THE DESIGN AND SYNTHESIS OF POLYMERIC ASSEMBLIES FOR MATERIALS APPLICATIONS: CHEMOSENSING, LIQUID CRYSTAL ALIGNMENT AND BLOCK COPOLYMERS

by

Jason R. Cox

B.S. (with Distinction), Chemistry
Worcester Polytechnic Institute, 2005

M.S., Chemistry
Worcester Polytechnic Institute, 2009

Submitted to the Department of Chemistry
in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

at the

Massachusetts Institute of Technology

June 2012

© Massachusetts Institute of Technology, 2012. All rights reserved.

Signature of Author: ____________________________

Department of Chemistry
May 24, 2012

Certified by: ____________________________

Timothy M. Swager
Thesis Supervisor

Accepted by: ____________________________

Robert W. Field
Chairman, Departmental Committee on Graduate Studies
This doctoral thesis has been examined by a Committee of the Department of Chemistry as follows:

Professor Stephen L. Buchwald: ______________________________ Thesis Committee Chair

Professor Timothy M. Swager: ______________________________ Thesis Supervisor

Professor Gregory C. Fu: __________________________________ Department of Chemistry
THE DESIGN AND SYNTHESIS OF POLYMERIC ASSEMBLIES FOR MATERIALS APPLICATIONS: CHEMOSENSING, LIQUID CRYSTAL ALIGNMENT AND BLOCK COPOLYMERS

by

Jason R. Cox

Submitted to the Department of Chemistry on May 24, 2012 in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Chemistry.

ABSTRACT

Conjugated polymers are an indispensable class of materials that have advanced the development of optoelectronic device architectures; in part, due to their outstanding electronic and mechanical properties. This thesis explores the utility of rationally designed energy transfer cascades involving conjugated polymers that can be used in applications such as chemosensing and liquid crystal alignment.

We begin by describing the design and development of a new transduction mechanism for the detection of cyclic ketones – molecules that are found in plasticized explosives. We discuss the synthesis of a new reporter dye bearing a receptor for cyclic ketones that is capable of undergoing efficient energy transfer with conjugated polymers. We further describe the optimization of a thin-film sensor comprised of these two components as well as its performance and selectivity.

In the next chapter we describe the design and synthesis of two new polymers that are capable of undergoing the di-π-methane rearrangement. We begin by describing the synthesis and photochemistry of the polymers as well as a model compound. The polymers contain triplet sensitizers built into the polymer backbone thereby creating an energy transfer cascade that facilitates the di-π-methane rearrangement. These materials are then evaluated as liquid crystal alignment layers for optoelectronic applications.

In the final chapter, we describe the end-capping of cross-coupling polymerizations using the hydroarylation of norbornadiene. This reaction is shown to be an efficient approach to generating macroinitiators which can be further polymerized using ring opening metathesis polymerization. These end-capped materials can also be crosslinked into hybrid materials that show promise as thin-film sensors for volatile organic compounds.

Thesis Supervisor: Timothy M. Swager, Title: John D. MacArthur Professor of Chemistry
Dedicated to my girls-Maegan and Norah Faith –
for their unwavering support and understanding
# TABLE OF CONTENTS

Title Page 1
Signature Page 3
Abstract 5
Dedication 6
Table of Contents 7
List of Abbreviations 9
List of Figures 10
List of Schemes 15
List of Tables 17

**Chapter 1. Introduction to Electronic Energy Transfer in Conjugated Systems** 19

1.1 Introduction 20
1.2 Photophysical Processes of Organic Materials 20
1.3 Mechanisms for Electronic Energy Transfer – FRET and Electron Exchange 22
1.4 Photophysical Processes in Conjugated Polymers 24
1.5 Summary 27
1.6 References 27

**Chapter 2. Interrupted Energy Transfer: Highly Selective Detection of Cyclic Ketones in the Vapor Phase** 30

2.1 Introduction and Motivation for Ketone Detection 31
2.2 Proposed Transduction Mechanism 33
2.3 Design Considerations and Synthesis of Emissive Receptor 34
2.4 Optimization of Dye Loading, Energy Transfer Efficiency and Ketone Detection 37
2.5 Development of a Reversible, Field-portable Detection System Using Interrupted Energy Transfer 43
2.6 Conclusion 48
2.7 Experimental Section 48
2.8 References 60

**Chapter 3. Liquid Crystal Alignment Layers Using an Axis-Selective Di-π-Methane Rearrangement** 62

3.1 Introduction to Liquid Crystals 63
3.2 The Di-π-Methane Rearrangement 66
3.3 Approach and Design Considerations 67
3.4 Synthesis of Monomers, Model Compounds and Photoalignment Polymers 69
3.5 Photochemistry of Model Compound and Photoalignment Polymer 70
3.6 Alignment of Liquid Crystal Phases using P1. 75
3.7 Conclusion 78
3.8 Experimental Section 79
Chapter 4. Norbornadiene End-Capping of Cross-Coupling Polymerizations: A Facile Route to Triblock Polymers

4.1 Introduction
4.2 The Hydroarylation of Norbornadiene
4.3 Model Reactions
4.4 Polymer End-capping
4.5 Formation of Triblock Copolymers
4.6 Applications of Macroinitiators
4.7 Conclusion
4.8 Experimental Section
4.9 References

Curriculum Vitae
Acknowledgements
**LIST OF ABBREVIATIONS**

- **AFP** amplifying fluorescent polymer
- **CP** conjugated polymer
- **DART** direct analysis in real time
- **DMF** dimethylformamide
- **DMSO** dimethyl sulfoxide
- **DNT** 2,4-dinitrotoluene
- **EET** electronic energy transfer
- **$E_T$** triplet energy
- **FRET** Förster resonance energy transfer
- **GRIM** Grignard metathesis reaction
- **HOMO** highest occupied molecular orbital
- **HRMS** high-resolution mass spectra
- **IC** internal conversion
- **IMS** ion mobility spectrometry
- **ISC** intersystem crossing
- **$k_{ET}$** rate of energy transfer
- **LCD** liquid crystal display
- **LCM** liquid crystal material
- **LOD** limit of detection
- **LUMO** lowest unoccupied molecular orbital
- **M$_n$** number-average molecular weight
- **MS** mass spectroscopy
- **NIR** near infrared
- **NMR** nuclear magnetic resonance
- **OLED** organic light emitting diode
- **OPV** organic photovoltaics
- **PDI** polydispersity index
- **PET** photoinduced electron transfer
- **PETN** pentaerythritol tetranitrate
- **POM** polarized optical microscopy
- **QCM** quartz crystal microbalance
- **RDX** 1,3,5-trinitro-1,3,5-triazacyclohexane
- **ROMP** ring-opening metathesis
- **SEC** size-exclusion chromatography
- **$T_g$** glass transition temperature
- **THF** tetrahydrofuran
- **THz-TDS** terahertz time domain spectroscopy
- **TNT** 2,4,6-trinitrotoluene
- **UV** ultraviolet
- **VOC** volatile organic compound
LIST OF FIGURES FROM MAIN TEXT

Figure 1.1 Jablonski diagram depicting the photophysical pathways available to an organic molecule after excitation with a photon. Photochemical transformations have been omitted; however, in many cases reactivity initiated from the excited state is the dominant pathway.

Figure 1.2 Schematic depiction of electronic energy transfer between a donor and acceptor. Both modes of non-trivial EET are described – FRET (left) and exchange transfer (right).

Figure 1.3 Schematic depiction of the band gap (E_g) of extended conjugated systems (left) and the relationship between semiconductor band structure and conjugated polymers (right).

Figure 1.4 Schematic depiction of conformational effects on band gap structure and photophysical properties of conjugated polymers. At the interface of the light blue and red subunits is a 90° twist in the polymer chain, this generates two separate chromophoric subunits.

Figure 1.5 Schematic depiction of energy migration to an emissive defect in a CP thin film.

Figure 2.1. Schematic depiction of the proposed transduction mechanism (blue barbed structure = AFP, red structure = NIR-emitting receptor, green structure = cyclohexanone).

Figure 2.2. Absorbance (solid line) and emission (line with squares) spectra of PPE1 (blue) and SQ1 (red). Spectra were taken in CHCl3, using the absorbance maximum for each component as the excitation wavelength for emission collection.
**Figure 2.3.** Plot expressing the relationship between dye-loading (wt%) and energy transfer efficiency. Thin-films containing both components were excited in a spectral region where only PPE1 absorbs (400 nm) and the ratio of SQ1:PPE1 was compared.

**Figure 2.4.** Thin-film fluorescence spectra before (blue) and after (red) exposure to the saturated vapor of acetone (top) and cyclohexanone (bottom) for 30 s ($\lambda_{ex} = 400$ nm).

**Figure 2.5.** Change in thin-film fluorescence intensity of polymer (blue) and squaraine dye (red) after 30 s exposure to the saturated vapor of the indicated ketone ($\lambda_{ex} = 400$ nm) (mean of three different films).

**Figure 2.6.** Mean frequency shift of a QCM crystal coated with a thin-film of the sensor formulation after 30 s exposure to the saturated vapor of the indicated ketone (mean of three sequential measurements).

**Figure 2.7.** Thermal ellipsoid representation of the X-ray structure of SQ1 (1:1 cocrystal with DMF). The displacement ellipsoids are drawn at the 50% probability level, hydrogen atoms are represented by a sphere of arbitrary radius (gray = carbon, green = fluorine, blue = nitrogen, red = oxygen, light blue = hydrogen, black dashed lines = hydrogen bonds).

**Figure 2.8.** Thin-film fluorescence spectra taken in the presence of the saturated vapor of toluene. The black trace represents the first collected spectrum with red and green traces following at intervals of approximately 30 s ($\lambda_{ex} = 400$ nm).

**Figure 2.9.** Sequential fluorescence spectra of sensor formulation. The film is first exposed to the saturated vapor of cyclohexanone until the
emission of SQ1 is suppressed (top, left). The film is then sparged with a stream of N₂ and a subsequent spectrum recorded (top, middle). The same film is heated to 120 °C for 10 minutes and an additional spectrum recorded (top, right). The resulting film is then re-exposed to the saturated vapor of cyclohexanone (bottom, middle) (λex = 400 nm).

**Figure 2.10.** Uncorrected response of FIDO® to the saturated vapor of acetone (first three reversible peaks) followed by saturated cyclohexanone vapor (four consecutive exposures). Note the ‘staircase’ structure of the data indicating that it is an irreversible response.

**Figure 2.11.** Uncorrected response of FIDO® to the saturated vapor of cyclohexanone using a plasticized film.

**Figure 2.12.** Calibration curve showing the response of the sensor system to different concentrations of cyclohexanone vapor (exponential fit). Inset figure is an expansion of the 0 – 200 ppm concentration range (linear fit).

**Figure 2.13.** Uncorrected response of the FIDO® instrument to the headspace of C-4 explosive.

**Figure 3.1.** Schematic depictions of the structure of liquid crystal mesogens (left) and the nematic phase (right). Small inset (lower left) displays the molecular structure of 4-cyano-4’pentylbiphenyl (5CB).

**Figure 3.2.** Schematic depictions of unaligned (left) and aligned (right) nematic liquid crystalline phases. The rod-like structure represents a liquid crystal mesogen such as 5CB. The black arrow on the right side represents the molecular director.
**Figure 3.3.** Various photochemical transformations that are applied in photoalignment mechanisms.

**Figure 3.4.** Overall transformation and mechanism of the di-π-methane rearrangement (top). Implications of the multiplicity of the di-π-methane rearrangement (bottom).

**Figure 3.5.** Molecular structure of P1 and the resulting photoproduct of the di-π-methane rearrangement.

**Figure 3.6.** Schematic depiction of the proposed photoalignment mechanism using the di-π-methane rearrangement. Red (green) structures represent P1 before (after) photolysis. Blue structures represent LC molecules.

**Figure 3.7.** Stacked ¹H NMR spectra obtained during photolysis of 5.

**Figure 3.8.** Stacked ¹H NMR spectra obtained during photolysis of P1.

**Figure 3.9.** Stacked ¹H NMR spectra obtained during photolysis of P2.

**Figure 3.10.** Fluorescence spectra of model compound 5 (left), P1 and P2 (right). Spectra were taken in dichloromethane solution using $\lambda_{ex} = 300$ nm with O.D. of 0.1 for all components.

**Figure 3.11.** Schematic depiction of LC cell fabrication using photoalignment polymer P2.

**Figure 3.12.** Optical micrographs of LC cells where the photopolymer P1 has not been irradiated (top) or has been irradiated with polarized light (bottom).
**Figure 3.13.** Optical micrographs of LC cells where the photopolymer P1 has been irradiated through a polarizer and striped photomask. Irradiation was carried out for 10 minutes in air (LC = MLC 6884). The alternating stripes correspond to features of 100 µm. Black arrows correspond to the orientation of the polarizers.

**Figure 4.1.** Crude $^2$H NMR spectrum (bottom) (CH$_2$Cl$_2$) of the indicated transformation (top). Spectrum was taken after the removal of volatiles from the reaction mixture.

**Figure 4.2.** $^1$H NMR spectrum of P2. Included is the molecular structure of P2 with the appropriate protons highlighted. The inset is a magnified portion of the spectrum.

**Figure 4.3.** (a) Synthesis of PNB-$b$-P1-$b$-PNB. (b) THF SEC (UV detection 450 nm) traces of P1 (black) and PNB-$b$-P1-$b$-PNB triblock copolymer (blue).

**Figure 4.4.** (a) Optical micrographs of PNB cross-linked with P1 in unstretched (left) and stretched (right) states. (b) Optical micrographs with 365 nm excitation light of the same material in unstretched (left) and stretched (right) states.

**Figure 4.5.** (a) Photoluminescence spectra of PNB cross-linked with P2 in water (red) and 1% THF/water (v:v) (black). (b) Optical micrograph (UV excitation at 365 nm) showing PNB cross-linked with P2 in water (right) and 1% THF/water (v:v; left). (c) Photoluminescence intensity decay (monitored at 450 nm) of the same film after exposure to the saturated vapor of THF.
LIST OF SCHEMES FROM MAIN TEXT

Scheme 2.1. Synthetic route to emissive receptor SQ1. 35

Scheme 2.2. Molecular structure of PPE1. 36

Scheme 3.1. Synthesis of model compound 5. 69

Scheme 3.2. Synthesis of comonomers 6 and 7. 70

Scheme 3.3. Synthesis of photoalignment polymers P1 and P2. 70

Scheme 3.4. Regiochemical possibilities during photolysis of model compound 5. 72

Scheme 4.1. Molecular structures of common conjugated polymers (top). Palladium catalyzed reactions that are employed in the synthesis of conjugated materials (bottom). 103

Scheme 4.2. Post-polymerization end-capping of PT using the Vilsmeier reaction. 104

Scheme 4.3. Proposed catalytic cycle for the hydroarylation reaction (top). Ring strain energies associated with norbornane derivatives (bottom). 105

Scheme 4.4. Conditions and yields for the formation of model compounds MC1, MC2, and MC3. 106

Scheme 4.5. Conditions used for the end-capping of cross-coupling polymerizations (top) and the resulting end-capped polymers synthesized 108
in this work (bottom).

**Scheme 4.6.** Conditions and monomers used for the formation of triblock copolymers.
LIST OF TABLES FROM MAIN TEXT

Table 2.1. Names, molecular structures and equilibrium vapor pressures of explosives and related compounds.

