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**The synthesis of cross-conjugated oligo(phenyleneethynylene)s and
investigation of their optical properties.**

by

JOON CHO



A Thesis

Submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the
requirement of the degree of Master of Science

Department of Chemistry

Edmonton, Alberta

Fall, 2001



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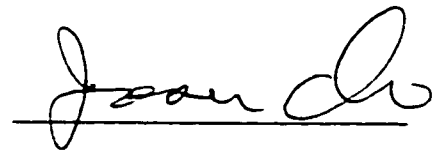
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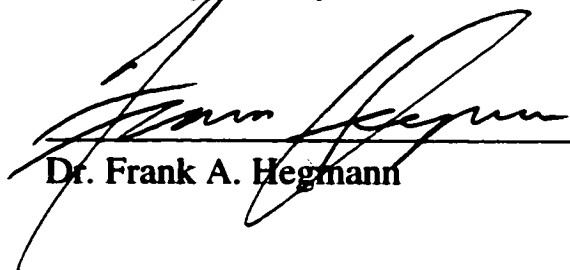
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Dr. Rik. R. Tykwinski, Supervisor



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August 3, 2001

Abstract

The synthesis and characterization of a series of novel cross-conjugated oligo(phenyleneendiyne)s have been reported in this thesis. Employing palladium catalyzed cross-coupling reactions, in which $\text{PdCl}_2(\text{PPh}_3)_2$ is used as a catalyst, CuI as a co-catalyst and in the presence of diisopropyl amine, the cross-conjugated oligo(phenyleneendiyne)s (**89**, **90**, **92** and **108**) that possess defined lengths and structures have been synthesized in an iterative approach. To probe the properties of higher oligomeric analogues, cross-conjugated oligo(phenyleneendiyne)s (**104**, **105**, **106** and **107**) have been synthesized in a one-pot polymerization route. The structural properties of these oligomers and polymers have been characterized by ^1H and ^{13}C -NMR, IR, high-resolution MS and electrospray mass spectroscopies. The electronic absorption and emission behavior of these cross-conjugated system were investigated via UV-Vis and fluorescence spectroscopies.

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TABLE OF CONTENTS

I. Introduction	
A. Background	1
B. Research Goals	35
II. Results and Discussion	
A. Synthesis and characterization of cross-conjugated oligomers	38
B. Investigation of electronic absorption and emission behavior of cross-conjugated oligomers	47
C. Synthesis and characterization of cross-conjugated oligomers from one-pot polymerizations	49
D. Investigation of electronic absorption and emission properties of cross-conjugated oligomers from one-pot polymerizations	68
III. Conclusions	72
IV. Experimental Section	74
V. References and Notes	108
VI. Appendix	115

List of Equation and Tables

Page

Table 1. Yields from desilylation reaction of monomer 89 with varying temperature. 2

Equation 1. 12

List of Abbreviations

Aq	Aqueous
Bu	Butyl
ca.	Approximately
cm	Centimeter
d	Doublet
DBMP	2,6-Di-<i>t</i>-Butyl-4-Methyl Pyridine
DP	Degree of Polymerization
E_g	The Solution Optical Gap
E_{max}	The Longest-Wavelength Absorption Energy
ECL	Effective Conjugation Length
EDTA	Ethylene Diamine Tetraacetic Acid
e. g.	For Example
EI	Electron Ionization
equiv	Equivalent
<i>et al.</i>	And Others
ES	Electrospray
g	Grams

h	Hours
HOMO	Highest Occupied Molecular Orbital
HRMS	High Resolution Mass Spectrometry
Hz	Hertz
<i>i</i>	Iso
IR	Infrared
LED	Light Emitting Diode
LUMO	Lowest Unoccupied Molecular Orbital
m	Multiplet
MC	Methylene Chloride
Me	Methyl
mg	Milligrams
MHz	Megahertz
mL	Milliliter
mmol	Millimole
mol	Mole
Mp	Melting Point
MS	Mass Spectrometry
<i>m/z</i>	Mass-to-Charge Ratio
n	Normal

nm	Nanometer
NMR	Nuclear Magnetic Resonance
ORTEP	Oak Ridge Thermal Ellipsoid Plot
PA	Polyacetylene
PDA	Polydiacetylene
Ph	Phenyl
PP	Polyphenylene
PPE	Polyphenyleneethynylene
ppm	Parts Per Million
PPV	Polyphenylenevinylene
Pr	Propyl
PT	Polythiophene
PTA	Polytriacetylene
q	Quartet
quint	Quintet
ROMP	Ring Opening Metathesis Polymerization
rt	Room Temperature
s	Singlet
SEC	Size Exclusion Chromatography
sept	Septet

S_N2	Nucleophilic Substitution Second Order
t	Triplet
TBAF	Tetrabutylammonium fluoride
TEE	Tetraethyleneethene
TES	Triethylsilyl
THF	Tetrahydrofuran
TIPS	Triisopropylsilyl
TLC	Thin Layer Chromatography
TMS	Trimethylsilyl
TPP	Tetra Phenyl Porphyrin
UV	Ultraviolet
Vis	Visible

I. Introduction

A. Background

a. Linearly-conjugated polymers

The area of organic conjugated polymers has received a fair amount of attention in the last decade. This interest results from the possibility of π -electron conjugation along the polymer backbone and the potential for electronic and photonic applications. Thus, structurally varied conjugated oligomers and polymers have been synthesized and their properties have been exploited.¹

Traditionally, inorganic crystals have been investigated as materials with commercially relevant electronic and photonic properties. However, these materials are often expensive and difficult to process. As an alternative, organic compounds have been explored. They offer many advantages over their inorganic counterparts. The ease of synthetic adjustment, potential ease of processing, and tailoring characteristic properties by changing functionality on the polymer backbone enticed chemists to pursue the study of organic conjugated oligomers and polymers.

The characterization and physical study of the high-molecular weight polymers are often difficult because of their poor solubility. In addition, structural defects along the polymer backbone reduce expected physical properties. As an abbreviated analogue of polymers, oligomers with precise length and structure facilitate characterization and can be used as models for polymers.^{2,3} Therefore, knowledge of the number of monomer units required in an oligomer to achieve a desired physical property is of interest. To accomplish this goal, estimation of effective conjugation length (ECL)

has become an essential measurement toward understanding physical properties of π -conjugated oligomers. A simple way to evaluate the ECL includes plotting a relevant physical property (e. g., the longest-wavelength absorption energy E_{\max} or the solution optical gap E_g) against the inverse number of monomer units (n^{-1}).⁴ Extrapolation to infinite chain length yields n_{ECL} .

Oligomers can be used as molecular wires in molecular scale electronics and nanotechnologic devices.⁵ A number of structurally varied oligomers have been realized and their physical properties have been investigated for these applications. With the development of synthetic methodologies, monodisperse linearly π -conjugated polymers and oligomers have been realized up to the 10 nm length.^{6,21b} Figure 1 shows monomer units of the most actively investigated oligomers.

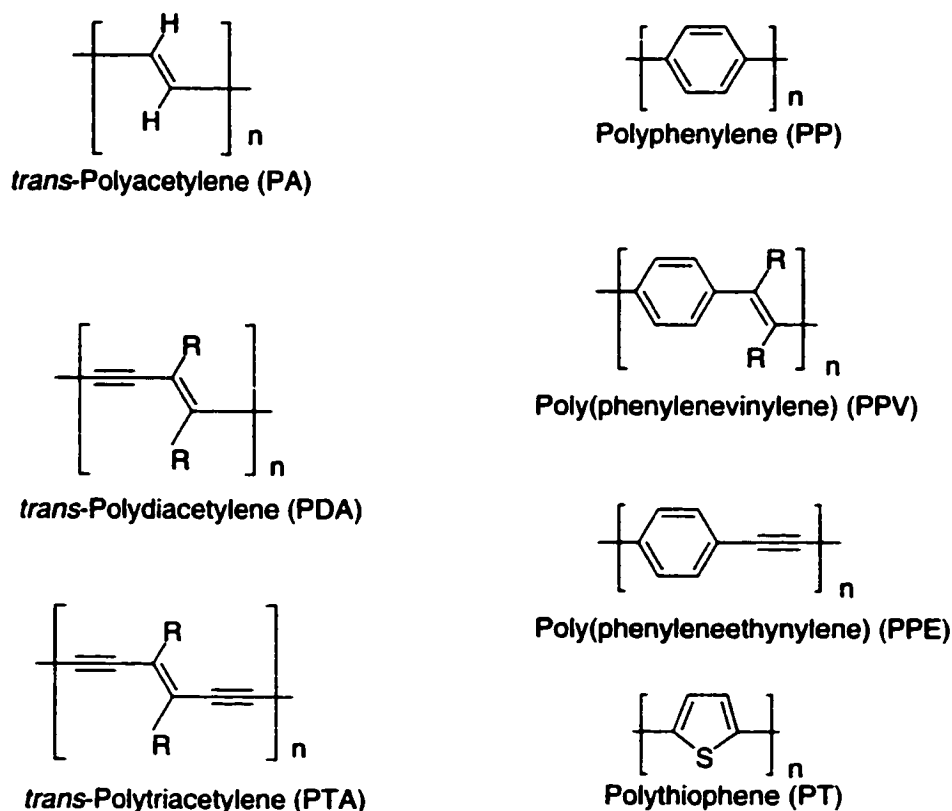
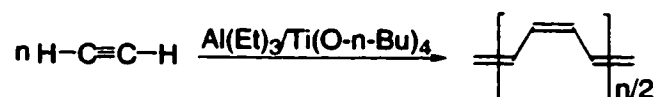


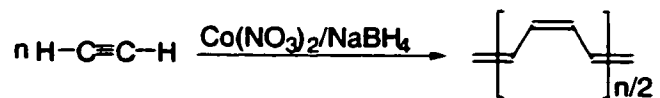
Figure 1: The structures of common linearly conjugated polymers.

Polyacetylene (PA), the simplest π -conjugated polymer with a non-aromatic carbon backbone, has been investigated because of its high electrical conductivity (up to 10^5 Scm^{-1}) upon doping (Insulator: 10^{-18} - 10^{-5} Scm^{-1} , Semiconductor: 10^{-5} - 10^2 Scm^{-1} , Conductor: 10 - 10^7 Scm^{-1}).^{7a} Natta *et al.* synthesized *cis*-polyacetylene from acetylene gas for the first time using $\text{Al}(\text{Et})_3/\text{Ti}(\text{OPr})_4$ in hexane in 1958.^{7b} Shirakawa later reported a route to polyacetylene and it is an extension of the work first described by Natta *et al.*⁸ The Shirakawa procedure prepared *cis*-polyacetylene by adapting the Al/Ti ratio within the range 1.5-4 (Scheme 1).⁸



Scheme 1: Shirakawa's route to polyacetylene.

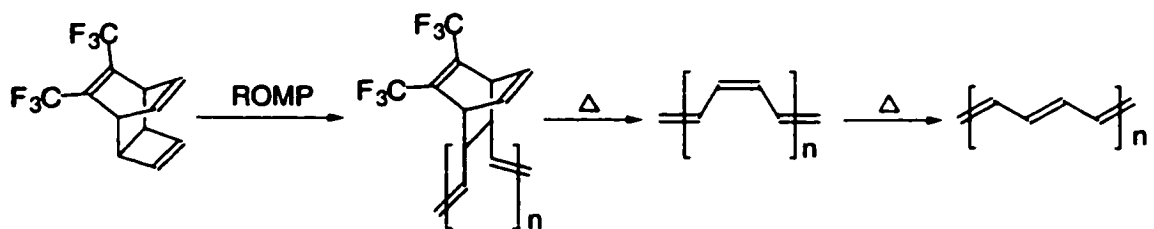
Contrasting the study of Shirakawa, Baker *et al.* prepare almost pure *trans*-PA by reducing the Al/Ti ratio to unity.⁹ In 1980, Enkelmann *et al.* discovered that the best results to *cis*-PA are obtained using Luttinger's catalyst $\text{Co}(\text{NO}_3)_2/\text{NaBH}_4$.¹⁰ The main advantage of this Luttinger's catalyst over that developed by Shirakawa is that it enables the polymerization reaction to be carried out even in the presence of water and oxygen (Scheme 2).



Scheme 2: Luttinger's route to Polyacetylene as developed by Enkelmann *et al.*

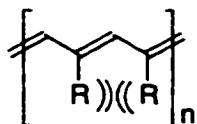
The inherent insolubility and infusibility of polyacetylene, coupled with its sensitivity to air, prevent processing the polymer. Therefore, attempts to make polyacetylene

more processible have been performed by using precursor polymer routes.¹¹ This approach mainly involves the synthesis of prepolymers, which can be thermally converted to polyacetylene, as first reported by Edward and Feast.¹² The initial monomer, 7,8-bis-(trifluoromethyl)tricyclo-[4,2,2,0]deca-3,7,9-triene, is readily polymerized in the presence of ring opening metathesis polymerization initiators, such as $WCl_6/SnMe_4$ (Scheme 3).¹² The resulting prepolymer is soluble in common organic solvents and is easily purified, characterized, and processed. Upon heating, the prepolymer is converted to polyacetylene.



Scheme 3: Polymer precursor route to polyacetylene by Edward and Feast.

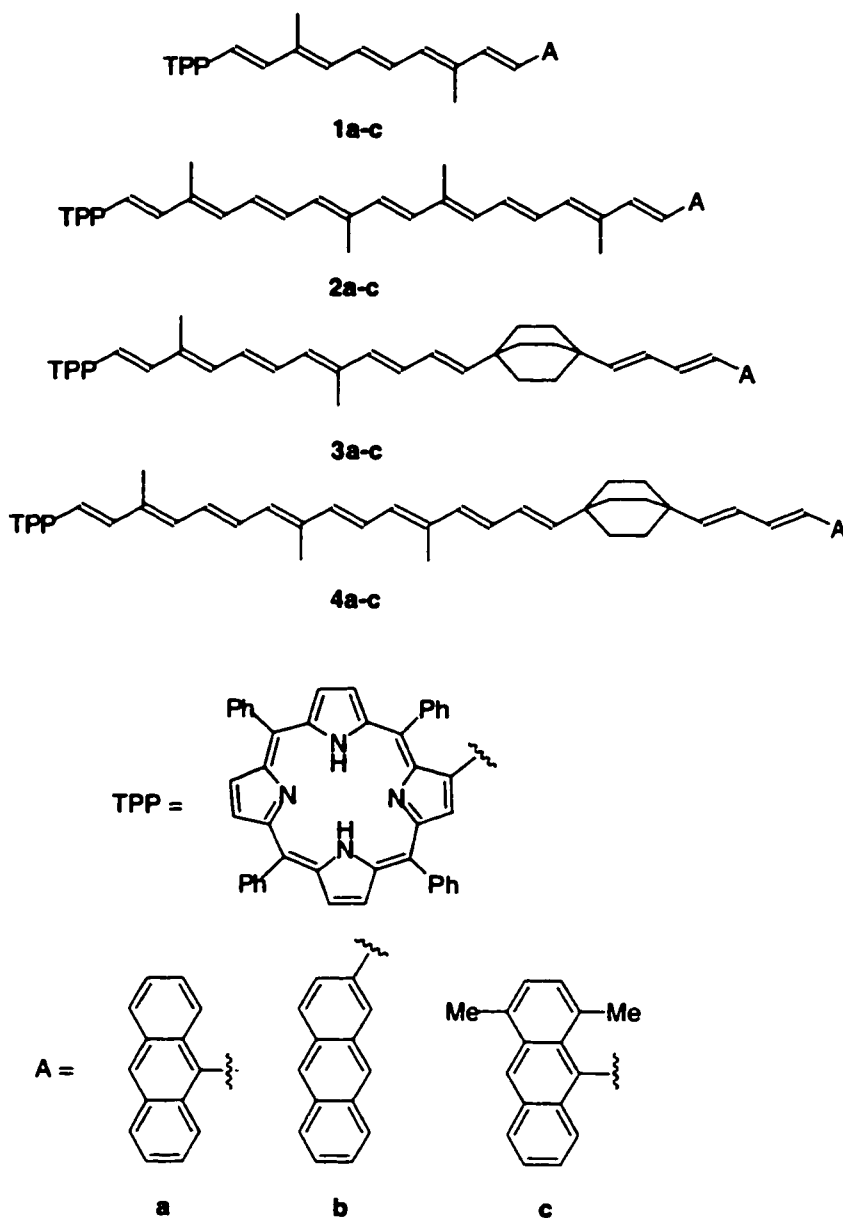
As an alternative approach, introduction of side-groups onto the polymer backbone has been carried out in order to obtain soluble polyacetylene analogues. This effort also caused problems in that replacement of ethylenic hydrogen atoms by solubility-gaining side chains leads to severe steric interactions and distorts the π -conjugated backbone from planarity. This results in the loss of conjugation and widening of the HOMO-LUMO gap (Scheme 4).



Scheme 4: The loss of planarity resulting from interaction between side chains.

Thus, many investigations have been made at the level of oligomers in this series. Various oligoenes end-capped with donor, acceptor or redox-active groups have been

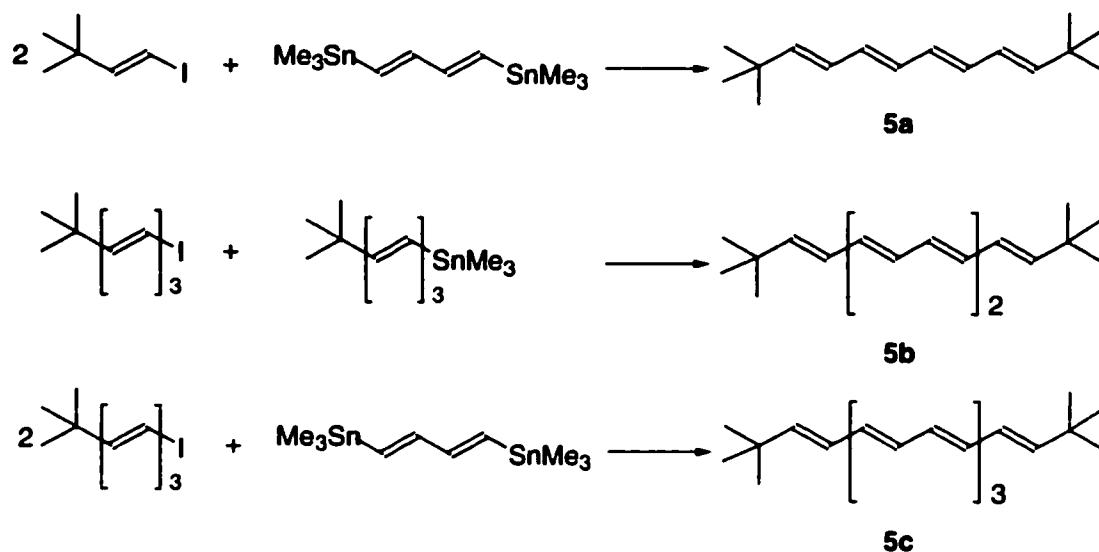
synthesized. For example, Effenburger and co-workers synthesized the carotenoid polyenes **1-4** with different end groups to study intramolecular energy transfer (Scheme 5).¹³ Interestingly, even though conjugation is interrupted by a bicyclo (2,2,2) alkane unit in oligomers **3** and **4**, energy transfer was nonetheless observed.¹⁴



Scheme 5: Donor-acceptor substituted oligoenes **1-4**.

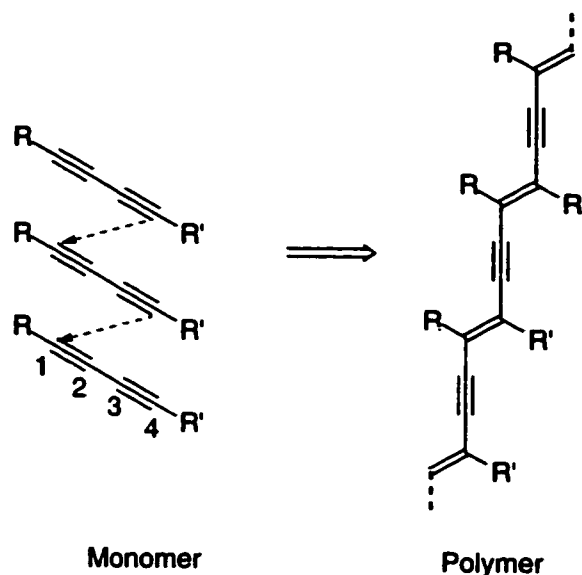
Müllen and co-workers applied the Stille-coupling reaction to synthesize **5a-c**.¹⁵ This reaction gives an alternative synthetic route toward the formation of C(*sp*²)-C(*sp*²)

single bonds to the Wittig reaction used by Effenburger (Scheme 6). These oligomers are highly redox-active and **5c** shows seven successive one-electron transfers from the tetraanion to the trication.



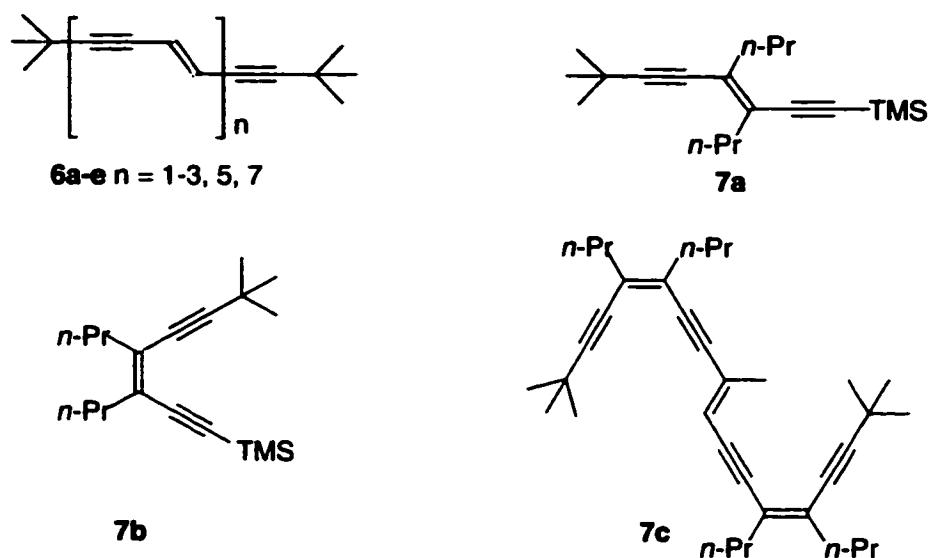
Scheme 6: All *trans*-PA oligomers **5a-c** prepared by Stille-coupling.

The second class of π -conjugated polymers with a non-aromatic carbon backbone is the poly(diacetylene)s (PDAs). PDA polymers are generally prepared by topochemical polymerization of diacetylene (Scheme 7). This solid-state synthesis of PDAs requires suitably pre-arranged and substituted diyne reactants in a single crystal.¹⁶ Oligo-PDAs are less numerous than oligo-PAs because of synthetic difficulties. Poly(diacetylene)s are not conductive upon doping but have large third-order nonlinear co-efficients.¹⁷



Scheme 7: Topochemical 1,4-addition polymerization of PDA.

Wudl and Bitler reported first synthesis of *trans*-enynol oligomers **6a-e** in 1986 (Scheme 8).¹⁸ *t*-Butyl end-capped oligomers **6a-e** show a color change from colorless (**6a,b**) to deep yellow (**6e**) with increasing length. In this series of oligomers, *t*-butyl end-capping gives thermal stability and the resulting oligomers are stable in air. Giesa and Schulz used **6a-e** and **7a-c** as model compounds of poly(diacetylene)s.¹⁹ They investigated UV/Vis and Raman spectroscopies of oligomers as a function of chain length and geometry. These results suggest that ECL in PDAs was around 10 monomer units. With the development of metal-catalyzed cross-coupling reactions to form C(*sp*)-C(*sp*²) bonds, it might be expected that more new PDAs could soon be realized.

