

Novel Reactions of a Neutral Organic Reductant:
Reductive Coupling and Nanoparticle Synthesis

by

Anna Jolene Mork

B.A. Chemistry, Physics
Carleton College, 2010

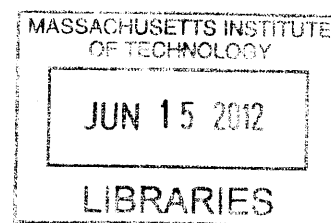
SUBMITTED TO THE DEPARTMENT OF CHEMISTRY IN PARTIAL
FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE IN CHEMISTRY
AT THE
MASSACHUSETTS INSTITUTE OF TECHNOLOGY

JUNE 2012

© 2012 Anna Jolene Mork. All rights reserved.

The author hereby grants to MIT permission to reproduce
and to distribute publicly paper and electronic
copies of this thesis document in whole or in part
in any medium known now or hereafter created.



ARCHIVES

Signature of Author: _____

Handwritten signature of Anna Jolene Mork in black ink.

Department of Chemistry
May 25, 2012

Certified by: _____

Handwritten signature of Timothy M. Swager in black ink.

Timothy M. Swager
John D. MacArthur Professor of Chemistry
Thesis Supervisor

Accepted by: _____

Handwritten signature of Robert Warren Field in black ink.

Robert Warren Field
Robert T. Haslam and Bradley Dewey Professor of Chemistry
Director of Graduate Studies

Novel Reactions of a Neutral Organic Reductant: Reductive Coupling and Nanoparticle Synthesis

by

Anna Jolene Mork

Submitted to the Department of Chemistry
on May 25, 2012 in Partial Fulfillment of the
Requirements for the Degree of
Master of Science in Chemistry

ABSTRACT

A recently developed bis-pyridinylidene neutral organic electron donor captured our interest as a potential source of new chemistries for reductive coupling and the synthesis of group IV nanoparticles. This super electron donor was used as a co-reductant for nickel-catalyzed reductive coupling of aryl halides in order for the reaction to be homogeneous and avoid the traditional co-reductant, zinc, previously reported for these Yamamoto-type dehalogenative couplings. Reductive coupling was somewhat successful for specific substrates, including 4-bromoanisole and 2,5-dibromothiophene, but competing hydrodehalogenation of the aryl halide was problematic for both expanding the substrate scope and increasing the length of the polymers generated from this reaction.

The attempt to synthesize silicon and germanium nanoparticles from reduction of the corresponding tetrachloride precursors using this super organic electron donor met limited success. Dimerization of silicon species occurred, but there was little conclusive evidence of nanoparticle formation.

Finally, in a brief side-project to explore other applications of the organic reductant, the molecule was shown to successfully n-dope both p-type and n-type organic electronic materials.

Thesis Supervisor: Timothy M. Swager
Title: John D. MacArthur Professor of Chemistry

ACKNOWLEDGEMENTS

I would like to thank my thesis advisor, Professor Tim Swager, for his unfailing support, his enthusiasm for chemistry, his understanding and guidance, and for his encouragement to find and pursue the science I love. It has been an honor and privilege to work for and with him for the past two years. I have learned not only about organic chemistry in the process, but also have valued the chance to observe the power of interdisciplinary and creating thinking for furthering research science.

I would like to also thank a number of my co-workers within the Swager laboratory. Firstly, thank you to Dr. Matthew Kiesewetter for answering thousands of questions, providing encouragement, and making every day fun. I would also like to thank Jon Weis and Kelvin Frazier, two of my year mates, for helpful discussions about chemistry and life. Similarly, I would like to thank Jose Lobez, Olesya Haze, Derek Schipper, and Balta Bonillo Fernandez for all their useful advice. Finally, the entire Swager family has been enormously helpful and supportive and deserves recognition for being a wonderful group of people to work with.

Several people outside of the Swager group have also been helpful throughout this work, and I would like to thank in particular Darcy Wanger for much advice about making devices and for serving as a mentor in a variety of capacities, Dr. Trisha Andrew for her help making FET devices, Dr. Tim Osedach for helping with troubleshooting FET devices and data analysis.

Finally, I would like to thank the people who helped me get here in the first place. Prof. Melissa Eblen-Zayas taught me the wonders of physics and materials science for four years at Carleton, and has never wavered in her encouragement to pursue whatever science most interests me. Prof. Dani Kohen, Prof. Joe Chihade, and Prof. Deborah Gross of the Chemistry Department and Prof. Bill Titus of the Physics Department at Carleton College have all been tremendously helpful and supportive as I have sought to find a place in the world of science. Thank you most of all to my family and friends who have believed in me throughout.

TABLE OF CONTENTS

Chapter 1. Introduction to Neutral Organic Electron Donors	
1.1 Introduction and Background	5
1.2 Synthesis and Characterization of Super Electron Donors	10
1.3 Conclusions	12
1.4 Experimental Methods	13
Chapter 2. Nickel-Catalyzed Reductive Coupling of Aryl Halides using an Organic Electron Donor as a Co-Reductant in the Catalytic Cycle	
2.1 Background and Motivation	15
2.2 Results and Discussion	18
2.3 Summary and Conclusions	26
2.4 Experimental Methods	28
Chapter 3. Reduction for Synthesis of Group IV Nanoparticles	
3.1 Introduction to the Synthesis of Group IV Nanoparticles	30
3.2 Results and Discussion	34
3.3 Summary and Conclusions	43
3.4 Experimental Methods.....	46
Chapter 4. N-doping of Organic Electronic Materials with Organic Electron Donor	
4.1 Background and Introduction	48
4.2 Results and Discussion.....	48
4.3 Experimental Methods	51
Chapter 5. References.....	53
Appendix A. Selected NMR Spectra	56
Appendix B. Curriculum Vitae	61

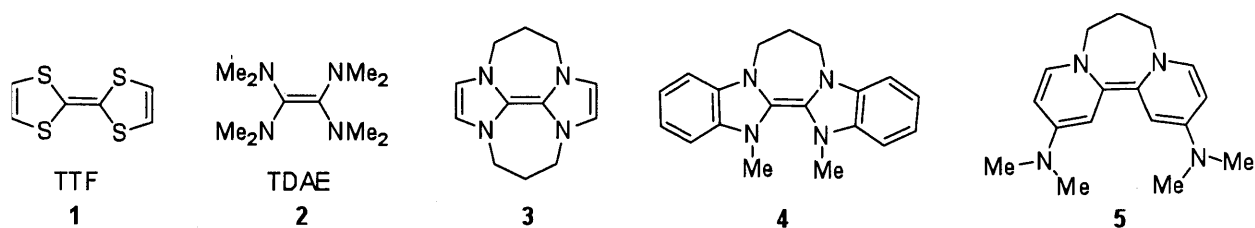
Chapter 1: Introduction to Neutral Organic Electron Donors

1.1 Background on Organic Electron Donors

Neutral, ground-state organic reducing agents are a rare but potentially very powerful tool in modern organic chemistry because they allow for reduction under mild conditions. Reduction can occur without the use of organometallics or reactive metals, without creating strong cationic Lewis acids, and without photochemical activation. Furthermore, a neutral organic reductant allows for a homogeneous reaction in organic solvents, a feat impossible with insoluble zero-valent metal reducers such as zinc or sodium chunk, which could potentially result in rate enhancements. We were interested in exploring the potential to use organic reductants in the transition-metal catalyzed reductive coupling of aryl halides for Yamamoto-type polymerizations as well as for the homogeneous phase reduction of silicon tetrachloride to make silicon nanoparticles. Finally, electron-donating organic molecules have potential use in n-doping of materials such as polymers for organic electronic applications, though we have only done preliminary work in this area so far.

Several neutral organic reducing agents have been reported in the literature, which have electrons in π bonds that are relatively easily removed. Molecules that readily give up electrons are those for which the cation and/or the radical form is resonance stabilized and therefore a relatively low energy species. Examples of reductants in this class include tetrathiafulvalene (TTF, **1**) and derivatives thereof as well as tetrakisdimethylaminoethylene (TDAE, **2**), which have been studied both for their electron transfer and transport capabilities. TTF has two reversible oxidation peaks at $E^1_{1/2}=0.37$ V and $E^2_{1/2}=0.67$ V in DCM versus SCE.¹ The two sulfur-containing five-membered rings of TTF each have seven π -electrons, so a one electron

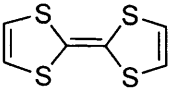
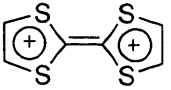
oxidation of each ring results in two 6π -electron Hückel aromatic cationic rings. The oxidative aromatization of the two rings provides a driving force for the facile removal of electrons in this molecule. TTF and its derivatives have been extensively studied as electron donating materials in organic conductors;² TTF is particularly well-known for its 1:1 complex with the electron accepting organic tetracyano-*p*-quinodimethane (TCNQ),^{3,4} which was the first reported “organic metal.” TTF as an electron donor for chemical reactions has also been shown to reduce both small-molecule arenediazonium salts as well as graphene oxide.⁵⁻⁷ Other powerful organic reductants include the nitrogen-containing TDAE molecule, which shows a single, two-electron oxidation peak at -0.62V vs. SCE in DMF which means it is about as reducing as zinc metal.⁸ TDAE can do single electron transfer to dope fullerenes,^{9,10} can reduce arenediazonium salts to aryl radicals,¹¹ can act as an electron source for Ni/Cr in the catalytic Nozaki-Hiyama reaction for alkenylation of aldehydes,¹² and can act as a co-reductant in palladium-catalyzed reductive couplings of aryl halides;⁸ however, TDAE is not a powerful enough reductant to reduce Ni(II) to Ni(0) for nickel-catalyzed reductive couplings.⁸ More recently, researchers have installed nitrogen atoms in place of some or all of the sulfur atoms in TTF because the *p* orbitals of nitrogen are better able to conjugate to the π -system which lends greater stability to the cation and facilitates oxidation.¹³ In analogy to TTF, the bridged neutral organic tetraazafulvalene **3**, formally a carbene dimer, was first reported in 1996,¹⁴ though it was not studied for its reduction properties at the time.

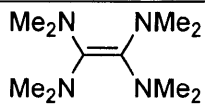
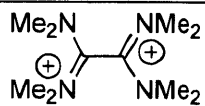
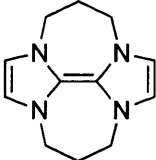
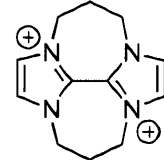
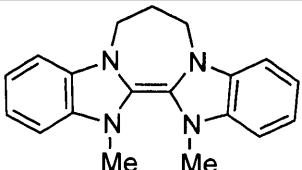
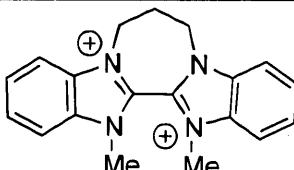
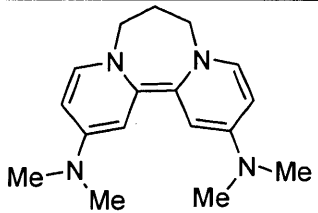
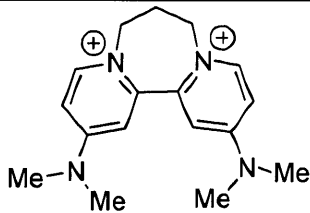
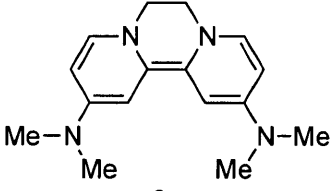
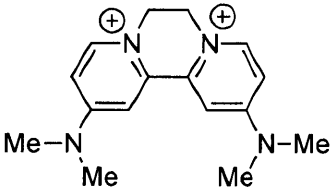
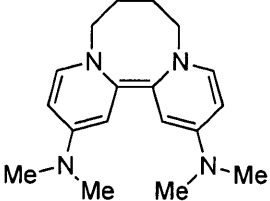
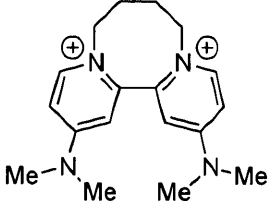
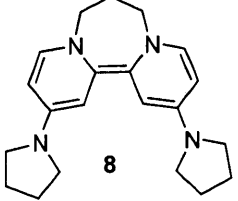
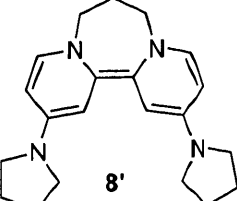


Scheme 1. Examples of neutral organic reducing agents.

Murphy, *et al.* first published the use of the neutral, benzimidazole-derived organic reducing agent **4** in 2005,¹⁵ and has since expanded the set of nitrogen-heterocycle-derived reductants to include, among others, molecule **5**.¹⁶⁻¹⁸ Their goal was to synthesize neutral organic molecules that were more powerful reductants than TTF or TDAE and could reduce aryl halides directly. Indeed, the tetraazafulvalene **4** shows two reversible sequential peaks in the cyclic voltammogram at -0.76V and -0.82V in DMF versus SCE,¹⁷ and molecule **5** shows a single two-electron peak at -1.24 V in DMF versus SCE, which means they are both more reducing than Zn.¹⁶ Murphy, *et al.* reason that molecules **4** and **5** are such powerful electron donors both because the nitrogen atoms are readily able to stabilize radicals/cations after electron donation and because of the 6- π Hückel aromatic nature of the cationic oxidized product. These neutral, nitrogen-containing super reducers have potential to be useful for a variety of chemistries where metal-free and homogeneous reaction conditions are desirable as they are equally or more reducing than many commonly used metals for the purpose. Electrochemical data, as well as the structure of the oxidized products for several neutral organic reductants, are summarized in Table 1.¹⁹ Organic electron donors **4** and, in particular, **5** were used for this thesis due to the combination of good electrochemical properties and ease of clean synthesis from cheap, readily available starting materials.

Table 1: Structures and oxidation potentials for selected organic electron donors. All values have been converted to comparison with SCE; the solvent used for measurement is DMF unless otherwise indicated. (Adapted from Murphy, *et al.*¹⁹)

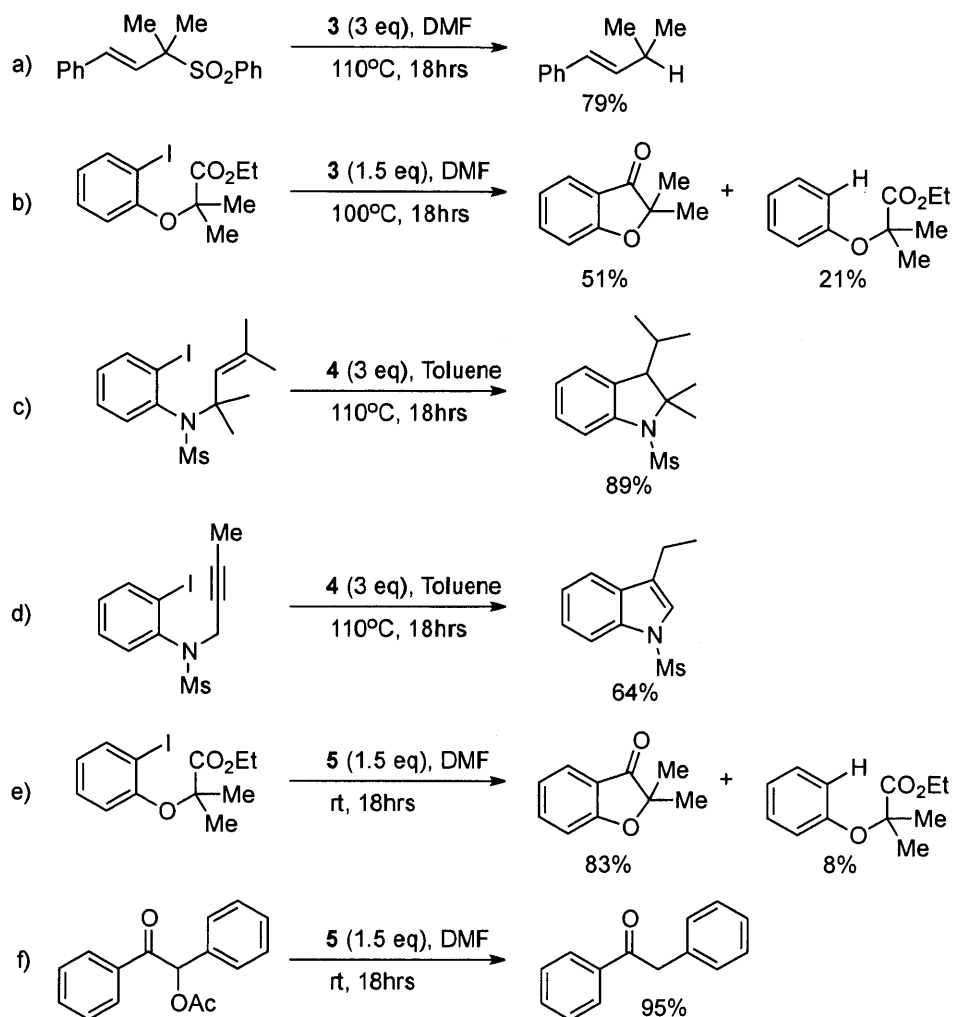
Structure of Neutral Reductant	Structure after oxidation	$E^1_{1/2}$	$E^2_{1/2}$
 <p style="text-align: center;">1</p>	 <p style="text-align: center;">1'</p>	0.37 V ^a	0.67 V ^a

 <p style="text-align: center;">2</p>	 <p style="text-align: center;">2'</p>	-0.78 V ^b	-0.61 V ^b
 <p style="text-align: center;">3</p>	 <p style="text-align: center;">3'</p>	-1.20 V ^c	
 <p style="text-align: center;">4</p>	 <p style="text-align: center;">4'</p>	-0.82 V	-0.76 V
 <p style="text-align: center;">5</p>	 <p style="text-align: center;">5'</p>	-1.24 V ^c	
 <p style="text-align: center;">6</p>	 <p style="text-align: center;">6'</p>	-1.21 V	-0.96 V
 <p style="text-align: center;">7</p>	 <p style="text-align: center;">7'</p>	-1.23 V ^c	
 <p style="text-align: center;">8</p>	 <p style="text-align: center;">8'</p>	-1.33 V	-1.24 V

- a. Measured in DCM.
b. Measured in acetonitrile.
c. Two-electron wave.