Table 4.1. Selected results of triblock copolymerizations.
Chapter 1

Introduction to Electronic Energy Transfer in Conjugated Systems
1.1 Introduction

In 1953, Hermann Staudinger received the Nobel Prize for his role in the development of macromolecular chemistry,\(^1\) a field that was surprisingly underdeveloped despite the ubiquity of polymers in naturally occurring systems. During his lecture he stated, "I sincerely hope that this great distinction will be the means whereby macromolecular chemistry will undergo further fruitful development."\(^2\) This wish was undoubtedly fulfilled as exemplified by the impact of polymeric materials in every aspect of human life.\(^3\) A second Nobel Prize was awarded to Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa in 2000 for their pioneering work with conductive (conjugated) polymers whereby a new sub-field of macromolecular chemistry was born.\(^4\) Conjugated polymers; that is, polymeric materials that contain alternating single and multiple bonds, occupy a venerable role in device architectures as they combine the optoelectronic properties of semiconductors with the mechanical properties of organic polymers.\(^5\) These materials are readily synthesized using standard carbon-carbon bond forming techniques and are typically soluble materials that can be processed into thin-films over large areas.\(^6\) Initially, these materials found utility in devices such as organic light emitting diodes (OLEDs) due to their excellent luminescent properties and have since matured into materials for organic photovoltaics (OPV) and sensing applications.\(^7\) The latter two applications take advantage of the electronic and photophysical properties of conjugated polymers, namely exciton migration, which will be described in the following sections.

1.2 Photophysical Processes of Organic Materials

In order to fully understand the photophysical properties of conjugated polymers, it is first necessary to understand the various transitions that are available to organic molecules when they interact with electromagnetic radiation. The different transitions are best explained with the
aid of a Jablonski diagram (Figure 1.1). The generation of an excited state is a direct result of the interaction of electrons in the highest occupied molecular orbital (HOMO) with the oscillating electric and magnetic fields of a photon. The oscillating electric field couples with the electron and if certain energetic (band gap) and geometric (field is oscillating in the same direction as the transition dipole moment) considerations are met, the electron will be promoted to the lowest unoccupied molecular orbital (LUMO) or higher unoccupied orbitals.

Figure 1.1 Jablonski diagram depicting the photophysical pathways available to an organic molecule after excitation with a photon. Photochemical transformations have been omitted; however, in many cases reactivity initiated from the excited state is the dominant pathway.

After excitation, the molecule will rapidly relax to the lowest vibrational level of the first excited singlet state in a process known as internal conversion (IC). From here, a number of pathways are possible including fluorescence, non-radiative decay, intersystem crossing (ISC) and phosphorescence. An additional deactivation process is called electronic energy transfer (EET) whereby the excited state of a molecule (donor) transfers its energy non-radiatively to a
nearby molecule (acceptor) (Figure 1.2). There are two possible mechanisms for energy transfer – Förster resonance energy transfer (FRET) and Dexter energy transfer.

\[ E_{\text{FRET}}(D) \rightarrow E_{\text{A}}(A) \]

\[ E_{\text{Dexter}}(D) \rightarrow E_{\text{A}}(A) \]

**Figure 1.2** Schematic depiction of electronic energy transfer between a donor and acceptor. Both modes of non-trivial EET are described – FRET (left) and exchange transfer (right).

### 1.3 Mechanisms for Electronic Energy Transfer – FRET and Electron Exchange

The excited state of an organic chromophore is itself an oscillating dipole; as such, it is capable of inducing a resonant interaction with nearby molecules whereby the excitation energy is transferred from the donor molecule to the acceptor molecule (Figure 1.2 left). This type of energy transfer is known as FRET and is the dominant form of energy transfer between organic compounds. It is not to be confused with trivial modes of energy transfer whereby the emission of a photon from a donor chromophore is reabsorbed by an acceptor molecule followed by emission. In the case of FRET, the transfer process results in a diminished lifetime of the donor which would not be observed in the trivial case. The rate of energy transfer \( k_{\text{ET}} \) is described by Equations 1-3 where \( \tau_D \) is the lifetime of the donor, \( R_0 \) is the Förster radius, \( R \) is the distance between donor and acceptor molecules, \( \kappa^2 \) is an orientation factor, \( F_{D}(\lambda) \) describes the
normalized fluorescence intensity of the donor, \( \varepsilon_A(\lambda) \) represents the molar extinction coefficient of the acceptor, and \( J \) is the spectral overlap integral.

\[
k_{ET} = \frac{1}{\tau_D} \cdot \frac{R_0}{R}^6 \quad (1)
\]

\[
R_0^6 = \frac{0.001n10}{128\pi^2N_A} \frac{k^2Q_D}{\pi^4} J \quad (2)
\]

\[
J = \int_0^\infty F_D \lambda \varepsilon_A \lambda^4 d\lambda \quad (3)
\]

These equations describe a system in which the efficiency of EET is directly proportional to the spectral overlap integral and inversely proportional to \( R^6 \). These predictable dependencies have made FRET an indispensable analytical tool for measuring sub-nanometer intermolecular separations.

The exchange, or Dexter mechanism, describes a situation where the donor and acceptor molecules formally exchange electrons (Figure 1.2 right). This implies that the two components exist at intermolecular separations small enough to permit overlap of the involved orbitals. The rate constant for the exchange mechanism is described by Equation 4 where \( K \) describes specific orbital interactions, \( J' \) is the normalized spectral overlap integral, \( R \) is the intermolecular separation between donor and acceptor, and \( L \) is the sum of the van der Waals radii.

\[
k_{ET} = KJ'\exp\left(-\frac{2R}{L}\right) \quad (4)
\]

Implicit in this description is the steep dependency of \( k_{ET} \) on the intermolecular separation of donor and acceptor. The exponential drop-off in exchange efficiency with increasing separation results in a process that can only occur over distances of 1 or 2 molecular diameters – a point that is central to the work described here.

It is worth summarizing the key differences between these two forms of EET: (i) the efficiency of energy transfer is dependent on the oscillator strength for the transitions \( D^* \rightarrow D \) and
$A \rightarrow A^*$ in the case of Förster energy transfer unlike the exchange mechanism, (ii) the distance dependence for Dexter energy transfer ($\exp(-2R/L)$) is much stronger than for FRET ($1/R^6$) and (iii) only for exchange interactions are triplet states allowed to transfer. The first difference highlights an important distinction between the two mechanisms – the spectral overlap integral for the exchange mechanism is not dependent on the intensity of the overlapping transitions. Conversely, the Förster mechanism is strongly dependent on the oscillator strength of the $A \rightarrow A^*$ transition.

1.4 Photophysical Processes in Conjugated Polymers

In many ways, the processes that have been described for small organic molecules thus far also pertain to larger systems such as conjugated polymers (CPs). Events such as absorption/emission of a photon, internal conversion, intersystem crossing and energy transfer have all been observed with CPs. However, there are some subtle differences between these two classes of materials that are a result of the extended conjugation in such systems.

As shown in Figure 1.3, the sequential addition of unsaturated centers results in a narrowing of the band gap ($E_g$) until the electronic system more closely resembles an inorganic semiconductor possessing valence and conduction bands. Absorption of a photon generates a strongly bound electron-hole pair (exciton) that is capable of diffusing along the polymer backbone as well as hopping from one polymer chain to another. The diffusion length of an exciton, ranging from 5 to 14 nm, means that a single excitation can sample many different polymer subunits prior to a photophysical process taking place. In Figure 1.3 (right) we have illustrated a process where the exciton is quenched by two sequential electron transfer events with an analyte – a process known as photoinduced electron transfer (PET). It is important to note that the diffuse nature of the exciton increases sensory gain as a single analyte molecule is
capable of quenching an entire polymer chain. The Swager group has devised a number of sensing applications that exploit this characteristic including a system that boasts the highest sensitivity for the detection of trinitrotoluene (TNT) vapor.

Figure 1.3 Schematic depiction of the band gap ($E_g$) of extended conjugated systems (left) and the relationship between semiconductor band structure and conjugated polymers (right).

In addition, the Swager group has shown that exciton migration is greatly increased when the polymer molecules are aggregated. The condensed nature of an aggregated system gives rise to decreased interpolymer separations thereby facilitating multidimensional exciton transport. Figure 1.3 depicts an idealized situation that assumes the polymer subunits are coplanar thus enforcing the band gap perturbations that result from extended conjugation. In practice, polymer molecules are typically coiled or aggregated to some degree, especially high molecular weight materials. The result is that there is a collection of chromophores within each polymer strand that differ in effective conjugation length and hence band gap. This point is illustrated schematically in Figure 1.4.
Figure 1.4 Schematic depiction of conformational effects on band gap structure and photophysical properties of conjugated polymers. At the interface of the light blue and red subunits is a 90° twist in the polymer chain, this generates two separate chromophoric subunits.

As shown in Figure 1.4, initial excitation of a smaller (larger band gap) conjugated subunit generates an exciton that rapidly diffuses to the lower energy (smaller band gap) subunit and then radiatively decays to the ground state. This exemplifies why conjugated polymers often exhibit broad structureless absorbance spectra yet also exhibit well structured emission spectra. This seemingly paradoxical situation arises from the fact that a coiled CP chain possesses a variety of different chromophoric subunits – each with a different band gap that can absorb a photon – while the emission spectra is controlled by exciton diffusion to the smallest band gap subunit in the chain.

Thus far we have described situations where an analyte may quench CP emission as well as how excitons will diffuse to and emit from small band gap subunits; however, we have not described the situation where a small band gap analyte acts as an emissive quencher. If we consider the fact that excitons readily diffuse to small band gap defects in CP chains then we would expect that amplified emission from an emissive quencher doped into a CP film should also occur. Indeed, the Swager group has shown that covalently attached emissive defects will emit strongly when the CP is excited as well as films that have been doped with small molecule dyes. This work showed that the CP unit can behave as a light-harvesting antennae which
funnels excitons to the small band gap traps and actually amplifies their emission via energy transfer (Figure 1.5).

![Diagram of exciton migration and energy transfer](image)

**Figure 1.5** Schematic depiction of energy migration to an emissive defect in a CP thin film.

### 1.5 Summary

In summary, the photophysical processes available to the excited states of organic molecules and conjugated polymers have been described. Behavioral distinctions between the two classes of materials are governed by exciton diffusion and energy transfer processes. This brief introduction highlights the essential characteristics of electronic energy transfer in order to be described in subsequent chapters including the detection of ketone molecules in the vapor phase (Chapter 2), alignment of liquid crystalline materials (Chapter 3) and the photophysical properties of crosslinked CP materials (Chapter 4).

### 1.6 References

Amsterdam, 1964.

(3) Polymers exhibit a wide range of properties that can be tuned for a given application ranging from high-strength materials to biopolymers. From elastomers to polyamides and conjugated polymers, polymer science has advanced nearly every scientific discipline.


(9) Lakowicz, J. R. Principles of Fluorescence Spectroscopy, 2nd ed.; Kluwer Academic/Plenum:


(13) These photophysical processes are observed in a variety of applications, the reader is directed to Refs 5, 6 and 7 for more information.


Chapter 2

Interrupted Energy Transfer: Highly Selective Detection of Cyclic Ketones in the Vapor Phase

Adapted and reproduced in part with permission from:
2.1 Introduction and Motivation for Ketone Detection

Plasticized explosives such as Composition C-4 and Semtex have drawn considerable interest from government agencies due to the worldwide increase in terrorism related events. These materials are typically comprised of approximately 90% energetic compounds and 10% binders/plasticizers. The molecular structures and relevant physical properties of some explosives and related materials are depicted in Table 2.1. In the case of C-4, the energetic material is 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX). This compound exhibits an extremely low equilibrium vapor pressure – approximately 6 ppt at 25 °C. Approaches to the detection of RDX rely upon mass spectroscopic (MS) techniques, ion mobility spectrometry (IMS), terahertz time domain spectroscopy (THz-TDS) and various colorimetric and fluorescence techniques.

Table 2.1. Names, molecular structures and equilibrium vapor pressures of explosives and related compounds.

<table>
<thead>
<tr>
<th>Name</th>
<th>Molecular structure</th>
<th>Equilibrium vapor pressure at 20 °C (Torr)</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3,5-trinitro-1,3,5-triazacyclohexane (RDX)</td>
<td><img src="image" alt="Molecular structure" /></td>
<td>4.1 x 10^{-9}</td>
<td>Energetic component of C-4</td>
</tr>
<tr>
<td>2,4,6-trinitrotoluene (TNT)</td>
<td><img src="image" alt="Molecular structure" /></td>
<td>1.1 x 10^{-6}</td>
<td>High explosive</td>
</tr>
<tr>
<td>Pentaerythritol tetranitrate (PETN)</td>
<td><img src="image" alt="Molecular structure" /></td>
<td>3.8 x 10^{-10}</td>
<td>Energetic component of Semtex</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td><img src="image" alt="Molecular structure" /></td>
<td>5 (25 °C)</td>
<td>Solvent used in the recrystallization of RDX</td>
</tr>
</tbody>
</table>
Each of these approaches carries with it a unique collection of advantages and limitations. Mass spectroscopic techniques, while providing excellent sensitivity and exquisite selectivity, requires the use of equipment that is not amenable to field-portable settings such as military operations. Canines have also proven effective in this regard; however, they require special handling and cannot be employed for long periods of time without significant rest periods. The Swager group recently reported an enzyme inspired approach to RDX detection using acridine-based hydride donors.\textsuperscript{7b}

As outlined previously, amplifying fluorescent polymers (AFPs) are excellent materials for chemosensing applications including the detection of trace energetic materials such as TNT.\textsuperscript{8} Despite the success of PET-based transduction mechanisms using AFPs in nitroaromatics detection, RDX cannot easily be detected. This is primarily due to the extremely low equilibrium vapor pressure and unfavorable reduction potential of this compound. In order to create a favorable electron transfer event for PET, a larger band gap AFP is required.\textsuperscript{7a} The increase in driving force for electron transfer also brings with it a loss in selectivity as many other analytes could potentially quench the AFP.

Plasticized explosives contain a percentage of binders and plasticizers that increase the stability of the energetic component while simultaneously enhancing favorable mechanical properties such as malleability. A recent study using solid-phase microextraction (SPME) techniques coupled with IMS reported the identities of the various additives in different samples of C-4.\textsuperscript{9} The two most prevalent compounds present in the air above these samples are cyclohexanone and 2-ethylhexanol. Cyclohexanone, whose molecular structure is depicted in Table 2.1, is used as a solvent in the production of RDX.\textsuperscript{4} Residual quantities of this compound survive the binding process and are present in C-4 samples in varying quantities. The branched
alcohol, 2-ethylhexanol, is used in the synthesis of a diester phthalate plasticizer known as DEHP and also finds its way into commercial C-4 samples. These two compounds exhibit much larger equilibrium vapor pressures than RDX and are speculated to be the compounds that trained canines actually smell when identifying C-4.\textsuperscript{10} Cyclohexanone is less prevalent than 2-ethylhexanol in non-explosives materials (present in plastic bottles/bags, glue etc.) thus limiting the number of false positives if using these components for an early warning detection system. These points served as inspiration for the development of an AFP-based sensor to detect cyclic ketones such as cyclohexanone in the context of plasticized explosives detection.

2.2 Proposed Transduction Mechanism

The detection of simple ketones using an AFP-based transduction mechanism has not been described in the literature. This is due, in part, to the lack of a favorable PET event between conjugated organic materials and unconjugated ketone moieties. This called for the formulation of an alternative transduction mechanism that does not rely on any electron transfer events involving the ketone. As described in previous sections, the efficiency of Dexter energy transfer is governed largely by the extent of orbital overlap between the donor and acceptor.\textsuperscript{11} The proposed transduction mechanism, outlined in Figure 2.1, is predicated on interrupted Dexter energy transfer. An AFP thin-film is used as a light-harvesting unit that can amplify the luminescence of a near-infrared (NIR) emitting receptor through the synergy of exciton migration and Dexter energy transfer. In the absence of any analytes, the selective excitation of the AFP component should yield fluorescence from both the AFP and the NIR fluorophore. In the presence of an analyte that is capable of interacting with the receptor, the interaction is thought to disturb the distance between the receptor and the AFP backbone thereby perturbing the efficiency of energy transfer and signaling the presence of the analyte.
Figure 2.1. Schematic depiction of the proposed transduction mechanism (blue barbed structure = AFP, red structure = NIR-emitting receptor, green structure = cyclohexanone).

