THE DESIGN AND SYNTHESIS OF LINEAR AND MACROCYCLIC POLY(*PARA*-ARYLENE)S

by

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Dedicated to my Malachi Chad Salandy

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ABSTRACT:

Poly(*para*-phenylene) (PPP) has generated sustained scientific interest due to its potential as a blue-emitting material for use in Organic Light Emitting Devices (OLEDs). However, due to its highly unfavorable solubility, most traditional synthetic routes to PPP are relatively limited in their scope. In Chapter 2 we discuss the synthesis of poly(*para*-arylene)s *via* the post polymerization functionalization of a completely soluble and easily accessible precursor polymer, utilizing the metal-catalyzed [2+2+2] reaction. We expect that this versatile strategy could lead to new and interesting PPP derivatives. In Chapter 3, we employed this [2+2+2] strategy once more in the synthesis of an defective, but otherwise inaccessible alkoxy substituted poly(phenylene triptycene). We discuss the limitations of this synthetic route for the installation of the three-dimensional triptycene scaffold along the polyphenylene backbone.

Recent interest in belt-shaped *p*-polyarylene macrocycles, otherwise known as nanohoops, has been high due to their potential as a starting template for the bottom-up synthesis of armchair carbon nanotubes (CNTs). The proposed strategy involves iterative Diels-Alder cycloadditions performed in the bay-region of a structurally appropriate nanohoop. However, the unique geometry of these macrocycles also makes them relatively challenging synthetic targets. Perylene has been identified as the smallest polycyclic aromatic hydrocarbon (PAH) capable of undergoing a Diels-Alder in its bay-region. Accordingly, in Chapter 4 we discuss progress towards the synthesis of a nanohoop containing this crucial perylene moiety, from which it is hoped the aforementioned bottom-up synthetic strategy can be successfully implemented.

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CHAPTER 1:

AN INTRODUCTION TO POLYAROMATIC MACROMOLECULES

1.1 Introduction: Historical Perspective

Friedrich August Kekulé von Stradonitz is widely credited with initially proposing the circular structure of benzene in 1865.[1a] However, closer examination of history records will show that the idea was originally reported 4 years earlier by an Austrian chemist, Josef Loschmidt, with whom it is believed Kekulé had previously corresponded.[1b] Although the empirical formula of benzene had long been known by this time, understanding the nature of its unsaturation was the major challenge.[1,2] Defining benzene as having alternating single and double bonds,[1] the work of Kekulé was arguably the first major milestone in the study of aromatic compounds. More than half a century later, deeper insight into the electronic make-up of these cyclic arrays was gained through the canonical work of Erich Hückel, published throughout the 1930s.[3] Aromaticity of a structure often leads to planarity and is characterized by several physical properties such as unexpectedly high thermal stability, nonalternant bond lengths, and diamagnetic anisotropy.[4] In defining molecules with $4n+2$ π-electrons as being aromatic, Hückel's theory simplified the process of determining whether or not a specific structure was aromatic.

Polyaromatic macromolecules, large structures consisting of multiple, covalently bonded aromatic motifs, have attracted the attention of material chemists for many years. Various related architectures can result in a wide range of interesting physical and electronic properties, often quite different to those of benzene.[5] The characteristics displayed by novel molecules of this sort are not always serendipitously achieved and can typically be understood and explained through fundamental organic chemistry concepts. It is arguably the further improvement and understanding of this useful structure-property relationship that serves as continued motivation for research into macromolecular synthesis amongst chemists today.

1.2 Conjugated Polymers

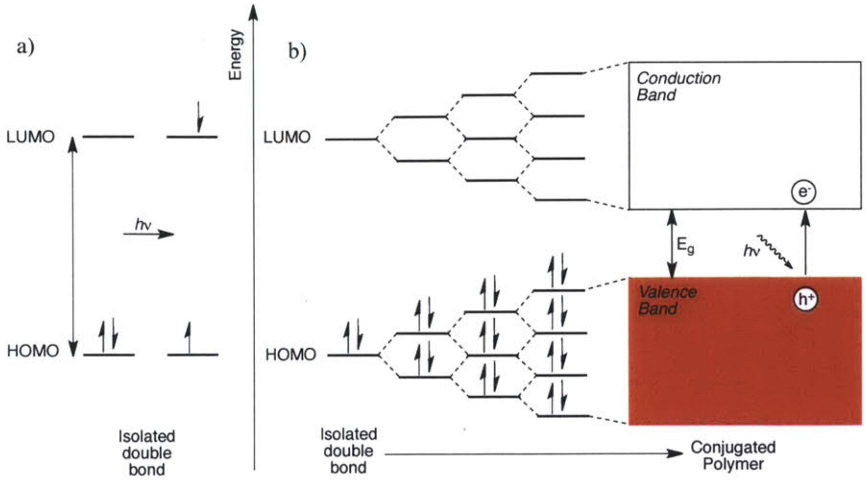


Figure 1.1. Schematic of the energy gap (E_g) between the HOMO and LUMO levels and the interaction of light with (a) small molecule MOs and (b) a conjugated polymer energy band system

Polymers have always been attractive for use in various technologies due to many advantageous properties including their strength, elasticity, flexibility, light-weight and low-cost of manufacturing, amongst others. As the main focus of a highly developed area of research, polymers have continuously received attention from a wide range of scientific disciplines in an effort to fully understand and control their properties. Accordingly, a significant portion of polymer research focuses on the development of new techniques by which the polymers may be modified, whether physically or chemically, for use in a specific application or process.[6]

The electronic properties of conjugated polymers can be influenced by organic synthesis via changes to their structural make-up.[7] Imagine an isolated double bond absorbing a photon of sufficiently high energy, E_g, the result is a π-electron from the highest occupied molecular orbital (HOMO) being promoted to the lowest unoccupied molecular orbital (LUMO), forming a singlet excited state. This excited electron may revert to its original ground energy state via non-radiative vibrational relaxation, emission of a photon from a triplet excited state which produces phosphorescence, or emission of a photon from the singlet excited state yielding fluorescence. Increased orbital overlap, facilitated by double bond conjugation, decreases the value of E_g by elevating the HOMO and depressing the LUMO. Additionally, as the extent of conjugation in a polymer increases, the density of molecular orbital states are more often thought of as an electronic band structure. The mixing of HOMO levels forms a broadened electron filled band known as the valence band and likewise, the LUMO levels form an empty conductance band (Figure 1.1). Consequently, the relatively more efficient pathway for an electron's relaxation from its excited singlet state to its ground state makes fluorescence a dominant feature of conjugated polymers.

Structural features of a conjugated polymer that influence the extent of conjugation along the polymer's backbone, such as the electron donating or withdrawing abilities of its substituents, help determine its energy band-gap (E_g). The size of the E_g is representative of the energy difference between the valence and conducting bands and is responsible for the electronic properties of the polymer. Accordingly, it is the synthetic manipulation of these interesting electronic properties that continues to make this a leading area of research amongst chemists.[8]

1.3 Polyphenylene

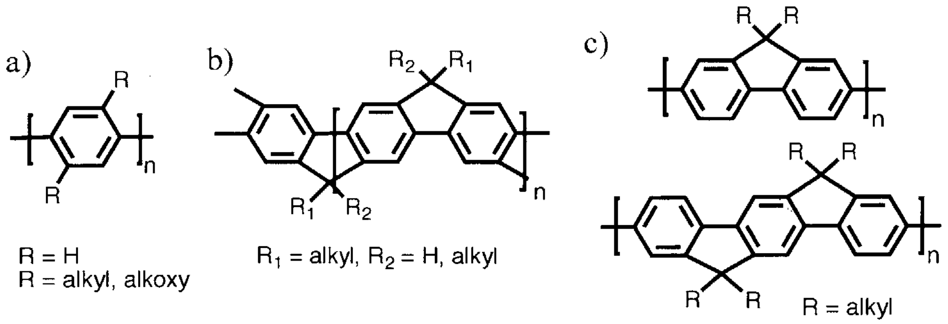
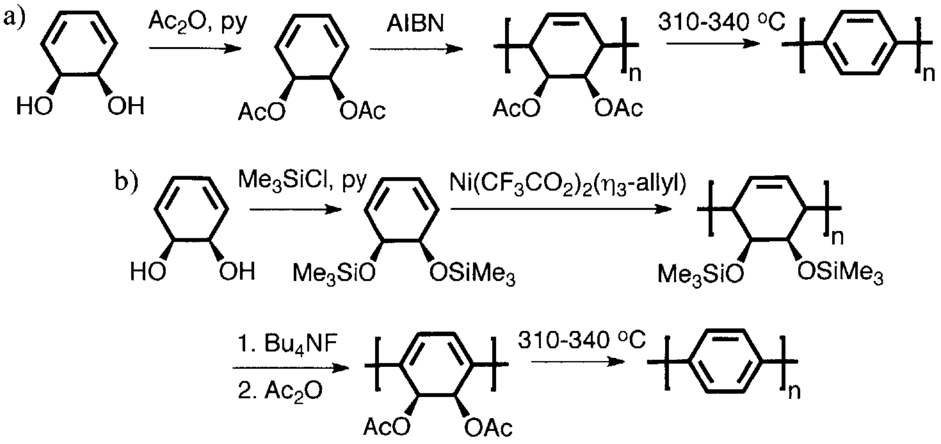
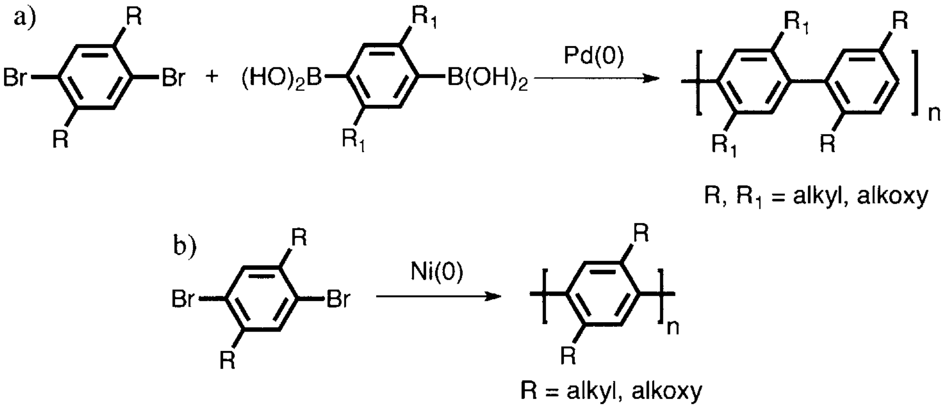


Figure 1.2. Examples of a) Poly(*para*-phenylene) (PPP) b) Ladder Poly(*para*-phenylene) (LPPP) c) a 'step-ladder' poly(*para*-phenylene)

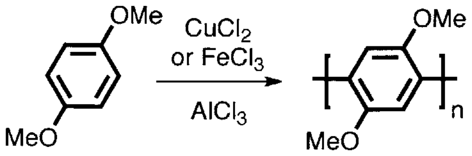
Multicolor displays such as computer monitors and televisions typically require the three basic colors, red, green and blue, which are then mixed accordingly to create other colors. However, achieving blue electroluminescence in devices using inorganic semiconductors is difficult and expensive.[9] Thus, conjugated polymers possessing a high HOMO-LUMO energy band-gap (~ 2.7-3.0 eV) and a short effective conjugation length were viewed as a viable alternative for yielding a stable, inexpensive and flexible, blue-emitting material. Due to its inherent phenyl-phenyl dihedral twist, poly(*para*-phenylene) (PPP) (Figure 1.2.a) emerged as a potentially suitable motif to achieve this goal.[10] In 1992 Leising *et al.* were the first to report blue electroluminescence (λ = 459 nm) from Organic Light Emitting Devices (OLEDs) employing PPP as the conducting layer in the device. However, due to the recalcitrant insolubility of PPP the use of a soluble polymer precursor is necessary for its incorporation into devices[11]. In light of this, solubilizing substituents were introduced on the polyphenylene backbones allowing for the synthesis of longer chains, imparting greater solubility and increasing deplanarization of the polymer. The reduced conjugation causes a hypsochromic-shift (blue-shift) in the PPP's emission due to an increased E_g, making the electronic properties of this class of polymers strongly dependent on the nature of its substituents.[12] Forced co-planarization of PPPs constitutional phenylenes corresponds with changes to the polymer's photophysical properties. The conjugation can be extended via coplanarization to a ladder poly(*para*-phenylene) (LPPP) (Figure 1.2.b) or a partially coplanarized or 'stepladder' PPP (Figure 1.2.c).[13] The inherent conformational rigidity of ladder polymers produces high photoluminescent quantum efficiencies that make them leading candidates for organic electronics.[14] Although LPPPs photoluminesce blue in solution, they are known to readily form yellow-emitting aggregates in thin films, problematic for their use in devices. Thus, research into LPPPs with structural moieties capable of inhibiting this aggregation is continually ongoing.[15]



Scheme 1.1. a) ICI route to PPP b) Grubbs' route to regioregular PPP (i.e. with all 1,4-linkages)



Scheme 1.2. Synthesis of a substituted PPP via a) Suzuki coupling b) Yamamoto coupling



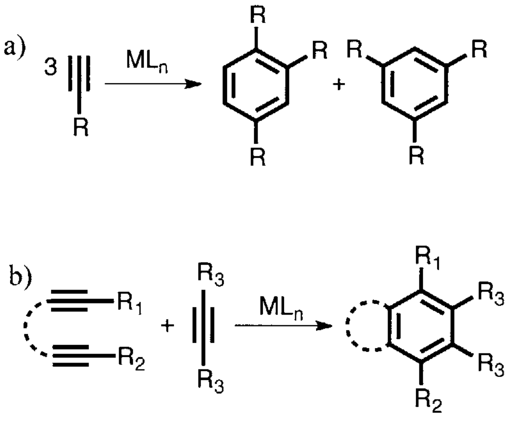
Scheme 1.3. Synthesis of substituted PPP via oxidative coupling using $AlCl_3$ with either $CuCl_2$ or $FeCl_3$

Poly(*para*-phenylene) and its derivatives are typically synthesized via direct, transition-metal catalyzed coupling between aromatic units or by aromatization of precursor polymers. The latter method, commonly used in the preparation of thin films of unsubstituted PPP, underwent initial development by ICI and Grubbs (Scheme 1.1).[16,17] More generally, substituted PPP derivatives are accessible using several tradition transition-metal coupling strategies.[18] These methods are capable of yielding longer and more soluble PPPs upon the introduction of solubilizing substituents, with the two most commonly used couplings being the Suzuki and Yamamoto polycondensations (Scheme 1.2).[19, 20, 21] Oxidative couplings employing only iron (III) chloride, or aluminum (III) chloride combined with either iron (III) chloride or copper (II) chloride, have also been shown to result in substituted PPPs (Scheme 1.3).[22] The Suzuki coupling has been reported as giving the highest degree of polymerization of the aforementioned methods.[23]

Lastly, despite the dependence of poly(*para*-phenylene)'s optical and electronic properties on its chain length, there exists a critical length beyond which no further photophysical changes are observed. This critical length is termed the 'effective conjugation length' or ECL. Due to the difficulties involved in obtaining pure, unsubstituted PPP oligomers of discrete lengths, its ECL is unknown. However, studies into the optical properties of substituted PPPs of well-defined lengths have determined its ECL to be eleven phenyl units for absorption, and seven for emission.[24]

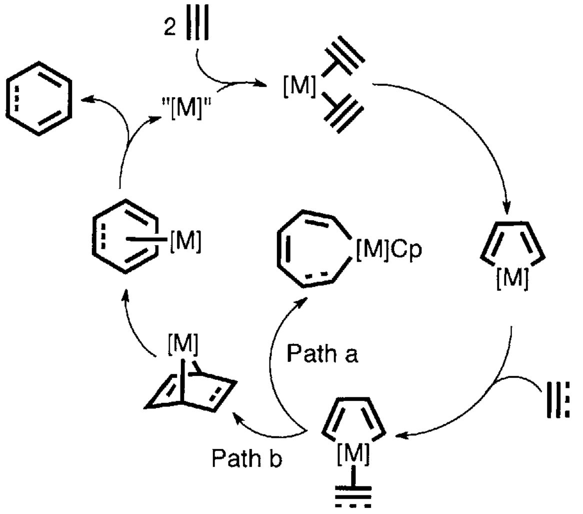
1.4 Metal-catalyzed [2+2+2] Reactions

Although the formation of benzene via the thermal cyclization of three acetylene molecules was discovered in 1866,[25] the metal catalyzed [2+2+2] trimerization of acetylene to give benzene derivatives wasn't reported until 1948 by Reppe (Scheme 1.4.a).[26] This atom-efficient, metal mediated cyclization was initially utilized in the synthesis of various polycyclic compounds. As the broad substrate scope, high functional group tolerance and efficient assembling capabilities of the [2+2+2] reaction eventually began to be realized, it soon became highly utilized in the synthesis of densely substituted aromatic substrates. Lead by researchers such Klaus Müllen, Peter Vollhardt and others, transition-metal catalyzed [2+2+2] reactions have greatly increased in popularity over the past fifteen years having been regularly employed in the assembly of large, and otherwise daunting, polycyclic aromatic hydrocarbon (PAH) structures.[27]



Scheme 1.4. a) A metal-catalyzed alkyne cyclotrimerization; a totally intermolecular [2+2+2] b) An intermolecular [2+2+2] between an α, ω-diyne and a monoalkyne

Although most early reports site cobalt complexes as the catalyst or mediating reagent for [2+2+2] cyclotrimerizations, there have since been successful applications of Ni, Pd, Rh, Ru, Ir, Fe, Zr, Cr and Nb based transition metal complexes. Due to its well known ability to promote powerful synthetic transformations and low-cost, γ^5-cyclopentadienyl dicarbonyl cobalt [$CpCo(CO)_2$] is arguably the most popular reagent for the [2+2+2] cyclization of alkynes. The use of this cobalt catalyst in the preparation of natural products, functional materials and pharmaceutically important molecules is well documented.[28] Typically, its presence in 5 mol % combined with refluxing conditions in xylenes, toluene or THF, under visible light irradiation produces good to excellent results. In some instances, a stoichiometric amount of the metal complex is required.[29] The growth of the reaction's substrate scope, coupled with increasingly complex targets, has inherently lead to the development of more specialized transition metal catalysts for the [2+2+2]. For example, γ^5-cyclopentadienyl bis(ethene) cobalt [$CpCo(C_2H_4)_2$] is commonly employed as a catalyst specifically for the co-cyclization of alkynes with alkenes. Another carbonyl containing cobalt catalyst of note is [$Co_2(CO)_8$], widely used in [2+2+2] cyclizations involving only alkynes. Recently, Okamoto *et al.* have developed a carbonyl free catalytic system employing a simple cobalt halide (such as $CoCl_2$) in combination with Zn powder and a suitable ligand for the regioselective synthesis of pyridines with all types of nitriles.[30] Despite cobalt's widespread prevalence, catalytic improvements to the [2+2+2] reaction have not been limited to only this transition metal. Although the inaugural alkyne cyclotrimerizations by Reppe were performed using a $NiBr_2$ and CaC_2 mixture, the intervening sixty-four years have seen the development of several more robust and general iterations of Nickel based catalytic systems for the [2+2+2].[31]



Scheme 1.5. The commonly accepted mechanism for a metal-mediated or catalyzed [2+2+2] cyclization.[32]

In 1974 Muller reported the formation of benzene derivatives from rhodacyclopentadienes, formed via reaction of [RhCl(PPh$_3$)$_3$] with α, ω-diynes, and monoynes.[33] Now commonly referred to as 'Wilkinson's catalyst', this metal complex has since become one of the most popular [2+2+2] catalysts due to its high reactivity with an exceptionally broad range of substrates.[34] However, Muller's work also offered some initial insight into the mechanism of the Rhodium catalyzed process.[35] In terms of mechanistic elucidation of the [2+2+2] cyclization, experimental results are often difficult to obtain and following the reaction by NMR is not possible due to the presence of paramagnetic species. Despite this, the isolation of reaction intermediates, as in Muller's case, coupled with exhaustive computational studies has proven crucial in determining the pathway of the cyclization. Although the mechanism of a specific [2+2+2] transformation is heavily dependent on the nature of the transition metal, ligands and substrate partners involved, a widely accepted mechanistic route is shown in Scheme 1.5. The first two alkynes, or the α, ω-diyne in certain instances, form a metallocyclopentadiene complex with the transition metal. This complex then incorporates the final alkyne or alkene partner via one of two mechanistic paths, prior to reductive elimination to finally furnish the cyclized product.[36]

1.5 Triptycene

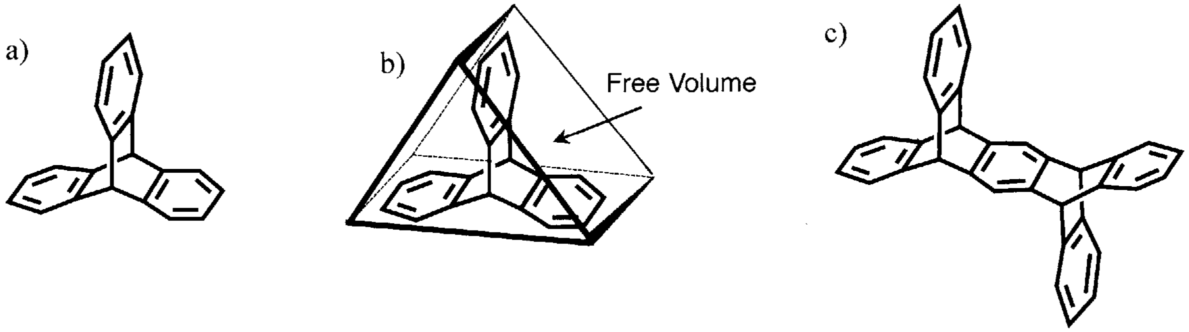
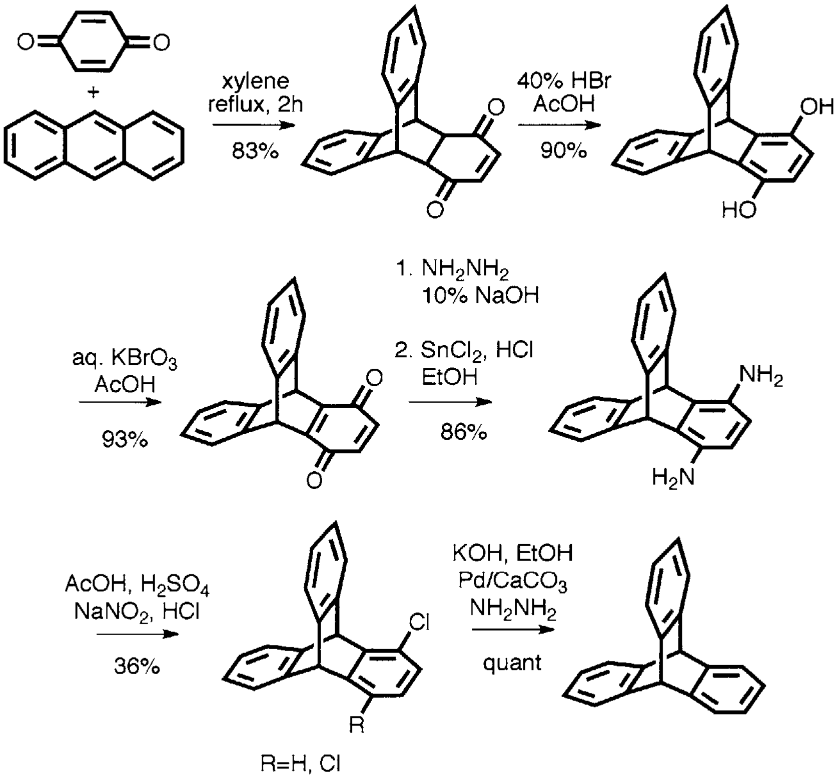


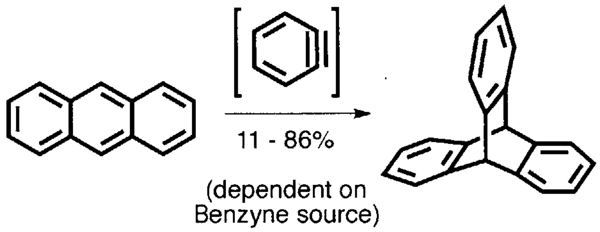
Figure 1.3. a) Triptycene; the smallest member of the iptycenes b) Schematic representation of triptycene's Internal Molecular Free Volume c) Pentiptycene

Triptycene, formally known as 9,10-dihydro-9,10-[1',2']-benzenoanthracene and comprising a rigid, three-pronged aromatic framework in a 120° orientation, is the smallest member of the iptycene family (Figure 1.3.a). Its synthesis was first reported by Bartlett in 1942 to test the stability of a radical located at one of its bridgehead positions, versus that of a geometrically unrestricted triphenylmethyl radical. The structure possesses D_{3h} symmetry and its name is derived from "the triptych of antiquity, which was a book with three leaves hinged on a common axis", in reference to its unusual shape.[37] Since the discovery of the triptycene motif, its three dimensional structure and unique electronic properties have seen it creatively applied to a variety of concepts. It has long been apparent that the three noncompliant, yet outwardly pointing, phenyl rings of triptycene are analogous to a rotary molecular machine capable of rotation through the axis of its bridgehead carbons. The scientific pursuit of continuously smaller motors stretches to before 1959 when Nobel laureate physicist Richard Feynman issued an award of $1000 to the first fabricator of an "operating electric motor only 1/64 inch cube."[38] Thus, the triptycene scaffold provided invaluable aid to researchers working on chemically powered rotary molecular motors.[39] This outwardly fixed arrangement of triptycene's constitutional phenyl rings creates a high degree of "internal molecular free volume" (IMFV) between adjacent rings (Figure 1.3.b). This structural characteristic confers several useful molecular properties to the triptycene molecule that have been exploited by researchers.[40] For instance, due to its suitably large IMFV triptycene has been reported to experience efficient host-guest interactions with molecules such as nitric oxide[41] and C_{60} fullerene.[42] Additionally, our lab has demonstrated that triptycene's uniquely high IMFV is responsible for improved porosity[43] and mechanical properties in polymers[44], an increased thin-film quantum yield of fluorescent polymers[45] and increased chromophore alignment in liquid crystals.[46]



Scheme 1.6. The first synthesis of triptycene.[37]

The original six-step procedure used in the pioneering synthesis of triptycene by Bartlett and co-workers is shown above in Scheme 1.6. Despite the slightly improved synthesis reported by Craig and Wilcox in the late 1950s,[47] it was an insightful synthesis published by Wittig around that same time employing a Diels-Alder cycloaddition of benzyne to anthracene, which enabled the molecule to be made in useful quantities (Scheme 1.7).[48] Derivatively, in the ensuing years the same Diels-Alder strategy was successfully applied to the synthesis of various substituted triptycenes and iptycene quinones.[49] Due to continuous advances in organic chemistry, recent times have witnessed the discovery of the two most synthetically efficient strategies for potentially useful triptycene derivatives, increasing the ease of their incorporation into macromolecules. In 2006 Chen and coworkers reported the selective nitration of triptycene by HNO_3 to yield two regioisomeric, trisubtituted derivatives.[50] Within the following year our lab reported a potentially useful synthesis of a functionalized triptycene diol derivatives made via a [2+2+2] cyclization.[51] This strategy allowed for the initial and subtle inclusion of a *syn*-oriented diyne into larger molecules prior to its conversion into the triptycene scaffold, potentially providing access to otherwise inaccessible structures.[52]



Scheme 1.7. Wittig's efficient synthesis of triptycene

The triptycene moiety has been successfully incorporated into several synthetic polymers, transferring its useful and unique molecular properties into a bulk system. Iptycene based ladder polymers that defy conventional wisdom about the poor solubility of rigid, shape-persistent polymers, have also been shown to form a highly porous material, akin to a "molecular cloth."[53] In another instance, the replacement of simple aromatic units in polymers made via ring-opening metathesis polymerization with non-compliant iptycene moieties, has been shown to produce materials with a lower dielectric constant. In regards to iptycene-containing conjugated polymers our lab has reported a poly(phenylene vinylene) and a poly(phenylene ethynylene), both containing the triptycene scaffold in their repeat unit, that employ their high IMFV to help improve the aspect ratio, and overall performance of liquid crystals via improved dye alignment

(Figure 1.4.a & b).[40] Additionally, we have also published the synthesis of a 2,6-polytriptycene polymer made via Yamamoto coupling (Figure 1.4.c).[54]

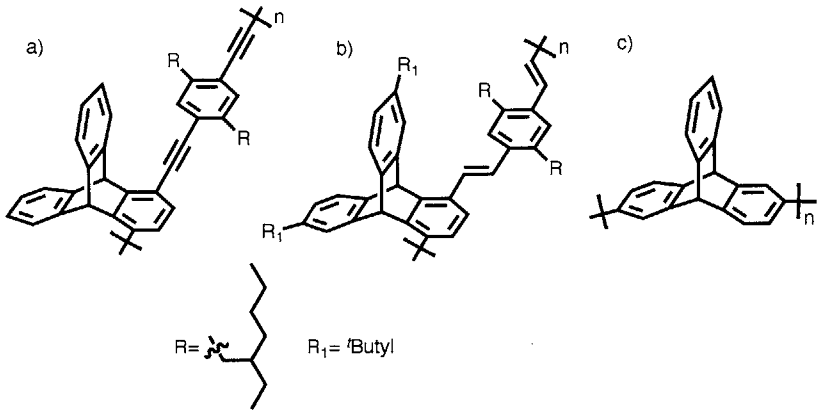
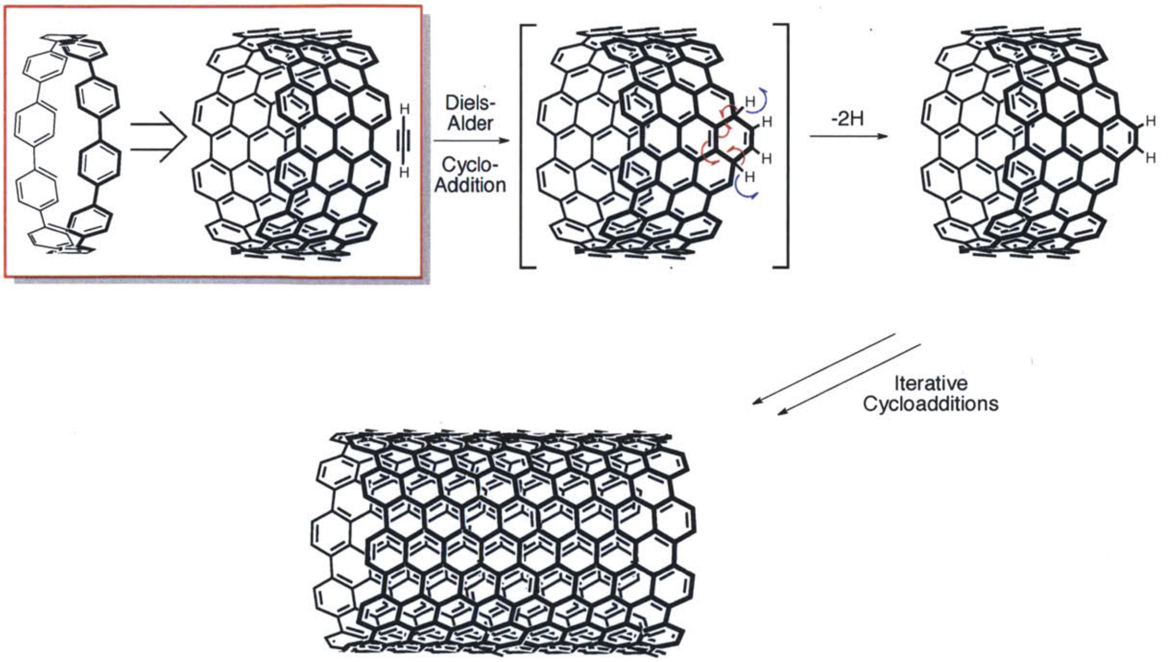


Figure 1.4. a) A triptycene-containing poly(phenyl ethynylene) b) A triptycene-containing poly(phenylene vinylene) c) Poly(2,6-triptycene)