Molecules **3**, **4** and **5** are powerful reducers, able to reduce a variety of molecules including not only aryl halides, but also aryl triflates and triflamides, sulfones, Weinreb amides, and diphenylcyclopropanes,^{15-17,20,21} which demonstrates the hugely electron donating nature of these molecules and suggests that they may be used for a variety of new reactions requiring a large reducing potential. Scheme 2 illustrates several examples of reported reactions with yields for these molecules. Molecule **3**, while more reducing than molecule **4**, requires a longer synthesis and therefore was not pursued in this work. However, it is interesting to note that the greater reducing power of **3** relative to **4** is attributed at least in part to the smaller reorganization energy of molecule **3** during oxidation; the benzimidazolium rings of **4** twist from 16° to 42° out of plane upon oxidation, while the imidazolium rings of **3** become more planar upon oxidation and twist from 10° to 1.5° out of plane.¹⁷ The smaller reorganization energy makes reduction by **3** kinetically more facile than reduction by **4**. Molecule **5** demonstrates similar reactivity to the super electron donor **3** (compare, for example, reactions *b* and *f* in Scheme 2) and is more straightforward to prepare in two steps, and therefore is the primary neutral organic electron donor studied in this work.

In this thesis, the reactivity of molecule **5** will be explored further in two general reaction schemes: firstly, as a co-reductant for metal-catalyzed reductive coupling of aryl halides in Chapter 2 with the ultimate goal of using molecule **5** for Yamamoto-type polymerizations with Ni(0), and secondly in reduction of silicon tetrachloride to elemental silicon for nanoparticle synthesis in Chapter 3. Finally, preliminary work will be discussed in Chapter 4 where **5** is shown to act as an electron dopant for semiconducting materials.

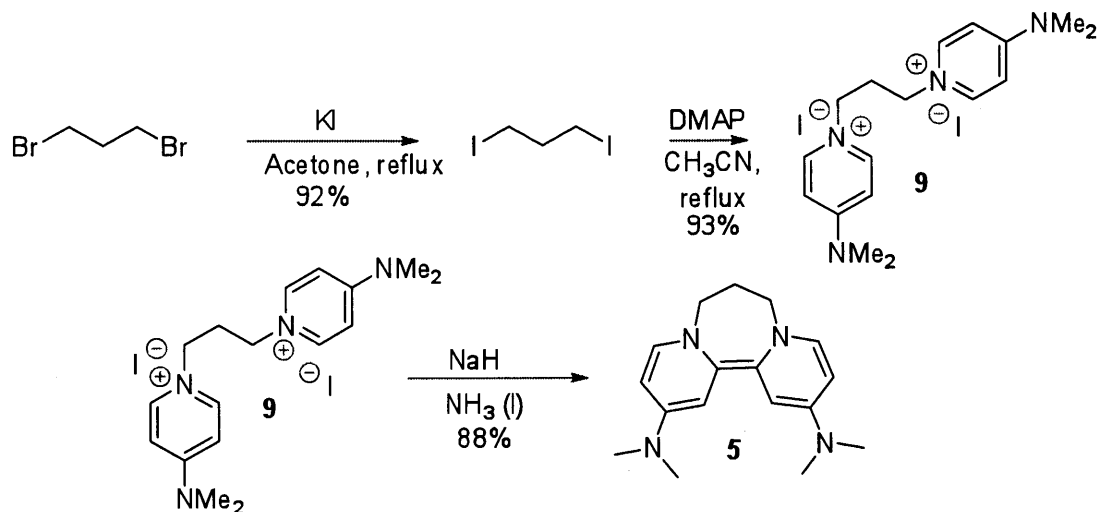


Scheme 2. Selected examples of reduction with neutral organic electron donors **3**, **4**, and **5**.^{15-17,22,23}

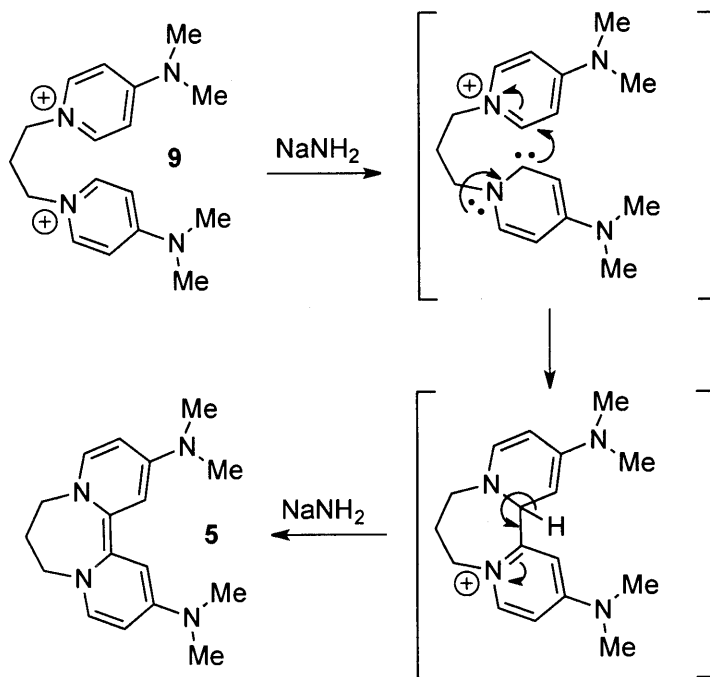
1.2 Synthesis and Characterization of Neutral Organic Super Electron Donors **4** and **5**

Super electron donor **5**, the primary molecule of interest for this thesis, was synthesized in three steps according to Scheme 3. Briefly, a Finkelstein reaction was used to convert 1,3-dibromopropane to 1,3-diiodopropane, which was then used as an S_N2 electrophile with dimethylaminopyridine (DMAP) to afford salt **9**. The diiodo salt **9** could be doubly deprotonated with a strong base to give bispyridinylidene **5**, formally a carbene dimer, as a dark purple-maroon solid. It is worth noting that the formation of **5** from NaH and **9** only proceeds in either

DMF or liquid ammonia as solvents. Several other solvents (dimethoxyethane, tetrahydrofuran, anisole, acetonitrile, dimethylacetamide) were attempted as well as other hydride sources (CaH_2), but no other conditions proved successful. The proposed mechanism for this transformation is outlined in Scheme 4, following Murphy, *et al.*¹⁶



Scheme 3. Synthetic scheme for preparation of **5** from salt **9**.



Scheme 4. Proposed mechanism for formation of bispyridinylidene **5**.¹⁶

Unfortunately, attempts to collect an NMR spectrum of **5** in deuterated benzene failed as a result of fast relaxation of the nuclei, presumably due the presence of a small concentration of the radical species. As a result, bispyridinylidene **5** was reacted with iodine to form the oxidized product **5'** which could be characterized by NMR and confirmed that the synthesized material was indeed **5**. The clean and facile synthesis of **5** in three steps made it an attractive molecule for further study as described in the remainder of this thesis.

Tetraazaalkene **4** was synthesized for comparison using a scheme essentially identical to that used above for bispyridinylidene **5**, with the exception that the final deprotonation and dimerization took place in DMF such that the product could be transferred immediately to a reaction mixture. **4** was characterized primarily by its bright yellow color, strongly reducing nature and the copious H₂ gas was evolved during the synthesis, as it was not isolated directly. Attempts to produce the precursor to tetraazafulvalene **3** resulted in a mixture of products, but as the reducing power of **3** is similar to **5**, no further steps were taken with that molecule.

1.3 Conclusions

The highly reducing nature of neutral organic super electron donors **4** and **5** in conjunction with their facile synthesis suggest their utility in a variety of organic transformations. While **5** is known to reduce aryl halides and has been shown to reduce diphenylcyclopropane, after excitation, to the radical anion, we hope to expand the range of uses for this molecule. Both molecules were synthesized cleanly in three steps to generate the highly colored carbene dimer super electron donor.

1.4 Experimental Methods

1.4.1 General Considerations

All experiments were performed using standard Schlenk techniques with dry solvents unless otherwise indicated. Nuclear Magnetic Resonance (NMR) spectra were collected on a Varian Mercury 300 MHz spectrometer with an Oxford Instruments Ltd. superconducting magnet 5 mm PFG autoswitchable probe.

1.4.2 Synthesis of 1,3-bis(*N,N*-dimethyl-4-aminopyridinium)propane diiodide **9**

A solution of 1,3-diiodopropane (6.43 g, 21.7 mmol) and 4-dimethylaminopyridine (5.3 g, 43.4 mmol) in acetonitrile (150 mL) was stirred at reflux under ambient for 24 hours. After cooling, the mixture was filtered, then diethyl ether was added to the eluent to precipitate more product. This was filtered again, and the solid was washed with diethyl ether then dried under vacuum to give **9** as a powdery white solid. Yield: 10.85g (96%). ¹H NMR (300MHz, CHCl₃): δ = 8.930 (d, 4H), 6.768 (d, 4H), 4.660 (m, 4H), 3.223 (s, 12H), 2.865 (m, 2H).

1.4.3 Synthesis of the bispyridinylidene *N,N,N',N'*-Tetramethyl-7,8-dihydro-6*H*-dipyrido[1,2-*a*;2',1'*c*][1,4]diazepine-2,12-diamine **5**

9 (10.25g, 19.7 mmol) was added to a Schlenk flask, and sodium hydride powder previously washed with hexanes (2.4g, 100 mmol) was added and the powders thoroughly mixed. Liquid ammonia (~80 mL) was condensed from a gas canister over dry ice/isopropanol, and the reaction mixture was stirred for several hours then allowed to warm to room temperature overnight as the ammonia evaporated. The product was pumped down under high vacuum, then brought into the glovebox where it was extracted with diethyl ether and filtered over a frit to remove the excess NaH and other salts. The diethyl ether was removed by distillation, leaving **5** as a dark

purple/maroon moisture and air sensitive solid that was not characterized by NMR. Yield: 3.95 g (71%).

1.4.4 Synthesis of N,N,N',N'-Tetramethyl-7,8-dihydro-6H-dipyrido[1,2a-2,1c][1,4]-diazepine-5,9-dium-2,12-diamine diiodide 5'

Iodine (0.279 g, 1.1 mmol) was dissolved in dry acetonitrile (5 mL) and the solution was degassed by bubbling argon for 20 minutes. The solution was cannula transferred onto solid **5** (0.284 g, 1.0 mmol) in a Schlenk flask and stirred at room temperature for 25 minutes. The reaction mixture was then filtered and washed copiously with diethyl ether, then dried under vacuum to give **5'** diiodide as a yellow-brown powder. Yield = 0.238g = 58%. ¹H NMR (300 MHz, DMSO): δ = 8.438 (d, 2H), 7.396 (d, 2H), 7.234 (dd, 2H), 4.532 (d, 2H), 3.974 (m, 2H), 3.314 (s, 6H), 3.274 (s, 6H), 2.382 (m, 2H).

1.4.5 Synthesis of 1,3-Bis[3-methyl-3H-benzimidazolium]propane diiodide, precursor to 4

Methylbenzimidazole (0.87 g, 6.6 mmol) and 1,3-diiodopropane (0.48 g, 1.6 mmol) were added to acetonitrile (50 mL) and stirred at reflux for 16 hours. The resulting white precipitate was filtered, then diethyl ether was added to the acetonitrile solution to precipitate more of the product salt which was filtered and dried under vacuum. Yield: 0.659g (67.5%). ¹H NMR (DMSO): δ = 9.800 (s, 2H), 8.072 (dd, 4H), 7.706 (d, 4H) 4.720 (dd, 4H), 4.109 (s, 6H), 2.627 (m, 2H).

1.4.6 Synthesis of tetraazaalkene 4

Sodium hydride (60% dispersion in mineral oil, 0.239g, 6.2 mmol) was washed copiously with hexanes, then dried under high vacuum for 30 minutes. The precursor to **4** described in 1.4.5 (0.56g, 1 mmol) was added, then anhydrous DMF (10 mL). The mixture was allowed to stir on ice for 1.5 hours. **4** was carried on for subsequent reactions without further characterization.

Chapter 2: Ni-Catalyzed Reductive Coupling of Aryl Halides using an Organic Electron Donor as a Co-Reductant in the Catalytic Cycle

2.1 Background and Motivation

Reductive coupling of aryl halides has been of interest for decades as a route to both symmetrical and unsymmetrical molecules, first realized with the Ullmann reaction using copper catalysis and subsequently achieved under more mild conditions with nickel and palladium catalysts.²⁴ The Ullmann reaction generally requires high temperatures, stoichiometric amounts of copper, and works best for electron-poor aryl halides, all of which limit the scope of the reaction.²⁴⁻²⁶ However, the ability to form aryl-aryl bonds directly from the aryl halide without having to first synthesize an organometallic species (*e.g.* a boronic ester, Grignard reagent, organozinc compound) is particularly useful for polymerization reactions, where then only a single monomer and catalyst are required and the reaction forms minimal by-products. This type of reductive coupling for polymerization has been achieved with the Yamamoto-type polymerization,^{27,28} a reductive coupling reaction using Ni(0) as a catalyst that has successfully been employed to polymerize a variety of monomers including thiophenes, pyridines, and *p*-phenylenes.²⁸ Because the reaction readily couples symmetrical aryl dihalides, it is particularly useful as a route to synthesize a wide variety of highly conjugated polymers, including block copolymers, for organic electronic applications.²⁹

One of the possible improvements on the Yamamoto polymerization method lies in the generation of the zero-valent nickel catalyst. The nickel catalyst can either be a ligated Ni(0) species such as Ni(COD)₂, in which case a stoichiometric amount of nickel is required for the reaction to proceed, or the Ni(0) can be generated *in situ* by the reduction of a Ni(II) salt, most commonly with metallic Zn, though other reductants, including sodium hydride, can be used.^{29,30}

A generalized schematic of the proposed catalytic cycle for stoichiometric Ni(0) is shown in Figure 1A, where oxidative addition of the monomer to the catalyst is followed by disproportionation of two molecules of X-Ni-Ar to a L_2NiR_2 species and NiX_2 ; the bisaryl nickel can then reductively eliminate the desired biaryl and Ni(0).³¹ It is worth noting, though it will not be discussed further here, that significant mechanistic studies have elucidated many complexities in this mechanism as it is reported to go through a radical chain process where four oxidation states of nickel ($Ni^0 - Ni^{III}$) are present in the reaction.³² The disproportionation of the Ar-Ni species is reported to be the slow step assuming the scheme shown in Figure 1A.³³ In this scheme, for every aryl-aryl bond formed, one molecule of NiX_2 (X = halogen) is also generated. Unless the nickel is reduced back to a Ni(0) species, the Ni(II) molecule cannot participate again in the catalytic cycle. As a result, in the absence of a co-reductant, a stoichiometric amount of Ni(0) is required for the reaction to proceed. This is problematic because Ni(0) species are expensive and air-sensitive, so using stoichiometric metal is not a scalable for large-scale production of conjugated polymers. Additionally, stoichiometric nickel also means that large polydispersities in the resulting polymer are expected due to significant competing chain-termination reactions because in the disproportionation step the Ar-Ni species can easily result in the coupling of chain ends.

A co-reductant can reduce NiX_2 back to Ni(0) to re-enter the catalytic cycle, and alleviate the several problems associated with of stoichiometric nickel. A more nuanced view of the coupling mechanism specifically for the case where Zn is a co-reductant is based on the work of Colon and Kelsey³⁴ and reproduced in Figure 1B. Zinc as a co-reductant is usually added in large excess as a finely ground insoluble powder which is problematic both in terms of atom efficiency and the heterogeneity of the reaction mixture. Sodium hydride as a co-reductant suffers similarly.

Neutral organic reductants offer the potential to relieve both of these challenges because they are soluble in organic solvents and may not require a significant excess in order for the reaction to run. We therefore were interested in exploring the potential to use neutral organic species for the reduction of nickel *in situ* for Yamamoto-type reductive couplings due to the potential to speed the reaction by reducing the induction period (a result of homogeneous reaction conditions) as well as increasing the atom efficiency.

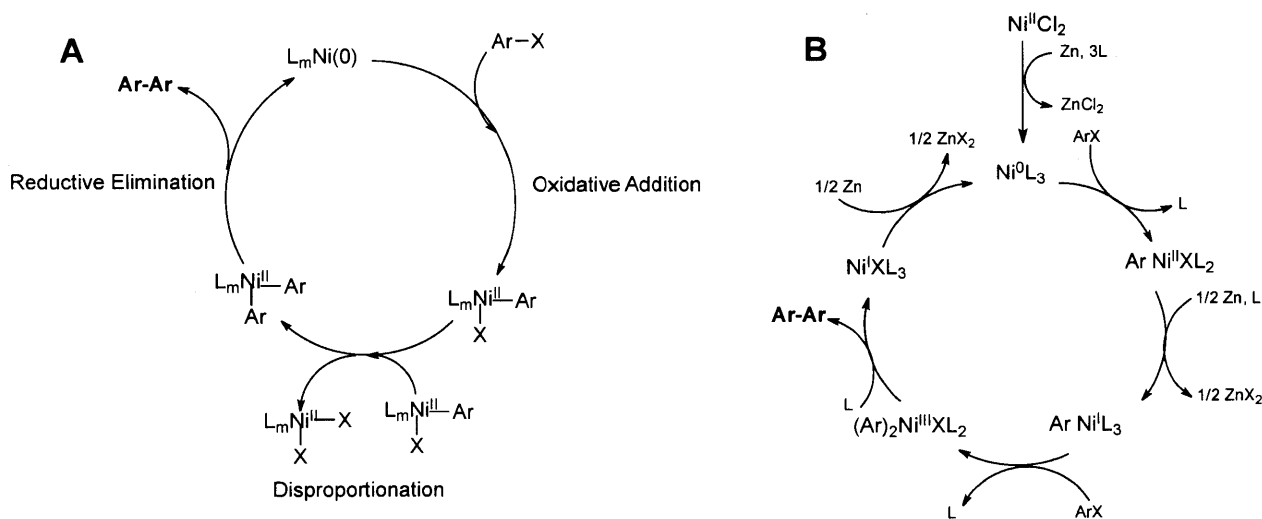
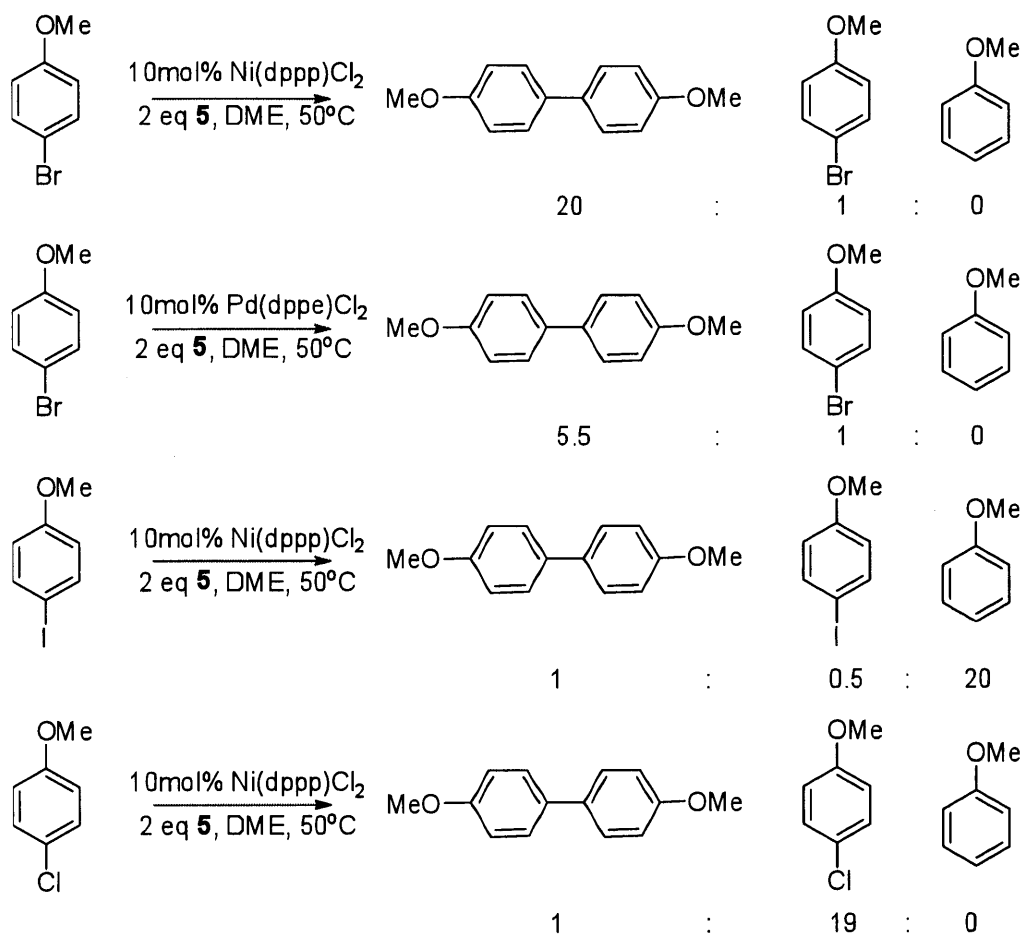


