 1121, 1088, 1015 cm$^{-1}$. $^1$H NMR (400 MHz, (CD$_3$)$_2$CO) δ 8.18 (d, J = 1.7 Hz, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.82 (dd, J = 8.1, 1.5 Hz, 1H), 7.69 (d, J = 8.6 Hz, 2H), 7.55 (d, J = 8.6 Hz, 2H), 7.34 (d, J = 8.6 Hz, 2H), 6.73 (d, J = 8.6 Hz, 2H), 5.25 (s, 2H), 2.47 (s, 3H). $^{13}$C NMR (100 MHz, (CD$_3$)$_2$SO) δ 193.7, 151.2, 150.2, 135.9, 135.6, 135.4, 134.0, 133.1, 130.4, 127.3, 125.9, 123.3, 115.9, 114.5, 107.6, 97.4, 97.3, 87.1, 85.8, 31.2. Anal. Calcd: C, 69.89; H, 3.91; N, 6.79. Found: C, 69.99; H, 3.89; N, 6.71.

4.10. 4-[4-(4-tert-Butoxycarbonylsulfanyl-phenylethynyl)-phenylethynyl]-benzenediazonium tetrafluoroborate (7). To a 100 mL round bottom was added BF$_3$OEt$_2$ (0.21 mL, 1.68 mmol) and cooled to −40 °C. 31 (0.24 g, 0.56 mmol) dissolved in THF (20 mL) was added dropwise. Following addition, t-BuONO (0.18 mL, 1.47 mmol) was added dropwise to the reaction mixture and allowed to warm to 0 °C. Et$_2$O (75 mL) was added to precipitate the diazonium salt. The product was collected by vacuum filtration and reprecipitated using Et$_2$O to afford 7 as an orange solid (0.23 g, 78%). FTIR (KBr) 2977, 2266, 2208, 1724, 1576, 1124, 1084 cm$^{-1}$. $^1$H NMR (500 MHz, (CD$_3$)$_2$CO) δ 8.90 (d, J = 9.0 Hz, 2H), 8.20 (d, J = 9.0 Hz, 2H), 7.74 (d, J = 8.43 Hz, 2H), 7.69 (d, J = 8.1 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.1 Hz, 2H), 1.51 (s, 9H).
13C NMR (100 MHz, (CD3)2CO) δ 167.0, 136.9, 135.5, 134.8, 134.1, 133.4, 132.92, 132.87, 130.8, 125.8, 124.3, 122.1, 114.6, 100.9, 92.3, 90.8, 90.0, 86.7, 28.2.

4.12. Thiocarbonic acid O-tert-butyl ester S-(4-iodo-phenyl) ester (8). To a solution of 1,4-diiodobenzene (4.00 g, 12.13 mmol) in THF (50 mL) at -78 °C was slowly added tert-butyllithium (14.3 mL, 24.25 mmol, 1.7 M in pentane). The resulting white slurry was stirred for 30 min and sulfur (0.43 g, 13.34 mmol) was added in one portion. The mixture was then allowed to warm to 0 °C for 10-15 min. The clear solution was cooled back to -78 °C and a solution of di-(tert-butyl)dicarbonate (3.18 g, 14.55 mmol) in THF (20 mL) was added via cannula. The reaction was allowed to warm to room temperature and poured into water. The mixture was extracted with EtOAc (1×) and the organic layer was washed with H2O (3×), brine (1×), and dried over anhydrous MgSO4. Flash chromatography, silica gel (4:1 hexane/CH2Cl2) gave 8 as colorless oil that slowly crystallized (2.91 g, 71%). mp: 58-60 °C. FTIR (KBr) 2976, 1717, 1565, 1469, 1365, 1220, 1201, 1128, 1090, 1005 cm−1. 1H NMR (400 MHz, CDCl3) δ 7.72 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.3 Hz, 2H), 1.51 (s, 9H). 13C NMR (100 MHz, CDCl3) δ 167.1, 138.3, 136.4, 128.7, 95.9, 86.1, 28.3. HRMS calcd for C11H13IO2S: 335.9681. Found: 335.9684.

4.13. 4-Bromo-1-iodo-2-nitrobenzene (9). To a 500 mL round bottom containing a stir bar was added BF3·OEt2 (9.95 mL, 78.53 mmol) and the flask was cooled to -30 °C.
Bromo-2-nitroaniline (4.05 g, 18.67 mmol) dissolved in THF (50 mL) was added dropwise. t-BuONO (8.17 mL, 68.72 mmol) was dissolved in THF (50 mL) and added dropwise. The reaction was allowed to warm to −5 °C at which time 100 mL of Et₂O was added and the mixture was allowed to stir at −5 °C for 10 min until a pale solid precipitated. The solid was filtered and washed with Et₂O to afford a pale solid which was then added in one portion to a 500 mL round bottom containing a stir bar, potassium iodide (4.40 g, 26.53 mmol), iodine (3.37 g, 13.27 mmol), and acetonitrile (75 mL). The reaction was allowed to stir at room temperature for 15 min. 150 mL of a saturated aqueous solution of sodium thiosulfate was added as well as 150 mL of CH₂Cl₂. The mixture was allowed to stir for 5 min, the layers were separated, the organics were dried using anhydrous MgSO₄, and the solvent was removed in vacuo. This afforded the product as a yellow solid (3.8 g, 62%). mp: 87-89 °C. FTIR (KBr) 3085, 1573, 1553, 1528, 1453, 1346, 1271, 1250, 1152, 1090, 1019 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, J = 2.8 Hz, 1H), 7.89 (d, J = 8.6, 1H), 7.40 (dd, J = 8.6, 2.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 153.9, 143.3, 136.9, 128.9, 123.1, 84.9. HRMS calcd for C₆H₃BrINO₂: 326.8392. Found: 326.8389.

4.14. (4-Bromo-2-nitro-phenylethynyl)-trimethyl-silane (10). See the general coupling procedure. Used were 9 (3.67 g, 11.19 mmol), trimethylsilylacetylene (1.58 mL, 11.19 mmol), PdCl₂(PPh₃)₂ (0.23 g, 0.33 mmol), CuI (0.13 g, 0.67 mmol), THF (20 mL), and triethylamine (5 mL). Flash chromatography, silica gel (1:1 CH₂Cl₂/hexanes) afforded the product as a yellow solid (3.16 g, 95%). mp: 30 °C. FTIR (KBr) 3093,
2959, 2164, 1599, 1553, 1531, 1469, 1409, 1341, 1280, 1250, 1216, 1152, 1092 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.15 (d, \(J = 2.1\) Hz, 1H), 7.67 (dd, \(J = 8.8\), 2.1 Hz, 1H), 7.50 (d, \(J = 8.8\) Hz, 1H), 0.27 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 150.7, 136.4, 136.2, 128.0, 122.6, 117.7, 105.8, 98.8, 0.0. HRMS calcd for \(\text{C}_{11}\text{H}_{12}\text{BrNO}_{2}\text{Si}\): 296.9802. Found: 296.9800.

4.15. Thioacetic acid \(S\)-(4-(3-nitro-4-trimethylsilanylethynyl-phenylethynyl)-phenyl] ester (11). See the general coupling procedure. Used were 10 (1.50 g, 5.03 mmol), 1-ethynyl-4-thiaoacetylbenezene\(^{14}\) (0.74 g, 4.19 mmol), \(\text{PdCl}_2(\text{PPh}_3)_2\) (0.18 g, 0.25 mmol), CuI (0.10 g, 0.50 mmol), THF (20 mL), and triethylamine (4 mL). Flash chromatography, silica gel (1:1 hexane/CH\(_2\)Cl\(_2\)) afforded the desired product as a yellow solid (0.48 g, 29%). mp: 104-107 °C. FTIR (KBr) 2961, 2206, 2155, 1699, 1588, 1536, 1520, 1499, 1396, 1351, 1249, 1223, 1180, 1131, 1113, 1089, 1013 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.16 (d, \(J = 1.5\) Hz, 1H), 7.67 (dd, \(J = 8.1\), 1.5 Hz, 1H), 7.63 (d, \(J = 8.1\) Hz, 1H), 7.57 (d, \(J = 8.6\) Hz, 2H), 7.44 (d, \(J = 8.6\) Hz, 2H), 2.46 (s, 3H), 0.30 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 193.1, 150.1, 135.22, 135.15, 134.4, 132.4, 129.5, 127.5, 124.1, 123.2, 118.0, 106.1, 99.3, 92.9, 88.3, 30.4, -0.3. HRMS calcd for \(\text{C}_{21}\text{H}_{19}\text{NO}_{2}\text{Si}\): 393.0855. Found: 393.0854.

4.16. Thioacetic acid \(S\)-(4-(4-ethynyl-3-nitro-phenylethynyl)-phenyl] ester (12). To a 100 mL round bottom containing a stir bar was added 11 (0.43 g, 1.09 mmol), THF (10
mL), acetic anhydride (0.21 mL, 2.19 mmol), acetic acid (0.13 mL, 2.19 mmol), and TBAF (1.31 mL of a 1.0 M solution in THF). The reaction was allowed to stir at room temperature for 15 min, poured into water and extracted with CH$_2$Cl$_2$ (3×). The organic layer was dried using anhydrous MgSO$_4$ and the solvent was removed in vacuo to give the product as an orange solid (0.29 g, 84%). mp: 143-145 °C. FTIR (KBr) 3277, 1695, 1540, 1524, 1352, 1112 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.18 (d, J = 1.1 Hz, 1H), 7.69 (dd, J = 8.1, 1.5 Hz, 1H), 7.66 (d, J = 8.1 Hz, 1H), 7.57 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 3.62 (s, 1H), 2.46 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 193.3, 150.4, 135.7, 135.5, 134.5, 132.5, 129.6, 127.7, 124.9, 123.2, 117.1, 93.2, 88.2, 87.1, 78.5, 30.5. HRMS calcd for C$_{18}$H$_{11}$NO$_3$S: 321.0460. Found: 321.0456.

![Chemical structure](image)

4.17. Thioacetic acid S-[4-[4-(4-tert-butoxycarbonylsulfanyl-phenylethynyl)-3-nitrophenylethynyl]-phenyl] ester (13). See the general coupling procedure. Used were 12 (0.95 g, 2.96 mmol), 8 (1.09 g, 3.25 mmol), Pd(dba)$_2$ (0.17 g, 0.30 mmol), PPh$_3$ (0.31 g, 1.2 mmol), CuI (0.11 g, 0.60 mmol), THF (30 mL) and $i$-Pr$_2$NEt (2.1 mL, 12 mmol). The reaction was stirred at room temperature overnight. Flash chromatography, silica gel (6:3:1 hexane/CH$_2$Cl$_2$/Et$_2$O) gave an oily residue. The oil was redissolved in Et$_2$O and diluted with hexane. The solution was carefully concentrated to remove most of the Et$_2$O. The formed precipitate was filtered to give 13 as an orange solid (0.93 g, 59%). mp: 106-112 °C. FTIR (KBr) 2982, 2209, 1713, 1536, 1502, 1396, 1349, 1198, 1124, 1078, 1012 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.23 (d, J = 2.0 Hz, 1H), 7.71 (dd, J = 8.6, 1.5 Hz, 1H), 7.69 (d, J = 8.6 Hz, 1H), 7.60 (d, J = 8.6 Hz, 2H), 7.57 (d, J = 8.5 Hz,
2H), 7.55 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 8.5 Hz, 2H), 2.46 (s, 3H), 1.53 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 193.3, 167.1, 149.6, 135.5, 134.8, 134.7, 134.5, 132.6, 132.5, 130.6, 129.5, 127.9, 124.1, 123.35, 123.27, 118.2, 98.3, 93.0, 88.5, 86.4, 86.3, 30.5, 28.4.

HRMS calcd for C$_{29}$H$_{23}$NO$_3$S$_2$: 529.1018. Found: 529.1018.

4.18. (4-Iodo-phenylethynyl)-trimethyl-silane (14). To a 500 mL round bottom flask containing a stir bar was added 4-bromo-phenylethynyl)-trimethyl-silane (3.58 g, 14.14 mmol). THF (40 mL) was added and the mixture was cooled to −78 °C. tert-Butyllithium (18.24 mL, 28.28 mmol of a 1.55 M solution in pentane) was added dropwise and the reaction was allowed to stir at −78 °C for 45 min at which time iodine (4.31 g, 16.97 mmol) dissolved in THF (50 mL) at −78 °C was added. The reaction mixture was then allowed to stir at −78 °C for 10 min followed by stirring at 0 °C for 25 min. The reaction was poured into an aqueous solution of sodium thiosulfate, extracted with CH$_2$Cl$_2$ (3×), dried using anhydrous MgSO$_4$ and the solvent removed in vacuo. Flash chromatography, silica gel (1:3 CH$_2$Cl$_2$/hexanes) afforded to product as a pale solid (4.04 g, 95%). mp: 52-54 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ δ 7.64 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 0.25 (s, 9H).

4.19. Thioacetic acid $S$-[4-(4-trimethylsilylphenylethynyl)-phenylethynyl]-phenyl] ester (15). See the general coupling procedure. Used were 14$^{16}$ (2.00 g, 6.67 mmol), 1-ethynyl-4-thioacetylbenzene$^{14}$ (1.29 g, 7.33 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.23 g, 0.33 mmol), CuI (0.13 g, 0.67 mmol), THF (30 mL), and triethylamine (5 mL). Flash
chromatography, silica gel (1:1 CH₂Cl₂/hexanes) afforded the product as an orange solid (1.40 g, 60%). mp: 113-116 °C. FTIR (KBr) 2970, 2150, 1737, 1713, 1694, 1598, 1502, 1406, 1365, 1247, 1220, 1135, 1116, 1091, 1011 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, J = 5.1 Hz, 2H), 7.46 (m, 4H), 7.40 (d, J = 5.1 Hz, 2H), 2.45 (s, 3H), 0.27 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 193.8, 134.6, 132.6, 132.3, 131.9, 128.7, 124.7, 123.6, 123.3, 105.0, 96.7, 91.1, 90.9, 30.7, 0.3. HRMS calcd for C₂₁H₂₀OSSi: 348.1004. Found: 348.1002.

4.20. Thioacetic acid S-{4-[4-(4-tert-butoxycarbonylsulfanyl-phenylethynyl)-phenylethynyl]-phenyl} ester (16). To a 100 mL round bottom flask containing a stir bar was added 15 (1.21 g, 3.47 mmol), THF (20 mL), acetic anhydride (0.66 mL, 6.95 mmol), acetic acid (0.40 mL, 6.95 mmol) and TBAF (4.17 mL of a 1.0 M solution in THF). The reaction was allowed to stir at room temperature for 20 min, poured into water and extracted with CH₂Cl₂ (3×). The organics were dried using anhydrous MgSO₄ and the solvent was removed in vacuo to afford the product as a white solid (0.71 g, 74%). mp: 127-130 °C. FTIR (KBr) 3272, 1696, 1509, 1493, 1125, 1104, 1090 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, J = 8.5 Hz, 2H), 7.49 (s, 4H), 7.42 (d, J = 8.5 Hz, 2H) 3.20 (s, 1H), 2.45 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 193.8, 134.7, 132.6, 132.5, 132.0, 128.8, 124.6, 123.8, 122.6, 91.0, 90.9, 83.6, 79.5, 30.7. HRMS calcd for C₁₈H₁₂O₃S: 276.0609. Found: 276.0603.
4.21. Thioacetic acid \( S\{-4-[4-(4\text{-}tert\text{-}butoxycarbonylsulfanyl\text{-}phenylethynyl}\}\text{-}phenylethynyl\}\text{-}phenyl \) ester (17). See the general coupling procedure. Used were 16 (0.65 g, 2.35 mmol), 8 (0.87 g, 2.59 mmol), \( \text{PdCl}_2(\text{PPh}_3)_2 \) (0.08 g, 0.12 mmol), CuI (0.05 g, 0.24 mmol), THF (20 mL), and TEA (3 mL). Flash chromatography, silica gel (2:1 \( \text{CH}_2\text{Cl}_2 \)/hexanes) afforded the product as a pale solid (0.64 g, 56\%). mp: 149-153 °C. FTIR (KBr) 2980, 1726, 1698, 1512, 1479, 1406, 1396, 1369, 1357, 1196, 1121, 1086, 1013 cm\(^{-1}\). \(^1\)H NMR (400 MHz, \( \text{CDCl}_3 \)) \( \delta \) 7.56-7.51 (m, 10H), 7.43 (d, \( J = 8.7 \) Hz, 2H), 2.45 (s, 3H), 1.53 (s, 9H). \(^{13}\)C NMR (100 MHz, \( \text{CDCl}_3 \)) \( \delta \) 193.6, 167.4, 134.7, 134.4, 132.4, 132.2, 131.8, 129.3, 128.5, 124.4, 124.2, 123.3, 123.2, 90.9, 90.8, 86.2, 30.5, 28.4. HRMS calcld for \( \text{C}_{29}\text{H}_{24}\text{O}_3\text{S}_2 \): 484.1167. Found: 484.1161.