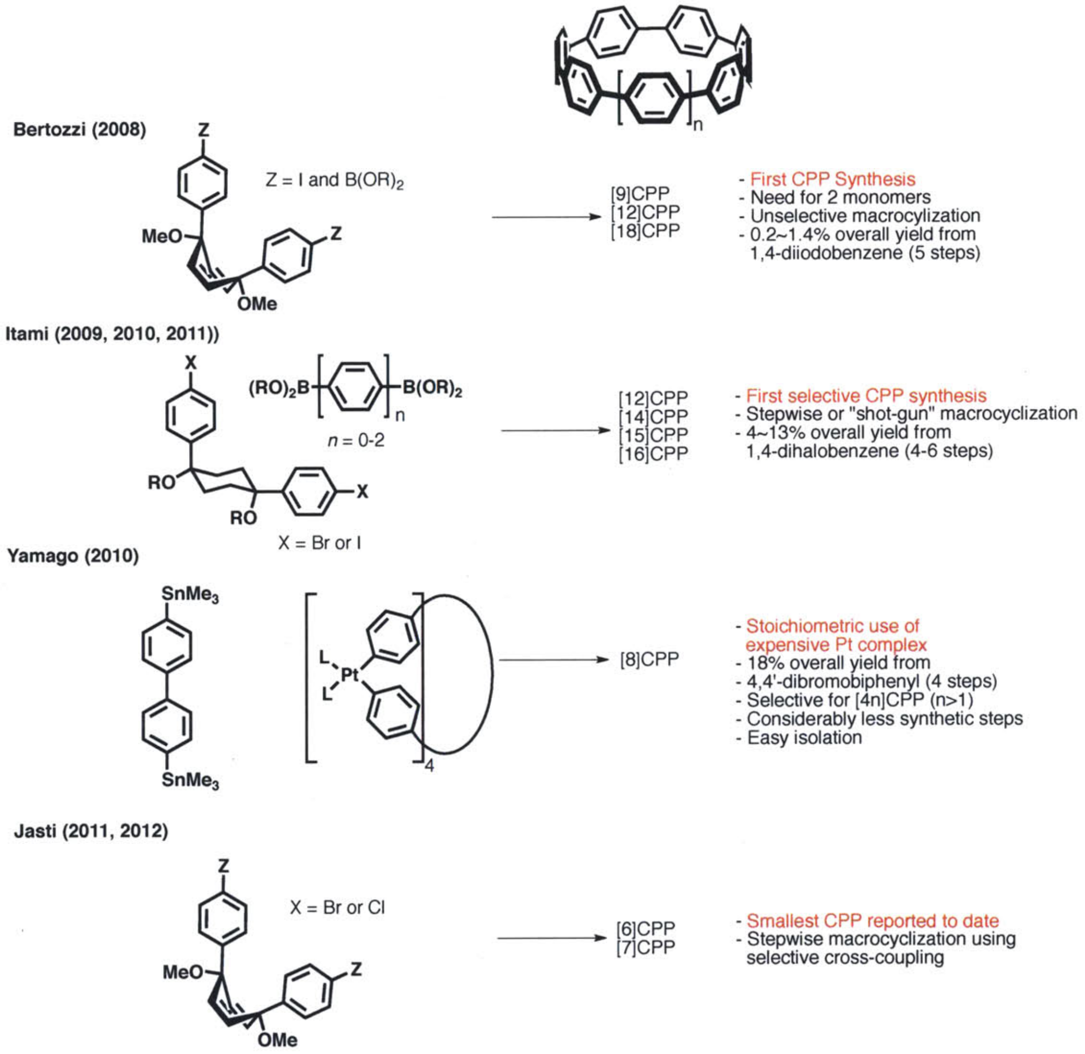
1.6 Nanohoops: Cross-Sections of Single-Walled Carbon Nanotubes

Despite continuously high interest in carbon nanotube (CNT) research, effective methods for the isolation and fabrication of chirally pure CNT samples are still relatively scarce. Due to the dependence of their electronic properties on chirality, new methods to achieve CNT samples of high purity are desirable.[55] If a carbon nanotube could be cut sideways into small segments, the resulting structures can be considered belt-like macrocycles, or nanohoops. Consequently, the synthesis of the shortest possible cross-sectional segment of an armchair CNT, a nanohoop known as cycloparaphenylene, became a noble target for many synthetic chemists with initial attempts reported as early as 1934.[56,57] Densely arranged, inwardly pointing *p*-orbitals aligned in the same plane of the macrocycle simultaneously experience electronic repulsion, making these macrocycles relatively high in energy and challenging to synthesize.[58]

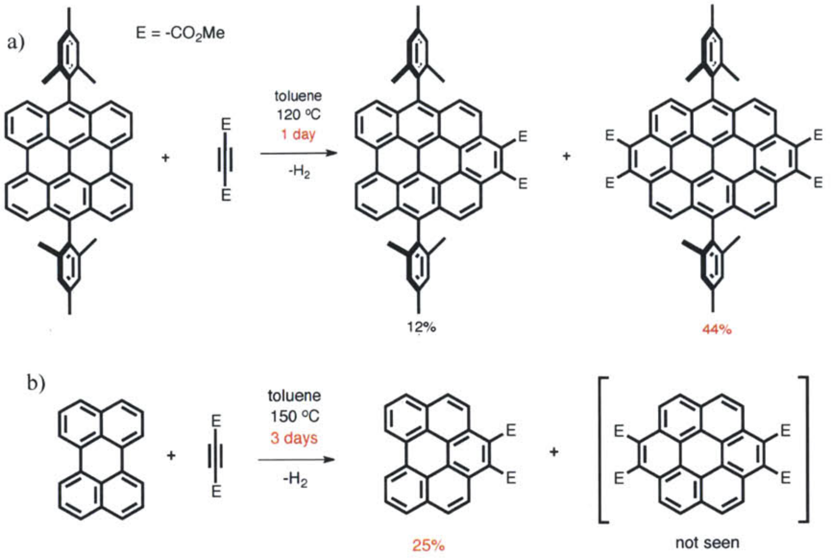


Scheme 1.8. A schematic representation of the bottom-up chemical synthesis of a short SWCNT segment. The red box highlights potential starting structures for the iterative Diels-Alder cycloadditions.[59]

Larry Scott is credited with envisioning the bottom-up chemical synthesis of short armchair CNT segments via iterative Diels Alder cycloadditions initiated in the bay-region of a structurally appropriate polyaromatic structure (Scheme 1.8).[60] Despite biphenyl's recalcitrant nature towards Diels-Alder cycloadditions, cycloparaphenylene represented a potentially appropriate starting structure for the methodology due to its unusually high macrocyclic strain energy. Thus, since the pioneering synthetic report of [9], [12] and [18]-cycloparaphenylene by Bertozzi and Jasti,[58] several research groups have actively pursued more efficient, selective syntheses of smaller cycloparaphenylenes. The past four years have seen a plethora of publications reporting [18]- to [6]-cycloparaphenylenes by the groups of Jasti, Itami and Yamago.[61] However, despite the precociously large volume of cycloparaphenylene-based literature, the great majority of its syntheses employ a similar synthetic strategy utilizing a *syn*-oriented quinoidal motif (Scheme 1.9). [62,63]



Scheme 1.9. A simplified overview of the synthetic strategies applied in accessing various cycloparaphenylenes.



Scheme 1.10. Comparison of the Diels Alder cycloadditions of Dimethyl acetylene dicarboxylate (DMAD) performed in the bay-regions of perylene and bisanthene.[59]

In a seminal 2009 communication Larry Scott *et al.* experimentally verified a crucial hypothesis involving Diels Alder cycloadditions performed with the diene-like bay-regions of PAHs. The degree of diene-character in the bay-region of a particular molecule was shown to increase correspondingly with its overall aromaticity. For instance, the activation energy barrier to a Diels Alder cycloaddition between acetylene and phenanthrene is considerably lower than that for acetylene and biphenyl. Similarly, a perylene moiety is significantly more likely to undergo a cycloaddition with a specific dienophile than is phenanthracene. This trend continues as expected for larger PAH molecules such as bisanthene, tetrabenzocoronene, etc.[59] Some researchers, such as the Scott research group, openly aim to utilize a semi-fullerene-like, corannulene-based structure for the initiation of the iterative Diels Alder strategy. However, for researchers seeking to perform the initial cycloaddition in the bay-region of cross-sectional macrocycles, or nanohoops, this 2009 report by Scott suggested that this task was perhaps beyond the capabilities of cycloparaphenylene. Accordingly, the newly issued challenge to organic chemists in this field became the synthesis of a nanohoop with an aromatic makeup akin to that perylene, or a larger PAH.

1.7 References

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CHAPTER 2:

POLY(*PARA*-ARYLENE)S VIA [2+2+2]

Adapted from: Batson, J. M.; Swager, T. M. "Poly(*para*-arylene)s *via* [2+2+2]," *Macro. Lett.* **2012**, *1*, 1121.

2.1 Introduction

Poly(*para*-phenylene)s (PPPs) are one of the most important semiconductive polymer structures with backbones comprised exclusively of phenylene groups. As a result of this centrality, these materials have received constant investigation for many years.[1] Particular interest in this class of polymers arises from their high thermal and oxidative stability and their use as a tunable blue-emitting material for organic light emitting devices (OLEDs).[2,3]

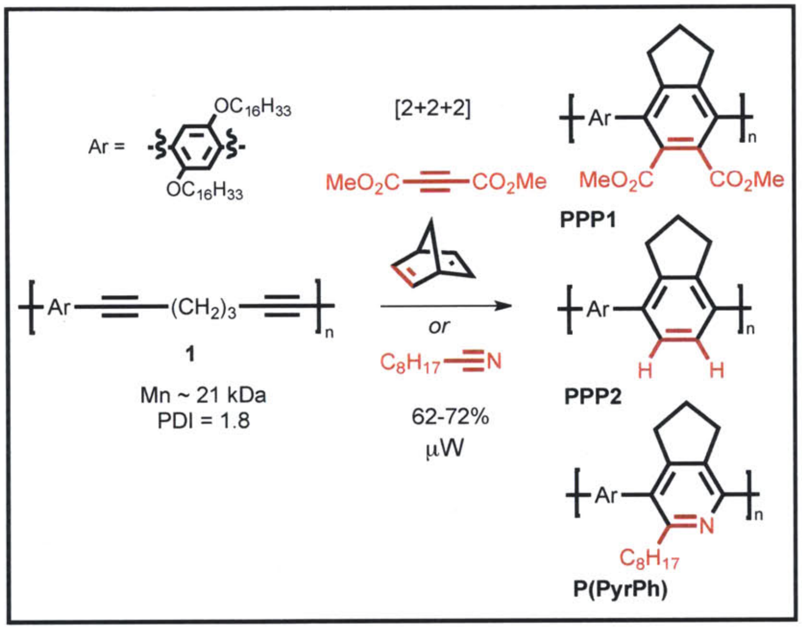
There are multiple established synthetic strategies to PPPs and related polyarylenes.[4] However, there are limitations to these different methods, particularly with regard to the creation of functional high molecular weight, and soluble PPP materials. Transition metal catalyzed cross-coupling of 1,4-functionalized phenyl groups was one of the most prominent strategies for accessing PPPs.[4] The coupling of phenyl groups lacking solubilizing side-chains by this method is limited to six repeat units.[5] Solubilizing substituents dramatically increase the length of PPPs that can be synthesized,[6] although, the polymerization rates are attenuated by the increased steric bulk. In addition, even with two substituents per phenyl group, these rigid rod polymers still exhibit limited solubility.[2,6,7] The synthesis of unsubstituted PPPs *via* the aromatization of soluble precursor polymers is the preferred route to this parent material.[1b,8,9] Although this strategy has resulted in considerably higher molecular weight polymers by circumventing insolubility issues, the resulting polymers can still possess structural irregularities resulting from incomplete aromatization.[4] Another synthetic strategy for accessing PPPs is the oxidative coupling of aryl monomers. The harsh conditions used in this process are less favorable and only low molecular weight oligomers are typically possible from these methods, regardless of solubilizing substituents.[4,9]

The substituents attached to PPP play an integral role in the polymer properties and can determine their intra- and interchain interactions.[7b] The most readily accessible 3,5-substitution pattern along the PPP backbone generates a regular structure that can promote inter-chain associations that affect the solubility of the polymer.[4] The phenyl-phenyl junctions are sensitive to the steric interactions induced by the substituents and thus substituted PPPs have twisted, non-planar conformations and absorption and emission spectra that are blue shifted relative to unsubstituted analogs.[10]

2.2 Synthesis

In considering new synthetic strategies for polyarenes, we decided to take a post-polymerization functionalization approach. This has the advantage that we could choose a polymerization that is known to provide access to higher molecular weight materials and then convert it to the final polymer. To accomplish this we selected the transition metal-mediated [2+2+2] reaction as a method capable of generating a polyarene with few defects. An added bonus of this approach was that [2+2+2] reactions are a proven method for efficiently forming dense substitution patterns in aromatic systems.[11] Additionally, by utilizing nitriles as one of the constituent elements,[11] *N*-heterocyclic analogs are readily accessible from a single precursor polymer (Scheme 2.1). In total, the combination of highly soluble starting polymers such as **1**, and the wide range of viable acetylene partners, offers an exciting new route to various poly(*para*-arylene)s.

The success of this method required a solubilizing phenylene group to be included in Polymer **1**. Previously, end-capped oligomers of Polymer **1** had been synthesized using traditional Sonogashira-polymerization methods.[12] Thus, with a slight excess of 1,6-heptadiyne and 1,4-bis(hexadecyloxy)-2,5-diiodobenzene, we were able to isolate Polymer **1** with a suitably high molecular weight for our studies $(M_n = 20.5\ k,\ PDI = 1.8\ \ DP \approx 32)$. However, considering that Sonogashira polymerizations performed between aryl co-monomers can produce much higher molecular weights,[13] we are confident that related structures of higher molecular weight analogs of **1** could be synthesized.



Scheme 2.1. The synthesis of poly(*para*-arylene)s *via* [2+2+2] with dimethyl acetylene dicarboxylate, norbornadiene and nonanenitrile.

PPP1 and **PPP2** were isolated in moderate yield after the reaction of Polymer **1** with dimethylacetylenedicarboxylate (DMAD) and norbornadiene respectively, using Wilkinson's catalyst $[Rh(PPh_3)_3Cl]$.[14] Accessing pyridine-containing compounds *via* [2+2+2] reactions using nitriles not activated with electron withdrawing groups was a challenging task relative to the phenyl-containing analogs.[11] Gratifyingly, we were able to achieve the desired transformation using nonanenitrile with a catalytic system comprised of hexahydrate cobalt (II) chloride, zinc and 1,2-bis(diphenylphosphino)ethane.[15]

2.3 Characterization of Poly(para-arylene)s

These reactions were initially performed under an argon atmosphere at 100 °C, in PhMe (16 hours) and the resulting polymers, **PPP1**, **PPP2** and **P(PyrPh)**, were analyzed by NMR, GPC, IR and UV-Vis spectroscopy to determine the efficiency of the [2+2+2] reaction as a post-polymerization functionalization reaction. Upon analysis of data from these conditions, it was evident that the desired transformation occurred but yet apparent via ^{13}C-NMR that alkyne functionality was still present within the polymers. This result reflects the challenge of synthesizing homogeneous polyarylenes by post-polymerization reactions, wherein quantitative yields are required.[12]

We hypothesized that the incomplete conversion in our post-polymerization reaction was the result of the poor solubility of our product polyarene under these reaction conditions. Thus, we turned to conditions wherein the reaction could be heated rapidly to higher temperatures to circumvent competitive aggregation/precipitation. Our optimized reaction reactions were therefore performed with microwave heating (1 hour, 150 °C, in PhMe). No solid precipitate was observed in the crude mixture when microwave conditions were employed. The resulting isolated polymers displayed a complete loss of detectable alkyne groups as determined by infrared spectroscopy and ^{13}C-NMR. As expected, the products have limited solubility in typical organic solvents, presumably as a result of their rigid-rod backbone structures.

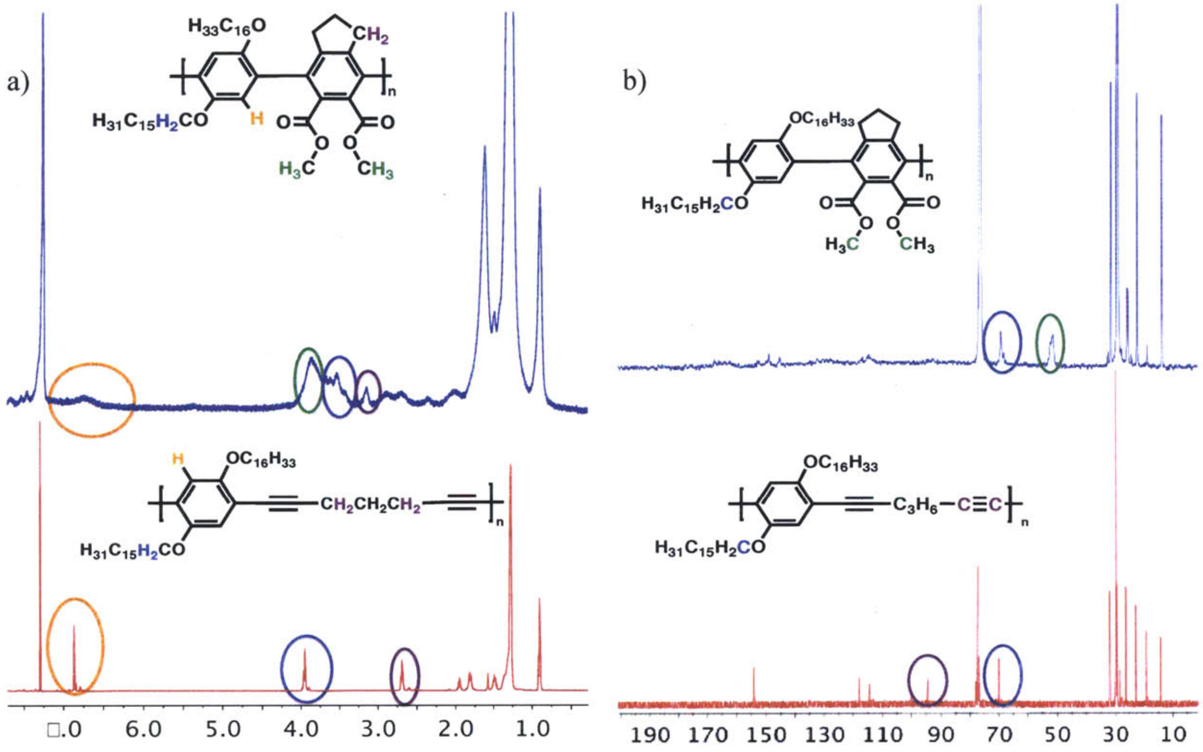


Figure 2.1. a) ^{1}H-NMR and b) ^{13}C-NMR spectra of Polymer **1** before (*red*) and after (*blue*) [2+2+2] reaction with DMAD (**PPP1**). Key functional groups and their resonances are indicated for clarity.

The NMR spectra of **PPP1**, **PPP2** and **P(PyrPh)** (Spectra 2.3, 2.5, 2.7 in Appendix) are best compared directly with Polymer **1** as shown for **PPP1** in Figure 2.1. Although the ^{1}H-NMR data alone is insufficient evidence for the complete conversion of **1** to a polyarene, it crucially shows the incorporation of key elements. Polymer **1**'s sharper ^{1}H-NMR spectrum relative to **PPP1** is due to its greater flexibility. As indicated in Figure 2.1a, the methylenes between the alkynes shift, and a new methyl ester signal is observed. Infrared Spectra of the product polyarenes proved to be the most convenient method for discerning the extent of conversion of the alkyne groups from Polymer **1** into aryl groups. Additionally, the incorporation of any further functional groups can be easily monitored this way. Representative infrared spectra of the optimized process are shown in Figure 2.2.

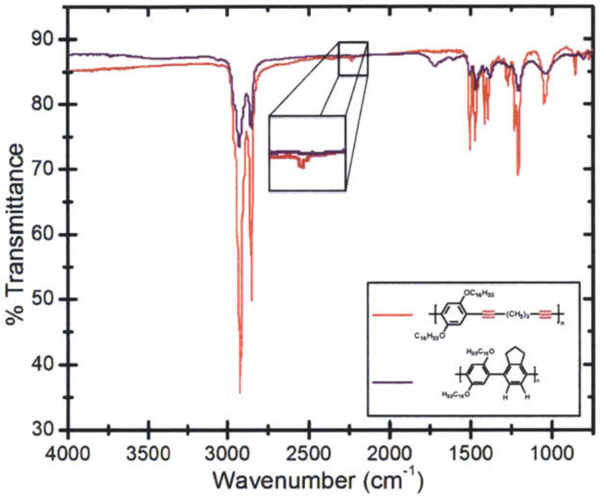


Figure 2.2. Infrared Spectra of polymer **1** (*red*) and **PPP2** (*purple*)

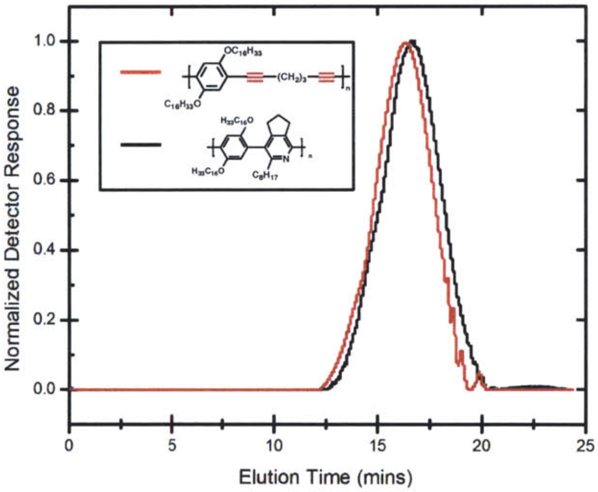


Figure 2.3. THF GPC traces (UV detection 254nm) of starting Polymer **1** (*red*) and **P(PyrPh)** (*black*).

We also considered that potential crosslinking reactions between alkynes in different polymer chains could yield defects in the final structures. However, it appears that we successfully negated cross-linked product formation by employing an excess of the DMAD, nobornadiene, or nonanenitrile partner during our reactions. As determined by GPC, the polymers before and after the [2+2+2] displayed a monomodal chromatogram with little change in the apparent molecular weight. Cross-linked material would have produced a considerably higher mass and a distorted GPC trace of the final polymers (Figure 2.3).

2.4 Discussion

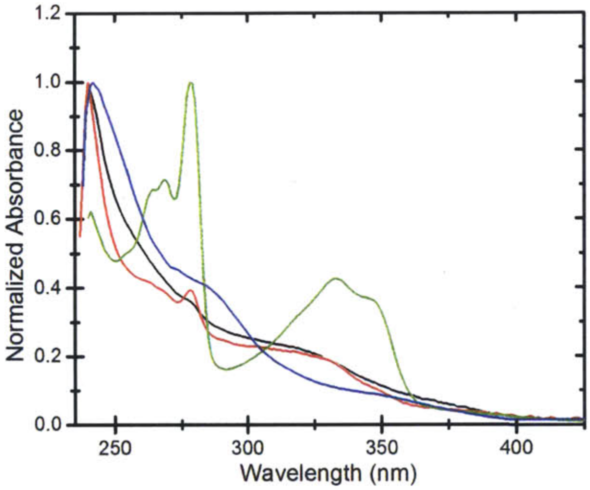


Figure 2.4. Comparison of the UV-Vis spectra for Polymer **1** (*green*), **PPP1** (*black*), **PPP2** (*red*) and **P(PyrPh)** (*blue*).

The conjugation length in poly(*para*-arylene)s is directly correlated to the dihedral twist between adjacent aryl groups. This twist is modulated by the steric interactions of the respective substituents.[4] As a result, the different acetylenic partners in our [2+2+2] reaction should produce varying optical bands gaps in the product polymers. These differences are revealed in the UV-Vis absorption spectroscopy (Figure 2.4). The minor differences in the absorption onset at long wavelength of the product polymers suggest that the interactions between the fused five-membered rings and the ethers on adjacent arylenes are the dominant steric interactions. This can be deciphered specifically in the band gap of **PPP2**, which lacks the ester or hydrocarbon substituents of **PPP1** or **P(PyrPh)** respectively, but still possesses a similar absorption spectrum. Comparisons of the absorption spectra can also be used as a crude estimate of extent of conversion as previously shown for oligomers of Polymer **1**.[16] Product polymers that possess a low degree of conversion from Polymer **1** have been seen to maintain absorption features of the starting polymer, once more suggesting that we have achieved a high degree of post-polymerization conversion[16,17].

2.5. Conclusion

In conclusion, we have demonstrated the viability of the metal-catalyzed [2+2+2] reaction to efficiently furnish minimally-defective, high-molecular weight poly(*para*-arylene)s starting from readily accessible, highly soluble polymers. In demonstration of the potential versatility of this strategy, we prepared two different poly(*para*-phenylene)s and a poly(*para*-pyridylene). We found the use of a microwave critical in obtaining high-quality PPPs. Further studies to extend the application of this strategy to other polymers is now underway in our lab.

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2.7 Experimental Procedures

Materials: All reactions were carried out under a flow of argon gas using standard Schlenk techniques unless otherwise stated. All photophysical experiments were performed with spectral grade chloroform. Toluene was obtained from a dry solvent still. 1,4-bis(hexadecyloxy)-2,5-diiodobenzene was prepared according to a literature procedure. 98 % purity 1,6-heptadiyne was procured specifically from Aldrich and all other reagent grade materials were purchased from various commercial sources and used as received unless otherwise stated.

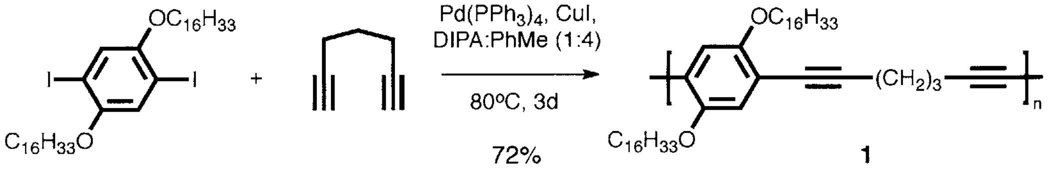
NMR Spectroscopy: ^{1}H- and ^{13}C- NMR spectra for all compounds were acquired on Varian Mercury 300 MHz, Varian Inova 500 MHz or Varian Inova 501 MHz spectrometers. The specific instrument is noted below each spectrum. Chemical shifts are reported in ppm and referenced to residual NMR solvent peaks. ($CDCl_3$: δ 7.26 ppm for ^{1}H, δ 77.2 ppm for ^{13}C. $C_6D_4Cl_2$: δ 128.5 ppm for ^{13}C.)

Gel Permeation Chromatography (GPC): Number average molecular weight (M_n) and polydispersity (PDI) of polymers were obtained on a Hewlett Packard series 1100 HPLC instrument equipped with a Mixed-C (300 x 7.5 mm) column. This GPC system utilized both UV (245 nm) and refractive index detection at a flow rate of 1.0 mL/min in tetrahydrofuran and calibrated relative with polystyrene standards purchased from Polysciences, Inc.

Infrared (IR) Spectroscopy: IR spectra were recorded on a Thermo Scientific, Smart-iTR, Nicolet 6700-FT-IR.

Absorption and Emission Spectroscopy: Fluorescence spectra were measured on a SPEX Fluorolog-τ3 fluorometer (model FL-321, 450 W Xenon lamp) using right-angle detection. Ultraviolet-visible absorption spectra were measured with an Agilent 8453 diode array spectrophotometer and corrected for background signal with a solvent filled cuvette.

Microwave: A CEM Discover Microwave was used for all microwave reactions (150W, 30PSI).



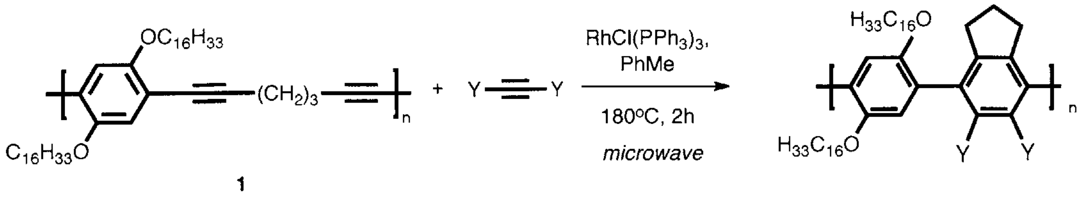
Polymer 1: 1,6-heptadiyne (681 mg, 7.40 mmol), 1,4-bis(hexadecyloxy)-2,5-diiodobenzene (5.92 g, 7.30 mmol), $Pd(PPh_3)_4$ (171 mg, 0.150 mmol), copper iodide (I) (139 mg, 0.730 mmol), dry toluene (20.0 mL) and diisopropylamine (5.00 mL) were added under a flow of argon to a flame-dried schlenk flask. The mixture was then purged *via* freeze, pump, thaw (3x) and heated to 80 °C for 3 days. Upon cooling, water was added to the reaction mixture followed by extraction with diethyl ether (3x). The combined organic layers were then washed with aq. NH_4Cl, and then with brine. After drying the separated organic layer with Na_2SO_4 it was then filtered and concentrated *in vacuo* to give a crude solid product. This residue was redissolved in a small volume of chloroform and precipitated into stirring methanol (~ 500 mL) to yield a light yellow product polymer (2.94 g, 72 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.83 (s, 1 H), 3.92 (t, 2 H), 2.66 (t, 2 H), 1.92 (t, 1 H), 1.78 (m, 2 H), 1.45 (m, 2 H), 1.24 (br s, 24 H), 0.87 (t, 3 H).

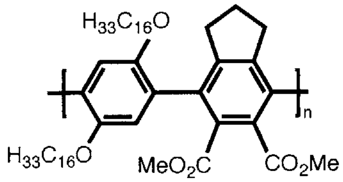
^{13}C NMR (500 MHz, $CDCl_3$): δ 153.7, 117.3, 113.9, 95.5, 77.6, 69.7, 32.1, 29.8 (multiple resonances), 29.6 (multiple resonances), 29.5, 28.4, 26.3, 22.9, 19.2, 14.3.

GPC (THF): M_w/M_n = 37 800/20 500.

IR: 2922.1, 2852.2, 2360.2, 2342.0 (CO_2), 2233.47, 1500.4, 1467.3, 1410.9, 1388.9,1341.4, 1307.3, 1270.9, 1228.1, 1205.4, 1034.2, 860.5, 721.0.



PPP1, PPP2



PPP1

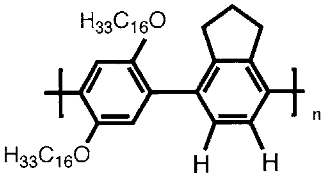
PPP1: Polymer **1** (160 mg, 0.247 mmol) and Wilkinson's catalyst/[$RhCl(PPh_3)_3$] (57.2 mg, 0.062 mmol) was added to a flame-dried microwave vial that had been back-filled with Argon. Once resealed, the microwave vial was then quickly purged and back-filled with argon three more times upon which dry toluene (4.0 mL) and dimethyl acetylene dicarboxylate (578 mg, 4.07 mmol) were added. The entire reaction mixture was then given a final purge *via* freeze, pump, thaw (3x) before being heated to 180 °C and stirred for 2.0 h in the microwave. Upon cooling to room temperature diethyl ether was added to the crude reaction mixture and washed with water (3x) and once with brine. After drying the separated organic layer with Na_2SO_4 it was then filtered and concentrated *in vacuo* to give a crude solid product. This residue was redissolved in a small volume of chloroform with the assistance of sonication and heat and precipitated from stirring hexanes (~ 500 mL) to yield a slightly orange solid as the product polymer (121 mg, 62 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.76 (br, 1 H), 4.11-3.34 (br m, 5 H), 3.26-3.09, 3.03-2.53, 2.35, 2.18-1.90, 1.90-1.03, 0.88 (br, 3 H).

^{13}C NMR (500 MHz, $CDCl_3$): δ 69.8 (br), 52.1 (br), 32.1, 29.9, 29.5, 26.3, 26.1, 22.8, 19.3, 14.2.

GPC (THF): M_w/M_n = 57 500/25 500.