Figure 1. General proposed catalytic cycle for Yamamoto-type reductive coupling of aryl halides with either (A) stoichiometric Ni(0),³¹ or (B) catalytic nickel and stoichiometric zinc.³⁴

Reductive coupling of aryl halides has been demonstrated previously using a TDAE (2) and palladium system,⁸ but TDAE was not sufficiently reducing to promote coupling with nickel catalysts. The standard reduction potential of nickel(II) is -0.26V, while that for TDAE is -0.62 V. Clearly, a significant overpotential is required to reduce nickel in the presence of ligands since TDAE was unsuccessful. The reduction potential for **5** is -1.24V; therefore, we were interested in testing the capability of **5** to allow reductive coupling using similar reaction conditions to the TDAE case but with a more powerful neutral organic reductant.

2.2 Results and Discussion

In order to test the capability of electron donor **5** as a co-reductant for nickel-catalyzed reductive couplings, a test system using 4-bromoanisole as the substrate was devised in analogy to the system described by Tanaka *et al.*⁸ with Pd/TDAE. Ni(II) was tested against Pd(II) with **5** as the co-reductant for coupling using the same substrate under the same conditions. Using 4-bromoanisole as a substrate, the nickel catalyzed reaction gave better yield of the coupled product 4,4'-dimethoxy-1,1'-biphenyl than the Pd-catalyzed reaction (results with ratios of products summarized in Scheme 5). When the substrate was changed to 4-iodoanisole in order to increase conversion for the nickel-catalyzed reaction, the primary reaction was dehalogenation to yield anisole rather than the biphenyl. For the chloroanisole substrate, after the same 15 hour reaction time used for the bromide and the iodide, a small amount of the dimethoxybiphenyl product was observed, but the predominant recovered material was the original 4-chloroanisole. We interpret the predominant dehalogenation of iodoanisole to suggest that it is reduced in solution by **5** before it is able to oxidatively add to the Ni species, as **5** is known to readily reduce aryl iodides. The small amount of coupling of chloroanisole suggests that **5** is able to result in some turnovers of the catalytic cycle but clearly the oxidative addition of the aryl chloride is slow. **5** does not reductively dehalogenate aryl chlorides except under photochemical conditions³⁵ which is why no dehalogenation was observed. In sum, **5** successfully served as a co-reductant for the nickel-catalyzed reductive coupling of aryl halides, though competing dehalogenation can be problematic particularly for the more labile C-X bonds.



Scheme 5. Results of coupling experiments with **5** in analogy to Tanaka, *et al.*⁸

Encouraged by the apparent ability of super electron donor **5** to participate in reductive coupling reactions, a variety of conditions and substrates were tested for nickel-catalyzed Yamamoto-style polymerization reactions with **5** as a co-reductant. The two monomers of greatest interest to our group are 2,5-dibromo-3-hexylthiophene and the family of 2,7-dibromofluorenes due to their important applications in organic electronics. Attempts at the reductive coupling 2,7-dibromofluorene and 9,9-dihexyl-2,7-dibromofluorene using Ni(dppp)Cl₂ resulted exclusively in either no reaction or hydrodehalogenation of the starting material to either 2-bromofluorene (partial dehalogenation) or fluorene (full dehalogenation). However, in the absence of any nickel catalyst the starting fluorene was largely preserved even after stirring in the presence of **5** for 15 hours at 50°C in THF. With this and other monomers, quenching the

reaction with deuterated methanol or deuterated water resulted in almost no deuteration observed by GCMS of the hydrodehalogenated product, suggesting that the proton added comes from the reaction mixture itself. The more electron poor monomer 2,5-dibromopyridine, one of the original substrates for nickel-mediated reductive coupling used by Yamamoto, also showed no evidence of polymerization by GPC.

Thiophenes, on the other hand, proved to be mildly successful substrates for reductive coupling by nickel in the presence of **5**. It is worth noting that 1.5 equivalents of **5** alone in the absence of nickel completely reduces 2,5-dibromothiophene to 2-bromothiophene at 50°C in THF, so all attempts at reductive polymerization of dibromothiophene must overcome the competing dehalogenation. However, both 2-bromothiophene and 3-bromothiophene were completely converted to 2,2'-bithiophene and 3,3'-bithiophene, respectively, using both NiBr₂ and Ni(dppp)Cl₂ as catalysts with **5** as measured by GCMS. Interestingly, when stoichiometric NiBr₂ and **5** were stirred with 2-bromothiophene at 50°C in THF, the products were a mixture of bithiophene as well as quarterthiophene, presumably due to the presence of nickel nanoparticles in the reaction mixture. These results show that reductive coupling of thiophenes using nickel as a catalyst is possible, and suggest that tweaking the reaction conditions may afford polymeric product.

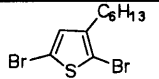
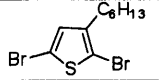
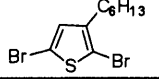
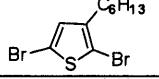
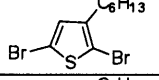
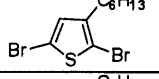
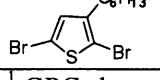
Several reactions using 2,5-dibromo-3-hexylthiophene as a substrate, the monomer frequently used to synthesize the celebrated polymer P3HT, were only successful in achieving, at most, tetramers. The results described below are summarized in Table 2. An initial attempt at polymerization using 10 mol% Ni(dppp)Cl₂ in DME at 50°C for 15 hours resulted in tetramers and lower oligomers, presumably as a result of chain termination by hydrodehalogenation. In order to suppress the competing dehalogenation reaction, the temperature of the reaction was

increased to 75°C on the presumption that a higher temperature may favor coupling over reduction, assuming a charged intermediate in the dehalogenation process, as a result of the Van't Hoff equation; however, the reaction produced only tetramers as the highest oligomer. Subsequently, the amount of Ni(dppp)Cl₂ catalyst used was increased to a stoichiometric amount in order to increase the probability that a monomer would meet a nickel complex in solution rather than **5** to try to reduce hydrodehalogenation. Nickel clearly mediates both reduction and coupling, however, because stoichiometric nickel produced only at most dimers. This is consistent with the previous finding that dibromofluorene is reduced substantially in the presence of a nickel species and **5** but very little in the presence of **5** alone. Additionally, we suspected that a less polar solvent may aid polymerization by suppressing dehalogenation as the presumed intermediate for dehalogenation has significant anionic character on the thiophene which should be destabilized in a non-polar solvent. However, the reaction in toluene at 80°C similarly only resulted in tetramers. We also suspected that a slow addition of the reductant **5** may result in polymerization over dehalogenation due to a smaller amount of the super electron donor available in solution to reduce monomers not coordinated to the small amount of nickel in solution. The slow addition of **5** via syringe pump over the course of almost seven hours resulted exclusively in either the complete or partial reduction of the dibromothiophene and only trace dimers (<1%) were detected. This suggests that the presence of **5** in solution over the course of the reaction is not entirely the problem, which again validates the suggestion that the nickel mediates dehalogenation in addition to coupling.

Finally, reductant **4** was used instead of **5** in order to test whether a less-reducing organic electron donor may reduce the rate of dehalogenation relative to polymerization. **4** has a reduction potential substantially greater than that required to reduce nickel to Ni(0) (Table 1), but

is less reducing than **5**. When a solution in DMF of **4** was added to a mixture of Ni^{II}/dibromothiophene in an equivalent amount of DME, after 6 hours at 80°C the only observed products of the reaction were the singly and doubly dehalogenated 3-hexylthiophenes (product ratio about 1.5:1) with no presence of coupled product. However, when the reaction was done in DMF alone, oligomers were generated. It appears that simply reducing the reactivity of the organic electron donor is insufficient to prevent dehalogenation based on the first experiment, but the second suggests that finding an optimal solvent system is crucial for the success of the reaction. Note that when the reaction with **5** rather than **4** was run in DMF, only dimers at best were generated. Despite the lack of resounding success in this reaction for the generation of high molecular weight polymers, it is worth noting that in the first reports on the Yamamoto coupling reaction with zinc as a co-reductant the polymeric molecular weights achieved were on the same order of magnitude (~700 Da) as those described here.³⁶

Table 2. Summary of results of thiophene reductive coupling reactions.

Monomer	Catalyst	Reductant	Mol % catalyst	Solvent	Temp (°C)	Equivalents reductant	M _w by GPC ¹
	Ni(dppp)Cl ₂	5	10	DME	50	2	726
	Ni(dppp)Cl ₂	5	5	DME	75	2	696
	Ni(dppp)Cl ₂	5	100	DME	50	3	366
	Ni(dppp)Cl ₂	5	10	Toluene	80	3	670
	Ni(dppp)Cl ₂	5	10	DMF	80	2	156
	Ni(dppp)Cl ₂	4	10	DMF/DME	80	5	Reduction only
	Ni(dppp)Cl ₂	4	10	DMF	80	2	762

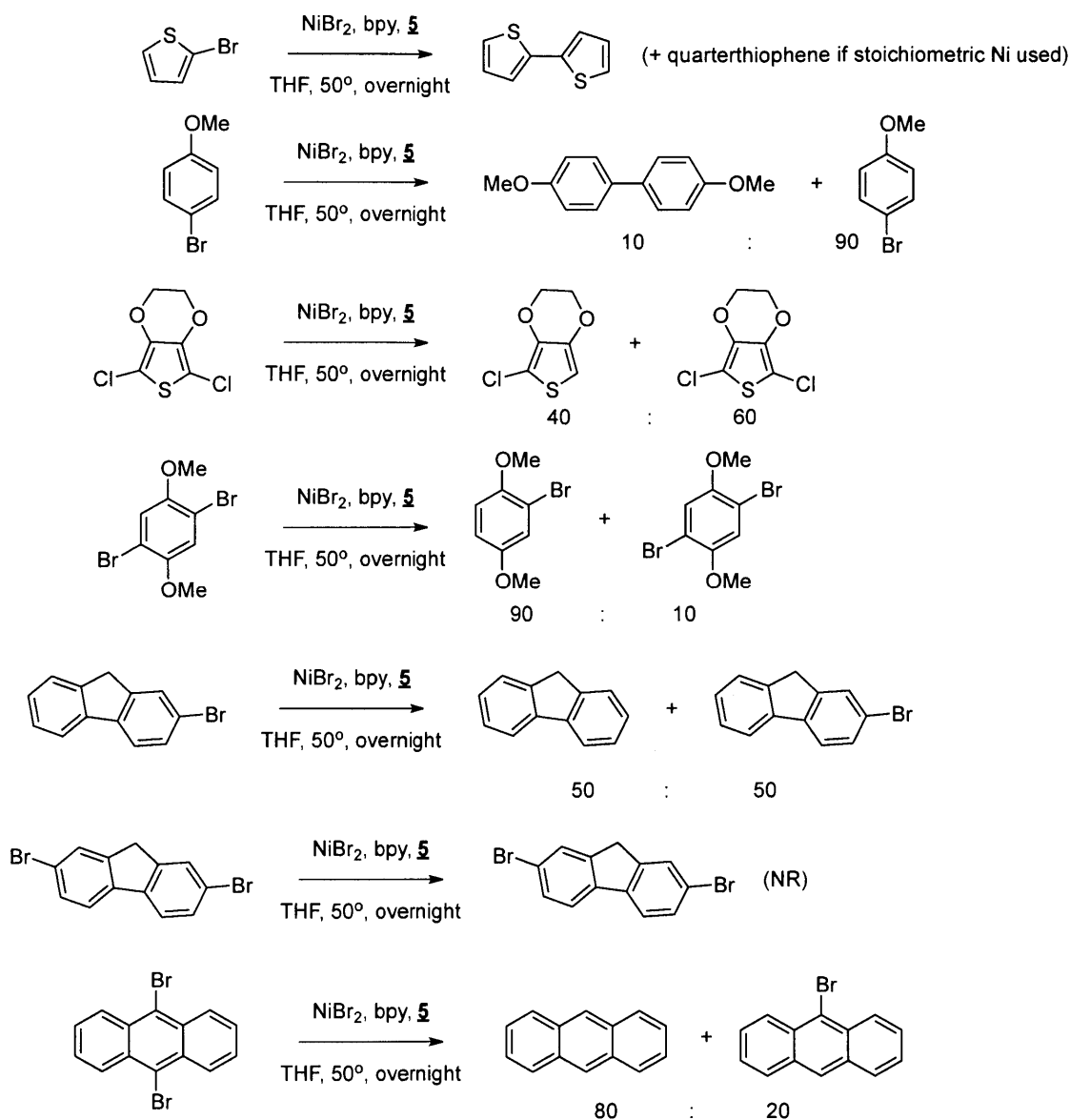
¹ GPC shows oligomers. The reported M_w is the highest M_w oligomer with retention time ~28 min.

Finally, a control reaction using sodium hydride and nickel in the absence of any organic reductant was carried out in order to determine whether trace quantities of sodium hydride left over from the synthesis of **4** and **5** could result in the observed dehalogenation. Sodium hydride is required for the synthesis of both neutral organic super electron donors, and while it is insoluble and therefore readily filtered out it could significantly complicate interpretation of the reaction results if it were present in trace amounts. Two equivalents of sodium hydride were stirred with the nickel catalyst and 2,5-dibromo-3-hexyl thiophene for 11 hours at 80°C and quenched with deuterated water. At the end of the reaction, the major product was the starting material, though there were some of both the singly and doubly dehalogenated thiophenes. The dehalogenated material did not show significant deuterium incorporation by GCMS, as was found when using **5** to reduce the nickel species, which again suggests that the hydrogen comes from the reaction mixture before the quench. Overall, these results imply that while a trace amount of sodium hydride may result in slight dehalogenation of the starting material, it is not sufficient to result in the frequently observed total dehalogenation of the monomer. Additionally, the fact that the proton in the hydrodehalogenation comes from the reaction mixture and not the protic quench both in the presence and absence of organic reductant, the proton does not come from molecule **5** itself. Molecule **5** is clearly more effective than NaH at dehalogenation of brominated monomers, perhaps because of its solubility in organic solvents, which also makes it a good candidate for homogeneous polymerizations.

In addition to the series of reactions using 2,5-dibromo-3-hexyl thiophene as the substrate monomer, chlorinated thiophenes were also tested for their reactivity in the Yamamoto polymerization using **5** as a co-reductant. Indeed, for poly(*p*-phenylenes), Yamamoto *et al.* found that dichlorobenzene produced superior polymers than dibromobenzene due to the reduced rate

of dehalogenation.³⁰ The reaction using 2,5-dichlorothiophene as the monomer resulted in no reaction. The reaction with 2,5-dichloro-3,4-ethylenedioxythiophene (EDOT) resulted exclusively in either no reaction or reduction to the monochloro EDOT (product ratio 70:30). Based on these results, it appears that use of the chloride rather than the bromide does indeed diminish the amount of hydrodehalogenated product, as expected, but it also seems that the dichlorothiophenes are not sufficiently reactive to go through the catalytic cycle with nickel, either, and are therefore not generally useful for reductive coupling polymerization reactions.

Nickel(II) bromide was also investigated as a nickel source for reductive coupling in order to determine if the nickel source affected the reaction. We suspected that **5** itself may serve as a ligand for the nickel and thus obviate the addition of other ligands, so a series of reactions with NiBr₂ and **5** were tested with a variety of substrates. The results of these reactions are summarized below in scheme 6. While 2-bromothiophene was successfully coupled by NiBr₂ and a small amount of product was observed for 4-bromoanisole coupling, NiBr₂ generally performed worse than Ni(dppp)Cl₂ in reductive coupling reactions.



Scheme 6. Reductive coupling of various aryl halides using NiBr_2 as nickel source and **5** as the co-reductant. All reactions used 10% catalyst loading if NiBr_2 unless otherwise indicated.

In order to diminish the amount of dehalogenation relative to coupling, **4** was tested as a co-reductant for the Ni-catalyzed Yamamoto-type coupling of aryl halides. Reductant **4**, as described above, was sufficiently reducing to dehalogenate 2,5-dibromothiophenes in the presence of a nickel catalyst. Alternative substrates were also tested for reactivity. 2,7-dibromofluorene underwent some reduction in the presence of **4**, with a product ratio of about

1:5:25 of fluorene : bromofluorene: dibromofluorene, indicating that, as observed with **5** as a co-reductant, molecule **4** reduces but does not couple fluorene substrates. Finally, to determine if **4** can participate in coupling reactions at all, the same reaction as described in Scheme 5 was tested except with molecule **4** as the reducing agent. Only a small amount of the desired biaryl was observed and the majority of the product was unreacted starting material (~1:6 ratio of product:reactant), and there were several other unidentified peaks in the GCMS spectrum presumably from decomposition of molecule **4**, though these peaks were not observed for the attempted fluorene coupling. The fact that molecule **4**, though less reducing than **5**, neither particularly decreased the amount of dehalogenated aryl bromide nor very successfully reductively coupled any monomer shows that there are more factors to consider in the nickel-catalyzed reductive coupling than merely the electron donating ability of the co-reductant.