\[
\begin{array}{c}
\text{AcS} \quad \text{---} \quad \text{---} \quad \text{---} \quad \text{---} \quad \text{---} \quad \text{---} \quad \text{---} \quad \text{---} \\
\text{SAc}
\end{array}
\]

4.26. Thioacetic acid \( S\{-12\text{-}acetylsulfanyl\text{-}dodecyl \) ester (22).\(^{19}\) To a 500 mL round bottom flask containing a stir bar was added potassium thioacetate (3.80 g, 33.28 mmol) and DMF\(^{18}\) (300 mL). 1,12-Dibromododecane (10.92 g, 33.28 mmol) was added in one portion while stirring. The reaction was then allowed to stir at room temperature for 24 h. The mixture was poured into a sepratory funnel, washed with water and extracted with \( \text{CH}_2\text{Cl}_2 \) (3×). The organic layer was dried using anhydrous MgSO\(_4\) and the solvent was removed in vacuo. Column chromatography, silica gel (1:1 \( \text{CH}_2\text{Cl}_2 \)/hexanes) afforded the product as a white solid (2.22 g, 21\%). mp: 44-46 °C. \(^1\)H NMR (400 MHz, \( \text{CDCl}_3 \)) \( \delta \) 2.85 (t, \( J = 7.28 \) Hz, 4H), 2.31 (s, 6H), 1.55 (quint, \( J = 7.56, 7.28 \text{ Hz}, 4\text{H} \), 1.35-1.20 (m, 16H).

\[
\begin{array}{c}
\text{HS} \quad \text{---} \quad \text{---} \quad \text{---} \quad \text{---} \quad \text{---} \quad \text{---} \quad \text{---} \quad \text{---} \\
\text{SH}
\end{array}
\]
4.27. Dodecane-1,12-dithiol (23).²⁰ To a 250 mL round bottom flask containing a stir bar was added 22 (1.00 g, 3.14 mmol) and 60 mL of degassed 3 M NaOH in acetone. The reaction was allowed to stir at room temperature for 4 h and neutralized to pH 7 with 1 M HCl. The organics were extracted with CH₂Cl₂ (3×), dried using anhydrous MgSO₄, and removed in vacuo. Column chromatography, silica gel (CH₂Cl₂) afforded the product as a white solid (0.41 g, 56%). mp: 31-32 °C. FTIR (KBr) 2952, 2917, 2850, 1471, 1280, 1231 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 2.52 (quart, J = 7.5 Hz, 4H), 1.59 (quint, J = 7.6 Hz, 4H), 1.39-1.24 (m, 18H). ¹³C NMR (100 MHz, CDCl₃) δ 34.5, 30.0, 29.9, 29.5, 28.8, 25.1. HRMS calcd for C₁₂H₂₆S₂₂: 234.1476. Found: 234.1476.

4.28. 4-Ethylnylaniline (24).²¹ See the general coupling procedure. Used were 4-idoaniline (8.76 g, 40.00 mmol), trimethylsilylacetylene (6.8 mL, 48.12 mmol), PdCl₂(PPh₃)₂ (1.40 g, 1.99 mmol), CuI (0.76 g, 3.99 mmol), THF (50 mL), and i-Pr₂NEt (28 mL). Flash chromatography, silica gel (4:1 hexane/EtOAc) gave a brown yellow solid. The solid (6.10 g, 32.22 mmol) was dissolved in MeOH (60 mL) and K₂CO₃ (13.40 g, 96.95 mmol) was added. The reaction was stirred for 8 h. The mixture was poured into water and extracted with EtOAc (2×). The extracts were washed with water (1×) and brine (1×). The organics were dried using anhydrous MgSO₄ and concentrated in vacuo, the brown oil residue was filtered through a short silica gel plug (CH₂Cl₂) to give 25 as a yellow solid (3.98 g, 85%). ¹H NMR (400 MHz, CDCl₃) δ 7.32 (d, J = 8.8 Hz, 2H), 6.62 (d, J = 8.8 Hz, 2H), 3.84 (s, 2H), 2.99 (s, 1H).
4.29. 4-(3-Nitro-4-trimethylsilyl-ethenyl-phenylethynyl)-phenylamine (25). See the general coupling procedure. Used were 24 (0.86 g, 7.34 mmol), 10 (2.65 g, 8.89 mmol), Pd(dba)$_2$ (0.19 g, 0.34 mmol), PPh$_3$ (0.36 g, 1.36 mmol), CuI (0.13 g, 0.67 mmol), THF (15 mL) and i-Pr$_2$NEt (3.5 mL). Flash chromatography, silica gel (3:1 hexane/EtOAc) gave 25 as red solid (1.53 g, 62%). mp: 121-123 °C. FTIR (KBr) 3477, 3383, 2198, 2150, 1630, 1599, 1537, 1519, 1347, 1323, 1298, 1249, 1221, 1177, 1156, 1134 cm$^{-1}$. $^1$H NMR (400 MHz, (CD$_3$)$_2$CO) $\delta$ 8.08 (d, $J = 1.5$ Hz, 1H), 7.74 (dd, $J = 8.1$, 1.5 Hz, 1H), 7.70 (d, $J = 8.1$ Hz, 1H), 7.31 (d, $J = 8.6$ Hz, 2H), 6.70 (d, $J = 8.6$ Hz, 2H), 5.22 (s, 2H), 0.27 (s, 9H). $^{13}$C NMR (100 MHz, (CD$_3$)$_2$CO) $\delta$ 151.5, 151.1, 135.9, 135.6, 134.2, 127.1, 126.7, 116.7, 114.9, 109.6, 104.8, 100.2, 96.9, 85.5, -0.3. HRMS caleed for C$_{19}$H$_{18}$N$_2$O$_2$Si: 334.1138. Found: 334.1131.

4.30. 4-(4-Ethynyl-3-nitro-phenylethynyl)-phenylamine (26). To a solution of 25 (1.53 g, 4.57 mmol) in THF (10 mL) and MeOH (25 mL) was added K$_2$CO$_3$ (1.90 g, 13.75 mmol). The mixture was stirred for 3 h and poured into THF (50 mL) and EtOAc (50 mL). The solution was washed with water, brine (2x), and dried over anhydrous MgSO$_4$. Removal of solvent followed by flash chromatography, silica gel (3:2 hexane/EtOAc) gave 26 as red solid (0.97 g, 80%). mp: 173-175 °C. FTIR (KBr) 3480, 3006, 2970, 1716, 1423, 1365, 1224 cm$^{-1}$. $^1$H NMR (400 MHz, (CD$_3$)$_2$CO) $\delta$ 8.09 (t, $J = 1.1$ Hz, 1H), 7.76 (d, $J = 1.1$ Hz, 2H), 7.31 (d, $J = 8.7$ Hz, 2H), 6.70 (d, $J = 8.7$ Hz, 2H),
5.23 (s, 2H), 4.26 (s, 1H). $^{13}$C NMR (100 MHz, (CD$_3$)$_2$CO) δ 151.0, 136.2, 135.6, 134.1, 127.1, 126.9, 116.0, 114.8, 109.5, 96.8, 88.0, 85.3, 78.9. HRMS calcd for C$_{16}$H$_{10}$N$_2$O$_2$: 262.0742. Found: 262.0737.

![Structure 30]

4.31. 4-(4-Ethynyl-phenylethynyl)-phenylamine (30)$^{25}$ Following the general coupling procedure 14 (0.75 g, 2.50 mmol) was coupled to 4-ethynylaniline$^{21}$ (0.35 g, 3.00 mmol) using PdCl$_2$(PPh$_3$)$_2$ (0.09 g, 0.13 mmol), CuI (0.05 g, 0.25 mmol), TEA (3 mL), and THF (10 mL). The reaction was stirred at 40 °C overnight. The mixture was poured in H$_2$O and extracted (3×) with CH$_2$Cl$_2$, dried using anhydrous MgSO$_4$ and concentrated in vacuo. Column chromatography, silica gel (CH$_2$Cl$_2$) afforded 4-(4-trimethylsilyl-phenylethynyl)-phenylamine as a yellow solid (0.64 g). Following the general procedure for the deprotection of TMS-protected alkynes, 4-(4-trimethylsilyl-phenylethynyl)-phenylamine (0.64 g, 2.21 mmol) was dissolved in a mixture of CH$_2$Cl$_2$ (15 mL), MeOH (15 mL), and K$_2$CO$_3$ (1.53 g, 11.05 mmol). The product was afforded without additional purification as an orange solid (0.47 g, 87%, 2 steps). $^1$H NMR (400 MHz, (CD$_3$)$_2$CO) δ 7.45 (m, 4H), 7.25 (d, $J = 6.7$ Hz, 2H), 6.68 (d, $J = 6.7$ Hz, 2H), 5.09 (s, 2H), 3.77 (s, 1H).

![Structure 31]

4.32. Thiocarboxylic acid $S'$-[4-[4-(4-amino-phenylethynyl)-phenylethynyl]-phenyl] ester O-tert-butyl ester (31). Following the general coupling procedure 30 (0.38 g, 1.75 mmol) was coupled to 8 (0.42 g, 1.26 mmol) using PdCl$_2$(PPh$_3$)$_2$ (0.04 g, 0.06 mmol),
CuI (0.02 g, 0.13 mmol), TEA (1 mL), and THF (5 mL). The reaction was stirred at room temperature overnight. The mixture was poured in H$_2$O and extracted (3×) with CH$_2$Cl$_2$, dried using anhydrous MgSO$_4$ and concentrated in vacuo. Column chromatography, silica gel (CH$_2$Cl$_2$) afforded the compound as a white solid (0.48 g, 64%). mp: 178-185 °C. FTIR (KBr) 3396, 2204, 1713, 1615, 1587, 1520, 1125 cm$^{-1}$. $^1$H NMR (400 MHz, (CD$_3$)$_2$CO) δ 7.59 (d, $J$ = 8.4 Hz, 2H), 7.56 (m, 4H), 7.50 (d, $J$ = 8.6 Hz, 2H), 7.27 (d, $J$ = 8.6 Hz, 2H), 6.69 (d, $J$ = 8.6 Hz, 2H), 5.09 (s, 2H), 1.51 (s, 9H). $^{13}$C NMR (100 MHz, (CD$_3$)$_2$CO) δ 167.2, 135.6, 133.8, 132.9, 132.6, 132.1, 130.3, 125.7, 124.9, 122.6, 114.9, 110.7, 94.3, 91.5, 90.8, 87.2, 86.7, 28.3. HRMS calcd for C$_{27}$H$_{23}$NO$_2$S: 425.1450. Found: 425.1441.

References:


Chapter 3

Synthesis, Self-Assembly, and Monolayer Analysis of Novel
Conformationally Restricted “U-Shape” Oligomers
1. Introduction

The rational design and synthesis of molecular candidates for inclusion in the fabrication of molecular-scale devices to be used in electronics and sensing is a focus of our research. In our experience it is best to start with a related series of candidate compounds and to verify their surface assembly characteristics before incorporating them into device test structures. When evaluating an organic molecule for potential application as a molecular device component, the electronic nature of its functional groups as well as its molecular geometry determine, to a great extent, the electronic characteristics.

Recent work has shown experimentally and theoretically that the metal-molecule interface in particular plays a crucial role in the overall conductivity and in some cases the behavior of the whole system. Several theoretical models have aided in understanding this observed switching behavior. Specifically, changes in electronic conduction of the molecules have been attributed to a wide variety of mechanisms, including reversible reduction and rotation of functional groups as well as conformationally induced tunnel barriers. Several OPEs have been identified as possessing favorable characteristics for nonlinear electronic responses, having a low HOMO-LUMO gap relative to the gap in aliphatic chains, and thereby providing electron delocalization along the length of the molecule. Moreover, by lowering the barrier for electron transport when covalently attached to metal surfaces, fully conjugated OPEs can have improved electrical transport. An extended π-conjugation throughout the backbone of the molecule is also thought to improve the overlap and delocalization of electron orbitals. With variation in the functional groups and structural rigidity of OPEs, members of this class of compounds have been shown to possess the physical properties
necessary to act as high-conductivity wires,\textsuperscript{18-21} rectifiers,\textsuperscript{22} components showing NDR,\textsuperscript{23-26} memory elements,\textsuperscript{27} and bistable latches,\textsuperscript{28,29} depending on the testbed used.

This has motivated us to pursue the synthesis of new OPEs that have an extended conjugation exemplified by a 1,3-bridging aromatic ring linking two linear phenylethynyl backbones. Six new "U-shaped" OPEs (1-6) have been synthesized, as shown in Figure 1, based on 3,3'-diethynyl-[1,1';3',1'']terphenyl and 1,8-diethynylantracene.\textsuperscript{30}

\textbf{Figure 1.} Target "U-Shape" compounds.

We propose that the use of U-shaped molecules will aid in developing a better physical understanding of the electronic properties of OPEs when they are present in active molecular electronic devices. Oligomers 3 and 6 bear nitro groups as potential
redox centers, and all targets are end-functionalized with acetyl-protected molecular alligator clips which upon deprotection afford the thiolates or thiols for covalent surface attachment. The terphenyl targets have a relatively low rotational barrier and larger dihedral angles at the central terphenyl ring, whereas the anthracene derivatives have higher rigidity based on the fully conjugated and planar 1,8-diethynylanthracene backbone.

The synthesis of the terphenyl targets began with commercially available 1,3-dibromobenzene, as shown in Scheme 1. A double lithium-bromide exchange reaction and stannylation afforded 7, which was used with 3-iodoaniline in a Stille coupling reaction\cite{31} to provide the terphenyl backbone 8. The anilines were then diazotized with isoamyl nitrite and BF$_3$·OEt$_2$\cite{32} followed by iodination with sodium iodide and iodine to afford 9. A final Sonogashira coupling\cite{33} with the free alkyne 10 gave the terphenyl 1 as the desired target.

Scheme 1. Synthesis of compound 1.
Intermediate 9 was also utilized for the synthesis of a longer terphenyl U-shaped oligomer, as depicted in Scheme 2. 4-Ethynylaniline\textsuperscript{34} (11) was used in a Sonogashira coupling to afford the bis-aniline 12. Diazotization and iodination conditions similar to those as in Scheme 1 were followed in order to isolate the terphenyl diiodide 13. A final coupling with the free alkyne 10 provided the final target 2 in moderate yield.

\begin{center}
\includegraphics[width=\textwidth]{scheme2.png}
\end{center}

**Scheme 2.** Synthesis of compound 2.

The third terphenyl U-shaped target 3 was prepared with a nitro group at the apex position as depicted in Scheme 3, starting with 14 which was prepared in 63\% yield over two steps from 1,3-dibromobenzene.\textsuperscript{35} A Stille coupling between 14 and 1,3-dibromo-5-nitrobenzene afforded 15. Alkaline deprotection of the alkynes gave 16, which was then coupled with alligator clip 17\textsuperscript{36} to afford the desired oligomer 3.

The synthesis of the anthracene-based U-shaped molecule 4 (Scheme 4) started with commercially available 1,8-dichloroantraquinone which was converted to 1,8-dichloroantraquinone 18 using zinc duct in concentrated ammonium hydroxide followed by refluxing in acidic conditions.\textsuperscript{37} Compound 18 was coupled to trimethylsilylacetylene magnesium bromide followed by deprotection using K\textsubscript{2}CO\textsubscript{3} to afford the bis-alkyne 19.\textsuperscript{38} Sonogashira coupling with alligator clip 17\textsuperscript{36} afforded the anthracene oligomer 4.

Conveniently, the bis-alkyne 19,\textsuperscript{38} and similar synthetic steps were used for the construction of a longer U-shaped target 5 as shown in Scheme 5. Compound 19 was coupled with iodide 20\textsuperscript{39} followed by deprotection of the alkyne affording 21. Subsequent coupling with alligator clip 17\textsuperscript{36} yielded the target oligomer 5.

Scheme 5. Synthesis of compound 5.

As illustrated in Scheme 6, a similar anthracene-based U-shaped molecule containing two nitro functional groups was also synthesized. 4-Bromo-3-nitroaniline\textsuperscript{40} (22) was coupled with TMSA to afford 23. The aniline was then diazotized and converted to the aryl iodide following known conditions\textsuperscript{32} to afford 24. Sonogashira coupling with 1,8-diethynylanthracene (19) gave the bis-TMS-protected alkyne 25. A final alkaline deprotection followed by coupling with alligator clip 17 gave the desired dinitro oligomer 6.