2.3 Design Considerations and Synthesis of Emissive Receptor

Realization of the aforementioned transduction mechanism requires the exclusion of any EET via the FRET pathway due to the fact that FRET can operate over very large distances. Condensed phases such as thin-films yield exceedingly small intermolecular distances; and as such, favor both the FRET and Dexter pathways. In order to favor the exchange mechanism, a chromophore with an absorbance spectrum that does not overlap with the emission spectrum of an AFP was necessary. Squaraine dyes are highly luminescent materials with narrow bandwidth absorbance spectra typically in the 650 - 700 nm range. Synthetic access to substituted squaraines is facile, making this class of molecules an excellent choice for interrupted energy transfer. Our proposed sensing scheme also requires that the squaraine dye possess a molecular recognition unit for the ketone moiety of cyclohexanone. Bifurcated hydrogen bond donors such as diaryl ureas and thioureas have been widely used as activators of carbonyl functionalities and serve as inspiration for our molecular recognition unit.
Our synthetic route towards SQ1 is displayed in Scheme 2.1. The synthesis begins with the formation of an unsymmetrical diaryl urea via the reaction of a phenylenediamine and 3,5-bis(trifluoromethyl)phenyl isocyanate. This compound underwent an electrophilic aromatic substitution/condensation reaction with squaric acid to afford SQ1 in good yield.

Scheme 2.1. Synthetic route to emissive receptor SQ1.

The resulting emissive receptor contains two strong intramolecular hydrogen bonds between the urea amide protons and the two oxygen atoms of the central four-membered ring. These interactions rigidify the dye scaffold thereby red shifting the absorbance spectrum (relative to unfunctionalized squaraine dyes) and also increasing the quantum yield of luminescence by removing rotational modes that could promote internal conversion. We chose to use pentiptycene containing PPE1 (structure displayed in Scheme 2.2) as the light harvesting unit for two reasons: (1) the pentiptycene unit reduces interpolymer π-π interactions that could compete as low energy trap sites and (2) the pentiptycene units increase the porosity of the polymer film thereby facilitating analyte diffusion into the film and also providing ample space for SQ1 to interact with the polymer backbone.15
Scheme 2.2. Molecular structure of PPE1.

The photophysical properties of SQ1 and PPE1 are displayed in Figure 2.2. The emission spectrum of PPE1 exhibits relatively little spectral overlap with the absorbance spectrum of SQ1 – an ideal scenario for the promotion of Dexter energy transfer. However, SQ1 does exhibit a small absorbance at approximately 415 nm which is due to a $S_0 \rightarrow S_n$ transition as the $S_0 \rightarrow S_2$ transition is symmetry forbidden.\(^\text{16}\) This low oscillator strength transition displays finite spectral overlap with the emission maximum of PPE1 and is believed to contribute to the energy transfer cascade. As mention previously, the efficiency of Dexter energy transfer is not dependent on the oscillator strength of the acceptor transition whereas FRET is strongly dependent on this variable; and as such, points towards Dexter energy transfer as the dominant mechanism.\(^\text{17}\)
2.4 Optimization of Dye Loading, Energy Transfer Efficiency and Ketone Detection

The efficiency of energy transfer was found to vary according to the dye-loading of SQ1 within thin-films of PPE1. Figure 2.3 displays the results of this study. Surprisingly, dye-loadings greater than approximately 0.5 wt% resulted in a decrease in the efficiency of energy transfer. We hypothesize that this seemingly counter intuitive result is due to the insolubility of SQ1 in films of PPE1 thereby causing phase separation of the two components and a net loss of energy transfer. Indeed, SQ1 was sparingly soluble in all organic solvents tested including chloroform, dichloromethane, DMSO and ethanol. In addition, dye loadings less than 0.5 wt% also resulted in decreased energy transfer. Given that excitons created in AFP thin-films have a finite migration sphere, and that the energy transfer efficiency drops off precipitously at dye loadings below 0.5 wt%, we hypothesize that a dye loading of 0.5 wt% results in a film where the average dye-dye distance is less than the radius of the exciton sphere.

Once the optimum dye-loading was established, the films were exposed to the saturated vapor of both cyclohexanone and acetone to ascertain whether the thin-films would elicit a
response. Interestingly, exposure to acetone vapor yielded no change in the emission spectra whereas cyclohexanone caused a dramatic shift in the ratio of emission of the two components as shown in Figure 2.4.

![Figure 2.3](image)

**Figure 2.3.** Plot expressing the relationship between dye-loading (wt%) and energy transfer efficiency. Thin-films containing both components were excited in a spectral region where only PPE1 absorbs (400 nm) and the ratio of SQ1:PPE1 was compared.

![Figure 2.4](image)

**Figure 2.4.** Thin-film fluorescence spectra before (blue) and after (red) exposure to the saturated vapor of acetone (top) and cyclohexanone (bottom) for 30 s ($\lambda_{ex} = 400$ nm).
Given the large disparity in equilibrium vapor pressure between cyclohexanone and acetone (acetone exhibits an equilibrium vapor pressure approximately 40 fold larger than cyclohexanone) and the small size of acetone relative to cyclohexanone, it was surprising to observe the results depicted in Figure 2.4. In order to further probe the selectivity of the sensor system, a number of other acyclic and cyclic ketones were screened. The ketone dependent responses of the sensor system are depicted in Figure 2.5.

![Figure 2.5](image)

**Figure 2.5.** Change in thin-film fluorescence intensity of polymer (blue) and squaraine dye (red) after 30 s exposure to the saturated vapor of the indicated ketone ($\lambda_{ex} = 400$ nm) (mean of three different films).

Close inspection of Figure 2.5 reveals two important trends. The most intriguing of the two trends lies in the sensor response to cyclic ketones. The three cyclic ketones elicited a ratometric response of the sensor system whereby the emission intensity of SQ1 decreased with a concomitant increase in the emission intensity of PPE1. This particular response matches the expected response if the transduction mechanism described in Figure 2.1 is operating. Conversely, exposure to acyclic ketones such as diisopropyl ketone, acetone, and 3-pentanone
yielded increases in the emission intensity of both components. The second trend is the overall increase in the magnitude of the response as a function of increasing alkyl character. This trend suggested that the hydrophobicity of the analyte may be a contributing factor to the observed selectivity.

To probe whether the observed selectivity was a function of the partition coefficient of the analytes, a quartz crystal microbalance (QCM) study was undertaken. The QCM instrument allows for high precision measurements of changes in mass by measuring the fluctuation of the resonant frequency of an oscillating quartz crystal. The results of this study are depicted in Figure 2.6. Each measurement was performed in a manner identical to the method used to produce the results in Figure 2.5.

![Image of frequency shift graph]

**Figure 2.6.** Mean frequency shift of a QCM crystal coated with a thin-film of the sensor formulation after 30 s exposure to the saturated vapor of the indicated ketone (mean of three sequential measurements).

In general, the results of the QCM study corroborate the hypothesis that the partition coefficient of the analytes is a contributing factor to the observed selectivity of the sensor. However, there are three important observations that suggest **SQ1** is intrinsically selective for cyclic ketones over acyclic ketones. The first point is that the results from Figure 2.6 suggest that
the partition coefficient of diisopropyl ketone is within an order of magnitude of the partition coefficient of cyclopentanone. Interestingly, despite the ability of both analytes to permeate the film, only cyclopentanone elicits a ratiometric response. Along similar lines, the partition coefficients of the cyclic ketones increase with increasing ring size – most likely a result of increased hydrophobicity. Despite this trend, cyclopentanone and cyclohexanone yield a greater response than cycloheptanone. This result suggests that SQ1 may be exhibiting some intrinsic structure-property selectivity; specifically, that the binding area in SQ1 cannot accommodate larger rings. The third point involves the response of the sensor to 2-methylcyclopentanone. This compound partitions into the films as efficiently as cyclopentanone; yet, it does not yield the expected ratiometric response thereby supporting the hypothesis that SQ1 possesses some degree of intrinsic selectivity.

Further supporting evidence comes from the cocrystal structure of SQ1 with dimethylformamide (DMF) shown in Figure 2.7. The structure displays the strong intramolecular hydrogen bonds that exist between the proximal urea protons and the central carbonyl functionalities of the central four membered ring as well as an intramolecular hydrogen bond between the distal urea protons and the amide carbonyl of DMF. The DMF molecules form intermolecular hydrogen bonds with two SQ1 molecules which are situated face to face due to strong π-π interactions. Attempts to produce cocrystals of SQ1 with cyclic ketones such as cyclohexanone failed due to the limited solubility of this compound.
Figure 2.7. Thermal ellipsoid representation of the X-ray structure of SQ1 (1:1 cocrystal with DMF). The displacement ellipsoids are drawn at the 50% probability level, hydrogen atoms are represented by a sphere of arbitrary radius (gray = carbon, green = fluorine, blue = nitrogen, red = oxygen, light blue = hydrogen, black dashed lines = hydrogen bonds).

To further understand the observed selectivity, we sought to investigate what causes the emission intensity of PPE1 to increase when exposed to acyclic ketones such as diisopropyl ketone. Thin-films solely comprised of PPE1 are known to elicit an increase in emission intensity when exposed to 'good' solvents such as toluene.\(^{19}\) This effect is due to solvent induced swelling of the film which removes low energy trap sites (π-π stacking) in the polymer film that act as quenching sites. To verify that solvent induced swelling was indeed the origin of the increase in PPE1 emission in the presence of acyclic ketones we exposed the sensor formulation to the saturated vapor of toluene (Figure 2.8).
Figure 2.8. Thin-film fluorescence spectra taken in the presence of the saturated vapor of toluene. The black trace represents the first collected spectrum with red and green traces following at intervals of approximately 30 s ($\lambda_{ex} = 400$ nm).

The results in Figure 2.8 are consistent with the notion that ‘good’ solvents such as toluene are capable of swelling thin-films of PPE1, as demonstrated by the large increase in the emission intensity of PPE1 during the exposure. Interestingly, the emission intensity of SQ1 remains relatively constant (slight decrease) during the exposure indicating that SQ1 maintains a small intermolecular distance with the backbone of PPE1 despite the surge of solvent molecules into the film. This result lends credence to the hypothesis that swelling, in the absence of any molecular recognition event, is not capable of eliciting a ratiometric response.

2.5 Development of a Reversible, Field-portable Detection System Using Interrupted Energy Transfer

In order to develop a truly field-portable sensor it is advantageous to use a reversible sensing system as this increases the lifetime of the sensor, decreases the number of consumables
and defrays some of the cost of the sensing element.\textsuperscript{20} Initially, our sensing system did not display reversibility as shown in Figure 2.9.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.9.png}
\caption{Sequential fluorescence spectra of sensor formulation. The film is first exposed to the saturated vapor of cyclohexanone until the emission of SQ1 is suppressed (top, left). The film is then sparged with a stream of N\textsubscript{2} and a subsequent spectrum recorded (top, middle). The same film is heated to 120 °C for 10 minutes and an additional spectrum recorded (top, right). The resulting film is then re-exposed to the saturated vapor of cyclohexanone (bottom, middle) (\textit{\lambda}_{\text{ex}} = 400 \text{ nm}).

The results displayed in Figure 2.9 show that the lack of reversibility was not due to residual cyclohexanone bound to the receptor site of SQ1 as sparging with an N\textsubscript{2} stream did not regenerate the emission from SQ1. However, annealing the film at 120 °C for 10 minutes restored the emission from SQ1 and the resulting film was capable of responding to additional cyclohexanone vapor. This result indicated that the initial exposure to cyclohexanone vapor may have displaced the dye molecules from the polymer backbone and heating (annealing) was necessary to restore the equilibrium positions of the dye molecules within the scaffold.
As discussed previously, chemosensing technology utilizing AFPs have been incorporated into a portable device known as FIDO®. This instrument allows for heating of the sensing element and, in principle, should interface easily with our sensing mechanism to create a field-portable, reversible sensor for cyclohexanone vapor. Unfortunately, despite continuous heating of the thin-film, the sensor did not exhibit any significant reversibility when exposed to cyclohexanone vapor as depicted in Figure 2.10.

![Figure 2.10](image)

**Figure 2.10.** Uncorrected response of FIDO® to the saturated vapor of acetone (first three reversible peaks) followed by saturated cyclohexanone vapor (four consecutive exposures). Note the 'staircase' structure of the data indicating that it is an irreversible response.

We surmised that lowering the glass transition temperature ($T_g$) of the polymer would increase the reversibility of the sensor formulation. Dioctyl phthalate was employed as a plasticizer, and at loadings of approximately 1 wt%, successfully increased the fluidity of the film. Gratifyingly, the plasticized film responded to cyclohexanone in a reversible manner as shown in Figure 2.11.
With a reversible sensor in hand, we focused our efforts on determining the analytical capabilities of the new system. Using a calibrated vapor delivery system, we generated precious concentrations of cyclohexanone vapor to challenge our new system. The resulting data was used to construct a calibration curve (Figure 2.12) and to determine the limit of detection (LOD). It is noteworthy that all measurements were collected in ambient air with (or without) 48% relative humidity—conditions that mimic those that would be encountered outside the laboratory. The LOD obtained under these conditions was 5 ppm cyclohexanone, a value that is significantly larger than what would be necessary for trace explosives detection. Despite this apparent drawback, we exposed the FIDO® system to the headspace above a sample of C-4 explosive. The instrument recorded small ‘hits’ in response to the headspace as shown in Figure 2.13. Using the calibration data from Figure 2.12 we estimated that the magnitude of the FIDO® response correlated to a concentration of approximately 17 ppm of cyclohexanone vapor. In order to verify this result, the headspace above the same sample of C-4 was sampled using SPME techniques and the concentration of cyclohexanone in the headspace was obtained using GC/MS. The obtained value of 27 ppm was very similar to the value reported by the FIDO® and lends
credence to the notion that the response of the sensor system was indeed due to cyclohexanone vapor in the headspace. The headspace GC/MS analysis also showed no traces of TNT or 2,4-dinitrotoluene (DNT) contaminants which could potentially interfere with the signal.

![Figure 2.12](image1.png)

**Figure 2.12.** Calibration curve showing the response of the sensor system to different concentrations of cyclohexanone vapor (exponential fit). Inset figure is an expansion of the 0 – 200 ppm concentration range (linear fit).

![Figure 2.13](image2.png)

**Figure 2.13.** Uncorrected response of the FIDO® instrument to the headspace of C-4 explosive.
2.6 Conclusion

In summary, we have developed a highly selective detection system for cyclic ketones. The transduction mechanism leverages the unique spatial requirements of Dexter energy transfer to generate a selective detector that does not require any type of PET in order to function. In addition, the synthesis and photophysical properties of emissive receptor SQ1 were described as well as the optimization of the energy transfer cascade utilizing this new fluorophore. The sensor was effectively interfaced with the FIDO® system and was shown to reversibly respond to concentrations of cyclohexanone vapor down to 5 ppm. The sensor also showed promise for the detection of cyclohexanone vapor in the headspace of the plasticized explosive C-4.