2.3 Summary and Conclusions

The highly reducing nature of molecule **5**, as well as its organic solubility, makes it promising for homogeneous phase reductive coupling reactions. While some coupling was achieved, especially with thiophene-based substrates as well as 4-bromoanisole, hydrodehalogenation was the major side reaction that prevented the synthesis of high molecular weight polymers. Hydrodehalogenation has been reported in the literature to be a competing reaction with polymerization even in the traditional zinc-nickel catalytic systems,³³ and the new reaction proposed here suffers similarly. The major obstacle to generation of higher molecular weight polymers will be decreasing the amount of dehalogenation. Increasing the reaction temperature, decreasing the solvent polarity, and decreasing the addition rate of **5** were all unsuccessful in eliminating dehalogenation, in part because the proton involved in the reduction

of the monomer appears to come from the reaction mixture itself, though the solvents used were rigorously dried over sodium/benzophenone, freeze-pump-thawed, and stored in the glovebox prior to use. It is possible that other solvent systems would improve yield of the coupled product over the dehalogenated product, and these are potentially worth further investigation.

The catalytic system investigated here appears to do better in the presence of more electron-rich substrates, such as thiophenes and anisoles, which gives it opposite selectivity to the traditional Ullmann reductive coupling which works best with electron-poor substrates. As a result, this reaction provides a complementary route for reductive coupling to synthesize symmetrical biaryls.

It appears that the reductive coupling reaction with super organic electron donors proceeds in the presence of nickel catalysts better than palladium catalysts, which means that if the reaction conditions are further optimized this polymerization scheme may mean cheaper reactions with fewer required steps as no organometallic compound (*e.g.* Grignard reagent) must be synthesized prior to use. This reaction also does not require the use of Ni(COD)₂, the standard stoichiometric Ni(0) source in many Yamamoto-type polymerizations, which is an air- and heat-sensitive flammable carcinogen. This also makes the current reaction scheme appealing, especially if the dehalogenation problem is successfully addressed.

Super organic electron donors have several advantages over traditional metal reductants such as zinc because they are highly soluble in organic solvents and their properties can be tuned by their molecular structures. Molecules **4** and **5** are both formally carbene dimers, yet they have significantly different reduction potentials due to the different connectivity and reactivity of the constituent functional groups. The molecular structure affects not only the reducing properties of the molecule, but also alters how it can interact with other organics in solution. It is possible, for

instance, that **4** and **5** coordinate/bind to nickel differently, which could play a role in their differing reactivities, as **5** was able to successfully couple 4-bromoanisole while **4** was not. This provides only a single example of how molecular design can be used to substantially change reactivity, and it is certainly possible that other organic reductants could be devised to optimize electron transfer to nickel without otherwise affecting the reaction substrate.

2.4 Experimental Methods

2.4.1 General Considerations

All ethereal solvents used were dried for at least 24 hours over sodium/benzophenone, then freeze-pump-thawed three times to remove oxygen before vacuum transfer to a receiving flask that was stored in the glovebox. Anhydrous DMF was used as purchased from Aldrich as required. Proton NMR spectra were recorded on a Varian Mercury 300 MHz instrument. Gas Chromatography Mass Spectrometry (GCMS) was performed using an Agilent 6890N Network GC System in conjunction with an Agilent 5973 Network Mass Selective Detector.

*2.4.2 General Reaction Conditions for Ni-catalyzed Reductive Coupling using **5** as co-reductant*

In a typical nickel-catalyzed reductive coupling experiment, 10 mol% of Ni(dppp)Cl₂ or NiBr₂ with equimolar 2,2'-bipyridine was added to a Schlenk flask and evacuated for at least ten minutes. The halogenated substrate was added to the flask, and the flask was purged with argon then evacuated. The Schlenk flask containing monomer and catalyst was then brought into a N₂-filled glovebox, where the organic reductant **5** was added to the flask followed by 5 mL of solvent (typically DME or THF). The reaction mixture was stirred inside the glovebox in a heated sand bath at 50°C for 15 hours unless otherwise indicated. At the end of the reaction, deuterated water or deuterated methanol was added to the flask to quench the reaction. Often

formation of bubbles was observed upon quenching, indicating the presence of a reducing species. The solvent was removed under reduced pressure, then water was added and the solution was extracted with either diethyl ether or chloroform. The organic phase was washed twice with water and once with brine before drying over anhydrous magnesium sulfate. The solvent was then removed with a rotary evaporator, and the resulting material was characterized by NMR, GCMS and/or GPC.

*2.4.3 General Reaction Conditions for Ni-catalyzed Reductive Coupling using **4** as a Co-Reductant*

4 was synthesized as described in section 1.4.6 and directly cannula transferred to a stirring flask containing monomer and Ni(dppp)Cl₂. The reaction was stirred at 80°C under argon atmosphere for six hours before quenching with deuterated water. The mixture was added to acidified water and extracted with chloroform. The chloroform layer was washed twice with water and once with brine before drying over anhydrous magnesium sulfate and removal of the solvent with a rotary evaporator. The resulting material was characterized by NMR, GCMS, and/or GPC.

Chapter 3: Reduction for Synthesis of Group IV Nanoparticles

3.1 Introduction to the Synthesis of Group IV Nanoparticles

Silicon nanoparticles (Si NPs) have a variety of potentially important technological applications stemming from their photoluminescent/optoelectronic properties as well as their potential as a material for energy storage. Both applications require the scalable (and ideally size-controlled) synthesis of the nanoparticulate material, as well as efficient capping of the resulting nanoparticles to stabilize them against oxidation to silica (SiO_2) upon prolonged exposure to ambient conditions. A technologically useful novel synthesis of silicon nanoparticles must therefore address both of these challenges, preferably starting with a readily available silicon source and using it to cleanly generate nanoparticles with minimal contamination.

Synthesis of monodisperse photoluminescent Si NPs with diameters ≤ 5 nm and high quantum yields could enable their use as a less-toxic non-heavy metal equivalent to Cd-rich quantum dots for imaging and other applications. The Bohr exciton radius of silicon is 4.9 nm, so nanoparticles of this size and smaller can show the effects of confinement in their optical properties. In the bulk, silicon is an indirect band gap semiconductor ($E_g = 1.12$ eV), but at nanometer scales it changes to a direct band gap semiconductor³⁷ and displays optical properties that vary in a size-dependent manner. The size-dependence of their absorption/emission features is due to confinement effects in analogy to quantum dots, and was first observed experimentally in 1990.³⁸ In particular, the maximum wavelength of emission becomes more blue-shifted relative to the bulk band-gap of silicon as the particle diameter decreases, and photon emission becomes more efficient because phonon-free transitions are allowed due to the direct band gap and radiative recombination pathways are accessible.³⁹ Silicon NPs generally emit light in the

spectral range from near infrared (NIR) to green when they are in the size range between 5nm and 1nm in diameter.³⁹ In addition to luminescence, Si NPs are also potentially useful energy storage materials. They have great potential for lithium ion storage in batteries due to their ability to absorb and release lithium ions over many electrochemical cycles without significant fracturing of the material,⁴⁰ and have also been shown to store hydrogen gas in the form of Si-H surface bonds which can release H₂ upon annealing.⁴¹ Both of these applications take advantage of the high surface area of nanocrystalline silicon particles in conjunction with the useful atomic properties of silicon. The variety of useful properties of nanoscale silicon crystals makes them relevant targets for robust and scalable synthetic methods which are currently lacking.

Many methods of synthesizing silicon nanoparticles exist, though they often either require harsh/unsafe reaction conditions, are gas-phase reactions and therefore non-scalable, or result in large size polydispersity. Examples of these include the gas-phase decomposition of silanes via laser ablation,⁴² reaction of Zintl salts (*e.g.* KSi) with silicon halides at elevated temperatures in the glovebox,⁴³ oxidation of Zintl salts such as MgSi with NH₄Br,⁴¹ reduction of silicon halides (in particular SiCl₄) with alkali metals⁴⁴ or sodium naphthalenide,⁴⁵ reduction of silica nanoparticles with magnesium powder,⁴⁶ or ball-milling of silicon wafers.⁴⁷ Many of these techniques are heterogeneous, generate several byproducts that are difficult to remove, and result in nanoparticles that are not necessarily crystalline and certainly not monodisperse. Therefore, the development of a novel synthetic method to achieve high-quality crystalline nanoparticles at reasonable temperatures and without the use of alkali metals could have a variety of applications in both industry and academia where usage is limited due to the infeasibility of the synthesis. Several of the above mentioned syntheses rely on the reduction of silicon tetrachloride (SiCl₄). We therefore imagined that a super organic reductant such as molecule **5** could potentially be

used to reduce silicon tetrachloride to elemental silicon and thereby form nanoparticles. This synthetic route is attractive because the oxidized form of molecule **5** is a dication and very water soluble, so not only would the reduction reaction be homogeneous in an organic solvent (both **5** and SiCl₄ are soluble in a variety of solvents) but the undesired byproduct of the reaction, the dichloride salt **5'**, could readily be washed away at the end of the reaction as it is unlikely to co-crystallize with the silicon.

All solution-based synthetic methods for generating silicon nanoparticles must address surface functionalization in addition to crystallinity and monodispersity, as the surface chemistry of nanoparticles affects their air stability and luminescent characteristics. Nanoparticles that have not been end-capped are vulnerable to oxidation, which degrades their photoluminescent and electronic properties. Common end-capping groups include octanol and other long-chain aliphatic alcohols, which result in Si-O-R linkages at the nanoparticle surface,⁴⁵ and organolithium compounds, such as *n*-butyllithium, or Grignard reagents, such as octylmagnesium bromide,^{48,49} which result in Si-C bonds at the surface. For H-terminated nanoparticles (*e.g.* generated from the metathesis of MgSi with NH₄Br), long-chain alkenes can be attached via a hydrosilation catalyst, which results in Si-C bonds on the surface of the nanoparticle.⁵⁰ In this work, both organometallic reagents as well as long-chain alcohols were investigated as capping groups for the silicon nanoparticles.

Similar methods to those enumerated above have been used to synthesize germanium nanoparticles (GeNPs) from various germanium precursors such as GeCl₄ and GeI₂.⁵¹⁻⁵³ Additionally, lithium aluminum hydride has been used to generate hydrogen-capped GeNPs which can be further functionalized to yield water-soluble amine-terminated nanoparticles.⁵⁴ The reduction potential for GeCl₄ is not readily available in the literature, but the fact that Ge(II) is a

stable oxidation state for the element where Si(II) is not suggests that the reaction may be easier to complete for a 2-electron donor such as **5** and may occur at lower potentials. As a result of its presumed greater ease of reduction, germanium tetrachloride was also investigated as a starting material for nanoparticle synthesis *via* reduction with **5**.

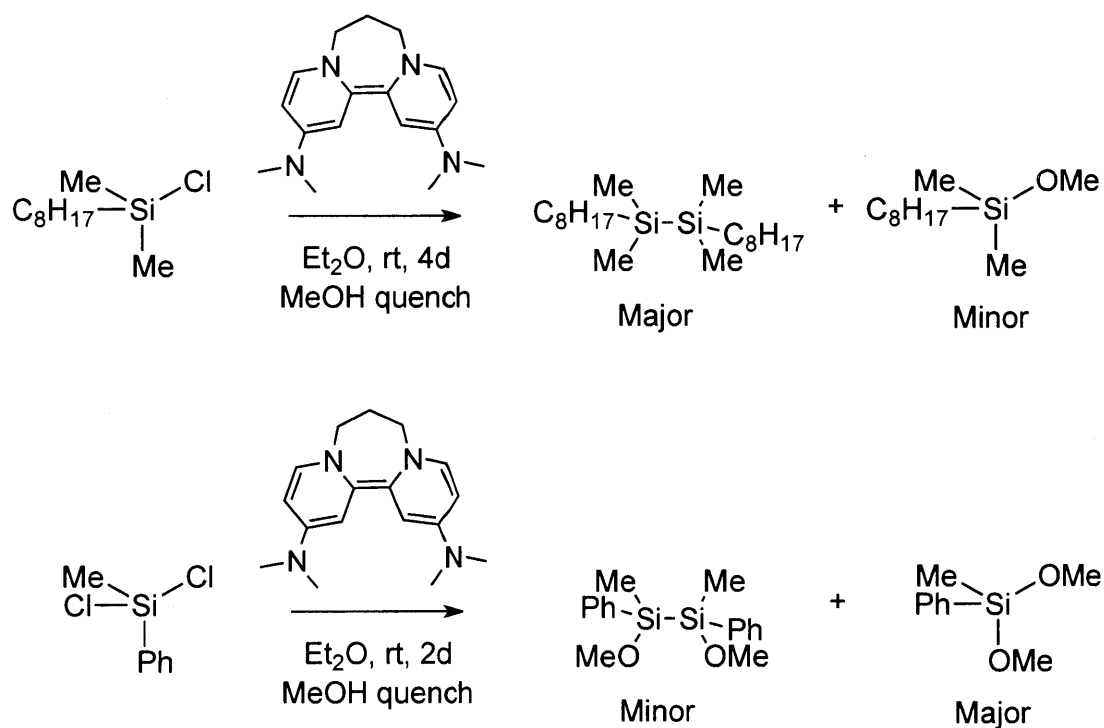
Finally, it is worth noting that very little is known about the kinetics of silicon nanoparticle growth in solution. Several models have been developed to describe silicon nanoparticle generation in the gas phase from silane (SiH_4),^{55,56} but nothing similar is readily available for solution-synthesized nanoparticles. The growth mechanism for traditional CdSe and related quantum dots has been more extensively studied,⁵⁷ and in general consists of the nucleation of dots in a supersaturated solution of monomeric precursor dissolved at high temperature in a suitable ligand (often TOPO = trioctylphosphine oxide), followed by a period of growth mediated by ligands popping onto and off of the nascent dot surface as more precursor is added fairly equally among dots, and finally (if the reaction is not quenched) a period of Ostwald ripening ensues where smaller particles redissolve and add their components to the larger particles.⁵⁸ The nucleation-growth-ripening scheme is much less pertinent for silicon nanocrystals for several reasons. Firstly, the concept of “ligands” does not hold as well for silicon as for zero-valent metal (*e.g.* Cd) precursors, so the concept of ligand-mediated uniform particle growth cannot be directly applied to silicon because there is no dynamic equilibrium where atoms are added and removed in a ligand-exchange-type process. Secondly, the bonds formed have more covalent character for elemental silicon than for CdSe and related materials, which affects both the conditions required for nucleation and for growth (for instance, it is not possible to spontaneously initiate growth using SiCl_4 no matter how saturated the solution is because there must be an electron source, whereas CdSe crystals grow spontaneously from

supersaturated solutions of monomers) as well as the Ostwald ripening process (smaller crystallites may not spontaneously dissolve to be deposited on larger particles). The best mechanism for silicon nanocrystal nucleation in solution has not been well studied, and remains an open question here. For monodisperse nanocrystal syntheses, control over the rate and timing of nucleation versus growth presents an important challenge. In this work, size control, monodispersity, and uniformity were not touched as the primary research question of interest lay in whether **5** could be used to reduce SiCl₄ to elemental silicon at all. Therefore, while various growth conditions and surface capping reagents were explored for the synthesis of silicon nanocrystals, the experiments required for understanding the mechanism of growth in order to tune growth rates and particle sizes were not explored.

3.2 Results and Discussion

In order to determine whether it was feasible to reduce silicon halides with **5**, we first developed a test system using di- and trialkyl silicon chlorides. The products of these reactions could readily be analyzed by NMR and GCMS, techniques not available for nanoparticle characterization, in order to determine if the reaction worked at all. First, chloro(*n*-octyl)dimethylsilane and **5** were stirred for four days in diethyl ether at room temperature, then the reaction was quenched with methanol. By GCMS, more than half of the product was the dimer and the rest was the alcohol-substituted methoxy(*n*-octyl)dimethylsilane. This initial result appeared promising because we observed conversion to the coupled product, indicating that reduction of the silicon-chlorine bond to generate a silicon-silicon bond was possible. Better yet, the starting materials for this reaction are expected to be less reactive than the desired substrate SiCl₄ because of the electron-donating nature of the alkyl groups which gave us hope that SiCl₄

could, in fact, be reduced. Similarly, when methyl(phenyl)dichlorosilane was stirred in toluene for two days at room temperature, a small degree of conversion to the dimer was observed, though there was no evidence by GPC of the formation of larger polymers. These results tentatively suggested that using **5** might prove a reasonable method for reducing silicon halides to generate the silicon-silicon bonds desired for nanoparticle formation, and elevated temperatures may certainly enhance the reaction.



Scheme 7. Reduction of silicon chlorides to dimers

Several general pitfalls are worth noting at the onset for future readers to avoid. While the most facile synthesis of **5** is *in situ* in DMF using a method analogous to that described for synthesis of **4** in section 1.4.6, DMF solutions of **5** cannot be cannula transferred to SiCl_4 because the SiCl_4 reacts with DMF instantaneously. As a result, **5** must be prepared as a dried powder in advance using the NaH/NH_3 method. Additionally, SiCl_4 must be bought and used as a neat liquid because solutions in DCM (as sold by Aldrich) are incompatible with strongly

reducing conditions because the DCM can react with, for example, **5** and makes carbenes as an undesirable side reaction.

Keeping this in mind, several types of reactions were attempted in order to synthesize silicium nanoparticles from the reduction of silicon tetrachloride by **5**. Firstly, in analogy to Gerbec, *et al.*,⁵⁹ the silicon halide/**5** reaction was tested using microwave conditions. Reactions in the microwave work best if either the molecule of interest itself is highly polarizable and therefore susceptible to microwave heating, or the solvent has a significant dipole moment that can be exploited to reach high temperatures and/or high pressures for the reaction. The polarizability of **5** suggests that it would make a good target for microwave heating. Phenyltrichlorosilane (PhSiCl₃) and **5** were added to a microwave reaction vessel in hexanes (a non-absorbing solvent) and heated to 100°C for 30 min then quenched with isopropanol. At the end of the reaction, the products were washed with water to remove the oxidized salts **5'** and the organic layer was analyzed with NMR, FTIR, GCMS and transmission electron microscopy (TEM). The GCMS trace revealed a small amount of dimer, but the TEM showed no nanoparticles and the FTIR/NMR mostly showed contamination from **5'**. The same reaction was conducted in THF since THF is a microwave absorbing solvent, but similar results were obtained. Microwave reactions were abandoned relatively early due to experimental hassle and no clear indication of the superiority of the method over standard thermal heating.