3. Assembly

The thioacetyl groups can be deprotected to afford the free thiol or thiolate by deacetylation with NH₄OH, as described previously.⁴¹ Subsequent exposure to a gold surface results in the formation of a Au-S bond. Unlike the assembly of oligomers containing one alligator clip,⁴² the U-shaped OPEs reported here feature two thiolates capable of forming Au-S bonds to the surface. While the planarity enforced by the anthracene backbone of OPEs 4-6 increased the probability that both thiols would participate in the SAM formation, the terphenyl backbone of OPEs 1-3 has more
rotational freedom that could result in incomplete SAM formation and higher defects in surface coverage.

Our calculations corroborated this conjecture. Figure 2 shows calculated energies for oligomer 2 at different dihedral angles of the terphenyl moiety.\textsuperscript{43}

Figure 2. Calculated energies for oligomer 2. The dihedral angle values correspond to $C_2-C_1-C_1-C_2'$ of the terphenyl moiety. The lowest calculated energies were observed at $39^\circ$ (structure a) and $139^\circ$ (zigzag structure b).
Two local minima were found, corresponding to dihedral angles of 39° and 139°. The range between the highest and the lowest energy (going from dihedral angle of 95° to 139°, Figure 2) is only 0.14 Kcal, indicating the free rotation of the terphenyl backbone. It is at the dihedral angle of 139° that the two alligator clips are at opposite ends of a zigzag structure, and it is this conformation that may lead to SAMs with defects and a less ordered organic monolayer. To better understand these calculations, experimental analysis at the interface level was performed using cyclic voltammetry (CV), single wavelength ellipsometry (SWE), and X-ray photoelectron spectroscopy (XPS).

4. Monolayer Analysis

Monolayer formation on a gold electrode was monitored by CV. Ion currents at the electrode under applied bias are an indirect measure of defect densities in the SAM. Figure 3 shows the results of CV tests done at increasing times for SAMs formed, using compound 4 on a working Au electrode by applying a potential in aqueous solutions with 1 mM K₃[Fe(CN)₆] and 0.1 M KCl.

After 15 min of assembly, CV showed that the redox current was decreased by slightly more than half, and the difference between redox peak potentials was increased compared to that of the bare Au electrode (Figure 3a). After a 30 min assembly (Figure 3c), the current was greatly decreased, and the CV showed an almost flattened capacitance shape. After 1 h, the CV indicated that the electrode was fully passivated (Figure 3d), resulting in no electrochemical response at the Au electrode. The passivation of the Au electrode is indicative of SAM formation from compound 4.
Figure 3. Cyclic voltammograms of SAMs formed with compound 4 on a gold electrode at different self-assembly times: (a) 0 min, (b) 15 min, (c) 30 min, (d) 60 min. A potential was applied to the SAM in aqueous solutions with 1 mM K₃[Fe(CN)₆] and 0.1 M KCl to show the passivation ability of the SAM prepared over the differing time intervals. The scan rate was 0.1 V/s at 23 °C, electrode surface area was 1 cm², and the initial scan direction was negative.

Additional data were gathered using SWE to measure SAM film thicknesses resulting from self-assembly experiments with OPEs 1-6. Table 1 summarizes the SWE thicknesses and theoretical values of monolayers formed on gold for each target compound. In general, measured values were slightly lower than theoretical ones, although it should be noted that the tilt angle from surface normal was set at 20°.⁴¹
<table>
<thead>
<tr>
<th>Compound</th>
<th>Experimental Thickness (nm)</th>
<th>Theoretical Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.9</td>
<td>1.5</td>
</tr>
<tr>
<td>2</td>
<td>1.8</td>
<td>2.1</td>
</tr>
<tr>
<td>3</td>
<td>1.4</td>
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<td>5</td>
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<td>2.3</td>
</tr>
<tr>
<td>6</td>
<td>2.3</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Table 1. Comparison of SWE results and theoretical thicknesses of a 24 h (+5 h at 40 °C) chemical assembly of compounds 1-6 on a Au substrate. Self-assembly was conducted in a solvent mixture solution of THF-EtOH (1:1), and the thioacetates were base-deprotected in situ with NH₄OH.⁴⁰ a Values with ± 10% of error. b At a 20° to surface normal angle.

Compounds 2, 3, 5, and 6 have thicknesses approaching the theoretical value for complete monolayer formation after 24 h provided consideration for molecular tilt and twist angles.⁴⁴,⁴⁵ Conversely, compounds 1 and 4 showed larger differences with respect to theoretical values, most likely due to formation of a less ordered SAM or, in the case of 1, possibly the preference of the molecule to assemble in a zigzag conformation similar to the structure represented in Figure 2b. As shown in Figure 4, further ellipsometric analysis was done by recording the growth kinetics of compound 5 while forming a SAM on Au and monitoring the thickness by SWE.
**Figure 4.** Growth kinetics profile of compound 5 assembled on Au in a THF/EtOH/NH₄OH solution.

SAM formation was rapid during the first 5 h, then slowed, and reached near-saturated coverage after 10 h. Similar phenomena have been observed in the adsorption kinetics of nitrated OPEs⁴² and alkanethiols⁴⁶,⁴⁷ on a Au surface. While alkanethiols show a faster film formation (1-2 min), the data in Figure 4 are in agreement with the assembly times reported for OPEs.⁴² The chemical integrity at the interface level of the SAMs was verified by XPS. Figure 5 shows multiplex spectra of the S(2p) region of the SAMs formed on Au using compounds 1-6.
Figure 5. High-resolution XPS multiplex for the S(2p) region of SAMs on Au of compounds 1-6 assembled for 24 h. For comparison, the signals shown in a are from oligomer 2 as the unreacted solid, and inset b is from a cleaned, bare Au sample with no SAM formed. Deconvolutions were made for the spin-orbit components S(2p^{3/2}) and S(2p^{1/2}) peaks. For the 6-SAM note that the deconvoluted doublet signal for the S(2p) of the unreacted 6 thioacetate is shown in green, while the doublet signal for the S(2p) of the
6 thiolate on Au is shown in blue. Comparison of the two doublets indicates there is a ~1:1 mixture of unreacted thioacetate to the thiol. XPS pass energy was 11.75 eV in a 45° takeoff angle. The Au(4f) binding energy of 84.00 eV was taken as a reference for all SAMs.

Similarly, Figure 6 summarizes high-resolution XPS signals at the C(1s) region for the same SAMs. High-resolution XPS multiplex of unreacted solids for S(2p) from the thioacetates of oligomers 1-6 were also recorded, and the corresponding signal for compound 2 is included in Figure 5 inset a for comparison purposes. For all unreacted solids, binding energies for S(2p\(^{1/2}\)) were about 2 eV higher than their corresponding SAMs. The signals for sulfur species, assigned at 162 and 163 eV,\(^{45}\) corresponding to the Au-S-oligomer bonding present in the SAM for every compound (Figure 5) was evidence for direct attachment of these oligomers to the Au surface. It is worth noting that the S(2p) signals for SAMs of compounds 4-6 showed small amounts of other sulfur species such as thioacetates or thiols from unreacted oligomer that did not undergo surface attachment. The SAM formed with compound 6 showed signals for both the SAM thiolate (in blue in the 6 SAM spectrum) and higher energy unreacted thioacetate (in green in the 6-SAM spectrum) in a ratio ~1:1,\(^{48}\) indicating incomplete SAM formation (Figure 5). Longer assembly times might improve the overall quality of the monolayer.\(^{45}\) These assignments fit well with the literature precedent from arylthiolate\(^{45}\) and alkanethiolate\(^{49}\) monolayers on gold.
Figure 6. High-resolution XPS multiplex for the C(1s) region of SAMs on Au of compounds 1-6. The bottom profile corresponds to a bare Au sample with no SAM formed. XPS pass energy was 11.75 eV in a 45° takeoff angle. The Au(4f) binding energy of 84.00 eV was taken as a reference for all SAMs.

Binding energies and relative concentrations for nitrogen, carbon, and sulfur species are summarized in Table 2. The difference in binding energies for unreacted thioacetate and the thiolate covalently attached to the Au surface is evident by comparing entries 1-6 corresponding to the different SAMs and entry 7 corresponding to the unreacted solid oligomer 6. The binding energy of 406.1 eV for an electron-deficient nitrogen species corresponds to the nitro group present on compounds 3 and 6. The C(1s)
signal at 284.6 ± 0.2 eV is assigned to carbon of 1-6 and is different from carbon contamination observed in a bare Au sample with no SAM formed (Figure 6).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound</th>
<th>Binding Energy (eV)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Relative Concentration (%)&lt;sup&gt;b&lt;/sup&gt;</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
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Table 2. Binding energies and relative concentrations for N, C, and S species observed by XPS on SAMs formed with each compound. SAM formation was in a solution of THF/EtOH/NH₄OH for 24 h. The Au(4f) binding energy of 84.00 eV was taken as a reference for all SAMs.<sup>a</sup> Values with ± 0.2 eV of error.<sup>b</sup> Values with ± 2% of error. For entries 1-6 Au comprised the remainder of the measured elements.

5. Summary

We report a new class of structurally isomorphic U-shaped OPEs containing two alligator clips that are capable of forming monolayers on Au surfaces. The quality of this process was analyzed by different techniques. SWE showed near-complete SAM formation after 10 h on a Au surface. Complete SAM formation was also observed on a working Au electrode monitored by CV when applying a potential in aqueous solution. XPS showed that the U-shaped oligomers produced chemisorbed SAMs with clear evidence for Au-S bond formation. Dihedral angle calculations for the terphenyl core of 2 showed that there are two energy minimized conformations, one in which both alligator clips would be situated for attachment to the same Au surface while in the other the two
alligator clips would be about 90° apart, possibly leading to incomplete SAM formation. The anthracene-based oligomers showed higher amounts of unreacted thioacetate in the XPS, probably due to a lower solubility and the need for longer self-assembly times than we used. The results of this molecule-metal interface analysis has encouraged us to pursue microscopy studies, a work currently in progress, with the aim of developing a better understanding of the role of these two classes of OPEs as future candidates for molecular electronics testing and development.

6. Experimental Section

6.1. Calculations. Total energies and energy minimizations of molecular structures were calculated using Spartan 5.1.43 The oligomers structures were geometry minimized at the parametric method No. 3 (PM3) level previous to a full optimization at the density functional theory (DFT) level.

6.2. Gold Substrates. Gold films were deposited by thermal evaporation of 200 nm thick Au onto Si wafers with a 25 nm Cr adhesion layer at a rate of 1 Å/s at 2 × 10^−6 Torr. Before use, the Au substrates were cleaned by a UV/O₃ cleaner (Boekel Industries, Inc., Model 135500) for 10 min in order to remove organic contamination and submerged in ethanol for 10 min before being dried in flowing N₂. This procedure was used to provide a reproducibly clean Au surface.50,51

6.3. Self-Assembly. The oligomer (1 mg) was dissolved in a solution of THF (3 mL) and EtOH (3 mL). Concentrated NH₄OH (10 μL) was then added, and the mixture was incubated for 10 min at room temperature in order to deprotect the thiol group. The cleaned Au substrates were immersed into the adsorbate solution at room temperature for
a period of 24 h, followed by 5 h at 40 °C, unless otherwise stated. All the solutions were freshly prepared, previously purged with N₂ for an oxygen-free environment, and kept in the dark during immersion to avoid photooxidation. After assembly, the samples were removed from the solution, rinsed thoroughly with EtOH, and blown dry with N₂.

6.4. SWE Measurements. Measurements of surface optical constants and molecular layer thicknesses were taken with a single wavelength (632.8 nm laser) Gaertner Stokes Ellipsometer. The \( n_s \) and \( k_s \) values were recorded for every clean Au sample and used for their corresponding SAM-adsorbed sample. The refractive index was \( n_f = 1.55 \) for all compounds \( (k_f = 0) \).\(^{41}\)

6.5. CV Monitored Electrode Passivation. The electrochemistry experiments were carried out using a BAS CV-50W voltammetric analyzer (Bioanalytical Systems, Inc). A conventional three-electrode cell was used with a gold substrate as the working electrode with surface area of 1 cm², a platinum wire as the counter electrode, and a Ag/AgNO₃ (10 mM AgNO₃ and 0.1 M Bu₄NBF₄ in acetonitrile) as the reference electrode. The scan rate was 0.1 V/s at 23 °C, and the initial scan direction was negative. Self-assembly on the working electrode was performed in an organic solution of 1 mM of the corresponding oligomer and base. After self-assembly for the designated time, samples were removed from the solutions and rinsed with EtOH.

6.6. XPS Measurements. A Physical Electronics (PHI 5700) XPS/ESCA system at 3 × 10⁻⁹ Torr was used to take photoelectron spectra. A monochromatic Al X-ray source at 350 W was used with an analytical spot size of 800 µm and 45° takeoff angle, with a pass energy of 11.75 eV. The Au(4f) binding energy of 84.00 eV was taken as a reference for all SAMs.
6.7. Material and General Procedures. Unless stated otherwise, reactions were performed in an oven-dried, nitrogen flushed glassware equipped with a magnetic stir bar and using freshly distilled solvents. Reagent grade Et₂O and THF were distilled from sodium benzophenone ketyl. PhMe and TEA were distilled from calcium hydride. Reagent grade n-hexanes, CH₂Cl₂, MeOH, EtOH, and EtOAc were used without further distillation. TMSA was donated by FAR Research Inc. All other commercially available reagents were used as received. Unless otherwise noted, reactions were magnetically stirred and monitored by TLC using E. Merck silica gel 60 F₂₅₄ precoated plates (0.25-mm). In general, the chromatography guidelines reported by Still were followed.⁵² Flash chromatography was performed with the indicated solvent systems using silica gel grade 60 (230-400 mesh). ¹H and ¹³C NMR spectra were observed at 400 and 100 MHz, respectively, on a Bruker Avance 400 spectrometer. NMR chemical shifts values for deuterated solvents were followed as reported.⁵³ FTIR spectra were obtained on a Nicolet Avatar 360 FTIR. Mass spectroscopy was performed at the Rice University Mass Spectroscopy Laboratory. Melting point values are uncorrected. All new compounds were named using the Beilstein AutoNom application of Beilstein Commander 2000 software. Compound 1-3 were prepared by others.³⁰

6.8. General Procedure for the Coupling of a Terminal Alkyne with an Aryl Halide Utilizing a Palladium-Copper Cross-Coupling (Castro-Stephens/Sonogashira Protocol).³³ To a screw cap tube or a round-bottom flask were added the aryl halide, PdCl₂(PPh₃)₂ (5 mol % based on aryl halide), and CuI (10 mol % based on aryl halide). Alternatively, a mixture of Pd(dba)₂ (0) (10 mol % based on aryl halide) and PPh₃ (10 mol % based on aryl halide) was used. The vessel was sealed with a rubber septum,
evacuated, and backfilled with nitrogen (3×). A cosolvent of THF was added followed by the amine base. The terminal alkyne was then added followed by replacing the septum with a screw cap and the reaction was heated if necessary. TLC was used to follow the progress of the reaction, and when complete, the reaction vessel was cooled to room temperature, and the mixture was quenched with water or a saturated solution of NH₄Cl. The organic layer was diluted with organic solvent and washed with brine (3×). The combined aqueous layers were extracted with organic solvent (3×), and the combined organic layers were dried over anhydrous MgSO₄, the slurry was filtered, and the solvent was removed from the filtrate in vacuo, followed by further purification of the residue as indicated.

6.9. General Procedure for Alkaline Deprotection of Trimethylsilyl-Protected Alkynes. The TMS-protected alkyne was added to an open round-bottom flask, and a solution of K₂CO₃ in MeOH was added to dissolve the organic compound. The reaction was monitored by TLC every 5 min until deprotection was complete. The reaction was quenched with water and extracted with organic solvents (3×). The combined organic layers were dried over anhydrous MgSO₄, the slurry was filtered, and the solvent was removed from the filtrate in vacuo to provide a crude product for further purification via flash chromatography.

6.10. Thioacetic Acid S-{4-[8-(4-Acetysulfanylphenylethynyl)anthracen-1-ylethynyl]phenyl} Ester (4). Following the Sonogashira coupling protocol, 17³⁶ (0.52 g,
1.88 mmol, 19 (0.20 g, 0.89 mmol), PdCl₂(PPh₃) (0.050 g, 0.08 mmol), and CuI (0.03 g, 0.15 mmol) were dissolved in THF (20 mL) and TEA (2 mL). The reaction was stirred overnight at room temperature. Purification by flash chromatography (CH₂Cl₂) afforded the desired product (0.21 g, 45% yield). mp 200 °C (decomp). FTIR (KBr) 1697, 1119, 1093 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 9.57 (s, 1H), 8.49 (s, 1H), 8.04 (d, J = 8.6 Hz, 2H), 7.82 (dd, J = 6.0, 0.9 Hz, 2H), 7.59 (d, J = 6.4 Hz, 4H), 7.50 (quart, J = 6.9, 1.6 Hz, 2H), 7.28 (d, J = 6.4 Hz, 4H), 2.48 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 193.5, 134.6, 132.5, 131.7, 131.6, 131.0, 129.5, 128.5, 127.8, 125.4, 124.6, 124.1, 121.3, 94.3, 89.4, 30.5. HRMS calcd for C₃₄H₂₂O₂S₂: 526.1061. Found: 526.1063.