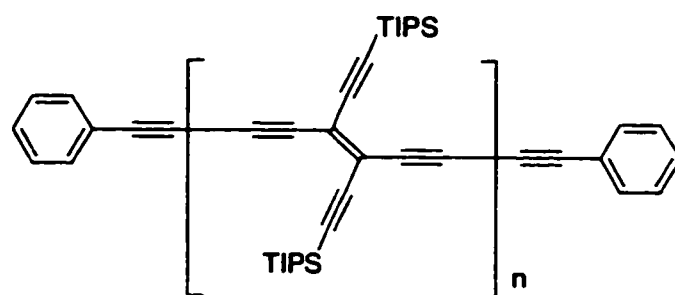


Scheme 8: The structures of PDA oligomers.

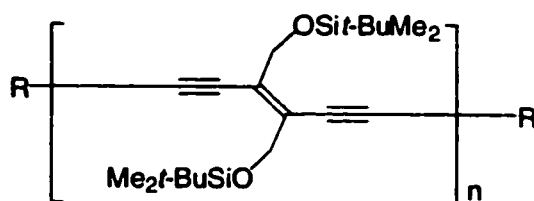
The third in this series of π -conjugated polymers without aromatic carbons in the repeat unit is poly(triacetylene)s (PTAs). Compared to PAs and PDAs, PTAs have been only recently realized. The first report of a PTA was in 1994 by Diederich and co-workers.²⁰ Although the PTA series has been synthesized lately, the ease of synthetic accessibility by simple oxidative acetylenic coupling make it more potentially versatile than the first two counterparts.

Phenylacetylene end-capped PTA oligomers **8a-e** extend up to about 5 nm and are kinetically stable (Scheme 9).²⁰ The X-ray crystal structure of dimeric **8b** shows a perfectly planar π -conjugated backbone. Trimethylsilyl end-capped oligoenediynes **9a-f** show significantly enhanced solubility and processibility compared to **8a-e** (Scheme 9).^{21a} This comes as a result of the more flexible $\text{Me}_2t\text{-BuSiOCH}_2$ side chains. In addition, oligoenediynes **10a-h**, which are end-capped with triethylsilyl groups, have been prepared (Scheme 9).^{21a,b} The tetracosameric PTA rod **10h** with its 24 carbon-carbon double and 48 carbon-carbon triple bonds and a length of 17.8 nm

between the terminal Si atoms is currently the longest linearly π -conjugated molecular wire that does not contain aromatic repeat units.^{21b} As an expansion of oligomer series **9** and **10**, the PTA oligomers **11** and **12** functionalized with donor-donor and acceptor-acceptor end-capping groups have also been prepared (Scheme 9).²²



8a-e $n = 1-5$

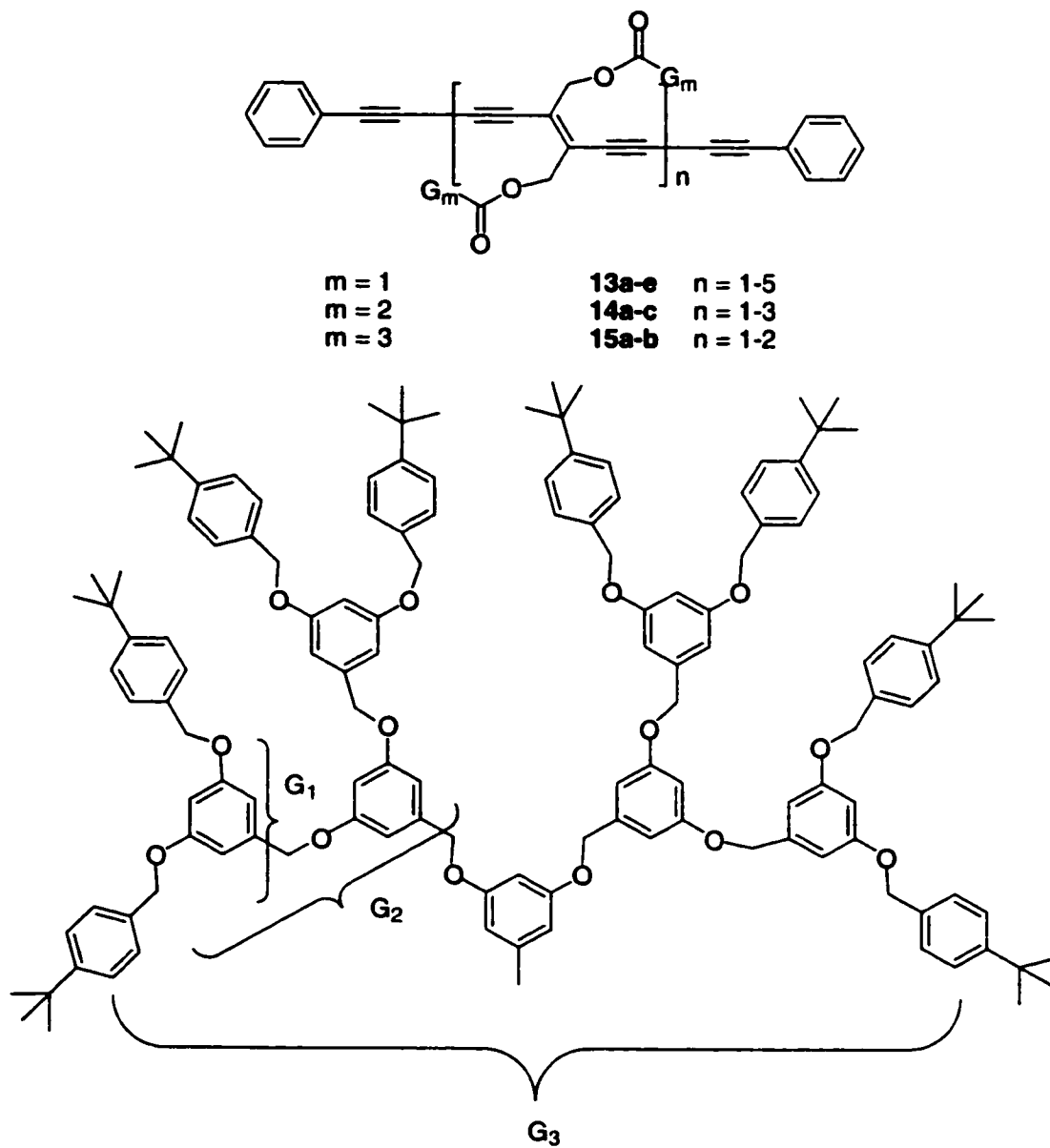


9a-f $n = 1-6$ $R = \text{TMS}$
10a-h $n = 1, 2, 4, 6, 8, 12, 16, 24$ $R = \text{TES}$
11a-f $n = 1-6$ $R = 4\text{-(dimethylamino)phenyl}$
12a-f $n = 1-6$ $R = 4\text{-nitrophenyl}$

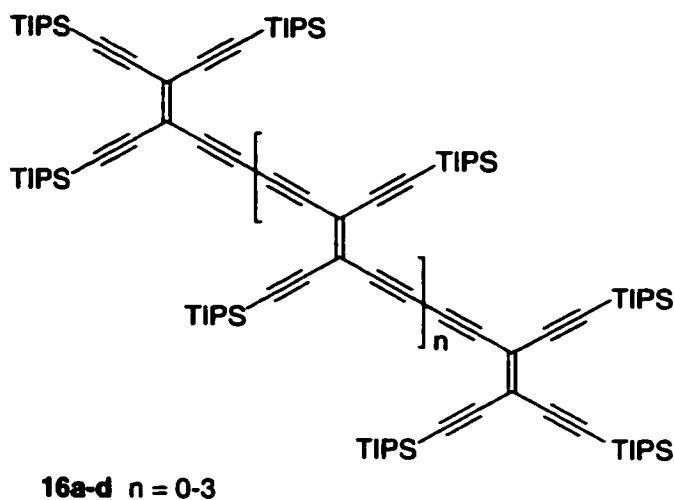
Scheme 9: The structures of PTA oligomers **8-12**.

The PTA oligomers **13-15** with dendritic side chains have also been synthesized by Diederich and co-workers to function as insulated molecular wires (Scheme 10).²³ Dendritic side chains work as a protector, which stabilize the central conjugated oligomer backbone. Furthermore, the presence of these side chains does not exert any effects on the electronic characteristics of PTA backbone. The PTA oligomers **16a-d**

have been prepared from oxidative coupling of tetraethynylethene subunits (Scheme 11).²⁴



Scheme 10: The structures of PTA oligomers 13-15.



Scheme 11: The structure of the oligomers **16a-d**.

In addition to oligomers and polymers with hydrocarbon backbones, various classes of oligomers and polymers with aromatic rings in the monomeric unit have been intensively investigated.^{25,26} Poly(*p*-phenylene), the simplest derivative, is excellent conductor upon doping. When PPP is in a neutral form, it functions as an insulator, with conductivity of $10^{-12} \text{ Scm}^{-1}$. In contrast, its conductivity is increased to the metallic region with values around 500 Scm^{-1} after doping with I_2 or AsF_5 .^{25,26} Another interesting property of PPP is that it can be used as a material for blue light-emitting diodes (LEDs) because its electronic absorption spectrum is limited to the UV region.^{27,28}

In parent PPP, steric interactions between the *ortho*-H atoms cause the planes of neighboring aryl rings to adopt dihedral angles up to 23° (Figure 2).²⁵ This significantly reduces π -overlap and prevents extended π -conjugation. The poor solubility of PPP has been addressed by attaching side-chain groups. The presence of these bulky side chain groups, however, further increases the dihedral angle and results in additional reduction of the π -orbital overlap along PPP backbone.

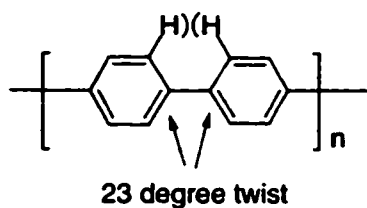
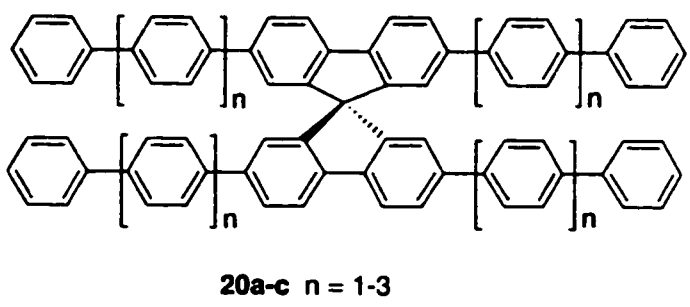
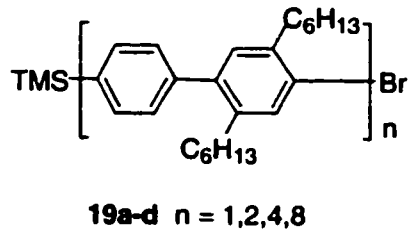
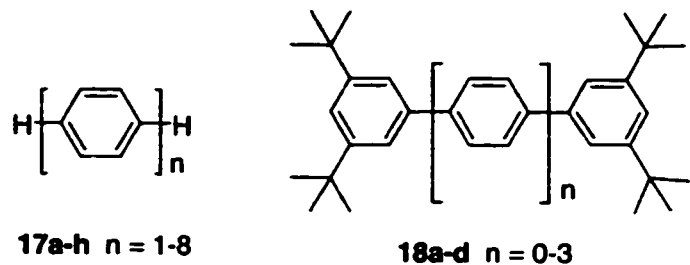


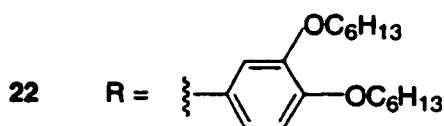
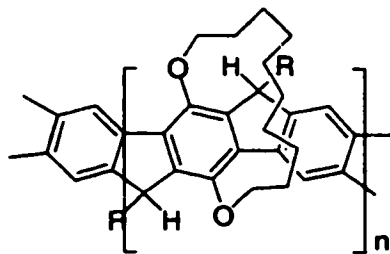
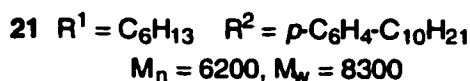
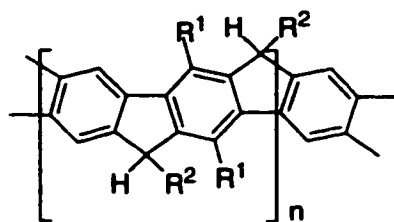
Figure 2: Steric interactions between *ortho* hydrogens.

In the oligomeric series of PPPs **17a-h**, solubility is significantly decreased by increasing chain length.^{29,30} Solubility is enhanced by introducing *t*-butyl groups on terminal phenyl rings in the oligomeric series **18a-d** (Scheme 12).^{31,32} Hensel and co-workers synthesized **19a-d**, and compound **19d** currently represents the longest monodisperse oligo(*p*-phenylene) (Scheme 12).³³ The attached alkyl substituents provides solubility in organic solvents. The longest wavelength absorptions from UV/Vis spectroscopic measurements of the oligomers **19a-d** show, however, identical absorptions at $\lambda_{\text{max}} = 261$ nm, which means the presence of bulky side groups impedes planarity of the oligomer backbone. Using a slightly modified PPP design, Salbeck and co-workers prepared spiro-linked oligo PPPs **20a-c** (Scheme 12).³⁴ These oligomers have high photoluminescence quantum efficiencies in the solid state, and they have potential as high molecular weight PPP oligomers for the construction of LEDs.³⁴



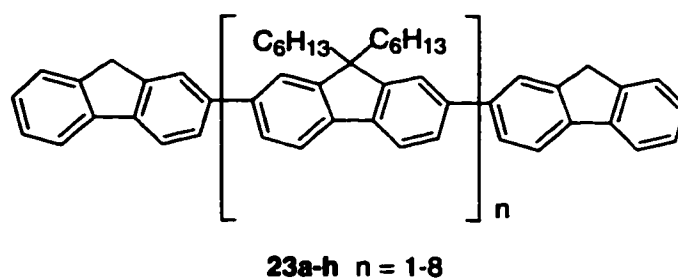
Scheme 12: The structures of PPP oligomers 17-20.

The planarization of the PPP backbone to maximize the extent of conjugation has been a goal of the notable interest. Planarization has been achieved by the introduction of methylene bridges between the ortho positions of adjacent phenylene rings to produce poly(fluorene)s. This effort gives polymers **21** and **22** (Scheme 13).³⁵⁻³⁷

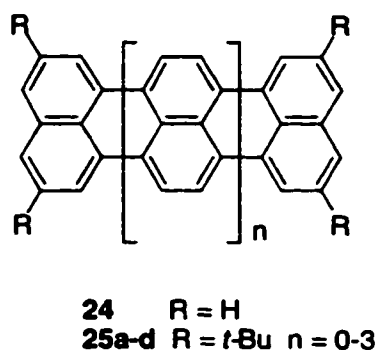


Scheme 13: Planarized PPP polymers 21-22 with bridging of *ortho*-positions of adjacent phenylene rings in the conjugated backbone, the poly(fluorene)s.

Klaerner and Miller prepared a series of poly(fluorene) oligomers 23a-h up to decamer, and their longest wavelength absorptions from UV/Vis spectroscopy are saturated at the stage of decamer (Scheme 14).³⁸ In addition, planarized poly(*peri*-naphthalene)s 24 and 25a-d have been synthesized, and the expected solubility problem was overcome by the introduction of *t*-butyl groups (Scheme 15).³⁹⁻⁴¹ Their UV/Vis spectroscopic analysis shows λ_{max} increases from 439 nm (25a) to 748 nm (25d) owing to extended planar π -conjugation.



Scheme 14: Poly(fluorene) oligomers **23a-h** prepared by Klaerner and Miller.

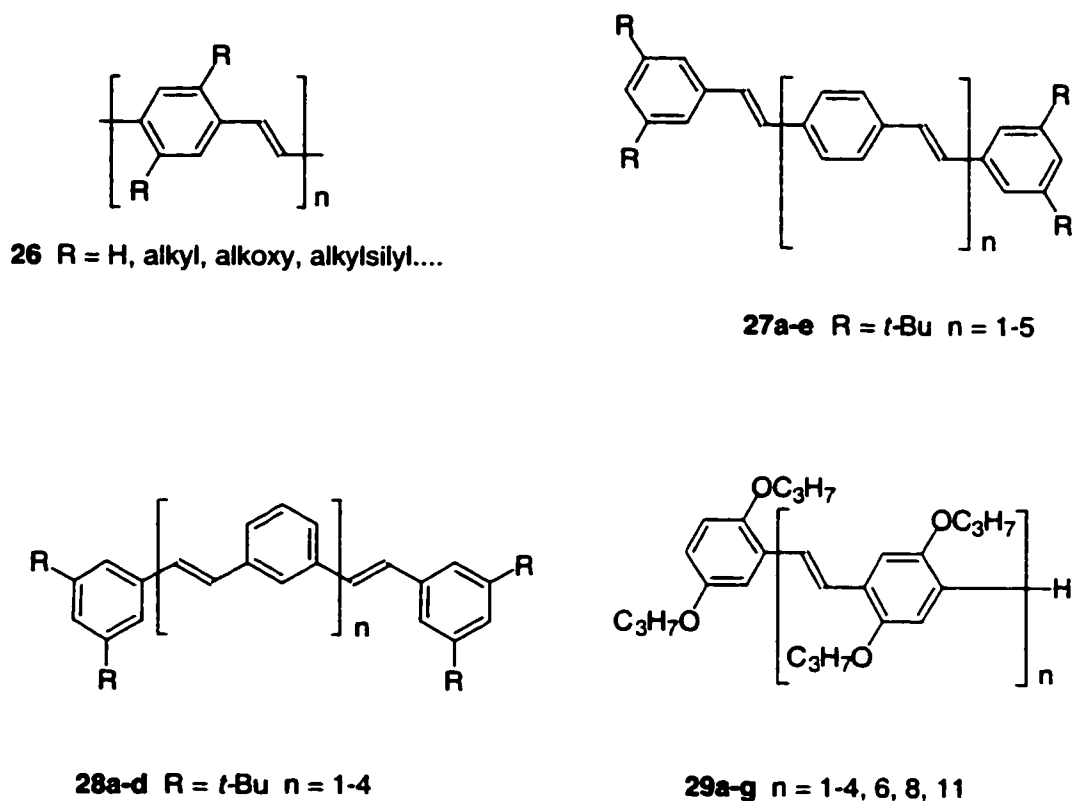


Scheme 15: Planarized poly(*peri*-naphthalene) oligomers **24** and **25a-d**.

Since Friend, Holmes and co-workers's first report⁴² in 1990 that light-emitting diodes (LED)s can be constructed from poly(*p*-phenylenevinylene)s (PPVs) **26** (Scheme 16), developments of PPV have become the most intensively studied field of π -conjugated organic molecules. With the development of varied synthetic methodologies, complete manipulation of the HOMO-LUMO gap has become possible. Therefore, light-emitting diodes that provide the entire visible spectrum have become available from this series.⁴³ The use of PPVs as an emitter material has also been successfully applied to the fabrication of organic-based lasers.⁴⁴⁻⁴⁶

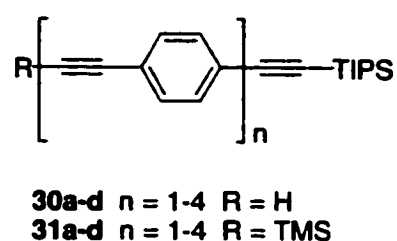
Müllen and co-workers prepared a series of oligo PPVs **27a-e**, and these oligomers suggested the chain length dependence of the longest-wavelength absorption

maximum to be 10 monomer units (Scheme 16).⁴⁷ *Meta*-phenylene containing PPV **28a-d** were also synthesized and investigated for their optical properties in comparison to the *para*-phenylene containing counterparts **27a-e** (Scheme 16).⁴⁷ The interesting difference is that bathochromic shift of the λ_{\max} by increasing number of monomer units is not observed for **28a-d**. Stalmach and co-workers introduced alkoxy side chains into the PPV backbone and were able to prepare oligomers **29a-g**, which span up to the 11-mer (Scheme 16).⁴⁸ The UV/Vis spectroscopic analysis gives λ_{\max} values from **29a** (354 nm) to **29g** (481 nm) as a result of extending the π -conjugation.



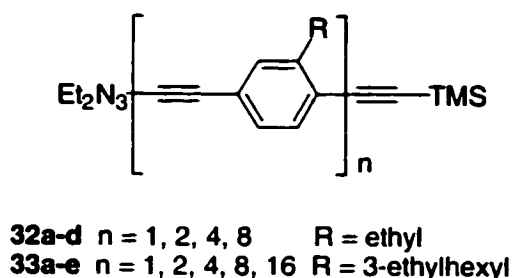
Scheme 16: PPV polymers **26** and oligomers **27-29**.

Poly(*p*-phenyleneethynylene)s (PPEs) have been developed as a relative of PPV.^{1d} PPEs show large photoluminescence efficiencies due to a high degree of rigidity. Furthermore, the rigid, linear backbone gives maximum orientation, which is an important property for the preparation of oriented films and blends.⁴⁹⁻⁵² Dixneuf and co-workers prepared **30a-d** and **31a-d** using iterative-convergent methods based on both Pd/Cu catalyzed carbon-carbon cross-coupling and selective desilylation reactions (Scheme 17).⁵³



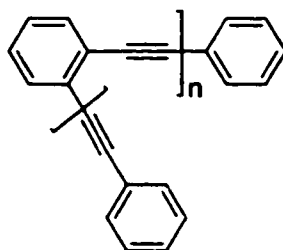
Scheme 17: PPE oligomers **30-31** prepared by Dixneuf and co-workers.

Tour and co-workers synthesized PPE oligomers **32a-d** and **33a-d** up to the 16-mer which has a backbone 128 Å long (Scheme 18).⁶ For oligomers **33a-d**, the ECL of this series is around 10. As found with other defined length oligomers, the presence of alkyl side chains in **32** and **33** leads to enhanced solubility.



Scheme 18: PPE oligomers **32-33** prepared by Tour and co-workers.

A series of *ortho*-linked oligo(*o*-phenyleneethynylene)s **34a-h** has been prepared by Grubbs and Kratz (Scheme 19).⁵⁴ Single crystal X-ray structure studies of **34c** and **34d** indicate that the compounds adopt a helical structure in the solid state.



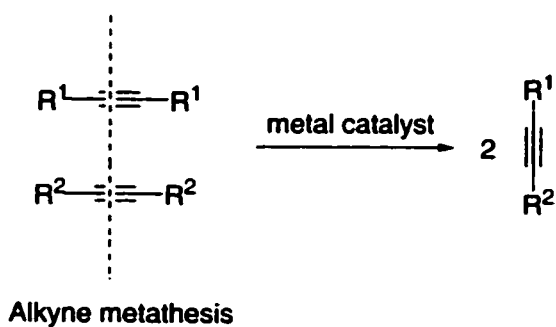
34a-h $n = 0-7$

Scheme 19: *Ortho*-linked PPE oligomers **34** prepared by Grubbs and Kratz.