2.7 Experimental Section

MATERIALS AND METHODS: All chemicals were of reagent grade, purchased from Sigma-Aldrich and used as received. All solvents used for photophysical experiments were of spectral grade. PPE1 was a gift from ICx Technologies (Lot#: BD15267). $^1$H and $^{13}$C NMR spectra were obtained on either a Varian Mercury (500 MHz) or Varian Mercury (501 MHz) spectrometer. NMR chemical shifts are referenced to either THF-$d_8$ or DMSO-$d_6$ and reported in units of δ (ppm). All $^{13}$C spectra are proton decoupled. All NMR experiments were conducted at room temperature. High-resolution mass spectra (HRMS) were obtained at the MIT Department of Chemistry using a peak-matching protocol to determine the mass and error range of the molecular ion. Electrospray or direct analysis in real time (DART), operating in negative ion mode, were used as the ionization techniques. UV-vis spectra were measured on an Agilent 8453 diode array spectrophotometer and corrected for background signal with a solvent filled cuvette. Fluorescence spectra were obtained using a SPEX Fluorolog-$\tau$3 fluorimeter using right-angle detection (solution measurements) or front-face detection (thin film measurements). Thin films
containing PPE1 and SQ1 were fabricated by spin-coating (5000 RPM for 1 min) chloroform solutions of the appropriate concentrations (Specialty Coating Systems™ G3P-8 Spincoat). The films were then placed under vacuum to ensure complete removal of the residual solvent. Thin-film quenching experiments were conducted by taking an initial photoluminescence spectrum ($\lambda_{ex} = 400$ nm, entrance/exit slits 2 nm) of the thin film, placing the surface over a glass vial loaded with 2 mL of the appropriate ketone for 30s, and taking an additional photoluminescence spectrum immediately after exposure. Quartz crystal microbalance measurements were performed with a home-built quartz crystal microbalance setup with crystals (10 MHz, Au electrodes) and oscillator from the International Crystal Manufacturing Co. Films were applied by spin-coating chloroform solutions of PPE1 and SQ1 on both sides of the crystal (5000 RPM for 1 min). Exposure of the QCM crystals to analyte was performed analogous to the photoluminescence experiments with data collection running continuously during the exposure. Film thicknesses were obtained according to previously published procedures. LOD measurements and experiments involving C-4 explosive were carried out at the Edgewood Chemical Biological Center and the methods are described in a subsequent section.

**SYNTHETIC PROCEDURES AND CHARACTERIZATION:**

1-(3,5-bis(trifluoromethyl)phenyl)-3-(3-dimethylamino)phenyl)urea. $N,N$-Dimethyl-$m$-phenylenediamine dihydrochloride (2.0 g, 9.56 mmols) was dissolved in 10 mL of methylene chloride and washed with 1M NaOH (aq). The resulting organic layer was isolated, dried over anhydrous MgSO₄, and added directly to a 25 mL round-bottom flask containing a stirred solution of 3,5-Bis(trifluoromethyl)phenyl isocyanate (2.68 g, 10.52 mmols) in 5 mL methylene
chloride. The mixture was stirred at room temperature for 12 h during which the precipitation of a white solid was observed. The precipitate was isolated by filtration, washed with cold methylene chloride and dried under vacuum to yield 2.47 g (66%) of a white solid. \(^1\)H NMR (501 MHz, DMSO-\(d_6\)): \(\delta\) 9.29 (s, 1H), 8.80 (s, 1H), 8.10 (s, 2H), 7.61 (s, 1H), 7.07 (t, \(J = 8.21\) Hz, 1H), 6.90 (s, 1H), 6.74 (d, \(J = 8.21\) Hz, 1H), 6.40 (d, \(J = 8.21\) Hz, 1H), 2.87 (s, 6H). \(^13\)C NMR (501 MHz, DMSO-\(d_6\)): \(\delta\) 153.5, 152.1, 143.1, 140.9, 131.9 (q, \(J_{C\text{-}CF_3} = 32.3\) Hz), 130.3, 125.6 (q, \(J_{C\text{-}F} = 272.8\) Hz), 119.0, 115.4, 108.3, 108.3, 104.0, 41.3. MS (DART) calc for C\(_{17}\)H\(_{15}\)F\(_6\)N\(_3\)O [M - H]: 390.10, found 390.10.

SQ1. A 50 mL round-bottom flask, equipped with a magnetic stir bar, Dean-Stark trap and reflux condenser, was charged with 1.0 g (2.56 mmols) 1-(3,5-bis(trifluoromethyl)phenyl)-3-(3-dimethylamino)phenyl)urea, 0.15 g (1.28 mmols) 3,4-dihydroxycyclobut-3-ene-1,2-dione, and 30 mL of a 3:1 mixture of toluene and \(n\)-butanol. The resulting mixture was refluxed under azeotropic distillation conditions for 6 h. During the reaction a color change from light yellow to dark green was observed with concomitant precipitation of a metallic green solid. The vessel was cooled to r.t. and allowed to sit overnight. The resulting metallic green solid was filtered, washed with methanol and hexanes, and dried under vacuum to yield 0.8 g (72%) of squaraine 2. \(^1\)H NMR (500 MHz, THF-\(d_8\)): \(\delta\) 11.87 (s, 2H), 8.42 (m, 6H), 8.29 (s, 4H), 7.99 (s, 2H), 7.60 (s, 2H), 6.58 (d, \(J = 9.1\) Hz, 2H), 3.21 (s, 6H). Due to the limited solubility of the compound satisfactory \(^13\)C spectra could not be obtained even after acquiring for 24 h. Anal. calc for
C$_{38}$H$_{28}$F$_{12}$N$_6$O$_4$ * 1H$_2$O: %C 51.94, %H 3.44, %N 9.56, %F 25.95; found %C 51.56, %H 3.27, %N 9.24, %F 26.90.
**FLUORESCENCE AND QCM DATA:**

![Photoluminescence spectra](image)

**Figure 2.7.1** Photoluminescence spectra of thin films before (blue) and after (red) 30 second exposure to the headspace of the indicated ketone ($\lambda_{ex} = 400$ nm).

![Photoluminescence spectra](image)

**Figure 2.7.2.** Photoluminescence spectra of thin films before (blue) and after (red) 30 second exposure to the headspace of the indicated ketone ($\lambda_{ex} = 400$ nm).
Figure 2.7.3. Photoluminescence spectra of thin films before (blue) and after (red) 30 second exposure to the headspace of the indicated ketone ($\lambda_{ex} = 400$ nm).

Figure 2.7.4. Photoluminescence spectra of thin films before (blue) and after (red) 30 second exposure to the headspace of acetone ($\lambda_{ex} = 400$ nm).
Figure 2.7.5. Photoluminescence spectra before (blue) and after (red) exposure to the headspace of the indicated solvent mixture. Note that both components exhibit an increase in emission intensity when exposed to pure ethanol and exhibit a small ratiometric response when exposed to a 3% (v/v) cyclohexanone/ethanol mixture.

Figure 2.7.6. Mean frequency shift of a QCM crystal coated with a thin-film of PPE 2 after 30 second exposure to the headspace vapor of cyclohexanone (mean of three sequential measurements).
Figure 2.7.7. Photoluminescence spectra of squaraine 1 in CHCl₃ (O.D. = 0.1 au) with excitation wavelength at 650 nm (red) and 400 nm (blue). The small bump at 650 nm in the red spectrum is due to the excitation wavelength.
RAW FIDO® DATA (ANALYTE = CYCLOHEXANONE):

Figure 2.7.9. Normalized responses of the FIDO® system to the indicated concentration of cyclohexanone vapor.
**$^1$H AND $^{13}$C NMR SPECTRA:**

Figure 2.7.10. $^1$H NMR spectrum of 1-(3,5-bis(trifluoromethyl)phenyl)-3-(3-dimethylamino)phenyl)urea (DMSO-$d_6$).

Figure 2.7.11. $^{13}$C NMR spectrum of 1-(3,5-bis(trifluoromethyl)phenyl)-3-(3-dimethylamino)phenyl)urea (DMSO-$d_6$).
Figure 2.7.12. $^1$H NMR spectrum of SQ1 (THF-$d_8$).
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR SQ1:

Identification code x10009

Empirical formula C41 H35 F12 N7 O5

Formula weight 933.76

Temperature 100(2) K

Wavelength 1.54178 Å

Crystal system Triclinic

Space group P-1

Unit cell dimensions
\[ a = 7.9149(2) \text{ Å} \quad \alpha = 89.6190(10)^\circ. \]
\[ b = 13.8805(3) \text{ Å} \quad \beta = 82.0830(10)^\circ. \]
\[ c = 18.1339(4) \text{ Å} \quad \gamma = 88.7430(10)^\circ. \]

Volume 1972.76(8) Å³

Z 2

Density (calculated) 1.572 Mg/m³

Absorption coefficient 1.259 mm⁻¹

F(000) 956

Crystal size 0.12 x 0.04 x 0.03 mm³

Theta range for data collection 3.18 to 66.91°.

Index ranges -9 ≤ h ≤ 9, -16 ≤ k ≤ 16, -17 ≤ l ≤ 21

Reflections collected 34262

Independent reflections 6956 [R(int) = 0.0338]

Completeness to theta = 66.91° 98.9 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.9632 and 0.8636

Refinement method Full-matrix least-squares on F²

Data / restraints / parameters 6956 / 373 / 614

Goodness-of-fit on F² 1.027

59
Final R indices [$\sigma$ > 2\sigma(I)]

\[ R_1 = 0.0397, \quad wR_2 = 0.1035 \]

R indices (all data)

\[ R_1 = 0.0441, \quad wR_2 = 0.1078 \]

Largest diff. peak and hole

0.477 and -0.397 eÅ⁻³

2.8 References


(19) Our laboratory has observed that solvents such as toluene and THF are capable of swelling CP films.


(21) Studies were conducted at the Edgewood Chemical Biological Center (ECBC).
Chapter 3

Liquid Crystal Alignment Layers Using an Axis-Selective Di-π-Methane Rearrangement
3.1 Introduction to Liquid Crystals

Liquid crystalline materials (LCMs) have permeated all areas of human life. It is difficult to imagine a world without liquid crystal displays (LCDs); yet, this particular application of LCMs represents only a small portion of technologies that exploit liquid crystalline phases. LCMs have been used as thermometers, optical switches, wavelength tunable filters, lasing media, sensing materials and much more. The utility of LCMs is derived from the special liquid crystalline phases that these materials can exhibit under appropriate conditions. Liquid crystalline phases, from a qualitative perspective, are phases that exhibit some of the anisotropic properties of solids (orientational or positional order) yet are free flowing liquids. This seemingly paradoxical state of matter was first described by an Austrian botanist named Friedrich Reinitzer at the University of Graz in 1888. While working with cholesteric molecules he observed that this material undergoes a thermal transition to yield an opaque liquid that subsequently melts to a clear liquid at higher temperatures. This observation was the catalyst for the understanding and development of LCMs.

The simplest liquid crystalline phase – the nematic phase – is schematically depicted in Figure 3.1. Molecules exhibiting this phase of matter possess orientational order but lack any positional order; in other words, the molecules are not correlated with each other. When nematic phases are formed on isotropic substrates, such as glass, many nematic domains form where the vectors that describe the orientational order (director) vary in direction across the mesophase (Figure 3.2). This is not an ideal situation as devices that utilize liquid crystalline phases require uniform alignment of the phase. In order to induce alignment, a technique known as rubbing was developed in 1911. In this process, a thin polymer film is rubbed in one direction using a cloth. The microscopic and molecular anisotropies that develop on the surface are believed to be
the origin of liquid crystal alignment on these films.\textsuperscript{10} Despite the crudeness of this approach, it is the major industrial technique for producing aligned LCMs. There are a number of problems associated with the rubbing process such as: (i) generation of static charges in the device, (ii) incorporation of dust particles on the surface and (iii) it serves as a bottleneck in the production of LCMs.\textsuperscript{11} In order to solve these problems, there has been considerable interest in developing non-contact alignment processes that utilize light.

Figure 3.1. Schematic depictions of the structure of liquid crystal mesogens (left) and the nematic phase (right). Small inset (lower left) displays the molecular structure of 4-cyano-4’pentylbiphenyl (5CB).

Figure 3.2. Schematic depictions of unaligned (left) and aligned (right) nematic liquid crystalline phases. The rod-like structure represents a liquid crystal mesogen such as 5CB. The black arrow on the right side represents the molecular director.
Non-contact alignment mechanisms that utilize light are collectively known as photoalignment mechanisms. The general approach is to coat a substrate with a photoresponsive polymeric film, and through polarized irradiation, generate anisotropy at the liquid crystal–polymer interface. The photoresponsive polymer films typically rely on simple photochemical transformations such as cis/trans isomerizations\(^2\) and cycloaddition reactions.\(^3\) The most commonly used transformations for photoalignment are shown in Figure 3.3.

![Photochemical Transformations](image)

**Figure 3.3.** Various photochemical transformations that are applied in photoalignment mechanisms.\(^4\)

The transformations outlined in Figure 3.3 are effective approaches for photoalignment; however, the listed reactions suffer from at least one of the following limitations: (i) the transformation is thermally reversible, (ii) more than one pathway is available, and/or (iii) extended irradiation destroys the alignment. To address these limitations, we sought to design robust photoalignment layers based on the di-π-methane rearrangement.
3.2 The Di-π-methane Rearrangement

The di-π-methane rearrangement is a high yielding photochemical transformation discovered by Zimmerman in 1966 (Figure 3.4). The scope of this reaction and related reactions has been thoroughly reviewed. The term di-π-methane refers to the arrangement of two vinylic moieties separated by a methylene unit, which is a general characteristic of substrates that undergo this rearrangement.

![Mechanism of the di-π-methane rearrangement](image)

**Figure 3.4.** Overall transformation and mechanism of the di-π-methane rearrangement (top). Implications of the multiplicity of the di-π-methane rearrangement (bottom).

As shown in Figure 3.4, the overall transformation consists of converting a skipped diene system to an allylic cyclopropane moiety. In the case of unconstrained, freely rotating, divinyl groups (top, Figure 3.4), reaction via the excited singlet state yields the desired product. If the same substrate is reacted through a triplet manifold, the only observed products are the result of isomerization about the double bonds. Conversely, constrained divinyl moieties, as is the case with 1 (Figure 3.4), behave in the opposite fashion - triplet sensitization of 1 yields the desired product whereas direct irradiation yields dibenzocyclooctatetraene. The multiplicity
dependence of this transformation with respect to dibenzobarrelene is essential to the work described in this chapter.

3.3 Approach and Design Considerations

The Swager group has exploited the intramolecular free volume (IFV) associated with triptycene-based structures to create polymers that are strongly aligned in liquid crystalline media. This design principle served as inspiration for the construction of P1 (Figure 3.5). The repeat unit of this polymer contains two functional units. The first unit, the diester substituted dibenzobarrelene structure, serves two purposes: (i) this structure exhibits a rigid carbocyclic structure similar to that of triptycene; as such, it is expected to form favorable interactions with an LC phase and (ii) the same structure also serves as a di-π-methane substrate. We hypothesized that the rearrangement would lead to a structure that exhibits a lower level of IFV and would therefore interact poorly with the LC phase. By using linearly polarized light to initiate the reaction, only chromophores with transition dipole moments oriented parallel to the polarized light source will undergo the transformation. The remaining chromophores would retain their IFV and lead to a net anistropy at the polymer LC phase and generate an alignment axis for the LC phase to couple with (Figure 3.6).

![Figure 3.5](image.png)

**Figure 3.5.** Molecular structure of P1 and the resulting photoproduct of the di-π-methane rearrangement.
Because it is a rigid system, the rearrangement proceeds through a triplet manifold thereby requiring the presence of a triplet sensitizer. During photoexcitation with linearly polarized light, the benzophenone units (exhibiting the proper orientation with respect to the light source) are excited to the first singlet state and then quickly crossover to the first excited triplet state through intersystem crossing. We surmised that incorporation of sensitizer units directly into the backbone would lead to facile Dexter energy transfer thereby exciting the dibenzobarellene units to their triplet state followed by the di-π-methane rearrangement.

Figure 3.6. Schematic depiction of the proposed photoalignment mechanism using the di-π-methane rearrangement. Red (green) structures represent P1 before (after) photolysis. Blue structures represent LC molecules.
3.4 Synthesis of Monomers, Model Compounds and Photoalignment Polymers

The core unit of P1 is a diester-substituted dibenzobarellene compound as mentioned previously. The synthesis of this compound is shown in Scheme 3.1. The synthesis begins with the double addition of trimethylsilylacetylide to 1,4-anthraquinone followed by SnCl₂ mediated reductive aromatization to afford 2 in good yield. This compound underwent a facile Diels Alder reaction with DMAD followed by fluoride deprotection of the silyl groups to yield 3. Double Sonogashira-Hagihara cross-coupling of 3 with 4 afforded the model compound 5.