6.11. **Thioacetic Acid**

S-\([4-(4-\{8-\{4-(4-\text{Acetylsulfanylphenylethynyl}\text{phenylethynyl}][\text{anthracen-1-}
\text{ylethynyl}][\text{phenylethynyl}]\text{phenyl}\}]\) Ester (5). Following the Sonogashira coupling protocol, 21 (0.050 g, 0.13 mmol), 17²⁶ (0.07 g, 0.26 mmol), Pd(dba)₂ (0.01 g, 0.01 mmol), PPh₃ (0.01 g, 0.01 mmol), and CuI (0.01 g, 0.03 mmol) were dissolved in THF (10 mL) and TEA (1 mL). The reaction was stirred overnight at room temperature. Purification by flash chromatography (CH₂Cl₂) afforded the desired product (0.05 g, 53%) as a yellow solid. mp 248 °C (decomp). FTIR (KBr) 2921, 2210, 1915, 1689, 1697, 1504, 1391, 1120, 1010 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 9.60 (s, 1 H), 8.51 (s, 1H), 8.06 (d, J = 8.5 Hz, 2H), 7.83 (d, J = 6.4 Hz, 2H), 7.55 (d, J = 8.5 Hz, 4H), 7.51 (dd, J = 6.4, 1.5 Hz, 2H), 7.45 (d, J = 8.2 Hz, 4H), 7.40 (d, J = 8.2 Hz, 4H), 7.24 (d, J = 8.2 Hz,
4H), 2.46 (s, 6H). $^{13}$C NMR (400 MHz, CDCl$_3$) δ 193.5, 134.4, 132.4, 131.98, 131.95, 131.8, 131.7, 130.9, 129.5, 128.5, 127.9, 125.5, 124.4 124.2, 123.5, 123.2, 121.4, 94.8, 90.9, 90.8, 89.8, 30.5. HRMS calc'd for C$_{50}$H$_{31}$O$_2$S$_2$: 727.1766. Found: 727.1754.

![Chemical structure image]

6.12. Thioacetic Acid S-[4-(4-[8-[4-(4-Acetysulfanylphenylethynyl)-3-nitrophophylethynyl]anthracen-1-ythynyl]-2-nitrophophylethynyl)phenyl] Ester (6). Combining the general deprotection of TMS-alkynes and the Sonogashira coupling protocol, 25 (0.35 g, 0.53 mmol) was dissolved in a mixture of CH$_2$Cl$_2$ (30 mL), MeOH (30 mL), and K$_2$CO$_3$ (0.72 g, 5.2 mmol), leaving the reaction mixture to stir for 3 h. Once an orange solid (0.22 g) was isolated as the free alkyne, 17$^{36}$ (0.23 g, 0.84 mmol), Pd(dba)$_2$ (0.02 g, 0.04 mmol), PPh$_3$ (0.02 g, 0.08 mmol), and CuI (0.02 g, 0.08 mmol) were added and dissolved in THF (20 mL) and TEA (2 mL). The reaction was stirred overnight at room temperature. Purification by flash chromatography (CH$_2$Cl$_2$) afforded the desired product (0.15 g, 35%) as a yellow solid. mp 204-208 °C. FTIR (KBr) 2212, 1700, 1540, 1520, 1501, 1343, 1113, 1088 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ 9.46 (s, 1H), 8.54 (s, 1H), 8.26 (d, J = 1.5 Hz, 2H), 8.10 (d, J = 8.6 Hz, 2H), 7.87 (d, J = 6.9 Hz, 2H), 7.66 (dd, J = 8.0, 1.5 Hz, 2H), 7.51 (m, 8H), 7.28 (d, J = 8.6 Hz, 4H), 2.46 (s, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 193.2, 149.5, 135.4, 134.8, 134.3, 132.8, 131.7, 131.6, 131.5, 130.3, 129.7, 128.2, 127.7, 125.5, 124.2, 123.7, 123.4, 120.4, 118.3, 98.6, 92.5,

6.13. 1,8-Dichloroantracene (18).\textsuperscript{37} To a 500 mL round bottom was added 1,8-
dichloroantracquinone (5.00 g, 18.04 mmol), zinc dust (24.85 g), and NH\textsubscript{4}OH (100 mL). 
The mixture was heated at 75 °C for 30 minutes at which time it was allowed to cool to
room temperature and filtered. The filter cake was washed with boiling \textit{CH}_2\text{Cl}_2 (3\times). 
The washings were combined and concentrated to give a light yellow powder which was
heated to reflux for 1 h in 250 mL \textit{i}-PrOH and 4 mL concentrated HCl. The solution was
cooled to RT and basified with an aqueous solution of NaHCO\textsubscript{3}, extracted with \textit{CH}_2\text{Cl}_2
(3\times), dried using MgSO\textsubscript{4} and concentrated to afford the desired product as a yellow solid
(2.33 g, 53%). \textit{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}) \textit{δ} 9.26 (s, 1H), 8.48 (s,1H), 7.95 (d, \textit{J} = 8.6
Hz, 2H), 7.64 (d, \textit{J} = 8.6 Hz, 2H), 7.42 (dd, \textit{J} = 7.2, 1.3 Hz, 2H).

6.14. 1,8-Diethynyl-antracene (19).\textsuperscript{37} To a 100 mL round bottom flask was added
ethylmagnesium bromide (26.2 mL of a 1.0 M solution in THF) and cooled to 0 °C. 
TMSA (3.77 mL, 26.7 mmol) was added dropwise and allowed to warm to RT during
which time gas was evolved. The grignard was then transferred into a 250 mL round
bottom flask with an attached reflux condenser containing 18 (1.31 g, 5.40 mmol),
Ni(acac)\textsubscript{2} (0.003 g), PPh\textsubscript{3} (0.005 mg), and THF (30 mL). The reaction was heated at
reflux for 24 h until reaction was complete by GCMS. The mixture was poured into H₂O, extracted with CH₂Cl₂ (3×), dried using MgSO₄ and concentrated to afford 1,8-Bis-trimethylsilanyleneathynyl-anthracene as yellow crystals (1.78 g, 89%). ¹H NMR (400 MHz, CDCl₃) δ 9.33 (s, 1H), 8.43 (s, 1H), 7.98 (d, J = 8.6 Hz, 2H), 7.89 (dd, J = 6.9, 0.9 Hz, 2H), 7.44 (dd, J = 8.5, 1.6 Hz, 2H), 0.40 (s, 18H). The crystals (4.12 g, 11.13 mmol), CH₂Cl₂ (100 mL), and MeOH (100 mL) were added to a 500 mL round bottom flask. K₂CO₃ (15.38 g, 111.3 mmol) was added and the reaction was allowed to stir at room temperature for 5 h. The reaction was poured into H₂O, extracted with CH₂Cl₂ (3×), dried using MgSO₄ and concentrated. The residue was purified via column chromatography, silica gel (1:1 CH₂Cl₂/hexanes) to afford the desired product as a yellow crystalline solid (2.9 g, 58%). ¹H NMR (400 MHz, CDCl₃) δ 9.44 (s, 1H), 8.45 (s, 1H), 8.03 (d, J = 8.62 Hz, 2H), 7.80 (dd, J = 6.9, 1.0 Hz, 2H), 7.45 (dd, J = 8.6, 1.6 Hz, 2H), 3.63 (s, 2H).

6.15. (4-Iodo-phenylethylnyl)-trimethyl-silane (20)⁸⁹ To a 500 mL round bottom flask containing a stir bar was added (4-Bromo-phenylethylnyl)-trimethyl-silane (3.58 g, 14.14 mmol). THF (40 mL) was added and the mixture was cooled to -78 °C. tert-Butyllithium (18.24 mL, 28.28 mmol of a 1.55 M solution in pentane) was added dropwise and the reaction was allowed to stir at -78 °C for 45 min at which time iodine (4.31 g, 16.97 mmol) dissolved in THF (50 mL) at -78 °C was added. The reaction mixture was then allowed to stir at -78 °C for 10 min followed by stirring at 0 °C for 25 min. The reaction was poured into an aqueous solution of sodium thiosulfate, extracted
with CH$_2$Cl$_2$ (3×), dried using anhydrous MgSO$_4$ and the solvent removed in vacuo. Column chromatography, silica gel (1:3 CH$_2$Cl$_2$/hexanes) afforded to product as a pale solid (4.04 g, 95%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.64 (d, $J$=8.4 Hz, 2H), 7.19 (d, $J$=8.4 Hz, 2H), 0.25 (s, 9H).

![Structure](image)

6.16. 1,8-Bis-(4-ethynylphenylethynyl)anthracene (21). Combining the Sonogashira coupling protocol and the general deprotection of TMS-alkynes, 19 (0.20 g, 0.89 mmol), 20 (0.55 g, 1.86 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.03 g, 0.04 mmol), and CuI (0.02 g, 0.09 mmol) were dissolved in THF (15 mL) and TEA (2 mL). The reaction was stirred overnight at room temperature. Purification by flash chromatography (1:1 hexanes/CH$_2$Cl$_2$) afforded a yellow solid that was immediately dissolved in a mixture of MeOH (30 mL), CH$_2$Cl$_2$ (30 mL), and K$_2$CO$_3$ (0.96 g, 7.01 mmol). The reaction was stirred for 6 h. Purification by flash chromatography (2:1 hexane/CH$_2$Cl$_2$) afforded the desired product (0.10 g, 27% yield) as a yellow solid. mp 240 °C (decomp). FTIR (KBr) 3296, 3041, 2923, 2201, 1919, 1637, 1497, 1392, 1336, 1255, 1159, 1097, 1023 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ 9.53 (s, 1 H), 8.46 (s, 1H), 8.02 (d, $J$ = 8.5 Hz, 2H), 7.80 (d, $J$ = 6.7 Hz, 2H), 7.49 (m, 6H), 7.37 (d, $J$ = 8.5, 4H), 3.23 (s, 2H). $^{13}$C NMR (400 MHz, CDCl$_3$) δ 132.4, 131.8, 131.7, 131.6, 131.0, 129.5, 127.8, 125.4, 124.1, 123.8, 122.4, 121.3, 94.5, 89.8, 83.4, 79.3. HRMS calcd for C$_{34}$H$_{18}$: 427.1487. Found: 427.1479.

![Structure](image)
6.17. 3-Nitro-4-trimethylsilanylethynylphenylamine (23). Following the Sonogashira coupling protocol, 4-bromo-3-nitroaniline\(^4\) (10.0 g, 45.9 mmol), TMSA (7.8 mL, 55.0 mmol), Pd(dba)\(_2\) (1.3 g, 2.3 mmol), PPh\(_3\) (1.2 g, 4.6 mmol), and CuI (0.6 g, 3.2 mmol) were dissolved in THF (200 mL) and TEA (35 mL). The reaction was stirred overnight at room temperature. Purification by flash chromatography (CH\(_2\)Cl\(_2\)) afforded the desired product (7.7 g, 71%) as an orange solid. mp 95-99 °C. FTIR (KBr) 3483, 3379, 2956, 2151, 1621, 1516, 1341, 1317, 846 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.40 (d, \(J = 8.4\) Hz, 1H), 7.24 (d, \(J = 2.4\) Hz, 1H), 6.78 (dd, \(J = 8.4, 2.4\) Hz, 1H), 4.03 (s, 2H), 023 (s, 9H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 151.4, 147.3, 136.3, 118.8, 109.8, 107.4, 100.4, 99.9, 0.0. HRMS calcd for C\(_{11}\)H\(_{14}\)N\(_2\)O\(_2\)Si: 234.0825. Found: 234.0826.

![Image of structure 24]

6.18. 4-Iodo-2-nitrophenylethynyltrimethylsilane (24). To a 250 mL round bottom flask containing borontrifluoride diethyletherate (16.60 mL, 130.9 mmol) at -40 °C was added 23 (7.70 g, 32.7 mmol) in THF (100 mL), followed by the addition of \(t\)-BuONO (13.60 mL, 114.5 mmol). The reaction was warmed to room temperature and ether was added to precipitate the diazonium salt. The solid was collected by vacuum filtration and washed with ether. The precipitate was then added to a solution of NaI (7.2 g, 48.3 mmol) and I\(_2\) (6.1 g, 24.1 mmol) in CH\(_3\)CN (150 mL). Purification by flash chromatography (1:1, hexanes:CH\(_2\)Cl\(_2\)) afforded the desired product (7.90 g, 69%) as a yellow oil. FTIR (neat) 2960, 2163, 1545, 1529, 1468, 1342, 1250, 879, 846 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.31 (d, \(J = 1.7\) Hz, 1H), 7.85 (dd, \(J = 8.2, 1.7\) Hz, 1H), 7.33 (d, \(J = 8.2\) Hz, 1H), 0.27 (s, 9H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 150.2, 141.7, 136.1,
133.3, 118.0, 105.8, 98.7, 93.0, -0.3. HRMS calcd for C_{11}H_{12}NO_{2}Si: 344.9682. Found: 344.9692.

6.19. 1,8-Bis-(3-nitro-4-trimethylsilanylenethynylphen-ylethynyl)anthracene (25).
Following the Sonogashira coupling protocol, 19 (0.35 g, 1.6 mmol), 24 (1.10 g, 3.3 mmol), Pd(dba)$_2$ (0.09 g, 0.16 mmol), PPh$_3$ (0.09 g, 0.33 mmol), and CuI (0.06 g, 0.33 mmol) were dissolved in THF (15 mL) and TEA (3 mL). The reaction was stirred overnight at room temperature. Purification by flash chromatography (1:1 hexanes:CH$_2$Cl$_2$) afforded the desired product (0.35 g, 34%) as a yellow solid. mp 157-161 °C. FTIR (KBr) 2958, 2198, 2158, 1545, 1346, 1246, 863, 843 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.36 (s, 1H), 8.50 (s, 1H), 8.19, (d, $J = 1.7$ Hz, 2H), 8.07 (d, $J = 8.6$ Hz, 2H), 7.85 (dd, $J = 6.9$, 0.9 Hz, 2H), 7.67 (dd, $J = 8.0$, 1.7 Hz, 2H), 7.51 (m, 4H), 0.33 (s, 18H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 150.4, 135.3, 135.0, 132.2, 131.7, 131.3, 130.3, 128.3, 127.4, 125.5, 124.4, 123.5, 120.4, 118.2, 106.4, 99.3, 92.4, 92.3, -0.1. HRMS calcd for C$_{40}$H$_{32}$N$_2$O$_4$Si$_2$: 660.1901. Found: 660.1906.

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5495.
2905.
43. Spartan version 5.1; 18401 Von Karman Avenue, Suite 370, Irvine, CA 92612 U.S.A.


48. SAM formation for compound 6 did not include the final 5 h assembly at 40 °C.


Chapter 4

Design and Synthesis of Azobenzene Oligo(Phenylene Ethynylene)s for Potential Molecular Electronic Devices
1. Introduction

Molecular electronics research in our group has centered around OPEs which, with the redox active nitro group, have demonstrated NDR at variable temperatures.\textsuperscript{1-3} Additionally, we have synthesized several new classes of potential molecular electronics compounds in our laboratory in order to develop further understanding of the switching process.\textsuperscript{4-7} Our group has focused on rational design principles prior to commencing our syntheses. We propose that for a molecule to behave as a molecular switch it must meet the following requirements; it must have a continuous current pathway (i.e. it must be conjugated), it must have a redox active site where a reduction or oxidation can occur, and it must contain "alligator clips" as a way to connect the molecule to macroscopic electrodes. This chapter presents the synthetic work on azobenzene derivatives that have been synthesized as possible device candidates that bear protected thiol end groups for self-assembled attachment to metallic probes.

The proposed mechanism of redox active nitro functionalized OPEs is that the redox center contributes to the switching behavior of the molecule.\textsuperscript{8} However, other theories have recently been put forth for NDR behavior including molecule/metal-based contact variations that could result in NDR-like performance.\textsuperscript{9,10} By incorporating an azo functionality into an OPE, an additional redox center is created where switching behavior is likely to be observed.\textsuperscript{11} In addition to the redox active site, azobenzenes are known to change between the $E$ and $Z$ configurations when irradiated with light, giving rise to other probable switching mechanisms,\textsuperscript{12} although we are not exploiting that manifold here. Recently azobenzene derivatized molecules have been used in host-guest molecular recognition systems,\textsuperscript{13} molecular switches,\textsuperscript{14} and as molecular scissors.\textsuperscript{15}
In addition to the syntheses, electrochemical testing of selected compounds has been performed, a method found to be useful for qualitative comparisons of molecular electronic devices.\textsuperscript{16}

2. Synthesis

The azobenzene derivatives synthesized are shown in Figure 1 as compounds 1-4 as well as the hydrazo compound 5.

\begin{center}
\includegraphics[width=0.4\textwidth]{azobenzene衍生物.png}
\end{center}

\textbf{Figure 1.} Azobenzene derivatized compounds 1-4 and hydrazo compound 5.