IR: 2922.6, 2852.4, 1732.7, 1501.4, 1466.4, 1436.1, 1379.0, 1208.3, 1034.9, 870.4, 808.7, 793.3, 781.6, 774.4, 754.7, 739.0, 734.1, 722.9.



PPP2

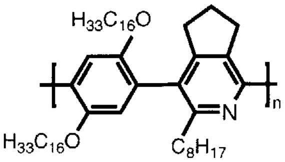
PPP2: The same procedure for **PPP1** was followed with the crude polymer being precipitated from rapidly stirring methanol instead of hexanes (70 %).

^{1}H NMR (500 MHz, $CHCl_3$): δ 4.32-3.51, 3.28-2.97, 2.86-2.57, 2.25-1.97, 1.36, 0.94, 0.27 (Dow Corning silicone grease).

^{13}C NMR (500MHz, $C_6D_4Cl_2$): δ 32.6, 30.4, 30.0, 26.8, 23.3, 13.4.

GPC (THF): **PPP2** was not soluble enough to yield a GPC trace in THF.

IR: 2923.0, 2852.7, 1716.9, 1700.1, 1683.7, 1652.8, 1500.6, 1466.5, 1377.2, 1303.7, 1262.1, 1205.1, 1035.7, 736.3, 733.4.



P(PyrPh)

P(PyrPh): Polymer **1** (160 mg, 0.247 mmol), cobalt (II) chloride hexahydrate (11.7 mg, 0.050 mmol, 0.20 eq), 1,2-Bis(diphenylphosphino)ethane (24.6 mg, 0.062 mmol) and zinc (4.80 mg, 0.074 mmol) were added to a flame-dried microwave vial back-filled with Argon. Once resealed, the microwave vial was then quickly purged and back-filled with argon three more times upon which dry *N*-methyl-2-pyrrolidone (2.00 mL) and nonanenitrile (3.50 mL, 19.8 mmol) were added. The reaction mixture was then sparged with argon for 30 minutes before being heated to 180 °C and stirred for 2 h in the microwave. Upon cooling to room temperature, distillation was used too isolate the crude product. Dichloromethane was added to this residue and this organic layer was then washed with water (3x) and once with brine. After drying the separated combined organic layer with Na_2SO_4 it was then filtered and concentrated *in vacuo* to give the crude solid product. This residue was redissolved in a small volume of chloroform and precipitated from stirring methanol (~ 500 mL) to yield a slightly yellow solid as the product polymer (139 mg, 72 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.83 (br, 1 H), 3.92 (br, 2 H), 2.66 (br, 2 H), 1.92 (br, 1 H), 1.78 (br, 2 H), 1.43-1.05 (br, 27 H), 0.87 (br, 3 H).

^{13}C NMR (500 MHz, $CDCl_3$): δ 154.2, 117.8, 70.2, 32.7, 30.5, 30.4, 30.2, 30.1, 30.0, 26.8, 23.4, 14.9.

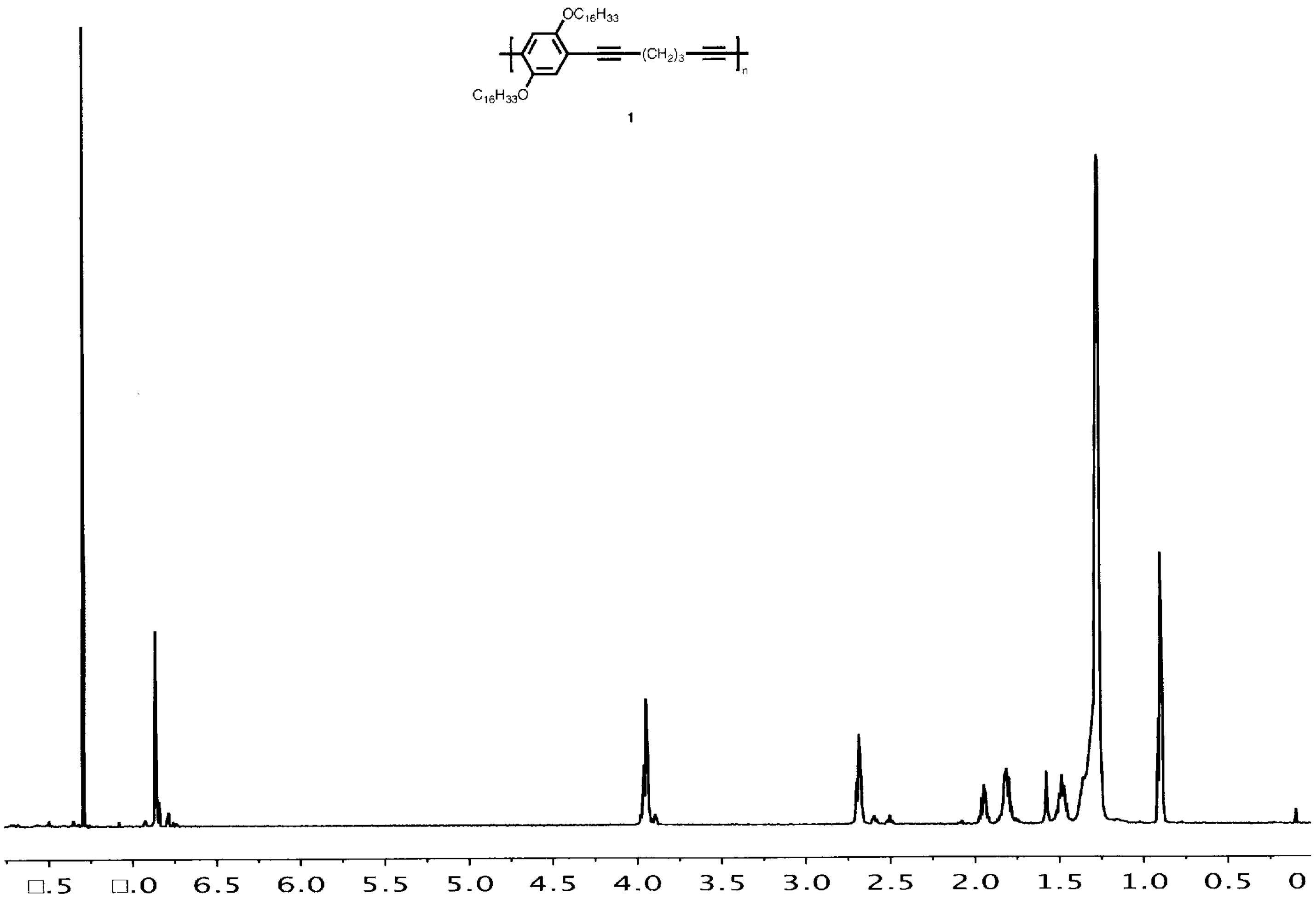
GPC (THF): M_w/M_n = 42 900/19 500.

IR: 2917.8, 2850.7,1501.8, 1493.7, 1479.0, 1468.1, 1451.4, 1442.4, 1426.7, 1411.4, 1390.9, 1370.4, 1344.7, 1228.2, 1205.8, 1048.5, 855.8, 748.7, 723.5.

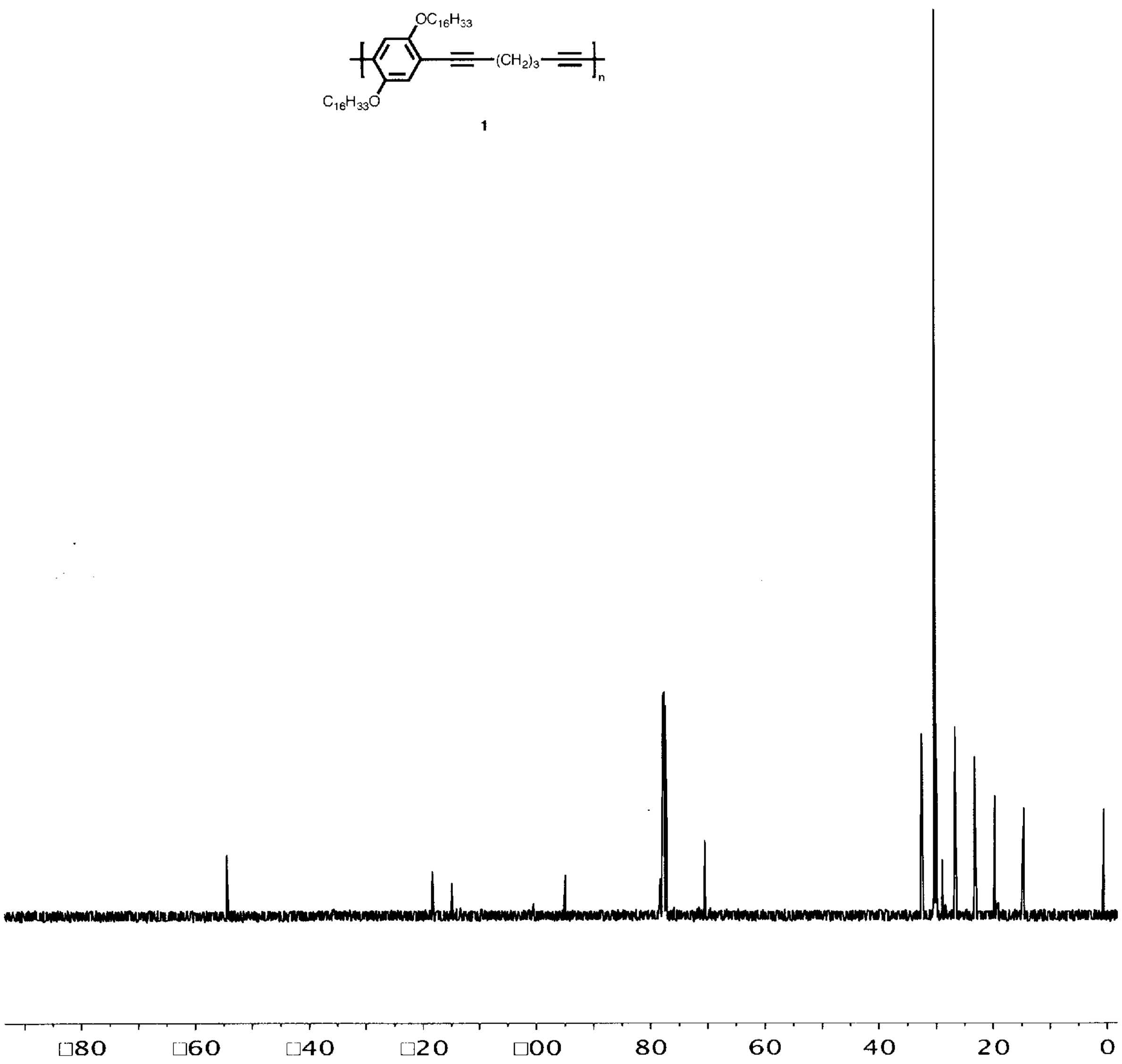
Chapter 2 Appendix:

^{1}H-NMR and ^{13}C-NMR Spectra

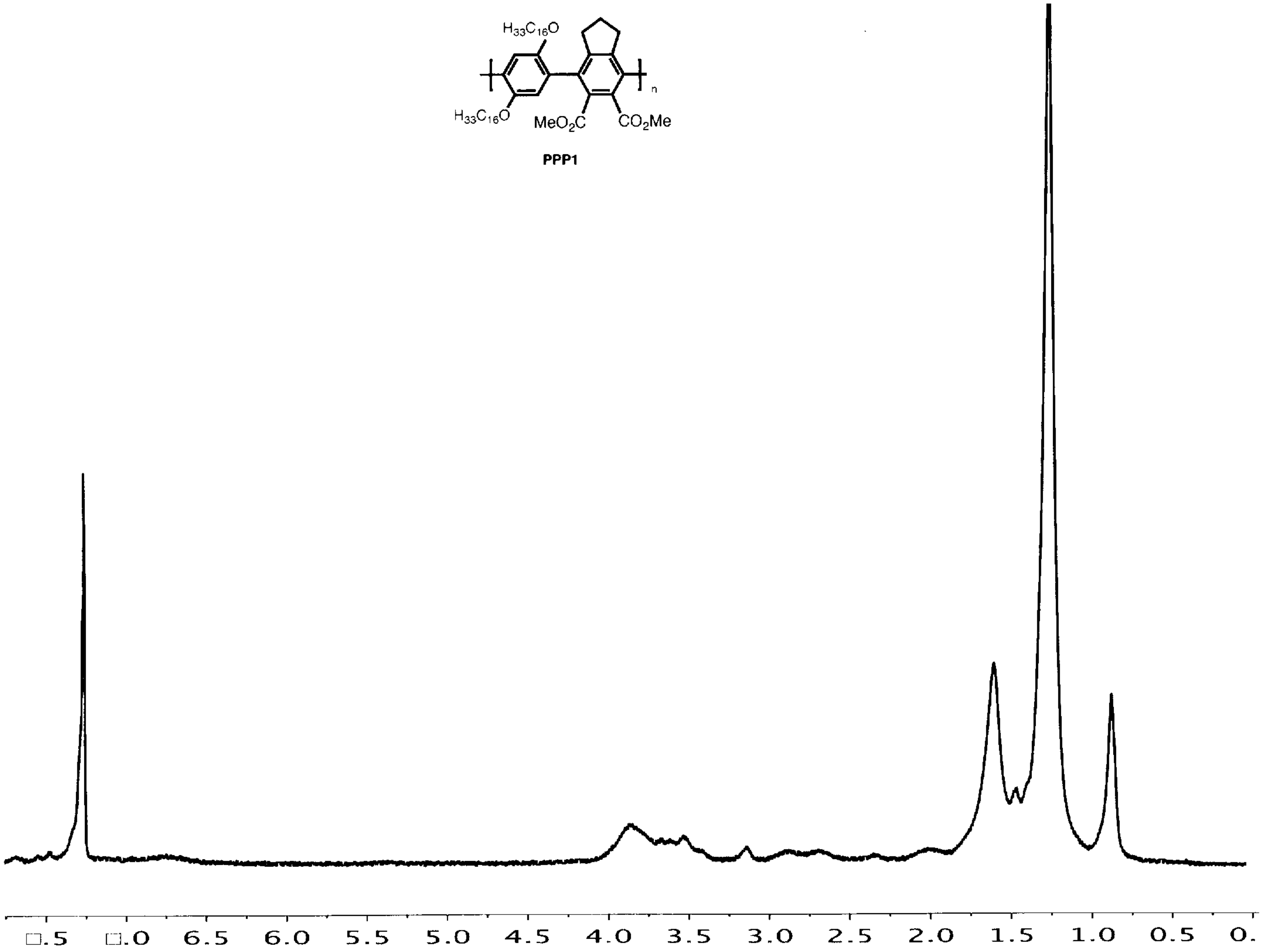
And Additional Figures



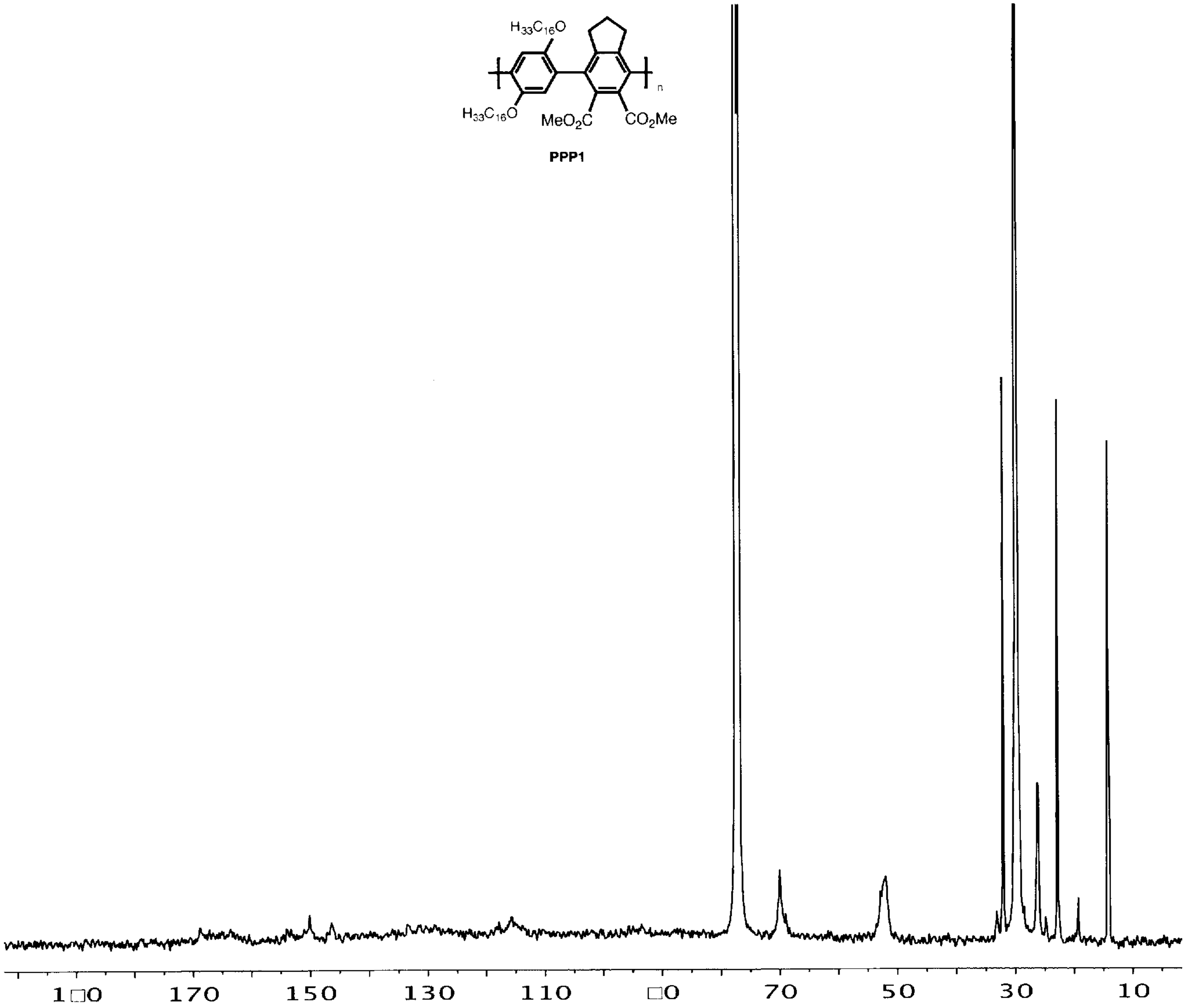
Spectrum 2.1. ^{1}H-NMR Spectrum of **Polymer 1** (500 MHz, $CDCl_3$).



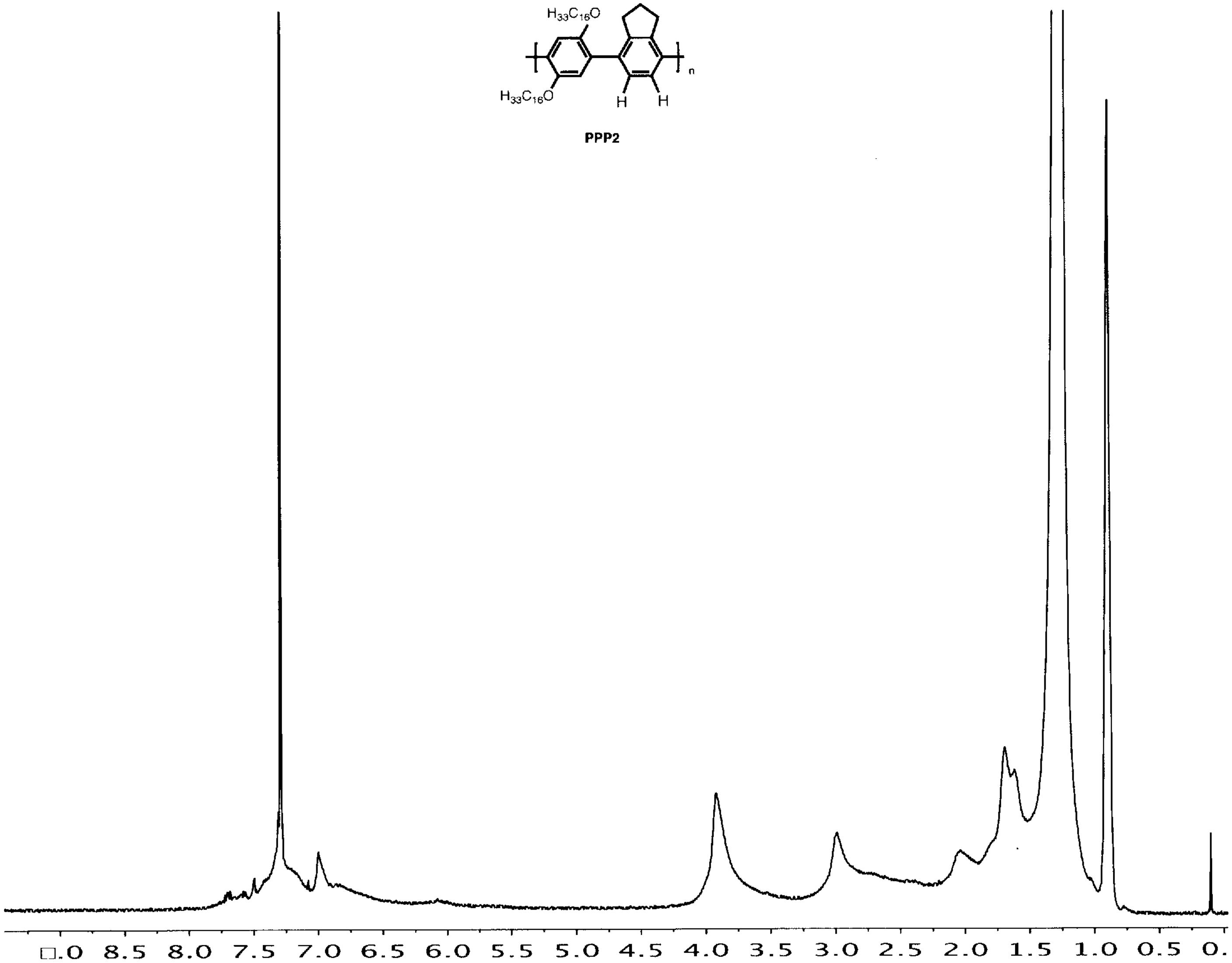
Spectrum 2.2. ^{13}C-NMR Spectrum of **Polymer 1** (501 MHz, $CDCl_3$).



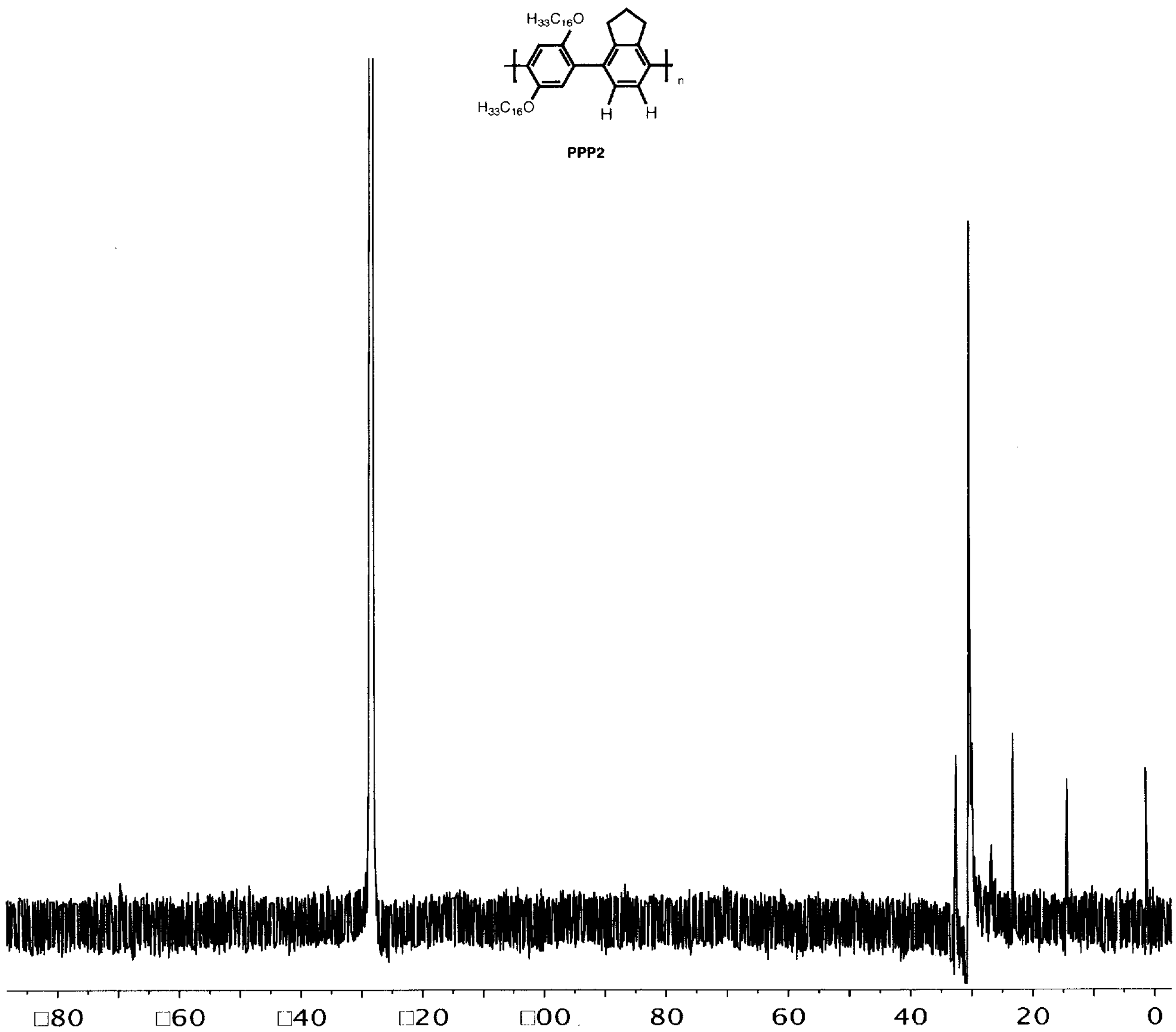
Spectrum 2.3. ^{1}H-NMR Spectrum of **PPP1** (500 MHz, $CDCl_3$).



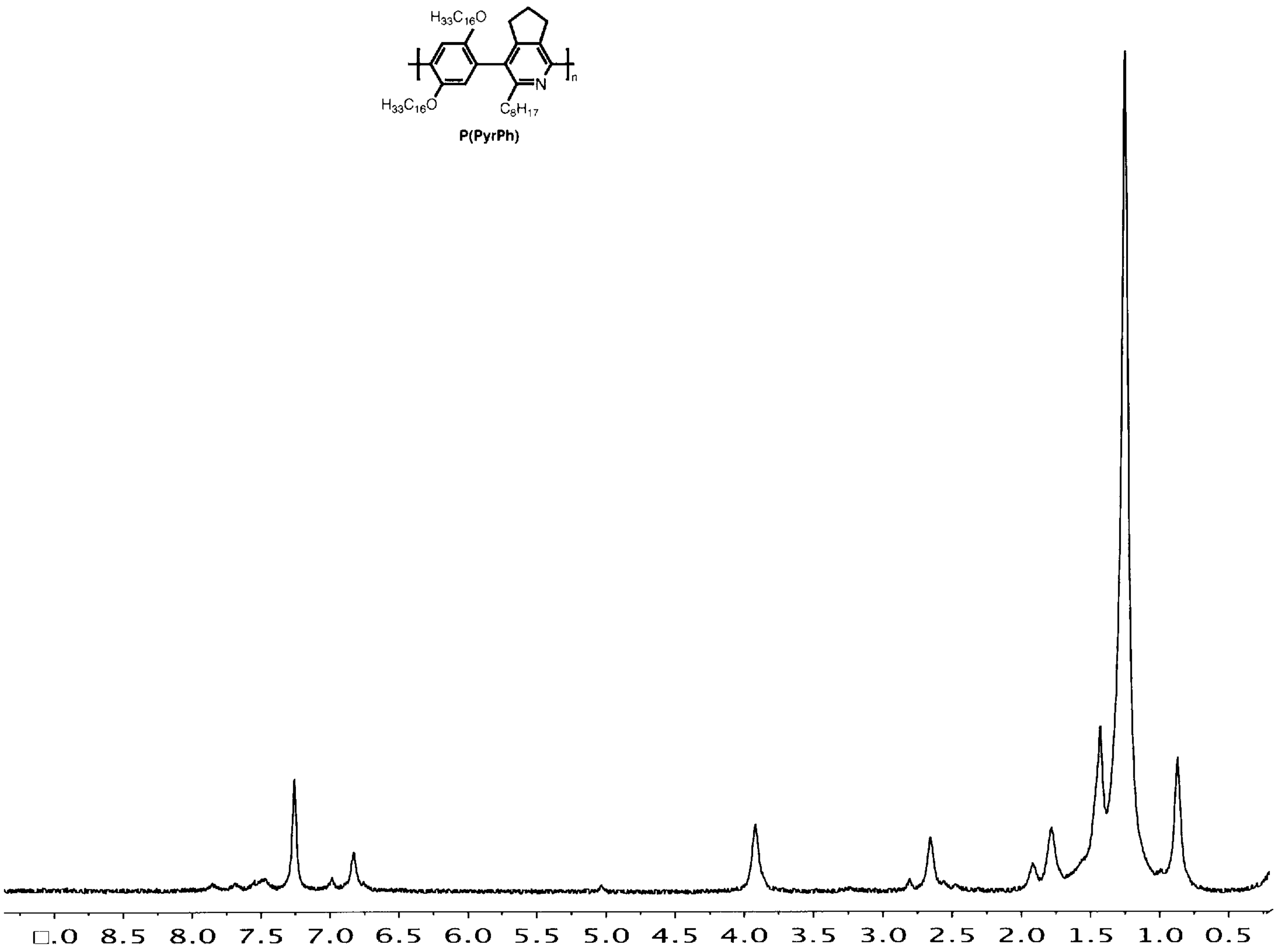
Spectrum 2.4. ^{13}C-NMR Spectrum of **PPP1** (501 MHz, CDCl$_3$).



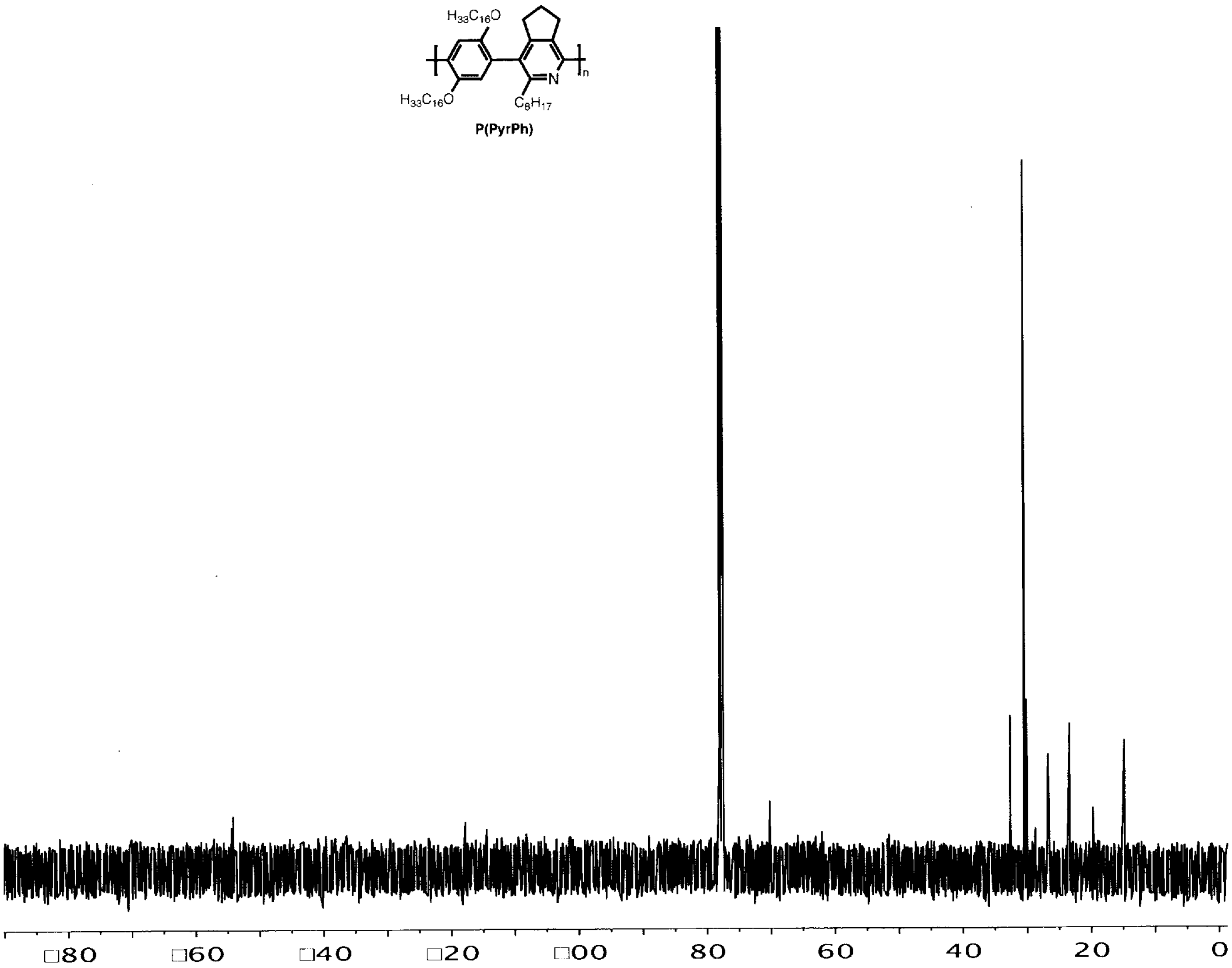
Spectrum 2.5. ^{1}H-NMR Spectrum of **PPP2** (500 MHz, CDCl$_3$, 40 °C).