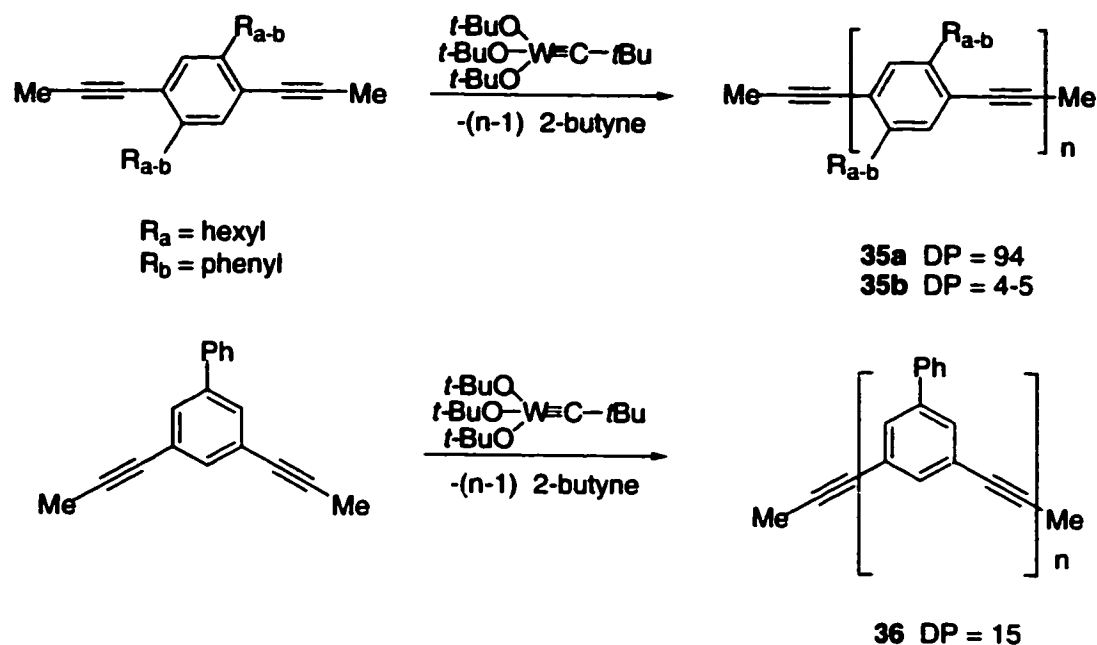
In addition to palladium catalyzed methodologies for preparing PPE oligomers and polymers, alkyne methathesis has become another useful way to produce PPEs (Scheme 20). Bunz and co-workers have investigated alkyne metathesis and prepared various series of PPE polymers **35-36** (Scheme 21). They reported a synthesis of polymers **35** and **36** using Schrock's tungsten-carbyne catalyst.⁵⁶ The degree of polymerization (DP) of polymer **35a** turns out to be 94. The degree of polymerization (DP) in a polymer molecule is the number (n) of repeating units in the polymer chain. These experimental results prove that alkyne methathesis can be an effective alternative to construct PPE polymers. Polymers **35b** and **36**, however, are achieved in only DP of 4-5 and 15, respectively. This low DP of polymer **35b** results from insolubility of diphenyl-PPE product. In addition to this problem of insolubility, the formation of cycle products from polymer **36** also lowers the DP. The adopted catalyst, $(t\text{BuO})_3\text{W}\equiv\text{CrBu}$, for alkyne methathesis is not commercially available, and it

is very sensitive toward air and water. Therefore, preparation of PPE polymers using this catalyst system requires extreme care.

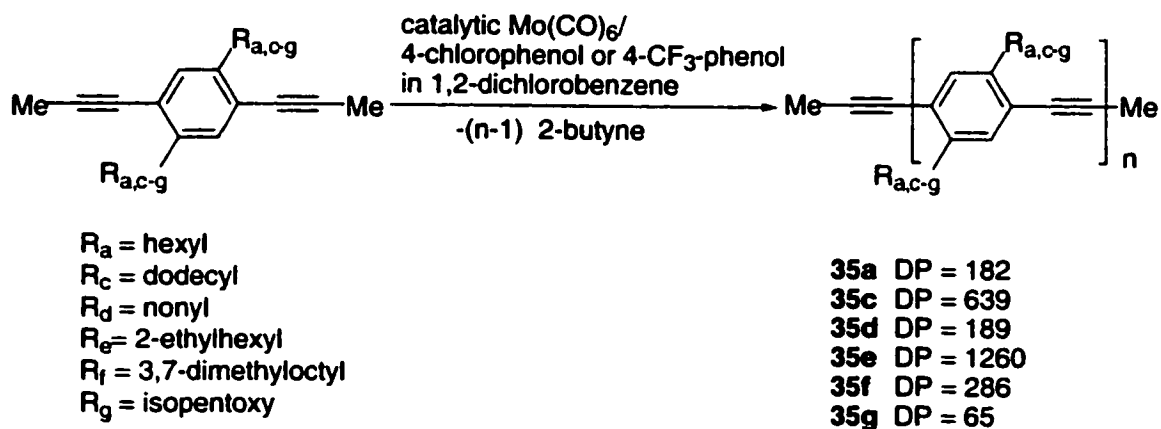
To circumvent these problems, Bunz and co-workers have used the Mortreux-Bunz catalyst system for the preparation of PPE polymers.^{56,57} This catalyst system consists of $\text{Mo}(\text{CO})_6$ with 4-chlorophenol or 4- CF_3 -phenol in 1,2-dichlorobenzene. Polymers **35a** and **35c-g** were thus realized with higher DPs using this catalyst system (Scheme 22).^{56,57} The catalyst system works great in non-dried, non-purified, off-the shelf solvents and offers an another useful way to prepare PPE polymers.



Scheme 20: The schematic presentation of alkyne metathesis.



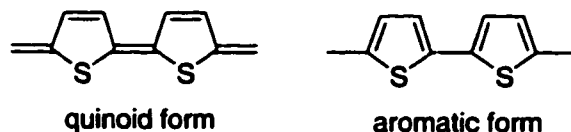
Scheme 21: The structure of PPE polymers from the Schrock catalyst system.



Scheme 22: The structure of PPE polymers from the Mortreux-Bunz catalyst system.

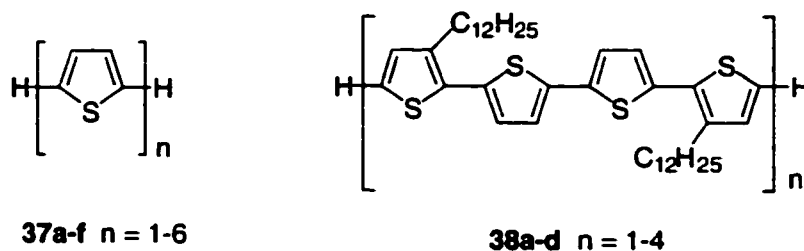
Poly(α -thiophene) (PT) can be generally viewed as a *cis*-PA chain in which the PA backbone is stabilized by the bridging sulfur atom.⁵⁸ This structural adjustment from polyacetylene provides some important features. First, PT is more environmentally stable than PA. Second, the electronic and photonic properties can be easily modified

by attaching side chains to the thienyl ring monomer units. Third, a nondegenerate ground state, related to the nonenergetic equivalence of the two limiting mesomeric forms (aromatic and quinoid), of PT are possible (Scheme 23).



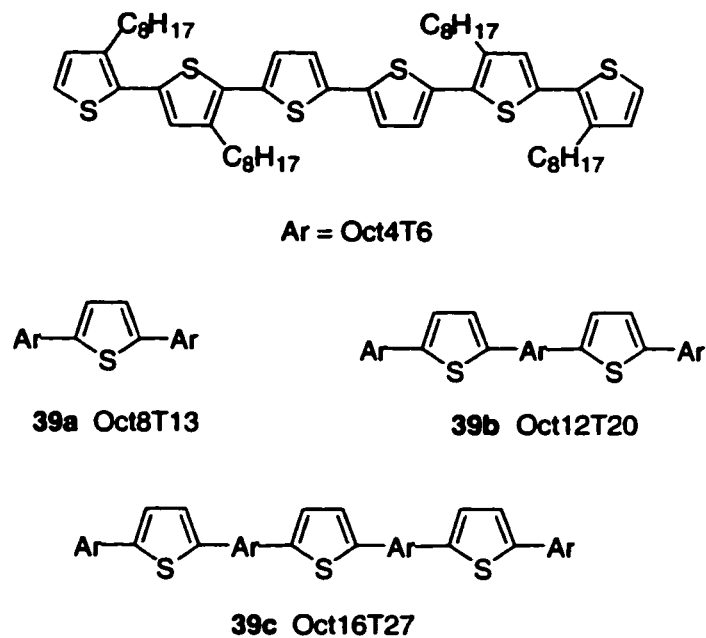
Scheme 23: Two limiting mesomeric forms of PT.

Oligomers **37a-f** have been prepared by Prasad and co-workers and used to study the nonlinear optical, second hyperpolarizability γ , values as a function of increasing chain length (Scheme 24).⁵⁹ Their λ_{\max} values, as measured by UV/Vis absorption spectroscopy, increase from 231 nm (**37a**) to 429.2 nm (**37f**), and the second hyperpolarizability γ values also increased as a function of chain length. The ECL of this series of oligomers is around 17. Bäuerle *et al.* prepared the solubilized series of oligomers **38a-d** (Scheme 24).⁶⁰ The ECL from UV-Vis spectroscopic measurements of this series is around 20.



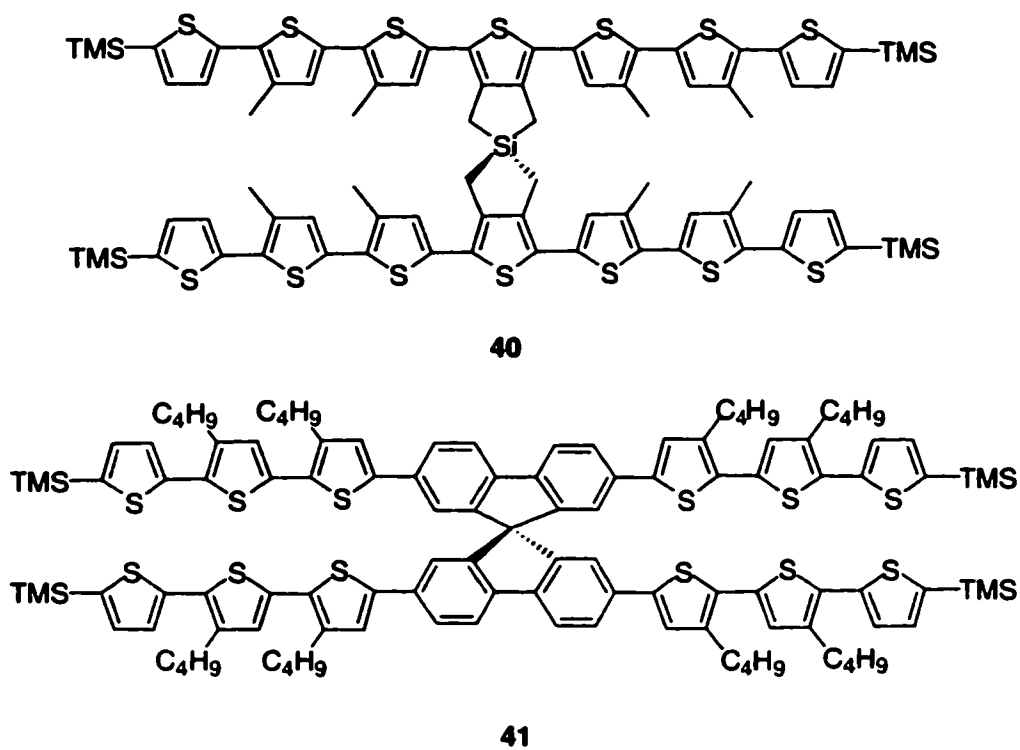
Scheme 24: The structures of PT oligomers **37-38**.

The longest reported mono-disperse and fully characterized oligo PT is the 27-mer **39c** synthesized by Otsubo and co-workers (Scheme 25).⁶¹ From the UV/Vis spectroscopic data, the ECL of this series of oligomers is also around the 20-mer.



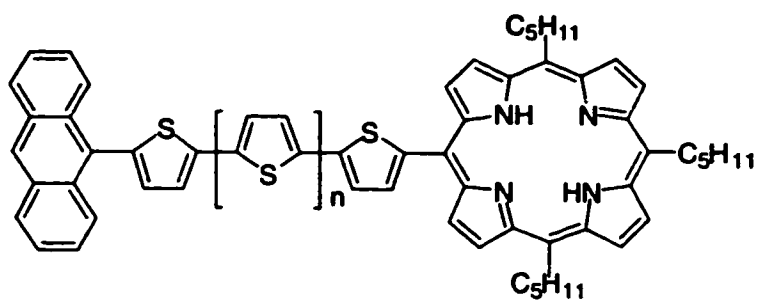
Scheme 25: The structures of PT oligomers **39a-c**.

Attempts to make orthogonally fused conducting polymers by Tour and co-workers afforded spiro-fused oligo(α -thiophene)s **40** and **41** (Scheme 26).⁶² However, electron communication through the two orthogonally connected oligomers was found to be very weak.⁶³

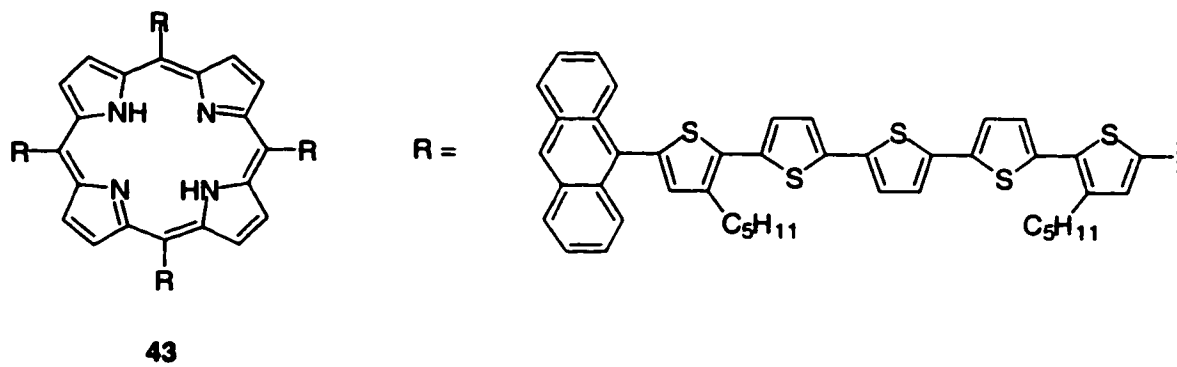


Scheme 26: The spiro fused PT oligomers **40** and **41**.

Oligo(α -thiophene) can function as a linker in donor-acceptor systems. Compounds **42** and **43** have been prepared and their intramolecular energy transfer properties investigated versus other oligoene systems (Scheme 27).⁶⁴ The studies demonstrate that oligo-PT spacers are better than oligoene spacers due to their thermal and chemical stability, higher fluorescence quantum yields, and larger degree of π -electron delocalization.⁶⁴



42a,b $n = 0,1$



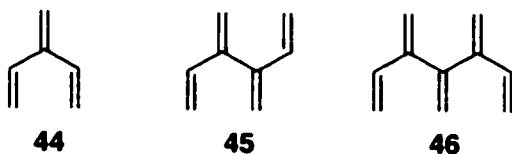
43

Scheme 27: The PT oligomers 42a-b and 43.

b. Cross-conjugated polymers

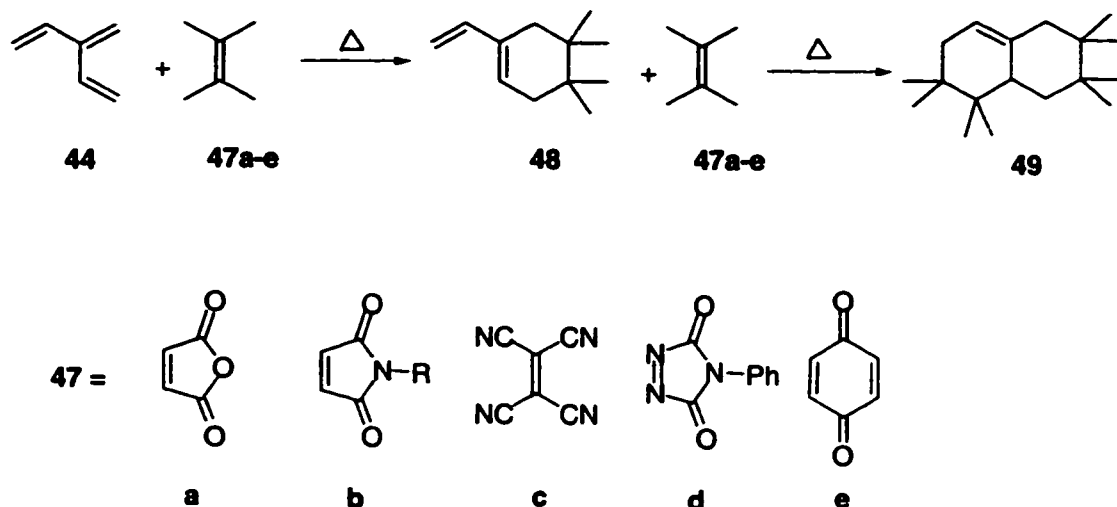
Cross-conjugation, another mode of π -electron communication, is defined as a system possessing three unsaturated groups, two of which, although conjugated to a third unsaturated center, are not conjugated to each other.⁶⁵

3-Methylene-1,4-pentadiene **44** is the simplest acyclic cross-conjugated hydrocarbon compound and the parent compound of a class of polyolefins known as dendralenes (Scheme 28).⁶⁶ In trivial nomenclature, **44** is [3]-dendralene and higher members of this series is achieved by replacing non-terminal hydrogen atoms by vinyl substituents (e. g., **45** [4]-dendralene, **46** [5]-dendralene).



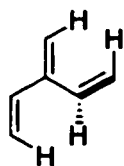
Scheme 28: The structures of [3]-, [4]-, and [5]-dendralenes.

Originally, [3]-dendralene **44** drew attention for synthetic applications rather than its unique π -electron communication. This compound has been used in [4+2] cycloadditions because it functions as a tandem-annelating reagent or diene in Diels-Alder additions (Scheme 29).^{67,68}



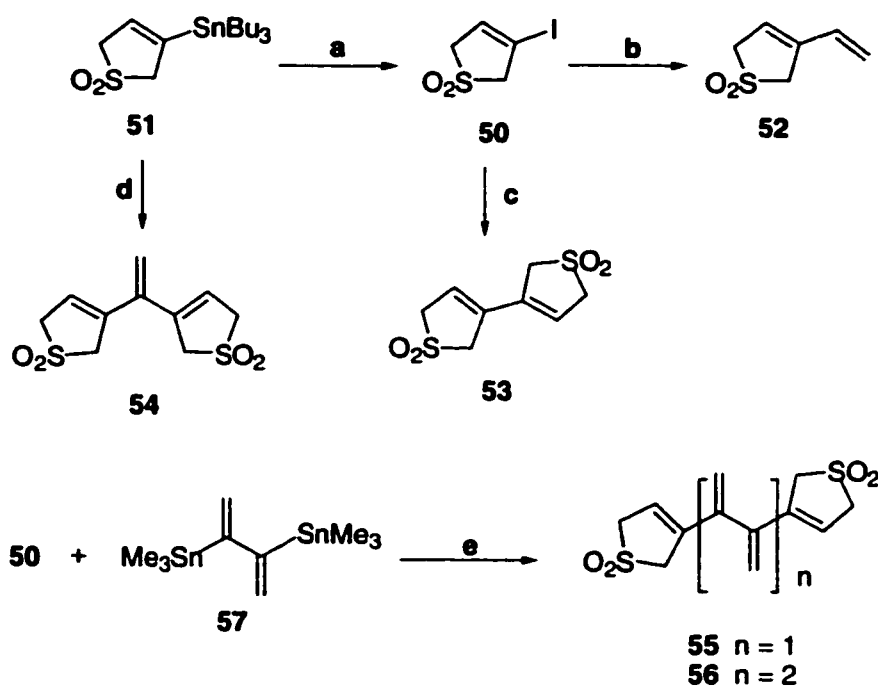
Scheme 29: [3]-dendralene **44** as a tandem-annulating reagent.

Almenningen *et al.* carried out a detailed structural analysis of **44** by electron diffraction, vibrational, NMR, and UV spectroscopies. The most stable conformation of **46**, from their investigation, is the *anti-skew* conformation (Scheme 30).⁶⁹



Scheme 30: The *anti-skew* conformation of [3]-dendralene **44**.

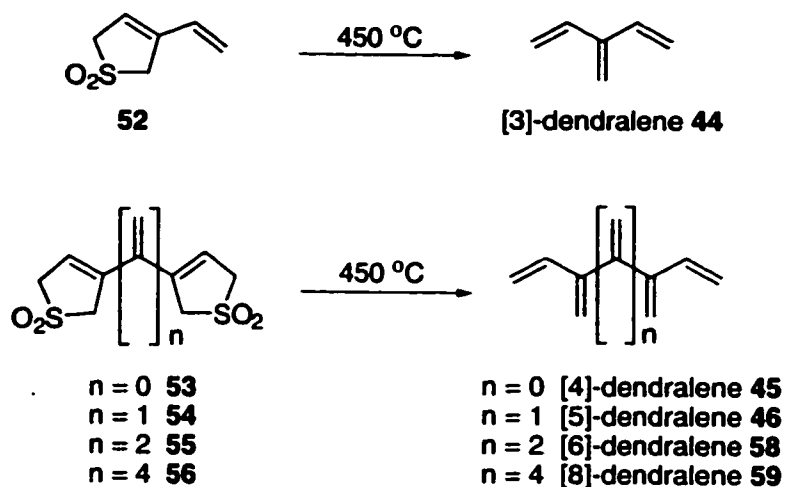
To present, only one series of unfunctionalized [n]-dendralenes has been prepared, and this elegant route was taken to the stage of the [8]-dendralene by Sherburn and co-workers.⁷⁰ The preparation of [3], [4], [5], [6] and [8]-dendralenes has been achieved by an masking-unmasking procedure. The synthetic route to the masked [n]-dendralenes is shown in Scheme 31.



Reagents and conditions : (a) I_2 , CH_2Cl_2 , Ar, 1 h. (b) $\text{Bu}_3\text{Sn-CH=CH}_2$ (1.2 equiv), $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (0.05 equiv), DMF, RT, Ar, 2 h.
 (c) **51** (1.0 equiv), $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (0.05 equiv), DMF, RT, Ar, 18 h.
 (d) $\text{CH}_2=\text{CBr}_2$ (0.5 equiv), $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (0.05 equiv), DMF, 40 °C, Ar, 36 h.
 (e) **57** (1.0 equiv), $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (0.05 equiv), DMF, 60 °C, Ar, 72 h.

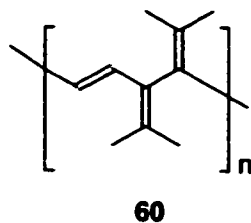
Scheme 31: The preparation of masked dendralenes.

The masked dendralenes **52-56** are converted to their corresponding unfunctionalized [n]-dendralenes upon heating (Scheme 32). The UV/Vis absorption maximum of [8]-dendralene **59** is only 226 nm. For comparison, [3]-dendralene **44** shows absorption maximum at 224 nm and these results confirm the non-planar, non-conjugated arrangement in these molecules.



Scheme 32: Unmasking the dendralenes.

The first and only polymer which has a [3]- dendralene structure in its monomer unit was reported by Swager and Grubbs (Scheme 33).⁷¹ The average molecular weight (relative to polystyrene standards) of this polymer **60** was 12000-51000 and polydispersity was as low as 2.1 (determined by gel permeation chromatography). Polymer **60** is not extensively delocalized due to its cross-conjugated nature. However, it shows modest conductivity (from 10^{-3} - 10^{-4} S/cm) and paramagnetism upon oxidative doping. The UV/Vis absorption maximum of the polymer **60** is only 278 nm and shows that π -system of this polymer is segregated into triene segments. The segregation of polymer **60** is the result of steric interactions causing distortions the π -conjugated backbone from planarity.