Compound 1 was synthesized from \textit{p}-iodoaniline as shown in Scheme 1. Oxidizing \textit{p}-iodoaniline using potassium permanganate and copper(II) sulfate afforded 6.\textsuperscript{17} Attempts to replace the diiodide using \textit{tert}-butyllithium at \(-78\) °C, followed by
adding sulfur and quenching with acetyl chloride were met with no success. However, using \( n \)-butyllithium, 1 was afforded, albeit in low yield.

\[
\begin{align*}
\text{I-} & \text{NHNH}_{2} \xrightarrow{\text{KMnO}_4, \text{CuSO}_4 \cdot 5\text{H}_2\text{O}} \text{I-} \text{N-} \text{N-} \text{I-} \\
1) \ n\text{-BuLi} & \\
2) \text{S}_8 & \\
3) \text{AcCl} & \\
\end{align*}
\]

Scheme 1. Synthesis of substituted azobenzene 1.

As shown in Scheme 2, coupling 6 with 4-ethynyl-1-thioacetylbenzene\(^{18}\) afforded the expected dicoupled product 2. Since our experiments have shown that compounds without thioacetyl ‘alligator clips’ for adhesion to metallic surfaces after acetyl removal) produced cleaner electrochemical results that are still quantitatively similar to the sulfur-bearing systems,\(^{16}\) we made 7 by coupling phenylacetylene to 6 under the same conditions as those used to make 2. It is important to note that in both of these coupling reactions, none of the hydrazo product was obtained.

\[
\begin{align*}
\text{I-} & \text{N-} \text{N-} \text{I-} \xrightarrow{\text{PdCl}_2(\text{PPh}_3)_2, \text{Cu}, \text{TEA, THF}} \text{X-} \text{N-} \text{N-} \text{X-} \\
2, \ X = \text{SAC, 43\%} \\
7, \ X = \text{H, 40\%} \\
\end{align*}
\]

Scheme 2. Synthesis of azo compounds 2 and 7.

Figure 2a shows the CV of 7. It is evident from the data that the azo linkage contains an additional redox center compared to the unfunctionalized OPE (Figure 2b). From Figure 2b, there are two clear reduction peaks at \(-1.3\) and \(-2.1\) V as well as smaller
features at −1.4 and −1.8 V. The reductions are reasonably reversible. However, because oxygen and water were not rigorously excluded, this data was used, as we have done in our prior work, only for comparison between molecules and to make relative assessments regarding solid-state behavior.

![Graphs](image)

**Figure 2.** CV of (a) compound 7 and (b) an unfunctionalized OPE.

The monothioacetate compound 3 was synthesized as shown in Scheme 3. Compound 6 was coupled to 1 equivalent of TMSA to give 8 followed by coupling with phenylacetylene to give 9. Compound 9 was treated with K$_2$CO$_3$ to give 10 which was finally coupled to 4-iodothioacetyl benzene$^{19}$ to afford 3.

Compounds 4 and 5 were synthesized from 2-nitro-4-iodoaniline as shown in Scheme 3. 2-Nitro-4-iodoaniline was oxidatively coupled using mercury(II) oxide and iodine$^{20}$ to afford the azo derivative 11, exclusively as the $E$ isomer. The poor yield is presumably due to the low reactivity of the electron deficient aniline and the sterically hindered azo product. Compound 11 was then subjected to palladium-catalyzed coupling with 4-ethynyl-1-thioacetylbenzene$^{18}$ to yield both the azo compound 4, and the hydrazo product 5.
Scheme 3. Synthesis of the azo 4 and hydrazo 5.

Figure 3 shows the CV of the dinitro azo compound 4 with multiple reduction peaks at $-1.3$, $-2.0$ and $-2.3$ V and a small peak at $-1.8$ V. We are currently awaiting solid-state testing of these compounds in order to assess their applicability for molecular electronics.

Figure 3. CV of the dinitro azo compound 4.

3. Summary
Azobenzene oligomers have been synthesized bearing functionalities to interface between proximal electronic probes for molecular electronics studies. Initial electrochemical results of unfunctionalized azobenzene oligomers show multiple reversible redox states compared to unfunctionalized OPEs.

4. Experimental

4.1. Materials and General Procedures. Unless stated otherwise, reactions were performed in oven-dried glassware under a nitrogen atmosphere using freshly distilled solvents. Reagent grade Et₂O and THF were distilled from sodium benzophenone ketyl. PhMe and TEA were distilled from calcium hydride. Reagent grade n-hexanes, CH₂Cl₂, MeOH, EtOH, and EtOAc were used without further distillation. TMSA was donated by FAR Research Inc. All other commercially available reagents were used as received. Unless otherwise noted, reactions were magnetically stirred and monitored by TLC using E. Merck silica gel 60 F₂₅₄ precoated plates (0.25-mm). Flash chromatography was performed with the indicated solvent systems using silica gel grade 60 (230-400 mesh). ¹H and ¹³C NMR spectra were observed at 400 and 100 MHz, respectively, on a Bruker Avance 400 spectrometer. NMR chemical shifts values for deuterated solvents were followed as reported. FTIR spectra were obtained on a Nicolet Avatar 360 FTIR. Mass spectroscopy was performed at the Rice University Mass Spectroscopy Laboratory. Melting point values are uncorrected. All new compounds were named using the Beilstein AutoNom application of Beilstein Commander 2000 software.

4.2. General Procedure for the Coupling of a Terminal Alkyne with an Aryl Halide Utilizing a Palladium-Copper Cross-Coupling (Castro-Stephens/Sonogashira Protocol).²⁰ To a screw cap tube or a round-bottom flask were added the aryl halide,
PdCl₂(PPh₃)₂ (5 mol % based on aryl halide), and CuI (10 mol % based on aryl halide). Alternatively, a mixture of Pd(dba)₂ (10 mol % based on aryl halide) and PPh₃ (10 mol % based on aryl halide) was used. The vessel was sealed with a rubber septum, evacuated, and backfilled with nitrogen (3×). A cosolvent of THF was added followed by the amine base. The terminal alkyne was then added followed by replacing the septum with a screw cap and the reaction was heated if necessary. TLC was used to follow the progress of the reaction, and when complete, the reaction vessel was cooled to room temperature, and the mixture was quenched with water or a saturated solution of NH₄Cl. The organic layer was diluted with organic solvent and washed with brine (3×). The combined aqueous layers were extracted with organic solvent (3×), and the combined organic layers were dried over anhydrous MgSO₄, the slurry was filtered, and the solvent was removed from the filtrate in vacuo, followed by further purification of the residue as indicated.

4.3. General Procedure for Alkaline Deprotection of Trimethylsilyl-Protected Alkynes.²¹ The TMS-protected alkyne was added to an open round-bottom flask, and a solution of K₂CO₃ in MeOH was added to dissolve the organic compound. The reaction was monitored by TLC every 5 min until deprotection was complete. The reaction was quenched with water and extracted with organic solvents (3×). The combined organic layers were dried over anhydrous MgSO₄, the slurry was filtered, and the solvent was removed from the filtrate in vacuo to provide a crude product for further purification via flash chromatography.

4.4. Thioacetic acid S-[4-(4-acetysulfanyl-phenylazo)- phenyl] ester (1). To a 100 mL round bottom flask was added bis-(4-iodo-phenyl)-diazene (6)¹⁷ (0.50 g, 1.15 mmol).
THF (50 mL) was added and the reaction cooled to -78 °C. n-Butyllithium (1.04 mL of a 2.21 M solution in hexanes) was added dropwise. The reaction was kept at -78 °C and stirred for 45 min. With a strong backfill of N₂, the septum was removed, sulfur powder (0.078 g, 2.419 mmol) was quickly added, and the septum replaced. The reaction mixture was warmed to 0 °C and stirred for 10 min. The reaction was recooled to -78 °C and acetyl chloride (0.20 mL, 2.76 mmol) was added. The solution was allowed to warm to room temperature overnight and the next day it was poured into H₂O (100 mL) and extracted with CH₂Cl₂ (3×). The organic extracts were combined, washed with brine, dried over anhydrous MgSO₄, and the solvent was removed in vacuo. Flash chromatography, silica gel (CH₂Cl₂) afforded the product (0.025 g, 7%). mp: 162-164 °C. FTIR (KBr) 3019, 1699, 1215, 1116 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, J = 8.8 Hz, 4H), 7.59 (d, J = 8.8 Hz, 4H), 2.48 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 193.6, 153.0, 135.4, 131.8, 124.0, 30.8. HRMS calcd for C₁₅H₁₄N₂O₂S₂: 330.0496. Found: 330.0495.

![Structure](image)

4.5. Thioacetic acid S-(4-(4-[4-(4-acetyl sulfanyl-phenylethynyl)-phenylazo]-phenylethynyl)-phenyl) ester (2). Bis-(4-iodo-phenyl)-diazene (6)¹⁷ (0.69 g, 1.59 mmol) was coupled to 4-ethynyl-1-thioacetylbenzene¹⁸ (0.63 g, 3.57 mmol) following the general coupling procedure at 50-60 °C for 20 min. The reaction was poured into ether and washed with a saturated aqueous ammonium chloride solution. The organic layer was dried using anhydrous MgSO₄ and concentrated in vacuo. The remaining solid was dissolved in hot CH₂Cl₂ and filtered. The filtrate was concentrated to afford the product
(0.36 g, 43%). mp: decomposes at 246 °C. FTIR (KBr) 3052, 2923, 2207, 1912, 1692, 1594, 1557, 1498, 1480, 1397, 1354, 1298, 1283, 1261, 1221, 1181, 1154, 1110, 1012 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, J = 9 Hz, 4H), 7.69 (d, J = 9 Hz, 4H), 7.6 (d, J = 9 Hz, 4H), 7.43 (d, J = 9 Hz, 4H), 2.45 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 193.8, 152.4, 134.7, 133.0, 132.7, 128.9, 125.8, 124.6, 123.5, 91.7, 91.4, 30.7. HRMS calcd for C₃₂H₂₂N₂O₂S₂: 530.1123. Found: 530.1122.

4.6. Thioacetic acid S-\{4-[4-(4-phenylethynyl-phenylazo)-phenylethynyl]-phenyl\} ester (3). Compound 10 (0.05 g, 0.16 mmol) was coupled to 4-iodothioacetyl benzene¹⁹ (0.06 g, 0.20 mmol) according to the general coupling procedure. Column chromatography, silica gel, CH₂Cl₂/hexanes (1:1) afforded the product as an orange solid (0.03 g, 40%). mp: 230-235 °C. FTIR (KBr) 1689, 1597, 1496, 1114, 1102 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, J = 8.6 Hz, 4H), 7.69 (d, J = 8.4 Hz, 4H), 7.57 (m, 4H), 7.43 (d, J = 8.2 Hz, 2H), 7.37 (m, 3H), 2.46 (s, 3H). Repeated attempts to obtain the ¹³C NMR, even at 125 MHz, were unsuccessful due to the insolubility of the material.

4.7. Thioacetic acid S-(4-\{4-(4-acetylsulfanyl-phenylethynyl)-2-nitro-phenylazo]-3-nitro-phenylethynyl\}-phenyl) ester (4). Bis-(4-iodo-2-nitro-phenyl)-diazene (11) (0.100 g, 0.286 mmol) was coupled to 4-ethynyl-1-thioacetylbenzene¹⁸ (0.11 g, 2.29 mmol) according to the general coupling procedure. After 30 min the reaction was complete and poured into CH₂Cl₂ (100 mL) and MeOH (100 mL). Care was taken to
remove mainly the more volatile CH₂Cl₂ on the rotovap. The precipitate was vacuum filtered and washed with MeOH to afford 4 (0.06 g, 30%). mp: decomposes at 350 °C. FTIR (KBr) 2360, 2341, 1715, 1529, 1088 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, J = 1.9 Hz, 2H), 7.82 (dd, J = 7.6, 1.9 Hz, 2H), 7.73 (d, J = 7.6 Hz, 2H), 7.62 (d, J = 9.0 Hz, 4H), 7.46 (d, J = 9.0 Hz, 4H), 2.47 (s, 6H). Repeated attempts to obtain the ¹³C NMR, even at 125 MHz, were unsuccessful due to the insolubility of the material. HRMS calcd for C₃₂H₂₀N₄O₆S₂: 620.0824. Found: 620.0820.

4.8. Thioacetic acid S-[4-(4-{N⁷-[4-(4-acetylsulfanyl-phenylethynyl)-2-nitro-phenyl]-hydrazino}-3-nitro-phenylethynyl)-phenyl] ester (5). The filtrate and MeOH washings from 4 were combined and the solvent was removed in vacuo. The residue was dissolved in a minimum amount of CH₂Cl₂ followed by the addition of hexanes (100 mL). Care was taken to remove only mainly the more volatile CH₂Cl₂ in vacuo. The solid was vacuum filtered and washed with hexanes. The solid was purified by flash chromatography, silica gel (CH₂Cl₂) to afford 5 as an orange solid (0.105 g, 59%). mp: 226-232 °C. FTIR (KBr) 3371, 3019, 2400, 1715, 1529, 1426, 1215 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 9.34 (s, 2H), 8.45 (d, J = 2.4 Hz, 2H), 7.64 (dd, J = 9.0, 2.4 Hz, 2H), 7.54 (d, J = 9.4 Hz, 4H), 7.42 (d, J = 9.4 Hz, 4H), 7.19 (d, J = 9.4 Hz, 2H), 2.45 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 193.8, 144.8, 139.7, 134.7, 133.0, 132.5, 130.3, 128.9, 124.2, 114.8, 114.7, 89.5, 88.9, 30.7. HRMS calcd for C₃₂H₃₃N₄O₆S₂: 623.1059. Found: 623.1054.
4.9. **Bis-(4-iodo-phenyl)-diazene (20).** Potassium permanganate (7.50 g, 86.3 mmol) and copper(II) sulfate pentahydrate (7.50 g, 30.0 mmol) were ground until homogenous and added to a 500 mL round bottom flask containing 4-iodoaniline (4.38 g, 20.0 mmol) and a magnetic stir bar. CHCl₃ (200 mL) was added and the reaction was allowed to stir for 4 days. Upon completion, the reaction was filtered through a silica gel plug, washed with CHCl₃, and the solvent was removed in vacuo. Flash chromatography, silica gel (CH₂Cl₂) afforded the desired product as an orange solid (1.25 g, 15%). ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, J = 9 Hz, 4H), 7.64 (d, J = 9 Hz, 4H).

4.10. **Bis-(4-phenylethynyl-phenyl)-diazene (7).** Bis-(4-iodo-phenyl)-diazene, 6 (0.25 g, 0.58 mmol) was coupled to phenylacetylene (0.15 mL, 1.38 mmol) according to the general procedure. Flash chromatography, silica gel (5:1 hexanes/CH₂Cl₂) afforded the product (0.088 g, 40%). mp: decomposes at 246 °C. FTIR (KBr) 3019, 2400, 1215 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, J = 6.4 Hz, 4H), 7.69 (d, J = 6.4 Hz, 4H), 7.58 (m, 4H), 7.39 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 152.2, 132.9, 132.1, 129.1, 128.9, 126.7, 123.5, 123.3, 92.6, 89.6. HRMS calcd for C₂₆H₁₈N₂: 382.1470. Found: 382.1469.

4.11. **(4-Iodo-phenyl)-(4-trimethylsilylene-phenyl)-diazene.** Bis-(4-iodo-phenyl)-diazene (6) (1.64 g, 3.78 mmol) was coupled to TMSA (0.56 mL, 3.97 mmol)
following the general coupling procedure. Flash chromatography, silica gel hexanes afforded the product as a bright orange solid (0.53 g, 35%). mp: 141-144 °C. FTIR (KBr) 2957, 2159, 1393, 1252, 1213, 1225, 1100, 1051, 1003 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.87 (m, 4H), 7.65 (d, J = 8.7 Hz, 2H), 7.60 (d, J = 8.7 Hz, 2H), 0.28 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 152.1, 151.9, 138.6, 133.1, 126.4, 124.7, 123.1, 104.8, 98.2, 97.6, 0.1. HRMS calcd for C₁₁H₁₇IN₂Si: 404.0206. Found: 404.0210.