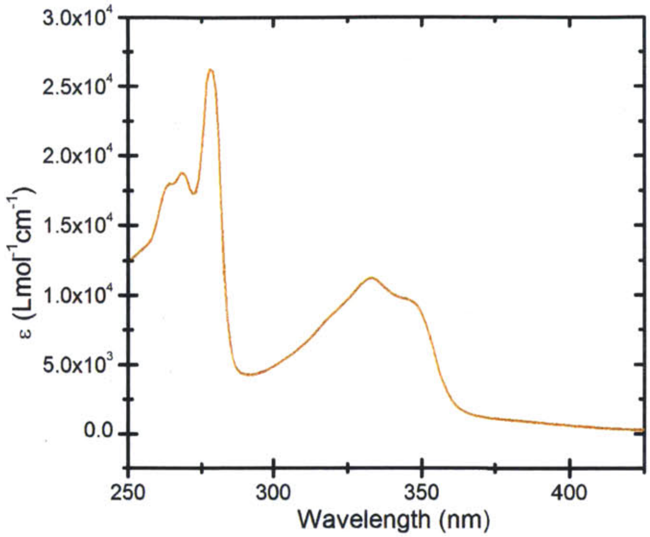
Spectrum 2.6. ^{13}C-NMR Spectrum of **PPP2** (501 MHz, $C_6D_4Cl_2$, 95 °C).



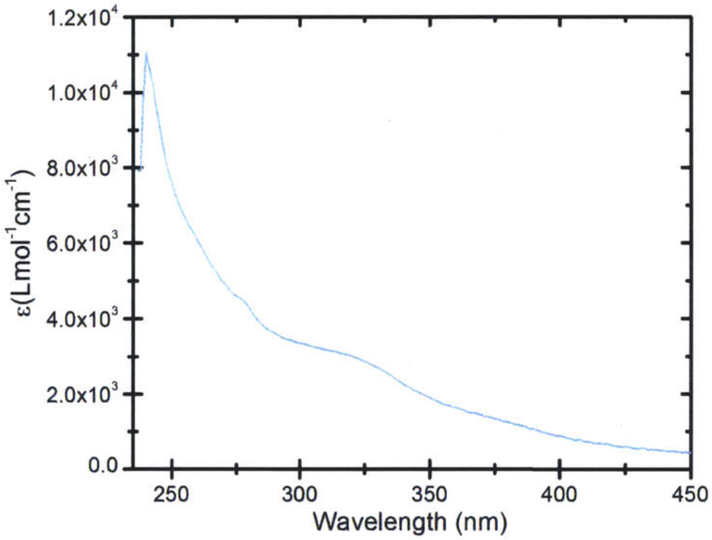
Spectrum 2.7. ^{1}H-NMR Spectrum of **P(PyrPh)** (500 MHz, CDCl$_3$).



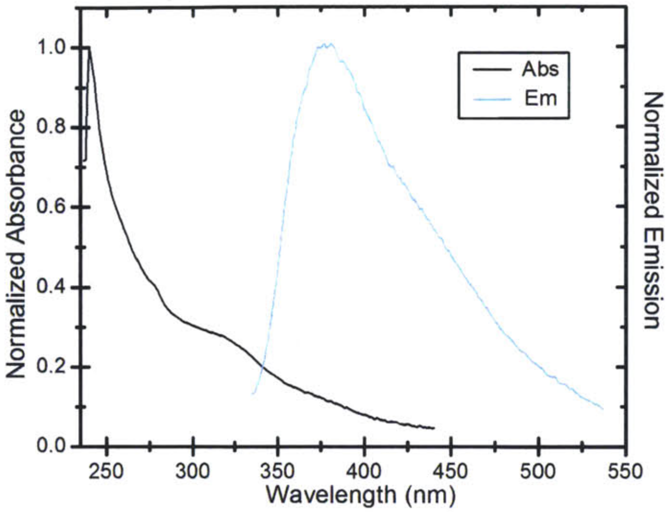
Spectrum 2.8. ^{13}C-NMR Spectrum of **P(PyrPh)** (501 MHz, CDCl$_3$).



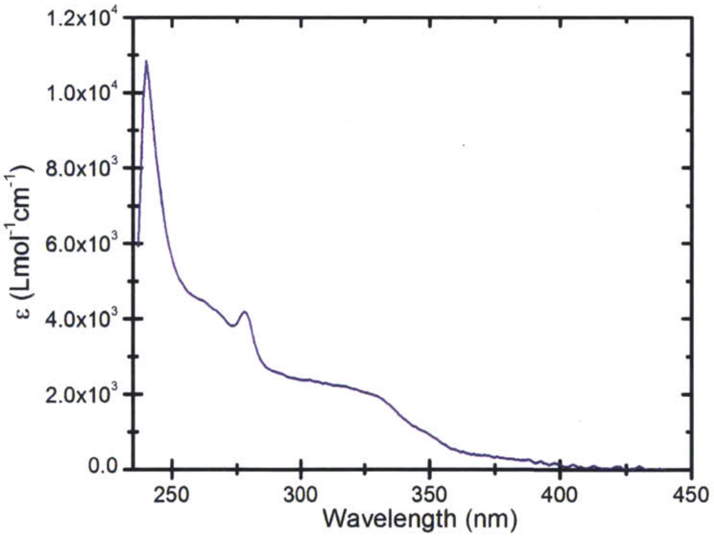
Spectrum 2.9. UV-Vis Absorption Spectrum of Polymer **1** in $CHCl_3$, λ_{max} = 278nm.



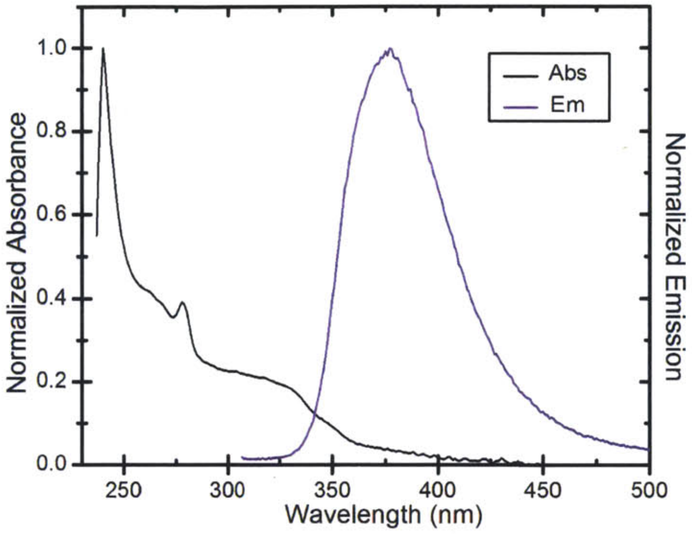
Spectrum 2.10. UV-Vis Absorption Spectrum of **PPP1** in $CHCl_3$, λ_{max} = 240nm.



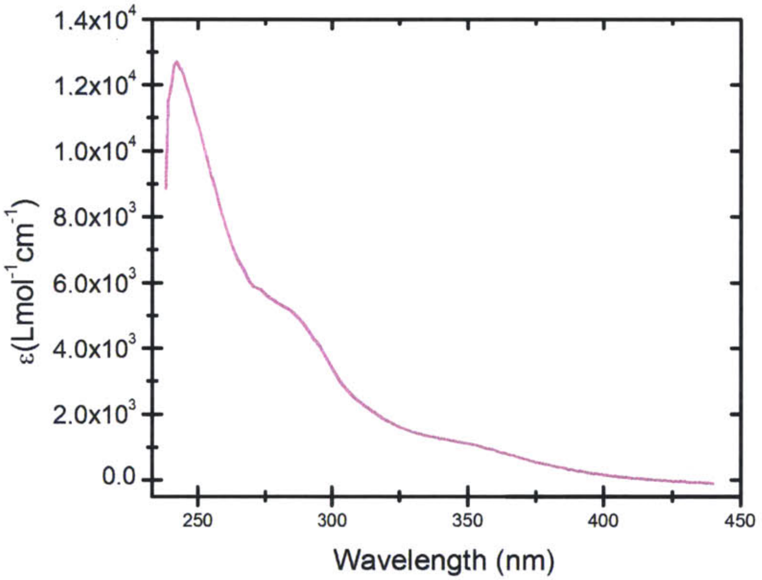
Spectrum 2.11. Absorption and Emission Spectra of **PPP1** in $CHCl_3$, $\lambda_{em} = 381$nm.



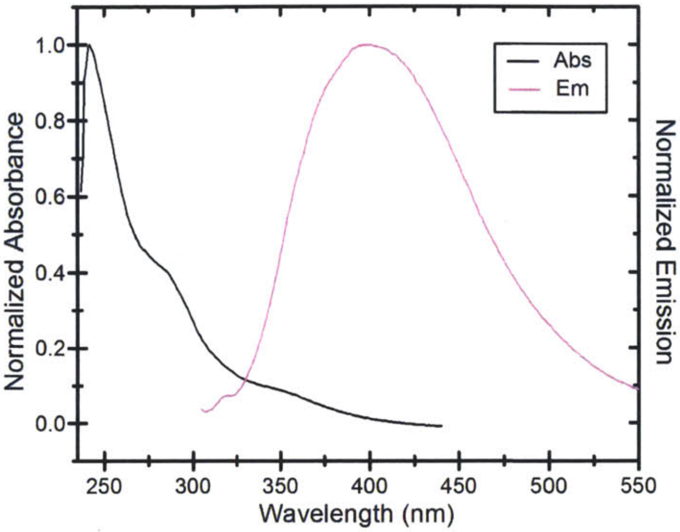
Spectrum 2.12. UV-Vis Absorption Spectrum of **PPP2** in $CHCl_3$, $\lambda_{max} = 240$nm.



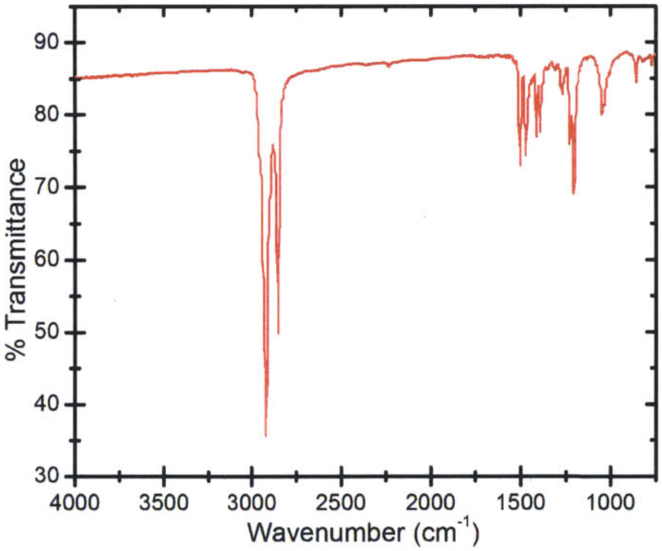
Spectrum 2.13. Absorption and Emission Spectra of **PPP2** in CHCl$_3$, λ_{em} = 377nm.



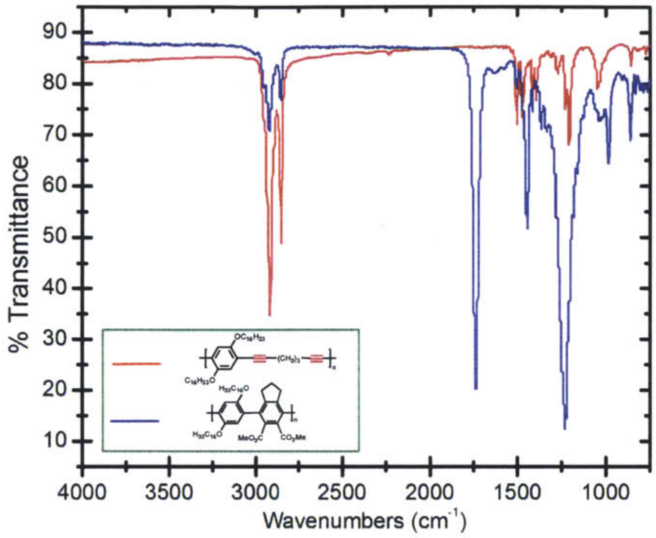
Spectrum 2.14. UV-Vis Absorption Spectrum of **P(PyrPh)** in CHCl$_3$, λ_{max} = 242nm.



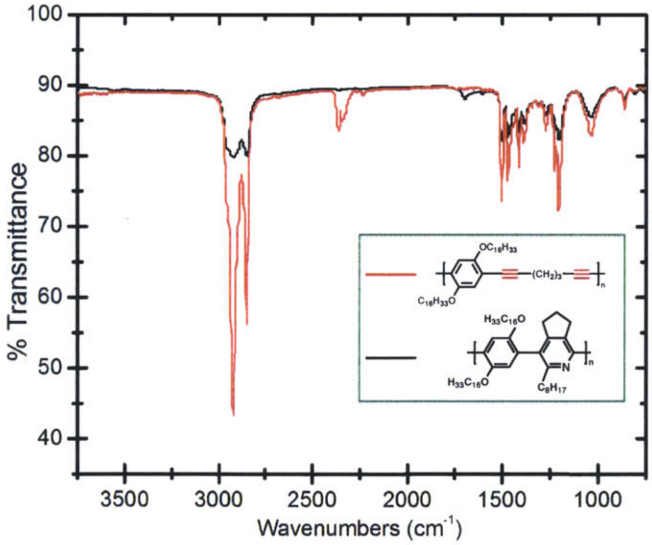
Spectrum 2.15. Absorption and Emission of **P(PyrPh)** in $CHCl_3$, λ_{em} = 401nm.



Spectrum 2.16. Infrared Spectrum of **Polymer 1**.



Spectrum 2.17. Infrared Spectra of **PPP1** (blue) with Polymer **1** (red).



Spectrum 2.18. Infrared Spectra of **P(PyrPh)** (black) with Polymer **1** (red).

CHAPTER 3:

APPROACHES TO POLY(PHENYLENE TRIPTYCENE) VIA [2+2+2]

Thanks to Dr. Derek Schipper for attempting the initial poly(phenylene triptycene) polymerizations depicted in **Scheme 3.2** and **Table 3.1**.

3.1 Introduction

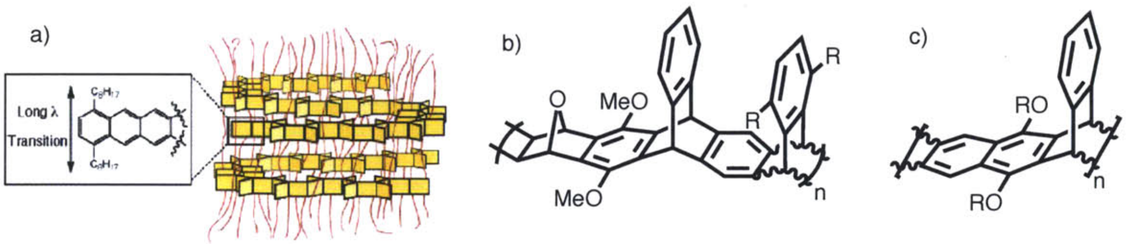


Figure 3.1. a) A schematic representation of a guest polymer (PVC), perpendicularly aligned by its host polymer (Ladder poly(iptycene) or LPI). (Reprinted with permission from Swager, T. M. *Acc. Chem. Res.* **2008**, *41*, 1186. Copyright 2013 American Chemical Society) b) The structure of the LPI used in the studies demonstrated by *(a)*. c) Another example of a Ladder poly(iptycene) reported by our group.[5]

The family of molecules in which multiple arene rings connect to form the bridges of [2.2.2] bicyclic ring systems were termed "iptycenes" by Hart three decades ago.[1] As the smallest member of this molecular family, triptycene's three-pronged aromatic framework has been utilized in several creative and useful ways. Its unique molecular architecture has seen it used in studies of atropisomerism,[2] host-guest chemistry,[3] ligand design, and as a component of "molecular machines".[4] One of triptycene's most convenient structural features is its internal molecular free volume (IMFV). The rigidity of its three constitutional aromatic rings, all set 120° apart from each other, creates a molecular-sized gap of free space between any two of these rings. This useful molecular property can be amplified and exploited in various manners by bulk systems *via* incorporation of the triptycene scaffold into different polymers.[5] This concept is readily demonstrated by the "ultimate iptycene polymer", a ladder poly(iptycene), which possesses desirable microporous characteristics.[6] Our lab has used iterative, high pressure Diels-Alder cycloadditions on small polyacene monomers to form high molecular weight, two-dimensional ladder polymers containing the crucial triptycene moiety.[7] The dense array of triptycenes formed by this method imparts a high degree of IMFV on the resulting polymer, yielding the desired porosity. Our lab has demonstrated the ability of a ladder poly(iptycene) (LPI, Figure 3.1,b) to engage its microporosity in the alignment of perpendicularly stretched poly(vinyl chloride) (PVC) chains as depicted in part (a) of Figure 3.1. Upon the introduction of the 'guest' polymer PVC to a solution of the LPI, the structures orient in the observed manner in an attempt to minimize the system's free volume. This perpendicular alignment of guest polymers is unprecedented and not only allows for many further possibilities, but also highlights the usefulness of triptycene containing polymers.[8]

In 2002 our group reported both triptycene-containing poly(phenylene vinylene) (PPV) and poly(phenylene ethynlene) (PPE) polymers as displaying enhanced alignment properties in a nematic phase liquid crystal (LC), with the directional properties controlled by an electric field.[9] Similarly conjugated polymers that do not possess the crucial triptycene moiety were found to be completely soluble in typical organic solvents, yet completely insoluble in the nematic phases of the two LCs examined, 1- -4-hexylcyclohexyl)-4-isothiocyanatobenzene (6CHBT) and 4-(trans-4-pentyl-cyclohexyl)benzonitrile (5PCH). Triptycene's rigid, three-dimensional architecture confers improved solubility on its polymers by preventing strong interpolymer aggregation which is responsible for the low solubilty of typical conjugated polymers. The homogeneity of the LC-polymer mixture in this instance results from the host-guest system seeking to lower its overall energy by minimizing the free volume in solution (Figure 3.2 d). This electrically controlled phase alignment employed as a new method of polymer organization in nematic solutions has the potential for widespread use in new molecular electronic devices. Additionally, the potential for improved electron transport properties could have beneficial applications for sensors, electroluminescent devices, and field effect transistors.[9]

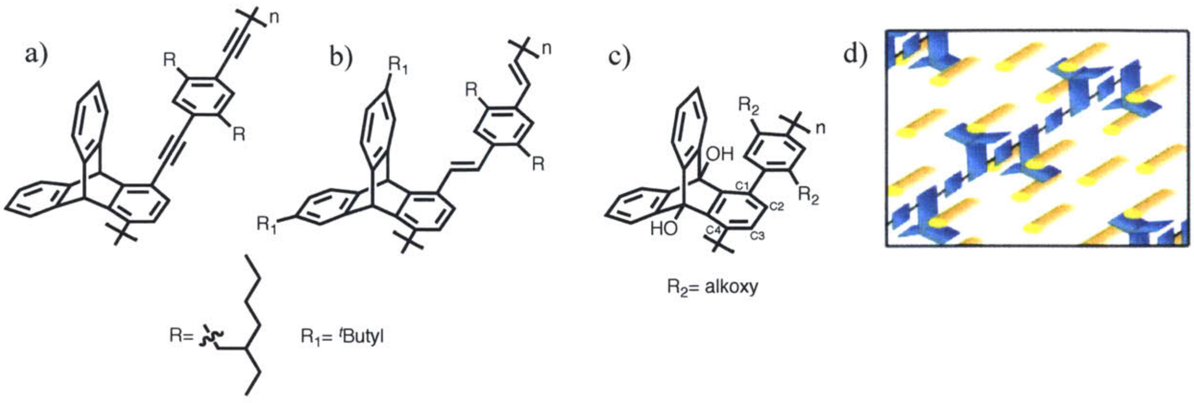
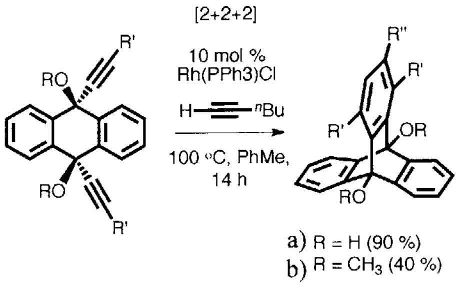
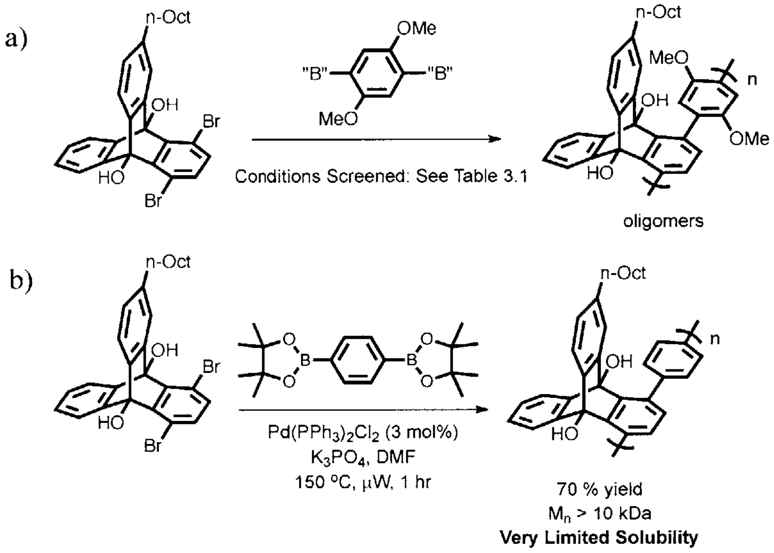


Figure 3.2. A triptycene-containing a) poly(phenylene ethynylene) (PPE) b) poly(phenylene vinylene) (PPV) c) previously unknown poly(*para*-phenylene) (PPP) d) A general illustration of a triptycene-containing conjugated polymer aligned with a nematic phase liquid crystal (Reprinted with permission from Swager, T. M. *Acc. Chem. Res.* **2008**, *41*, 1184. Copyright 2013 American Chemical Society).

Several years later Taylor and Swager reported the synthesis of a triptycene diol, which is easily functionalized at the 1,4-positions (Scheme 3.1).[10] This metal-mediated [2+2+2] cyclization of a *syn*-oriented diyne offered what is perhaps the most efficient synthetic route to the 1,4-functionalized triptycene scaffold reported to date. In addition to the two potentially advantageous bridgehead hydroxyl groups, Taylor's synthetic route also provided the option to install substituents at triptycene's 2,3-positions *via* the selection of an appropriate [2+2+2] alkyne partner. This ease of functionalization of triptycene's core aromatic frame lead us to consider the possibility of a triptycene-containing poly(*para*-arylene), or more specifically, a poly(phenylene triptycene). We envisioned that removal of the two vinyl or ethynyl moieties from the repeat unit of a triptycene-containing PPV or PPE could result in a conjugated polymer with its triptycenes fixed in greater proxmity. Coupled with the reduction in intrinsic chain disorder due to the polymer's increased stiffness relative to a PPV or PPE, this denser arrangement of triptycene's IMFV in poly(phenylene triptycene) could potentially furnish some interesting LC alignment properties.



Scheme 3.1. Mark Taylor's synthesis of a functionalized triptycene a) diol and b) dimethoxy *via* a transition metal-catalyzed [2+2+2] cyclization.[12]



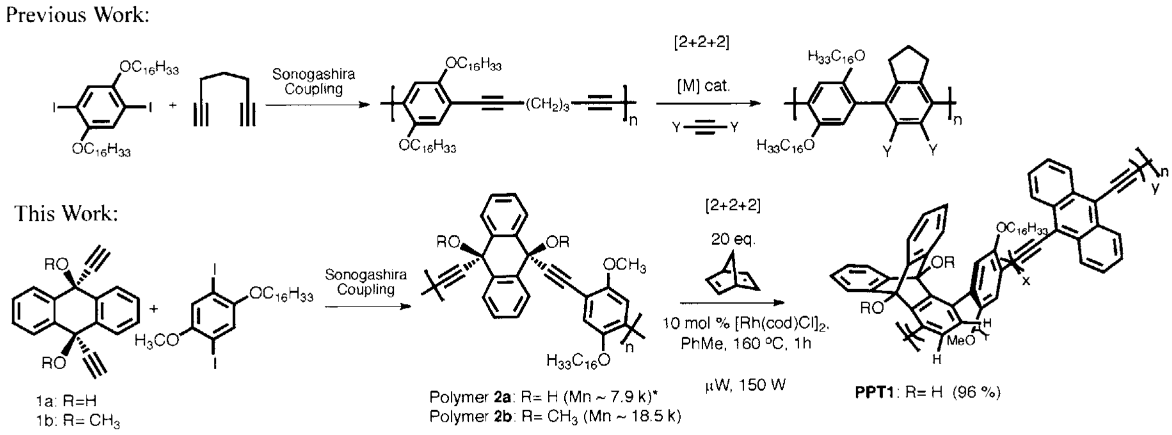
Scheme 3.2. Initial efforts towards the synthesis of a) a substituted poly(phenylene triptycene) b) a poly(phenylene triptycene) without alkoxy substituents.

"B" screened	Pd Source	Ligand	Base	Solvent	Heating
$B(OH)_2$	$Pd(PPh_3)_2Cl_2$	PPh_3	K_2CO_3	DMF	Microwave
BF_3K	$Pd_2(dba)_3$	$P(o\text{-tolyl})_3$	K_3PO_4	Dioxane	Benchtop/Schlenk
Bu_4NBF_3	PEPPSI-Ipr	S-Phos	KOH	H_2O	

Table 3.1. A variety of Suzuki cross-coupling conditions attempted in the polymerization in part (a) of Scheme 3.2.

Our initial attempts at synthesizing poly(phenylene triptycene) with alkoxy substituents were unsuccessful. We easily accessed a 1,4-dibromo triptycene diol monomer by employing Taylor's metal-catalyzed [2+2+2] synthesis of triptycene derivatives (Scheme 3.1), starting from 1,4-dibromo-9,10-anthraquinone. We first utilized our triptycene monomer in a Suzuki cross-coupling polymerization with (2,5-dimethoxy-1,4-phenylene) diboronic acid as a co-monomer, but only achieved oligomers despite screening a wide variety of reaction conditions (Table 3.1). We hypothesized that the resistance to polymerization was likely due to unfavorable steric interactions between the bridgehead hydroxyl groups of our triptycene diol and the ether substituents of our alkoxy co-monomer. We validated this hypothesis by repeating the polymerization with an unsubstituted co-monomer, 1,4-diboronic acid benzene, successfully yielding polymers with a number average molecular weight (M_n) of over 10 kDa (Scheme 3.2). Unfortunately, the resulting polymer displayed a prohibitively low solubility in typical organic solvents leading us to consider alternative options for the synthesis of more soluble, alkoxy substituted poly(phenylene triptycene)s (PPTs).

We previously demonstrated the synthesis of poly(*para*-phenylene) derivatives *via* a post-polymerization [2+2+2] cyclization of a diyne-containing precursor polymer[11] and envisioned that a similar approach could produce alkoxy substituted poly(phenylene triptycene) derivatives (Scheme 3.3). Taylor's strategy was essential once more as we successfully co-polymerized the triptycene diol precursor, a *syn*-oriented diyne (Scheme 3.1.), with 1-(hexadecyloxy)-2,5-diiodo-4-methoxybenzene. Previously, only Taylor's *anti*-diyne isomer had been utilized in polymerization efforts, leading to the synthesis of poly(anthrylenebutadiynylene).[12] The choice of comonomer utilized with **1a** in the synthesis of polymer **2a** was crucial. As a result of **1a**'s *syn*-orientation it has an inherent tendency to form macrocyclic oligomers rather than linear polymers and so an initial screening was required to determine structurally suitable comonomers. Following this, we employed traditional Sonogashira-polymerization techniques and were able to isolate polymers **2a** and **2b** in moderate yields and with suitably high molecular weights for our study. In conctrast to the high solubility of the bridgehead substituted dimethoxy polymer **2b**, the diol analog **2a** was only partially soluble in typical organic solvents. This lack of solubility not only increased the difficulty of **2a**'s characterization, but also prevented accurate determination of its molecular weight by Gel Permeation Chromatography (GPC).



Scheme 3.3. A comparison of the post-polymerization [2+2+2] cyclization strategy a) previously used to access poly(*para*-arylene)s and b) presented in this work as a route to alkoxy-substituted poly(phenylene tripycene)s with minor defects (*Longer chains filtered out of GPC sample due to lower solubility).

Subjecting polymer **2a** to [2+2+2] reaction conditions with norbornadiene and $[Rh(cod)Cl]_2$ generated a material [**PPT1**] in nearly quantitative mass-based yield. Interestingly, **PPT1** possessed significantly improved solubility in contrast to its precursor polymer, **2a**, likely due to the partial installation of the triptycene scaffold along the polymer's backbone. Aiming to optimize the yields of the individual cyclizations in order to furnish PPTs as structurally homogeneous as possible, the post-polymerization [2+2+2] reaction was performed with microwave heating (1 h, PhMe, 160 °C). As is discussed later in this chapter, the material **PPT1** likely has at least trace level defects as a result of reductive dehydroxylation of the monomer forming dialkynl anthracene moeitites (i.e. $y > 0$ in Scheme 3.3) during the [2+2+2] cyclization. Similar defects appear to be minimally present in polymers **2a** and **2b** also. This reductive transformation has been previously reported by Taylor from our group as a route to low bandgap polymers.[12] The bridgehead substituted dimethoxy PPT analogs from polymer **2b** appear to increase the susceptibility to reductive aromatization. Indeed, it was shown by Taylor that the presence of the bridgehead methoxy substituents drastically lowers the efficiency of the [2+2+2] conversion relative to the diol analog from 90 % to 40 % (Scheme 3.1),[12] an obstacle that even our microwave conditions, which proved effective in other schemes, could not overcome. The diol-containing **PPT1** was analyzed by NMR, GPC, IR and UV-Vis spectroscopy to determine its structure and the efficiency of the post-polymerization [2+2+2] reaction. All data obtained strongly suggests that the bulk cyclization reactions proceeded favorably to yield a structure with PPT repeating groups that is minimally defective.