Scheme 33: The structure of polymer **60** prepared by Swager and Grubbs.

Iso-polydiacetylenes **61**, the cross-conjugated constitutional isomers of polydiacetylenes **62**, have been realized, and their properties resulting from π -electron communication through the cross-conjugated backbone have been explored by Tykwinski's group (Fig 3).⁷²⁻⁷⁴

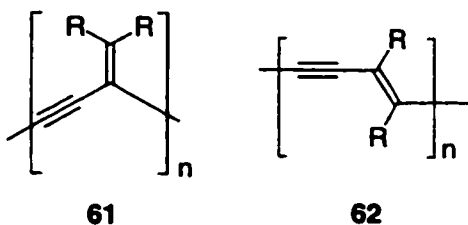
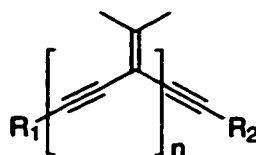


Figure 3: The generalized structure of *iso*-PDA **61** and PDA **62**.

Zhao and Tykwinski synthesized the first series of *iso*-PDAs **63a-d**, **64** and **65a-d** up to the nonamer **65d** (Scheme 34).⁷² The length of nonamer **65d** is 3.4 nm and it is the longest *iso*-PDA oligomer to be reported to date. UV-Vis spectroscopic analysis suggests that electronic communication along the conjugated framework increases as a function of oligomer length.



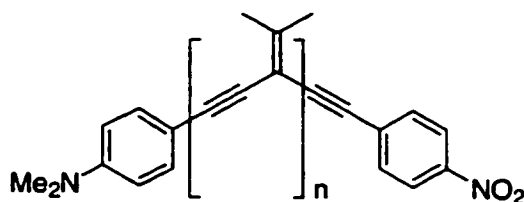
63a-d $R_1, R_2 = \text{TMS}$ $n = 1, 3, 5, 7$

64 $R_1 = \text{TMS}$ $R_2 = \text{TIPS}$ $n = 1$

65a-d $R_1, R_2 = \text{TIPS}$ $n = 3, 5, 7, 9$

Scheme 34: The structure of *iso*-PDA oligomers **63-65**.

Ciulei and Tykwinski prepared donor and acceptor substituted *iso*-PDAs **66a-c** and structure-property relationships for these oligomers have been reported (Scheme 35).⁷³ UV/Vis absorptions reveals that, whereas D/A monomer **66a** shows D/A electronic communication through the cross-conjugated framework, such communication in **66b** and **66c** appears to be considerably limited.

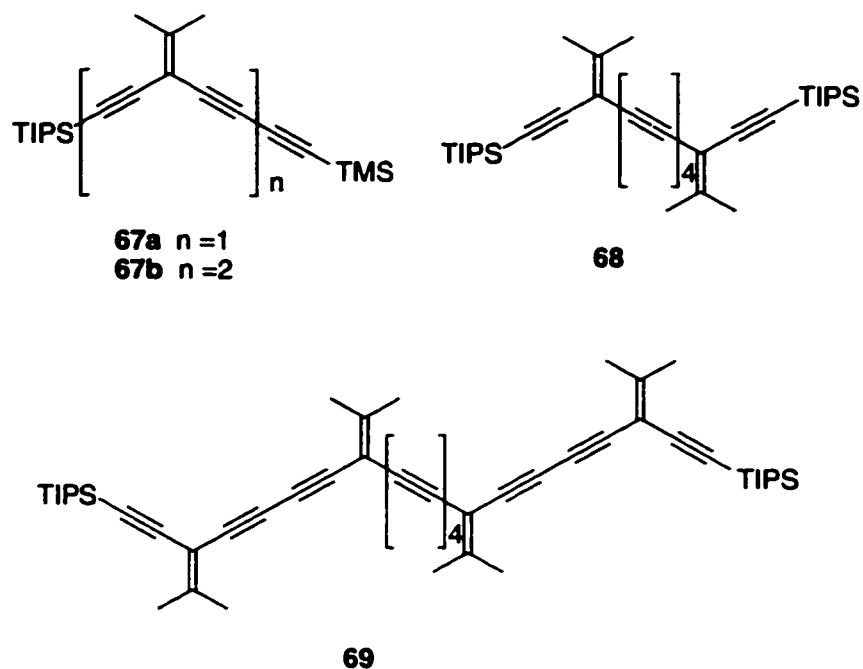


66a-c $n = 1-3$

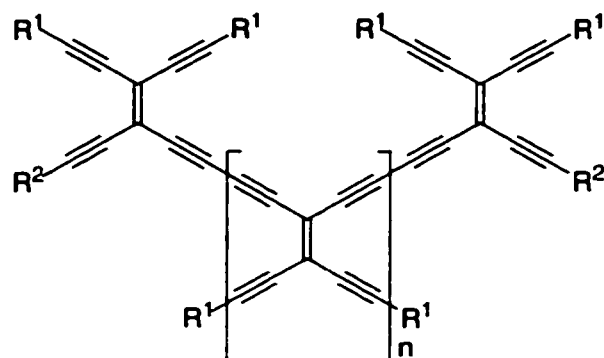
Scheme 35: The structure of D/A end-capped *iso*-PDA oligomers **66a-c**.

As an extension of the *iso*-PDA synthesis, Zhao and Tykwinski prepared a series of cross-conjugated polyenynes **67-69** (Scheme 36).⁷⁴ Oligomers **67a** and **67b** can be classified as members of *iso*-polytriacetylenes, *iso*-(PTA)s. For these oligomers, no electronic communications through the cross-conjugation framework was observed. In addition to *iso*-PTA oligomer **67a-b**, tetraethynylethene subunits oligomer **70** and **71**

prepared by Diederich and co-workers can also be classified as members of *iso*-PTA (Scheme 37).²



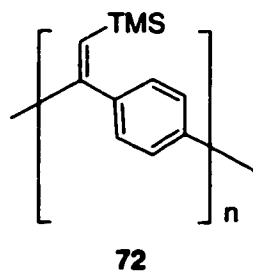
Scheme 36: The structures of polyenyne oligomers **67-69**.



70a-c $n = 0-2$ $R^1 = R^2 = \text{TIPS}$
71 $n = 1$ $R^1 = \text{TIPS}$ $R^2 = \text{TES}$

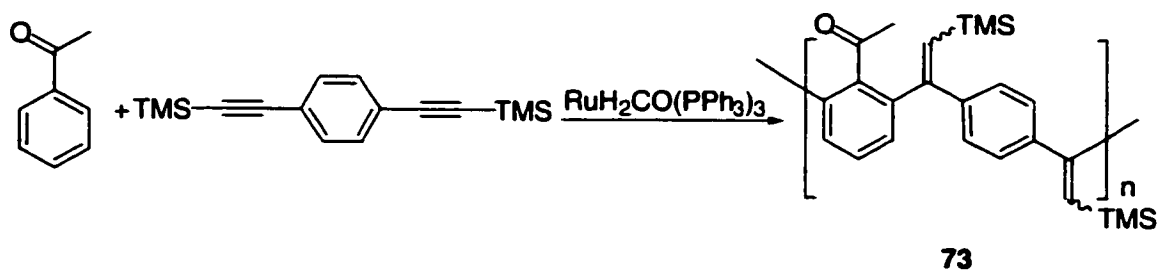
Scheme 37: The structures of *iso*-PTA oligomer **70-71**.

Iso-polyphenylenevinylenes, the constitutional isomer of its linearly conjugated counterpart, polyphenylenevinylene (PPV), have been synthesized by several groups. Mao and Tilley prepared the cross-conjugated polymer **72** (Scheme 38).⁷⁵ The molecular weight of polymer **72** is not high ($M_w/M_n=2700/1700$) and λ_{max} of this polymer at 270 nm is also not quite high as a result of its cross-conjugated structure.



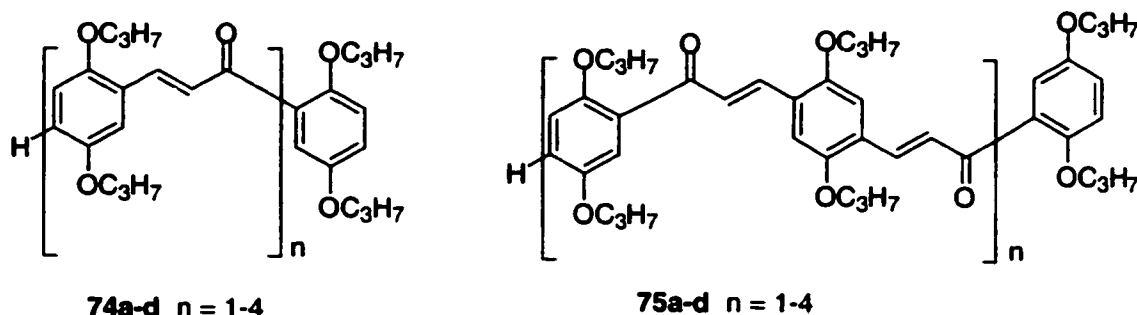
Scheme 38: The structure of *iso*-PPV polymer **72**.

Londergan *et al.* synthesized cross-conjugated co-poly(arylene/1,1-vinylene) **73** by using ruthenium catalysis (Scheme 39).⁷⁶ From the topology of this polymer **73**, it can be classified in the *iso*-polyphenylenevinylene category. The large band gap of this polymer **73** ($\lambda_{max}=240, 284$ nm and fluorescence at 420 ± 5 nm) make it useful in organic LED and other optoelectronic applications.



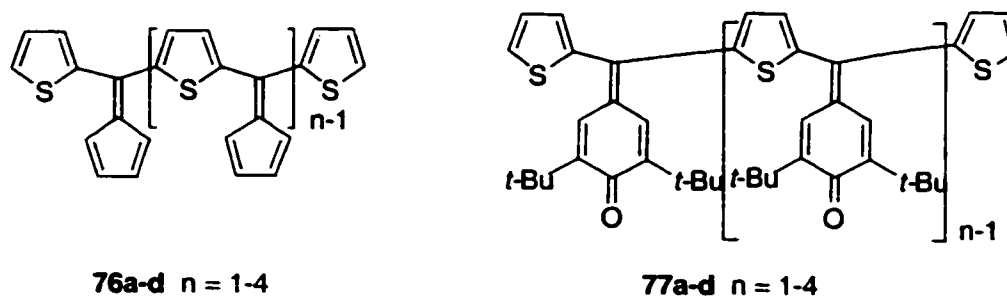
Scheme 39: The synthetic route to *iso*-PPE polymer **73**.

Meier *et al.* have prepared cross-conjugated oligomers **74a-d** and **75a-d** that contain chalcone building blocks (Scheme 40).^{77,78} Their absorption and fluorescence spectra reveal that bathochromic shifts occur as a result of the cross-conjugated ketone present in this system. The ECL of oligomers **74a-d** and **75a-d** is 6 and 14 chalcone building blocks, respectively.⁷⁹



Scheme 40: The structures of oligomers **74-75**.

The thiophene ring can be a part of a cross-conjugated oligomer structure as well. Oda and co-workers reported a series of oligomers **76a-d** in 1994 (Scheme 41).⁸⁰ Their UV/Vis spectra demonstrate that no electronic communication is achieved through each unit. Also, Oda and co-workers prepared an alternative set of oligomers **77a-d** (Scheme 41).⁸¹ These oligomers possess better stability than **76a-d** and high electron affinity as measured by cyclic voltammetry (CV).

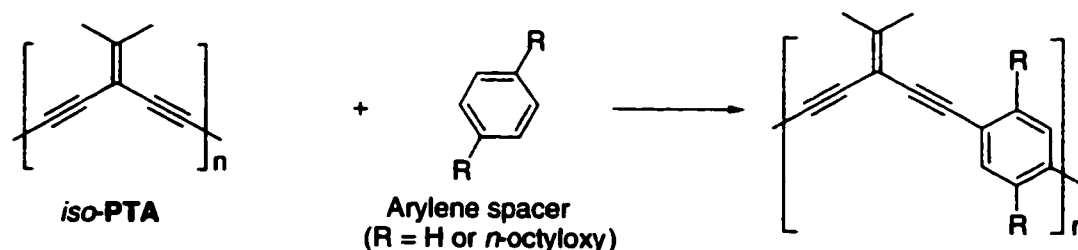


Scheme 41: The structures of thiophene contains cross-conjugated oligomers **76-77**.

The synthesis and investigation of organic linearly- and cross-conjugated oligomers and polymers has become a notable topic in recent years. The number of papers regarding this area published through various scientific journals continues to grow. As many new organic-based materials will be used in our daily life in the near future, an understanding of organic material chemistry will become all too important.

B. Research goals

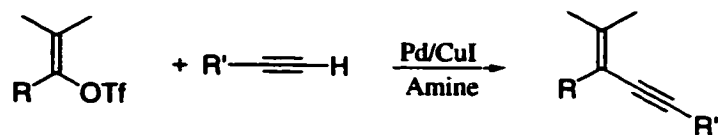
Our interest in constructing cross-conjugated polymers stems from curiosity about their unique π -delocalization. According to previous studies on cross-conjugated *iso*-polydiacetylenes (*iso*-PDAs)⁷² and *iso*-polytriacetylenes (*iso*-PTAs)⁷⁴, reduced π -electron communication along the polymer framework has been observed relative to the analogous linearly conjugated materials. In order to understand structure-property relationships, as well as develop novel polymeric systems for the purpose of specific electronic and optical properties, we extend our investigation of cross-conjugated systems toward insertion of arylene spacers into the *iso*-PTA structures (Scheme 42).



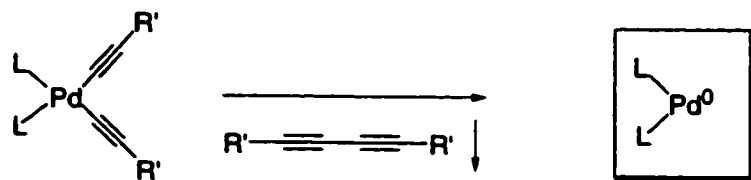
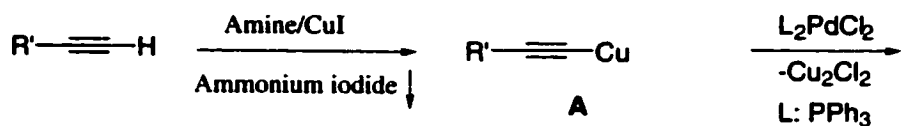
Scheme 42: Proposed cross-conjugated polymers.

These polymers are similar in structure to the linearly conjugated PPEs, which have become important organic polymers as photoluminescent and fluorescent chemosensor materials.¹⁶ To construct and study these polymers, two different synthetic approaches can be employed. First, oligomeric systems with defined length and structure can be assembled iteratively in order to facilitate the ease of purification and characterization. Palladium-catalyzed coupling reactions between vinyl triflates and terminal alkynes would be used in this approach and the mechanism is described in Scheme 43.⁸²

I. Overall reaction

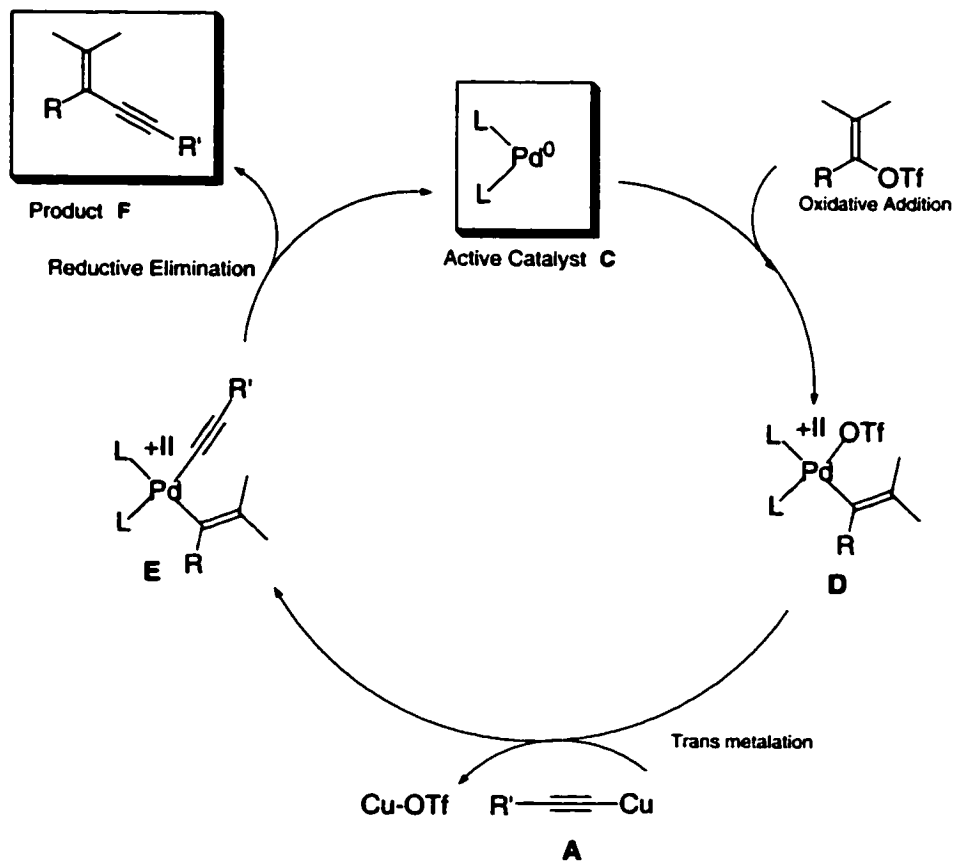


II. Catalyst Activation



B

III. Catalytic Cycle



Scheme 43: The mechanism of Pd-catalyzed coupling reaction.

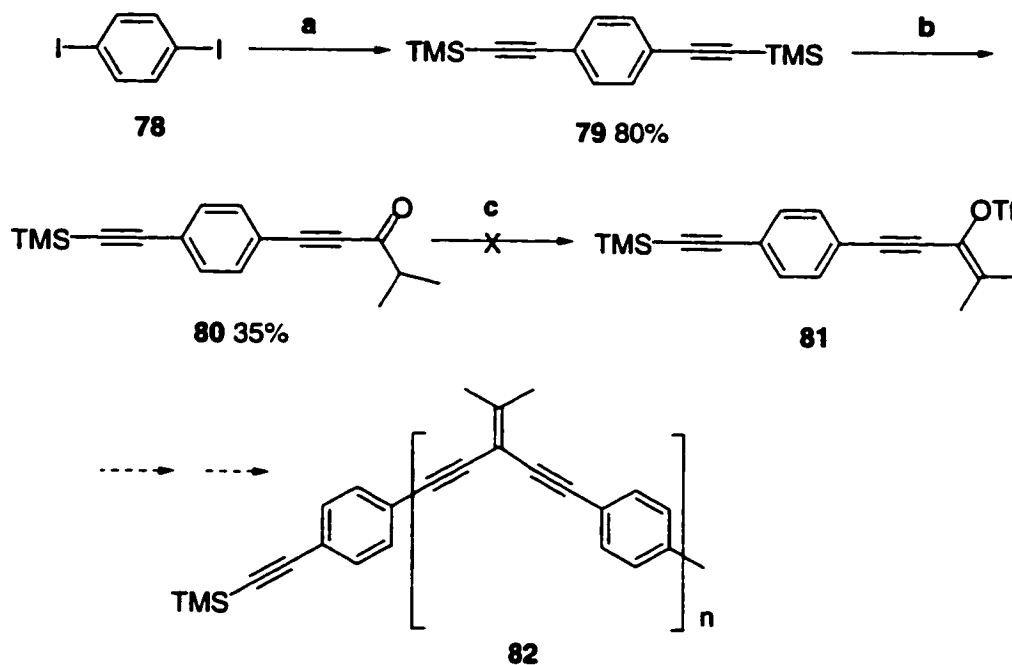
It was predicted that a series of oligomers with defined length could thus be obtained. The challenge of using this approach, however, is that it requires numerous steps to reach the polymeric stage. To circumvent this problem, an alternative approach, one-pot polymerization, was targeted to obtain cross-conjugated higher oligomers in a single step. Unlike the stepwise approach, this route leads to a mixture of oligomers with a distribution of different chain lengths. The determination of structural characteristics is thus far more difficult.

In this thesis, both iterative and one-pot polymerization syntheses of cross-conjugated oligomers are outlined, compared and discussed. Their structural properties have been studied via ^1H and ^{13}C -NMR and IR spectroscopies, and MS spectrometry. Their electronic absorption and emission characteristics have been investigated in order to understand their π -electronic properties.

II. RESULTS SECTION

A. Synthesis and characterization of cross-conjugated oligomers.

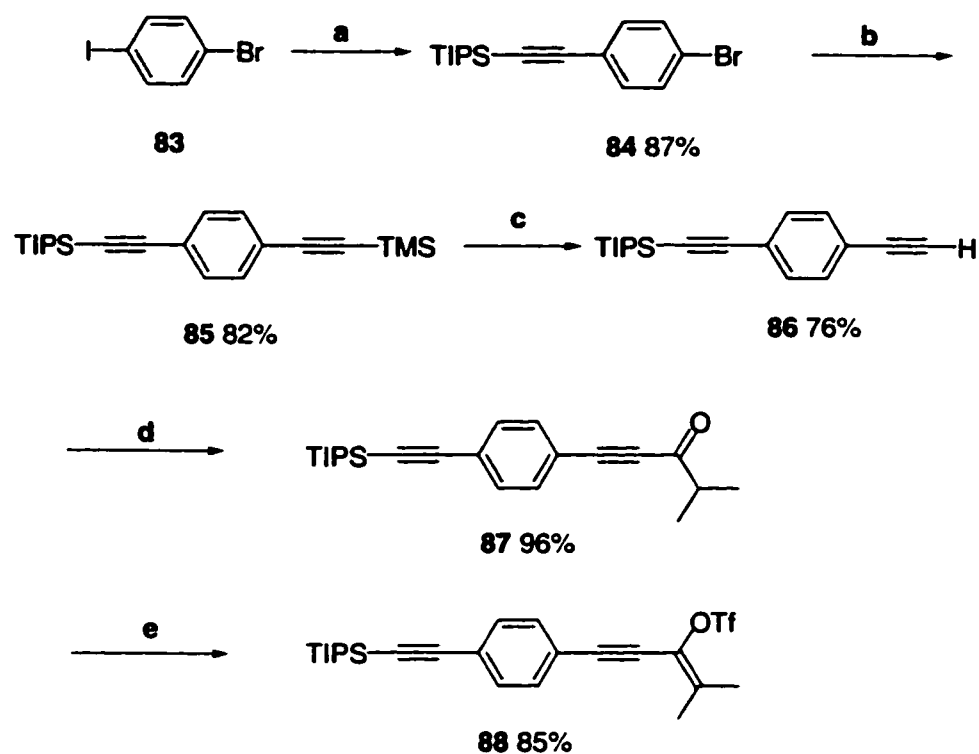
Several synthetic routes toward cross-conjugated oligomers are outlined in this chapter. Oligomeric structures that possess cross-conjugation via the insertion of an arylene spacer into the *iso*-PTA structure have been designed and realized. The initial attempt is summarized in Scheme 44.



Reagents and conditions: (a) Trimethylsilylacetylene (2.4 equiv), $\text{PdCl}_2(\text{PPh}_3)_2$ (5 mol%), CuI (10 mol%), triethylamine, rt, 15 h. (b) AlCl_3 (1 equiv), *iso*-butyryl chloride (1 equiv), CH_2Cl_2 , rt, overnight. (c) 2,5-di-*tert*-Butyl-4-methyl-pyridine (1.25 equiv), triflic anhydride (1.5 equiv), CH_2Cl_2 .