Several reductions of GeCl₄ with **5** were attempted under the assumption that Ge(IV) may be easier to reduce than Si(IV). In analogy to a method developed by Lee *et al.*,⁵¹ GeCl₄, hexadecylamine, hexadecene, and **5** were heated to 180°C for one hour in the microwave before quenching with methanol and “crashing out” the reaction by centrifugation. The resulting precipitate was resuspended in MeOH/Hexanes twice more and reprecipitated in order to clean

the solid brown material that was then characterized by FTIR (Figure 2, line A). There are no visible C-H stretches, and the absorption features all appear below 1500 cm^{-1} , which is where Ge-O and Ge-C stretches should be. Essentially the same FT-IR was obtained when the reaction was heated to only 100°C and quenched with methanol (Figure 2, line C) and when *n*-butyllithium was added to cap the NPs (Figure 2, line D), which seemed promising until SiCl_4 was used instead of GeCl_4 and the FT-IR spectrum appeared almost identical (Figure 2, line B). SiCl_4 does not react with hexadecene, and the SiCl_4 reaction was run in the absence of hexadecylamine for fear of side reactions; similarly, a control reaction with GeCl_4 and hexadecylamine with no reductant resulted in minimal formation of precipitate which had a different IR signature from that shown in Figure 2. The similarities between the IR spectra of the SiCl_4 and GeCl_4 reactions suggest that the precipitate may not, in fact, be the desired metal nanoparticles and could instead represent some form of degradation product from heating **5**. The NMR signals corresponding to **5'** in the supernatant for these reactions show significant decomposition of the molecule, more than was ever observed under reductive coupling conditions, which indicates that high temperatures destroy **5**. The reaction of GeCl_4 with **5** in DME in the absence of ligands also generates a black precipitate with an FTIR signature identical to the other GeCl_4 -based reactions described above. Attempts at reducing GeCl_4 using inverse micelles as per Prabakar, *et al.*⁵⁴ with tetraoctylammonium bromide as a surfactant in toluene yielded a similar black, insoluble precipitate. All germanium-based reactions resulted in the same precipitate which could be, or at least include, a germanium compound, but TEM images of the black precipitate were not promising for nanocrystals due to the negligible quantity of material and its amorphous appearance. Several example TEM images are given in Figure 3.

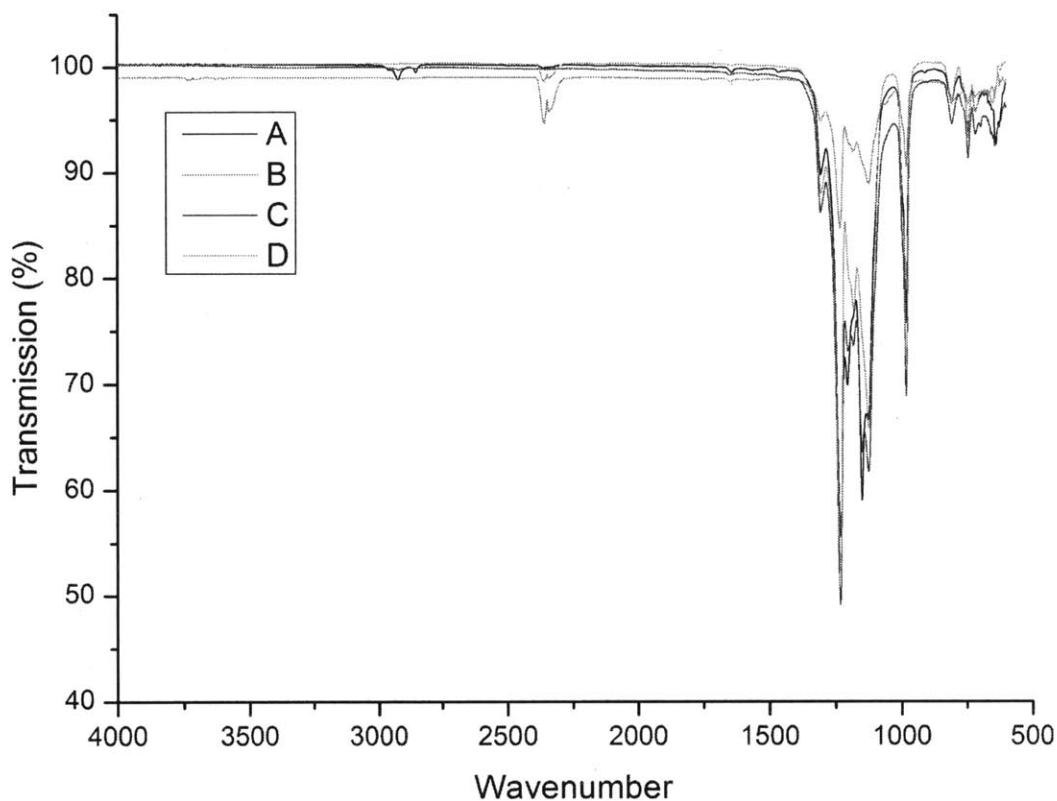


Figure 2. FT-IR spectra for (A) GeCl_4 , 180°C, microwave, MeOH quench (B) SiCl_4 , 150°C, MeOH quench (C) GeCl_4 , 100°C, MeOH quench (D) GeCl_4 , 100°C, *n*-butyllithium termination

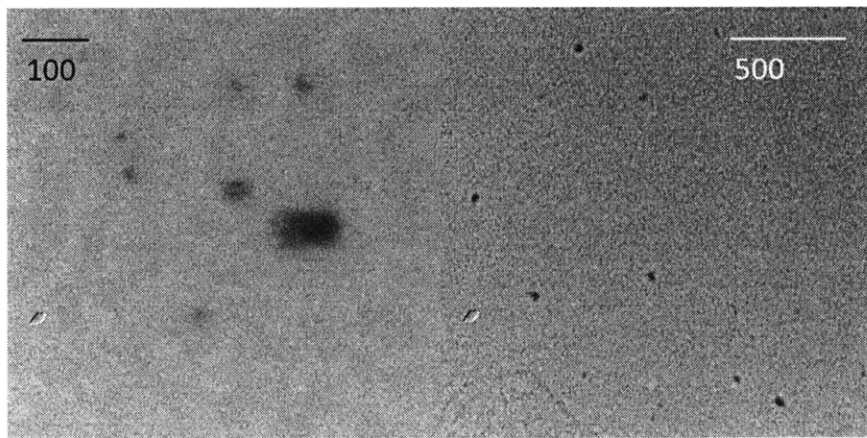


Figure 3. TEM images of potential Ge nanoparticles from black precipitate after reaction of GeCl_4 with **5** in DME at 100°C for one hour.

As discussed in the introduction to this chapter (Section 3.1), capping nanoparticles with a suitable end group to passivate dangling bonds is an essential element of nanoparticle

synthesis. In the reactions described above, methanol was used to quench the reaction and therefore presumably served as the capping material. In addition to alcohols, organometallic compounds such as Grignard reagents or organolithium reagents can be used to cap group IV nanoparticles at the end of synthesis as the organometallic presumably displaces the Si-Cl or Ge-Cl bond to create a Si-C or Ge-C bond. A number of experiments using *n*-butyllithium or octylmagnesium bromide as capping groups always resulted in the formation of an orange/brown precipitate upon crash out by centrifugation. A control experiment in which **5** went through the same reaction conditions as used for attempts at synthesizing nanoparticles but with no Si or Ge source also resulted in an orange/brown precipitate after addition of octylmagnesium bromide and the material had an identical UV/Visible absorption spectrum to the precipitated material when a Si source was added (Figure 4). The precipitate formed in the absence of a silicon source, as well as the precipitated material in the presence of SiCl₄, were both resuspended in methanol and drop cast onto TEM grids. Both TEM grids had large polygonal regions of dark material presumably corresponding to products of side reactions, but only the reaction including a silicon source exhibited small dots in regions outside these large dark crystals by TEM (Figure 5A). These same TEM grids were analyzed with scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDX) as well (Figure 5C, 5D). The SEM images did not show strong evidence of nanoparticles, but did elucidate the nature of the large polygonal crystals as the EDX spectra showed they were predominantly magnesium salts. The EDX spectrum for particles from the reaction including a silicon source did show silicon signal (Figure 5C) unlike these salts in the absence of silicon, but the form the silicon is unclear as it could well be silicon oxide. Interestingly, no precipitate was formed in control reactions in the absence of **5** where *n*-butyllithium or octylmagnesium bromide were added to SiCl₄ or GeCl₄, suggesting that the

observed magnesium salt precipitate is likely due to a reaction between the organometallic reagent and molecule **5** or its oxidized form **5'**.

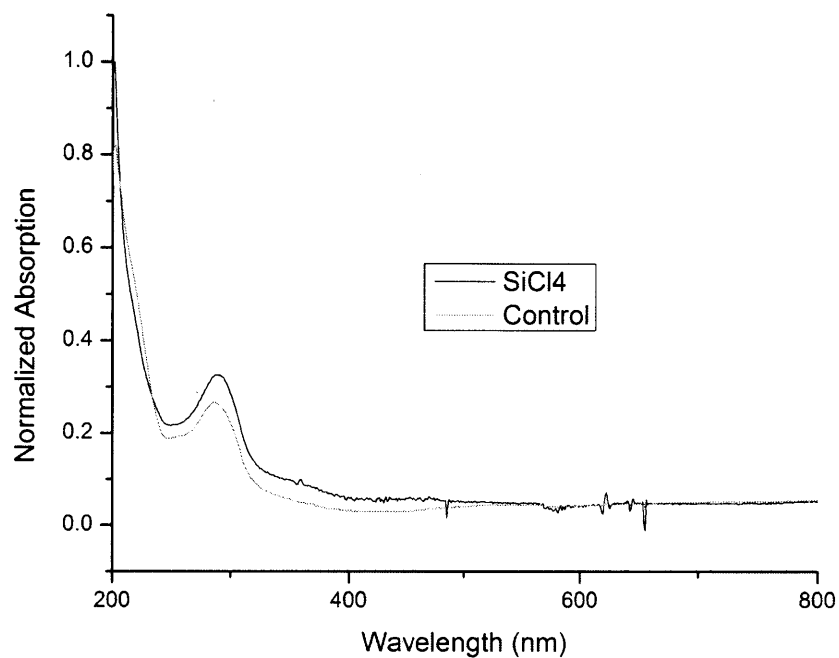


Figure 4. UV-Vis absorption spectra for precipitate after reduction of SiCl_4 with **5** and subsequent addition of octyl-MgBr, and control where no Si source was added. The absorption is clearly due to reactions of the reductant **5** rather than the Si.

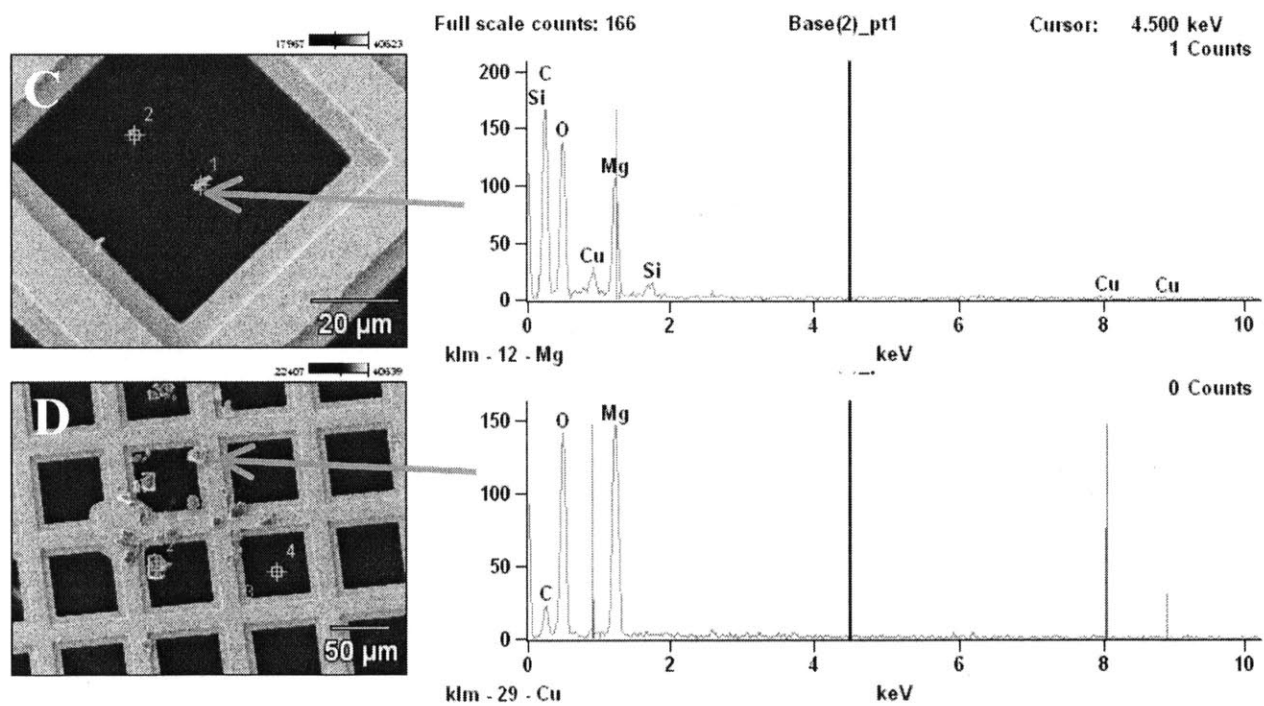
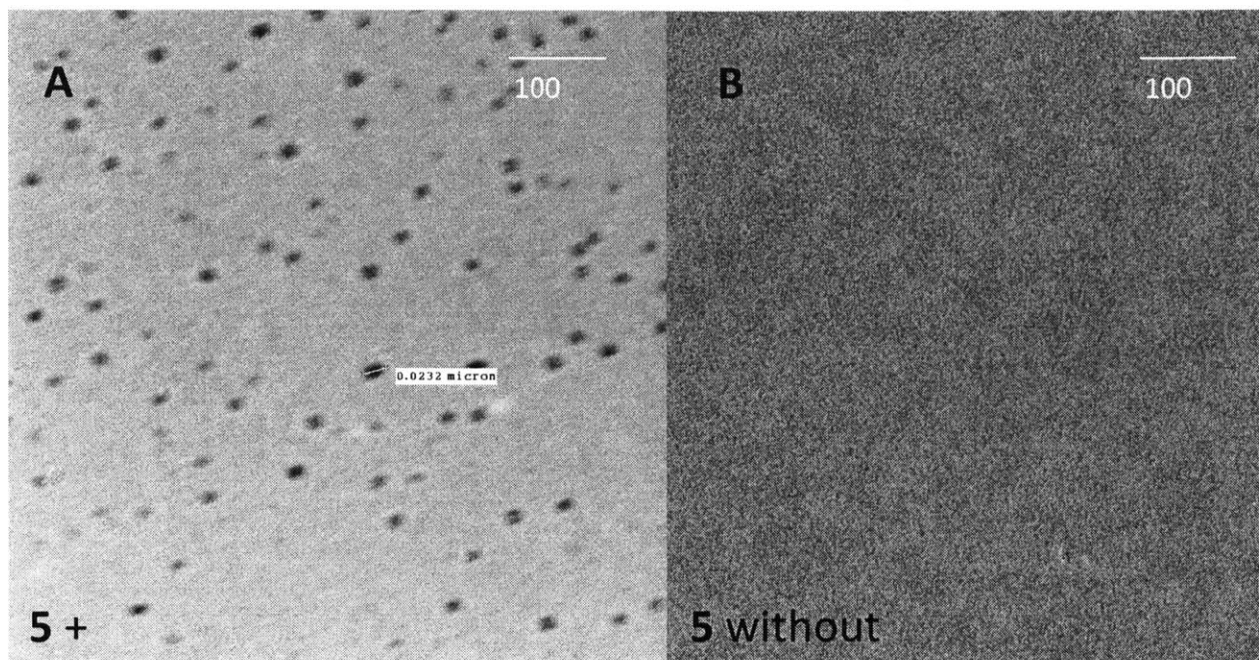


Figure 5. TEM (A,B) and SEM (C,D) images of the same TEM grids with solid precipitate. A,C: SiCl_4 was added to reaction; B,D: reaction in absence of Si source. EDX spectra are given which correspond to the region marked with crosshairs as 1 in the SEM image.

In order to avoid the side reactions observed when organometallic species were added to solutions of **5**, octanol was chosen as a capping agent to produce hydrophobic nanoparticles.⁴⁵

No precipitate was formed in a control reaction between only **5** and octanol under conditions used to synthesize nanoparticles. When SiCl_4 or GeCl_4 were added, a small amount of precipitate formed upon centrifugation of the octanol-quenched material. Representative TEM images of this precipitate show giant spheres that are high contrast but do not appear crystalline, as well as lower contrast amorphous material (Figure 6). We decided these materials were not promising for further study as their composition, crystallinity, and size distribution are neither well controlled nor well defined. Additionally, the fact that **5** cannot be heated above about 100°C without decomposing and it reacts with organometallic capping agents means it has limited practical utility for nanoparticle synthesis.