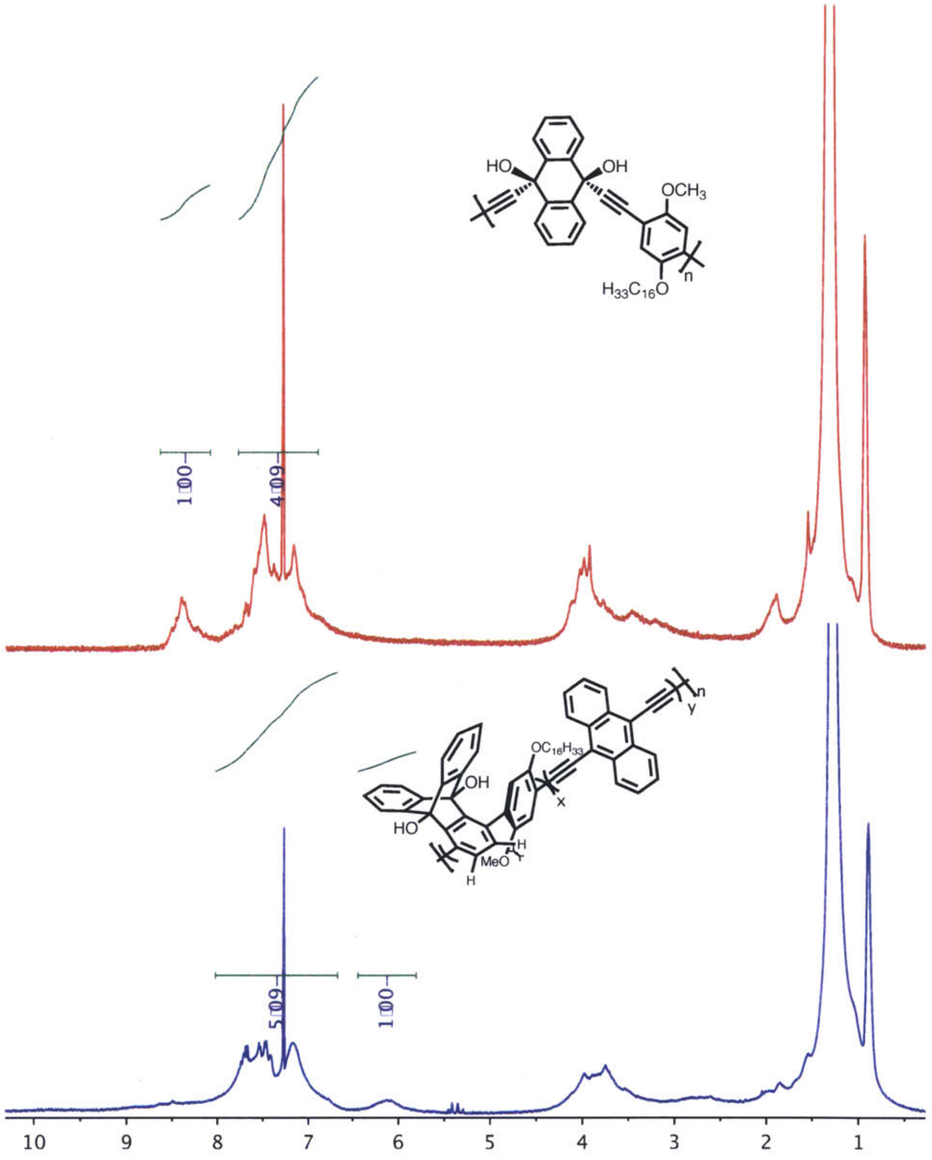


Figure 3.3. ^{1}H-NMR spectrum of polymer **2a** before (*red*) and after (*blue*) [2+2+2] reaction with norbornadience (**PPT1**). The relative integrals of peaks in the aromatic region are shown (both in $CHCl_3$ at 50 °C)

The NMR spectra of **PPT1** were directly compared to that of polymer **2a** as shown in Figure 3.3. The ^{1}H-NMR spectrum of **PPT1** shows the clear introduction of a non-equivalent proton signal at 6.1 ppm. This observation corroborates the installation of new aromatic hydrogen units, consistent with the desired polyphenylene backbone. Addtionally, there is almost a complete disappearance of the anthraquinoidal proton signal at 8.5 ppm. The change in structure upon cyclization of **2a** is likely responsible for the significant change in this chemical shift. Comparison of the ^{13}C-NMR spectra is equally vital in determining the outcome of the post-polymerization reaction. However, despite collecting ^{13}C-NMR data for the polymer **2a** and **PPT1** at elevated temperatures and over long periods of time (Spectrum 3.2. and 3.6 in Appendix), we were unable to achieve a sufficiently high signal-to-noise ratio from these spectra to further discern the extent of the post-polymerization conversion.

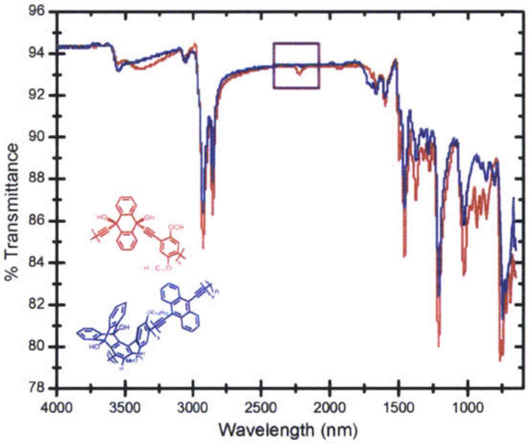


Figure 3.4. Infrared (IR) Spectra of polymer **2a** (*red*) versus **PPT1** (*blue*) showing the disappearance of the alkyne IR stretch highlight in the purple box .

Complementary to the NMR data, we collected IR spectra of the polymers before and after the [2+2+2] reaction in an attempt to qualitatively monitor any functional groups gained or lost (Figure 3.4.). Fortunately, the IR spectra clearly showed the complete disappearance of the weak alkyne stretch in further support of our structural assignment of **PPT1**. Lastly, as with our previous work synthesizing poly(*para*-phenylene) derivatives, it behooved us to demonstrate that inter-polymer [2+2+2] reactions potentially resulting in cross-linking did not occur. We anticipated that triptycene's rigid, three-dimensional framework would minimize the risk of this unwanted side reaction. A monomodal chromatogram of our products as determined by GPC, with little change in the apparent molecular weight confirmed this hypothesis, as cross-linked material would have resulted in a considerably higher mass.

3.4 Results and Discussion

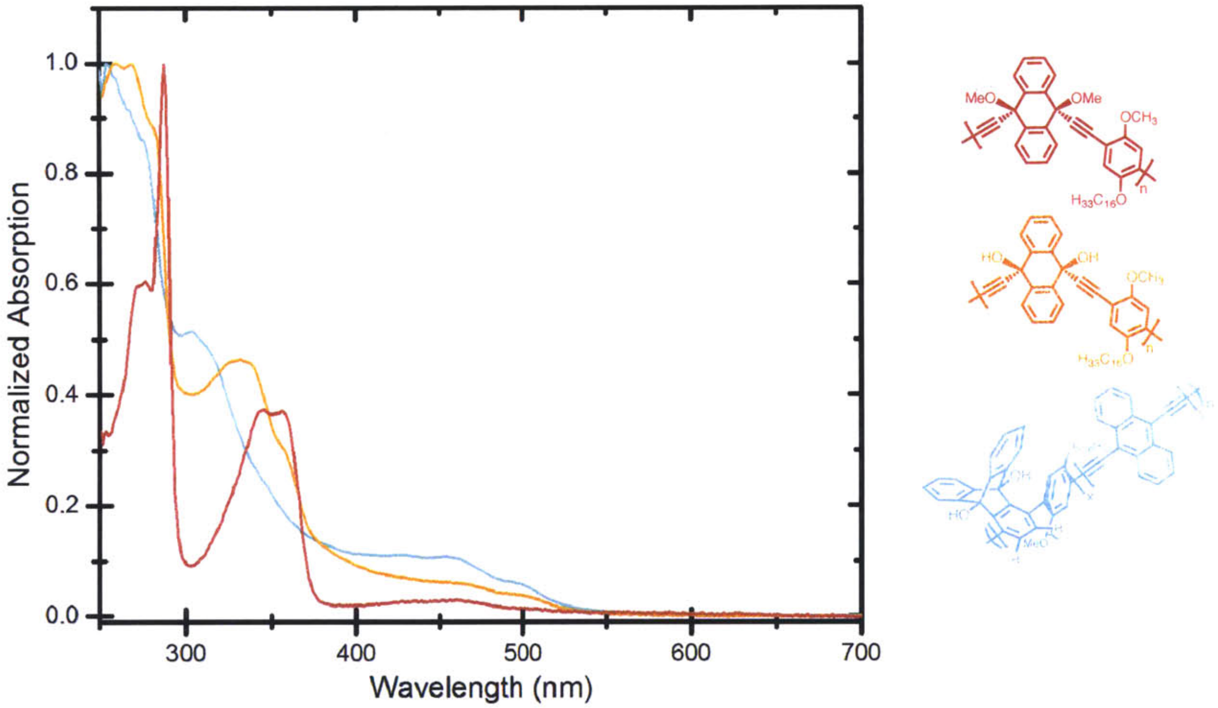
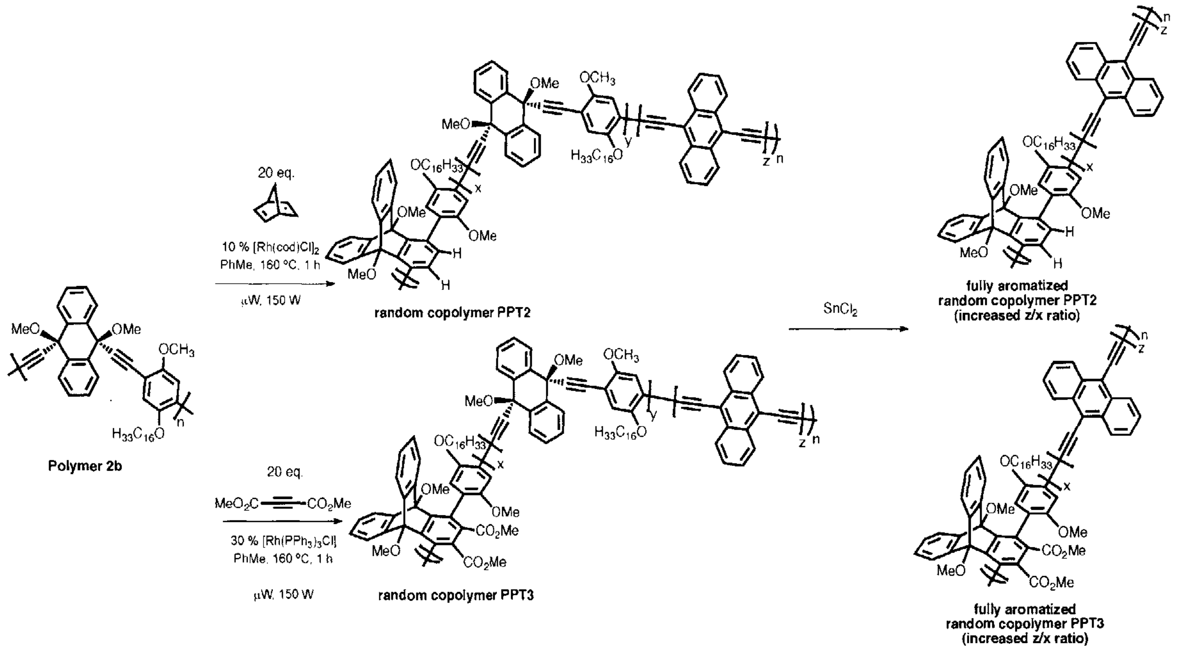


Figure 3.5. Normalized Absorption Spectra of Polymer **2a** (*orange*), Polymer **2b** (*red*), **PPT1** (*cyan*)

As a result of the correlation between conjugation lengths in poly(*para*-arylene)s and the dihedral angles between adjacent arylenes, the photoluminescence of highly twisted, substituted PPPs is dominated by lower wavelength (higher energy) absorptions as a result of their poor conjugation.[13] Thus, similar to the photophysical properties of the previously synthesized poly(*para*-arylene)s,[11] we expected **PPT1** to possess a sharply blue-shifted absorption spectrum with subtle features. Gratuitously, we observed the characteristically "benzene-like" aromatic π → π* absorption band[14] at ~ 255 nm with minor differences at higher wavelengths in the absorption spectra. The earlier difficulties encountered utilizing 1,4-dibromo triptycene diol and (2,5-dimethoxy-1,4-phenylene)diboronic acid as comonomers in a Suzuki polymerization suggested that densely crowded steric interactions likely exist between adjacent aryl units in **PPT1**, further rationalizing its hypsochromic UV-Vis profile. The absorptions at longer wavelengths between 400 and 500 nm are likely the result of very minor impuritires, which based upon previous results and other experiments (*vide infra*), we attribute to reductive aromatization.

All the [2+2+2] cyclization attempts with polymer **2b** resulted in product polymers with an unusual absorption band located just above 500 nm. In the original report of this triptycene-forming strategy, a significantly higher yield was obtained for the [2+2+2] cyclization with the diol-containing *syn*-diyne, in comparison to its dimethoxy-containing anolog (Scheme 3.1).[12] Taylor attributes this disparity to unfavorable steric interactions associated with the larger bridgehead methoxy substituents. Additionally, the increased tendency for reductive aromatization of the dimethoxy anthraquinoidal moiety, relative to its diol analog, could potentially result in the unwanted incorporation of anthracene along the polymer's backbone. This facile aromatization, exploited by Taylor in his synthesis of poly(anthrylenebutadiynylene), seemed the likely cause of this surprising red-shift in absorption also witnessed to a lesser extent in **PPT1**, polymer **2a** and polymer **2b**.[12]



Scheme 3.4. A depiction of the partial [2+2+2] cyclization of polymer **2b** and the reductive aromatization of the resulting polymers.

In an effort to further understand this unexpected photophysical observation we performed a reduction on the product polymers using $SnCl_2$, thereby converting any remnant anthraquinoidal moieties to anthracene. Although still qualitative, this strategy appeared to be the most reliable method for determining the efficiency of the post-polymerization [2+2+2] reaction. Considering the low yield reported for the synthesis of the bridgehead substituted dimethoxy triptycene (Scheme 3.1), the bulk [2+2+2] cyclizations with polymer **2b** were expected to furnish poorly converted polymers. Although requiring different lengths of time, common reductive conditions for quinoidal moieties ($SnCl_2$ in THF and 1,4-dioxane, heat) leading to fully aromatized derivatives were successfully applied to monomers **1a** and **1b**. Upon treatment with the same reaction conditions, the product polymers from the [2+2+2] cyclization efforts with polymer **2b** displayed a significant enhancement of their red-shifted absorption bands located near 500 nm (Scheme 3.4 & Figure 3.6.). These results unequivocally confirmed the low degree post-polymerization conversion experienced by polymer **2b**. However, when the diol-containing **PPT1** was subjected to the same reaction conditions used for aromatizing monomer **1a**, no discernible changes to its absorption or NMR spectra were observed. This negative result indicates that only a minimal amount of remnant anthraquinoidal moieties are left in **PPT1**. Additionally, although no anthracene signals were observed in **PPT1** via ^{1}H-NMR, these photophysical observations do not rule out the possibility of minor 1,4-diethynl anthracene defects present in the final product polymer.

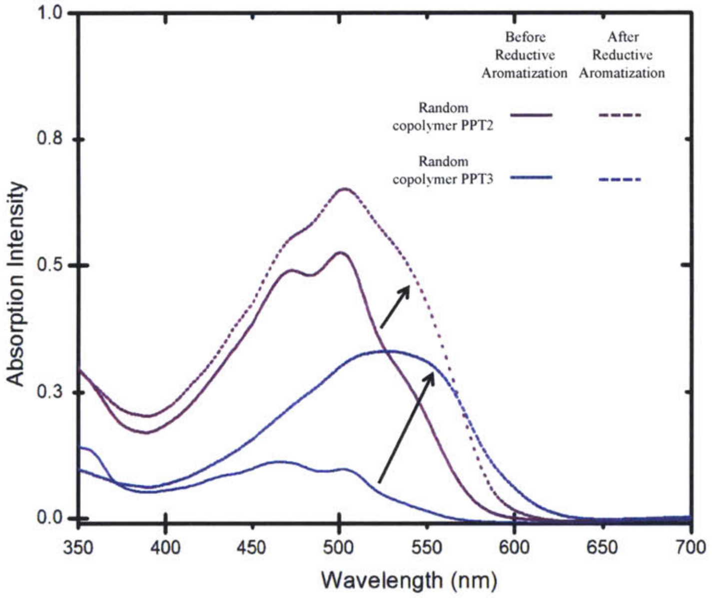
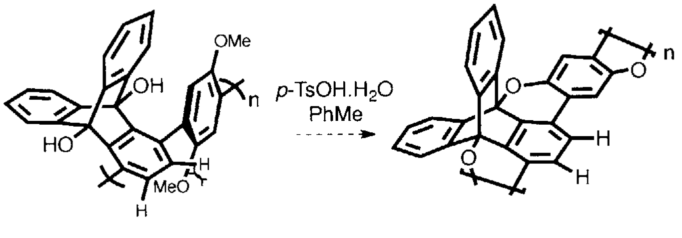


Figure 3.6. UV-Vis spectra displaying the absorption changes experienced by random copolymers PPT2 and PPT3 upon treatment with $SnCl_2$.

3.5 Conclusion

We were able to efficiently synthesize an otherwise inaccessible alkoxy substituted poly(phenylene triptycene), **PPT1**, *via* a post-polymerization, metal-catalyzed [2+2+2] cyclization reaction. It has been reliably demonstrated that the post-polymerization transformation proceeds with a relatively high degree of conversion. We are in the initial stages of investigating the alignment capabilities of **PPT1** in commercially available nematic phase liquid crystals, 1-(trans-4-hexylcyclohexyl)-4-isothiocyanatobenzene (6CHBT) and 4-(trans-4-pentyl-cyclohexyl)benzonitrile (5PCH), relative to the previously reported triptycene-containing PPV and PPE polymers. Additionally, efficient access to triptycene-containing polymers with hydroxyl substituents, such as **PPT1**, augurs well for our future synthetic efforts towards a triptycene-containing ladder polyphenylene (Scheme 3.5) via a transetherification cyclization reaction utilizing these rigidly postioned hydroxyl bridgehead substituents of triptycene .[15]



Scheme 3.5. The potential transetherification cyclization of PPTs to triptycene-containing ladder polyphenylenes.

3.6 References

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3.7 Experimental Procedures

Materials: All reactions were carried out under a flow of argon gas using standard Schlenk techniques unless otherwise stated. All photophysical experiments were performed with spectral grade chloroform. Toluene was obtained from a dry solvent still. 1-(hexadecyloxy)-2,5-diiodo-4-methoxybenzene was prepared according to available literature procedures. All reagent grade materials were purchased from various commercial sources and used as received unless otherwise stated.

NMR Spectroscopy: ^{1}H and ^{13}C NMR spectra for all compounds were acquired on a Varian Inova 500 MHz or Varian Inova 501 MHz spectrometers. The specific instrument is noted below each spectrum. NMR data collected at elevated temperatures are noted below the respective spectra. Chemical shifts are reported in ppm and referenced to residual NMR solvent peaks. ($CDCl_3$: δ 7.26 ppm for ^{1}H, δ 77.2 ppm for ^{13}C.)

Gel Permeation Chromatography (GPC): Number average molecular weight (M_n) and polydispersity (PDI) of polymers were obtained on a Hewlett Packard series 1100 HPLC instrument equipped with a Mixed-C (300 x 7.5 mm) column. This GPC system utilized both UV (245) and refractive index detection at a flow rate of 1.0 mL/min in tetrahydrofuran and calibrated relative with polystyrene standards purchased from Polysciences, Inc.

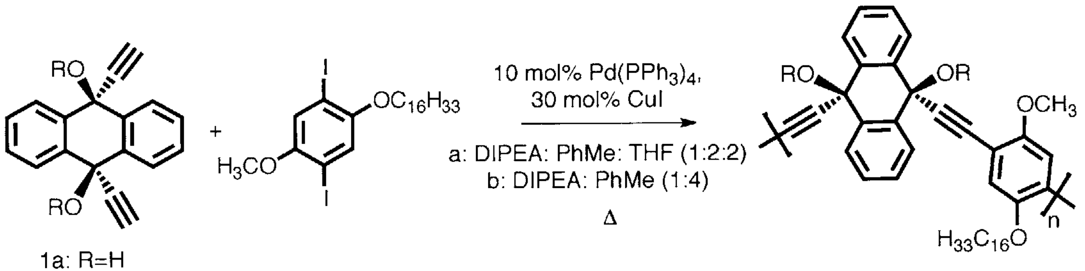
Infrared (IR) Spectroscopy: IR spectra were recorded on a Thermo Scientific, Smart-iTR, Nicolet 6700-FT-IR.

Absorption and Emission Spectroscopy: Fluorescence spectra were measured on a SPEX Fluorolog-τ3 fluorometer (model FL-321, 450 W Xenon lamp) using right-angle detection.

Ultraviolet-visible absorption spectra were measured with an Agilent 8453 diode array spectrophotometer and corrected for background signal with a solvent filled cuvette.

Microwave: A CEM Discover Microwave was used for all microwave reactions (150 W, 30 PSI).

1a and **1b** were synthesized according to literature procedures.



1a: R=H
1b: R= CH_3

2a: R=H (63 %)
2b: R= CH_3 (52 %)

Polymer 2a: 1a (108 mg, 0.415 mmol), 1-methoxy-4-(hexadecyloxy)-2,5-diiodo benzene (247 mg, 0.412 mmol), *N,N*-diisopropylethylamine (0.50 mL), THF (1.00 mL) and PhMe (1.00 mL) were added to a schlenk flask and sparged with nitrogen gas for 30 minutes. Tetrakis(triphenylphosphine) palladium (0) (47.6 mg, 0.041 mmol) and copper (I) iodide (23.4 mg, 0.123 mmol) were then added under a flow of argon to the reaction mixture which was then left to stir at 60 °C under reflux. After 3 days the reaction mixture was cooled and then quenched with saturated aqueous ammonium chloride. One extraction of the crude reaction mixture was performed with ethyl acetate. The organic layers were then collected and washed twice with aqueous ammonium chloride and once with brine. The organic layer was once more collected, dried with sodium sulfate, filtered and concentrated *en vacuo* to yield a red solid. This crude product was then transferred to a small round bottom flask and dissolved in a minimal amount of chloroform with the assistance of heat and sonication. Using a disposable pipette, the concentrated solution of the crude polymer was added to rapidly stirring hexanes (~ 500 mL) to yield the red product polymer via precipitation (156 mg, 0.235 mmol).

^{1}H NMR (500 MHz, $CDCl_3$, 50 °C): δ 8.37, 7.47, 7.14, 3.89, 1.87, 1.27, 0.91

^{13}C NMR (501 MHz, $CDCl_3$, 50 °C): δ 100.5, 32.6, 30.3, 30.0, 23.3, 14.7

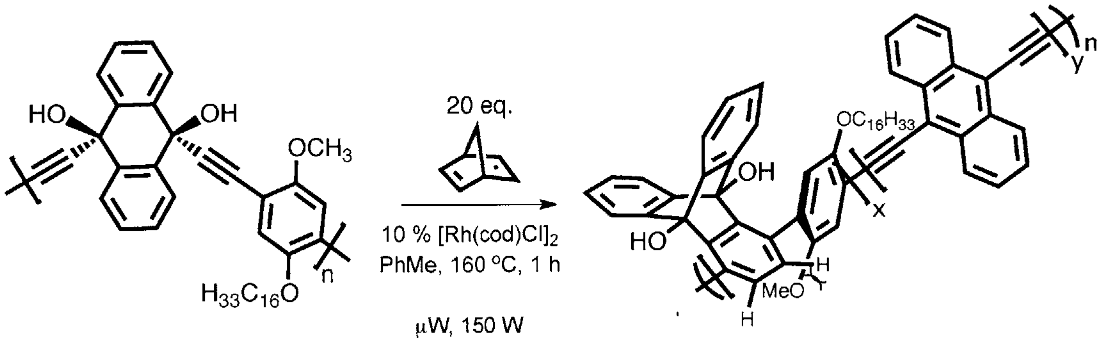
GPC (THF): M_w/M_n = 13 000/7 880

Polymer 2b: The same general procedure described for the synthesis of Polymer 2a was utilized with 1b (182 mg, 0.632 mmol) employed as the corresponding diyne monomer. Additionally, *N,N*-diisopropylethylamine (1.00 mL) and PhMe (3.00 mL) were instead used as the solvent system. After stirring at 60 °C for 3 days under reflux, the reaction mixture was quenched with aqueous ammonium chloride. Three extractions of the crude reaction mixture were performed with dichloromethane. The organic layers were then collected and washed twice with aqueous ammonium chloride and once with brine. The organic layer was once more collected, dried with sodium sulfate, filtered and concentrated *en vacuo* to yield a red solid. This crude product was then transferred to a small round bottom flask and dissolved in a minimal amount of chloroform with the assistance of heat and sonication. Using a disposable pipette, the concentrated solution of the crude polymer was added to rapidly stirring methanol (~ 500 mL) to yield the red product polymer via precipitation (202 mg, 0.320 mmol).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (br s, 4 H), 7.50 (br s, 4 H), 7.00 (s, 2 H), 3.98 (s, 2 H), 3.86 (s, 4 H), 3.20 (s, 6 H), 1.83 (s, 2 H), 1.47 (s, 2 H), 1.25 (br s, 26 H), 0.81 (t, 3 H)

^{13}C NMR (501 MHz, $CDCl_3$): δ 155.2, 154.9,136.8, 136.7, 130.2, 129.4, 117.2, 116.4, 114.0, 113.9, 95.4, 95.0, 86.2, 75.8, 70.1, 57.3, 52.9, 32.6, 30.4, 30.3, 30.2, 30.1, 30.0, 26.8, 23.4 32.6, 30.3, 30.0, 23.3, 14.7

GPC (THF): M_w/M_n = 33 900/18 500



Polymer 2a: R= H

PPT1: R= H (96 %)

PPT1: Polymer 2a (49.5 mg, 0.082 mmol) and [Rh(cod)Cl]$_2$ (4.00 mg, 0.008 mmol) were added to a microwave reaction vial prior to placing the cap on and evacuating the system through a syringe needle via a high vacuum pump. The reaction vial was then backfilled with Argon (x3) before norbornadiene (0.17 mL, 1.64 mmol) and PhMe (4.00 mL) were added via a syringe through the cap once more. The reaction mixture was then sparged for 30 minutes with nitrogen before being stirred and heated in the microwave reactor (160 °C, 150 W, 1 hour). Upon cooling, the reaction mixture was quenched with aqueous ammonium chloride and extracted with dichloromethane (x3). The organic layers were then collected and washed with aqueous ammonium chloride and brine respectively, dried with sodium sulfate, filtered and concentrated *en vacuo* to give a red crude product. We transferred the crude product to a small vial before washing with several drops of hexane (x3) and then decanting the solvent. This step was also repeated with methanol (x3). The isolated polymer was then attached to a vacuum pump and dried of excess solvent overnight to furnish red PPT1 (49.7 mg, 0.079 mmol).

^{1}H NMR (500 MHz, CDCl$_3$, 50 °C): δ 7.92 - 7.37, 7.16, 6.14, 3.99, 3.76, 1.85, 1.54, 1.28, 0.89.

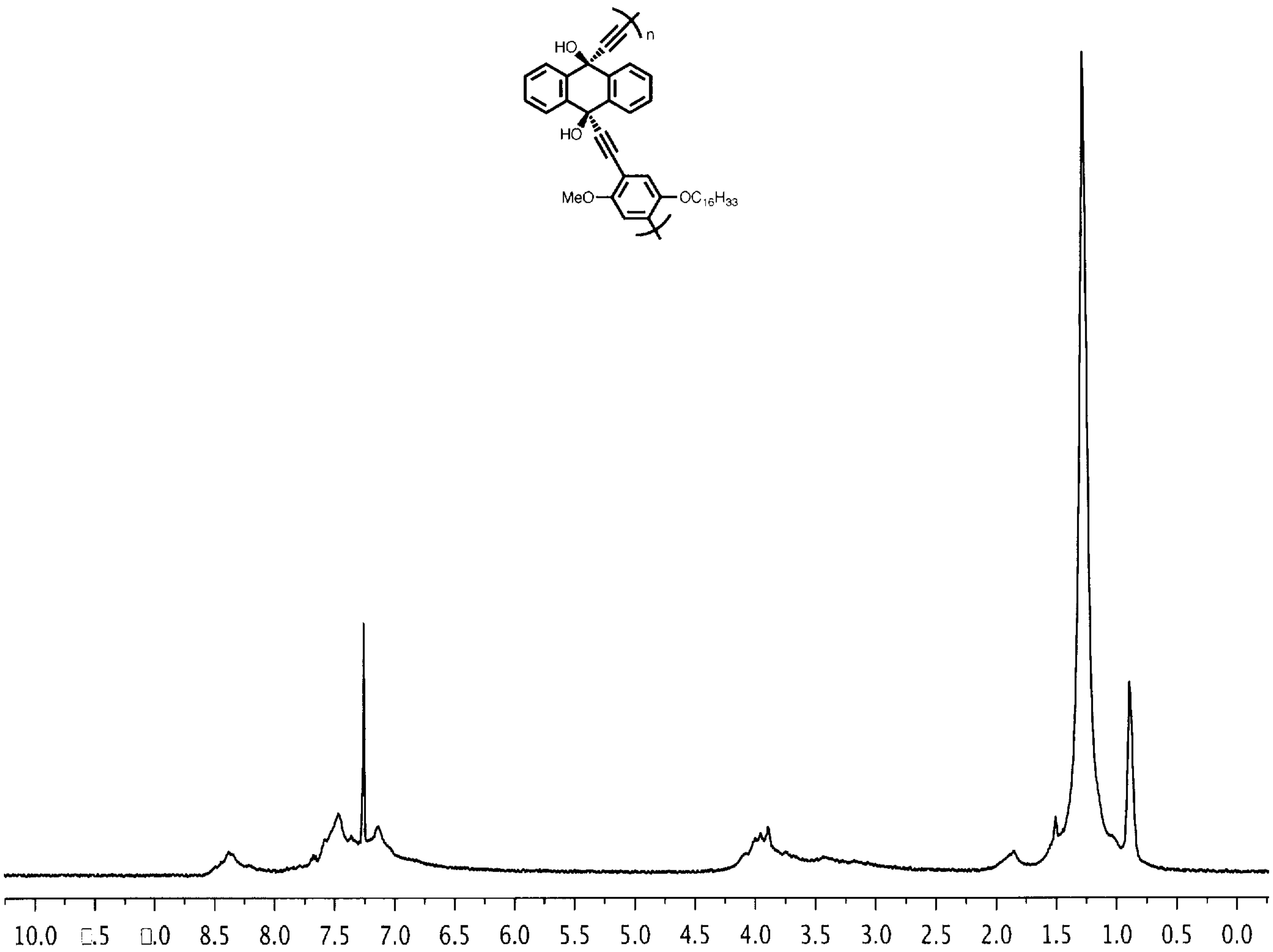
^{13}C NMR (501 MHz, CDCl$_3$, 50 °C): δ 132.8, 132.8, 129.2, 129.0, 100.5, 32.6, 30.3, 30.0, 23.3, 14.7