Scheme 44: The synthetic route toward a series of cross-conjugated poly(phenyleneenediynes).

1,4-Diiodobenzene **78** was coupled with 2.4 equiv of trimethylsilylacetylene under the palladium-catalyzed coupling conditions, to give **79** as a yellow solid in 80% yield.⁸³ To access ketone **80**, compound **79** was thus reacted with *iso*-butyryl chloride in the presence of aluminium chloride catalyst in CH₂Cl₂.⁸⁴ Unfortunately, this reaction gave a complex mixture, suggesting that aluminium chloride is too strong a Lewis acid. Column chromatography (silica gel, hexanes/CH₂Cl₂, 3:1) did, however, successfully give compound **80** as a yellow oil in 35% yield. Compound **80** was then carried on toward the corresponding vinyl triflate **81**, using 2,6-di-*tert*-butyl-4-methyl pyridine (DBMP) and triflic anhydride.⁸⁵ The reaction gave only desilylated product. This reaction indicated that the trimethylsilyl group may not be a suitable protecting group for this synthesis of cross-conjugated arylene oligomers. Realizing this, the bulky triisopropylsilyl (TIPS) group was used to replace the trimethylsilyl (TMS) moiety as the protecting group in this oligomer synthesis because of its better chemical stability. The oligomers protected with a TIPS moiety were targeted as summarized in Scheme 45.

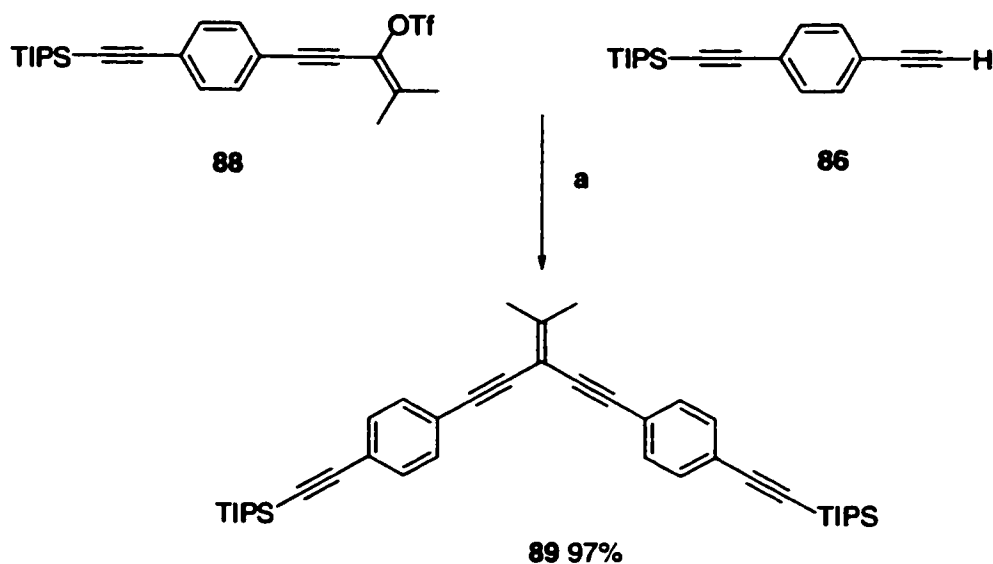


Reagents and conditions: (a) Triisopropylsilylacetylene, $\text{PdCl}_2(\text{PPh}_3)_2$ (5 mol%), CuI (10 mol%), triethylamine, rt, 15 h. (b) Trimethylsilylacetylene, $\text{PdCl}_2(\text{PPh}_3)_2$ (5 mol%), CuI (10 mol%), triethylamine, reflux, overnight. (c) K_2CO_3 , THF/MeOH (1:1), rt, 30 min. (d) CuI (5 mol%), triethylamine, *iso*-butyryl chloride, rt, 4 h. (e) 2,5-di-*tert*-Butyl-4-methyl-pyridine (1.25 equiv), triflic anhydride (1.5 equiv), CH_2Cl_2 , rt, 4 h.

Scheme 45: The synthetic route to vinyl triflate **88**.

To construct this series of oligomers, vinyl triflate **88** was targeted as a building block. 1-Bromo-4-iodobenzene **83** was selected as a starting material because the two halogens possess different reactivities toward palladium catalyzed cross-couplings with acetylenes.⁸⁶ Starting with compound **83**, cross-coupling with triisopropylsilylacetylene under the palladium-catalyzed coupling conditions gave **84** in 87% yield.⁸⁶ A cross-coupling between compound **84** and trimethylsilylacetylene was then conducted under reflux, as the bromine substituent is less reactive than the iodine. Compound **85** was formed in 82% yield. Generally, Friedel-Crafts acylation would be appropriate for the synthesis of ketone **87**. The strong reaction conditions,

however, resulted in many by-products and lowered the yield of the reaction. To circumvent this problem, an alternative method was used.⁸⁷ For this, deprotection of the TMS group from compound **85** was necessary. This reaction was carried out with potassium carbonate as a catalyst in a 1:1 ratio of wet methanol and THF.⁸⁸ Wet methanol functions as a proton donor, and THF was used to solvate the compound. After 30 min of stirring, desilylated compound **86** was obtained in 76% yield. From compound **86**, ketone **87** can be obtained under the catalysis of CuI and in the presence of *iso*-butyryl chloride and triethylamine.⁸⁷ This reaction gave a yellow oil **87** in 96% yield. Two reasons likely account for the success of this reaction, including the increased stability of the TIPS group and the ability to form monodeprotected **86** so that the milder CuI coupling conditions can be employed. Ketone **87** can be converted into vinyl triflate **88** using a procedure adapted from that described by Stang *et al.*⁸⁵ In contrast to the attempt to make triflate **81**, the reaction to **88** gave the desired product. After reaction, the solvent was removed and the residue was redissolved by pentane. The undissolved solid, [DBMP-H⁺]OTf, was removed by filtration. The purification by column chromatography gave **88** as an orange oil in 85% yield. This result confirmed that the triisopropylsilyl group is a much better protecting group than the trimethylsilyl group for these reactions.

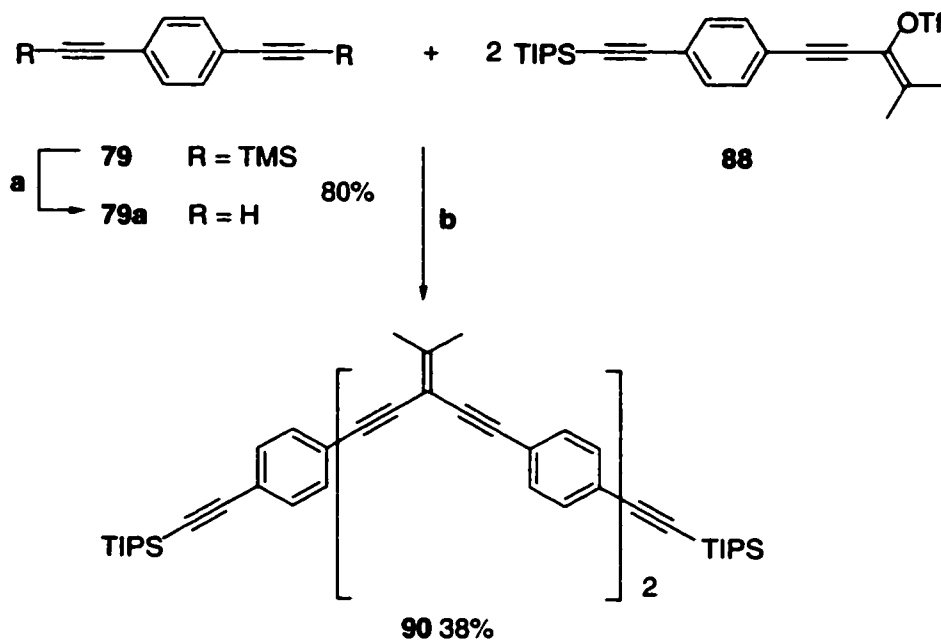


Reagents and conditions: (a) $\text{PdCl}_2(\text{PPh}_3)_2$ (5 mol%), CuI (10 mol%), $i\text{-Pr}_2\text{NH}$, THF, rt, 4 h.

Scheme 46: The synthetic route to monomer **89**.

From the vinyl triflate **88**, monomer **89** can be generated by cross-coupling **88** with mono-protected **86** under palladium-catalyzed coupling conditions,⁸² which utilized $\text{PdCl}_2(\text{PPh}_3)_2$ as a catalyst, CuI as a co-catalyst, degassed THF as a solvent and in the presence of diisopropylamine for 4 h (Scheme 46). This reaction was monitored by TLC and one major product was found. Column chromatography (silica gel, 1:10 CH_2Cl_2 /hexanes) gave **89** as an orange oil in 97% yield. The ^1H NMR spectrum gives signals of eight phenyl protons as a singlet at 7.40 ppm, six hydrogens from two methyl group as a singlet at 2.07 ppm and forty-two protons of the triisopropylsilyl group as a singlet at 1.11 ppm. In the ^{13}C -NMR spectrum of monomer **89**, four signals are observed in the region of 88-106 ppm, assigned to the four *sp* carbons; four signals are observed between 123-132 ppm for the carbons of the phenylene rings; the alkylidene methyl carbons resonate at 23.0 ppm; two signals at 101.3 and 155.3 ppm

are representative of sp^2 alkylidene carbons; and two signals at 11.4 and 18.7 ppm are assigned to carbons of the trisopropylsilyl group.



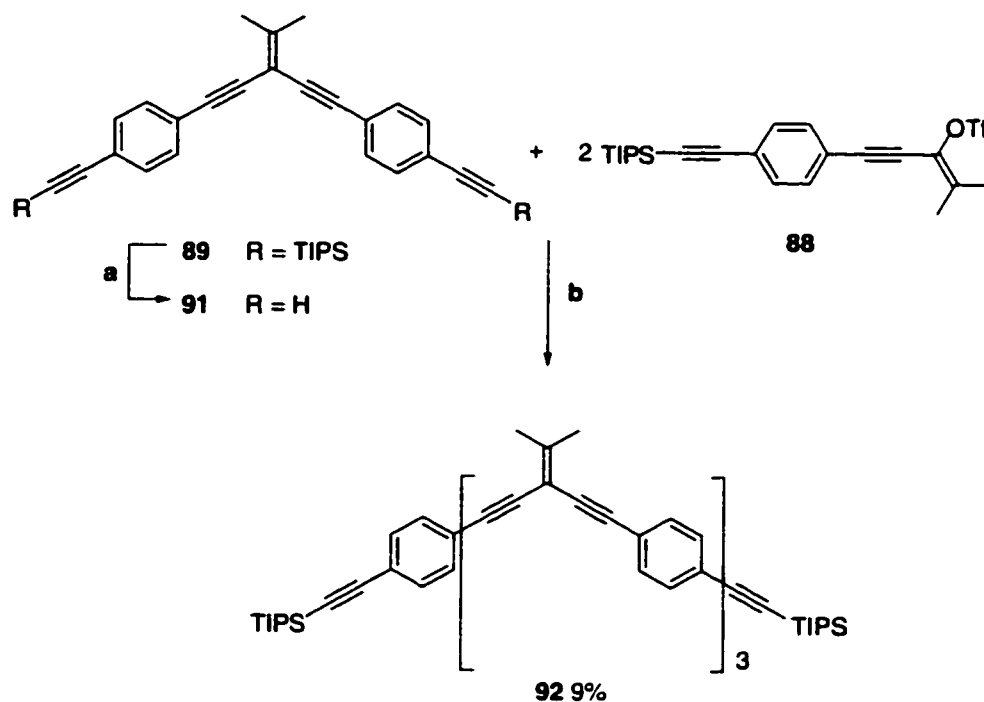
Reagents and conditions: (a) K_2CO_3 , THF/MeOH (1:1), rt, 30 min.
 (b) $\text{PdCl}_2(\text{PPh}_3)_2$ (5 mol%), CuI (10 mol%), $i\text{-Pr}_2\text{NH}$, THF, rt, 2 h.

Scheme 47: The synthetic route to dimer **90**.

The synthesis of the next member of the series, dimer **90**, is outlined in Scheme 47. First, desilylated compound **79a** was easily prepared by deprotecting **79** with potassium carbonate in 1:1 wet MeOH/THF.⁸⁸ Dimer **90** can be then generated by coupling **88** (2 equiv) with desilylated compound **79a** (1 equiv) under the palladium-catalyzed coupling conditions for 2 h (Scheme 47).⁸² Column chromatography (silica gel, 1:7 CH_2Cl_2 /hexanes) afforded **90** as an orange oil in 38% yield.

The ^1H NMR spectrum of **90** gives signals of four phenyl protons as a singlet at 7.42 ppm, eight phenyl protons as a singlet at 7.40 ppm, 12 hydrogens from four methyl

group as a singlet at 2.14 ppm and forty-two protons from trisopropylsilyl group as a singlet at 1.11 ppm. In the ^{13}C -NMR spectrum of dimer **90**, six signals are observed in the region of 123-132 ppm, assigned to the six aromatic carbons; five signals are observed between 88-107 ppm, representative of six types of sp carbons (one coincident signal); two signals at 101.3 and 155.3 ppm are assigned as the two alkyldiene sp^2 carbons; a single resonance at 23.0 ppm is observed for both alkyldiene methyl carbons; and two signals at 11.3 and 18.7 ppm are assigned to carbons of the trisopropylsilyl group. Electrospray Mass (ESMS) spectra of dimer **90** shows the molecular ion signal, $[\text{M} + \text{Ag}]^+$, at 903.4.



Reagents and conditions: (a) TBAF, THF, -10°C , 10 min. (b) $\text{PdCl}_2(\text{PPh}_3)_2$ (5 mol%), (10 mol%) CuI , $i\text{-Pr}_2\text{NH}$, THF, rt, 4 h.

Scheme 48: The synthetic route to trimer **92**.

Trimer **92**, the next member of this oligomer series, was synthesized as shown in Scheme 48. Monomer **89** can be desilylated to form bisterminal alkyne **91** using

tetrabutylammonium fluoride (TBAF) at $-10\text{ }^{\circ}\text{C}$ in dilute THF solution.⁸⁹ Unfortunately, the yield of the desilylation reaction was low. Decomposition by-products were observed via TLC during the reaction. In attempts to optimize the yield of this reaction, experiments of varying reaction temperature were carried out (Table 1).

Temperature ($^{\circ}\text{C}$)	Yield (%)
rt	0 ^a
0	trace
-10	27
-30	0 ^b

a. Reaction generated only unidentified decomposition products.

b. No reaction takes place at this temperature.

Table 1: Yields from desilylation reaction of monomer **89** with varying temperature.

From these observations, the reaction gives the best yield of 27% at $-10\text{ }^{\circ}\text{C}$. As compound **91** is not sufficiently stable enough for long-term storage, it was quickly converted to trimer **92** using palladium-catalyzed coupling conditions. (Scheme 48).⁸² Column chromatography (silica gel, 1:3 CH_2Cl_2 /hexanes) gave **92** as an orange oil in 9% yield from **89**. The ^1H NMR spectrum of **92** gives signals as a singlet for eight aromatic protons at δ 7.42, eight aromatic protons at 7.40 ppm, eighteen hydrogens from six methyl group at 2.14 ppm and forty-two protons from triisopropylsilyl group at 1.11 ppm. In the ^{13}C -NMR spectrum of trimer **41**, six signals are observed in the region of 123-132 ppm, assigned to the eight aromatic carbons (two coincident

signals); six signals are observed in the range of 88-107 ppm, representing eight *sp* carbons (two coincident signals); signals at 101.3, 155.20 and 155.24 ppm are assigned as the four alkylidene *sp*² carbons (one coincident signal); a signal at 23.0 ppm is observed for the three alkylidene methyl carbons; and two resonances at 11.4 and 18.7 ppm are assigned as the carbons of the trisopropylsilyl group. Electrospray Mass (ESMS) spectra of trimer **92** shows the molecular ion signal, [M + Ag]⁺, at 1081.

With the increasing oligomeric length, the stability of the oligomer decreases correspondingly. In attempts toward longer oligomers, the desilylation of either dimer **90** or trimer **92** led to only unidentified decomposition products immediately after the addition of TBAF. It was therefore impossible to access longer oligomers via this approach.

B. Investigation of electronic absorption and emission behavior of cross-conjugated oligomers.

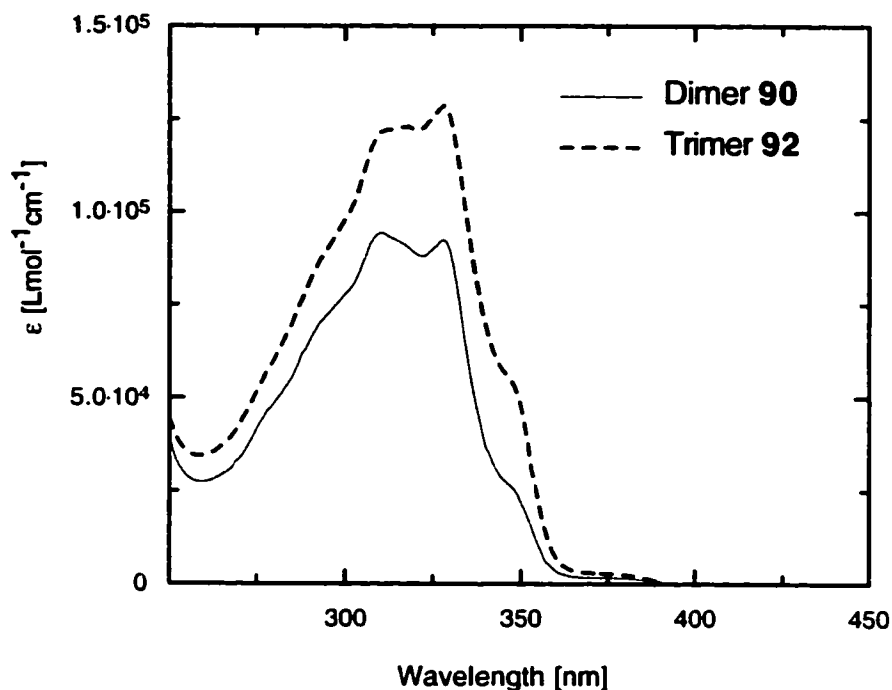


Figure 4: UV-Vis spectra of dimer **90** and trimer **92** in CHCl_3 .

UV-Vis spectroscopic analysis of dimer **90** and trimer **92** was performed to investigate their electronic absorption behavior (Figure 4). This spectrum shows that both dimer **90** and trimer **92** possess similar absorption bands at 310 and 328 nm and a shoulder absorption at 350 nm, as well as a broad, less intense absorption ($\epsilon < 1000$) from 360-390 nm, likely resulting from the presence of butadiyne moieties by means of homo-coupling side reaction. The similar UV-Vis characteristics for dimer **90** and trimer **92** suggest that there is little π -electron communication via the framework of the oligomers as the chain length increases, even at the trimeric stage. This effect can be attributed to the contribution of both cross-conjugation as well as the phenylene spacer unit, which both diminish the π -delocalization along the oligomer backbone.

As a result, only the accumulated effect in molar absorptivity takes place with additional number of oligomeric units.

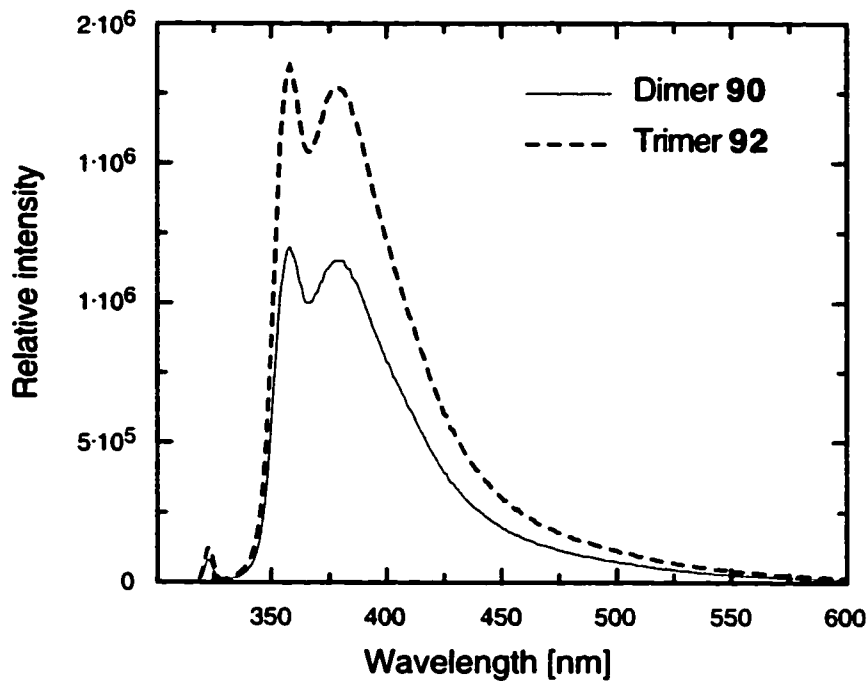


Figure 5: Fluorescence spectra of dimer **90** and trimer **92** in CHCl₃.

Fluorescence spectra of dimer **90** and trimer **92** were obtained in dilute solutions of degassed chloroform and are shown in Figure 5. When irradiated at 326 nm, both oligomers exhibit exactly the same emission bands at 359 and 381 nm respectively. With the increasing oligomeric chain length, there is no apparent red-shift in emission energy. It can be explained that their electronic properties are virtually identical and that increased communication is not obtained by increasing oligomeric units. Varying the excitation wavelength from 250 to 347 nm, both dimer **90** and trimer **92** give the same emission maxima indicating that the emission is insensitive to the excitation wavelength.

C. Synthesis and characterization of cross-conjugated oligomers from one-pot polymerization.

Attempts to prepare a new series of cross-conjugated oligomers was successful only at the stage of trimer. Therefore, one-pot polymerization was adopted to realize the longer oligomers. It was expected that a comparison of electronic absorption and emission characteristics among oligomers from iterative divergent and one-pot polymerization syntheses would describe properties resulting from increased chain length.