Scheme 3.1. Synthesis of model compound 5.

Comonomers for the synthesis of P1 and P2 were synthesized according to Scheme 3.2. These comonomers were iodinated meta to the carbonyl group in order to limit the effective conjugation length of the resulting polymers. Typically, electronically deactivated arenes such as benzophenone and benzil are sluggish substrates for electrophilic halogenations; however, the use of concentrated sulfuric acid and N-iodosuccinimide (NIS) at low temperature successfully
iodinated both compounds in good yield. Presumably, the concentrated sulfuric acid is capable of protonating the succinimide groups thereby yielding a strongly electrophilic source of iodine.  

\[
\text{Scheme 3.2. Synthesis of comonomers 6 and 7.}
\]

Polymers P1 and P2 were synthesized using standard Sonogashira-Hagihara cross-coupling chemistry as depicted in Scheme 3.3. In order to preserve the processability/solubility of the targeted polymers, the polymerization reactions were conducted for only 24-36 hours yielding number-average molecular weights (Mn) of 15,000 – 33,000 g/mol.

\[
\text{Scheme 3.3. Synthesis of photoalignment polymers P1 and P2.}
\]

3.5 Photochemistry of Model Compound and Photoalignment Polymers

Polymers P1 and P2 contain di-π-methane substrates that each can yield two different regioisomers upon photolysis. To probe the regiochemical behavior of the dibenzobarrelene scaffold, the photochemistry of model compound 5 was investigated. As shown in Scheme 3.4,
the photolysis of 5 may give rise to racemic mixtures of two regioisomers. The regiochemistry of this transformation is controlled by the formation of the bridged diradical species shown in Scheme 3.4. There are two possibilities present, in one case the diradical could be centered on the lone arene ring (Diradical 2, Scheme 3.4). However, loss of aromaticity makes this diradical particularly unstable. We hypothesized that the extended conjugation of the ethynyl-bridged arene system would make this particular diradical (Diradical 1, Scheme 3.4) more stable and give rise to photoproduct rac-DP1 as the major product.

Indeed, photolysis of 5 in chloroform using benzophenone as the triplet sensitizer gave rise to predominantly one set of new peaks as shown in Figure 3.7. It is noteworthy that the NMR spectrum in Figure 3.7 is of the crude mixture and that only signals from starting material and product can be observed. This point exemplifies the efficiency of the di-π-methane transformation and its possible utility as a photoalignment reaction. In order to unambiguously determine the regiochemistry of the rearrangement the major photoproduct was isolated by column chromatography. The product was analyzed via 2D NMR techniques and determined to be rac-DP1.
Scheme 3.4. Regiochemical possibilities during photolysis of model compound 5.

Figure 3.7. Stacked $^1$H NMR spectra obtained during photolysis of 5.
After investigating the photochemistry of model compound 5, we turned our attention to the photochemistry of photoalignment polymers P1 and P2. The reactions were carried out in CDCl₃ and monitored by ¹H NMR spectroscopy. The results of the photolysis of P1 are shown in Figure 3.8.

![Diagram of photolysis of P1]

**Figure 3.8.** Stacked ¹H NMR spectra obtained during photolysis of P1.

As shown in Figure 3.8, the photolysis of P1 in CDCl₃ cleanly yields the di-π-methane photoproduct. The new methine resonances at 5.5 and 4.5 ppm closely match the chemical shifts of the methines formed during the photolysis of model compound 5. The generation of only two new methine peaks is indicative of the high regioselectivity of this transformation and is analogous to the observed regioselectivity of the model compound. It is noteworthy that the photolysis of P1 was carried out in the presence of air. Typically, triplet sensitized photochemical transformations are carried out in degassed solutions as oxygen can easily quench the triplet state of the sensitizer.¹⁹ In the case of P1, incorporation of the triplet sensitizer in the polymer backbone positions the sensitizer adjacent to the di-π-methane substrate and enhances
the rate of energy transfer. This enhancement alleviates the need to remove oxygen as the rate of energy transfer is faster than the diffusion rate of oxygen in solution. From a practical standpoint, this is an ideal situation as the photolysis of photoalignment films can be carried out in air as opposed to an inert atmosphere.

The photolysis of P2 closely resembled that of P1 (Figure 3.9). The major difference between these two polymers is the choice of the triplet sensitizer. Both benzil and benzophenone are efficient triplet sensitizers with intersystem crossing rates of near unity. However, the triplet energy of benzil is substantially lower than that of benzophenone ($E_{T, \text{benzil}} = 54$ kcal/mol, $E_{T, \text{benzophenone}} = 69$ kcal/mol). This indicates that energy transfer from benzophenone to the di-n-methane substrate should be more exothermic and therefore more efficient than energy transfer from benzil. Interestingly, the rates of rearrangement for the two polymers are very similar (11% product formation P2, 17% product formation P1 after 20 minutes of continuous irradiation) suggesting that the rate limiting step does not involve energy transfer.

![Figure 3.9. Stacked $^1$H NMR spectra obtained during photolysis of P2.](image)
Close inspection of the fluorescence spectra of 5, P1, and P2 reveals that the emission from P1 exhibits a bathochromic shift of approximately 100 nm compared to model compound 5 and also lacks the well resolved vibrational structure characteristic of these chromophores. It is interesting that neither polymer exhibits any emission similar to that of 5 (despite using a $\lambda_{ex} = 300$ nm), this suggests that the emission from the dibenzobarrelene core is sufficiently quenched by the triplet sensitizer. This is consistent with an energy transfer cascade whereby excitation of the dibenzobarrelene core is followed by energy transfer (Dexter or FRET) to the sensitizer which then undergoes intersystem crossing to the lowest triplet state followed by back energy transfer (Dexter) to the dibenzobarrelene unit with subsequent rearrangement. The origin of the emission from P1 is unknown and may be due to an impurity or defect site in the polymer backbone (alkyne homocoupling).

![Fluorescence spectra of 5, P1, and P2](image)

**Figure 3.10.** Fluorescence spectra of model compound 5 (left), P1 and P2 (right). Spectra were taken in dichloromethane solution using $\lambda_{ex} = 300$ nm with O.D. of 0.1 for all components.

### 3.6 Alignment of Liquid Crystal Phases using P1.

Benzil is known to react with oxygen during extended exposure to visible wavelengths greater than 400 nm to form peroxides.\textsuperscript{20} This characteristic is not ideal for devices and required us to direct our attention towards P1. In order to test the alignment capabilities of P1 we
fabricated simple LC devices as shown in Figure 3.11. The fabrication process begins with formation of a thin film of P1 on a clean glass substrate followed by polarized irradiation. This process is repeated on a second substrate and the two slides are sandwiched together with 6 μm spacers and sealed with epoxy. The cells are then filled with the LC material at a temperature above the clearing point of the LC and allowed to slowly cool to the nematic phase. The alignment was observed via polarized optical microscopy (POM) on a rotating stage with crossed polarizers. In the case where the photoalignment layers are oriented parallel to each other we expect no light to pass through the cell when the LC director is parallel to either of the two polarizers when crossed. However, if the cell is rotated off-axis (45° angle relative to either polarizer), then we expect light to pass through the cell. Figure 3.12 exemplifies this situation.

Figure 3.11. Schematic depiction of LC cell fabrication using photoalignment polymer P2.
Figure 3.12. Optical micrographs of LC cells where the photopolymer P1 has not been irradiated (top) or has been irradiated with polarized light (bottom). Irradiation was carried out for 10 minutes in air (LC = MLC 6884). Black arrows correspond to the orientation of the polarizers.

As can be seen in Figure 3.12, LC cells that have not been irradiated display no alignment whatsoever. This is indicated by the consistent brightness of the cells when rotated by the indicated amount. When the cells have been irradiated with polarized light the alternation between bright and dark states becomes evident and is consistent with alignment. To further probe the utility of this approach we attempted to create more elaborate patterns by using photomasks in conjunction with the polarized irradiation. Figure 3.13 displays an open-faced cell where a striped photomask was employed to generate alternating regions of irradiated and not-irradiated P1.
Figure 3.13. Optical micrographs of LC cells where the photopolymer P1 has been irradiated through a polarizer and striped photomask. Irradiation was carried out for 10 minutes in air (LC = MLC 6884). The alternating stripes correspond to features of 100 µm. Black arrows correspond to the orientation of the polarizers.

We anticipated that the non-irradiated regions would exhibit no alignment; however, we were surprised to find that both irradiated and non-irradiated regions displayed significant alignment. Interestingly, Figure 3.13 shows that the two regions are aligned orthogonal to one another – a completely unexpected result. We hypothesize that this result may be due to swelling of the polymer in the irradiated regions which would generate a surface topography of alternating ridges and valleys. It has been shown previously that such surface patterns are capable of aligning LC mesogens.21

3.7 Conclusion.

In conclusion we have shown the design and synthesis of two new photoresponsive polymers that are capable of undergoing the di-π-methane rearrangement. The polymers contain triplet sensitizers within the polymer backbone that are capable of sensitizing the reaction via triplet-triplet Dexter energy transfer. In addition, these polymers are capable of aligning liquid
crystal mesogens by exploiting the IFV of dibenzobarrelene structures. Further work is currently underway in our laboratory to probe the scope of this approach.

3.8 Experimental Section.

**MATERIALS AND METHODS:** Toluene, CH₂Cl₂ and THF were purified by passage through solvent purification columns containing activated alumina. N,N-Dimethylformamide (DMF) was distilled from MgSO₄ and stored over 4Å molecular sieves. Diisopropylamine was distilled from CaH₂. All other reagents were obtained from commercial sources and used as received unless otherwise noted.

**INSTRUMENTATION:** NMR spectra were recorded on Varian Mercury 300 MHz, Varian Inova 500 MHz or Varian Inova 501 MHz spectrometers. Chemical shifts were reported in ppm and referenced to residual NMR solvent peaks (CDCl₃: δ 7.27 ppm for ¹H, δ 77.23 ppm for ¹³C). High-resolution mass spectra (HRMS) were obtained at the MIT Department of Chemistry using a peak-matching protocol to determine the mass and error range of the molecular ion. Electrospray or direct analysis in real time (DART), operating in negative ion mode, were used as the ionization techniques. Melting points were measured on a Mel-Temp II apparatus (Laboratory Devices INC) and were not corrected. Number average molecular weights (Mn) and polydispersity (PDI) of polymers were obtained on a HP series 1100 gel permeation chromatography (GPC) system in THF and calibrated with polystyrene standards and utilizing both UV (450 nm) and refractive index detection. UV-vis spectra were measured on an Agilent 8453 diode array spectrophotometer and corrected for background signal with a solvent filled cuvette. Fluorescence spectra were obtained using a SPEX Fluorolog-3 fluorimeter using right-
angle detection (solution measurements) or front-face detection (thin film measurements). Thin films containing P1 and P2 were fabricated by spin-coating (5000 RPM for 1 min) chloroform solutions of the appropriate concentrations (Specialty Coating Systems\textsuperscript{TM} G3P-8 Spincoat). The films were then placed under vacuum to ensure complete removal of the residual solvent. Photolysis experiments were carried out using a BlueWave\textsuperscript{®} 200 light curing system from Dymax. A FGUV W53199 UV filter from Thorlabs, Inc. was used generate 360 nm light output (36 mW/cm\textsuperscript{2}). Linearly polarized irradiation was achieved using a Glan-Taylor polarizer.

**SYNTHETIC PROCEDURES AND CHARACTERIZATION:**

1,4-Bis[(trimethylsilyl)ethynyl]anthracene (2). Compound 2 was prepared based on a preparation described by Tannaci et al.\textsuperscript{22} A flame dried flask was charged with dry THF (40 mL) and ethynyltrimethylsilane (1.42 g, 14.41 mmol). To this solution was added butyllithium (8.8 mL, 1.6 M) drop-wise over a period of 30 minutes at 0 °C under a nitrogen atmosphere. This solution was stirred and allowed to warm to room temperature (~1 hour). After 1 hour, 1,4-anthraquinone (1 g, 4.80 mmol) was added as a single solid portion to the stirring solution. The reaction mixture immediately turned purple upon addition of the solid. The solution was stirred at room temperature for 12 h at room temperature and monitored by TLC. To this solution was added saturated SnCl\textsubscript{2} in 10% aqueous HCl (10 mL). The solution immediately changed from a
purple to orange color and the reaction monitored by thin-layer chromatography. Upon completion, the reaction mixture was partitioned between water and hexanes. The organic phase was washed three times with water and passed through a plug of silica gel. The resulting yellow solid was further purified by recrystallization from ethanol to yield 1.2 g (66%) of a brilliant yellow solid. mp 169 °C. $^1$H NMR (125 MHz, CDCl$_3$): δ 8.93 (s, 2H), 8.06 - 8.11 (m, 2H), 7.69 (s, 2H), 7.54 - 7.58 (m, 2H), 0.45 (s, 18H). $^{13}$C NMR (501 MHz, CDCl$_3$): δ 132.90, 131.23, 130.45, 129.24, 126.93, 126.44, 122.44, 103.90, 102.59, 0.89.

**Dimethyl 1,4-bis[[(trimethylsilyl)ethynyl]-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate.** The title compound was prepared using a procedure similar to that reported by McNeil et al.$^{23}$ To a flame dried 50 mL round-bottom flask was added compound 2 (1.0 g, 2.69 mmol), DMAD (1.53 g, 10.79 mmol), and 10 mL of dry o-xylene. The reaction was refluxed under a nitrogen atmosphere for 12 h. The reaction was cooled to room temperature, concentrated in vacuo and purified by column chromatography using 90/10 hexanes/EtOAc. The material was then triturated with cold methanol to remove any residual DMAD. The off-white solid was dried in vacuo to yield .99 g (1.94 mmol) of the target compound. $^1$H NMR (501 MHz, CDCl$_3$): δ 7.40-7.41 (m, 2H), 7.04-7.06 (m, 2H), 5.95 (s, 2H), 3.82 (s, 6H), 0.35 (s, 18H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 166.16, 147.77, 146.902, 143.812, 128.65, 126.37, 124.95, 119.51,
102.48, 100.71, 53.14, 51.41, 0.71. MS (DART) calc for C\textsubscript{30}H\textsubscript{32}O\textsubscript{4}Si\textsubscript{2} [M + H]: 513.1912, found 513.1912.