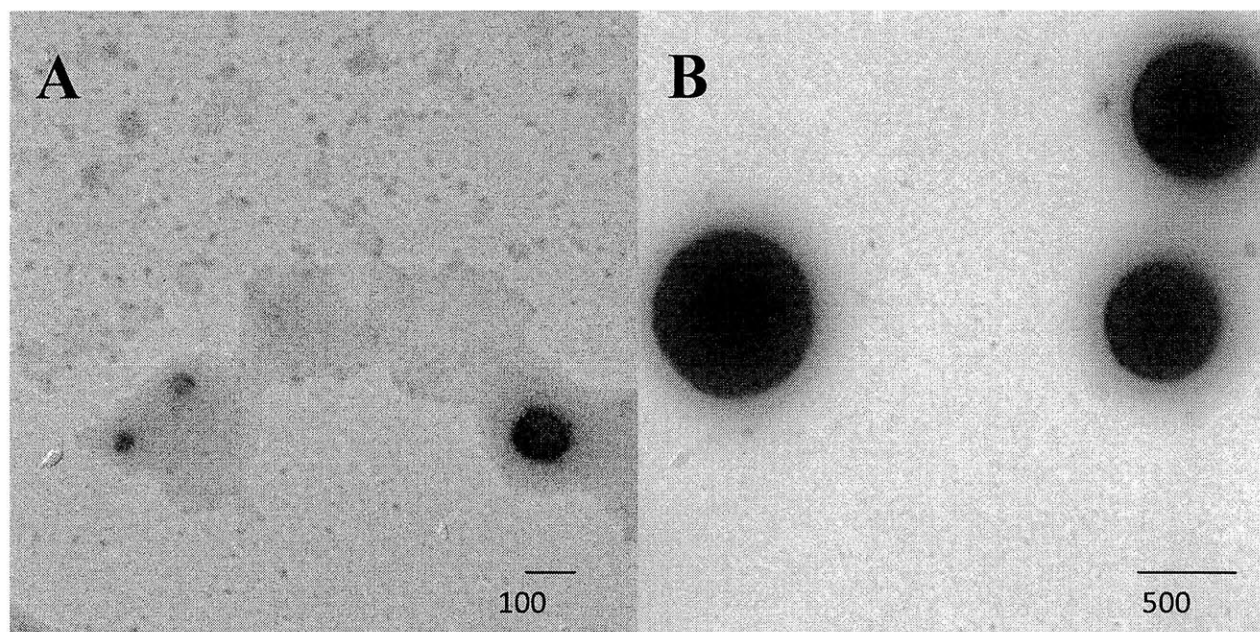


Figure 6. TEM images of precipitate formed upon centrifugation of **A)** GeCl_4 or **B)** SiCl_4 reduced with **5** and terminated with octanol.

3.3 Summary and Conclusions

We were unable to demonstrate strong evidence for the successful synthesis of group IV nanoparticles using **5** to reduce silicon and germanium halides. There are several possible reasons for the failure to produce observable Si or Ge NPs, which will be the focus of this section.

Firstly and most obviously, it is possible that molecule **5** is not sufficiently reducing to dehalogenate silicon halides. The standard reduction potential for the half reaction $\text{SiO}_2 + 4\text{e}^- + 4\text{H}^+ \rightarrow \text{Si(s)} + 2\text{H}_2\text{O}$ is -0.87 V, and as silicon tetrachloride is in the same +4 oxidation state we assumed that it could be reduced by the electron donor **5** as per Table 1. Relatively little work has been done using electrochemical reduction of SiCl_4 . Agrawal and Austin⁶⁰ used electrochemistry to deposit amorphous silicon onto an electrode from a solution of 1.0M SiHCl_3 in propylene carbonate containing 0.1M tetrabutylammonium chloride as the supporting electrolyte; in this case, the cyclic voltammogram showed the reduction wave at -2.3V vs Pt. Over several cycles, as amorphous silicon was deposited on the electrode the reduction peak shifted slightly to more negative potentials. Gobet and Tannenberger⁶¹ measured the reduction potentials of SiHCl_3 , SiCl_4 and SiBr_4 in THF using tetrabutylammonium perchlorate as the supporting electrolyte and Ag/AgClO₄ as the reference electrode. They measured -2.7 V as the reduction peak for SiHCl_3 , -3.0 V as the reduction peak for SiCl_4 , and -2.2 V for the reduction of SiBr_4 . These peaks are shifted -0.8 V relative to Ag/AgCl, so the corrected reduction potential for SiCl_4 would be -1.4 V vs. Ag/AgCl. However, **5** shows a half-wave reduction peak at only -1.13 V vs Ag/AgCl in DMF. This suggests that **5** may not be sufficiently reducing to make Si(s) from SiCl_4 .

The reduction of germanium (IV) takes two steps, as Ge(II) is a stable oxidation state of the element, and occurs at less negative potentials. The standard reduction potential for $\text{GeO}_2 + 2\text{e}^- + 2\text{H}^+ \rightarrow \text{GeO} + \text{H}_2\text{O}$ is -0.37 V, and for $\text{GeO} + 2\text{e}^- + 2\text{H}^+ \rightarrow \text{Ge(s)} + \text{H}_2\text{O}$ is +0.26 V, suggesting that it should be possible to reduce Ge(IV) with **5**. The reduction potential for GeCl_4 is not readily available, but is assumed to be somewhat higher than that of GeO_2 in analogy with the SiCl_4 system. Even so, molecule **5** should be sufficiently reducing to make Ge(0), though admittedly the evidence for this occurring was ambiguous at best.

Secondly, it is possible that the separation methods used to remove the oxidized **5'** from the reaction mixture after quenching were insufficient and the nanoparticles were lost in the separation process. Using separation by aqueous/organic extraction, this would be unlikely if the particles were successfully capped with some long-chain alkane which should render them organic-soluble rather than water-soluble; however, if the capping were unsuccessful, small silicon or germanium particles could be oxidized to small hydrophilic silica/germanium oxide particles and go into the aqueous phase of the extraction. Separation by precipitation could also result in loss of material if the nanoparticles were too small or too organic-soluble to be efficiently precipitated.

Thirdly, it is possible that the reactions were not run at sufficiently high temperatures to allow for reduction and group IV nanoparticle growth. Many papers reporting the solution synthesis of Si NPs use elevated temperatures (up to $\sim 300^\circ\text{C}$) in order to provide a sufficient enthalpic driving force for the reaction and the formation of the covalent Si-Si bonds. Elevated temperatures are also favorable for driving reduction using **5**; however, if the reaction temperature was raised much above 100°C the organic reductant appeared to decompose, which limited the temperature range accessible for testing. **5** has also been shown to be a stronger

reductant upon photochemical excitation, as it can then reduce aryl chlorides as well as diphenylcyclopropanes, which it cannot do with thermal activation alone.³⁵ It is possible that photochemical excitation may be simultaneously a way around both the thermal decomposition problem and the slightly too small reducing power problem mentioned above. Photochemical excitation of **5** is a reasonable next step to try to drive this reaction forward in lieu of higher temperatures.

Fourthly, the concentration of monomers and the solvent systems employed may have been insufficient to achieve particle nucleation and/or growth. Sugimoto⁶² extensively describes systems requirements for the synthesis of monodisperse nanoparticulate materials, and a key feature of these syntheses is the supersaturation above a critical concentration of the monomer at the time of nucleation. Supersaturation is required to separate the nucleation stage from the growth stage (a fact often illustrated with La Mer diagrams⁵⁸), and well-resolved nucleation is a key feature of monodisperse colloidal growth systems. It is possible, therefore, that because neither the silicon source nor the reductant were supersaturated in solution, there was no defined nucleation phase and (assuming **5** is reducing enough to reduce the SiCl₄ in the first place) only dimers/trimers were formed due to the lack of a defined nucleated surface on which more silicon monomers could be deposited.

In sum, there are a number of sensible reasons why this reaction failed to produce clear evidence of silicon/germanium nanoparticles, and a more comprehensive study of these different potential explanations is required to pinpoint the shortfalling of this method. However, as described in Section 3.2, molecule **5** was able to reduce small amount of silicon halides to the corresponding dimers, which suggests that the desired reaction to produce nanoparticles is not completely out of the question and rather requires further work.

3.4 Experimental Methods

3.4.1 General Considerations

All experiments were conducted in a N₂ filled glovebox, unless otherwise indicated. SiCl₄ (Strem Chemicals, 99.99%), GeCl₄ (Strem Chemicals, 99.99%), and molecule **5** were all stored in the glovebox until use. All ethereal solvents were dried over sodium benzophenone, freeze-pump-thawed three times, and vacuum transferred to a dry receiving flask before use. Hexane was dried over an activated alumina solvent column. Octylmagnesium bromide (Aldrich Chemicals) and n-butyllithium (Acros Organics) were used as received. Octanol was dried over calcium hydride and distilled prior to use.

TEM images were collected on a JEOL 200CX instrument in the Center for Materials Science and Engineering at the Massachusetts Institute of Technology. FT-IR spectra were collected using either a ZnSe or a Ge attenuated total reflectance (ATR) crystal on a Nicolet 6700 FT-IR spectrometer from Thermo Scientific. Microwave reactions were conducted using a CEM Discover CW microwave.

3.4.2 General Procedure for SiCl₄ Reduction

For a typical experiment, four equivalents of reductant **5** was dissolved in a solvent (hexanes, toluene, THF, DME) for a final concentration of 0.6 mM and heated to the desired temperature (50°C, 80°C, 100°C, 150°C). Neat silicon tetrachloride or powdered SiCl₄•Pyr₂ complex (Pyr = pyridine, prepared according to the literature⁶³) was then added into the reaction mixture, and the mixture was stirred for 30min to 12 hours for different reactions. At the end of the prescribed time, the reaction mixture was removed from the glovebox and four equivalents of the appropriate capping agent (n-butyllithium, octylmagnesium bromide, octanol) were added at room temperature and stirred for at least one hour. Methanol was added and the mixture

centrifuged at 10000 rpm for 10 minutes to crash out any precipitate. The precipitate was resuspended in 50:50 hexanes:methanol and reprecipitated twice to remove the salt **5'** from any particles. The precipitate was resuspended in HPLC grade methanol and drop cast onto carbon film TEM grids for imaging. The supernatant from the precipitation was dried under vacuum, then resuspended in water and extracted with either CHCl₃ or diethyl ether. ¹H NMR spectra of the organic phase never showed significant signal beyond residual solvent, small amounts of **5'**, and grease presumably left over from the NaH used to synthesize **5**. Attempts to collect ²⁹Si NMR spectra were unsuccessful.

3.4.3 General Procedure for GeCl₄ Reduction

Attempts at reduction of GeCl₄ were either entirely analogous to those described above in 3.4.2 or required the addition of hexadecylamine and hexadecene. In the latter case, GeCl₄ was added to hexadecylamine (24 equivalents) and stirred at 50°C until the hexadecylamine was entirely melted, then a solution of hexadecene (20 equivalents), **5** (4 equivalents) and toluene was injected and the reaction was further heated to either 80 or 100°C. The reaction was quenched and precipitated as per 3.4.2.

3.4.4 General Procedure for Microwave Reactions

For microwave reactions, SiCl₄ or GeCl₄ or a 5:1 mixture of SiCl₄:PhSiCl₃ was added to a solution in a microwave reactor vial of **5** in either THF or hexanes. The vial was brought out of the glovebox and put into the microwave (CEM Discover), then stirred at either 100°C or 150°C for 30 min or one hour with a maximum power of 200 W. The reaction was quenched with isopropanol and precipitated, and the supernatant was extracted from water with chloroform or diethyl ether.

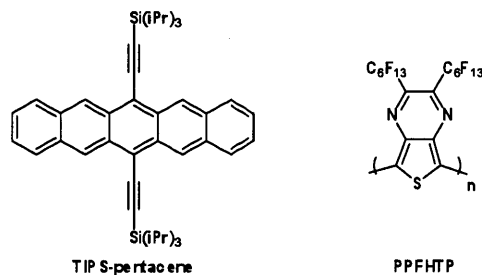
Chapter 4: N-doping of Organic Electronic Materials with Organic Electron Donor

4.1 Background and Introduction

Organic electronic materials have recently been highly studied for their use in organic photovoltaics, organic light emitting diodes, organic field effect transistors, and other applications where the semiconducting properties of highly conjugated organic materials can be utilized.⁶⁴ While hole-conducting p-type organic materials are abundant, synthesis of electron-conducting n-type materials remains challenging. One potential solution is doping p-type materials with electrons in order to change the dominant charge carrier. Guo *et al.* have successfully doped TIPS-pentacene as well as several p-type polymers using rhodacene and ruthenacene dimer derivatives, which both increased the Fermi level of the parent organic and increased its conductivity.⁶⁵ We were interested in whether **5** could analogously serve as an electron dopant for organic electronic materials.

4.2 Results and Discussion

In order to determine whether **5** could serve as an electron dopant for organic materials, we chose two test molecules: 1,3-bis(tri(isopropyl)silyl ethynyl) pentacene (TIPS-pentacene), a known p-type organic small molecule, and poly(2,3-bis(perfluorohexyl)thieno[3,4-*b*]pyrazine (PPFHTP), a novel n-type fluorous organic polymer recently developed in the Swager laboratory (Scheme 8). Bottom gate, bottom contact field-effect transistors (FETs) were used to measure conductivities and electron mobilities for both materials both with and without **5** added as an electron dopant.



Scheme 8. Molecules used for electron doping experiments with **5**.

TIPS-pentacene is a well-known small molecule organic semiconductor with a hole mobility of $0.17 \text{ cm}^2/\text{Vs}$ that has been used for organic field effect transistors and organic solar cells.⁶⁶⁻⁶⁸ TIPS-pentacene was synthesized from pentacene quinone using the Swager modification of Anthony's procedure.⁶⁹ Three solutions of 10mg/mL TIPS-pentacene in toluene were stirred with 0%, 5%, or 10 wt % **5** in a glovebox for 30 min, then were spin coated onto clean FET substrates and allowed to dry at room temperature overnight. The substrates were measured for their field-effect transistor electronic properties in a N_2 filled glovebox. The best performing devices were those doped with 5 wt % **5**, and they showed a clear change from standard p-type conduction (observed in the 0% devices, Figure 7 left) to n-type conduction (Figure 7 right). Additionally, the saturation *hole* mobility measured for the best undoped device was $\mu_{\text{sat}} = 1.5 \times 10^{-5} \text{ cm}^2/\text{Vs}$ while the saturation *electron* mobility measured for the best doped device was $\mu_{\text{sat}} = 3.9 \times 10^{-4} \text{ cm}^2/\text{Vs}$. These results were obtained without any optimization of device fabrication, and could almost certainly be improved upon changing deposition conditions for the TIPS-pentacene as well as the concentration of **5** used. This demonstrates that molecule **5** can not only dope TIPS-pentacene to make an n-type material, but could, in fact, increase the conductivity of the thin film.

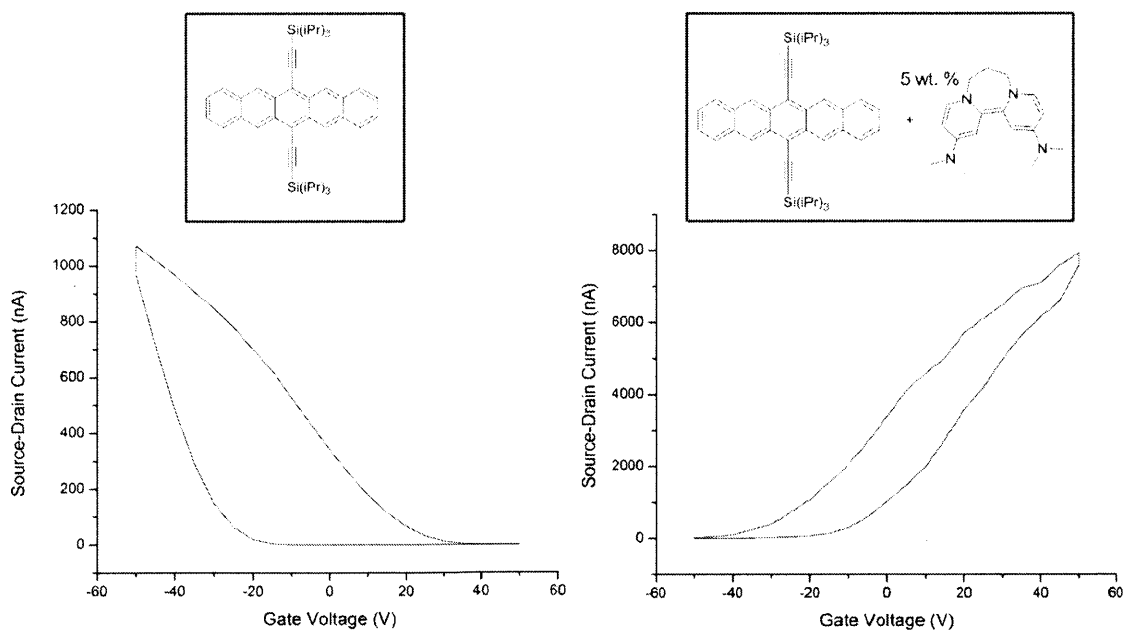


Figure 7. Field-effect transistor transfer curves for TIPS-pentacene in the absence (left) and presence (right) of 5 wt % **5**. For both curves, the source-drain voltage $V_d = 50\text{V}$.

Encouraged by the results using TIPS-pentacene, we investigated whether **5** could dope PPFHTP, a novel fluorinated organic polymer developed in the Swager lab (*Takeda, et al. in progress*). This low bandgap n-type polymer has measured electron mobility in the top contact/bottom gate configuration of $2 \times 10^{-6} \text{ cm}^2/\text{Vs}$. The polymer is known to turn from brilliant blue to purple upon both electrochemical doping and doping with sodium naphthalenide. Here, a filtered solution of 10 mg/mL PPFHTP in perfluoro(methyl)cyclohexane was spin cast onto bottom gate/bottom contact FET substrates and 12 μL of 0.1 mM **5** in toluene were drop cast onto devices (attempting to stir **5** into PPFHTP in solution caused the polymer to aggregate significantly and precipitate out of solution). The devices were dried at room temperature for 30 minutes, then measured in a N_2 filled glovebox. While these deposition conditions did not yield the best possible devices, the **5**-doped polymer showed significantly different FET performance than the native polymer. The devices doped with **5** do not turn on when the gate voltage is varied, and merely show a linear decrease in current over time as the gate voltage is swept which is responsible for the shape of the transfer curve in Figure 8B. The same behavior is also manifest in the lack of source-drain current (I_{sd}) modulation with changing gate voltages observed in the output curves for the doped polymer (Figure 8D). In the absence of **5**, PPFHTP demonstrated standard organic field effect transistor properties, albeit with low mobility (Figure 8A, 8C). The fact that the electronic properties of PPFHTP when doped with **5** were independent of gate voltage coupled with the fact that the doped polymer passed much higher currents for a given source-drain voltage than the undoped polymer together indicate that **5** successfully doped the polymer and made it conducting rather than semiconducting.

In sum, super electron donor **5** successfully doped organic semiconductors and was both able to change the sign of the charge carrier for a p-type small molecule semiconductor as well

as change the properties of an n-type polymeric semiconductor to make it conductive. Electron donor **5** is therefore potentially useful in future applications where an n-type dopant is required.