In addition to preparation of oligomer **104**, oligomers **105-107** have also been targeted and realized (Figure 6). The presence of fluorene ring in the cross-conjugated backbone of polymers **106-107** was predicted to impart interesting emission properties as a result of its highly luminiscence nature.^{90,91} It was envisioned that each oligomer could be obtained from a coupling reaction between an enediyne and diiodo component (Figure 7). Furthermore, an end-capping reagent was incorporated both to prevent the presence of reactive terminal acetylene moiety and to determine chain length via ¹H-NMR intergrations.⁹²

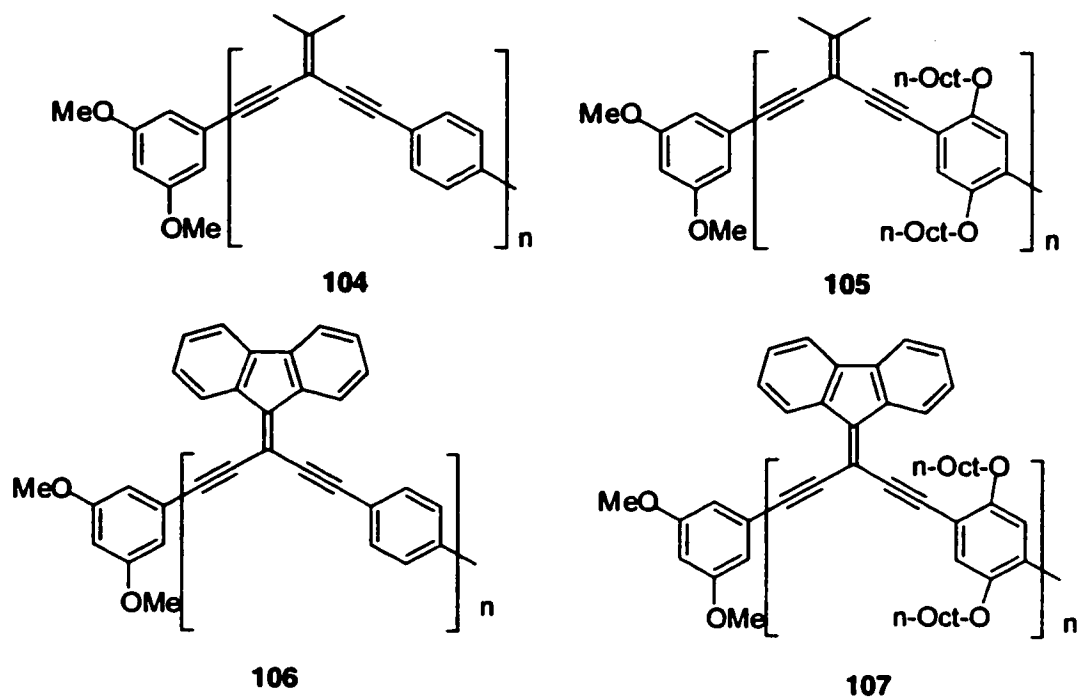


Figure 6: The monomer units of cross-conjugated polymers.

In this thesis, two types of diiodo compounds were used, 1,4-diiodo-benzene **78** and 1,4-dioctyloxy-2,5-diiodo-benzene **100**. The synthetic flexibility of using the dioctyloxy substituted diiodobenzene is that it can provide the oligomer with better solubility and luminescence efficiency.

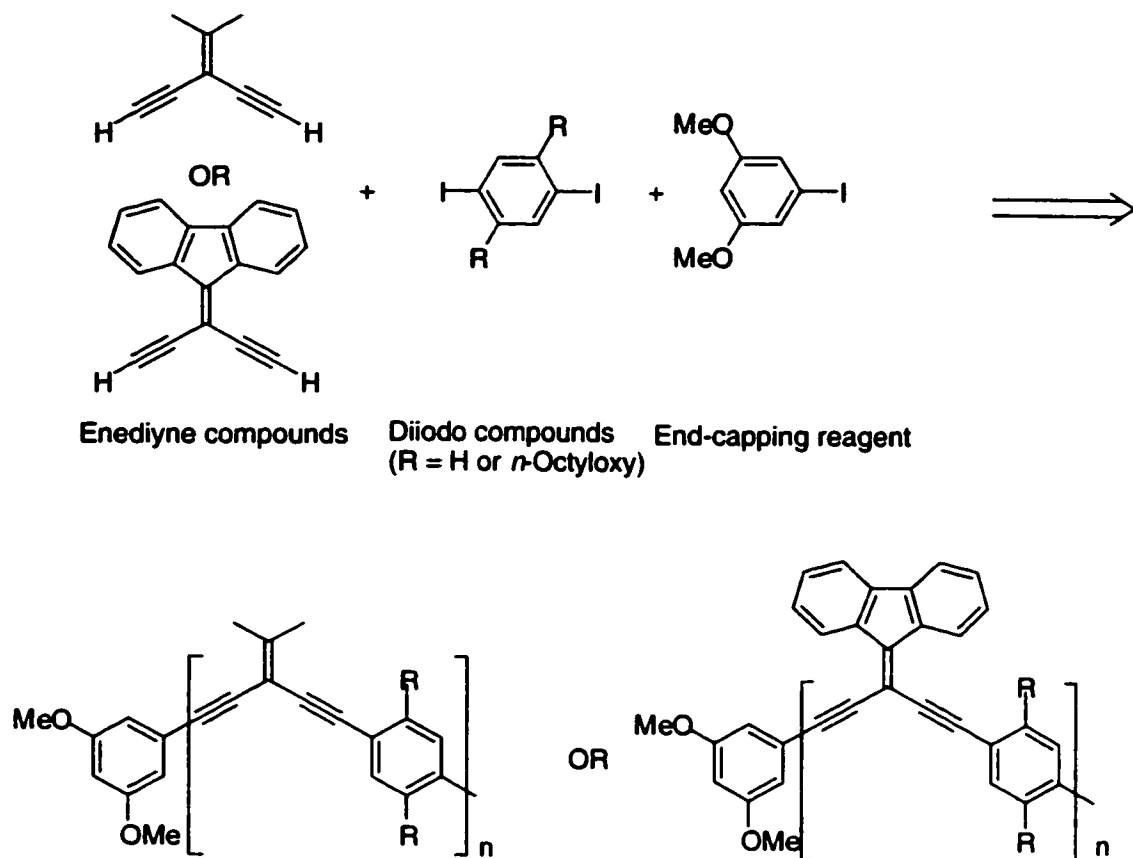
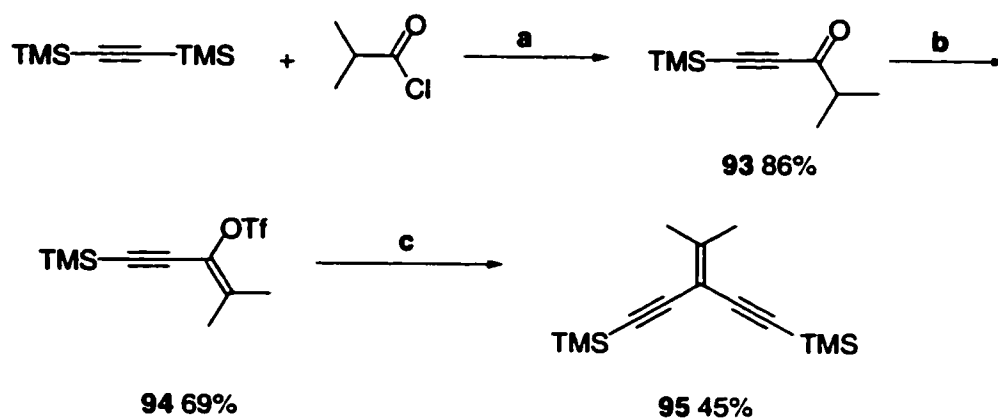


Figure 7: The schematic representation of one-pot polymerization.

As a building block of oligomer **104** and **105**, enediyne compound **95** was targeted (Scheme 49). *iso*-Butyryl chloride was reacted with bis(trimethylsilyl)acetylene in the presence of aluminium trichloride in CH_2Cl_2 , as previously reported.⁸⁵ After distillation, the reaction gave compound **93** as a yellow oil in 86% yield.



Reagents and conditions: (a) AlCl_3 (1 equiv), CH_2Cl_2 , 0 °C, 3 h.

(b) 2,5-di-*tert*-Butyl-4-methyl-pyridine (1.25 equiv), triflic anhydride (1.5 equiv), CH_2Cl_2 , rt, 4 h.

(c) Trimethylsilylacetylene, $\text{PdCl}_2(\text{PPh}_3)_2$ (5 mol%), CuI (10 mol%), *i*- Pr_2NH , THF, rt, 4 h.

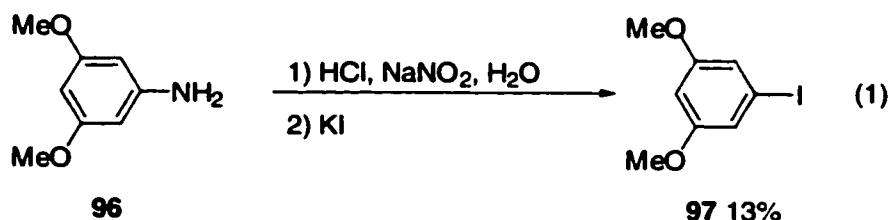
Scheme 49: The synthetic route to compound 95.

Compound 93 was then used to make the corresponding vinyl triflate 94 using the procedure as described by Stang *et al.*^{85a} Column chromatography (silica gel, 1:1 CH_2Cl_2 /hexanes) gave the orange-colored oil compound 94 in 69% yield.⁷² Eneidyne 95 was then obtained via a coupling reaction between 1.3 equiv of trimethylsilylacetylene and compound 94 under palladium-catalyzed coupling conditions as previously reported.⁷² This compound was purified by column chromatography (silica gel, hexanes) to give compound 95 as a yellow oil in 45% yield.

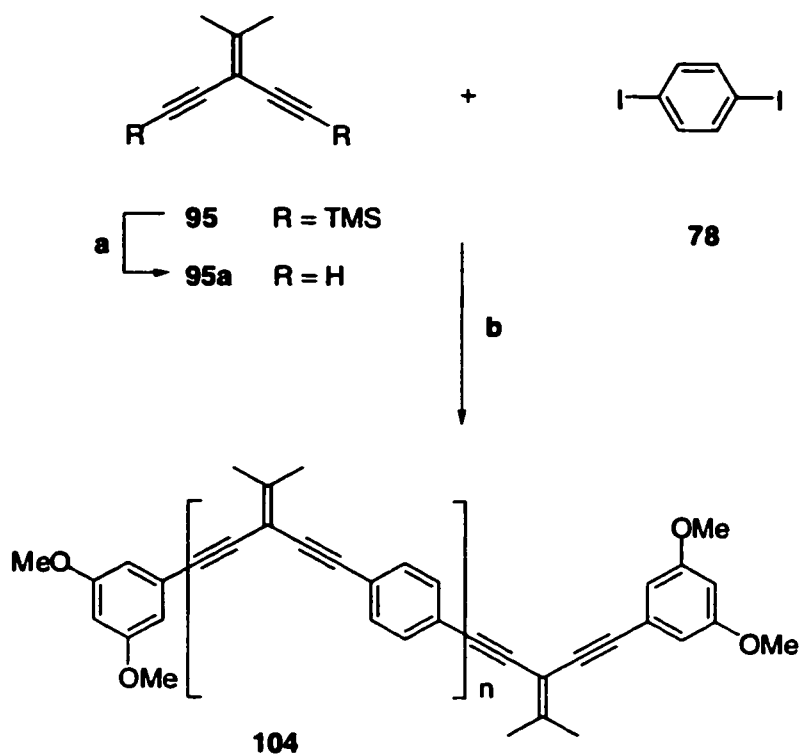
3,5-Dimethoxyiodobenzene 97 was chosen as an end-capping reagent to eliminate the possibility of residual and unstable terminal acetylenes in the oligomeric structure. The methoxy groups in this compound appear as a singlet at 3.84 ppm. It was expected that the other resonances in the ^1H NMR spectra of the desired oligomers would not overlap with this methoxy proton signal. This would allow for comparison

of the integration of the methoxy groups with that of other hydrogens of the oligomers, and would provide a means to estimate the average chain length of the oligomers.⁹²

Compound **97** was synthesized directly from the commercially available compound **96** using Sandmeyer reaction conditions (Eq. 1). Despite its low yield, the Sandmeyer reaction is a strong tool used to synthesize various organic compounds possessing different functionalities from aromatic amine compounds. After column chromatography (silica gel, hexanes), compound **97** was obtained as white solid in 13% yield.⁹³



Toward the synthesis of oligomer **104**, enediyne **95** was desilylated using K₂CO₃ in THF/MeOH (Scheme 50).⁸⁸ After workup, desilylated **95a** was used directly without any further purification. It was coupled to commercially available 1,4-diiodobenzene **78** in the presence of 8 mol% of end-capping reagent **97** under palladium catalyzed cross-coupling conditions (Scheme 50).⁹⁴

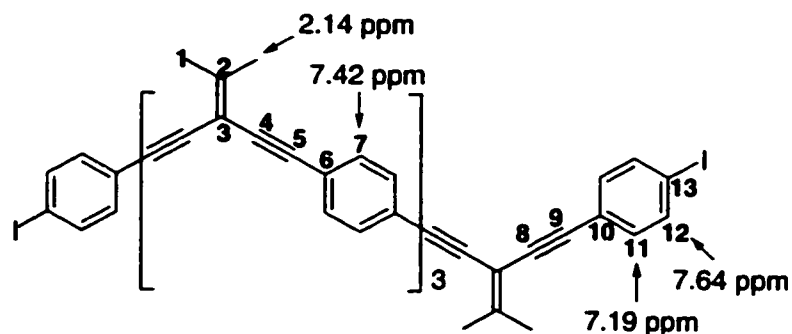


Reagents and conditions: (a) K_2CO_3 , THF/MeOH (1:1), rt, 30 min.
 (b) **97** (8 mol%), $\text{PdCl}_2(\text{PPh}_3)_2$ (5 mol%), Cul (10 mol%),
 $i\text{-Pr}_2\text{NH}$, THF, rt, 2 days.

Scheme 50: The synthetic route to polymer **104**.

To reduce the extent of homo-coupled products, oxygen was removed by bubbling nitrogen through the solution at room temperature for 2 h before the reaction. After workup, the solvent was removed under reduced pressure and the residue was redissolved in a minimal amount of CH_2Cl_2 . Precipitation by addition of hexanes gave the dark-brown colored oligomer **104** in 29% yield. Unfortunately, $^1\text{H-NMR}$ spectroscopy reveals that this polymerization gave only a mixture of oligomers without end-capping (DP is only 4). The low DP of this polymerization results from the severe lack of solubility of the products. In addition, desilylated **95a** is so volatile and unstable that it was likely lost prior to completion of the reaction. The shortage of

95a in the reaction was therefore a probable reason for the absence of end-capping in the oligomer backbone.



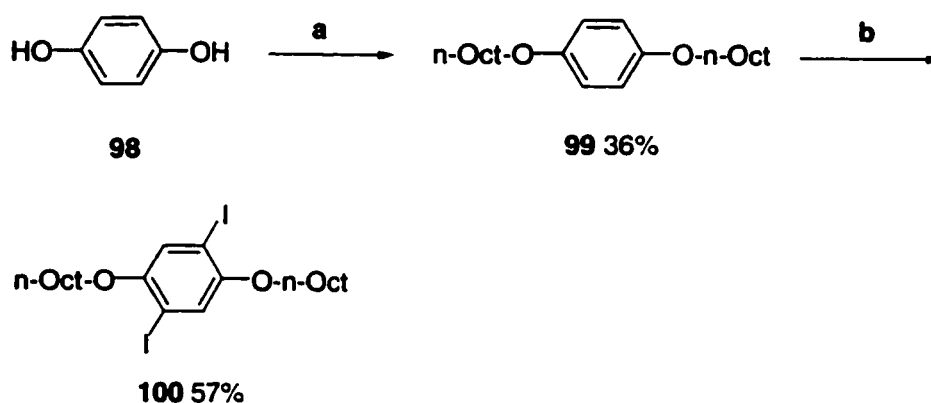
C1: 23.0-23.19 ppm.
 C2 and C3: 155.3 and 101.3 ppm.
 C4,8 and C5,9: ~88.0 and ~91.1 ppm.
 C6 and C7: ~123.0 and 131.3 ppm.
 C10, C11, C12 and C13: 123.0, 132.9, 137.4 and 93.9 ppm.

Figure 8: The ^1H -NMR characterization of oligomer **104**.

Although difficult to characterize as a result of the mixture of products, the following spectral details could be assigned (Figure 8). In the ^1H -NMR spectrum, a signal at 7.42 ppm is assigned as the aromatic protons of an internal aryl component; two symmetrical doublets at 7.19 and 7.64 ppm are observed for the aromatic protons of aryl component terminated with iodine; a resonance at 2.14 ppm represents methyl protons of alkylidene component. The ^{13}C -NMR spectrum was obtained with low signal/noise ratio as a result of poor solubility. Although some of the signals are missing from this low resolution, presence of following signals were suggestive of its structure. The resonance at 131.3 ppm is assigned as the C7; resonances at 132.9 and 137.4 ppm belong to C11 and C12; a series of signals around 123.0 ppm result from C6 and C10; a signal at 93.9 ppm is assigned as C13; two signals at 101.3 and 155.3 ppm are from C3 and C2; a series of signals at 88.0 and 91.1 ppm are assigned as C4,8 and C5,9; the signal at 23.0 ppm are observed as C1. There is no absorption band at

$\sim 3300\text{ cm}^{-1}$ in IR spectrum, suggesting that all enediyne reactants were consumed during the reaction. This fact supports that resulting products are a mixture of oligomers terminated with iodine.

As the attempt to prepare oligomer **104** was hampered by poor solubility, a solubility-gaining side chain was introduced to the diiodo moiety. 1,4-Dioctyloxy-2,5-diiodobenzene **100** was prepared using the synthetic path outlined in Scheme 51.⁹⁵



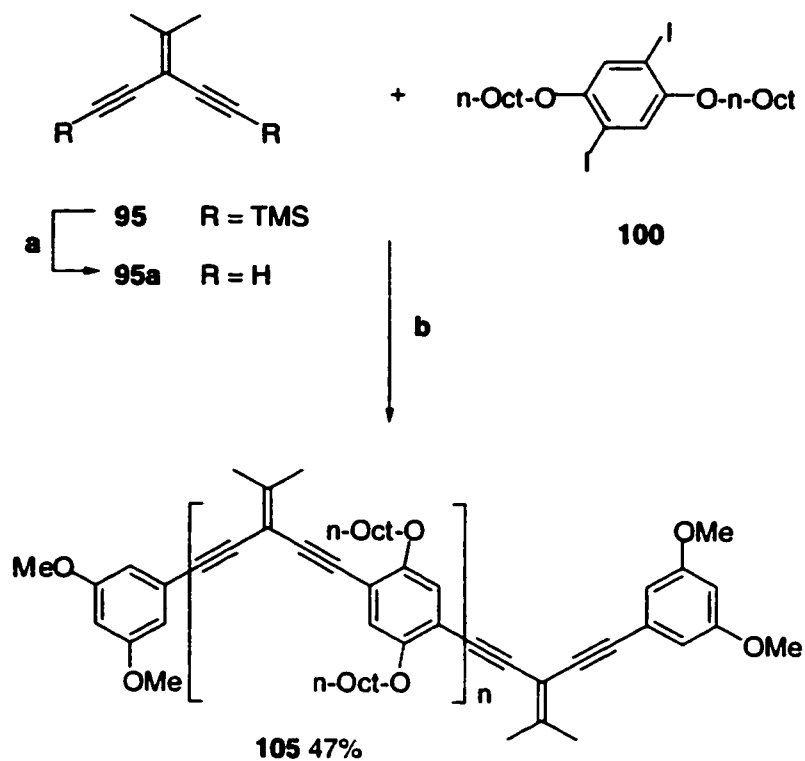
Reagents and conditions: (a) *n*-Octyl iodide (2.2 equiv), K_2CO_3 , acetone, reflux, 3 days. (b) 1) KIO_3 , I_2 / AcOH, H_2SO_4 , H_2O , reflux, 6h, 2) 20% aq $\text{Na}_2\text{S}_2\text{O}_4$.

Scheme 51: The synthetic route to compound **100**.

In the presence of potassium carbonate, compound **98** reacted with *n*-octyl iodide in an $\text{S}_{\text{N}}2$ fashion. This reaction gave **99** as a transparent solid in 36% yield.⁹⁵ Iodination of compound **99** using iodine and KIO_3 in the presence of acetic and sulfuric acid and gave the colorless solid **100** in 57% yield.⁹⁵

For the synthesis of oligomer **105**, compound **95** was desilylated using K_2CO_3 in THF/MeOH to give **95a**, which was then coupled to **100** in the presence of 8 mol% of

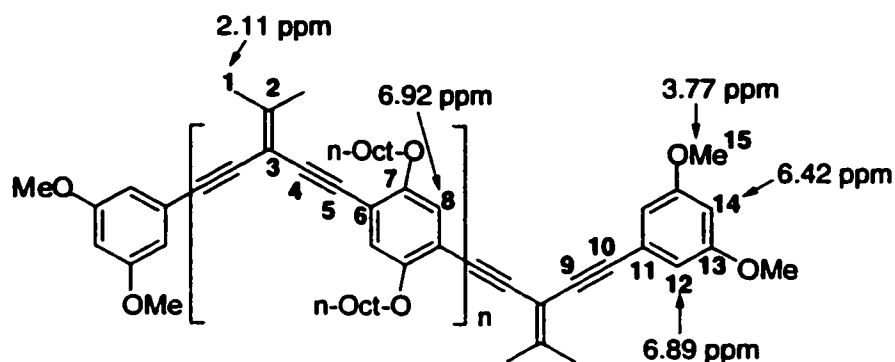
end-capping reagent **97** under the standard palladium-catalyzed coupling conditions (Scheme 52).⁹⁴



Reagents and conditions: (a) K_2CO_3 , THF/MeOH (1:1), rt, 30 min.
(b) **97** (8 mol%), $PdCl_2(PPh_3)_2$ (5 mol%), CuI (10 mol%),
 iPr_2NH , THF, rt, 2 days.

Scheme 52: The synthetic route to oligomer **105**.

After workup and precipitation from MeOH/ CH_2Cl_2 , this reaction gave a dark-brown oligomer **105** in 47% yield. The chain length estimation from end-capping analysis indicates that DP of this oligomer is 11. Comparing to the reaction for oligomer **104**, introduction of alkoxy-chain to the oligomer backbone improved its solubility and length.



C1: 23.0-23.2 ppm.
 C2 and C3: 154.9 and 101.3-102.0 ppm.
 C4,9 and C5,10: 87.8-88.8 and 90.8-92.0 ppm.
 C6, C7, and C8: 113.4-114.0, 153.5, and 116.1-116.2 ppm.
 C11, C12, C13, and C15: 124.9, 109.3-109.4, 160.6, and 55.5 ppm.
 C14: Missing.

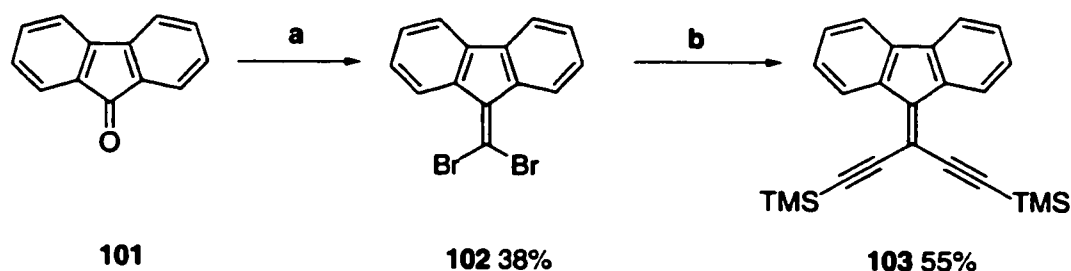
Figure 9: The ^1H - and ^{13}C -NMR characterization of oligomer **105**.

The spectroscopic data acquired for oligomer **105** suggested the structural and composition properties of this polymer mixture (Figure 9). The ^1H NMR spectrum of oligomer **105** is consistent with its proposed structure. The resonance at 6.92 ppm is assigned as the aromatic protons of the aryl component introduced from **100**; signals from 3.77, 6.42 and 6.89 ppm belong to the protons from the end-capping moiety; a resonance from 2.11 ppm is representative of the methyl protons of alkylidene component and signals from 0.85-1.76 and 3.95 ppm are assigned as the protons from the octyloxy side chain. The higher integration (1.5 times higher than expected) of methyl protons of alkylidene can be explained by the formation of enediyne homo-coupled by-product. The presence of this by-product is also demonstrated at the ^{13}C NMR studies.