4.12. (4-Phenylethynyl-phenyl)-(4-trimethylsilanylethynyl-phenyl)-diazene (9). Compound 8 (0.15 g, 0.37 mmol) was coupled to phenylacetylene (0.05 mL, 0.45 mmol) according to the general coupling procedure. Flash chromatography, silica gel hexanes/CH₂Cl₂ (5:1) afforded the product as a bright orange solid (0.13 g, 93%). mp: 164-167 °C. FTIR (KBr) 2154, 1251, 867, 852 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, J = 8.4 Hz, 2H), 7.95 (d, J = 8.3 Hz, 2H), 7.77 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 8.3 Hz, 2H), 7.61 (m, 2H), 7.45 (m, 2H), 0.27 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 152.1, 152.0, 133.1, 132.7, 131.9, 128.9, 128.6, 126.5, 126.2, 123.3, 123.14, 123.09, 104.8, 97.5, 92.4, 89.4, 0.1. HRMS calcd for C₂₅H₂₂N₂OSi: 378.1552. Found: 378.1553.

4.13. (4-Ethynyl-phenyl)-(4-phenylethynyl-phenyl)-diazene (10). The TMS group was removed according to the general procedure using 9 (0.08 g, 0.21 mmol), K₂CO₃ (0.14 g, 1.03 mmol), CH₂Cl₂ (10 mL), and MeOH (10 mL). No further purification was necessary. The product was isolated as an orange solid (0.06 g, 99%). mp: 171-174 °C.
FTIR (KBr) 3277, 1384, 1154, 1103 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.91\) (m, 4H), 7.67 (m, 4H), 7.58 (m, 2H), 7.38 (m, 3H), 3.25 (s, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 152.4, 151.9, 133.2, 132.7, 131.9, 128.9, 128.7, 126.6, 125.1, 123.3, 123.1, 92.4, 89.4, 83.5, 79.9.\) HRMS calcd for C\(_{22}\)H\(_{14}\)N\(_2\): 306.1157. Found: 306.1154.

4.14. **Bis-(4-iodo-2-nitro-phenyl)-diazene** (11). To a 250 mL round bottom flask charged with a magnetic stir bar was added 4-iodo-2-nitroaniline (2.00 g, 7.58 mmol), mercury(II) oxide (2.46 g, 11.36 mmol), and iodine (2.88 g, 11.36 mmol). CH\(_2\)Cl\(_2\) (80 mL) was added and the reaction mixture was allowed to stir overnight. The next day the reaction was filtered through a silica gel plug and washed with copious amounts of CH\(_2\)Cl\(_2\). The filtrate was then washed with a saturated aqueous solution of sodium thiosulfate, dried over anhydrous MgSO\(_4\), and the solvent removed in vacuo. Flash chromatography, silica gel (1:1 petroleum ether/Et\(_2\)O) afforded the product as brown crystals (0.15 g, 4%). mp: 244 °C. FTIR (KBr) 3076.3, 3019.1, 1517.1, 1336.1, 1215.1, 1090.6, 840.0, 756.3, 666.5 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.31\) (d, \(J = 2.0\) Hz, 2H), 8.05 (dd, \(J = 8.1, 2.0\) Hz, 2H), 7.40 (d, \(J = 8.1\) Hz, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 148.4, 144.8, 143.3, 133.6, 120.3, 97.6.\) HRMS calcd for C\(_{12}\)H\(_8\)N\(_4\)O\(_4\)I\(_2\): 523.8478. Found: 523.8492.

**References:**


Chapter 5

Fabrication of Carbon Nanotube-Molecule-Silicon Junctions and Molecular Grafting to Silicon Surfaces in Air Using Organic Triazenes as Stable Diazonium Sources and HF as a Constant Hydride-Passivation Source
1. Introduction

As the semiconductor industry approaches the limits of CMOS technology, efforts are underway to develop strategies to extend the life of silicon technology.\textsuperscript{1} These processes could involve building functional structures atop semiconductors by relying on the spontaneous self-assembly and self-patterning of organic molecules at the surface of the substrate. In our previous work on NanoCell molecular memories,\textsuperscript{2} we found that formation of metallic nanofilaments via electromigration was the likely source of the observed switching effect. It is often difficult to avoid metallic nanofilament formation; hence the recording of molecular behaviors in metallic junctions can be complicated.\textsuperscript{3,4} The direct covalent grafting of aryl molecules onto hydride passivated silicon surfaces via the reaction of aryldiazonium salts\textsuperscript{4} creates an opportunity for developing molecular electronic devices that do not have metal electrodes in direct contact with molecular species, thereby obviating the formation of metallic filaments and providing a venue for recording of molecular electronic behavior.

Previous work in our laboratory has demonstrated covalent attachment of arenes via aryldiazonium salts to Si (hydride passivated single crystal or poly Si; <111> or <100>, p-doped, n-doped or intrinsic), GaAs, and Pd surfaces.\textsuperscript{5} In the case of Si, this provides a direct arene-Si bond with no intervening oxide. We also reported on the use of aryldiazonium salts for the direct covalent linkage of arenes to SWNTs where the nanotubes can exist either as bundles or individual structures\textsuperscript{6,7} (when surfactant-wrapped). Here, we merge these two concepts for the covalent attachment of individualized (unroped) SWNTs to Si surfaces via orthogonally functionalized OPE aryldiazonium salts.\textsuperscript{8-14} To our knowledge this is the first procedure\textsuperscript{15} to covalently
attach SWNTs to a silicon surface that does not require a CVD growth process. In addition to functioning as the linker units, OPEs and related conjugated molecules can serve as electronically active moieties in sensor and device embodiments. Hence the union of easily patterned silicon with the often hard-to-affix nanotubes can provide a critical interface methodology for electronic and sensor arrays.

Also presented in this chapter is a procedure to covalently graft aryl molecules to hydride-passivated Si(100) surfaces (Si-H) by the in situ conversion of aryl-diethyltriazenes into aryl-diazonium salts using 2% HF, followed by spontaneous surface grafting of the aryl species to the silicon surface. Major advances are, first, reactive diazonium species need not be isolated, and second, by using aqueous HF as the triazene-to-diazonium conversion promoter, the entire process can be carried out in air since any Si-oxide is continuously converted to the Si-H species. Molecular layers from a monolayer to 200 nm thick could be formed depending on reaction conditions. In one case where the molecule bore an α-triazene and ω-aniline, after grafting of the molecular layer onto Si-H via the triazene, the remaining aniline moiety was converted into a diazonium salt in situ with NOBF₄, and then permitted to react with functionalized SWNTs, thereby providing an alternative route to covalently attaching carbon nanotubes to the silicon surface using the aryl molecular layer generated from an aryldiethyltriazenes as the tethering unit.

2. Results

Chemical orthogonality provides chemoselection for dual substrate/nanotube attachment while OPEs provide a rigid structure to minimize molecular looping upon surfaces. The target OPE molecules contain a diazonium salt on one end and an aniline
moiety on the other end as shown in Figure 1. This design allows for selective assembly via the first diazonium salt onto a hydride passivated silicon surface followed by diazotization of the aniline using an alkyl nitrite.17 Once formed, the new diazonium salt, covalently bound to the Si surface, will react with an aqueous solution of individualized SDS-wrapped SWNTs18 (SWNT/SDS) resulting in covalent attachment of the SWNTs19 to the silicon surface using the OPEs as shown in Scheme 1.

**Figure 1.** Oligo(phenylene ethynylene)s 1 and 2 used to covalently attach SWNTs to silicon.

**Scheme 1.** Stepwise attachment of carbon nanotubes to silicon via 1.
The key to developing an orthogonal attachment chemistry was the formation of a diazonium species with a latent diazonium salt at the other end. An α-dialkyltriazenyl-ω-aniline proved to be efficacious upon the demonstration that the triazene could be converted to a diazo species\textsuperscript{20} without affecting the aniline. The synthesis of the mononitro compound 1 is shown in Scheme 2. 4-Iodoaniline was first treated with t-BuONO in BF\textsubscript{3}·OEt\textsubscript{2}\textsuperscript{17} to generate the diazonium salt followed by conversion to the triazene 3\textsuperscript{21} using diethylamine and K\textsubscript{2}CO\textsubscript{3}.\textsuperscript{22} 4-Iodo-2-nitrophenylethynyltrimethylsilane (4) was coupled to 4-ethynylaniline\textsuperscript{23} followed by deprotection of the alkyne to give 5. Compound 5 was coupled to compound 3 to give compound 6. Treatment of the triazene moiety on 6 was readily converted to the diazonium salt upon treatment with HBF\textsubscript{4} while the aniline remained intact; the latter thereby serving as a masked diazonium salt ready for generation after surface attachment. Attempts to use an α,ω-bis-diazonium salt OPE were unsuccessful due to the spontaneous loss of the terminal diazonium during the silicon assembly.\textsuperscript{5}
Scheme 2. Synthesis of compound 1.

The synthesis of compound 2 is shown in Scheme 3. Compound 7 was coupled to 4-ethynylaniline\textsuperscript{23} followed by deprotection of the TMS group to give 8.\textsuperscript{24} Compound 8 was then coupled to 3\textsuperscript{21} to afford 9 which was converted to the diazonium salt 2 in good yield.


In a typical experiment, the diazonium salt (1 or 2) in anhydrous CH\textsubscript{3}CN (2.0 mM) was exposed to a hydride passivated silicon <111> surface according to our previous report\textsuperscript{5} in a nitrogen-filled glove box for the desired reaction time (vide infra). Following monolayer assembly, the substrate was removed from the glove box and placed in a 0.3 M solution of isoamyl nitrite in CH\textsubscript{3}CN for 5 min to diazotize the terminal aniline (Scheme 1). The substrate was then removed and immediately immersed in an aqueous SWNT/SDS suspension\textsuperscript{18} (0.7 μM) at pH 10 for 24 h. The SWNT remained predominantly as individualized SWNTs rather than in bundles. Following nanotube
attachment, the substrate was removed, rinsed with water, CH$_3$CN and dried with a stream of nitrogen to afford the desired structure (Scheme 1).

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<thead>
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<th>Molecule</th>
<th>Thickness (nm)</th>
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<tr>
<td></td>
<td>found$^a$</td>
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<tr>
<td>1</td>
<td>2.0$^c$</td>
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<tr>
<td>2</td>
<td>1.4$^c$, 2.1$^d$</td>
</tr>
</tbody>
</table>

*Table 1.* Calculated and observed thicknesses of 1 and 2 on Si $<111>$. $^a$Value measured by ellipsometry with ca. ±0.2 nm error. $^b$The theoretical thickness calculated by molecular mechanics (not including the arene-silicon bond). All reported values are an average of three measurements for reactions of a 2.0 mM solution of diazonium salt in CH$_3$CN. $^c$Assembly performed inside a nitrogen filled glove box for 1 h and $^d$16 h.

Molecular attachment to the silicon substrate was analyzed using ellipsometry as shown in Table 1. Monolayer formation for 1 reached the theoretical height after 1 h. However, monolayer thicknesses for 2 averaged slightly below the theoretical SAM thickness, although thicknesses close to the theoretical value were attained by reacting the substrate with a solution of 2 for longer time periods.
Figure 2. XPS spectrum of the N1s region of a SAM of compound 1 (45° take off angle).

Figure 2 shows the XPS spectrum of the N1s region of a monolayer of 1. The smaller peak at 405.8 eV is due to the nitrogen atom of the nitro group and the peak at 399.7 eV is due to the aniline plus nitrogen gas adsorbed from the atmosphere. Attempts to measure the nitrogen signal of the surfaced tethered diazonium salt were unsuccessful due to its rapid decomposition during transfer in air.

SWNT attachment was further verified using atomic force microscopy (AFM) (Figure 3). The AFM image (Figure 3a) shows a high coverage of SWNTs bound to the silicon substrate via the OPE molecules. The architectures are highly robust and able to withstand rinsing and 1 min of sonication. Many surface-bound nanotubes exist as individuals although there may be small bundles present as well. While the nanotube diameters range from 0.95-3.1 nm as recorded by the height measurements, they can be difficult to precisely ascertain due to their projection upward off the molecule-grafted surface. We found SWNT coverage to be controllable by varying the SDS/SWNT reaction time with the terminal diazonium salt from 3-16 h.

Control experiments were performed to ensure both the OPE and diazotization steps were required for SWNT attachment. When the OPE was not employed or when the second diazotization step was eliminated (Figure 3b), there were few if any SWNTs bound to the silicon surface. This leads us to conclude that the SWNTs are indeed
covalently attached\textsuperscript{19} to the assembled organic molecule via the in situ generated diazonium salt.

Figure 3. Tapping mode AFM image of SWNTs covalently bound via 1 (not seen) on a silicon surface (a) and AFM image when the isoamyl nitrite diazotization reaction of the terminal aniline is not employed (b). Few if any SWNTs are seen on the surface.

It is important to note that when using NOBF\textsubscript{4} to perform the diazotization (as opposed to the alkynitrite) on the assembled monolayer, surface roughening in the form of large peaks and valleys (10-20 nm) was observed and there were no surface-bound nanotubes. For anhydrous assembly conditions, NOBF\textsubscript{4} could be used (vide infra).

The lightly functionalized surface-bound SWNTs are likely to retain significant degrees of their electronic and optical properties since it takes functionalization of ca. 1 in 100 carbons along a SWNT to even cause a loss of the sensitive UV van Hove singularities.\textsuperscript{25} Furthermore, when applied only to the end-segments of SWNTs that straddle patterned gap arrays, the active central portions of the SWNTs will remain unperturbed by the surface hybridization moieties. Thus this Si-nanotube assembly strategy could provide the basis for directing SWNTs to precise junctions in electronic, optical and sensor arrays.
This technique of fabricating carbon nanotube-molecule-silicon arrays\textsuperscript{15} and forming self-assembled monolayers of organic molecules on silicon surfaces\textsuperscript{5} depends solely on the covalent attachment of arenes on hydride passivated silicon surfaces. In the reaction of aryl diazonium salts with silicon hydride surfaces, radicals are believed to be the reactive intermediate, thus forming an organic molecular layer as shown in Figure 4 for the Si(100) surface.\textsuperscript{5}

\textbf{Figure 4.} Proposed mechanism for the reaction of aryl diazonium salts with Si(100) surface.\textsuperscript{5} Monolayer formation is achievable; however, multilayer formation can be facilitated through higher reaction concentrations and prolonged reaction times (hours).
Described here is a method to covalently graft organic arenes to hydride-passivated Si(100) surfaces (Si-H) by the in situ conversion of aryldiethyltriazenes, 3, 9-13,26,27 (Figure 5), into diazonium salts using dilute aqueous HF. Reactive diazonium species need not be isolated, and by using aqueous HF in the reaction medium, the entire process can be carried out in air since any Si-oxide is continuously converted to the Si-H species. Therefore the process is compatible with simple organic device fabrication methods and paves the way for diverse silicon-molecule studies in, for example, molecular electronics, sensors, and photo-electrochemical-based conversion arrays.

Also described is the formation of carbon nanotube-molecule-silicon junctions using an α-dialkyltriazenyl-ω-aniline 9 to covalently attach carbon nanotubes to silicon surfaces, similar to what was described earlier. By dovetailing with the methods here, we show that the aryltriazene 9 can be grafted to a hydride passivated silicon surface, converted to a terminal diazonium salt and reacted with carbon nanotubes for the bridging of SWNTs to silicon surfaces via the molecular layer.

![Chemical structures](image)

**Figure 5.** Triazenes used in the present study.
It is not uncommon for diazonium salts to be unstable in the presence of oxygen, hence monolayer formation on the silicon surface must be conducted in a glove box, under a nitrogen atmosphere. Furthermore, some diazonium species are not stable to isolation; therefore their direct reaction with Si-H can not be carried out. There are also potential safety hazards involved with the production and storage of some diazonium salts. The use of organic triazenes overcomes these limitations by offering an air stable compound that can be converted in situ to the corresponding diazonium salt with the use of an appropriate acid, as shown in Scheme 4. When the diazonium salt is generated by acid treatment in the presence of a hydride passivated silicon surface, a covalently bound organic layer is formed. This process was performed under ambient conditions in air (vide infra). In some cases, butylated hydroxytoluene (BHT) was added in an attempt to retard multilayer formation. The calculated molecular lengths of triazenes 3, 10-13 are shown in Table 2 and the film thicknesses generated, measured by ellipsometry, under different reaction conditions are listed in Table 3.

Scheme 4. Formation of aryldiazonium salts from aryltriazenes.

<table>
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<tr>
<th>compound</th>
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<tr>
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<td>1.3</td>
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<tr>
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Table 2. Calculated molecular length for triazenes.
<table>
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<th>compound</th>
<th>conc. (mM)</th>
<th>time (h)</th>
<th>measured film thickness (nm)\textsuperscript{a}</th>
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<tr>
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<td>1.2 ± 0.3</td>
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<td>13</td>
<td>0.3</td>
<td>16</td>
<td>3.2 ± 0.3</td>
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</table>

Table 3. Film thickness for in situ reaction of triazenes 3, 10-13 in 2% HF solution on Si(100). \textsuperscript{a}The measured values are the average of three identically prepared samples. \textsuperscript{b}Solid BHT was added to a final conc. of 0.01 M.