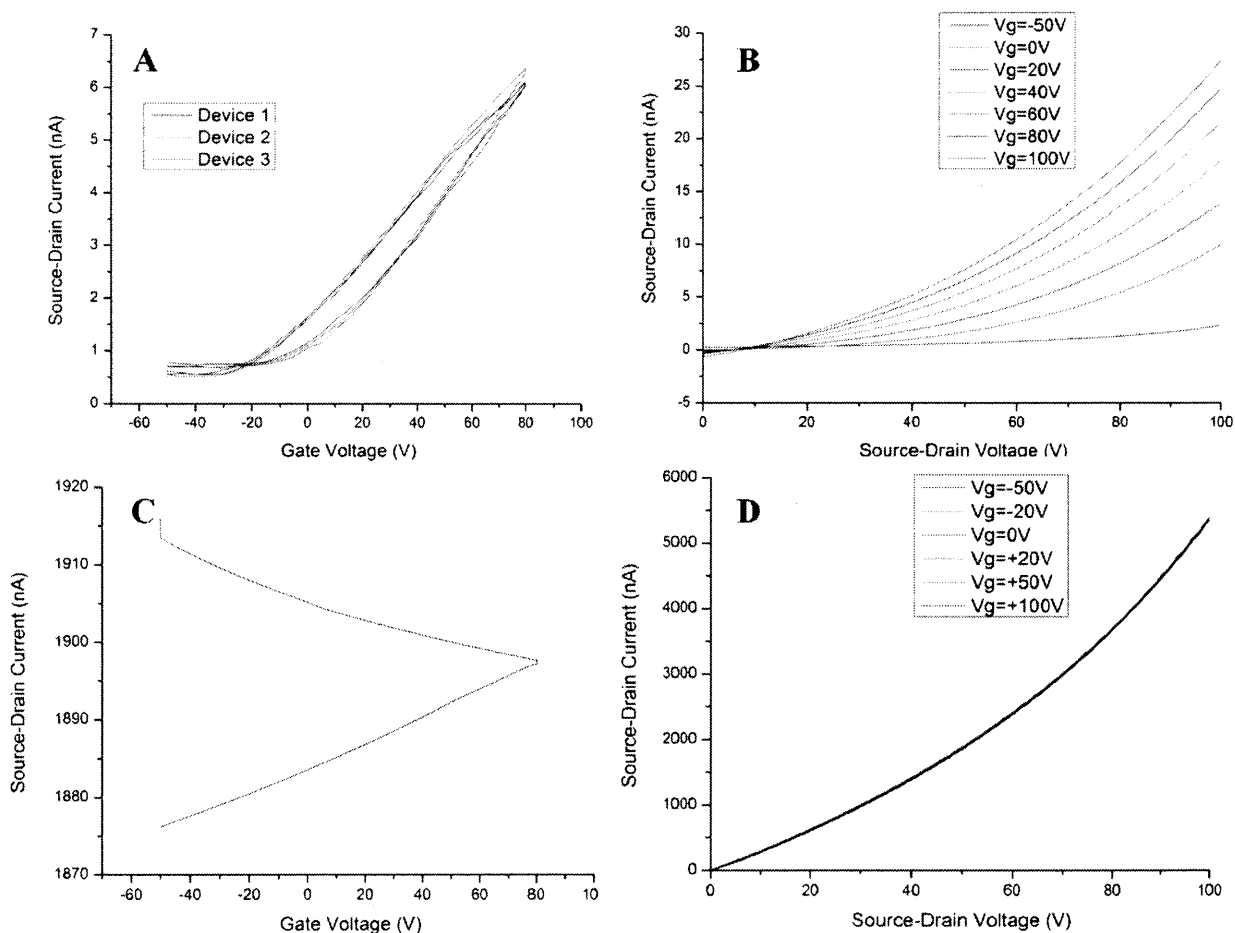


Figure 8. Transfer (A, B) and output (C, D) curves for PPFHTP in the absence (A, C) and presence (B, D) of **5**. Transfer curves were collected with a drain voltage of $V_d = 50V$, and output curves were collected with the series of gate voltages listed in the legend.

4.3 Experimental Methods

4.3.1 Organic Materials

TIPS-pentacene was synthesized from pentacene quinone in two steps with an overall yield of 89% as described previously.⁶⁹ PPFHTP was synthesized as described in an upcoming paper (Takeda, *et al.*).

4.3.2 Field-Effect Transistor Fabrication and Measurement

Field-Effect transistors were made from substrates fabricated at the Technology Research Laboratory at the Massachusetts Institute of Technology. The substrates were fabricated on 4" p-type silicon wafers (boron doped, resistivity 30-50 Ωcm , 500 nm thermal oxide) and had 5 nm of Cr under 50 nm of Au patterned using standard photolithography techniques, with channel widths of 10 μm . The substrates were cleaned with sonication in Micro-90 surfactant, water, acetone, and boiling isopropanol prior to overnight deposition of the self-assembled monolayer (1 $\mu\text{L}/\text{mL}$ PhSiCl_3 in hexanes). After monolayer growth, the substrates were cleaned by sonicating in acetone and toluene, then dried under N_2 and pumped into a glovebox where a 10 mg/mL solution of the desired organic was spin cast at 1000 rpm for 1 minute. The contact pads of the thin film transistor were cleaned with an appropriate solvent and the substrate was allowed to dry before transferring to another N_2 filled glovebox for measurement using a Keithley 2636 source-meter operated by a standard LabView program.

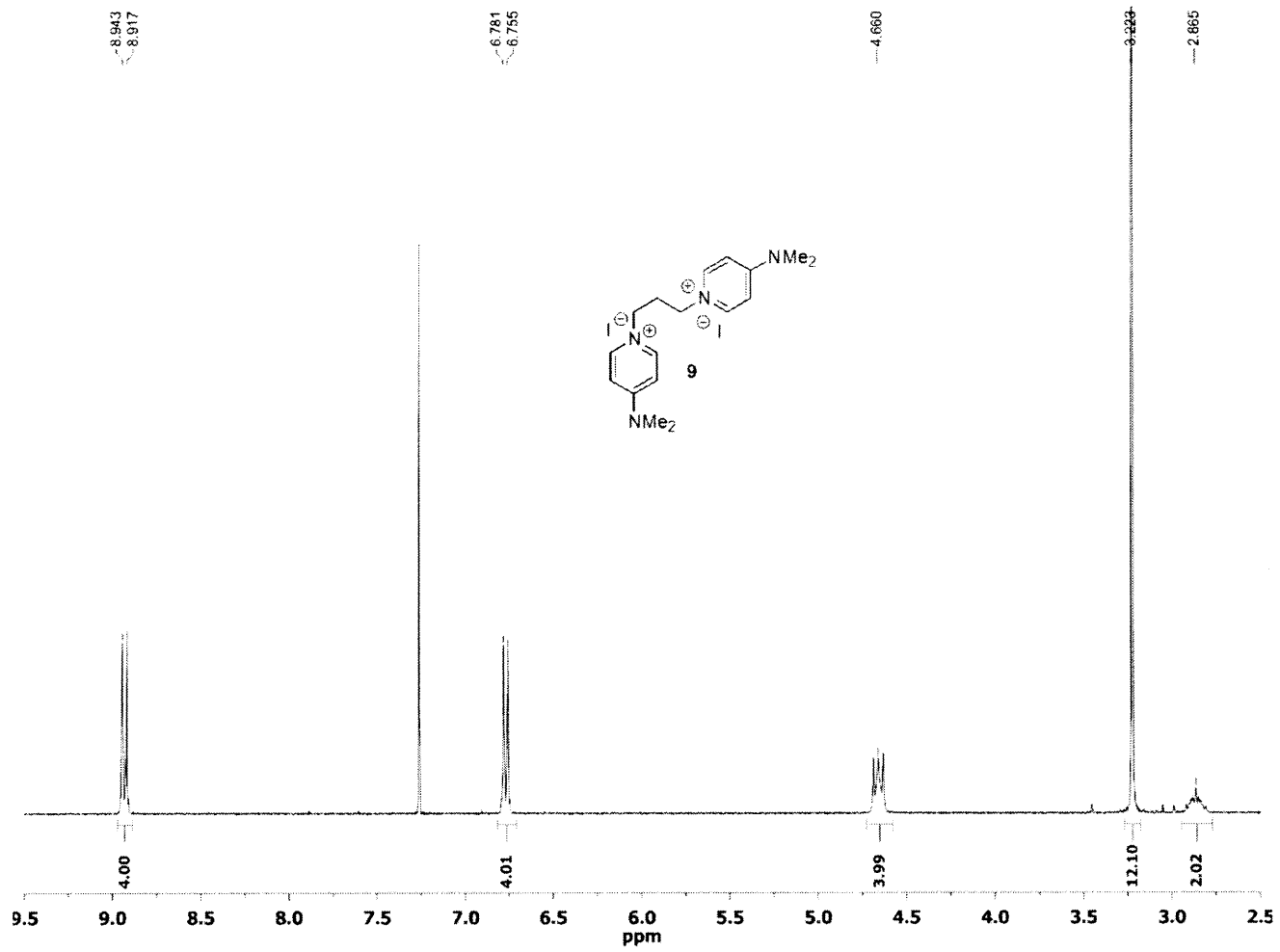
Chapter 5: References

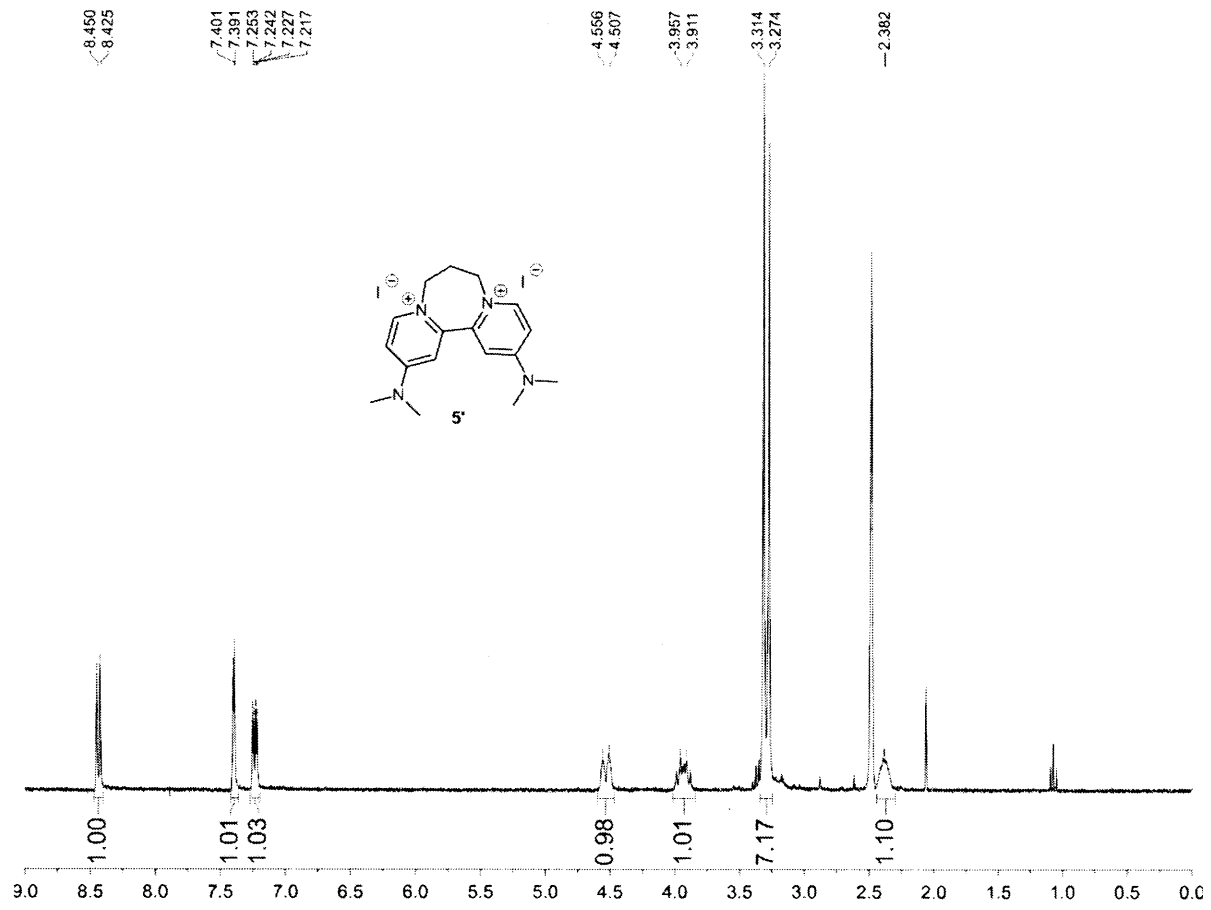
- (1) Segura, J.; Martin, N. *Angewandte Chemie-International Edition* **2001**, *40*, 1372.
- (2) Brunetti, F.; Lopez, J.; Atienza, C.; Martin, N. *Journal of Materials Chemistry* **2012**, *22*, 4188.
- (3) Garito, A.; Heeger, A. *Accounts of Chemical Research* **1973**, *435*, 232.
- (4) Ferraris, J.; Cowan, D. O.; Walatka, V.; Perlstein, J. H. *Journal of the American Chemical Society* **1973**, *95*, 948.
- (5) Murphy, J. A. In *Radicals in Organic Synthesis*; Renaud, P., Sibi, M., Eds.; Wiley-VCH Verlag GmbH: Weinheim, Germany, 2001.
- (6) Yang, G.; Zhang, G.; Sheng, P.; Sun, F.; Xu, W.; Zheng, D. *Journal of Materials Chemistry* **2012**, *22*, 4391.
- (7) Kaminska, I.; Das, M.; Coffinier, Y.; Niedziolka-Jonsson, J.; Woisel, P.; Opallo, M.; Szunerits, S.; Boukherroub, R. *Chemical Communications* **2012**, *48*, 1221.
- (8) Kuroboshi, M.; Waki, Y.; Tanaka, H. *Journal of Organic Chemistry* **2003**, *68*, 3938.
- (9) Pederson, M. R.; Laouini, N. *Journal of Cluster Science* **1999**, *10*, 557.
- (10) Yamaoka, H.; Kambe, T.; Sato, T.; Ishida, Y.; Matsunami, M.; Eguchi, R.; Senba, Y.; Ohashi, H. *Physical Review B* **2011**, *84*, 161404.
- (11) Mahesh, M.; Murphy, J.; LeStrat, F.; Wessel, H. P. *Beilstein Journal of Organic Chemistry* **2009**, *5*, 2009.
- (12) Kuroboshi, M.; Tanaka, M.; Kishimoto, S.; Goto, K.; Mochizuki, M.; Tanaka, H. *Tetrahedron Letters* **2000**, *41*, 81.
- (13) Wang, H.-J.; Shi, J.; Fang, M.; Li, Z.; Guo, Q.-X. *Journal of Physical Organic Chemistry* **2010**, *23*, 75.
- (14) Taton, T. A.; Chen, P. *Angewandte Chemie-International Edition* **1996**, *35*, 1011.
- (15) Murphy, J. A.; Khan, T. A.; Zhou, S. Z.; Thomson, D. W.; Mahesh, M. *Angewandte Chemie-International Edition* **2005**, *44*, 1356.
- (16) Murphy, J. A.; Garnier, J.; Park, S. R.; Schoenebeck, F.; Zhou, S.-Z.; Turner, A. T. *Organic Letters* **2008**, *10*, 1227.
- (17) Murphy, J. A.; Zhou, S.-z.; Thomson, D. W.; Schoenebeck, F.; Mahesh, M.; Park, S. R.; Tuttle, T.; Berlouis, L. E. A. *Angewandte Chemie-International Edition* **2007**, *46*, 5178.
- (18) Sword, R.; Baldwin, L. A.; Murphy, J. A. *Organic & Biomolecular Chemistry* **2011**, *9*, 3560.
- (19) Garnier, J.; Kennedy, A. R.; Berlouis, L. E. A.; Turner, A. T.; Murphy, J. A. *Beilstein Journal of Organic Chemistry* **2010**, *6*, 4.
- (20) Jolly, P.; Fleary-Roberts, N.; O'Sullivan, S.; Doni, E.; Zhou, S. Z.; Murphy, J. A. *Organic & Biomolecular Chemistry* **2012**, *Advance Article*.
- (21) Cahard, E.; Schoenebeck, F.; Garnier, J.; Cutulic, S.; Zhou, S. Z.; Murphy, J. A. *Angewandte Chemie-International Edition* **2012**, *51*.
- (22) Schoenebeck, F.; Murphy, J.; Zhou, S. Z.; Uenoyama, Y.; Mielo, Y.; Tuttle, T. *Journal of the American Chemical Society* **2007**, *129*, 13368.
- (23) Cutulic, S.; Findlay, N.; Zhou, S. Z.; Chrystal, E. J. T.; Murphy, J. A. *Journal of Organic Chemistry* **2009**, *74*, 8713.
- (24) Hassan, J.; Sevignon, M.; Gozzi, G.; Schulz, E.; Lemaire, M. *Chemical Reviews* **2002**, *201*, 1359.
- (25) Fanta, P. E. *Chemical Reviews* **1946**, *38*, 139.
- (26) Fanta, P. E. *Chemical Reviews* **1964**, *64*, 613.
- (27) Yamamoto, T. *Chemistry Letters* **1988**, 153.