Dimethyl 1,4-diethynyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (3). To a flame-dried 50 mL round-bottom flask was added dry THF (20 mL) and dimethyl 1,4-bis[(trimethylsilyl)ethyl]yl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (0.5 g, 0.975 mmol) under a nitrogen atmosphere. TBAF (2.05 mL, 1.0 M) was added slowly via a syringe and allowed to stir overnight. The reaction mixture was concentrated in vacuo and purified by silica gel column chromatography using 2:1 (hexanes/CH\textsubscript{2}Cl\textsubscript{2}) to afford a off-white solid (0.33 g, 0.897 mmol, 92%). \textsuperscript{1}H NMR (501 MHz, CDCl\textsubscript{3}): \( \delta \) 7.47-7.45 (m, 2H), 7.16 (s, 2H), 7.06-7.08 (m, 2H), 5.99 (s, 2H), 3.8 (s, 6H), 3.43 (s, 2H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): \( \delta \) 165.83, 146.97, 146.70, 143.18, 128.90, 126.04, 124.56, 118.39, 82.58, 80.49, 52.81, 50.69. MS (DART) calc for C\textsubscript{24}H\textsubscript{16}O\textsubscript{4} [M + H]: 369.1121, found 369.1135.
Dimethyl 1,4-bis (p-tolylethynyl)-9,10-ethenoanthracene-11,12-dicarboxylate (5). To a flame-dried 10 mL Schlenk flask was added dry toluene (5 mL), dry diisopropylamine (2 mL), compound 3 (0.05 g, 0.136 mmol), and compound 4 (0.062 g, 0.285 mmol) under a nitrogen atmosphere. The flask was evacuated and refilled with nitrogen three times followed by addition of a spatula tip of tetrakis(triphenylphosphine)palladium and Cul. The vessel was sealed and heated to 80 °C for 4 h with stirring under a nitrogen atmosphere. The reaction mixture was then cooled to room temperature, concentrated in vacuo and partitioned between CH₂Cl₂ and water. The organic phase was washed with saturated NH₄Cl (aq) solution followed by three washes with water. The organic phase was concentrated in vacuo and purified by silica gel column chromatography using 2:1 (Hexanes:CH₂Cl₂). The light brown powder was dried in vacuo to yield 0.66 g (0.119 mmol, 88%) of the title compound. ¹H NMR (501 MHz, CDCl₃): δ 7.53-7.54 (d, J = 7.85 Hz, 4H), 7.47-7.48 (m, 2H), 7.24-7.25 (d, J = 7.85 Hz, 4H), 7.17 (s, 2H), 7.05-7.07 (m, 2H), 6.07 (s, 2H), 3.83 (s, 6H), 2.43 (s, 6H). ¹³C NMR (125 MHz, CDCl₃): δ 166.37, 147.74, 146.36, 143.94, 139.61, 132.34, 129.99, 128.73, 126.40, 125.01, 120.71, 119.60, 95.35, 86.46, 53.25, 51.54, 22.34. MS (DART) calc for C₃₈H₂₈O₄ [M + H]: 549.2060, found 549.2059.
Bis(3-iodophenyl)methanone (6). The title compound was prepared by following the literature procedure reported by Chaikovskii et al.\textsuperscript{18} To a round-bottom flask was added 30 mL of sulfuric acid (90%) and cooled to 0 °C with an ice bath. To this solution was added N-iodosuccinimide (2.25 g, 10 mmol) and the reaction was stirred until it became homogenous. To this solution was added benzophenone (0.46 g, 2.5 mmol) as a single solid portion and the solution was stirred for 4 h. The reaction mixture was then poured onto a 100 mL ice/water mixture and treated with Na\textsubscript{2}SO\textsubscript{3} solution. The mixture was partitioned between CH\textsubscript{2}Cl\textsubscript{2} and water and the organic phase was washed three times with water. The organic phase was concentrated \textit{in vacuo} and the resulting solid purified by recrystallization (EtOH) to yield 0.69 g (1.58 mmol, 63%) of a white crystalline solid. mp 146 °C. \textsuperscript{1}H NMR (501 MHz, CDCl\textsubscript{3}): \( \delta \) 8.12 (s, 2H), 7.93-7.95 (d, \( J = 7.48 \) Hz, 2H), 7.70-7.72 (d, \( J = 7.48 \) Hz, 2H), 7.23-7.26 (t, \( J = 8.39 \) Hz, 2H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): \( \delta \) 194.18, 142.27, 139.47, 139.25, 130.77, 129.80, 94.96.

1,2-bis(3-iodophenyl)ethane-1,2-dione (7). The title compound was prepared using the same procedure and quantities described above. Yield = 0.70 g (58%). mp 127 °C. \textsuperscript{1}H NMR (501 MHz, CDCl\textsubscript{3}): \( \delta \) 8.31 (s, 2H), 7.99-8.01 (d, \( J = 6.89 \) Hz, 2H), 7.89-7.92 (d, \( J = 6.89 \) Hz, 2H),
7.25-7.28 (t, J = 8.01 Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 192.04, 144.03, 138.67, 134.55, 130.92, 129.44, 94.95.

P1. To a flame-dried 25 mL Schlenk flask was added dry toluene (5 mL), dry diisopropylamine (3 mL), compound 3 (0.1 g, 0.271 mmol) and compound 6 (0.118 g, 0.271 mmol). The reaction vessel was subjected to one cycle of freeze-pump-thaw where during the freeze cycle a spatula tip quantity of tetrakis(triphenylphosphine)palladium and CuI was added. The reaction mixture was then subjected to two additional freeze-pump-thaw cycles and heated to 80 °C for 36 h under a nitrogen atmosphere. The solution was cooled to room temperature and reprecipitated directly into cold acetone (200 mL). The white polymeric material was partitioned between CHCl$_3$ and water, washed once with sat. NH$_4$Cl (aq) and washed three times with water. The organic phase was concentrated in vacuo to a volume of approximately 1 mL and reprecipitated from cold acetone to yield 0.09 g (61%) of a white powder. GPC gave $M_n = 15,000$; PDI = 1.8, DP = 26.

$^1$H NMR (501 MHz, CDCl$_3$): δ 8.08 (broad, 2H), 7.84 (broad, 4H), 7.57 (broad, 2H), 7.44 (broad, 2H), 7.17 (broad, 2H), 7.00 (broad, 2H), 6.03 (broad, 2H), 3.77 (broad, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 166.18, 147.58, 146.81, 143.58, 138.29, 136.31, 133.65, 130.77, 129.39, 128.93, 126.51, 125.04, 124.36, 119.30, 94.11, 88.14, 53.25, 51.48.
**P2.** To a flame-dried 25 mL Schlenk flask was added dry DMF (5 mL), dry diisopropylamine (3 mL), compound 3 (0.1 g, 0.271 mmol) and compound 7 (0.125 g, 0.271 mmol). The reaction vessel was subjected to one cycle of freeze-pump-thaw where during the freeze cycle a spatula tip quantity of tetrakis(triphenylphosphine)palladium and Cul was added. The reaction mixture was then subjected to two additional freeze-pump-thaw cycles and heated to 80 °C for 24 h under a nitrogen atmosphere during which time the target polymer appeared to crash out of the reaction. The vessel was cooled and the precipitate isolated by filtration. This white powder was taken up in CHCl₃ and washed with sat. NH₄Cl (aq) and water (3 times). The organic layer was isolated and concentrated to a volume of approximately 1 mL and then reprecipitated from cold methanol (200 mL) to yield 0.064 g (41%) of the target polymer. GPC gave $M_n = 33,000$; PDI = 3.1, $DP = 60$. $^1$H NMR (501 MHz, CDCl₃): $\delta$ 8.3 (broad, 2H), 8.07 (broad, 2H), 7.97 (broad, 2H), 7.66 (broad, 2H), 7.51 (broad, 2H), 7.23 (broad, 2H), 7.10 (broad, 2H), 6.07 (broad, 2H), 3.85 (broad, 6H). $^{13}$C NMR (125 MHz, CDCl₃): $\delta$ 193.70, 166.24, 147.66, 146.93, 143.63, 138.63, 133.73, 133.65, 130.76, 130.68, 130.10, 129.12, 126.7, 125.14, 119.33, 93.63, 88.68, 53.39, 51.54
**rac-DP1.** The title compound was synthesized by the bulk photolysis of compound 5 in CHCl₃ using benzophenone as a triplet sensitizer. To a rubber septum-stoppered quartz cuvette was added dry CHCl₃ (3.0 mL), compound 5 (0.05 g, 0.091 mmol) and benzophenone (0.083 g, 0.456 mmol). The cuvette was sparged with argon for 15 minutes and then irradiated with a lamp for 4 h. After photolysis, the reaction mixture was concentrated *in vacuo* and purified via silica gel column chromatography using hexanes/acetone (30:1).
$^1$H and $^{13}$C NMR Spectra:

Figure 3.8.1. $^1$H NMR spectrum of 2 (500 MHz, CDCl₃).

Figure 3.8.2. $^{13}$C NMR spectrum of 2 (125 MHz, CDCl₃).
Figure 3.8.3. $^1$H NMR spectrum of pictured compound (500 MHz, CDCl$_3$).

Figure 3.8.4. $^{13}$C NMR spectrum of pictured compound (125 MHz, CDCl$_3$).
Figure 3.8.5. $^1$H NMR spectrum of 3 (500 MHz, CDCl$_3$).

Figure 3.8.6. $^{13}$C NMR spectrum of 3 (125 MHz, CDCl$_3$).
Figure 3.8.7. $^1$H NMR spectrum of 5 (500 MHz, CDCl$_3$).

Figure 3.8.8. $^{13}$C NMR spectrum of 5 (125 MHz, CDCl$_3$).
Figure 3.8.9. $^1$H NMR spectrum of 6 (500 MHz, CDCl$_3$).

Figure 3.8.10. $^{13}$C NMR spectrum of 6 (125 MHz, CDCl$_3$).
Figure 3.8.11. $^1$H NMR spectrum of 7 (501 MHz, CDCl$_3$).

Figure 3.8.12. $^{13}$C NMR spectrum of 7 (125 MHz, CDCl$_3$).
Figure 3.8.13. $^1$H NMR spectrum of P1 (500 MHz, CDCl$_3$).

Figure 3.8.14. $^{13}$C NMR spectrum of P1 (125 MHz, CDCl$_3$).
Figure 3.8.15. $^1$H NMR spectrum of P2 (500 MHz, CDCl$_3$).

Figure 3.8.16. $^{13}$C NMR spectrum of P2 (125 MHz, CDCl$_3$).
Figure 3.8.17. $^1$H NMR spectrum of rac-DP1 (500 MHz, CDCl$_3$).

Figure 3.8.18. $^{13}$C NMR spectrum of rac-DP1 (125 MHz, CDCl$_3$).
Figure 3.8.19. NOESY NMR spectrum of rac-DP1 (500 MHz, CDCl$_3$).
Figure 3.8.20. HMBC NMR spectrum of rac-DP1 (500 MHz, CDCl3).
Figure 3.8.21. HSQC NMR spectrum of \textit{rac-DP1} (500 MHz, CDCl\textsubscript{3}).
Figure 3.8.22. gCOSY NMR spectrum of rac-DP1 (500 MHz, CDCl₃).

3.9 References

(3) Ohman, Y. Nature 1938, 157, 291.
(7) Reinitzer, F. Monatsh. Chem. 1888, 9, 421.


(12) The examples are too numerous to list. For a representative example see: Ichimura, K.; Suzuki, Y.; Seki, T. Hosoki, A.; Aoki, K. Langmuir 1988, 4, 1214.


(14) See the following and references cited therein: Yaroshchuk, O.; Reznikov, Y. J. Mater. Chem. 2012, 22, 286.


Chapter 4

Norbornadiene End-Capping of Cross-Coupling Polymerizations: A Facile Route to Triblock Polymers

Adapted and reproduced in part with permission from:

* This work was initiated by T. Igarashi and H A Kang. H A Kang is responsible for the initial syntheses and characterization of MC1-MC3 and P1, P3 and P4, as well as initial triblock copolymer formation. J.R. Cox is responsible for the synthesis of P2, cross-linking experiments and sensing experiments, as well as Figures 4.1 and 4.3 and part of Table 4.1.
4.1 Introduction

The previous chapters described the utility of PPEs in applications such as chemosensing and liquid crystal alignment. Scheme 4.1 displays the molecular structures of other classes of conjugated polymers that are used in device applications. The development of transition metal catalyzed carbon-carbon bond forming reactions has increased both the ease in which these materials are synthesized as well as the variety of available structures. However, despite these advances, conjugated polymers continue to suffer from problems related to processability. The rigidity and self-associating properties of conjugated polymers limits the utility of these building blocks in materials applications exhibiting the full spectrum of mechanical properties. Specifically, the low molecular weights of these materials limits the mechanical durability necessary to realize the often-stated goal of enabling flexible electronic/photonic devices.

Scheme 4.1. Molecular structures of common conjugated polymers (top). Palladium catalyzed reactions that are employed in the synthesis of conjugated materials (bottom).
In order to retain the interesting optoelectronic characteristics of these polymers, while concomitantly maximizing their mechanical properties, groups have focused on the development of block copolymers that contain a conjugated segment. This approach is best exemplified by the elegant work of McCullough, schematically shown in Scheme 4.2.

**Scheme 4.2.** Post-polymerization end-capping of PT using the Vilsmeier reaction.

In this work, PT is formed via the Grignard Metathesis reaction (GRIM) and the bromine end-groups are removed via a quenching procedure. This is then followed by a Vilsmeier reaction and subsequent reduction to generate reactive end-groups that can be converted to macroinitiators for further radical and condensation based polymerizations. This approach is mechanistically representative of standard approaches to triblock copolymer formation and typically requires at least one change in reaction conditions after polymer formation thereby necessitating additional purification and isolation cycles to generate a competent macroinitiator. We were interested in developing an end-capping reaction that is compatible with standard palladium-mediated cross-coupling reactions and would yield a macroinitiator in a single pot reaction thereby removing the numerous isolation/purification cycles.
4.2 The Hydroarylation of Norbornadiene

The proposed catalytic cycle for the hydroarylation reaction of norbornadiene is pictured in Scheme 4.3. The transformation is mechanistically similar to the Heck reaction with one major difference – the product of carbopalladation does not possess a properly oriented β-hydrogen atom for elimination to generate the product alkene.\(^5\) Instead, formic acid is used as a hydride source to generate a palladium hydride species which subsequently undergoes reductive elimination to generate the hydroarylation product.\(^6\)

**Scheme 4.3.** Proposed catalytic cycle for the hydroarylation reaction (top). Ring strain energies associated with norbornane derivatives (bottom).

Some key features of this reaction are as follows: (i) the relief of ring strain associated with norbornadiene accelerates carbopalladation, (ii) the conditions are compatible with standard palladium catalyzed cross-coupling methods and (iii) the product norbornene is a competent monomer for ring opening metathesis polymerization (ROMP). This last feature is of utmost...
In addition, the use of deuterium labeled formic acid (DCOOH) afforded the hydroarylated product with the deuterium label on the norbornene scaffold (Figure 4.1) as anticipated from the proposed catalytic cycle. Also, there is a small resonance associated with an aryl methine (6.8 ppm) suggesting that the major side product is hydrodehalogenation. However, this product accounts for only 3-18% of the product distribution based on the results shown in Scheme 4.4. This result, in conjunction with the model reactions, suggests that hydrodehalogenation of the aryl halide is slower than carbopalladation and should not interfere with the end-capping reaction.

![Figure 4.1. Crude $^2$H NMR spectrum (bottom) (CH$_2$Cl$_2$) of the indicated transformation (top). Spectrum was taken after the removal of volatiles from the reaction mixture.](image)

### 4.4 Polymer End-capping

With an efficient coupling reaction in hand we turned our attention to the end-capping of conjugated polymers. Scheme 4.5 displays the structures of the polymers that were end-capped in this work. The conditions that were employed for the end-capping of polymerization reactions mirrored those that were used in the model reactions. Small excesses of the dihaloarene were used to increase the percentage of conjugated polymer chains that were capped with an aryl
halide thereby facilitating the incorporation of norbornene units on both ends of a given polymer chain.

Scheme 4.5. Conditions used for the end-capping of cross-coupling polymerizations (top) and the resulting end-capped polymers synthesized in this work (bottom).

All end-capped polymers were characterized via $^1$H and $^{13}$C NMR spectroscopy as well as size-exclusion chromatography (SEC). Figure 4.2 displays the $^1$H NMR spectrum of P2. The end-capped polymer displays the expected methines belonging to the norbornene end-groups
(red protons) as well as the bridgehead methines (green protons) of the triptycene unit and the \( \alpha \)-methylenes (blue) of the dialkoxy comonomer. Of particular interest is the ratio of near end-cap \( \alpha \)-methylenes of the dialkoxy monomer (small blue integral) to the norbornene methines (red protons). A perfectly efficient end-capping reaction would yield a ratio of 3:4 (red/blue); our ratio of 3:5 suggests that the reaction proceeded in a highly efficient manner.

![Figure 4.2](image-url)

**Figure 4.2.** \(^1\)H NMR spectrum of P2. Included is the molecular structure of P2 with the appropriate protons highlighted. The inset is a magnified portion of the spectrum.