GPC (THF): M_w/M_n = 12 150/7 790

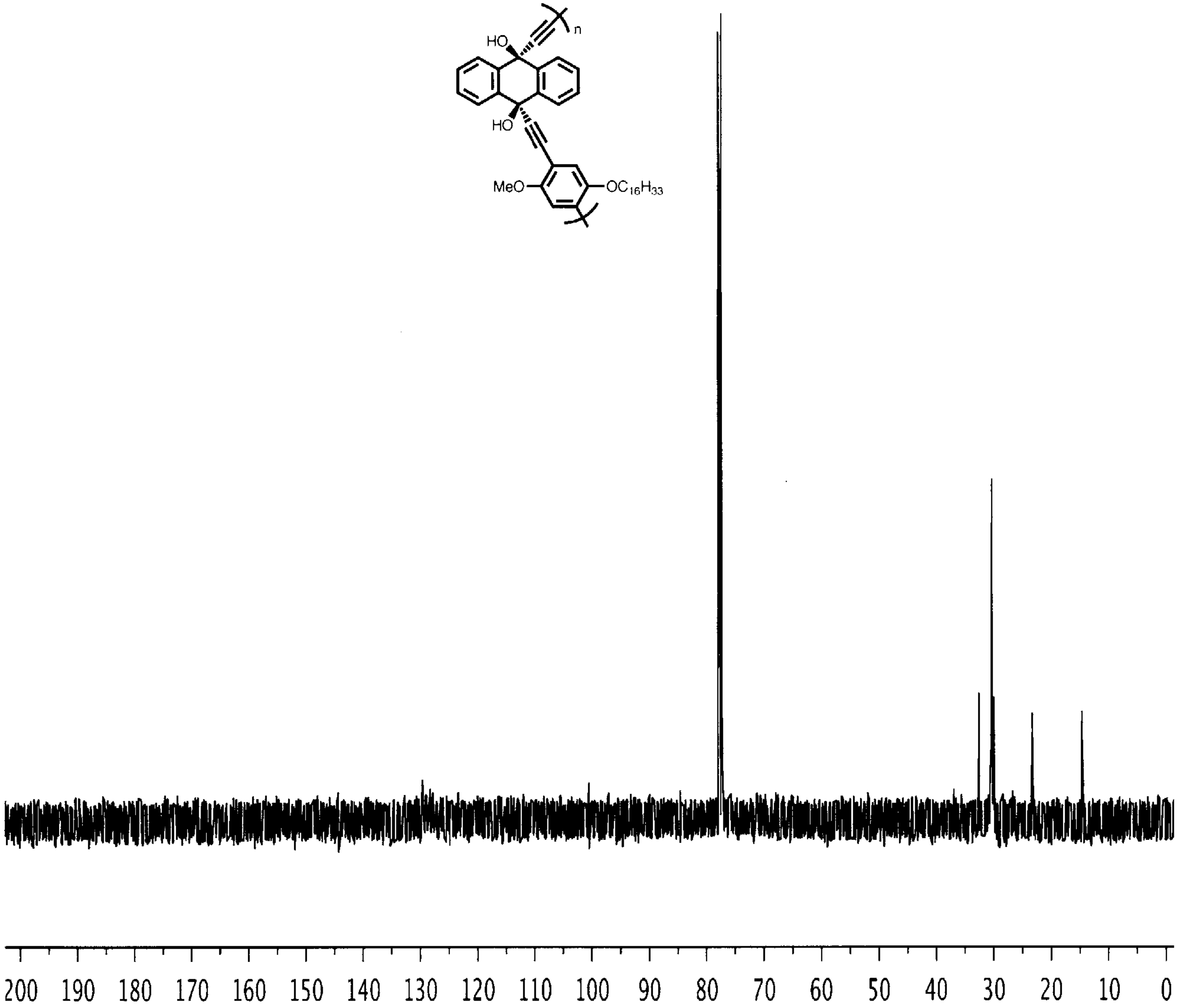
Chapter 3 Appendix:

^{1}H-NMR and ^{13}C-NMR Spectra

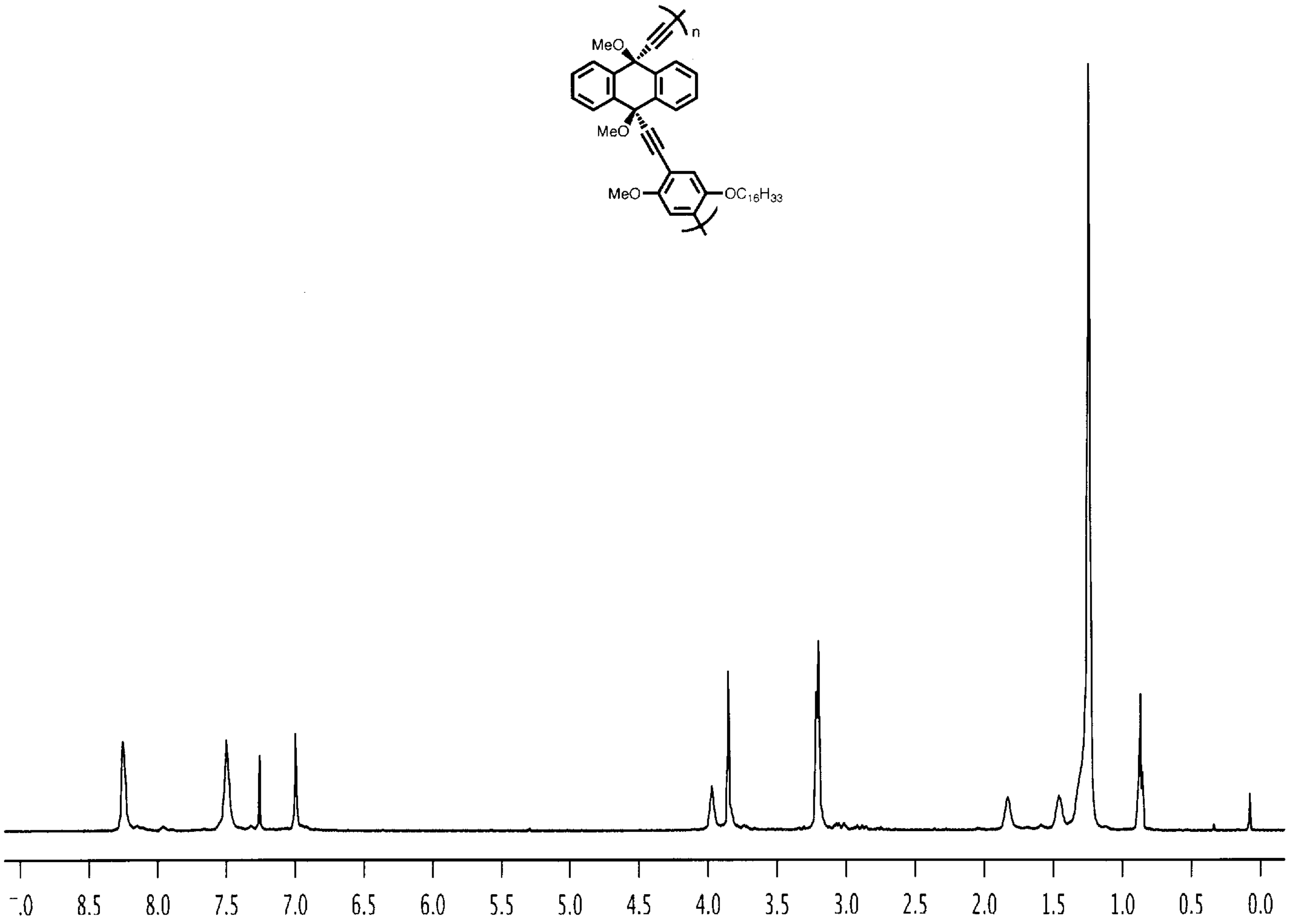
And Additional Figures



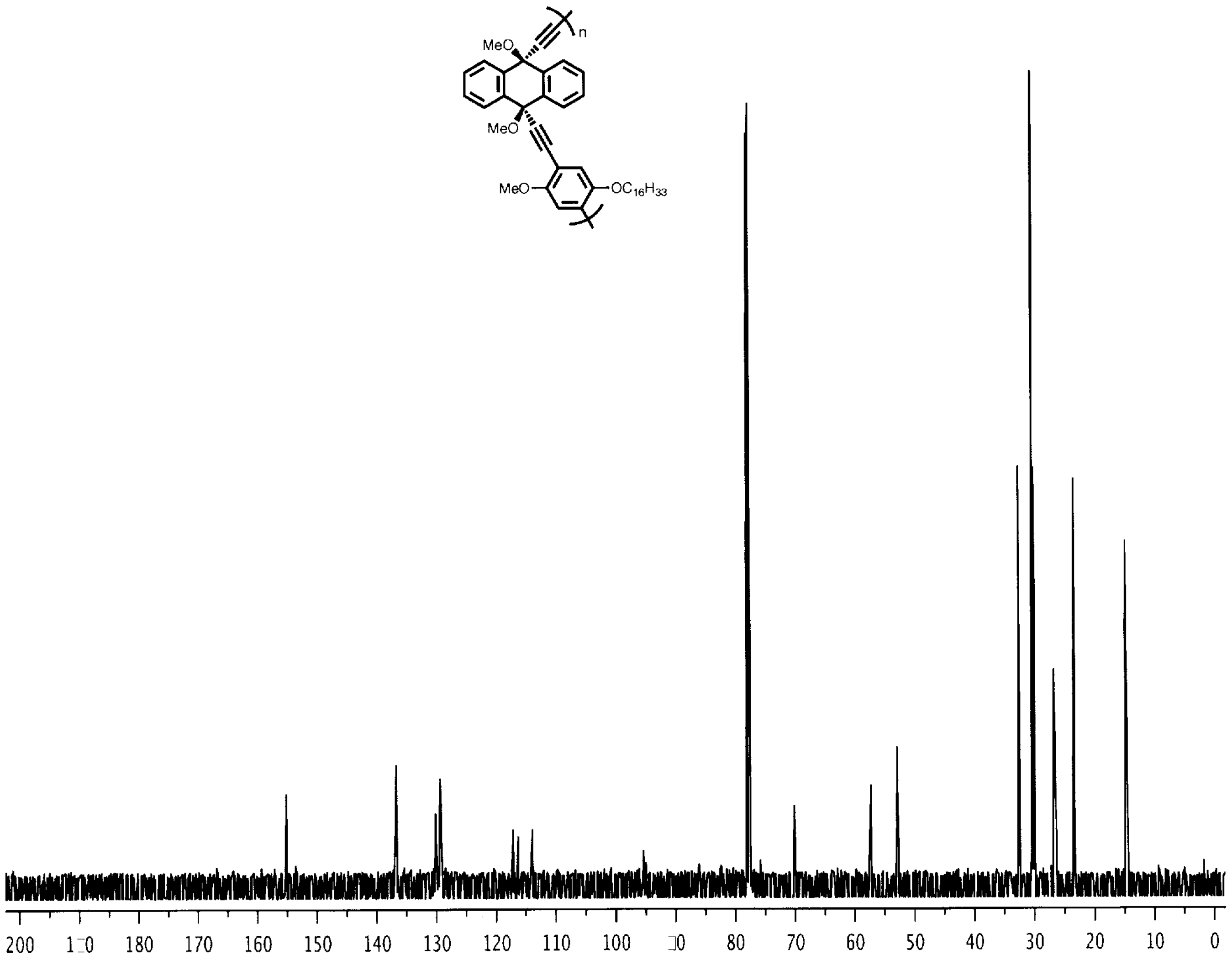
Spectrum 3.1. ^{1}H-NMR Spectrum of **Polymer 2a** (500 MHz, CDCl$_3$, 50 °C).



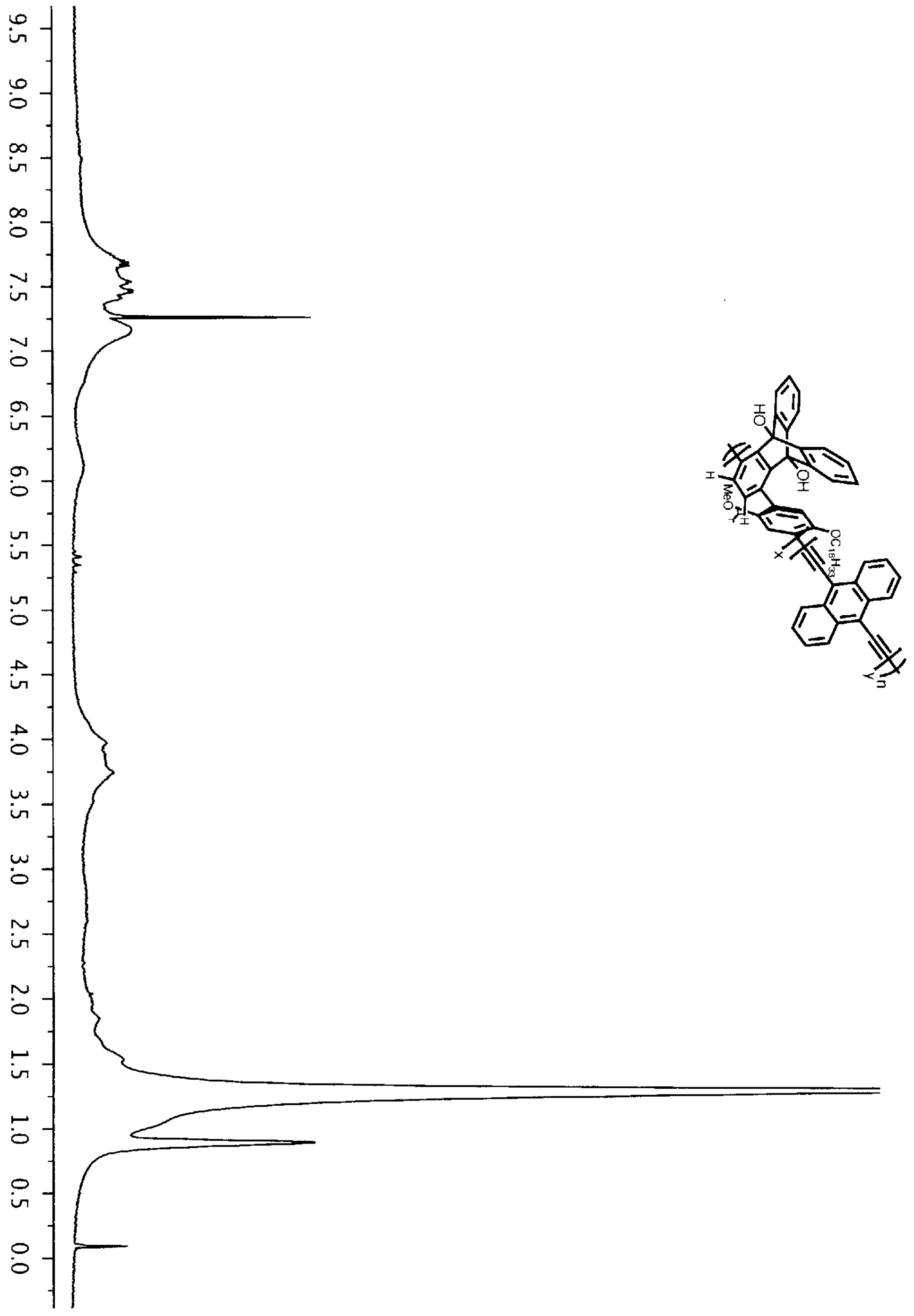
Spectrum 3.2. ^{13}C-NMR Spectrum of **Polymer 2a** (501 MHz, CDCl$_3$, 50 °C).



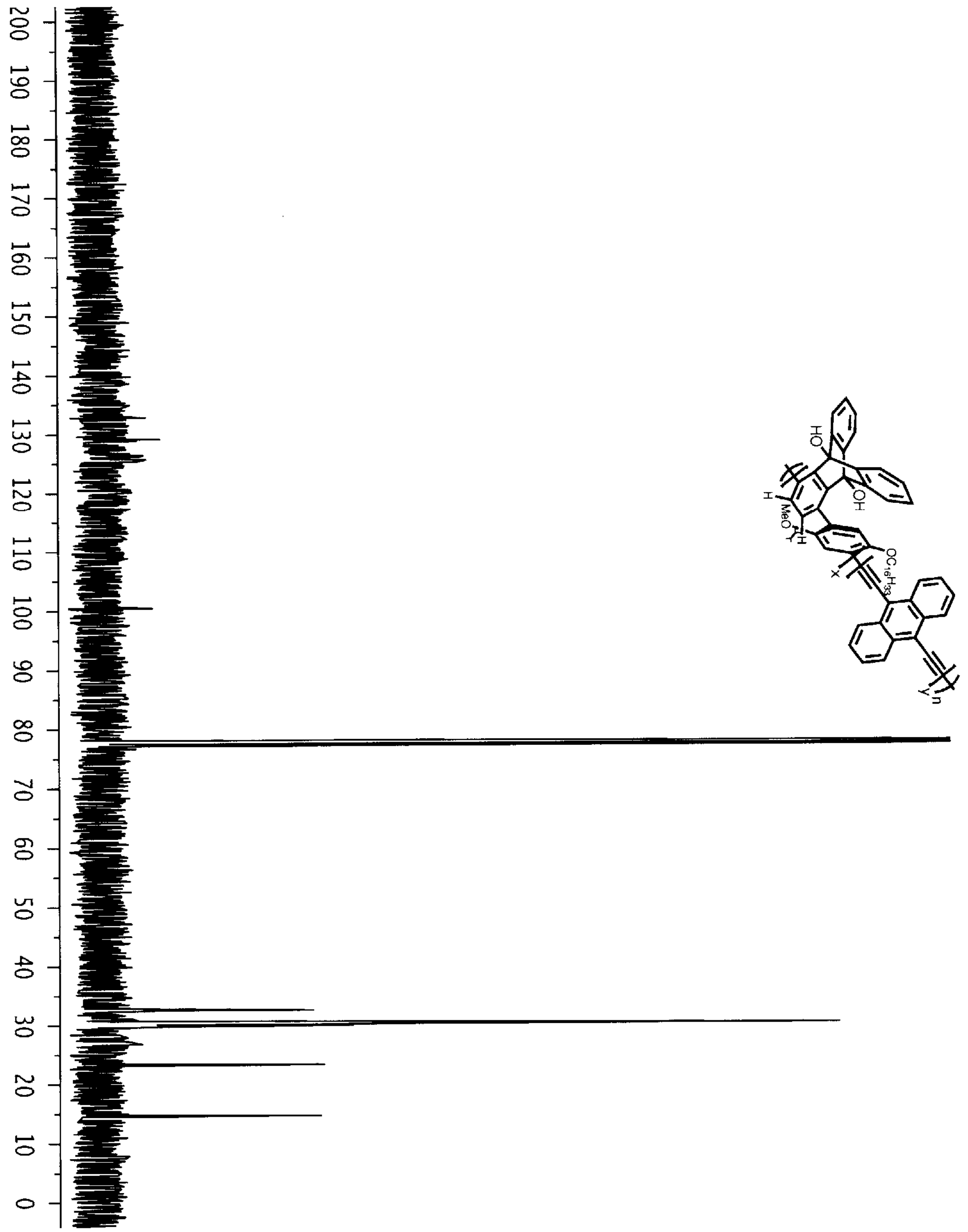
Spectrum 3.3. ^{1}H-NMR Spectrum of **Polymer 2b** (500 MHz, $CDCl_3$).



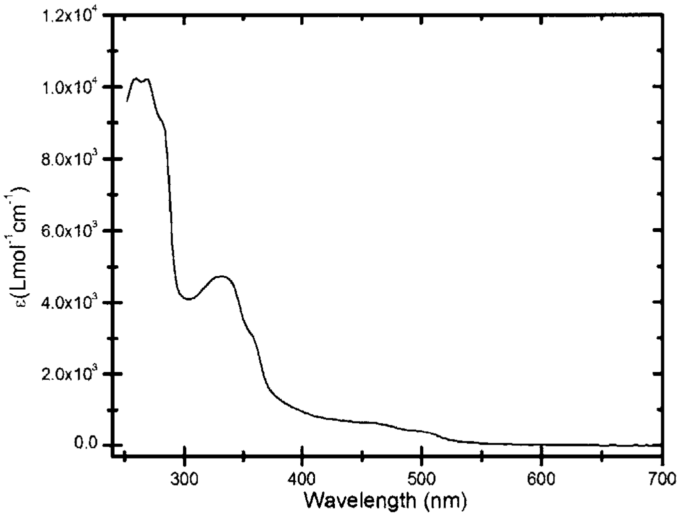
Spectrum 3.4. ^{13}C-NMR Spectrum of **Polymer 2b** (500 MHz, CDCl$_3$).



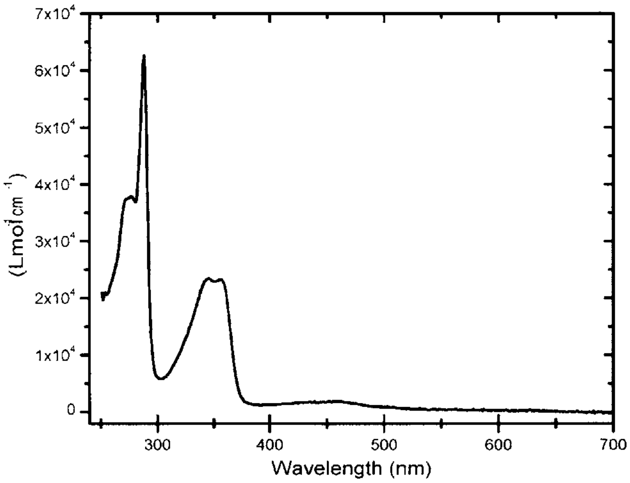
Spectrum 3.5. ^{1}H-NMR Spectrum of **PPT1** (500 MHz, CDCl$_3$, 50 °C).



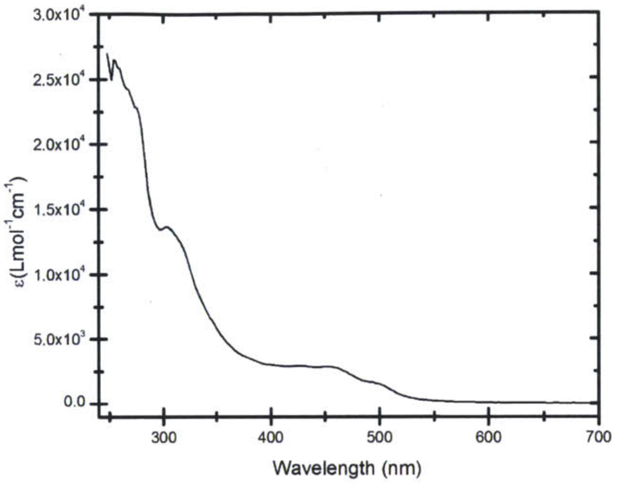
Spectrum 3.6. ^{13}C-NMR Spectrum of **PPT1** (501 MHz, CDCl$_3$, 50 °C).



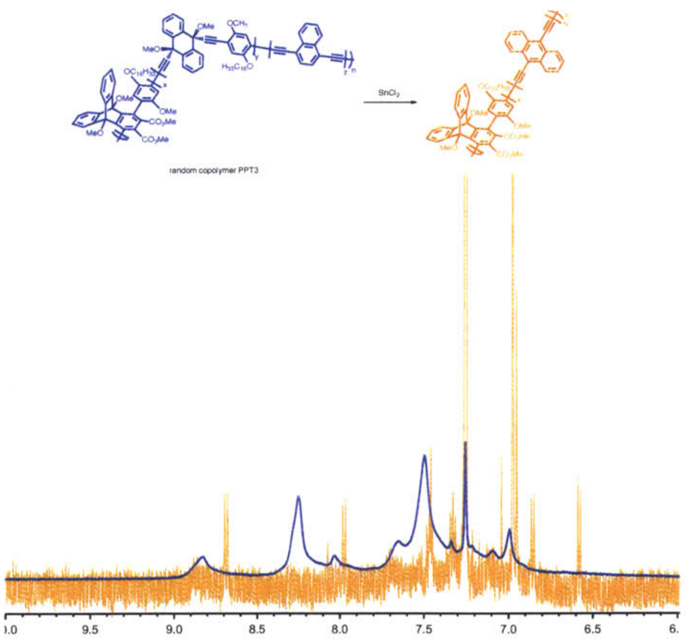
Spectrum 3.7. UV-Vis Spectrum of **Polymer 2a**



Spectrum 3.8. UV-Vis Spectrum of **Polymer 2b**



Spectrum 3.9. UV-Vis Spectrum of **PPT1**

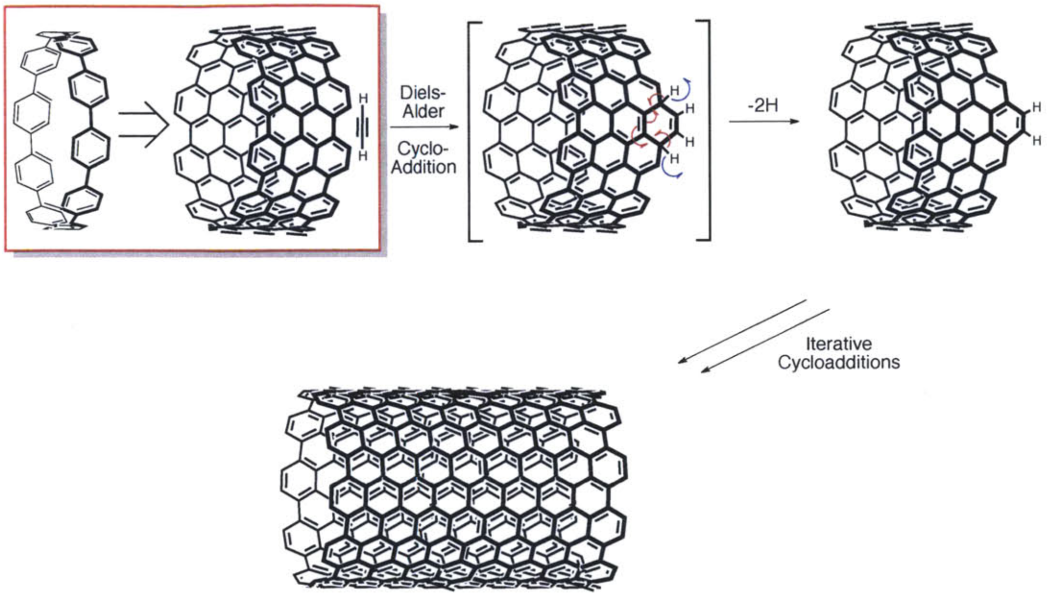


Spectrum 3.10. Overlapped ^{1}H-NMR spectra (in the aromatic region) in $CHCl_3$ of a random copolymer obtained from subjecting polymer 2b to [2+2+2] reaction conditions (*blue*) and its reductively aromatized analog (*orange*). The downfield signal matches exactly with that of the anthracenediacetylene polymer reported by Taylor.[12]

CHAPTER 4:

TOWARDS A PERYLENE-CONTAINING NANOHOOP: MACROCYCLIC, CROSS-SECTIONS OF ARMCHAIR SWCNTs

4.1 Introduction



Scheme 4.1. Schematic representation of the bottom-up chemical synthesis of an armchair SWCNT segment of a single chirality via iterative Diels-Alder cycloadditions performed in the bay-region of a nanohoop (potential starting structures highlighted in red square).[1]

Tremendous attention has recently been given to carbon nanohoops due to their potential utility in the bottom-up chemical synthesis of single chirality, armchair single-walled carbon nanotube (SWCNT) segments.[2] This strategy employs iterative Diels-Alder cycloadditions followed by oxidative re-aromatizations, with the initial cycloaddition being performed in the bay-region of a structurally suitable *p*-polyarylene macrocycle, or nanohoop (Scheme 4.1).[1,2] The simplest of these nanohoops is cycloparaphenylene (CPP), a belt-shaped macrocycle consisting entirely of 1,4-connected phenylenes. This macrocycle is considered the shortest possible cross-section of an armchair SWCNT.[3] Bertozzi and Jasti's pioneering synthesis[3] of CPP in 2008 preceeded numerous publications by three research groups demonstrating the selective synthesis of progressively smaller CPPs.[4] This culminated four years later with Jasti's report of [6]-

cycloparaphenylene, theoretically the smallest CPP.[5] Although it is well known that 1,1'-biphenyl is unable to undergo a Diels-Alder cycloaddition in its bay-region, we hypothesized that the significant macrocyclic strain of CPP[6] could significantly improve the feasibility of a cycloaddition in its bay-region. The belt-like shape of CPP means that its constitutional *p*-orbitals are radially aligned in the same plane as the macrocycle[3], resulting in high orbital density at the center of the macrocycle which is responsible for the unusually high strain energy of these compounds (Figure 4.1.a).[6] This feature, coupled with its structural resemblance to carbon nanotubes, qualifies CPP and other structurally similar macrocycles as potential starting points for the rational, chemical synthesis of armchair SWCNTs (Figure 4.1.b & c).[7]

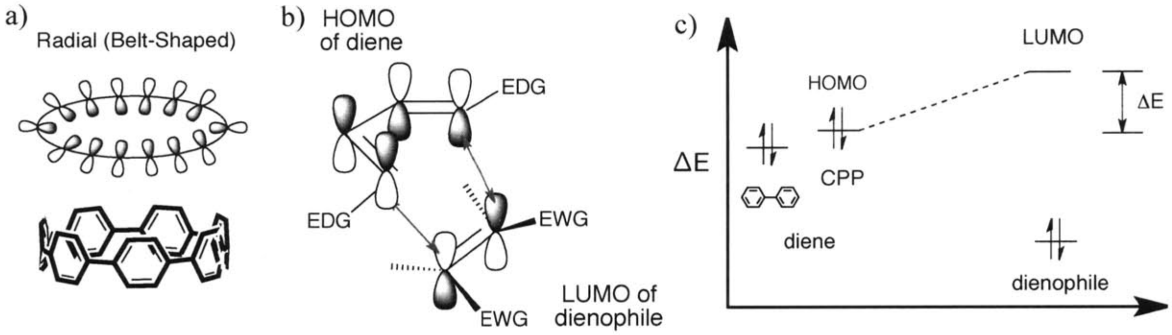
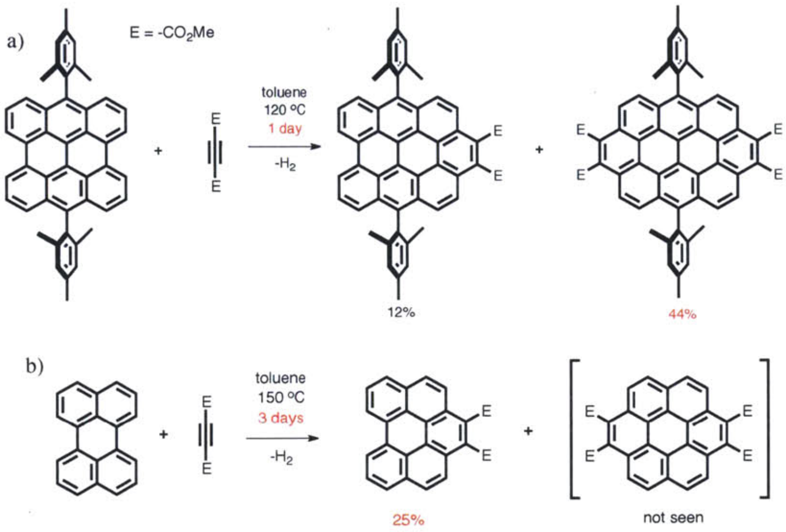


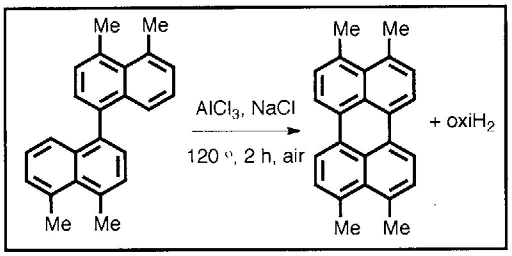
Figure 4.1. Schematic representations of a) the radially aligned *p*-orbitals in a CPP b) typical HOMO-LUMO interactions in a Diels-Alder cycloaddition and c) the energetically higher HOMO in the bay-region of a CPP relative to 1,1'-biphenyl due to its macrocyclic strain (ΔE is smaller for CPPs)

We initially synthesized and subjected [12]-cycloparaphenylene to typical Diels-Alder conditions utilizing various Lewis Acids and dienophiles, with the addition of an oxidant in some instances to assist with the re-aromatization of any potentially formed cycloadducts. Despite our best efforts we could not perform a Diels-Alder cycloaddition within the bay-region of [12]-CPP. However, considering the crucial dependence of macrocyclic strain-energy on ring size[8], we were still uncertain about the viability of the bottom-up strategy (Scheme 4.1.) starting from a CPP smaller than the [12]-membered analog.