In the ^{13}C NMR spectrum, a signals at 153.5 ppm is assigned as C7; three signals are seen in the region of 116.1-116.3 ppm from C8; and four signals at 113.4-114.0 ppm are from C6. Signals at 124.9, 109.3-109.4, 160.5 and 55.5 ppm are assigned as C11,

C12, C13, and C15 from end-capping reagent. The one signal of C12 from end-capping reagent is missing. A series of signals from 87.8-88.8 and 90.8-92.0 ppm are assigned as C4,9 and C5,10; three signals from 154.9 and 101.3-102.1 ppm are from C2 and C3; and a series of resonances from 23.0-23.2 ppm are observed as alkylidene methyl carbon C1. Two signals at 75.9 and 79.0 ppm represents the *sp* carbons from homo-coupled butadiyne by-products. Additional carbon signals are also observed in the ^{13}C NMR spectrum. It was concluded that this reaction yielded a mixture of oligomers with various lengths.

Fluorene substituted enediyne **103**, a key component to oligomers **106** and **107**, was synthesized as summarized in Scheme 53. Fluorenone **101** was subjected to Corey-Fuchs dibromo-olefination using $\text{CBr}_4/\text{PPh}_3$ and gave **102** as a yellow solid in 38% yield.⁹⁶ Compound **103** was synthesized by coupling **102** with 2.4 equiv of trimethylsilylacetylene using palladium-catalyzed coupling conditions for 24 h, as previously reported.⁹⁷



Reagent and conditions: (a) CBr_4 , PPh_3 , rt, 15 h. (b) Trimethylsilylacetylene (2.4 equiv), $\text{PdCl}_2(\text{PPh}_3)_2$ (5 mol%), CuI (10 mol%), $i\text{-Pr}_2\text{NH}$, THF, reflux, 24 h.

Scheme 53: The synthetic route to enediyne **103**.

The structure of compound **103** was confirmed by X-ray crystallographic analysis of a single crystal from recrystallization in $\text{CH}_2\text{Cl}_2/\text{MeOH}$. The ORTEP drawings of

compound **103** are shown in Figure 10 and 11. All the alkyne moieties are slightly bent with angles at $176.94(18)^\circ$ and $179.13(18)^\circ$ that are less than an ideal 180° . The angle of enediyne segment C(2)-C(3)-C(5) at $113.94(14)^\circ$ is smaller than that observed for the dimethyl analog **65a** at $115.0(4)^\circ$.⁷² Compound **103** maintains planarity throughout the fluorene segment and the extended cross-conjugated structure, as evidenced by a torsional angle for C(2)-C(3)-C(4)-C(21) of only 0.1° . By comparing fluorene segment included oligomers **106** and **107** with **105** and **106**, the influence of this fluorene moiety in the oligomer backbone toward absorption and emission properties will be discussed later.

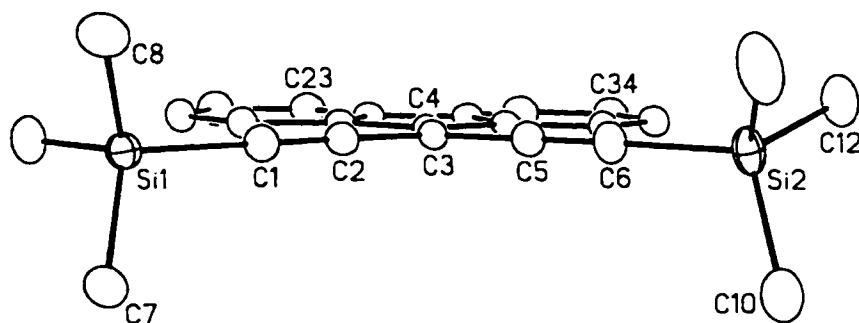


Figure 10: The edge-on view of compound **103**.

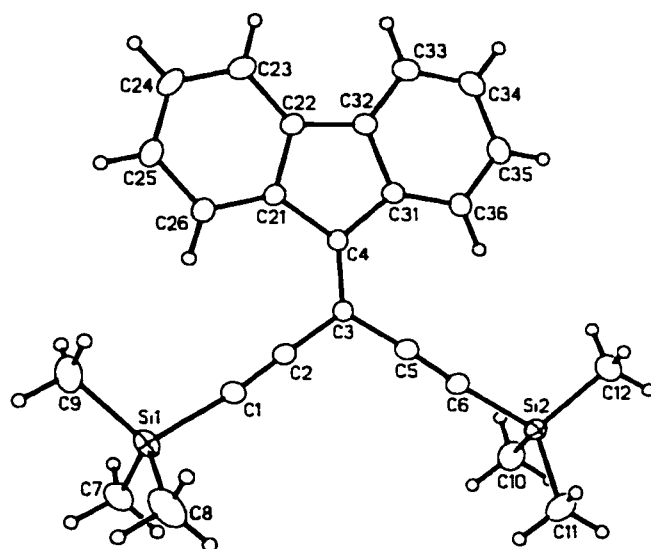
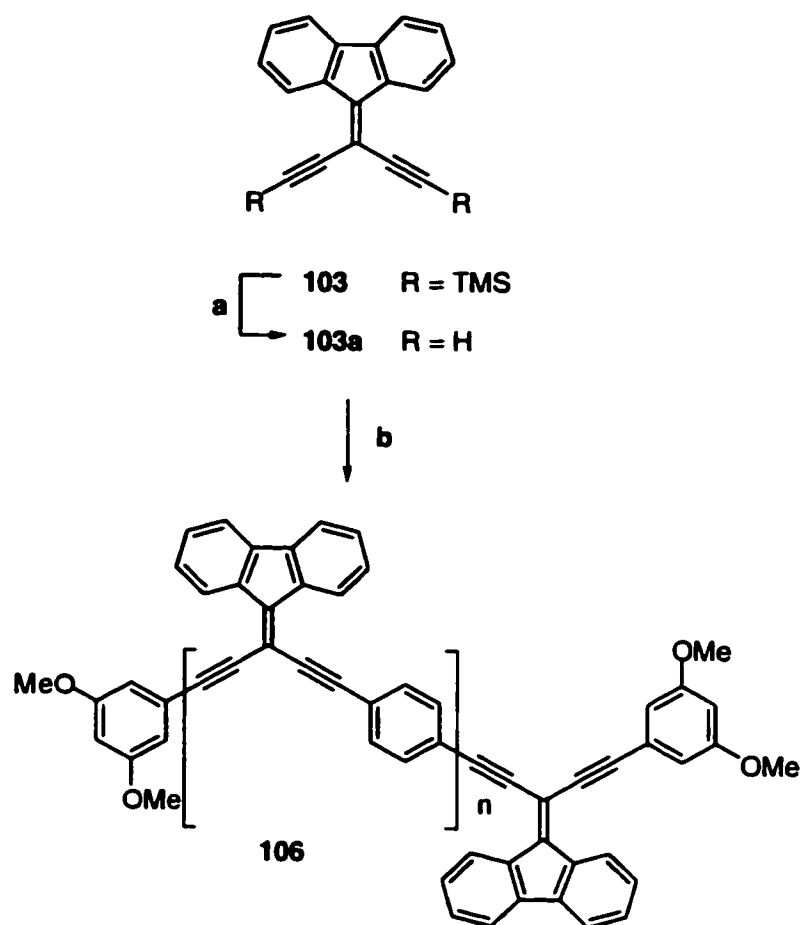


Figure 11: The perspective view of compound **103**.

Toward the synthesis of oligomer **106**, desilylation of compound **103** was carried out using K_2CO_3 in THF/MeOH (1:1).⁸⁸ After workup, desilylated **103a** was used directly without any further purification. It was coupled to 1,4-diiodobenzene **78** in the presence of 8 mol% of 3,5-dimethoxy-1-iodo-benzene **97** under the palladium-catalyzed coupling conditions (Scheme 54).

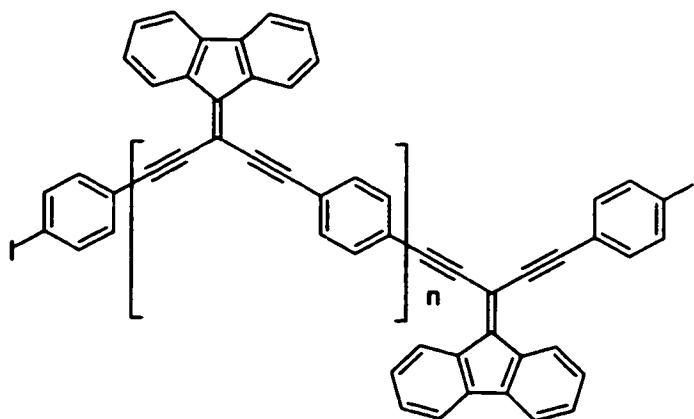


Reagents and conditions: (a) K_2CO_3 , THF/MeOH (1:1), rt, 30 min.
 (b) **78**, **97** (8 mol%), $\text{PdCl}_2(\text{PPh}_3)_2$ (5 mol%), CuI (10 mol%),
 $i\text{-Pr}_2\text{NH}$, THF, rt, 2 days.

Scheme 54: The synthetic route to oligomer **106**.

To prevent the formation of homo-coupled products, oxygen was removed by bubbling nitrogen through the solution at room temperature for 2 h before reaction. The reaction mixture was stirred for 2 days at room temperature and polymeric material eventually precipitated out from the solution toward the end of the reaction. This precipitate was extracted with CH_2Cl_2 and washed with a solution of EDTA to remove any metal impurities. Oligomer **106** was then purified by size exclusion chromatography (SEC, toluene) and obtained as a brown solid in 7% yield. As found

in the preparation of oligomer **104**, poor solubility was certainly detrimental to this reaction.



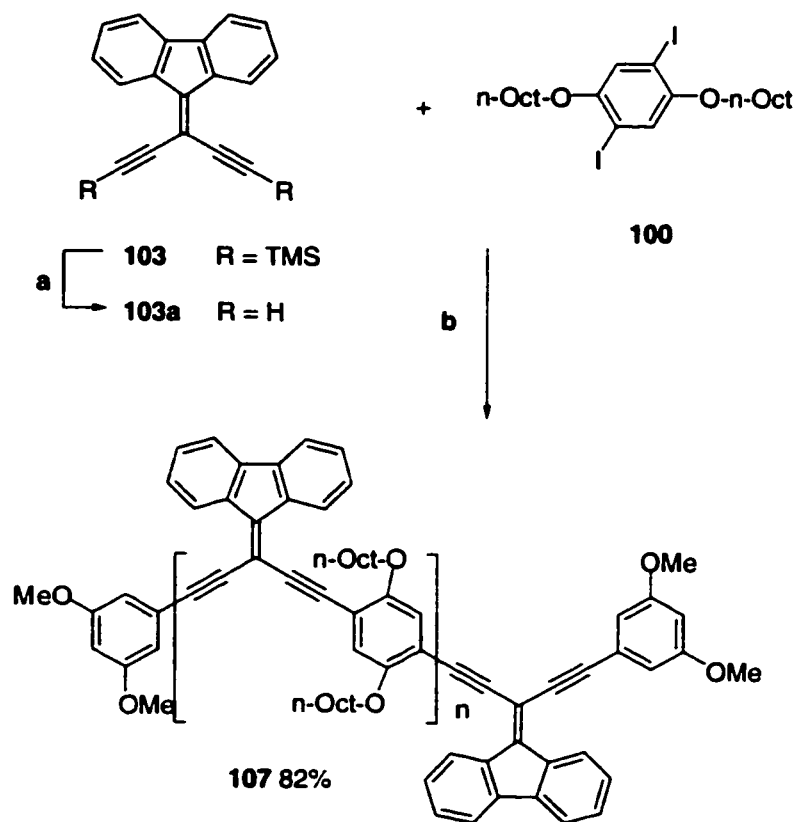
H from aryl component: 7.7 ppm.
H from end-capped ring: 7.4 and 7.7 ppm.
H from fluorene component: 7.3, 7.4, 7.8 and 8.7 ppm.

Figure 12: The ^1H -NMR spectroscopic characterization of oligomer **104**.

The spectroscopic data acquired for oligomer **106** suggested the structural and composition properties of this polymer mixture (Figure 12). According to the ^1H NMR spectroscopic characterization of the product from this reaction, a slightly higher integration ratio is observed in the region of 7.70 ppm as a result of aryl component proton in the polymer backbone. Most of resulting products, however, are end-capped with iodine. The integration ratio of three proton peaks around 7-9 ppm verified this estimation. The degree of end-capping with **97** is pretty low, as observed in the preparation of oligomer **104**. Lack of solubility during the oligomerization process forces the oligomers product to precipitate from solution and most of the product is thus not end-capped with **97**. For this reason, end-capping analysis for the estimation of the chain length was impossible. The ^{13}C NMR spectra also could not be obtained due to limited solubility. Attempts to acquire ^{13}C NMR spectra resulted in

spectra with very weak signals. As all protons of oligomer **106** are aromatic and overlapped, chain length estimation by comparison of the each segment integration ratio is also impossible. Analogous to the synthesis of oligomers **104** and **105**, solubility-gaining side chain needed to be introduced onto benzene ring.

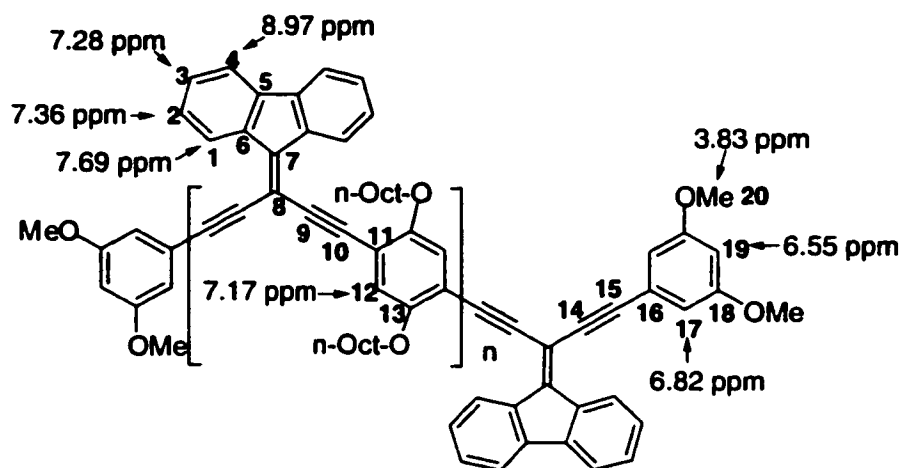
For the synthesis of oligomer **107**, enediyne **103** was desilylated using K_2CO_3 in THF/MeOH (1:1).⁸⁸ The resulting **103a** was coupled to **100** in the presence of 8 mol% of end-capping reagent **97** under the palladium-catalyzed coupling conditions (Scheme 55)



Reagents and conditions: (a) K_2CO_3 , THF/MeOH (1:1), rt, 30 min.
 (b) **97** (8 mol%), $PdCl_2(PPh_3)_2$ (5 mol%), CuI (10 mol%),
 $i\text{-Pr}_2\text{NH}$, THF, rt, 2 days.

Scheme 55: The synthetic route to oligomer **107**.

After workup and purification by SEC, this reaction gave oligomer **107** in 82% yield (Scheme 55). The presence of the octyloxy group on the benzene ring was obviously beneficial, leading to higher yield and better solubility.

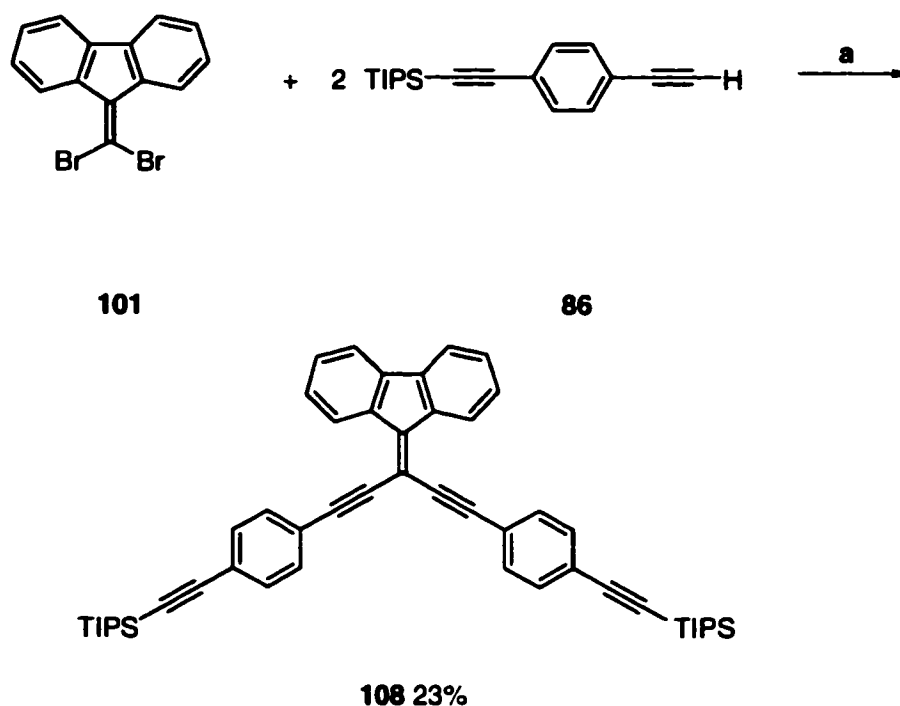


C1-C6: 130.1, 126.2, 128.0, 137.7, 119.9 and 140.6 ppm.
 C7-C8: 145.5 and 101.5 ppm.
 C9-C10: 94.7 and 95.5 ppm.
 C11-C13: 114.7, 117.4 and 154.4 ppm.
 C14-C15: Missing.
 C17, C18 and C20: 109.9, 161.3 and 55.9 ppm.
 C16 and C19: Missing.

Figure 13: The ^1H - and ^{13}C -NMR characterization of oligomer **107**.

The spectroscopic data acquired for oligomer **107** suggested the structural and composition properties of this polymer mixture (Figure 13). In the ^1H NMR spectrum, signals from 0.76-1.86 and 4.12 ppm are assigned as the protons from octyloxy side chain; signals at 3.83, 6.55 and 6.82 ppm verified the existence of end-capping reagent in the polymer chain; and resonances from 7.17-8.97 ppm are assigned as the aromatic protons from the fluorene and aryl component. In the ^{13}C NMR spectrum of oligomer **107**, three signals are observed at 109.9, 161.3 and 55.9 ppm from C17, C18 and C20 (C16 and C19 signals are missing) as end-capping moiety; ten signals are seen from the enediyne component which has twelve unique types of carbons (the signals of

the enediyne component which has twelve unique types of carbons (the signals of C14 and C15 are missing as a result of low signal/noise ratio); and signals at 114.7, 117.4 and 154.4 ppm are assigned as C11, C12 and C13. Also, an estimation of the average chain length from end-capping results gave a mixture of 24-mer. The presence of octyloxy side chain in the polymer backbone results in the high degree oligomerization.



Reagents and conditions: (a) PdCl₂(PPh₃)₂ (5 mol%), CuI (10 mol%), *i*-Pr₂NH, THF, rt, overnight.

Scheme 56: The synthetic route to monomer **108**.

In order to make comparisons with oligomer **106**, monomer **108** was synthesized via coupling compound **101** and 2 equiv of compound **86** using palladium-catalyzed coupling conditions (Scheme 56).⁹⁴ Purification of **108** gave a yellow solid **108** in

observed for proton of phenyl ring; and a signal at 1.16 ppm belongs to the protons of triisopropylsilyl group. In the ^{13}C NMR spectrum, signals from 145.9, 140.7, 137.6, 130.3, 128.0, 125.84, 120.1 and 101.0 ppm are assigned to carbons from enediyne component; signals at 132.5, 131.9, 124.7, 122.8 ppm belong to carbons from the phenyl ring; resonances at 106.8, 97.9, 94.2 and 90.6 ppm belong to *sp* carbons; and signals at 18.8 and 11.7 ppm are assigned to carbons from triisopropylsilyl group.

D. Investigation of electronic absorption and emission properties of cross-conjugated oligomers from one-pot polymerization.

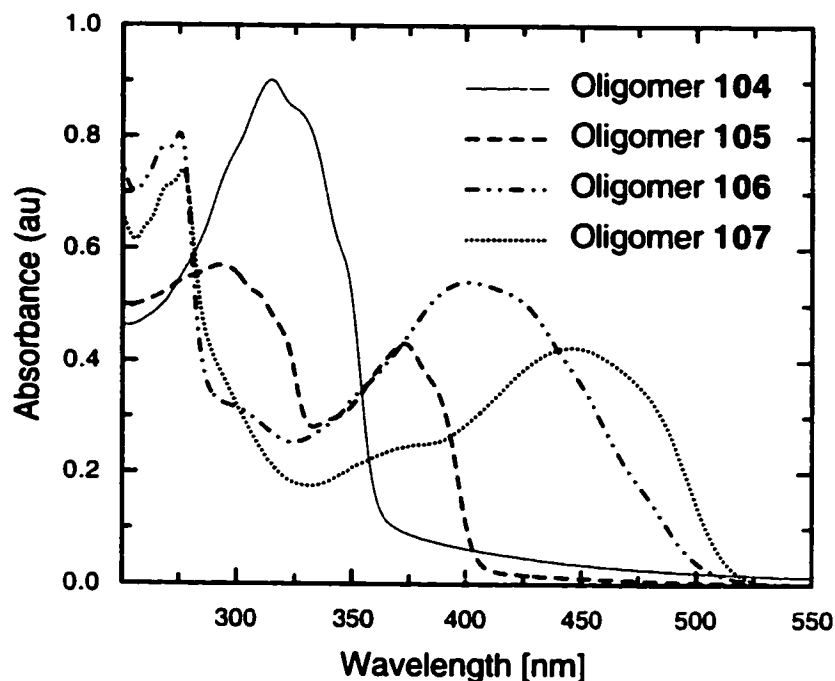


Figure 14: The UV-Vis spectra of polymer **104**, **105**, **106** and **107** in CHCl_3 .

The electronic absorption spectra of **104**, **105**, **106** and **107** are shown in Figure 14. Oligomer **104** possess absorption bands at 310 and 328 nm and a shoulder absorption at 350 nm, as well as a broad, less intense absorption ($\epsilon < 1000$) from 360-390 nm. These absorption bands are quite similar to those of dimer **90** and trimer **92**. This effect also can be attributed to the contribution of both cross-conjugation as well as the phenylene spacer unit. The oligomers **106** and **107** possess identical absorption bands at 243 and 273 nm that are attributed to the fluorenyl conjugation subunit. As the *n*-octyloxy group acts as a chromophore, it causes a red-shift band to 375 nm in polymer **105** relative to the band observed 310 nm for oligomer **104**. Similarly, this band in **107** at 445 nm is red-shifted relative to the absorption observed for oligomer **106** at

401 nm as a result of the narrowing HOMO-LUMO gap. Comparing absorption maxima between oligomers **106-107** and their enediyne subunit **103** (354 nm), more red-shifted maxima are observed from the oligomers **106** (401 nm) and **107** (445 nm). This result indicates that fluorene segment participates in linearly extended conjugation through phenylene spacer.