Additional evidence for the efficient incorporation of norbornene end-caps comes from the behavior P2 when exposed to a catalytic quantity of Grubbs’ third generation catalyst (G3). Prior to addition of G3, P2 exhibited a \( M_n \) of 10,400 g/mol (PDI = 1.7). The \( M_n \) increased to 20,400 g/mol (PDI = 3.7) after exposure to G3 for 12 hours at room temperature indicating that P2 is a competent macroinitiator.
(red protons) as well as the bridgehead methines (green protons) of the triptycene unit and the α-methylenes (blue) of the dialkoxy comonomer. Of particular interest is the ratio of near end-cap α-methylenes of the dialkoxy monomer (small blue integral) to the norbornene methines (red protons). A perfectly efficient end-capping reaction would yield a ratio of 3:4 (red/blue); our ratio of 3:5 suggests that the reaction proceeded in a highly efficient manner.

![NMR spectrum](image)

**Figure 4.2.** $^1$H NMR spectrum of P2. Included is the molecular structure of P2 with the appropriate protons highlighted. The inset is a magnified portion of the spectrum.

Additional evidence for the efficient incorporation of norbornene end-caps comes from the behavior of P2 when exposed to a catalytic quantity of Grubbs’ third generation catalyst (G3). Prior to addition of G3, P2 exhibited a $M_n$ of 10,400 g/mol (PDI = 1.7). The $M_n$ increased to 20,400 g/mol (PDI = 3.7) after exposure to G3 for 12 hours at room temperature indicating that P2 is a competent macroinitiator.
4.5 Formation of Triblock Copolymers

The formation of triblock copolymers from P1 is schematically outlined in Figure 4.3 and is representative of our general strategy. The isolated macroinitiators P1 was treated with stoichiometric quantities of G3 for approximately 30 minutes at room temperature. The ruthenium-alkylidene terminated polymer was isolated by reprecipitation into cold hexanes and then redissolved in CH₂Cl₂. Subsequent exposure of this macroinitiator to a solution of norbornene resulted in the formation of high molecular weight triblock copolymer PNB-b-P1-b-PNB.

Figure 4.3. (a) Synthesis of PNB-b-P1-b-PNB. (b) THF SEC (UV detection 450 nm) traces of P1 (black) and PNB-b-P1-b-PNB triblock copolymer (blue).

The SEC trace in Figure 4.3 confirms the following two points: (i) the vast majority of P1 chains are end-capped with norbornene units and (ii) The ruthenium-alkylidene terminated
chains are competent macroinitiators for ROMP. The scope of this approach is shown in Scheme 4.6 and Table 4.1.

![Diagram](image)

Scheme 4.6. Conditions and monomers used for the formation of triblock copolymers.

Table 4.1. Selected results of triblock copolymerizations\(^a\).

<table>
<thead>
<tr>
<th>CP</th>
<th>macroinitiator</th>
<th>Monomer</th>
<th>block copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\text{Mn}^b) (g/mol)</td>
<td>PDI</td>
<td>Monomer (\text{Mn}^b) (g/mol)</td>
</tr>
<tr>
<td>P1</td>
<td>130,900</td>
<td>2.5</td>
<td>5</td>
</tr>
<tr>
<td>P1</td>
<td>36,400</td>
<td>1.9</td>
<td>4</td>
</tr>
<tr>
<td>P3</td>
<td>29,000(^c)</td>
<td>1.69</td>
<td>5</td>
</tr>
<tr>
<td>P4</td>
<td>23,600</td>
<td>1.8</td>
<td>6</td>
</tr>
<tr>
<td>P4</td>
<td>23,600</td>
<td>1.8</td>
<td>5</td>
</tr>
</tbody>
</table>

\(^a\)Conditions: See Scheme 4.6 for general conditions, specific conditions are outlined in the Experimental Section. \(^b\)Determined using SEC relative to polystyrene standards in THF. \(^c\)This macroinitiator was formed using Grubbs’ 2nd generation catalyst. \(\text{G3}\) exhibited significant oligomerization of the end-capped polymer.
As can be seen in Table 4.1, our approach yielded high molecular weight materials using three different strained alkenes. It has to be noted; however, that the formation of high molecular weight macroinitiators is not without limitations. Specifically, in some cases the end-capped polymers showed a tendency to oligomerize yielding intractable materials. The use of G3 which exhibits an excellent initiation to propagation ratio was an effective solution to this problem.8

4.6 Applications of Macroinitiators

In addition to functioning as macroinitiators, the end-capped CPs can also act as cross-linkers to form functional plastics/rubbers. Polynorbornene (PHB), commercially known as Norsorex, is an elastomeric material with a tunable glass transition temperature ($T_g$) that can vary from 35 to -60 °C.9 When the material is plasticized with an aromatic or hydrocarbon additive, the $T_g$ drops below room temperature and the material behaves as an elastomer. We envisioned using P1-P4 as cross-linkers for the formation of functionalized elastomers, materials that exhibit the mechanical properties of polynorbornene and the optical properties of the conjugated cross-linker.

The cross-linked materials were formed by treating a mixture of P1 norbornene with a catalytic amount of G3. The polymerizations were carried out in Teflon® wells and the resulting plastics could be peeled from the wells. Figure 4.4 displays optical images of polynorbornene cross-linked with P1 under both ambient and UV (365 nm) illumination. The material exhibits elastomeric behavior while also exhibiting the optical characteristics of P1. The material exhibited greater than 80% recovery after being uniaxially stretched to six times its initial length.
Figure 4.4. (a) Optical micrographs of PNB cross-linked with P1 in unstretched (left) and stretched (right) states. (b) Optical micrographs with 365 nm excitation light of the same material in unstretched (left) and stretched (right) states.

P2 is a soluble conjugated polymer that exhibits red-shifted photoluminescence in thin films as a result of π-π interactions. We surmised that PNB rubber cross-linked with P2 would exhibit photophysical perturbations as a result of swelling in the presence of organic solvents, possibly acting as a sensor for detection of volatile organic compounds (VOCs) in water. Figure 4.5 displays the photoluminescence spectra of this material in aqueous solutions with or without tetrahydrofuran (THF). In water, the film exhibits broad red-shifted emission consistent with interpolymer interactions such as π-π stacking. After addition of a small amount of THF (1% v:v) the emission shifts to shorter wavelengths suggesting that the material is swelling with concurrent loss of interpolymer interactions. In addition, exposure of the cross-linked material to the saturated vapor of THF shows a similar response and the emission decay at 450 nm is depicted in Figure 4.5c.
Figure 4.5. (a) Photoluminescence spectra of PNB cross-linked with P2 in water (red) and 1% THF/water (v:v) (black). (b) Optical micrograph (UV excitation at 365 nm) showing PNB cross-linked with P2 in water (right) and 1% THF/water (v:v; left). (c) Photoluminescence intensity decay (monitored at 450 nm) of the same film after exposure to the saturated vapor of THF.

4.7 Conclusion

To summarize, we have shown the utility of the hydroarylation of norbornadiene in the context of multiblock copolymer synthesis. The end-capping protocol is compatible with Stille, Sonogashira and Suzuki cross-coupling polymerizations – methods that are typically employed for the synthesis of CPs. This reaction can be carried out in a single pot fashion and generates end-capped polymers that can be subsequently transformed into ruthenium-alkylidene macroinitiators for the generation of triblock copolymers via ROMP. In addition, these end-capped materials can be used as cross-linking agents for the formation of functional rubber
scaffolds that exhibit the mechanical properties of the peripheral ROMP segments and the optical
properties of the conjugated portion. These materials also displayed utility as possible sensor
materials for VOCs. Further work is currently underway in our laboratory to use this method to
generate highly functionalized conjugated polymer nanoparticles.

4.8 Experimental Section

MATERIALS AND METHODS: Toluene, CH$_2$Cl$_2$ and THF were purified by passage through solvent
purification columns containing activated alumina. N,N-Dimethylformamide (DMF) was
distilled from MgSO$_4$ and stored over 4Å molecular sieves. Diisopropylamine was distilled from
CaH$_2$. Bicyclo[2.2.1]hepta-2,5-diene was distilled from alumina. Bicyclo[2.2.1]hept-2-ene was
distilled from sodium. 1,4-bis((2-ethylhexyloxy)-2,5-diiodobenzene$^{10}$ (1), 1,4-bis($n$-octyloxy)-
2,5-diiodobenzene$^{11}$ (3), 1,4-bis($n$-dodecyloxy)-2,5-diiodobenzene$^{12}$ (2), 5,5'-trimethylstanny1-
2,2'-bithiophene$^{13}$ (M1), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-
dioctylfluorene$^{14}$ (M3), 2,3-exo-dicarboxylic acid dimethyl ester-7-oxabicyclo[2.2.1]hept-5-ene$^{15}$
(5), and 2,3-exo-bis($ tert$-butyldimethylsilyloxy)methyl)-7-oxabicyclo[2.2.1]hept-5-ene$^{16}$ (6) and
M2b$^{17}$ were prepared according to literature procedure. All other reagents were obtained from
commercial sources and used as received unless otherwise noted.

INSTRUMENTATION: NMR spectra were recorded on Varian Mercury 300 MHz, Varian Inova 500
MHz or Varian Inova 501 MHz spectrometers. Chemical shifts were reported in ppm and
referenced to residual NMR solvent peaks (CDCl$_3$: $\delta$ 7.27 ppm for $^1$H, $\delta$ 77.23 ppm for $^{13}$C).
Mass spectra (MS) were obtained at the MIT Department of Chemical Instrumentation Facility
(DCIF) using Bruker Daltonics APEX II 3T FT-ICR-MS. Melting points were measured on a
Mel-Temp II apparatus (Laboratory Devices INC) and were not corrected. Number average molecular weights ($M_n$) and polydispersity (PDI) of polymers were obtained on a HP series 1100 gel permeation chromatography (GPC) system in THF and calibrated with polystyrene standards and utilizing both UV (450 nm) and refractive index detection.

SYNTHETIC PROCEDURES AND CHARACTERIZATION:

1,4-Bis(bicyclo[2.2.1]hept-5-en-2-yl)-2,5-bis((2-ethylhexyl)oxy)-benzene (MC1). Compound 1 (0.50 g, 0.85 mmol) and PdCl$_2$(PPh$_3$)$_2$ (II) (12.6 mg, 17.9 µmol) were placed in a Schlenk flask with a stir bar. The flask was evacuated and backfilled with nitrogen three times before addition of bicyclo[2.2.1]hepta-2,5-diene (0.40 mL, 3.93 mmol) DMF (4.0 mL) and diisopropylamine (1.0 mL). This reaction flask was subjected to three cycles of freeze-pump-thaw. Formic acid (0.20 mL, 5.30 mmol) was added slowly, and the reaction mixture was heated at 80 °C for overnight. Then, the mixture was cooled to room temperature, diluted with CH$_2$Cl$_2$ and washed with water and brine several times. After drying over MgSO$_4$, the solution was filtered, and the solvent was distilled off under reduced pressure. Column chromatography of the crude material on silica gel (CH$_2$Cl$_2$ :hexane (3:10)) provided the product as a viscous oil (0.431 g, 97%). $^1$H NMR (500 MHz, CDC$_1$$_3$): δ 6.79 (s, 2H), 6.26 (dd, 2H, $J$= 5.61 Hz, $J$= 3.05 Hz), 6.19 (dd, 2H, $J$= 5.61 Hz, $J$= 2.88 Hz), 3.85 (m, 4H), 2.97 (s, 2H), 2.93 (m, 2H), 2.90 (s, 2H), 1.71 (m, 2H), 1.63 (m, 4H), 1.59 (d, 4H, $J$= 7.85),1.56 - 1.41 (m, 8H), 1.37 - 1.31 (m, 8H), 0.97 - 0.91 (m, 12H). $^{13}$C NMR (125 MHz, CDC$_1$$_3$): δ 151.08, 137.53, 137.40, 132.26, 110.10, 70.44, 47.12,
46.27, 42.47, 40.09, 37.21, 33.14, 31.00, 29.43, 24.35, 23.32, 14.35, 11.56. HR-MS (ESI): calcd for C₃₆H₅₄O₂ [M+Na]⁺, 541.402; found 541.399.

1,4-Bis(bicyclo[2.2.1]hept-5-en-2-yl)-2,5-bis(n-dodecyloxy)-benzene (MC2). This compound was synthesized by the same procedure as described for compound MC1 using the following quantities of reagents: compound 2 (1.0 g, 1.43 mmol), bicyclo[2.2.1]hepta-2,5-diene (1.5 mL, 14.7 mmol), Pd(PPh₃)₄ (0) (40.0 mg, 35 μmol), CuI (20.0 mg, 0.10 mmol), formic acid (0.70 mL, 18.5 mmol), diisopropylamine (2.5 mL) and toluene (10.0 mL). Purification by column chromatography provided the product as a white solid (0.849 g, 93%). The final purification was achieved by recrystallization from acetone; mp 64 °C. ¹H NMR (500 MHz, CDC1₃): δ 6.77 (s, 2H), 6.25 (dd, 2H, J = 5.64 Hz, J = 3.08 Hz), 6.17 (dd, 2H, J = 5.64 Hz, J = 2.75 Hz), 3.92 (t, 4H, J = 6.3 Hz), 2.95 (s, 2H), 2.92 - 2.89 (m, 4H), 1.76 (m, 4H), 1.64 (m, 2H), 1.57 (m, 4H), 1.50 - 1.43 (m, 6H), 1.36 - 1.26 (m, 32H), 0.89 (t, 6H, J = 6.94 Hz). ¹³C NMR (125 MHz, CDC1₃): δ 151.26, 137.51, 137.41, 132.63, 110.71, 69.03, 46.89, 46.31, 42.49, 37.16, 33.52, 32.15, 29.91, 29.89, 29.88, 29.85, 29.81, 29.62, 29.58, 26.43, 22.92, 14.36. HR-MS (ESI): calcd for C₄₄H₇₀O₂ [M+H]+, 631.545; found 631.545.
1,4-Bis(bicyclo[2.2.1]hept-5-en-2-yl)-9,9-dioctylfluorene (MC3). This compound was synthesized by the same procedure as described for compound MC1 using the following quantities of reagents: 2,7-diiodo-9,9-dioctyl-fluorene (0.022 g, 0.034 mmol), bicyclo[2.2.1]hepta-2,5-diene (0.02 mL, 0.20 mmol), Pd(PPh$_3$)$_4$ (0) (1.0 mg, 0.86 µmol), aliquat® 336 (0.01 mL), tetraethylammonium hydroxide solution 20% in water (0.10 mL), formic acid (0.01 mL, 0.26 mmol), diisopropylamine (0.20 mL) and toluene (1.0 mL). Column chromatography of the crude material on silica gel (10% CH$_2$Cl$_2$ in hexane) provided the product as a viscous oil (0.016 g, 82%). $^1$H NMR (500 MHz, CDC$_1$$_3$): $\delta$ 7.57 (d, 2H, $J= 7.63$ Hz), 7.23 - 7.21 (m, 4H), 6.30 (dd, 2H, $J= 5.64$ Hz, $J= 3.05$ Hz), 6.20 (dd, 2H, $J= 5.64$ Hz, $J= 2.90$ Hz), 3.00 (s, 2H), 2.94 (s, 2H), 2.81 (m, 2H), 1.96 - 1.91 (m, 4H), 1.80 (m, 2H), 1.68 (m, 2H), 1.64 (d, 2H, $J= 8.39$ Hz), 1.46 (m, 2H), 1.23 - 1.07 (m, 20H), 0.83 (t, 6H, $J= 7.17$ Hz), 0.67 (m, 4H). $^{13}$C NMR (125 MHz, CDC$_1$$_3$): $\delta$ 151.07, 144.84, 138.90, 137.58, 126.16, 122.24, 119.16, 54.97, 48.82, 45.98, 44.19, 44.19, 42.57, 40.41, 34.05, 32.00, 30.13, 29.37, 29.30, 23.91, 22.84, 14.30. HR-MS (ESI): C$_{43}$H$_{58}$ [M]$^+$, 574.453; found 574.452.
P4. Compound 1 (1.28 g, 2.19 mmol), compound M1 (1.03 g, 2.08 mmol) and Pd(PPh₃)₄ (0) (0.088 g, 76 μmol) were placed in a Schlenk flask with a stir bar. The flask was consecutively evacuated and backfilled with argon three times prior to addition of DMF (20 mL) and THF (20 mL). This reaction flask was subjected to three cycles of freeze-pump-thaw, and the reaction mixture was heated at 70 °C. After stirring for 24 h, THF (10 mL), diisopropylamine (0.60 mL), bicyclo[2.2.1]hepta-2,5-diene (0.40 mL, 3.9 mmol) and formic acid (0.20 mL, 5.2 mmol) were added successively. The mixture was stirred for another 24 h at 70 °C, cooled to room temperature, diluted with CHCl₃, and washed with saturated ammonium chloride solution and water. After drying over MgSO₄, the solution was filtered and the filtrate was passed through a short column of silica gel with CHCl₃. The solvent was removed, and the residue was redissolved in a small volume of CH₂Cl₂ and precipitated into stirred acetone. The precipitate was separated, washed with acetone and dried in vacuo. This afforded 1.01 g of P4 as a red solid.