Scheme 4.2. Diels-Alder cycloadditions with dimethyl acetylene dicarboxylate (DMAD) as the dienophile successfully performed in the bay-regions of a) protected bisanthene and b) perylene. Note the different reaction conditions used, and the varying outcomes (mono- vs. bis-cycloadducts and the respective yields)[1]

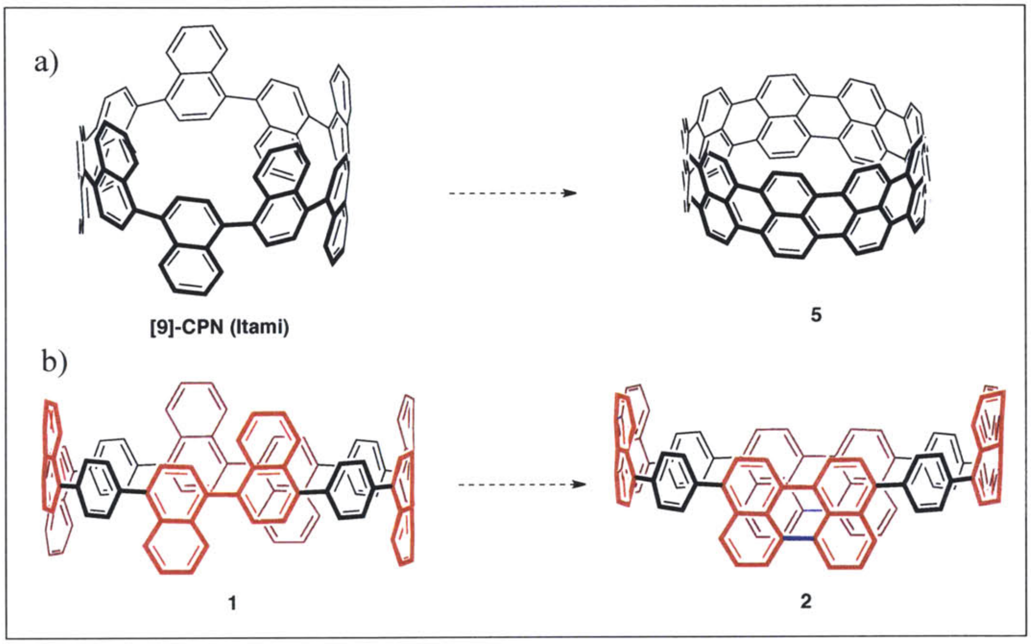
Larry Scott is widely credited with the development of the concept for the bottom-up chemical synthesis of SWCNTs. His group published a seminal report in 2009 strongly suggesting that successful initiation of this strategy required the use of a polycyclic aromatic hydrocarbon (PAH)-containing nanohoop, versus the structurally smaller CPP. Scott's research group then experimentally validated the correlation between increasing polycyclic aromaticity of a bay-region-containing compound and its decreasing activation energy barrier to cycloadditions within its respective bay-regions (Scheme 4.2).[1] This unequivocally demonstrated that the "diene-like character" associated with the bay-region of a PAH moeity increases with its size (i.e. bi-phenyl < phenanthrene < perylene < bisanthene, etc. are increasingly likely to undergo cycloaddtions in their bay-regions with a specific dienophile). The asymptotic nature of this correlation meant that a nanohoop containing the desirable perylene moiety soon emerged as a synthetic target for several organic chemists.[9] The increased desirability of a perylene-containing nanohoop was due to a combination of its improved Diels-Alder feasibility and its plausible synthetic viability.



Scheme 4.3. The Scholl cyclization of a 1,1'-binaphthalene derivative to form a perylene containing compound.[11]

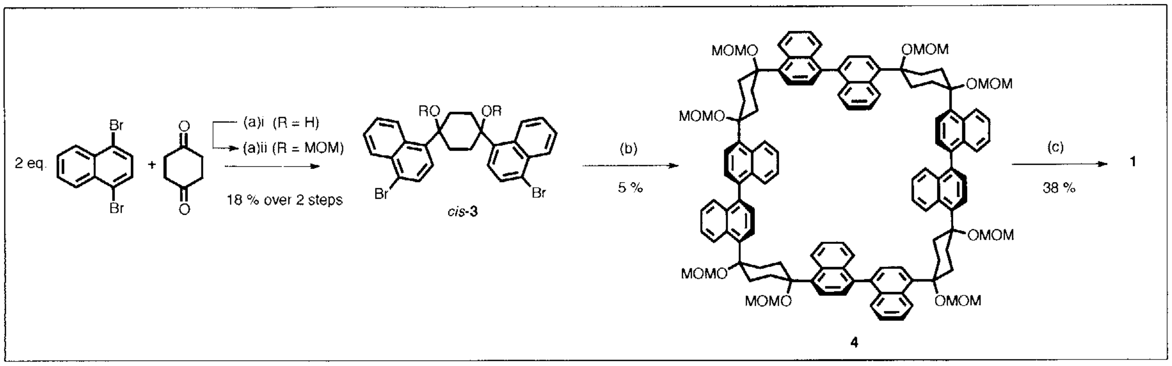
Extending the aromaticity of a given substrate increases its rigid planarity, [10] simultaneously diminishing its inclination to curve or bend as is necessary in the formation of a nanohoop. Thus, rather than attempt to access a nanohoop possessing a rigid, pre-installed perylene unit, we opted for a more logical synthetic approach by aiming to synthesize a belt-shaped macrocycle containing the 1,1'-binaphthalene moiety, a precursor to perylene. The extensively studied Scholl reaction has been previously used to facilitate the cyclization of 1,1'-binaphthyl derivatives to perylene-containing compounds[11] (Scheme 4.3.). However, this powerful coupling reaction often reacts indiscriminately to leading to molecular re-arrangement of its substrate, with a strong dependence on the makeup of the specific substrate involved.[12]

With the subsequent goal of synthesizing a short cross-section of an armchair SWCNT, one naphthyl unit in length and structurally similar to perylene (**5**), the Itami research group reported the synthesis of [9]-cycloparanaphthalene ([9]-CPN) in early 2012.[9] The high energy due to the radially aligned *p*-orbitals increases the likelihood of producing a dispersion of conformers upon subjecting 9-CPN to Scholl reaction conditions, so we decided to pursue the synthesis of a similar, but simpler, nanohoop. We envisioned that a nanohoop possessing 1,1’-binaphthyls that were isolated from each other by a *para*-connected phenyl (**1**) could potentially result in improved selectivity for the crucial perylene forming step (Scheme 4.4.b).



Scheme 4.4. Potential conversion of a) Itami’s [9]-CPN to a perylene-like nanohoop b) previously unreported **1** to a perylene-containing nanohoop (with the isolated 1,1’-binaphthyls and isolated perylene groups highlighted in red).

4.2. Synthesis and Characterization



Scheme 4.5. Conditions: (*(a)i*) *1.* 2.2 eq. *n*BuLi, TMEDA, PhMe/Et_2O, -78 °C, 1 h *2.* 1 eq. 1,4-cyclohexanedione, rt, 16 h (*(a)ii*) DCM, 2.0 eq. DIPEA, 2.0 eq. MOMCl, 0 °C to rt, 16 h (*b*) 2.0 eq. $Ni(COD)_2$, 2.0 eq. 2,2'-bipy, reflux, THF [15mM], 36 h (*c*) excess *p*-TsOH, PhMe, μW, O_2, 150 °C, 150 W, 1 h.

1,4-cyclohexanedione was slowly added in three equivalent portions to mono-lithiated 1,4-dibromonaphthalene stirring in a toluene/diethyl ether solvent mixture cooled to -78 °C. The reaction was left to stir for 16 hours at room temperature and then worked up to furnish a crude mixture of *cis*- and *trans*-diol products. The diol of the crude product was then protected with methyoxy methyl (MOM) groups via reaction with Hünig's base and chloromethyl methyl ether. The desired isomer was isolated by column chromatography. Once isolated, *cis*-**3** was utilized in a high-dilution Yamamoto coupling which furnished a *tetra*-cyclized product, **4**, in low yields. Applying conditions similar to those employed by Itami in the aromatization of *cis*-tetrasubstituted-1,4-cyclohexane moieties[4d], we performed an acid mediated aromatization of **4** using *p*-toluene sulfonic acid in toluene coupled with microwave heating to yield compound, **1**.

Typical organic characterization techniques such as Nuclear Magnetic Resonance (NMR) and High Resolution Mass Spectroscopy (HRMS) were applicable to *cis*-**3** and macrocycle **4**, making their structural determination relatively simple. However, the poor bond rotation around **1**'s rigid naphthyl-naphthyl bond and the molecule's high asymmetry required the use of increased temperatures (150 °C, Spectrum 4.6 in Appendix.) to simplify the NMR spectra via coalescing of the peaks. In addition, due to **1**'s exclusively aromatic, non-polar composition, MALDI-TOF was the required method for determining its mass.

4.3. Results and Discussion

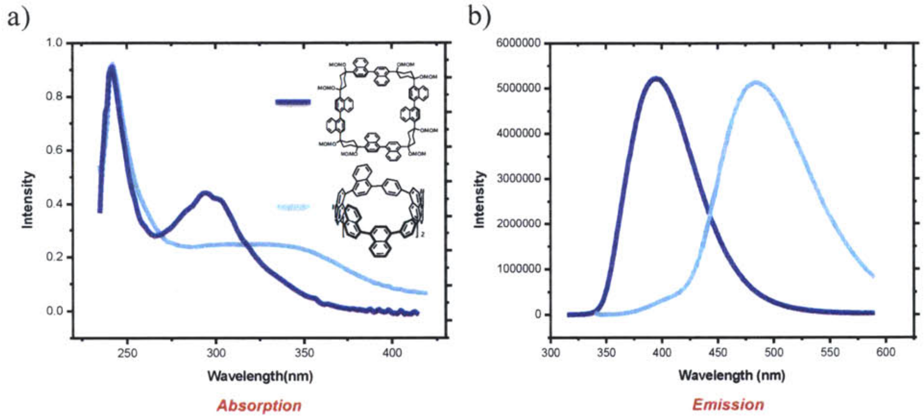


Figure 4.2. A comparison of the a) Absorption and b) Emission spectra upon conversion of **4** (*blue*) to target compound **1** (*cyan*). (**4**: **ε** @ 293 nm: 1.97 X 10^4 L mol^{-1} cm^{-1}, **ϕ**: 0.23 in $CHCl_3$ relative to Anthracene in EtOH. **1**: **ε** @ 305 nm: 3.16 X 10^4 L mol^{-1} cm^{-1}, **ϕ**: 0.29 in DMSO relative to Anthracene in EtOH, τ: 1.852 ns relative to POPOP)

We examined the photophysical spectra of **4** and **1** (Figure 4.2.) to gain some insight into the relative electronic properties of our target compound, given its high degree of curvature. Direct comparison of the absorption properties via normalized UV-Vis spectra (Figure 4.2a), shows a noticeable diminishing of **4** absorption band close to 300 nm upon conversion to **1**. The four saturated cyclohexane moieties in **4** allow for structural flexibility in the precursor macrocycle, enabling relatively efficient naphthyl-naphthyl π-orbital overlap. However, the severe curvature introduced upon aromatization to **1** reduces the efficiency of this binaphthyl π-conjugation and correspondingly, the strength of the absorption band located at ~ 300 nm decreases. Overall, it is the increasingly poor geometry for efficient orbital overlap that is responsible for the observed differences in the absorption profiles. The emission of **4** is red-shifted by nearly 100 nm upon formation of **1** (Figure 4.2.b). For *p*-polyarylenes, such strongly bathochromic emission is characteristic of high-energy macrocycles, instead of their linear analogs. As highlighted in Chapter 2, linear poly(*para*-arylene)s usually emit blue due to their rigid structures and the large dihedral angles between their adjacent aryl rings. However, the relatively large Stokes shift observed for **1** is governed by the extent of structural relaxation in the optically excited state of the fully aromatic macrocycle, or nanohoop.[3] The enhancement of curvature upon formation of **1** results in greater sp^3 hybridization and increasingly asymmetric *p*-orbitals, with their smaller lobes oriented towards the inside of the nanohoop. These changes reduce steric interactions, simultaneously decreasing the dihedral angles in the excited state relative to the very sterically hindered ground state. As a result, relative to their linear analogues, macrocyclic *p*-polyarylenes have the potential for considerably greater structural relaxation explaining the characteristally large Stokes shift observed in Figure 4.2b.

Despite the wealth of useful literature on the Scholl reaction, it has been shown to explicitly promote unwanted rearrangements in a variety of polyaromatic substrates.[12] Furthermore, previously reported nanohoops are commonly only accessed in milligram quantities due to a number of synthetic limitations, with very few exceptions.[4c, 13] This disadvantageous circumstance also hindered the synthesis of large quantities of **1** in this study. Taking these factors into consideration, we synthesized 4,4'-dimethyl-1,1'-binaphthalene[14] as a model compound and are screening various Scholl reaction conditions in search of those most convenient for the transformation of **1** to **2**.

4.4. Conclusion

We have reported the synthesis of **1**, a nanohoop containing four 1,1'-binaphthyl units, each separated by a phenyl ring. We are currently seeking to identify the most appropriate cyclization reaction conditions to furnish a perylene-containing nanohoop (**2**) from this precursor macrocycle (**1**).

4.5 References

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4.6 Experimental Procedures

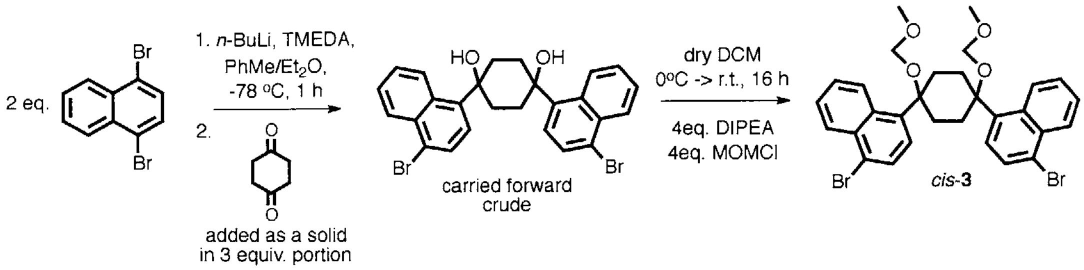
Materials: All reactions were carried out under a flow of argon gas using standard Schlenk techniques unless otherwise stated. All photophysical experiments were performed with spectral grade chloroform. Toluene was obtained from a dry solvent still. All reagent grade materials were purchased from various commercial sources and used as received unless otherwise stated.

NMR Spectroscopy: ^{1}H and ^{13}C NMR spectra for all compounds were acquired on a Varian Inova 500 MHz or Varian Inova 501 MHz spectrometers. The specific instrument is noted below each spectrum. NMR data collected at elevated temperatures are noted below the respective spectra. Chemical shifts are reported in ppm and referenced to residual NMR solvent peaks. ($CDCl_3$: δ 7.26 ppm for ^{1}H, δ 77.2 ppm for ^{13}C. CD_2Cl_2: δ 5.30 ppm for ^{1}H. d^6-DMSO: δ 2.50 ppm for ^{1}H, δ 39.52 ppm for ^{13}C)

Absorption and Emission Spectroscopy: Fluorescence spectra were measured on a SPEX Fluorolog-τ3 fluorometer (model FL-321, 450 W Xenon lamp) using right-angle detection. Ultraviolet-visible absorption spectra were measured with an Agilent 8453 diode array spectrophotometer and corrected for background signal with a solvent filled cuvette.

MALDI-TOF Mass Spectroscopy: A Bruker Omniflex MALDI-TOF was used for determining the mass of **1.** 9-nitroanthracene was used as the matrix as reported by Itami in the synthesis of 9-CPN.[9]

Microwave: A CEM Discover Microwave was used for all microwave reactions (150 W, 30 PSI).

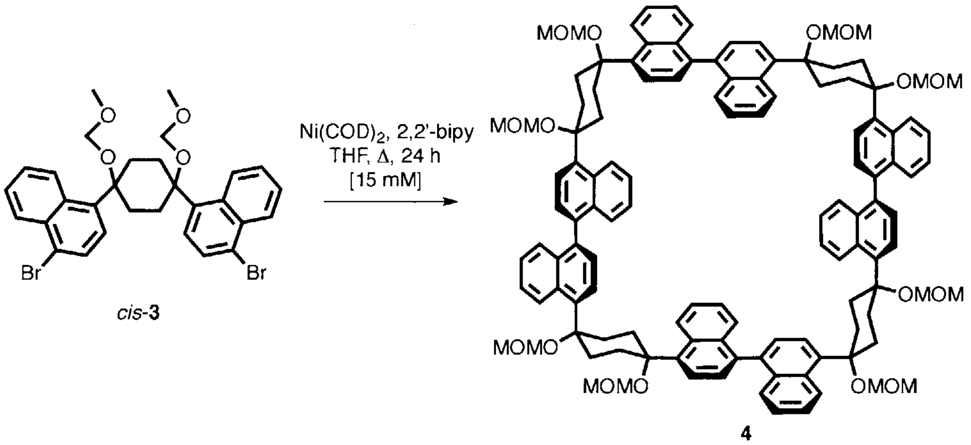


***cis*-3**: 1,4-dibromonaphthalene (25.0 g, 87.4 mmol), diethyl ether (400 mL) and PhMe (400 mL) were added to a flame-dried, 1 L round-bottom schlenk flask equipped with a magnetic stir bar. A solution of *n*-butyllithium (60.0 mL, 1.60 M, 96.2 mmol) was then added to the flask dropwise at -78 °C via an addition funnel. After stirring the mixture for 1.5 hours at -78 °C cyclohexane-1,4-dione (4.90 g, 43.7 mmol) was added in three equal portions and allowed to stir for 16 hours after warming up to room temperature. The reaction mixture was then quenched with aqueous ammonium chloride solution, extracted with ethyl acetate (x3), dried with sodium sulfate, and concentrated *in vacuo*. The residue was passed through a short silica-gel plug using 40 % DCM: 60 % Hexane to afford crude 1,4-bis(4-bromonaphthyl)cyclohexane-1,4-diol as an off-white solid that was carried forward as is. This crude diol product was then added to a flame-dried schlenk flask under a flow of Argon and capped with a rubber septum. Diisopropylethylamine (15.2 mL, 87.4 mmol) and dry dichloromethane (30 mL) were then added to the flask via a syringe needle before cooling the entire mixture down to 0 °C. Chloromethyl methyl ether (6.64 mL, 87.4 mmol) was thereafter added dropwise to the cooled, stirring mixture, which was then warmed to room temperature and allowed to stir for 16 hours. Aqueous ammonium chloride was added to quench the reaction upon its completion before the organic and aqueous layers were separated. The aqueous layer was then extracted with dichloromethane (x3). The cumulative organic layers were then washed with brine, dried with sodium sulfate and concentrated *in vacuo*. The desired product was then isolated from the resulting residue via column chromatography (50 % DCM: 50 % hexanes => 100 % DCM) to yield a white solid (4.78 g, 7.79 mmol, 18 % over 2 steps).

^{1}**H NMR** (500 MHz, CD$_2$Cl$_2$): δ 8.98 (d, J=7.9 Hz, 2 H), 8.33 (d, J=7.3 Hz, 2 H), 7.74 (d, J=8.0 Hz, 2 H), 7.63-7.57 (m, 4 H), 7.35 (d, J=8.1 Hz, 2 H), 4.47 (s, 4 H), 3.38 (s, 6 H), 3.02 (td, J=10 Hz, 2 H), 2.86 (dψt, J=13 Hz, 2 H), 2.35 (dt, J=15 Hz, 2 H), 2.20 (ψt, J=12 Hz, 2 H)

^{13}**C NMR** (500 MHz, CDCl$_3$): 133.0, 132.9, 128.8, 128.3, 127.7, 127.0, 126.4, 124.2, 92.9, 80.4, 56.6, 34.1 (br).

HRMS (ESI): calc for C$_{30}$H$_{30}$Br$_2$O$_4$ [M+Na] 635.0403, found 635.0374.

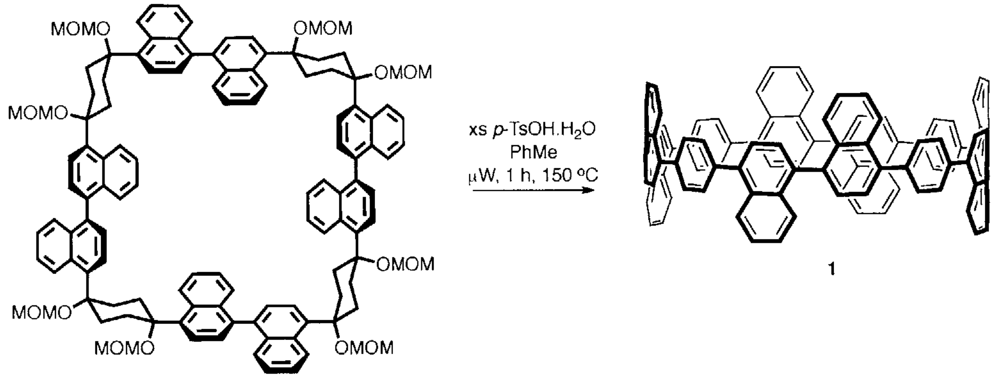


4: *cis*-**3** (2.23 g, 3.63 mmol), Ni(COD)$_2$ (2.00 g, 7.27 mmol) and 2,2'-bipyridine (1.13 g, 7.27 mmol) were added to a flame-dried 500 mL round-bottom schlenk flask equipped with a magnetic stir bar under a flow of Argon. Dry tetrahydrofuran (480 mL) was added to the flask. The reaction mixture was then set to reflux and left for 36 hours after which it was cooled to room temperature and then quenched with aqueous ammonium chloride. The organic and aqueous layers were then separated and the aqueous layer then extracted with ethyl acetate (x3). The cumulative organic layers were then washed with brine, dried with sodium sulfate and concentrated *in vacuo*. The desired product was then isolated from the crude residue via repeated column chromatography ([5 % ethyl acetate/ 95 % hexanes => 20 % ethyl acetate/ 80 % hexanes] followed by [15 % ethyl acetate/ 85 % hexanes => 20 % ethyl acetate/ 80 % hexanes]) to give a white solid (33.3 mg, 0.182 mmol, 5 %)

^{1}H-NMR (500 MHz, $CDCl_3$): 8.70 (d, *J*=8.7 Hz, 8 H), 7.99 (d, *J*=8.5 Hz, 8 H), 7.48 (ψt, *J*=15.2 Hz, 8 H), 7.34 (ψt, *J*=15.0 Hz, 8 H), 6.87 (d, *J*=7.6 Hz, 8 H), 6.59 (d, *J*=7.5 Hz, 8 H), 4.77 (d, *J*=7.5 Hz, 8 H), 4.57 (d, *J*=7.3 Hz, 8 H), 3.49 (s, 24 H), 2.77 (m, 8 H), 2.60 (br s, 8 H), 2.45 (m, 8 H), 2.24 (br s, 8 H).

^{13}C-NMR (500 MHz, $CDCl_3$): 138.5, 133.7, 132.7, 127.4, 127.3, 127.0, 125.6, 125.5, 93.5, 80.7, 56.3, 37.5, 36.8, 32.5

HRMS (ESI): calc for $C_{120}H_{120}O_{16}$ [M+H]+Na 1840.8475, found 1840.8521.



4

1

A 7 mL microwave vial containing a magnetic stirring bar was flame-dried under vacuum and back-filled with argon after cooling to room temperature. To this vial was added **4** (18.2 mg, 10 μmol), TsOH.H_2O (30.4 mg, 0.16 mmol), and dry PhMe (3.00 mL). After degassing the mixture with Argon for 30 minutes, the vial was then sealed and heated in the microwave reactor apparatus, stirring at 150 °C for 60 minutes. After the reaction mixture was cooled down to room temperature, it was made up with dichloromethane. This organic layer was then washed with 1 M NaOH (aq) (x3). The organic and aqueous layers were then separated prior to washing the organic layer with brine. The cumulative organic layer was then dried with sodium sulfate, filtered and concentrated *in vacuo*. The resulting residue was subjected to column chromatography (20 % CH_2Cl_2/ 80 % hexane) to afford **1** (4.9 mg, 38 %) as an off-white, slightly yellow solid.

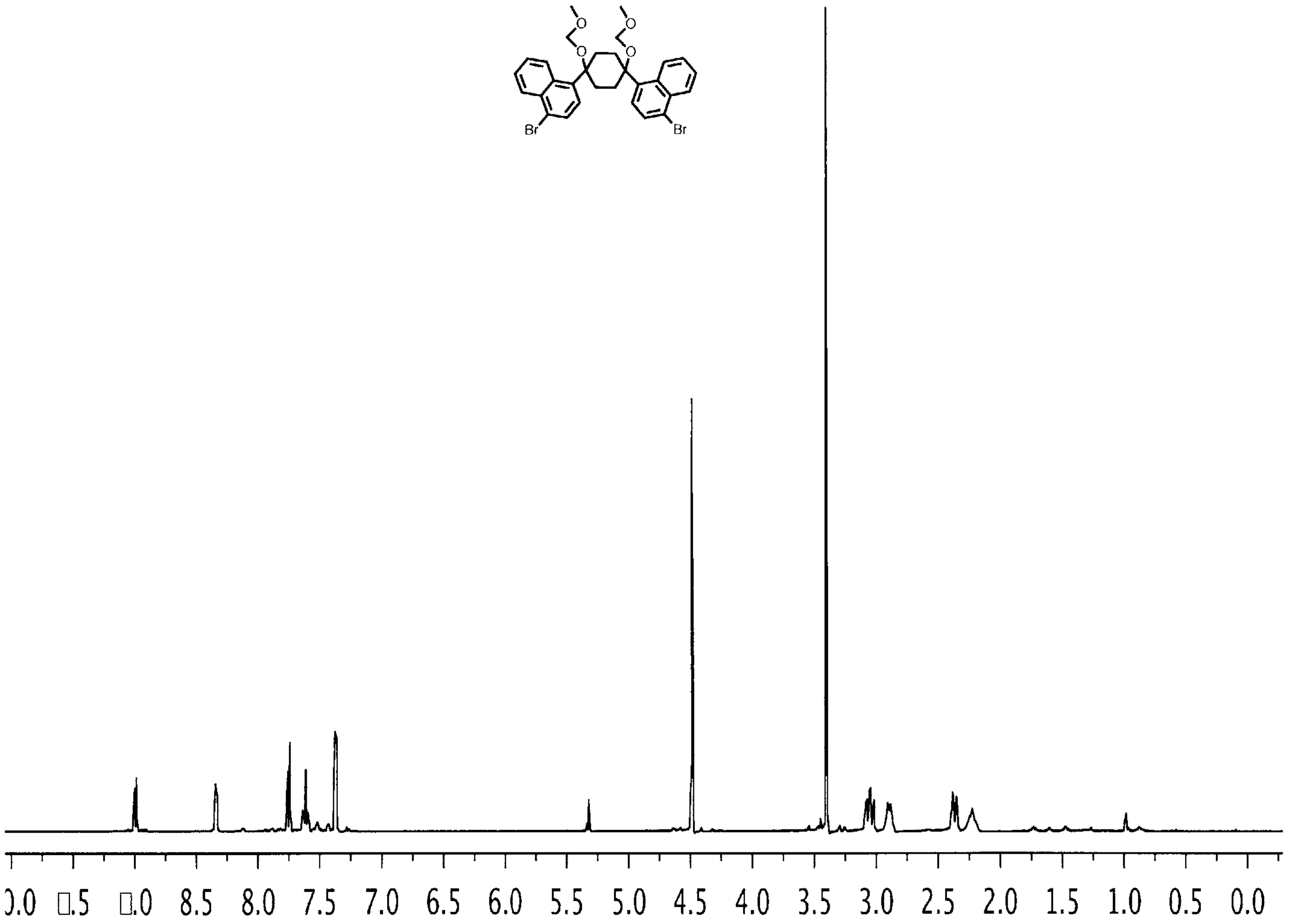
^{1}H-NMR (500 MHz, d^6-DMSO, 150 °C): 8.13 (1 H), 8.02 (2 H), 7.77 (1 H), 7.71 (3 H), 7.56 (5 H), 7.43 (2 H)

MADLI-TOF MS: calc for $C_{102}H_{70}$: 1306.55, found 1306.84.