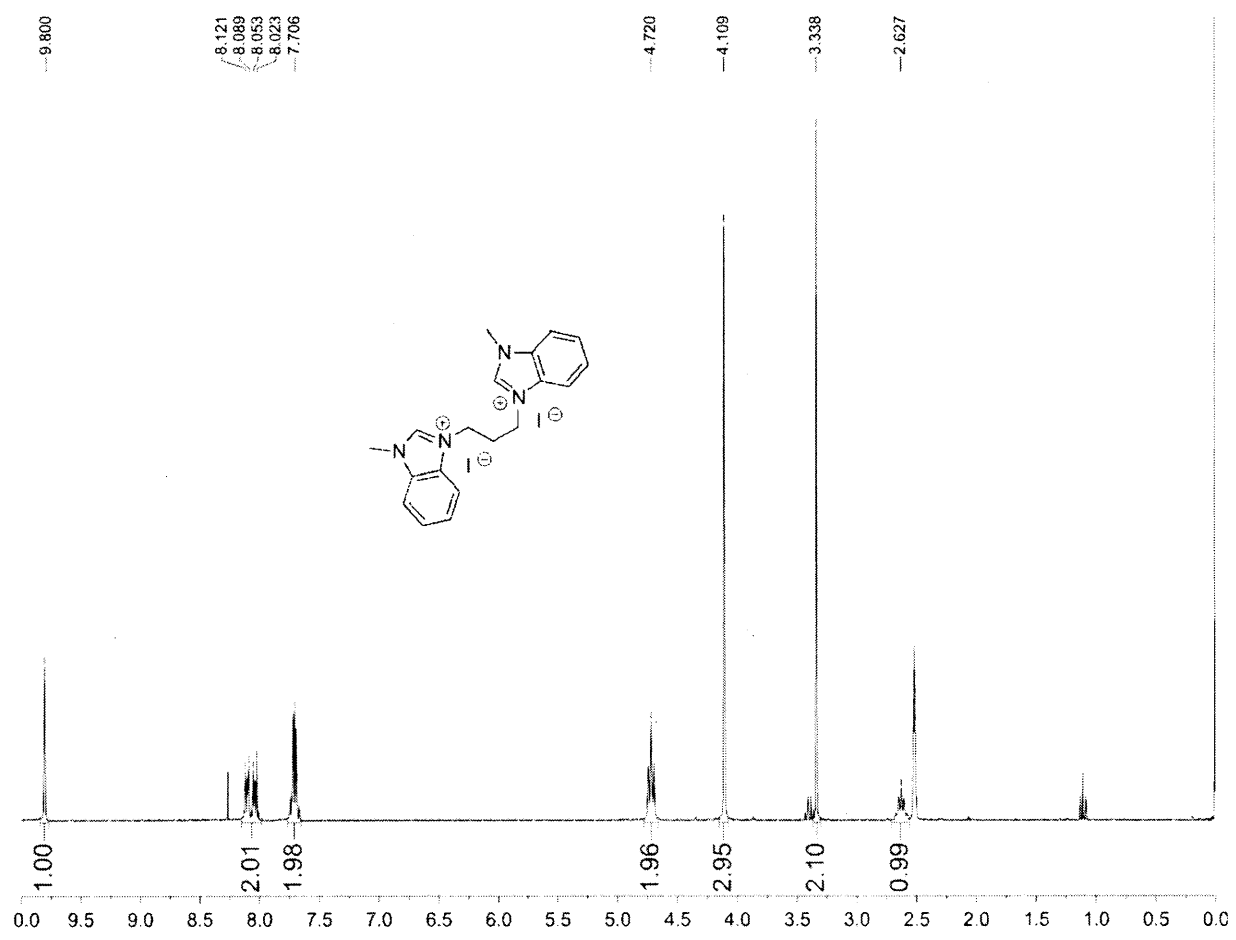
- (28) Yamamoto, T.; Morita, A.; Miyazaki, Y.; Maruyama, T.; Wakayama, H.; Zhou, Z. H.; Nakamura, Y.; Kanbara, T.; Sasaki, S.; Kubota, K. *Macromolecules* **1992**, *25*, 1214.
- (29) Yamamoto, T. *Bulletin of the Chemical Society of Japan* **1999**, *72*, 621.
- (30) Yamamoto, T.; Hayashida, N.; Maruyama, T. *Macromolecular Chemistry and Physics* **1997**, *198*, 341.
- (31) Yamamoto, T.; Maruyama, T.; Zhou, Z.-H.; Ito, T.; Fukuda, T.; Yoneda, Y.; Begum, F.; Ikeda, T.; Sasaki, S. *Journal of the American Chemical Society* **1994**, *116*, 4832.
- (32) Tsou, T. T.; Kochi, J. K. *Journal of the American Chemical Society* **1979**, *101*, 6319.
- (33) Ueda, M.; Ichikawa, F. *Macromolecules* **1990**, *23*, 926.
- (34) Colon, I.; Kelsey, D. *Journal of Organic Chemistry* **1986**, *51*, 2627.
- (35) Cahard, E.; Schoenebeck, F.; Garnier, J.; Cutulic, S. P. Y.; Zhou, S.; Murphy, J. A. *Angewandte Chemie International Edition* **2012**, *51*, 3673.
- (36) Yamamoto, T.; Kashiwazaki, A.; Kato, K. *Makromol. Chem.* **1989**, *190*, 1649.
- (37) Ledoux, G.; Guillois, O.; Porterat, D.; Reynaud, C.; Huisken, F.; Kohn, B.; Paillard, V. *Physical Review B* **2000**, *62*, 15942.
- (38) Takagi, H.; Ogawa, H.; Yamazaki, Y.; Ishizaki, A.; Nakagiri, T. *Applied Physics Letters* **1990**, *56*, 2379.
- (39) Cullis, A.; Canham, L.; Calcott, P. *Journal of Applied Physics* **1997**, *82*, 909.
- (40) Wu, H.; Zheng, G.; Liu, N.; Carney, T.; Yang, Y.; Cui, Y. *Nano Letters* **2012**, *12*, 904.
- (41) Neiner, D.; Chiu, H. W.; Kauzlarich, S. M. *Journal of the American Chemical Society* **2006**, *128*, 11016.
- (42) Werwa, E.; Seraphin, A. A.; Chiu, L. A.; Zhou, C. X.; Kolenbrander, K. D. *Applied Physics Letters* **1994**, *64*, 1821.
- (43) Bley, R. A.; Kauzlarich, S. M. *Journal of the American Chemical Society* **1996**, *118*, 12461.
- (44) Heath, J. R. *Science* **1992**, *258*, 1131.
- (45) Baldwin, R. K.; Pettigrew, K. A.; Ratai, E.; Augustine, M. P.; Kauzlarich, S. M. *Chemical Communications* **2002**, 1822.
- (46) Kravitz, K.; Kamyshny, A.; Gedanken, A.; Magdassi, S. *Journal of Solid State Chemistry* **2010**, *183*, 1442.
- (47) Verdoni, L.; Fink, M.; Mitchell, B. *Chemical Engineering Journal* **2011**, *172*, 591.
- (48) Mayeri, D.; Phillips, B. L.; Augustine, M. P.; Kauzlarich, S. M. *Chemistry of Materials* **2001**, *13*, 765.
- (49) Yang, C. S.; Bley, R. A.; Kauzlarich, S. M.; Lee, H. W. H.; Delgado, G. R. *Journal of the American Chemical Society* **1999**, *121*, 5191.
- (50) Rosso-Vasic, M.; Spruijt, E.; van Lagen, B.; de Cola, L.; Zuilhof, H. *Small* **2008**, *4*, 1835.
- (51) Lee, D.; Pietryga, J.; Robel, I.; Werder, D.; Schaller, R.; Klimov, V. *Journal of the American Chemical Society* **2009**, *131*, 3436.
- (52) Taylor, B. R.; Kauzlarich, S. M.; Delgado, G. R.; Lee, H. W. H. *Chemistry of Materials* **1999**, *11*, 2493.
- (53) Chiu, H. W.; Chervin, C.; Kauzlarich, S. M. *Chemistry of Materials* **2005**, *17*, 4858.
- (54) Prabakar, S.; Shiohara, A.; Hanada, S.; Fujioka, K.; Yamamoto, K.; Tilley, R. *Chemistry of Materials* **2010**, *22*, 482.
- (55) Menz, W.; Shekar, S.; Brownbridge, G.; Mosbach, S.; Kormer, R.; Peukert, W.; Kraft, M. *Journal of Aerosol Science* **2012**, *44*, 46.
- (56) Wong, H.; Li, X.; Swihart, M.; Broadbelt, L. *Journal of Physical Chemistry A* **2004**, *108*, 10122.
- (57) Owen, J. S.; Chan, E. M.; Liu, H.; Alivisatos, A. P. *Journal of the American Chemical Society* **2010**, *132*, 18206.
- (58) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Annual Review of Materials Science* **2000**, *30*, 545.

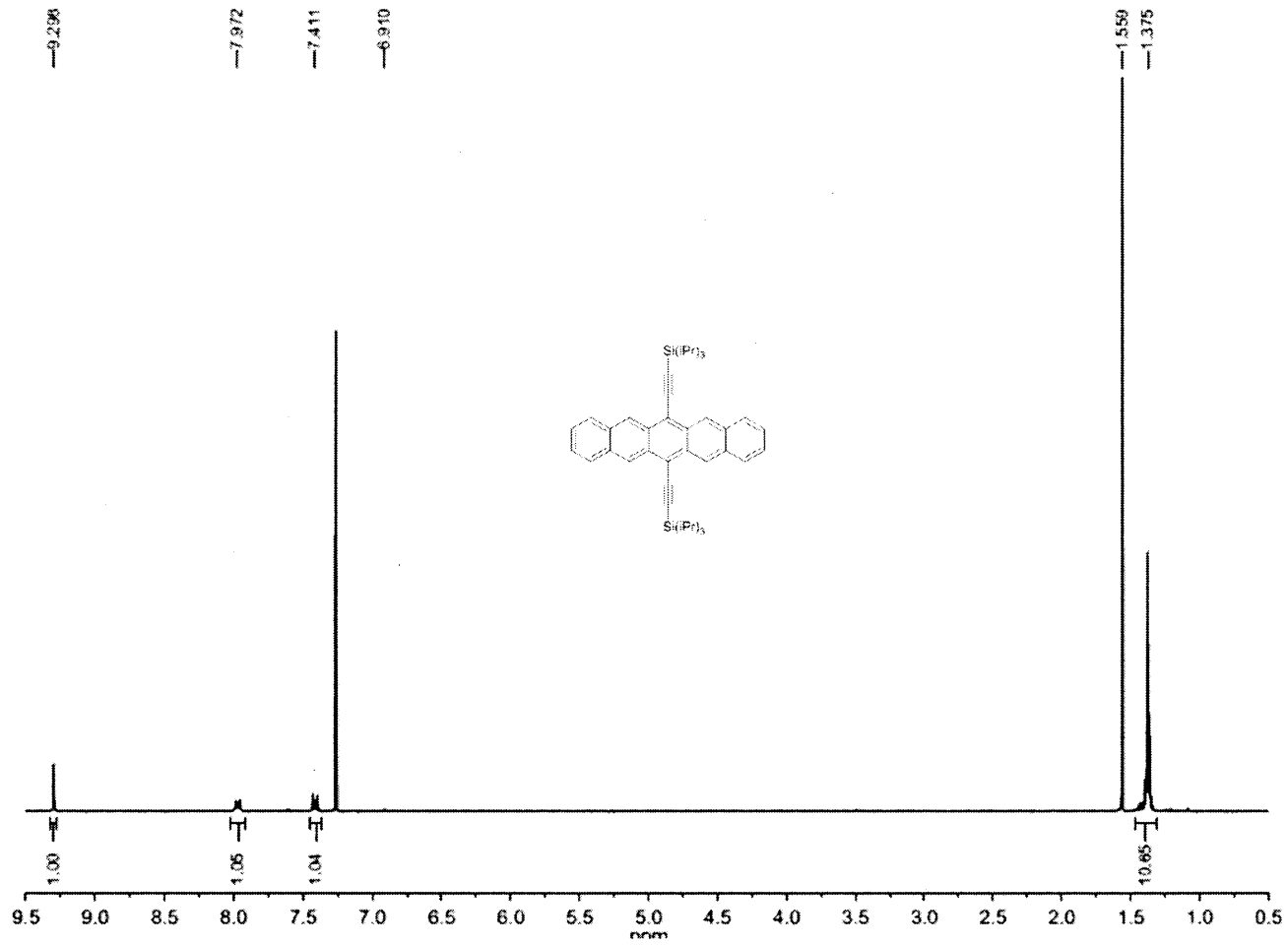
- (59) Gerbec, J.; Magana, D.; Washington, A.; Strouse, G. *Journal of the American Chemical Society* **2005**, *127*, 15791.
- (60) Agrawal, A.; Austin, A. *Journal of the Electrochemical Society* **1981**, *128*, 2292.
- (61) Gobet, J.; Tannenberger, H. *Journal of the Electrochemical Society* **1988**, *135*, 109.
- (62) Sugimoto *Advances in Colloid and Interface Science* **1987**, *28*, 65.
- (63) Piper, T. S.; Rochow, E. G. *Journal of the American Chemical Society* **1954**, *76*, 4318.
- (64) Katz, H.; Huang, J. *Annual Review of Materials Science* **2009**, *39*, 71.
- (65) Guo, S.; Kim, S. B.; Mohapatra, S. K.; Qi, Y.; Sajoto, T.; Kahn, A.; Marder, S. R.; Barlow, S. *Advanced Materials* **2012**, *24*, 699.
- (66) Lloyd, M.; Mayer, A.; Tayi, A.; Bowen, A.; Kasen, T.; Herman, D.; Mourey, D.; Anthony, J.; Malliaras, G. *Organic Electronics* **2006**, *7*, 243.
- (67) Payne, M.; Parkin, S.; Anthony, J.; Kuo, C.; Jackson, T. *Journal of the American Chemical Society* **2005**, *27*, 4986.
- (68) Sheraw, C.; Jackson, T.; Eaton, D.; Anthony, J. *Advanced Materials* **2003**, *15*, 2009.
- (69) Kim, Y.; Whitten, J.; Swager, T. *Journal of the American Chemical Society* **2005**, *127*, 12122.

Appendix A. Selected NMR Spectra









ANNA JOLENE MORK
Massachusetts Institute of Technology
Department of Chemistry
Cambridge, MA 02139

jmork@mit.edu
206.407.7364

EDUCATION:

S.M. Organic Chemistry, 2012

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA

Thesis: "Novel Reactions of a Neutral Organic Reductant: Reductive Coupling and Nanoparticle Synthesis"

B.A. Carleton College, 2010

Departments of Chemistry and Physics, Northfield, MN

Summa Cum Laude

Majors: Chemistry with Distinction, Physics with Distinction

American Chemical Society Certified Chemistry degree

Chemistry Thesis: "Organic Photovoltaics: The Chemistry of Carbon Based Solar Cells"

Physics Thesis: "Molecular Electronics: Exploring the Limits of Small"

RESEARCH EXPERIENCE:

Graduate Student in Organic Chemistry, MIT, Sept 2011-June 2012

- Advisor: Timothy M. Swager, Department of Chemistry, Massachusetts Institute of Technology
- Studied a novel fluorous semiconducting polymer (manuscript submitted), used organic super electron donor for new chemistries including nickel-catalyzed reductive coupling and silicon nanoparticle synthesis
- **Publication in preparation:** Takeda, Y., Andrew, T., Lobez, J., Mork, A., Swager, T. "An Air-Stable Low Bandgap N-Type Polymer Semiconductor Exhibiting Selective Solubility in Fluorous Solvents".

National Science Foundation Research Experience for Undergraduates (NSF-REU) Student for the Center on Polymer Interfaces and Macromolecular Assemblies (CPIMA), Summer 2009

- Advisor: Dr. Robert Waymouth, Chemistry Department, Stanford University
- Conducted research that involved the synthesis of a monomer, polymerization, and characterization of resultant cyclic and linear polymers with NMR, GPC, DSC, and rheological methods.

Kolenkow Reitz Funded Biology Student Intern, Fred Hutchinson Cancer Research Center, Winter 2008

- Advisor: Dr. Wenying Shou, Basic Sciences Division
- Developed method to image yeast cells growing in nutrient gradient using fluorescence microscopy in order to understand how cells respond to an inhomogeneous environment.

Carleton College Research Student in Chemistry, June 2008-November 2009

- Advisor: Dr. Joe Chihade, Chemistry Department, Carleton College
- Created novel hybrid tRNAs and examined their interaction with synthetase protein using radiolabeled sequencing gels and kinetics assays in a 5 student team working to understand tRNA-protein recognition.

Independent Study Research Student in Biology, January 2007-June 2008

- Advisor: Dr. Susan Singer, Biology Department, Carleton College
- Cloned and sequenced untranslated regions of the gene *PIM* from both DNA and mRNA transcripts from the species *Chamaecrista fasciculata* to understand gene regulation in floral development.

NSF-REU Student, University of Washington Engineered Biomaterials Program, Summer 2007

- Advisor: Dr. Gerald Pollack, Bioengineering Department, University of Washington
- Built chambers and developed imaging methods as part of a study in properties of water at air-water interface
- **Publication:** Mork, J. and Pollack, G. New Observations at the Air-Water Interface. *Journal of Undergraduate Research in Bioengineering*. 2008/2009.

High School Research Intern, June 2005-December 2006

- Advisor: Dr. Dina Mandoli, Biology Department, University of Washington
- Developed and used methods for confocal and epifluorescence microscopy imaging of marine alga *Acetabularia* to characterize cellular autofluorescence
- Presented results at Intel Science Talent Search (2006) and National Governors Association Conference (2006)

TEACHING & OUTREACH EXPERIENCE:

Head Teachers Assistant, Organic Chemistry I, Massachusetts Institute of Technology Fall 2011

- Coordinated other TAs and acted as liaison between > 120 students and the professor in addition to teaching my own section

Teachers Assistant, Organic Chemistry I, Massachusetts Institute of Technology Fall 2010

- Taught two recitation sections, graded homework and exams

Physics and Chemistry tutor, Laboratory Assistant, General Assistant, Carleton College, Fall 2007-June 2010

- Atomic and Nuclear Physics, Classical Mechanics, and Organic Chemistry tutor
- Analytical Chemistry and Introduction to Biology Laboratory TA
- Biology and Chemistry Laboratory Set-up assistant

Department of Chemistry Outreach Volunteer, Massachusetts Institute of Technology, Spring 2012

- Performed live demonstrations and explained chemical principles to ~100 sixth graders at Weston Middle School over course of two days

Department of Materials Science Middle School Outreach Volunteer, Massachusetts Institute of Technology, Summer 2011

- Taught middle school students principles of polymer science through live demonstrations and discussions

LEADERSHIP ROLES:

- *Swager Lab Safety Officer* (Jan 2011-June 2012)-Responsible for training new lab members, attending meetings, communicating with group, and enforcing policy
- *Swager Lab Subgroup Captain* (Jan 2011 – June 2012) – organized subgroup activities for 4-6 people

- *SYNFACTS Contributor* (Jan 2012 – June 2012) – found, discussed, and wrote articles for the “Materials and Unnatural Products” section of the Thieme monthly publication SYNFACTS

FELLOWSHIPS AND HONORS:

- *National Science Foundation Graduate Research Fellowship* (2010)
- *Chapin Fellowship* (2010) – MIT Graduate Fellowship
- *Phi Beta Kappa* (2010)
- *Goldwater Scholar* (2008)
- *Intel Science Talent Search Finalist* (2006) – National research competition, 40 finalists out of >2000 applicants
- *American Institute of Chemists Outstanding Student in Chemistry at Carleton College* (2010)
- *Frank E. Stinchfield Prize* (2010) – Awarded to an academically outstanding member of the senior class at Carleton College
- *Patricia V. Damon Scholar* (2009) – awarded to top 6 students out of class of 500
- *Carleton College Dean’s List* (2007, 2008, 2009) – top 10% of students
- *Robert C. Byrd Honors Scholar* (2006)
- *National Merit Scholar* (2006)

SOCIETIES:

- *Phi Beta Kappa*
- *Sigma Xi*