¹H NMR (500 MHz, CDCl₃): δ 7.53 (br, d, 2H, J= 3.58 Hz), 7.29 (br, s, 2H), 7.24 (br, d, 2H, J= 2.78 Hz), 6.28, 6.22 (br, m, end group), 4.06 (br, d, 4H, J= 5.19 Hz), 3.00, 2.94 (br, end group), 1.94 (br, m, 2H), 1.72 - 1.49 (br, m, 8H), 1.41 (br, m, 8H), 1.04 - 0.94 (br, m, 12H). ¹³C NMR (125 MHz, CDCl₃): δ 149.60, 138.28, 237.81, 126.30, 123.35, 122.79, 111.96, 72.12, 39.95, 31.01, 24.36, 23.36, 14.40, 11.55.
P3. This polymer was synthesized by the similar procedure as described for P4 at reflux condition for the polymerization and 80 °C for the end-capping reaction using the following quantities of reagent: 2,7-dibromo-9,9-dioctyl-fluorene (0.562 g, 1.02 mmol), compound M3 (0.642 g, 0.998 mmol), Pd(PPh₃)₄ (0) (3.0 mg, 2.6 µmol), 2M Na₂CO₃ (2.0 mL), aliquat® 336 (0.06 g), toluene (4.5 mL), bicyclo[2.2.1]hepta-2,5-diene (0.40 mL, 3.9 mmol), formic acid (0.20 mL, 5.3 mmol), diisopropylamine (0.50 mL). This afforded 0.722 g of P3 as a bright yellow solid. ¹H NMR (500 MHz, CDC1₃): δ 7.86 (br, d, 2H, J= 7.86 Hz), 7.73 - 7.70 (br, m, 4H), 6.32, 6.22 (br, m, end group), 3.03, 2.97 (br, end group), 2.14 (br, 4H), 1.30 - 1.07 (br, m, 20H), 0.83 (br, t, 6H, J= 7.01 Hz), 0.70 (br, 4H). ¹³C NMR (125 MHz, CDC1₃): δ 152.02, 140.69, 140.22, 126.37, 125.75, 121.70, 120.19, 55.57, 40.61, 32.03, 30.54, 30.27, 29.47, 24.13, 22.84, 14.31.

P2. This polymer was synthesized by the similar procedure as described for P4 at 80 °C using the following quantities of reagent: M2b (0.201 g, 0.665 mmol), compound 3 (0.370 g, 0.632 mmol), Pd(PPh₃)₄ (0) (15 mg, 13 µmol), Cul (7 mg, 38 µmol), toluene (5 mL), diisopropylamine (1 mL), bicyclo[2.2.1]hepta-2,5-diene (0.2 mL, 2 mmol) and formic acid (0.1 mL, 2.6 mmol). This afforded 0.09 g of orange solid. ¹H NMR (501 MHz, CDCl₃): δ 7.55 (br, 4H), 7.23 (br, 4H),
7.07 (br, 4H), 6.30 (br, endcap), 6.22 (br, 2H), 4.28 (br, 4H), 2.99 (br, endcap), 2.12 (br, 4H), 1.66 (br, 4H), 1.44 (br, 4H), 1.33-0.85 (m, 18H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 154.38, 148.03, 145.55, 128.62, 126.07, 117.60, 100.50, 70.47, 32.55, 32.51, 30.51, 30.17, 29.99, 26.87, 26.83, 23.40, 23.34, 14.77.

P1. This polymer was synthesized by the similar procedure as described for P4 at 80 °C using the following quantities of reagent: compound 2 (0.176 g, 0.25 mmol), compound M2a (0.117 g, 0.24 mmol), Pd(PPh$_3$)$_4$ (0) (11 mg, 9.5 μmol), CuI (7.2 mg, 38 μmol), toluene (3.0 mL), diisopropylamine (0.80 mL), bicyclo[2.2.1]hepta-2,5-diene (0.20 mL, 2.0 mmol) and formic acid (0.10 mL, 2.6 mmol). This afforded 0.188 g of P1 as a yellow solid. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.50 (br, 8H), 7.44 (br, 2H), 7.03 (br, 8H), 6.34, 6.26 (br, m, end group), 6.10 (br, 4H), 4.46 (br, 4H), 3.05, 3.03 (br, end group), 2.23 (br, 4H), 1.73 (br, 4H), 1.46 (br, 4H), 1.26 - 1.17 (br, 28H), 0.86 (br, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 145.29, 144.29, 125.48, 124.05, 70.38, 32.11, 30.18, 30.04, 29.89, 29.83, 29.79, 29.56, 26.53, 22.91, 14.36.

**General Procedure for ROMP Homopolymerizations.** Under nitrogen atmosphere in a glovebox, a solution of the desired monomer in CH$_2$Cl$_2$ (0.1 g/mL) was added rapidly and as one portion to a vigorously stirred solution of a desired concentration of either Grubbs’ catalyst II or III in CH$_2$Cl$_2$. The resulting mixture was stirred at room temperature for a specified period of
time before being quenched by addition of an excess amount of ethyl vinyl ether. The resulting polymers were purified by precipitating into either methanol or hexane followed by drying in vacuo.

**General Procedure for Block Copolymerizations.** A solution of the norbornene endcapped CP (P1, P2, P3, or P4) in CH$_2$Cl$_2$ (concentration of solution depended on the CP's solubility) was added in one portion to a vigorously stirred solution of an excess of Grubbs’ 3$^{rd}$ generation catalyst (~10 equiv.) in CH$_2$Cl$_2$ under nitrogen. The reaction mixture was stirred at room temperature for 30 min - 2 h before precipitation into hexanes. Isolated macroinitiator was dried in vacuo and redissolved in CH$_2$Cl$_2$. To this solution, the ROMP monomer solution of norbornene, 5 or 6 in CH$_2$Cl$_2$ was added. The copolymerization was allowed to stir 20 h and quenched by addition of a drop of ethyl vinyl ether. The reaction mixture was poured into acetone or hexane to precipitate the block copolymer. Then, the polymer was dissolved in THF and reprecipitated in hexane and collected by a centrifuge, which was dried in vacuo. All protons of each block in copolymers corresponded to those of the appropriate homopolymers in 1H NMR spectra.

**General Procedure for Cross-linked Rubber Formation.** A teflon® well was filled with 1mL of a concentrated solution of norbornene in CH$_2$Cl$_2$ (0.5 g/mL) also containing 1 mL of 0.05 g/mL P1. To this solution was added in one portion (1 mL) a solution of (0.1 g/mL) G3 catalyst. Immediately upon addition, the solution became viscous and finally ‘gel-like’. After 1 hr, the material was removed from the well and dried in vacuo.
$^1$H and $^{13}$C NMR Spectra:

**Figure 4.8.1.** $^1$H NMR Spectrum of MC1 (500 MHz, CDCl$_3$)

**Figure 4.8.2.** $^{13}$C NMR Spectrum of MC1 (125 MHz, CDCl$_3$)
Figure 4.8.3. $^1$H NMR Spectrum of MC2 (500 MHz, CDCl$_3$)

Figure 4.8.4. $^{13}$C NMR Spectrum of MC2 (125 MHz, CDCl$_3$)
Figure 4.8.5. $^1$H NMR Spectrum of MC3 (500 MHz, CDCl$_3$)

Figure 4.8.6. $^{13}$C NMR Spectrum of MC3 (125 MHz, CDCl$_3$)
Figure 4.8.7. $^1$H NMR Spectrum of P4 (500 MHz, CDCl$_3$)

Figure 4.8.8. $^{13}$C NMR Spectrum of P4 (125 MHz, CDCl$_3$)
Figure 4.8.9. $^1$H NMR Spectrum of P3 (500 MHz, CDCl$_3$)

Figure 4.8.10. $^{13}$C NMR Spectrum of P3 (125 MHz, CDCl$_3$)
Figure 4.8.11. $^1$H NMR Spectrum of P2 (501 MHz, CDCl$_3$)

Figure 4.8.12. $^{13}$C NMR Spectrum of P2 (125 MHz, CDCl$_3$)
Figure 4.8.13. gCOSY Spectrum of P2 (501 MHz, CDCl₃)
Figure 4.8.14. $^1$H NMR Spectrum of P1 (500 MHz, CDCl$_3$)

Figure 4.8.15. $^{13}$C NMR Spectrum of P1 (125 MHz, CDCl$_3$)
Figure 4.8.16. $^1$H NMR Spectrum of PNB5 (500 MHz, CDCl$_3$)

Figure 4.8.17. $^{13}$C NMR Spectrum of PNB5 (125 MHz, CDCl$_3$)
Figure 4.8.18. $^1$H NMR Spectrum of PNB6 (500 MHz, CDCl₃)

Figure 4.8.19. $^{13}$C NMR Spectrum of PNB6 (125 MHz, CDCl₃)
Figure 4.8.20. $^1$H NMR Spectrum of PNB-P4-PNB (500 MHz, CDCl$_3$)

Figure 4.8.21. $^1$H NMR Spectrum of PNB-P3-PNB (500 MHz, CDCl$_3$)
Figure 4.8.22. $^1$H NMR Spectrum of PNB-P1-PNB (500 MHz, CDCl$_3$)

Figure 4.8.23. $^1$H NMR Spectrum of PNB5-P4-PNB5 (500 MHz, CDCl$_3$)
Figure 4.8.24. $^1$H NMR Spectrum of PNB5-P3-PNB5 (500 MHz, CDCl$_3$)

Figure 4.8.25. $^1$H NMR Spectrum of PNB5-P1-PNB5 (500 MHz, CDCl$_3$)
Figure 4.8.26. $^1$H NMR Spectrum of PNB6-P4-PNB6 (500 MHz, CDCl$_3$)

4.9 References

(3) For a recent discussion on the synthesis of block copolymers containing conjugated blocks, see the following and references cited therein: Brochon, C.; Hadziioannou, G. ACS Symp. Ser. 2009, 1023, 243.


Jason R. Cox  
Organic Materials Chemist

32 Providence St  
Unit #5  
Worcester, MA 01604

Mobile: 508-579-3609
Email: jrcox3@mit.edu

Education

MASSACHUSETTS INSTITUTE OF TECHNOLOGY (MIT)  
Cambridge, MA
Ph.D. in Organic Chemistry  
June 2012
Advisor: Professor Timothy M. Swager (tswager@mit.edu)

Worcester Polytechnic Institute (WPI)  
Worcester, MA
M.S. in Chemistry  
June 2009
Advisor: Dr. Venkat R. Thalladi (vthalladi@gmail.com)

Worcester Polytechnic Institute (WPI)  
Worcester, MA
B.S. in Chemistry with Distinction  
June 2005

Experience

MIT, Department of Chemistry  
Cambridge, MA
Graduate Research Assistant  
2008-PRESENT
• Focused on the rational design, synthesis and application of photoresponsive polymeric coatings capable of aligning nematic liquid crystalline phases.
• Designed and synthesized new organic chromophores with pendant receptors for trace detection of energetic materials in collaboration with Edgewood Chemical Biological Center (ECBC).
• Designed and synthesized organic electronic materials suitable as electron-accepting units in organic photovoltaic applications.
• Trained over 50 researchers in atomic force microscopy (AFM), fluorescence spectroscopy, and UV-Vis spectroscopy.
• Mentored 1 visiting undergraduate student in organic synthesis, purification and characterization.
• Familiar with NMR, GPC, FT-IR, AFM, and DSC analysis of polymers and small molecules.

United States Marine Corps Reserves  
Devens, MA
Infantry Platoon Sergeant  
2003-2011
• Supervised the training, welfare and combat operations of a platoon of infantry Marines.
• Redesigned the perimeter security systems of a forward operating base (FOB) during a combat deployment to Fallujah, Iraq.
• Designed and implemented a thermal sensor for the detection of improvised explosive devices (IEDs) while deployed to Fallujah, Iraq. This work resulted in a Navy Achievement Medal (NAM) and was featured by a number of media outlets.
Jason R. Cox

WPI, DEPARTMENT OF CHEMISTRY WORCESTER, MA
Graduate Research Assistant 2005-2009

- Fabricated self-assembled monolayers (SAMs) capable of controlling the polymorphism of active pharmaceutical ingredients (APIs).
- Familiar with surface characterization using GATR-IR, contact angle goniometry and electrochemistry.
- Synthesized and characterized polymorphs of APIs using various crystallization techniques.
- Familiar with powder X-ray diffraction (PXRD), FT-IR, DSC and TGA analysis of organic solids. Specifically, in the identification of different polymorphs.
- Mentored 3 undergraduate students in the fabrication and applications of SAMs.
- Performed as a teaching assistant for four semesters of general chemistry.

Publications


Patents


Conferences


Awards

- Corning Fellowship (MIT) 2009
- Sigma Xi Membership (WPI) 2008
JASON R. COX

- American Institute of Chemists Award (WPI) 2008
- Navy Achievement Medal (USMC) 2008
- GRAD 2007 for most outstanding research (WPI-campus wide) 2007
- Certificate of Commendation (USMC) 2006
- Combat Meritorious Promotion (USMC) 2006
- Presidential Major Qualifying Project Award for Thesis (WPI) 2005
ACKNOWLEDGEMENTS

I must begin by thanking my advisor, Professor Timothy Swager, for instilling in me the passion and scientific creativity that is a staple of his personality and leadership style. His sense of humor and understanding have made the past four years some of my most memorable years.

I would also like to thank Professors Buchwald and Fu for serving on my committee. Their guidance and suggestions have been excellent and are greatly appreciated. Professor Joannopoulos has also served as a mentor during my time at the ISN and his commitment to ensuring the safety of our service members is unparalleled.

The research described in this thesis, and countless others, would not have been possible without the hard work of Kathy and Caitlin at Building 18 and Steve, Bill, John, Franklin, Maureen, Josh, Kurt, Marlisha, Ivan, Donna and Amy at the ISN.

The past four years in the Swager group have been amazing. I have to thank Brett, John, and Derek for all of the time spent at the board discussing chemistry, it will certainly be missed when I leave. My ISN-mates John, Yu Lin, Derek, Carlos, Stefanie, and Lionel have been excellent colleagues and I appreciate all of their advice/help in numerous endeavors over the years. I also would like to thank my colleagues at Building 18 - Jan, Olesya, Joel, Shuang, Eilaf, Birgit, Yossi, Dave, and Jeewoo – for all of their assistance and guidance.

Finally, I have to thank my beautiful wife Maegan and wonderful daughter Norah for all of their support and understanding these years. It has been such a long, long journey but I know the best years are yet to come!