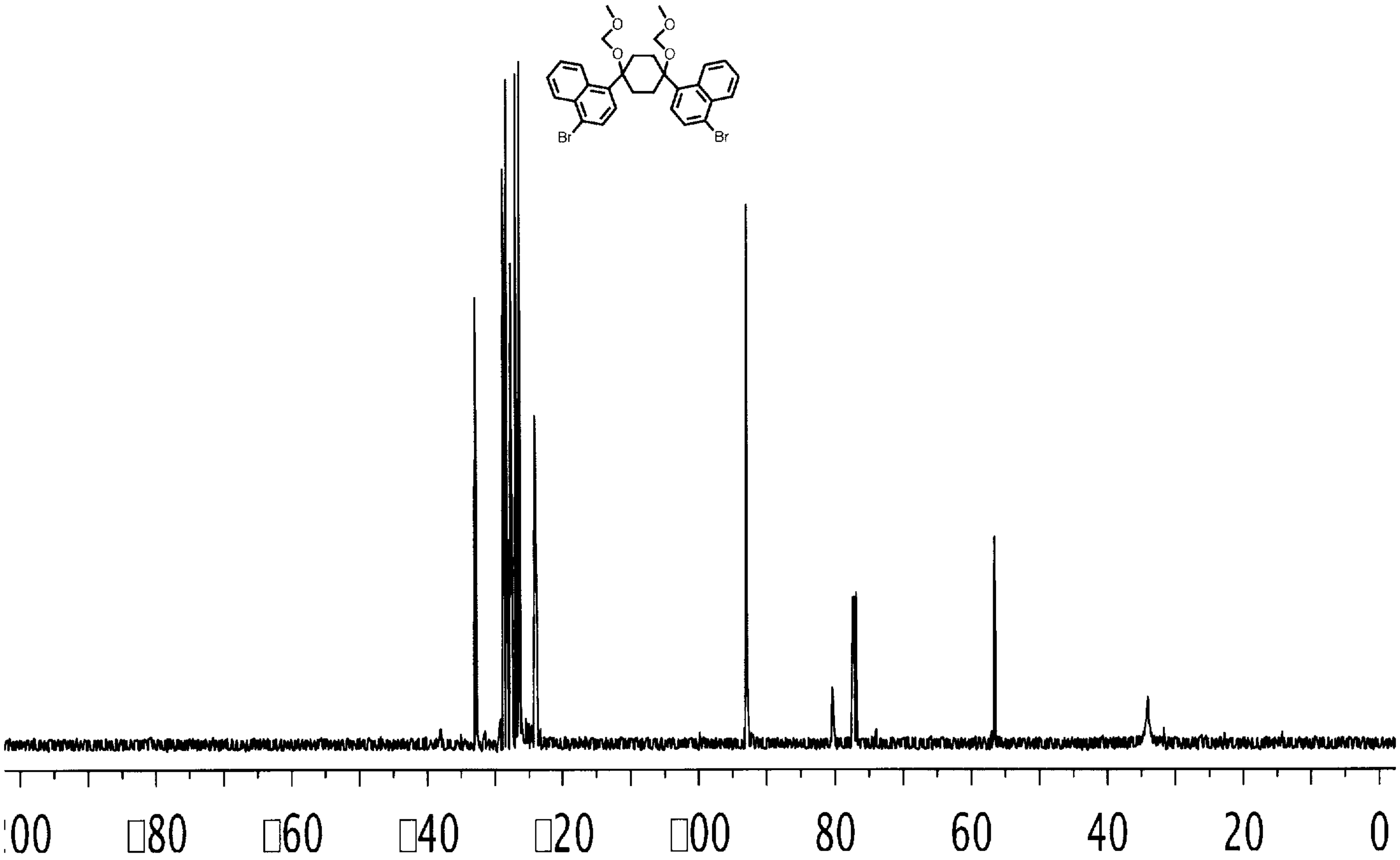
Chapter 4 Appendix:

^{1}H-NMR and ^{13}C-NMR Spectra

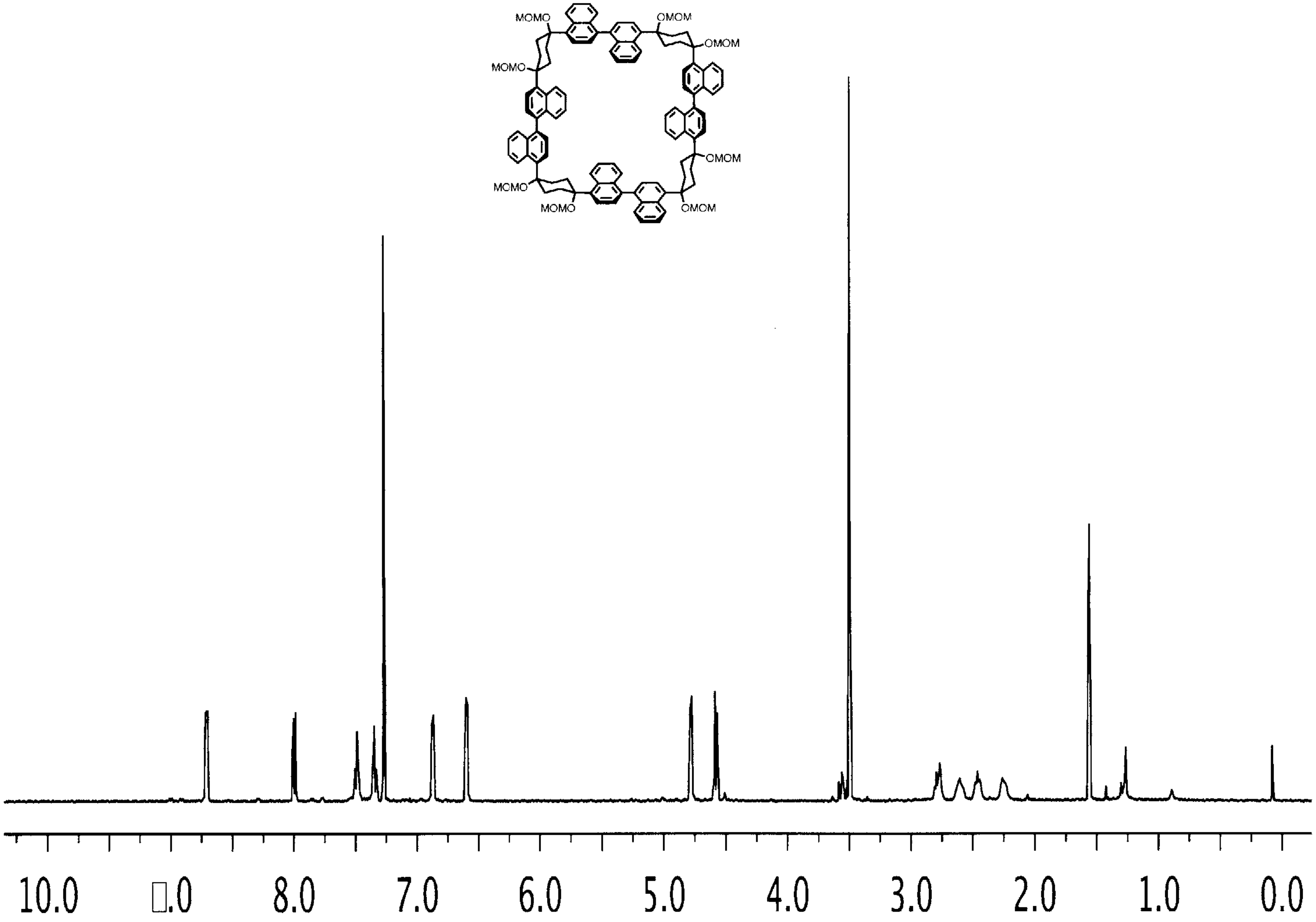
And Additional Figures



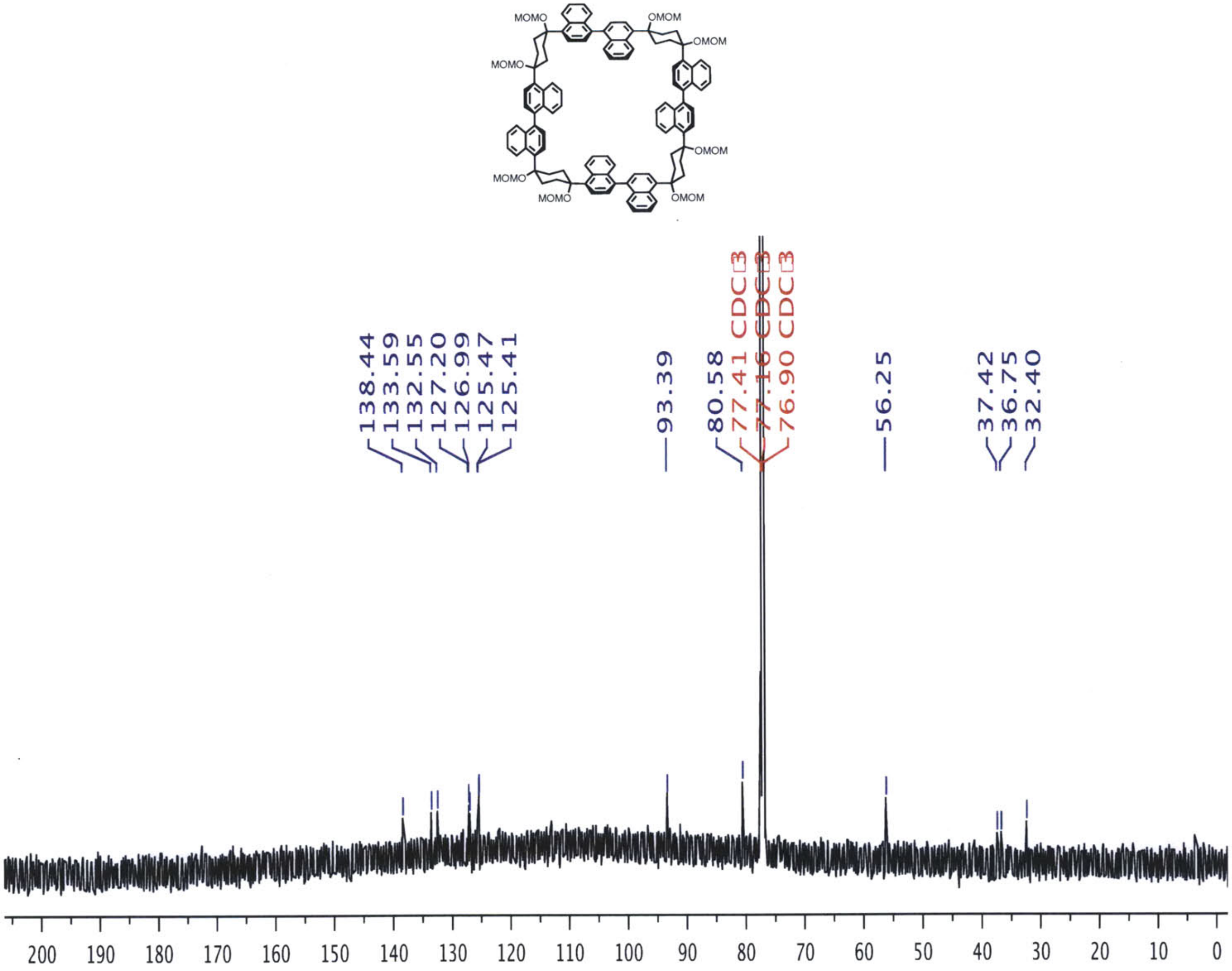
Spectrum 4.1. ^{1}H-NMR of *cis*-**3** (500 MHz, CD$_2$Cl$_2$).



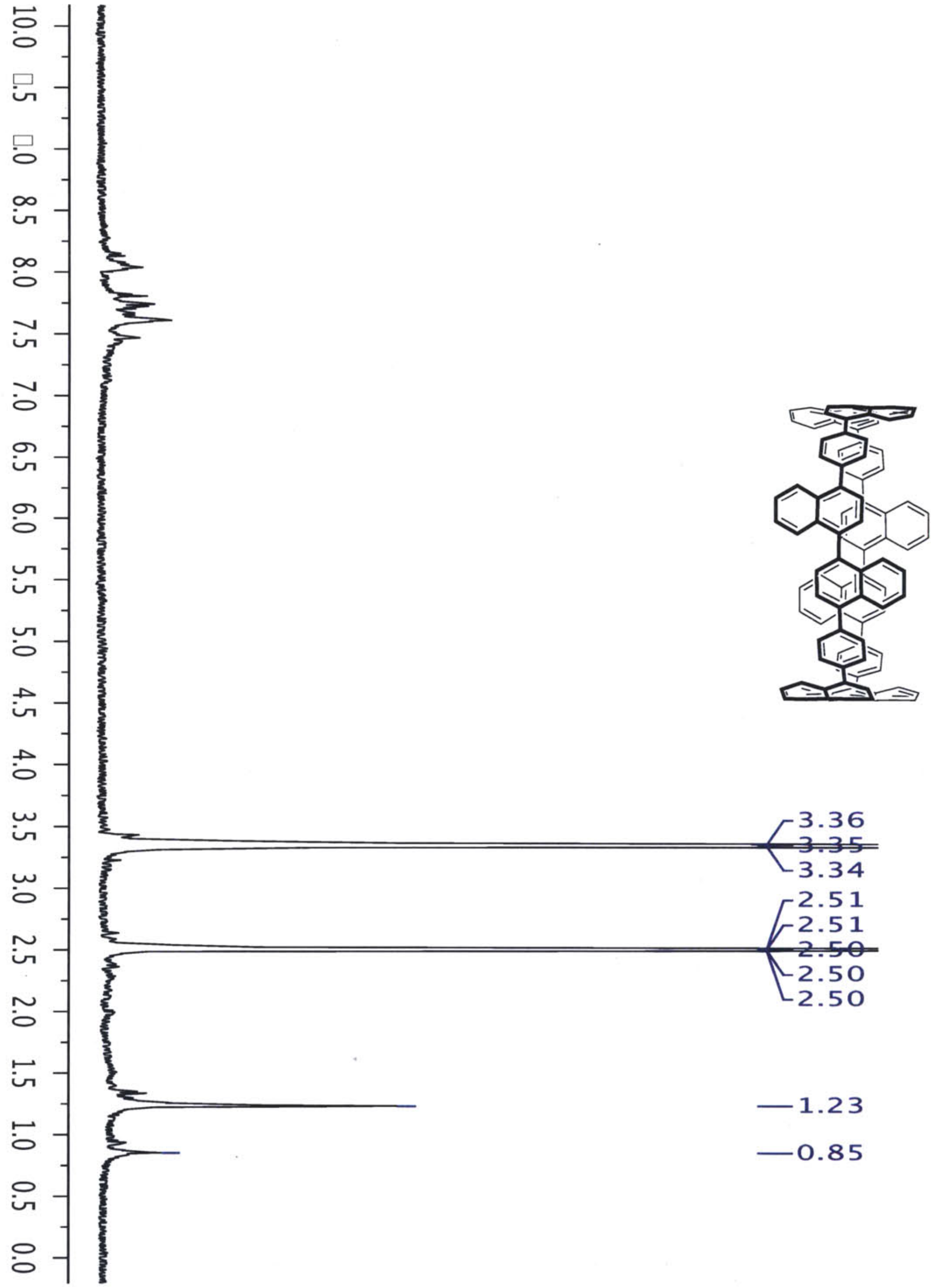
Spectrum 4.2. ^{13}C-NMR of *cis*-**3** (501 MHz, CDCl$_3$)



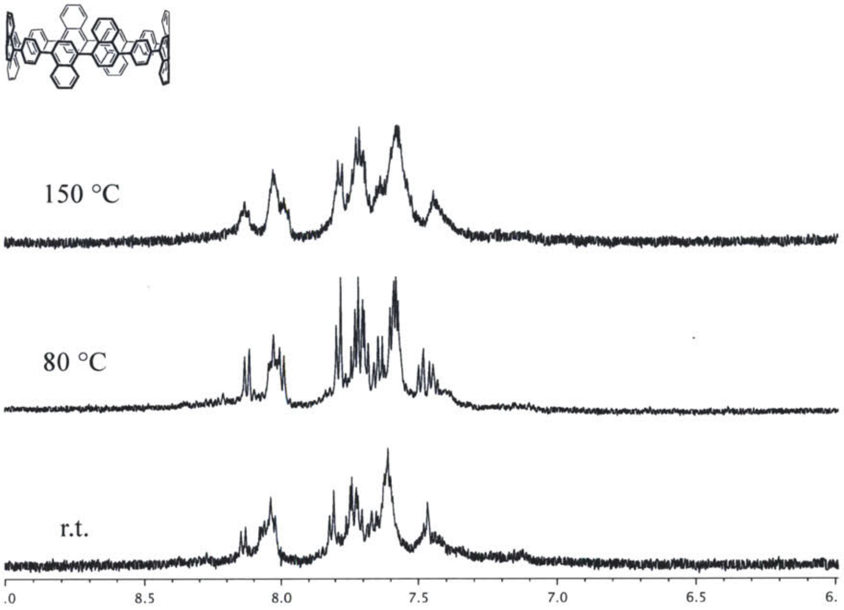
Spectrum 4.3. ^{1}H-NMR of **4** (500 MHz, $CDCl_3$).



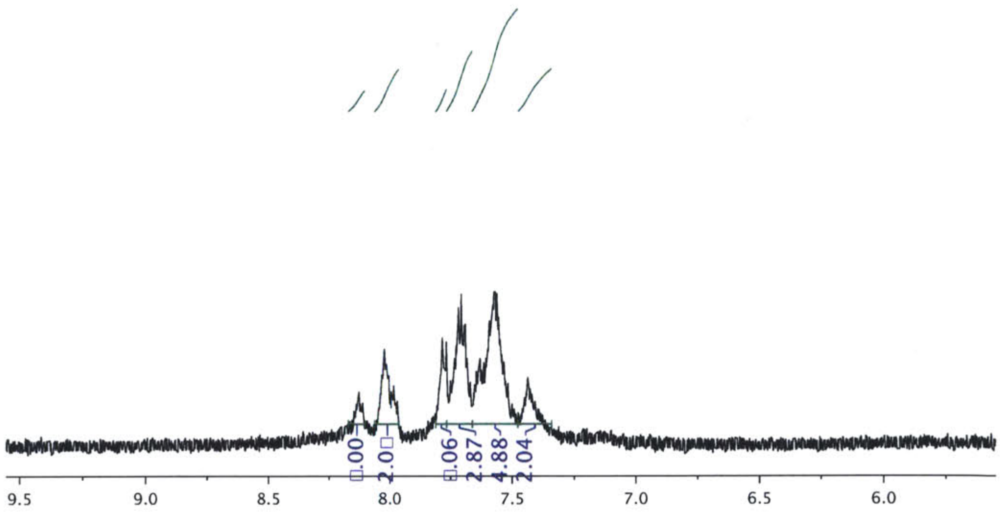
Spectrum 4.4. ^{13}C-NMR of **4** (501 MHz, CDCl$_3$).



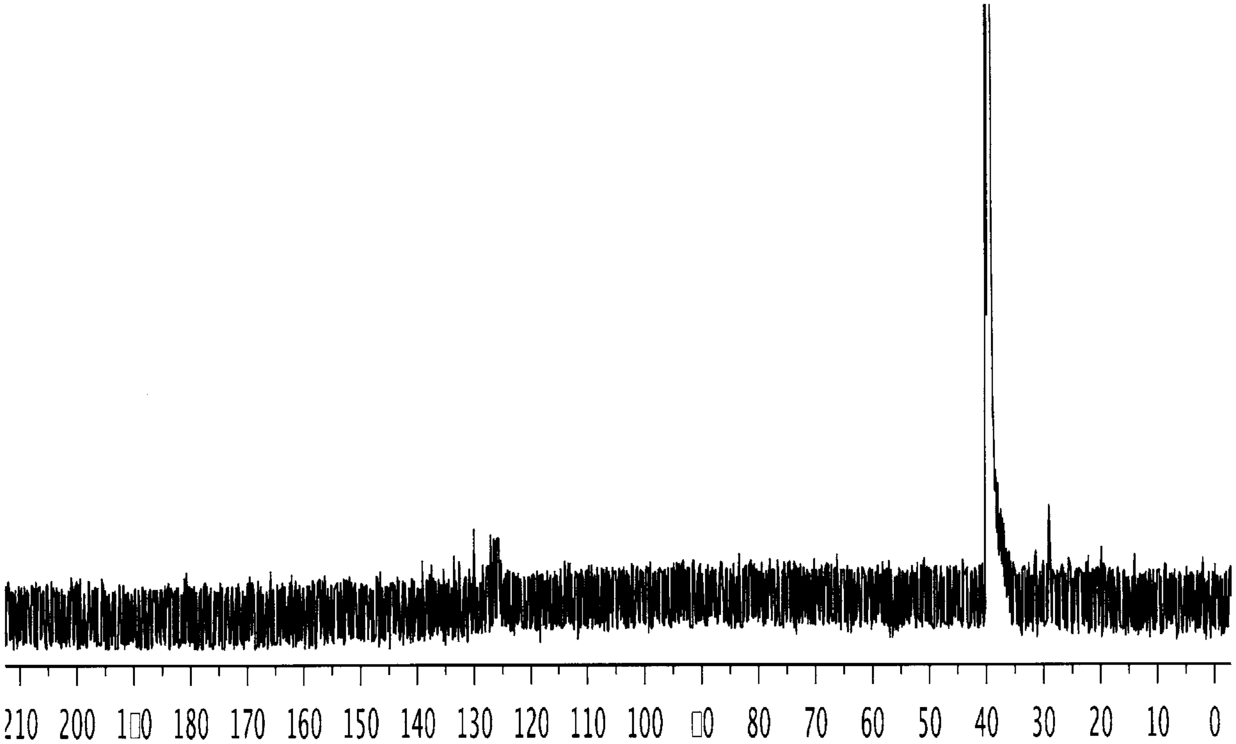
Spectrum 4.5. ^{1}H-NMR spectrum of Macrocycle **1** in d^6-DMSO acquired at room temperature and showing *n*-hexanes with slightly lowered chemical shifts.



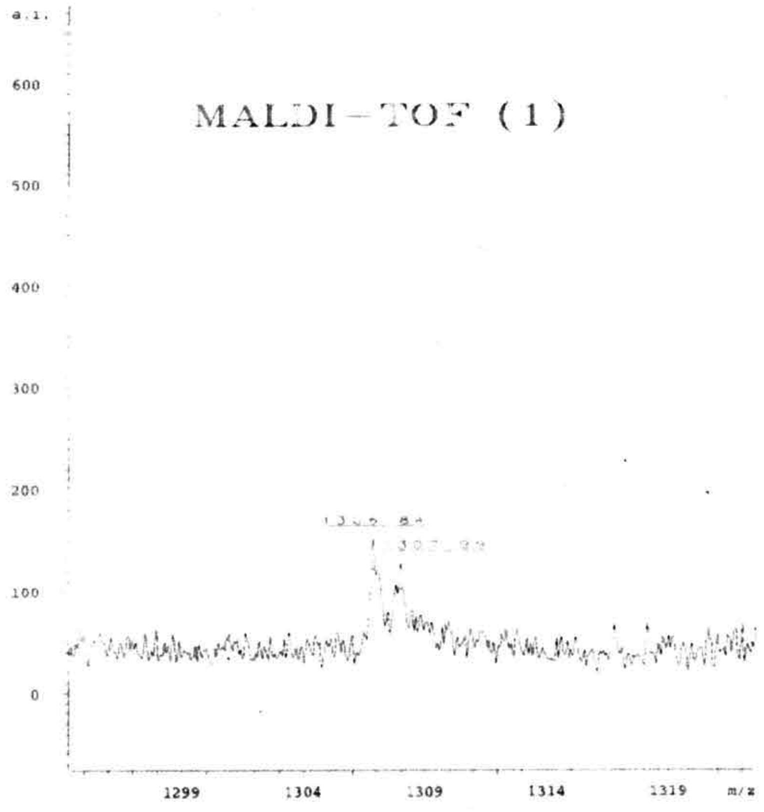
Spectrum 4.6. ^{1}H-NMR spectra of Macrocycle **1** in d^6-DMSO acquired at variable temperatures and showing the coalescing of the signals between 6.0 and 9.0 ppm.



Spectrum 4.7. ^{1}H-NMR of Macrocycle **1** in d^6-DMSO acquired at room temperature and with the related peak integral values displayed. The sum of the integrals represents a total of ***14 unequivalent protons***.



Spectrum 4.8. ^{13}C-NMR of **1** (501 MHz, d^6-DMSO)



Spectrum 4.9. MALDI-TOF MS of Macrocycle **1**.

JOEL M. BATSON

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EDUCATION

Massachusetts Institute of Technology (MIT) Cambridge, MA
Ph.D. Candidate, Organic Chemistry 2008 - June 2013

Research Focus: The application of synthetic chemistry to new and interesting macromolecules and conjugated polymers

- Reported a novel and versatile post-polymerization synthesis of densely substituted, poly(*para*-phenylene)s
- Developed a useful synthesis of polyphenylenes with fluorescence tunable between blue to yellow
- Nurtured a functional understanding of the role between the chemical structure and properties of conjugated polymers and macromolecules
- Synthesized a belt-shaped, polyaromatic macrocycle in progress of the bottom-up chemical synthesis of a single-walled carbon nanotube segment
- Developed a working knowledge of graphitic materials (carbon nanotubes & graphene related materials)

Morehouse College Atlanta, GA
Bachelor of Science, Chemistry (*magna cum laude*) 2004 - 2008

Presentation College, Chaguanas Trinidad, W.I.

- Achieved Grade A's in Cambridge Advanced Level Examinations (Mathematics, Physics & Chemistry) 1997 - 2004
- Earned a National Further Additional Scholarship from the Government of Trinidad and Tobago
- Earned a Full Academic Scholarship from Morehouse College

EXPERIENCE

Thieme Chemistry/ Synfacts Cambridge, MA
Assistant Editor July 2009 - Dec. 2010

- Screened, selected, evaluated, and summarized newly reported literature in the organic chemistry field of "Materials and Unnatural Products" for publication in Synfacts Journal, adding personal comments and opinions on the subject matter
- Produced two informative, concise reviews on literature articles per month
- Participated in a seven-member review team that highlighted noteworthy research results in synthetic organic chemistry each month

Massachusetts Institute of Technology, Department of Chemistry Cambridge, MA
Teaching Assistant Sept. 2008 - May 2009
Course: General Chemistry Undergraduate Lab (5.310), Advanced Chemical Experimentation and Instrumentation (5.33)

- Instructed a class of over 20 students on the synthesis of a highly emissive poly(*p*-phenylene vinylene) (PPV) polymer
- Directed the students' fabrication and measurement of an Organic Light Emitting Device (OLED) using the PPV polymer

Massachusetts Institute of Technology, Department of Chemistry Cambridge, MA
Research Intern June 2007 - Aug. 2007

- Developed an efficient synthetic route for large scale preparation of a monomer to be used in a polymer (PPV) synthesis, subsequently utilized in teaching an undergraduate lab course (5.33)

Rensselaer Polytechnic Institute, Department of Chemistry — Troy, NY

Research Intern — June 2006 - Aug. 2006

- Performed Anionic Polymerizations to produce Polystyrene (PS) samples of well defined sizes
- Studied the effect of differing pore sizes and solvents on the degree of adsorption of the PS samples in silica nanopores

TECHNICAL COMPETENCIES

- Small Molecule Organic Synthesis Characterization Techniques
- Air-Free Schlenk Techniques Techniques
-
- Conjugated Polymer Synthesis
- UV-Vis/Fluorescence Analysis
- Small Molecule
- Polymer Characterization

PUBLICATIONS & PRESENTATIONS

Publications (Peer Reviewed):

- Batson, J.; Swager, T. "Poly(*para*-arylene)s via [2+2+2]," *Macro. Lett.* **2012**, *1*, 1121-1123.

Publications (Non Peer Reviewed):

- Ryu, Chang Y.; Kim, Chansu; Batson, Joel; Kumar, Sanat "Displacer Effect On Adsorption of Polystyrenes in Nanoporous Silica," *Polymer Preprints (American Chemical Society, Division of Polymer Chemistry).* **2007**, *48 (1)*, 678-679.

Presentations:

- Batson, J.; Swager, T. "Synthesis of Linear and Macrocyclic Poly(*para*-arylene)s," International Conference on Science and Technology of Synthetic Metals (ICSM), Atlanta, GA. 7/12/2012. (Talk)
- Batson, J.; Swager T. "Synthesis of Linear and Macrocyclic Polyarenes," 2012 MIT Polymer Day Symposium, Cambridge, MA. 3/7/2012. (Poster)
- Batson, J.; Swager, T. "The Design and Synthesis of Linear and Macrocyclic Poly(*para*-arylene)s," Invited Speaker @ Rensselaer Polytechnic Institute's Polymer Center, Troy, NY. Date TBD.

LEADERSHIP

Treasurer, MIT ChemREFS (Resources for Easing Friction & Stress, Chemistry Department) — Jan. 2011 - *present*

- Formally trained in conflict resolution by "Mediation@MIT"
- Helped students resolve personal and professional conflicts as a member of this student-run support organization
- Served as a peer advocate and counselor
- Interacted with newly hired faculty members in an effort to improve their communication with students
- Prepared guidelines intended for less ambiguous academic expectations and communication for all Chemistry professors, which they then personalized and disseminated to their lab members
- Managed the annual budget of this organization for 2 years

Student-Advocate, Chemistry Department, MIT — July 2012 - Oct. 2012

- Composed and administered a detailed survey to the entire MIT Chemistry graduate student body as part of a 8 person team
- Exceeded goal of 70% participation
- Provided quantitative measures of satisfaction levels with various aspects of the chemistry department for future advocacy efforts and comparison to other departments (department comparisons performed by the MIT Graduate Student Council)

MIT Chemistry Outreach, Chemistry Department, MIT 2009 - 2012

- Visited two Boston-area (elementary, middle or high) schools each spring
- Performed two or three one hour-long chemistry demonstrations as a tool for teaching/exciting young students about science

HONORS & AWARDS

- Phi Beta Kappa National Honor Society inducted 2008
- Phi Beta Sigma Fraternity Incorporated, Chi Chapter; Education Committee Chair 2007, 2008
- Frederick E. Mapp Award for "Most Accomplished Senior in Chemistry Research 2008
- Recognized for having the highest GPA of the Chemistry majors, Morehouse College c/o '08 2008
- Recipient of Departmental Awards for Linear Algebra and Calculus III, Mathematics Department, Morehouse College 2005
- National Junior Track & Field Team of Trinidad and Tobago (1999, 2002-2003)

I cannot express my eternal gratitude to my advisor, *Tim Swager*, for the amazing experience of being his student over the past five years. My tenure in the Swager lab has been just as much, if not more in my instance, a learning experience about life as it was about chemistry. During the times that I struggled, and there were many, I could always depend on Tim to offer a reassuring thought. Likewise, whenever it was clear to him that I wasn't fully utilizing my potential, blunt words of motivation were never far behind. Tim's unmatched work ethic and generosity are a perpetual inspiration to me, and a constant reminder that I can aim for better. Lastly, I would be remiss if I didn't mention my favourite trait of Tim's, his management style. While it is no secret that there is a widespread lack of "good management" in academia, specifically in chemistry, Tim has found a healthy balance between keeping his workers happy, while still prodding them sufficiently to achieve continuous productivity. His performance of this delicate balancing act will surely stand out as one of my most fond memories of graduate school.

I would like to thank the other members of my thesis committee, *Rick Danheiser* and *Tim Jamison*. Rick, to me, you have constantly been a reminder of the excellence and dedication that is this M.I.T. and for that I am thankful. Tim, I have always enjoyed all my interactions with you throughout my time here. In a place that has its fair share of supersized egos, you have always exuded humility. Your pleasant demeanor and overall charm have made my Course 5 experience more tolerable, and for that I am deeply appreciative.

John Donne famously said in the Meditation XVII "No Man Is An Island," in reference to people's dependence on one another. In no other area of my life thus far have I found this saying to hold truer than in scientific research. Additionally, given the type of advisor that Tim is, I have leaned very heavily on past and present members of the *Swager lab* for guidance and support. I am positive I will forget to include several names here. This writing is due tomorrow, so please forgive me. *Kathy* and *Caitlin*, you have both played crucial roles in ensuring that there have been minimal distractions in my time here and for this I say thank you. I hope you both aware that you firmly belong in the friend category, and Caitlin, I wish you the best in your budding scientific career. *Dr. Ellen Sletten*, *Dr. Eilaf Ahmed* and *Dr. Matthew Kiesewetter*, I will sorely miss our regular lunch-time discussions and debates on topics ranging from ridiculous political views (yes, Eilaf. I'm looking at you), to the latest crazy thing that Jay did (or didn't do) along with the bits of chemistry here and there. *Dr. Barney Walker*, you are a weird and unique person and I love you dearly for that. You taught me to always ensure that the lowest R_f spot moves beyond the baseline on a TLC plate and "a million" other lab related things that I now take for granted. I could never repay you for this and I eagerly look forward to our future adventures. *Dr. Brett VanVeller*, without our two years of doing mechanism problems each day at lunch I would probably be a much worse organic chemist than I already am and I am thankful for your effort.

John Goods, it was a great pleasure getting to know you outside of lab and I suspect that our friendship will last beyond my time in lab. *Jon Weiss*, I'm still amazed by how unbelievably early you get to lab each day. You have a ridiculously intense work ethic that will get you very far in life. I would say to chill out, but after three years of working with you, I've decided for myself that you enjoy being stressed out. It has been remarkable fun sharing a lab space with *Markrete*, *Kelvin* and *Dr. Jisun Im* over the past couple years. We've had some truly great conversations while working late at night. Which brings me to *Dr. "Balta" Bonillo*, the owl of the lab in recent times. I already miss our numerous late-night discussions about how much synthesis sucks, and how much life also sucks in general. Be that as it may, relax. You're a very good chemist and will have an amazing life if you allow it. A breathe of fresh air in the latter stages of my doctorate has been *Dr. Jens Ravnsbaek*, one of the few people in lab that understands how I think about things. Dr. Jason Cox, you are a great man: a gentleman and a scholar and I will certainly continue to miss your presence in my life.

It would be impossible to acknowledge past co-workers with mentioning *Professor Trisha Andrew*. I am sure you already know it, but you played a very crucial role in my scientific development and are a truly a good friend. Thank you. *Dr. Rebecca Parkhurst, Dr. Jan Schnorr, Dr. Stefanie Sydlik, Dr. Jose Lobez, Dr. Jeewoo Lim, Dr. Shuang Liu*; you all have been like the elder siblings I never had. I look up to, and have tremendous respect for all of you for the part that you have played in my scientific and personal growth. For this I am eternally grateful. In particular, living with Dr. Parkhurst for one year was quite fun and enlightening. You see, I have always attempted to compartmentalize my life and create an explicit distinction between my work and home lives. However, in my time spent living with Becca, I learnt that given the nature of one's job, this is not always possible. In fact, the hyper social atmosphere of our advisor is reflected in the friendly interactions amongst lab members each day. Thus, the formation of wonderful friendships was always going to be inevitable. *Dr. Rocha, Dr. Rochat, Dr. Frantz, Dr. Zuniga, Dr. Schipper, Greg, Grace, Heartbreak, Sarah, Olyessa, Dr. Esser, Dr. Walsh, Sophie, Lionel, Tran, Lily, Brendan, Zeke, Dr. De Boer, Dr. Belger;* please know that I am only ever a phone call or an email away. Finally, it is only right that I express my deepest appreciation to *Dr. Koushik Venkatesan* for his role in teaching me many of the fundamental concepts of organic synthesis. Although he no longer remembers me, I am earnestly indebted to him for life for this initial training in synthetic chemistry.

I will for always have many fond memories of my time at M.I.T., especially in the earlier years, largely due to *Dr. Todd Senecal, Dr. Alyssa Larson, Dr. Peter Goldman, Bryan Hsu, Stephanie Tumidjaski, Jeremey Setser* and others. They ensured that fun was never too far away from Building 18. *Dr. Lesley-Ann Giddings*, without your support this journey would have been nearly impossible and I'm sure I can never fully repay you. Last, but not least, I want acknowledge my amazing family. Despite taking their "awesomeness" for granted throughout my childhood, it wasn't till I got older and had a larger data set for comparisons, that I eventually realized how lucky I truly was to have parents and a sibling such as mine. I left the shores of Trinidad to pursue a degree in Chemical Engineering with the intention of being able to easily return home to work in our local oil and natural gas industry. Nine years later, I am painfully aware that the career path I have followed now means I will be returning home later, rather than sooner. Despite not fully understanding the motivation behind several key decisions that I have made during this intervening time, their support and dedication to me has never faltered. Thank you, and I only hope that I can make the three of you all as nearly as proud as you have made me.