Five dilute acids, HF, HCl, HBF\textsubscript{4}, AcOH, and trifluoroacetic acid (TFA) were surveyed to discover which acid generated diazonium salts in situ most effectively by measuring film formation on the silicon surface. After a reaction time of 1 h, it was found that film formation only occurred in the HF solution. Apparently, the presence of HF was necessary to assure a fresh hydrogen-terminated silicon surface in the presence of
the water (from the acid) and atmospheric oxygen. Using these conditions, dilute aqueous HF acts both as an acid for the triazene-to-diazonium conversion as well as an etching agent for the continuous silicon-oxide to Si-H conversion. By increasing the concentrations of the triazene solutions of 3 and 10 to 20 mM (Table 3), we found that they formed multilayers up to 200 nm thick in 1 h. This could prove to be useful if seeking, for example, extended low κ dielectrics for electronic pattern layering on Si-wafers. The addition of BHT to the triazene reaction mixture, in order to hinder a radical processes, led to thinner films in some cases (Table 3, compare entry 1 to entry 2), while in several other cases there was little to no effect; the proposed radical mechanism may be too fast for interception of radical intermediates by the BHT at the surface.

When diazonium salt 14 was subjected to the assembly conditions described here (aqueous HF/CH$_3$CN in air), in the absence or presence of BHT, monolayer films were assembled on the Si(100) surface, with thickness of 1.4 nm and 1.3 nm, respectively. This result is identical to film assembly using the standard diazonium reaction procedure in a glovebox, and confirms that direct grafting of the film can take place in a mixture of HF and CH$_3$CN.

Brown precipitates were observed during film assembly of triazenes 3 and 10 at the 20 mM concentrations (but not at the lower concentrations) after 1 h. This could indicate that I$_2$ may have formed during the reaction with concomitant multilayer formation. This was further investigated using 10, by repeating the reaction in air or under Ar for 1 h at 20 mM. After film formation the substrate was rinsed with water and
acetonitrile and dried with nitrogen. The film thickness was measured and XPS data were collected for the films. The film thickness and the atomic concentration for C, O, F, and I from multiplex scans for the two samples are listed in Table 4.

<table>
<thead>
<tr>
<th>entry</th>
<th>conditions</th>
<th>atomic concentration</th>
<th>film thickness (nm)</th>
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<td></td>
<td></td>
<td>C_{1s}</td>
<td>O_{1s}</td>
</tr>
<tr>
<td>1</td>
<td>air</td>
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<tr>
<td>2</td>
<td>Ar</td>
<td>78.1</td>
<td>5.3</td>
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</table>

Table 4. Atomic concentration and film thickness of 10 in the presence and absence of air.

When the reaction was performed in air (entry 1), the film thickness (~195 nm) was much greater than when the film was assembled under Ar (~25 nm, entry 2). By XPS the oxygen content of the film produced in air is about three times that of the film produced in Ar. The incorporation of oxygen into the film indicates that oxygen might an important role in multilayer formation.

Figure 5 shows XPS C1s core level spectra in the films from entries 1 and 2, Table 4. The main peak at 284.5 eV is attributed to the aryl carbons, and the sub-peak at around 286.5 eV is the contribution from –C-O bond or –C=O bond. However, there is no detectable peak C-F peak at 288eV, indicating that no C-F species are present in the film.\textsuperscript{11} Based on the observation of the dark precipitate and the XPS data, both the iodo- and fluoro- groups were lost from the aryl rings during the assembly process. The F1s signal remained even after sonicating the samples in water for a few min, indicating that F is trapped in the film. Since the loss of iodine and fluorine from the aromatic ring of 10 occurred both in the presence and absence of air, the mechanism by which oxygen is
incorporated into the film, may not be connected to the loss of the halides. Further work is ongoing to discern the details of this process.

![Graph showing C1s XPS spectrum of 10 from entry 1 and 2 films (Table 4) under air and Argon atmosphere.]

**Figure 5.** C1s XPS spectrum of 10 from entry 1 and 2 films (Table 4) under air and Argon atmosphere.

To further evaluate the effectiveness of this procedure, we sought to use an α-dialkyltriazenyln-ω-aniline compound (9), instead of the diazonium salt (1 or 2) to form carbon nanotube-molecule-silicon junctions stated previously. The aniline moiety that remained after grafting a layer derived from 9 to the silicon surface was further converted to a diazonium salt in situ using NOBF₄ in the presence of functionalized SWNTs to produce the desired layer of SWNTs bound to the silicon surface via the intermediate layer of aryl molecules (Scheme 5). The diazonium-terminated surface-grafted molecules were stable enough to permit the in situ assembly to occur.
Scheme 5. Assembly of the functionalized SWNTs to the film derived from 9 on Si(100).

The AFM image of the SWNT-aryl-Si assembly formed from triazene 9 (Scheme 5) is shown in Figure 6. It can be seen that the substrate surface is well-covered with SWNTs similarly to Figure 3a.
Figure 6. AFM image of SWNTs covalently bound to the organic thin film derived from 9 on the silicon surface. The height of the SWNTs ranges from 0.8 nm to 3.2 nm. Black bar in lower right = 100 nm.

Based on the height measurement in the AFM, it can be determined that the nanotubes from this experiment are again most likely individuals or small bundles with heights ranging from 0.8 nm to 3.2 nm. Since the silicon surface itself is not flat after the in situ film assembly process, with increases in roughness due to the layer of organic film and the fact that NOBF₄ slowly etches silicon surfaces (as shown by our control tests), some of the tubes may be extending out of the surface plane. Also, there are likely molecules or other nanotubes underneath the SWNTs, yielding a higher apparent height. The surface-bound SWNTs were again stable to rinsing and short sonication (30 s) under solvent. Control experiments were also performed to ensure that the NOBF₄ diazotization step was required for SWNT attachment. Indeed, when the NOBF₄
diazotization step was eliminated, there was no attachment of the SWNTs to the silicon surface. In previous study for grafting SWNTs to Si using compound 1 or 2, NOBF₄ could not be used since, in the presence of water, severe etching of the Si surface ensued. However, anhydrous conditions (CHCl₃-CH₂CN) were utilized in this case. Therefore, nanotube-molecule-silicon junctions prepared using either methodology could prove to be excellent non-metallic molecular electronic interfaces.

3. Summary

This chapter presents the covalent attachment of carbon nanotubes to Si:H (111) or (100) surfaces using orthogonally functionalized OPEs. These carbon nanotube-molecule-silicon junctions hold promise for both molecular electronic and chemical sensor devices. To our knowledge this is the first reported procedure to covalently attach SWNTs to silicon via a surface bound organic molecule. Also presented is an in situ film assembly using organic triazenes for the formation of Si-molecule assemblies under ambient conditions. Dilute aqueous HF serves as the reagent necessary for the organic conversion (triazene to diazonium) and concomitantly acts as an in situ etchant for Si-O to Si-H conversion, thereby making the reactions possible in air. Most of the triazenes formed thin films, with several forming layers up to 200 nm thick. Using the latter methodology were also able to successfully attach functionalized SWNTs to the monolayers derived from an aryldiazonium intermediate grafted onto a Si(100) surface. Use of these Si-molecule-SWNT junctions for electronic device formation is currently being explored and the device behavior will be reported elsewhere.

4. Experimental Section
4.1. **Reagents and Solvents for Surface Characterization.** CH$_3$CN, 99.5+\% was purchased from Aldrich and stored in an nitrogen filled glove box. Reagent grade CH$_3$CN and pure water (resistivity $> 18 \text{ M}\Omega\text{ cm}$) were used for rinsing. Semi-conductor grade NHF$_4$ 40\% was purchased from Aldrich. Concentrated HCl, concentrated NH$_4$OH, concentrated H$_2$SO$_4$, 49\% HF, and 30\% H$_2$O$_2$ were purchased at reagent grade.

4.2. **Ellipsometric Measurements.** The film thickness was measured using a single wavelength (632.8 nm laser) Gaertner Strokes ellipsometer. The $n$ and $k$ values were taken for each substrate. The thickness was modeled as a single absorbing layer on the top of an infinitely thick substrate (fixed $n_a$). The observed error for repeat measurements of the same spot was typically less than 0.2 nm.

4.3. **AFM Measurements.** A Digital Instruments Nanoscope IIIa tapping mode instrument was used to obtain AFM images of SWNTs. The images were taken in air without the use of a purge box and immediately imaged following assembly.

4.4. **XPS Measurements.** A Quantera XPS Scanning Microprobe was used in collecting the XPS data, the takeoff angle was 45\°, and 114.8W monochromatic Al X-ray source was applied for all the measurements.

4.5. **Preparation of SWNT-Molecule-Silicon Junctions Using Compound 1 or 2.** Si(111) shards (prime grade, boron doped) were cleaned in piranha solution (2:1 H$_2$SO$_4$:H$_2$O$_2$) at 100 \degree C for 30 min, and rinsed with pure water (resistivity $> 18 \text{ M}\Omega\text{ cm}$). The shards were immersed in Ar-sparged 40\% NH$_4$F solution for 15 min to generate the hydrogen-terminated surface. The shards were rinsed thoroughly with water and dried in a stream of nitrogen gas. The fresh surfaces were immediately brought into an N$_2$ glove box. A 0.2 mM solution of 1 or 2 in anhydrous CH$_3$CN was freshly prepared in the
glove box and the hydrogen terminated silicon substrates were immersed in the solution. The reaction vessel was sealed for the desired reaction time. Following assembly, the substrates were removed from the glove box, rinsed with CH$_3$CN, and dried with N$_2$. The film thickness was immediately measured with by ellipsometry and XPS data was collected. The substrate was removed from the glove box and placed in a 0.3 M solution of isoamyl nitrite in CH$_3$CN for 5 min to diazotize the terminal aniline. The substrate was removed and immediately immersed in a sodium dodecylsulfate (SDS)/SWNT suspension$^{6,7}$ (0.2 µM) at pH 10 for 3-16 h (depending on coverage requirements). Following nanotube attachment, the substrate was removed, rinsed with water, CH$_3$CN and dried with a stream of nitrogen to afford the desired structure.

4.6. Assembly of Organic Triazenes. Si(100) shards (prime grade, As doped) were cleaned in piranha solution (2:1 H$_2$SO$_4$:H$_2$O$_2$) at 100 °C for 30 min, and then rinsed with pure water (resistivity > 18 MΩ cm$^{-1}$). The shards were immersed in etching solution, a mixture of 4% aqueous HF and CH$_3$CN (v:v, 1:1; hence 2% HF overall) for 5 min under Ar atmosphere. The triazenes were dissolved in 10 mL CH$_3$CN at the concentrations indicated in Table 3 before being added to the etching solution containing the Si(100) wafer. The reaction vessel was sealed with a fitted lid and the container was agitated on a platform shaker at 100 rpm. After the reaction, the substrates were copiously rinsed with deionized H$_2$O and CH$_3$CN then dried with a stream of N$_2$.

4.7. Preparation of Functionalized SWNTs.$^{6,7}$ An SDS suspension of SWNTs, 600 mL (40 mg/L, 0.024 g, 2.0 m equiv of carbon) was treated with 4-tert-butyldiazobenzene tetrafluoroborate (0.992 g, 4.0 mmol). The pH of the solution was adjusted to 10 with 6 M NaOH, at which point the mixture was allowed to stir for 3 h. After completion of the
reaction, the mixture was diluted with acetone and filtered over a polycarbonate membrane (1 μm pore size). The filter cake was washed with water (100 mL) and acetone (200 mL), and then dried (30 mg). The TGA mass loss was 31.5%. The Raman D to G- band ratio was 0.30.

4.8. Preparation of SWNT-Molecule-Silicon Junctions Using Compound 9. Organic triazene 9, was assembled on a hydride-passivated silicon surface using the same protocol as that used for compounds 10-14. Following assembly, the silicon shard was immersed in a dilute solution of t-butylphenyl-functionalized SWNTs in chloroform. An NOBF₄ solution (0.5 mM, 5 mL) in anhydrous CH₂CN was then added to the mixture containing the silicon shard; the NOBF₄ converted the aniline moiety into the diazonium salt in situ and the SWNTs reacted with the diazonium functionality. After 30 min, the sample was removed, rinsed with acetonitrile and chloroform, and dried using a stream of N₂.

4.9. General Synthetic Methods. Unless stated otherwise, reactions were performed in oven-dried, nitrogen flushed glassware equipped with a magnetic stir bar using freshly distilled solvents. Reagent grade THF was distilled from sodium benzophenone ketyl. TEA was distilled from calcium hydride. TMSA was donated by FAR Research Inc. All other commercially available reagents were used as received. Unless otherwise noted, reactions were magnetically stirred and monitored by TLC using E. Merck silica gel 60 F₂₅₄ precoated plates (0.25-mm). Flash chromatography was performed with the indicated solvent systems using silica gel grade 60 (230-400 mesh). ¹H and ¹³C NMR spectra were observed at 400 and 100 MHz, respectively, on a Bruker Avance 400 spectrometer. NMR chemical shifts are reported in ppm downfield from tetramethylsilane (TMS). FTIR spectra were obtained on a Nicolet Avatar 360 FTIR. Mass spectroscopy was performed
at the Rice University Mass Spectroscopy Laboratory. Melting point values are uncorrected. All new compounds were named using the Beilstein AutoNom application of Beilstein Commander 2000 software.

4.10. General Procedure for the Coupling of a Terminal Alkyne with an Aryl Halide Utilizing a Palladium-Copper Cross-Coupling (Castro-Stephens/Sonogashira Protocol).\(^{29}\) To a screw cap tube or a round-bottom flask were added the aryl halide, PdCl\(_2\)(PPh\(_3\))\(_2\) (5 mol % based on aryl halide), and CuI (10 mol % based on aryl halide). The vessel was sealed with a rubber septum, evacuated, and backfilled with nitrogen (3×). A cosolvent of THF was added followed by the amine base. The terminal alkyne was then added followed by replacing the septum with a screw cap and the reaction was heated if necessary. TLC was used to follow the progress of the reaction, and when complete, the reaction vessel was cooled to room temperature, and the mixture was quenched with water or a saturated solution of NH\(_4\)Cl. The organic layer was diluted with organic solvent and washed with brine (3×). The combined aqueous layers were extracted with organic solvent (3×), and the combined organic layers were dried over anhydrous MgSO\(_4\), the slurry was filtered, and the solvent was removed from the filtrate in vacuo, followed by further purification of the residue as indicated.

4.11. General Procedure for Alkaline Deprotection of Trimethylsilyl-Protected Alkynes.\(^{30}\) The TMS-protected alkyne was added to an open round-bottom flask, and a solution of K\(_2\)CO\(_3\) in MeOH and CH\(_2\)Cl\(_2\) was added to dissolve the organic compound. The reaction was quenched with water and extracted with organic solvents (3×). The combined organic layers were dried over anhydrous MgSO\(_4\), the slurry was filtered, and
the solvent was removed from the filtrate in vacuo to provide a crude product for further purification via flash chromatography.

\[ \text{H}_2\text{N}-\text{NO}_2 \]

4.12. 4-[4-(4-Amino-phenylethynyl)-2-nitro-phenylethynyl]-benzenediazonium tetrafluoroborate (1). Compound 6 (0.10 g) was dissolved in THF (20 mL). HBF\(_4\) (48% in water) (0.20 mL) was added dropwise. The mixture turned red and was stirred for 2 min. Et\(_2\)O (50 mL) was added and a yellow precipitate formed. The mixture was filtered and washed with excess Et\(_2\)O under a stream of nitrogen gas to afford 1 (0.07 g, 67%). FTIR (KBr) 3418, 2819, 2574, 2264, 2211, 1574, 1541, 1513, 1346, 1077 cm\(^{-1}\). \(^1\)H NMR (400 MHz, (CD\(_3\))\(_2\)CO) \(\delta\) 8.95 (d, \(J = 9.0\) Hz, 2H), 8.42 (s, 1H), 8.25 (d, \(J = 9.0\) Hz, 2H), 8.05 (s, 2H), 7.92 (d, \(J = 8.6\) Hz, 2H), 7.72 (d, \(J = 8.6\) Hz, 2H). Attempts to acquire \(^{13}\)C NMR spectral information were unsuccessful due to the instability of compound 1 in solution for extended time periods.

\[ \text{H}_2\text{N} \]

4.13. 4-[4-(4-Amino-phenylethynyl)-phenylethynyl]-benzenediazonium tetrafluoroborate (2). Compound 9 (0.12 g) was dissolved in THF (10 mL). HBF\(_4\) (48% in water) (0.20 mL) was added dropwise. The mixture turned red and was stirred for 2 min. Et\(_2\)O (50 mL) was added and a yellow precipitate formed. The mixture was filtered and washed with excess Et\(_2\)O to afford 2 (0.10 g, 80%). FTIR (KBr) 3440, 2849, 2576, 2270, 2208, 1574, 1516, 1079 cm\(^{-1}\). \(^1\)H NMR (500 MHz, (CD\(_3\))\(_2\)CO) \(\delta\) 8.90 (d, \(J = 9.1\) Hz, 2H), 8.21 (d, \(J = 9.1\) Hz, 2H), 7.85 (d, \(J = 8.7\) Hz, 2H), 7.76 (d, \(J = 8.5\) Hz, 2H), 7.72
(d, J = 8.5 Hz, 2H), 7.69 (d, J = 8.7 Hz, 2H). Attempts to acquire \(^{13}\)C NMR spectral information were unsuccessful due to the instability of compound 2 in solution for extended time periods.

4.14. **1-(4-Iodophenyl)-3,3-diethyltriazene (3).**\(^{21}\) 4-Iodoaniline (5.00 g, 22.83 mmol) was added to a 250 mL round bottom flask. THF (25 mL) was added and the reaction was cooled to -30 °C. Boron trifluoride diethyl etherate (11.57 mL, 91.32 mmol) was added dropwise followed by the dropwise addition of \(t\)-BuONO (9.50 mL, 79.91 mmol). The reaction was warmed to room temperature and Et\(_2\)O (150 mL) was added. The mixture was vacuum filtered and washed with Et\(_2\)O to afford the aryl diazonium salt which was dissolved in CH\(_3\)CN (80 mL) and cooled to 0 °C. A solution of H\(_2\)O (40 mL), K\(_2\)CO\(_3\) (8.34 g, 60.41 mmol), and diethylamine (4.20 mL, 40.27 mmol) was added to the reaction which turned deep red. The mixture was allowed to warm to room temperature over 3 h at which point it was poured in H\(_2\)O and extracted (3×) with CH\(_2\)Cl\(_2\), dried using anhydrous MgSO\(_4\) and concentrated in vacuo. Column chromatography, silica gel (3:1 CH\(_2\)Cl\(_2\)/hexane) afforded 3 as a viscous red oil (5.13 g, 74%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.65 (d, \(J = 8.8\) Hz, 2H), 7.19 (d, \(J = 8.8\) Hz, 2H), 3.79 (q, \(J = 7.1\) Hz, 4H), 1.25 (s broad, 6H).

4.15. **4-Iodo-2-nitrophenylethynyltrimethylsilane (4).** To a 250 mL round bottom flask containing BF\(_3\)-OEt\(_2\) (16.60 mL, 130.9 mmol) at -40 °C was added 3-Nitro-4-
trimethylsilanylethynylphenylamine (7.70 g, 32.7 mmol) in THF (100 mL), followed by
the addition of t-BuONO (13.60 mL, 114.5 mmol). The reaction was warmed to room
temperature and ether was added to precipitate the diazonium salt. The solid was
collected by vacuum filtration and washed with ether. The precipitate was then added to
a solution of NaI (7.2 g, 48.3 mmol) and I₂ (6.1 g, 24.1 mmol) in CH₃CN (150 mL).
Purification by flash chromatography (1:1, hexanes:CH₂Cl₂) afforded the desired product
(7.90 g, 69%) as a yellow oil. FTIR (neat) 2960, 2163, 1545, 1529, 1468, 1342, 1250 cm⁻¹
¹H NMR (400 MHz, CDCl₃) δ 8.31 (d, J = 1.7 Hz, 1H), 7.85 (dd, J = 8.2, 1.7 Hz, 1H),
7.33 (d, J = 8.2 Hz, 1H), 0.27 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 150.2, 141.7,
136.1, 133.3, 118.0, 105.8, 98.7, 93.0, -0.3. HRMS calcd for C₁₁H₁₂INO₂Si: 344.9682.
Found: 344.9692.

4.16. 4-(4-Ethynyl-3-nitro-phenylethynyl)-phenylamine (5). Following the general
coupling procedure (4-Iodo-2-nitro-phenylethynyl)-trimethyl-silane (1.20 g, 3.43 mmol)
was coupled to 4-ethynylaniline¹² (0.44 g, 3.77 mmol) using PdCl₂(PPh₃)₂ (0.12 g, 0.17
mmol), CuI (0.06 g, 0.34 mmol), TEA (4 mL), and THF (20 mL). The reaction was
stirred at 40 °C for 3 days until the starting material was consumed as judged by TLC.
The reaction was poured in H₂O and extracted (3×) with CH₂Cl₂, dried using anhydrous
MgSO₄ and concentrated in vacuo. Column chromatography, silica gel (CH₂Cl₂)
afforded the TMS protected alkyne as a yellow solid (0.87 g, 75%). Following the
general deprotection of TMS-protected alkynes, the yellow solid (0.87 g, 2.56 mmol) was
dissolved in a mixture of CH₂Cl₂ (25 mL), MeOH (25 mL), and K₂CO₃ (1.77 g, 12.81
mmol). The product 5, was afforded without addition purification as an orange solid (0.63 g, 92%). mp: 173-175 °C. FTIR (KBr) 3480, 3006, 2970, 1716, 1423, 1365, 1224 cm\(^{-1}\). \(^1\)H NMR (400 MHz, (CD\(_3\))_2CO) \(\delta\) 8.09 (t, \(J = 1.1\) Hz, 1H), 7.76 (d, \(J = 1.1\) Hz, 2H), 7.31 (d, \(J = 8.7\) Hz, 2H), 6.70 (d, \(J = 8.7\) Hz, 2H), 5.23 (s, 2H), 4.26 (s, 1H). \(^{13}\)C NMR (100 MHz, (CD\(_3\))_2CO) \(\delta\) 151.0, 136.2, 135.6, 134.1, 127.1, 126.9, 116.0, 114.8, 109.5, 96.8, 88.0, 85.3, 78.9. HRMS calcd for C\(_{16}\)H\(_{10}\)N\(_2\)O\(_2\): 262.0742. Found: 262.0737.

![Image](image.png)

4.17. 4-(4-(3,3-Diethyl triazene)-phenylethynyl)-3-nitro-phenylethynyl-phenylamine (6). Following the general coupling procedure 5 (0.63 g, 2.36 mmol) was coupled to 3\(^{21}\) (0.65 g, 2.14 mmol) using PdCl\(_2\)(PPh\(_3\))\(_2\) (0.08 g, 0.12 mmol), CuI (0.04 g, 0.21 mmol), TEA (3 mL), and THF (20 mL). The reaction was stirred at room temperature overnight. The reaction was poured in H\(_2\)O and extracted (3x) with CH\(_2\)Cl\(_2\), dried using anhydrous MgSO\(_4\) and concentrated in vacuo. Column chromatography, silica gel (CH\(_2\)Cl\(_2\)) afforded 6 as a yellow solid (0.50 g, 53%). mp: 172-175 °C. FTIR (KBr) 3496, 3390, 2972, 2204, 1619, 1602, 1538, 1518, 1393, 1343, 1302, 1271, 1099 cm\(^{-1}\). \(^1\)H NMR (400 MHz, (CD\(_3\))_2CO) \(\delta\) 8.14 (d, \(J = 0.9\) Hz, 1H), 7.77 (d, \(J = 2.9\) Hz, 2H), 7.56 (d, \(J = 8.4\) Hz, 2H), 7.5 (d, \(J = 8.5\) Hz, 2H), 7.32 (d, \(J = 8.5\) Hz, 2H), 6.71 (d, \(J = 8.5\) Hz, 2H), 5.21 (s, 2H), 3.83 (q, \(J = 8.1\) Hz, 4H), 1.32 (s, broad, 3H), 1.23 (s, broad, 3H). \(^{13}\)C NMR (125 MHz, (CD\(_3\))_2CO) \(\delta\) 153.1, 150.9, 150.6, 135.7, 135.3, 134.1, 133.5, 127.3, 125.8, 121.4, 119.0, 117.5, 114.9, 109.6, 99.5, 96.5, 85.60, 85.55. HRMS calcd for C\(_{26}\)H\(_{23}\)N\(_5\)O\(_2\): 437.1852. Found: 437.1844.
4.18. (4-Iodo-phenylethynyl)-trimethyl-silane (7). To a 500 mL round bottom flask containing a stir bar was added (4-Bromo-phenylethynyl)-trimethyl-silane (3.58 g, 14.14 mmol). THF (40 mL) was added and the mixture was cooled to -78 °C. tert-Butyllithium (18.24 mL, 28.28 mmol of a 1.55 M solution in pentane) was added dropwise and the reaction was allowed to stir at -78 °C for 45 min at which time iodine (4.31 g, 16.97 mmol) dissolved in THF (50 mL) at -78 °C was added. The reaction mixture was then allowed to stir at -78°C for 10 min followed by stirring at 0 °C for 25 min. The reaction was poured into an aqueous solution of sodium thiosulfate, extracted with CH₂Cl₂ (3×), dried using anhydrous MgSO₄ and the solvent removed in vacuo. Column chromatography, silica gel (1:3 CH₂Cl₂/hexanes) afforded to product as a pale solid (4.04 g, 95%). ¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, J=8.4 Hz, 2H), 7.19 (d, J=8.4 Hz, 2H), 0.25 (s, 9H).

4.19. 4-(4-Ethynyl-phenylethynyl)-phenylamine (8). Following the general coupling procedure 7 (0.75 g, 2.50 mmol) was coupled to 4-ethynylaniline (0.35 g, 3.00 mmol) using PdCl₂(PPh₃)₂ (0.09 g, 0.13 mmol), CuI (0.05 g, 0.25 mmol), TEA (3 mL), and THF (10 mL). The reaction was stirred at 40 °C overnight. The mixture was poured in H₂O and extracted (3×) with CH₂Cl₂, dried using anhydrous MgSO₄ and concentrated in vacuo. Column chromatography, silica gel (CH₂Cl₂) afforded 4-(4-trimethylsilylphenylethynyl)-phenylamine as a yellow solid (0.64 g).
Following the general procedure for the deprotection of TMS-protected alkynes, 4-(4-trimethylsilanylmethyl-phenylethynyl)-phenylethynyl)phenylamine (0.64 g, 2.21 mmol) was dissolved in a mixture of CH₂Cl₂ (15 mL), MeOH (15 mL), and K₂CO₃ (1.53 g, 11.05 mmol). The product 8, was afforded without additional purification as an orange solid (0.47 g, 87%, 2 steps). ¹H NMR (400 MHz, (CD₃)₂CO) δ 7.45 (m, 4H), 7.25 (d, J = 6.7 Hz, 2H), 6.68 (d, J = 6.7 Hz, 2H), 5.09 (s, 2H), 3.77 (s, 1H).

4.20. 4-[4-[4-(3,3-Diethyl triazene)-phenylethynyl]-phenylethynyl]-phenylethynyl)phenylamine (9).
Following the general coupling procedure 8 (0.48 g, 2.21 mmol) was coupled to 3 (0.61 g, 2.01 mmol) using PdCl₂(PPh₃)₂ (0.07 g, 0.10 mmol), CuI (0.04 g, 0.20 mmol), TEA (5 mL), and THF (20 mL). The reaction was stirred at room temperature for 1 h until the starting material was consumed as judged by TLC. The mixture was poured in H₂O and extracted (3×) with CH₂Cl₂, dried using anhydrous MgSO₄ and concentrated in vacuo. The residue was dissolved in a minimum amount of CH₂Cl₂ followed by the addition of hexane. The CH₂Cl₂ was carefully removed in vacuo and the precipitate was collected using vacuum filtration to afford 9 as a pale solid (0.62 g, 79%). mp: 169-173 °C. FTIR (KBr) 3463, 3371, 2973, 2932, 2208, 1618, 1599, 1519, 1396, 1239, 1291, 1237, 1095 cm⁻¹. ¹H NMR (500 MHz, (CD₃)₂CO) δ 7.52 (d, J = 6.9 Hz, 2H), 7.48 (d, J = 6.9 Hz, 2H), 7.42 (d, J = 6.8 Hz, 2H), 7.26 (d, J = 6.8 Hz, 2H), 6.68 (d, J = 6.8 Hz, 2H), 5.20 (s, 2H), 3.83 (q, J = 5.6 Hz, 4H), 1.31 (s, broad, 3H), 1.22 (s, broad, 3H). ¹³C NMR (100 MHz, (CDCl₃) δ 151.3, 147.0, 133.2, 132.5, 131.6, 131.4, 125.0, 123.7, 123.0, 120.6,
119.4, 115.0, 112.6, 92.2 91.9, 89.3, 87.5. HRMS caled for \( \text{C}_{26}\text{H}_{24}\text{N}_4 \): 392.001. Found: 392.2011.

4.21. 4-Phenylamino-benzenediazonium tetrafluoroborate (14). To a 250 mL round bottom flask was added \( N \)-phenyl-\( p \)-phenylenediamine (1.00 g, 5.43 mmol). THF (30 mL) was added and cooled to -50 °C. \( \text{BF}_3 \cdot \text{OEt}_2 \) (2.75 mL, 21.72 mmol) was added dropwise, followed by the dropwise addition of \( t \)-BuONO (0.86 mL, 6.52 mmol) in THF (5 mL). The reaction was allowed to warm to -10 °C at which point \( \text{Et}_2\text{O} \) (150 mL) was added. The suspension was allowed to stir for 10 min. The precipitated solid was collected by vacuum filtration to afford a mixture of 14 and the \( N \)-nitroso adduct. The collected solid was dissolved in a minimum of \( \text{CH}_3\text{CN} \) (10 mL) and \( \text{Et}_2\text{O} \) (150 mL) was added. The green solid was collected by vacuum filtration to afford the title compound as a light green solid (0.31 g, 20%). FTIR (KBr) 2244, 2186, 1603, 1579, 1531, 1493, 1366, 1323, 1112 cm\(^{-1}\). \(^1\)H NMR (400 MHz, \( \text{CD}_3\text{CN} \)) \( \delta \) 8.80 (s, 1H), 8.06 (d, \( J = 10.6 \) Hz, 2H), 7.49 (t, \( J = 8.1 \) Hz, 2H), 7.34 (m, 3H), 7.10 (d, \( J = 10.6 \) Hz, 2H). \(^{13}\)C NMR (100 MHz, \( \text{CD}_3\text{CN} \)) \( \delta \) 156.5, 137.3, 135.3, 130.5, 127.8, 124.5, 116.2, 92.6.

References


Haroz, E. H.; Rialon, K. L.; Boul, P. J.; Noon, W. H.; Kittrell, C.; Ma, J.; Hauge,


22. K. H. Saunders, The Aromatic Diazo Compounds, 2nd ed., Longmans, Green and
Co., New York, **1949**.

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26. Jian, H. *Synthetic Approaches to Molecular Motors and Conjugated Oligomer


5495.
Design, Synthesis, and Testing of Novel Organic Oligomers for Use as Molecular-Scale Electronic Devices

by

Austen Kyle Flatt

Volume II

Spectral Data

Houston, Texas

June, 2005
Chapter 1

Synthesis and Testing of End-Functionalized Oligoanilines for Molecular Electronic Device Candidates
Chapter 2

Synthesis and Self-Assembly of Orthogonally Functionalized Oligomers

for Molecular Electronics and NanoCell Architectures
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AKF-II-92

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**ATLANTIC MICROLAB, INC.**

Sample No. **AkF-III = 92**

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**SUBMITTER**

Company / School **Rice University**
Address **Rice University, Dept. of Chemistry**
1842 Main St.,
Houston, TX 77005

**NAME**

**Austin Flatf**

**DATE** 9-26-03

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- **Vac.**:
- **Time**:
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- **FAX Phone #**: 713-348-6250
- **Rush Service**: (SEE CURRENT PHONE SERVICE PRICE LIST)
- **Phone No.**

**Date Received**: OCT 06 2003

**Date Completed**: OCT 06 2003

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- **Remarks:**

  - Printed on 310 page.
Sample No. **AKF-II-137**

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PROFESSOR/SUPERVISOR: James Tour

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- **Temp.**
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- **Rush Service □** (SEE CURRENT PRICE LIST)
- **Phone Service □**
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Date Completed: **OCT 06 2003**

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Phone No.:

Sample No. □ A □ Z40-I-43

Company/School: Rice University
Address: Rice University Dept. of Chem. 6100 Main St.

Houston, TX 77005

NAME: Austin Flott
DATE: 9-26-03

Date Received: OCT 6 2003
Date Completed: OCT 6 2003
Remarks:
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Chapter 3

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Rush Service: (SEE CURRENT PHONE SERVICE: PRICE LIST)

Date Received: FEB 23 2004  Date Completed: FEB 23 2004

Remark: Please return unused sample.

\[ \text{NO CHARGE FOR DUPLICATES} \]

\[ \text{AKF-III-171} \]
Chapter 4

Design and Synthesis of Azobenzene Oligo(Phenylene Ethynylene)s for Potential Molecular Electronic Devices
Chapter 5

Fabrication of Carbon Nanotube-Molecule-Silicon Junctions and Molecular Grafting to Silicon Surfaces in Air Using Organic Triazenes as Stable Diazonium Sources and HF as a Constant Hydride-Passivation Source