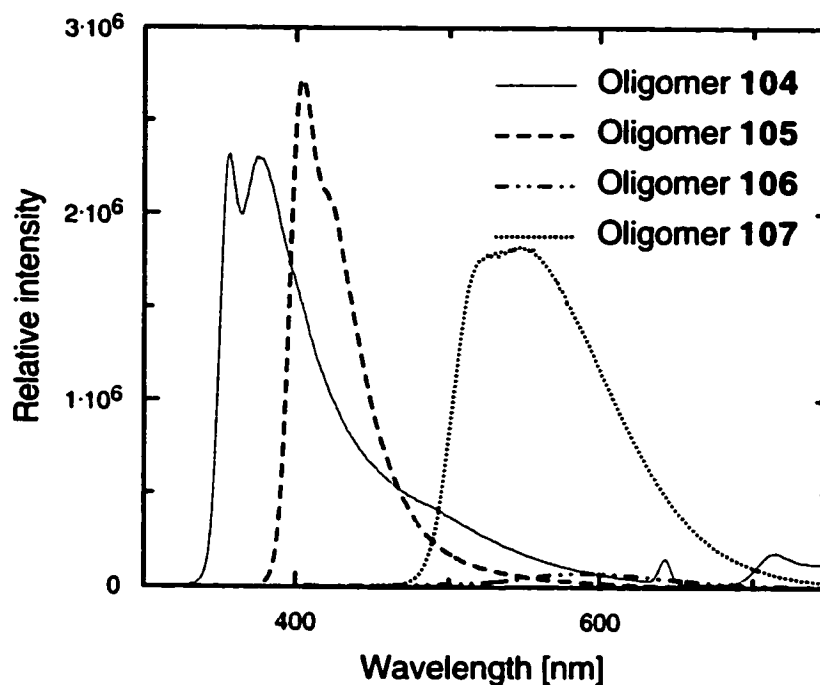


Figure 15: Fluorescence spectra of polymer **104**, **105**, **106** and **107** in CHCl_3 .

Electronic emission behavior of oligomers **104**, **105**, **106**, and **107** are shown in Figure 15. When irradiated at 326 nm, oligomer **104** exhibits exactly the same emission bands as dimer **90** and trimer **92** at 359 and 381 nm. Oligomer **105** gives an emission band at 407 nm when irradiated at 373 nm. When irradiated at 400 nm, oligomer **106** shows an emission band at 593 nm, whereas **107** gives an emission band at 555 nm when irradiated at 445 nm. Varying the excitation wavelength does not change the emission maxima of all oligomers. This result indicates that the emission

behavior of these oligomers is insensitive to the excitation wavelength. For oligomers **104**, **105** and **107**, the intensity of the emission is much stronger than that of **106**. This result can be attributed to the presence of the n-octyloxy group that stabilizes the excited state and prevents the interactions between the polymer chains and solvents for polymer **105** and **107**.^{ib,h} Because most reported oligomers and polymers with strong emission properties possess long side chains, strong emission from oligomer **104** is quite interesting.

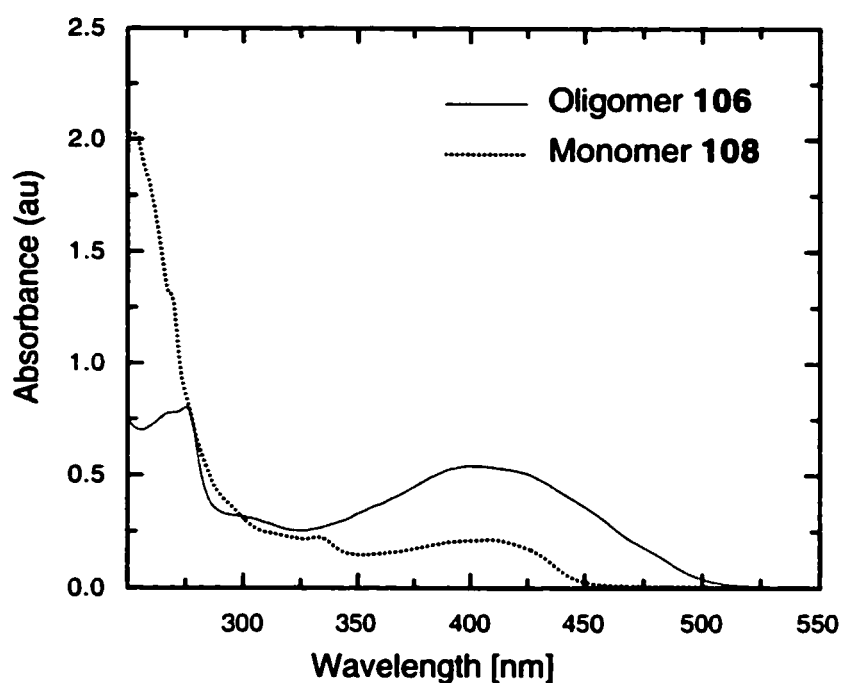


Figure 16: The UV-Vis spectra of of oligomer **106** and monomer **108** in CHCl₃.

Electronic absorption behaviors of oligomer **106** and monomer **108** are shown in Figure 16. Monomer **108** shows absorption at 332 and 410 nm. Oligomer **106** shows absorption bands at 295, 403 nm and shoulder absorptions extending into the visible region. It shows the effect of lengthening the longest linearly conjugated chain through oligomer backbone.

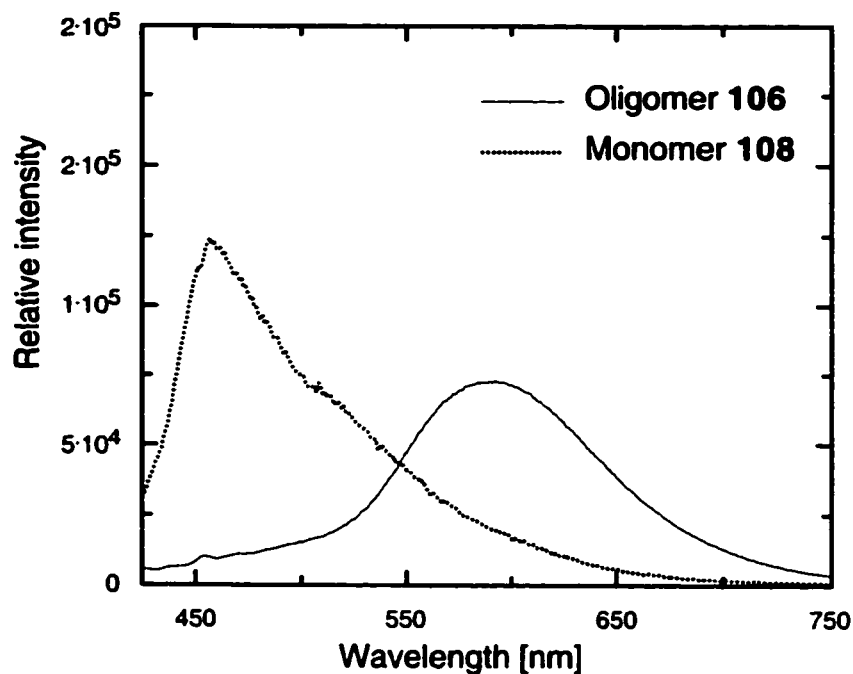


Figure 17: Fluorescence spectra of oligomer **106** and monomer **108** in CHCl₃.

Electronic emission behavior of monomer **108** and oligomer **106** are also shown in Figure 17. Both give a weak emission band, which is found at 479 nm for monomer **108** and 593 nm for oligomer **106**. The absence of the *n*-octyloxy side chain affects the emission properties among this oligomer series **106** and **108**. Oligomer **106** shows more red-shifted absorptions as a result of lengthened linearly-conjugated structure.

III. CONCLUSIONS

Cross-conjugated oligomers have been designed and synthesized by adopting an iterative divergent synthesis and a one-pot polymerization. Palladium-catalyzed coupling reactions between vinyl triflates and terminal alkynes gave monomer **89**, dimer **90** and trimer **92**. Attempts to prepare the higher homologues of this oligomer series were unsuccessful due to instability of the terminal alkyne moieties of the precursor molecules. Palladium catalyzed coupling reaction between enediyne and diiodo benzene derivatives in the presence of an end-capping reagent gave oligomers **104-107**. The severe lack of solubility of the oligomer **104** and **106** resulted in low degree of polymerization of both oligomers. The introduction of alkoxy-chain to the oligomer **105** and **107** improved their solubility and length. The electronic absorption and emission behavior of these oligomers have been examined. It appears that there is little electronic communication via the conjugated framework due to contributions from cross-conjugation. The presence of fluorene segment in the oligomers **106-107** results in dramatic red-shift as a result of linearly extended conjugation. Fluorescence spectra of the oligomers **90**, **92**, **104**, **105** and **107** show strong emission bands. Strong blue fluorescence from oligomer **105** and yellow fluorescence from oligomer **107** are observed. Thus, the manipulation of the polymer backbone enables enhancement of photoluminescence properties.

Searching for the materials with better electronic and photonic properties, the synthesis and studies of structure-property relationships for the newly structured oligomers and polymers have been highly demanded over the past years. By the development of synthetic methodologies and analysis technologies, much more intense studies will be carried out about their structure even in their molecular level

and we can totally understand their structure-property relationships of the organic materials.

IV. EXPERIMENTAL SECTION

General. Infrared (IR) spectra were recorded on a Nicolet Magna 750 fourier transform spectrometer and are reported in reciprocal wave numbers (cm^{-1}). Infrared determination was done on compounds applied as a film on KCl salt plates. Nuclear magnetic resonance (NMR) spectra were recorded on Varian Gemini-300, Varian Unity Inova 500 [500 MHz (^1H) and 126 MHz (^{13}C)] and Bruker AM-300 [300 MHz (^1H) and 75.5 MHz (^{13}C)] spectrometers at rt in CD_2Cl_2 or CDCl_3 ; solvent peaks (5.27 and 7.24 ppm for ^1H and 53.8 and 77.0 ppm, respectively for ^{13}C) as reference. Chemical shifts are reported in parts per million (ppm, δ) and coupling constants (J) were reported in hertz (Hz). X-ray crystallographic analysis was done on a Siemens P4/RA X-ray diffractometer. EI MS (m/z) was obtained on a Kratos MS-50 spectrometer and electrospray mass spectra were acquired from a Micromass ZABSPEC-OATOF instrument. UV-Vis spectra of chloroform solutions were acquired on a Cary 400 Scan UV-Vis spectrometer and are reported in wavelength (nm). Chloroform was degassed for 2 h prior to use. Fluorescence spectra were performed on a PTI LPS-220B spectrometer. Elemental analyses were performed by the Microanalytical Laboratory at the University of Alberta.

Flash column chromatographic separations⁹⁸ were performed on silica gel-60 (230-400 mesh) from General Intermediates of Canada and Silicycle. Size exclusion chromatographic separations were performed on Bio-Beads S-X8 (200-400 mesh, toluene). Thin Layer Chromatography (TLC) was carried out on plastic sheets coated with silica gel-60 F_{254} with the fluorescent indicator UV_{254} from Macherey-Nagel and on aluminium sheets coated with silica gel-60 F_{254} from E. Merck. Visualization was

accomplished under UV light or with KMnO_4 stain. Melting points were acquired from a Gallenkamp apparatus; uncorrected.

1,4-Bis-trimethylsilylethynyl-benzene **79**.⁸³



To a solution of **78** (5.9 g, 18 mmol) and trimethylsilylacetylene (4.2 g, 43 mmol) in degassed triethylamine (80 mL) were added $\text{PdCl}_2(\text{PPh}_3)_2$ (0.46 g, 0.66 mmol) and CuI (38 mg, 0.20 mmol). The reaction mixture was stirred at rt under a nitrogen atmosphere for 15 h, then diluted with benzene (100 mL). The solution was washed with water (2 x 100 mL) and dried over MgSO_4 . After solvent was removed, purification by column chromatography (silica gel, hexanes) gave **79** (3.9 g, 80%) as a shiny-yellow solid. Mp = 121-122 °C (lit mp = 122 °C⁸³); R_f = 0.62 (hexanes); ¹H NMR (300 MHz, CDCl_3) δ 7.37 (s, 4H), 0.22 (s, 18H); ¹³C NMR (75.5 MHz, CDCl_3 , APT) δ 131.8, 123.2, 104.6, 96.4, -0.4; EIMS m/z 270.1 (M^+ , 49.5), 255.1 ($[\text{M} - \text{CH}_3]^+$, 100); HRMS (EI) calcd. for $\text{C}_{16}\text{H}_{22}\text{Si}_2$ (M^+) 270.1260, found 270.1258.

1,4-Diethynylbenzene **79a**.⁹⁴



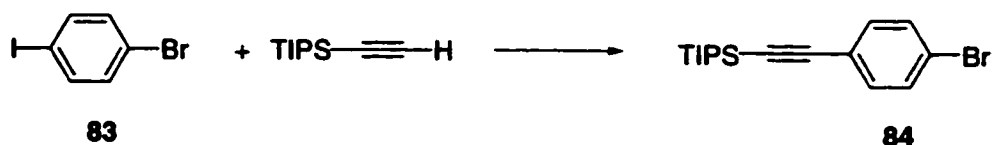
To a solution of **79** (2.3 g, 8.5 mmol) in THF/ MeOH (1:1, 30 mL) was added potassium carbonate (10 mg, 0.07 mmol). The solution was stirred at rt for 30 min. The solution was then extracted with ether (50 mL), washed with water (50 mL), then dried over MgSO₄. After the solvent was removed, purification by column chromatography (silica gel, hexanes) of the residue afforded **79a** (0.86 g, 80%) as a light-yellow solid. Mp = 95-96 °C (lit mp = 95 °C⁹⁴); *R*_f = 0.80 (hexanes); ¹H NMR (300 MHz, CDCl₃) δ 7.42 (s, 4H), 3.15 (s, 2H); ¹³C NMR (75.5 MHz, CDCl₃, APT) δ 132.1, 122.6, 83.1, 79.1; EIMS *m/z* 126.0 (M⁺, 6.27), 101.0 ([M - C₂H]⁺, 100); HRMS (EI) calcd. for C₁₀H₆ (M⁺) 126.0470, found 126.0464.

4-Methyl-1-(4-trimethylsilylethynyl-phenyl)-pent-1-yn-3-one **80**.



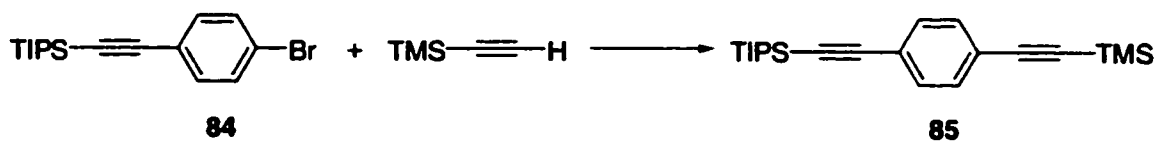
In a 100 mL flask, **79** (1.0 g, 3.7 mmol) was dissolved in CH_2Cl_2 (50 mL) and cooled to 0 °C. *iso*-Butyryl chloride (0.39 g, 3.7 mmol) and aluminium chloride (0.49 g, 3.7 mmol) were added successively. The reaction mixture was raised to rt and stirred overnight. The reaction mixture was then poured into a mixture of 10% HCl soln (50 mL) and ice (50 mL) and the organic layer was then collected. The aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined organic layers were washed with saturated aq. NaHCO_3 and saturated aq. NaCl, successively. The resulting solution was dried over MgSO_4 . After the solvent was removed, purification by column chromatography (silica gel, hexanes/ CH_2Cl_2 3:1) gave **80** (0.35 g, 35%) as a yellow oil. $R_f = 0.34$ (CH_2Cl_2 /hexanes 1:3); ^1H NMR (300 MHz, CDCl_3) δ 7.48 (AB q, $J = 8.1$ Hz, 2H), 7.44 (AB q, $J = 8.1$ Hz, 2H), 2.73 (sept, $J = 6.9$ Hz, 1H), 1.24 (d, $J = 6.9$ Hz, 6H), 0.23 (s, 9H); ^{13}C NMR (75.5 MHz, CDCl_3 , APT) δ 192.0, 132.8, 132.1, 125.5, 120.0, 104.0, 98.0, 90.8, 88.2, 43.1, 18.1, -0.1; EIMS m/z 268.1 (M^+ , 30), 225.1 ($[\text{M} - i\text{-Pr}]^+$, 100); HRMS (EI) calcd. for $\text{C}_{17}\text{H}_{20}\text{OSi}$ (M^+) 268.4338, found 268.1284.

(4-Bromo-phenylethynyl)-triisopropyl-silane 84.⁸⁶



To a solution of **83** (5.1 g, 18 mmol) and triisopropylsilylacetylene (3.3 g, 18 mmol) in degassed triethylamine (80 mL) were added PdCl₂(PPh₃)₂ (0.23 g, 0.328 mmol) and CuI (19 mg, 0.10 mmol). The reaction mixture was stirred at rt under a nitrogen atmosphere for 15 h, then diluted with benzene (100 mL). The solution was washed with water (2 x 100 mL) and dried over MgSO₄. After the solvent was removed, purification by column chromatography (silica gel, hexanes) of the residue afforded **84** (5.2 g, 87%) as a slightly yellow liquid. *R*_f = 0.7 (hexanes); IR (CDCl₃, film) 2942, 2864, 2157 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.41 (d, *J* = 9 Hz, 2H), 7.31 (d, *J* = 9 Hz, 2H), 1.11 (s, 21H); ¹³C NMR (75.5 MHz, CDCl₃, APT) δ 133.5, 131.5, 122.5 (one Ar-C is not observed), 105.9, 95.1, 18.7, 11.4; EIMS *m/z* 336.1 (M⁺), 295.0 ([M - *i*-Pr]⁺, 100); HRMS (EI) calcd. for C₁₇H₂₅Si⁷⁹Br (M⁺) 336.0909, found 336.0903 and calcd. for C₁₇H₂₅Si⁸¹Br (M⁺) 338.0888, found 338.0887.

1-[(Triisopropylsilyl)-ethynyl]-4-bromo-ethynyl-benzene **84.**



To a solution of **84** (5.4 g, 16 mmol) and trimethylsilylacetylene (1.9 g, 19 mmol) in degassed triethylamine (80 mL) were added PdCl₂(PPh₃)₂ (0.56 g, 0.80 mmol) and CuI (0.31 g, 1.6 mmol). The reaction mixture was stirred at reflux under a nitrogen atmosphere overnight. The solution was then diluted with benzene (100 mL), washed with water (2 x 100 mL), and dried over MgSO₄. After the solvent was removed, purification by column chromatography (silica gel, hexanes) gave **85** (4.7 g, 82%) as a yellow liquid. *R*_f = 0.54 (hexanes); ¹H NMR (300 MHz, CDCl₃) δ 7.37 (s, 4H), 1.10 (s, 21H), 0.23 (s, 9H).

(4-ethynyl-phenylethynyl)-triisopropyl-silane **86.**⁸⁸



To a solution of **85** (0.33 g, 0.93 mmol) in THF/ MeOH (1:1, 30 mL) was added potassium carbonate (10 mg, 0.07 mmol). The solution was stirred at rt for 30 min. The solution was then extracted with ether (50 mL), washed with water (50 mL), and dried over MgSO₄. After the solvent was removed, purification by column chromatography (silica gel, hexanes) of the residue afforded **86** (0.20 g, 76%) as an orange liquid. *R_f* = 0.44 (hexanes); ¹H NMR (300 MHz, CDCl₃) δ 7.40 (s, 4H), 3.14 (s, 1H), 1.11 (s, 21H).

4-Methyl-1-(4-triisopropylsilylethynyl-phenyl)-pent-1-yn-3-one **87**.



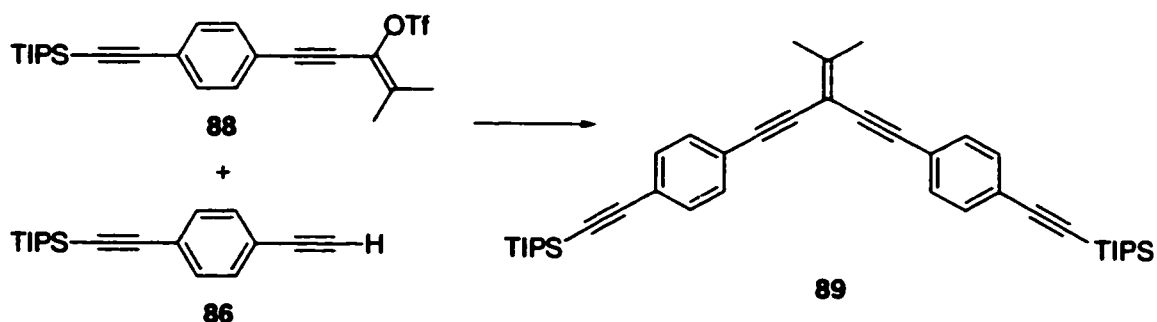
To a solution of **86** (0.26 g, 0.93 mmol) and *iso*-butyryl chloride (0.20 g, 1.9 mmol) in triethylamine (20 mL) under nitrogen atmosphere at 0 °C was added copper iodide (9.5 mg, 0.05 mmol). The reaction mixture was stirred at rt for 4 h. Triethylamine was then removed under reduced pressure. Methanol (50 mL) was added to quench remaining *iso*-butyryl chloride and the volatile components were removed under reduced pressure. The residue was extracted by diethyl ether (2 x 25 mL). This solution was washed with water (50 mL) and dried over MgSO₄. After the solvent was removed, purification by column chromatography (silica gel, CH₂Cl₂/hexanes 1:1) gave **87** (0.32 g, 96%) as an orange oil. *R*_f = 0.55 (CH₂Cl₂/hexanes 1:1); IR (CDCl₃, film) 2942, 2865, 2198, 1673 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.48 (AB q, *J* = 8.4 Hz, 2H), 7.45 (AB q, *J* = 8.6 Hz, 2H), 2.74 (sept, *J* = 6.9 Hz, 1H), 1.24 (d, *J* = 6.9 Hz, 6H), 1.11 (s, 21H); ¹³C NMR (75.5 MHz, CDCl₃, APT) δ 191.9, 132.8, 132.1, 125.9, 119.8, 106.1, 94.7, 90.8, 88.2, 43.1, 18.6, 18.0, 11.3; EIMS *m/z* 352.2 (M⁺, 8.6), 309.2 ([M - *i*-Pr]⁺, 100); HRMS (EI) calcd. for C₂₃H₃₂OSi (M⁺) 352.2222, found 352.2226.

Trifluoro-methanesulfonic acid 2-methyl-[(4-triisopropylsilylethynyl-phenyl)-ethynyl]-propenyl ester 88.



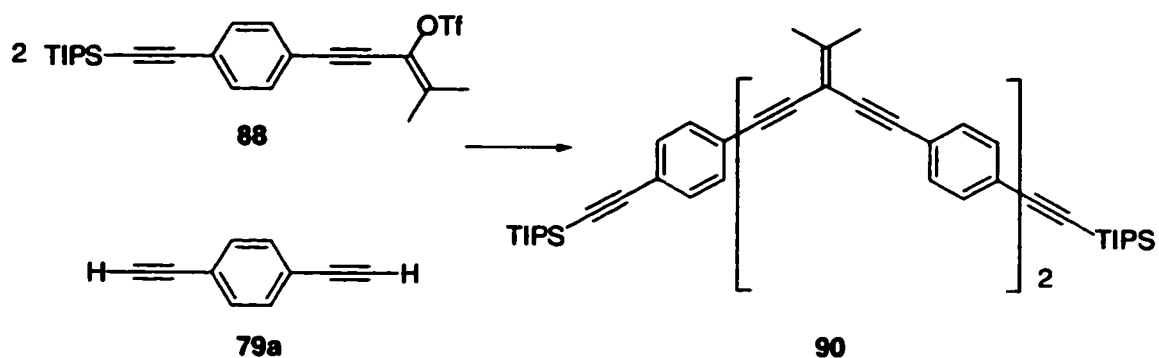
To a solution of **87** (0.74 g, 2.1 mmol) and 2,6-(*di-tert*-butyl)-4-methyl-pyridine (0.53 g, 2.6 mmol) in CH₂Cl₂ (30 mL) at 0 °C was added dropwise triflic anhydride (0.90 g, 3.2 mmol) under a nitrogen atmosphere. The reaction mixture was stirred at rt for 4 h. The solvent was then removed, the residue was dissolved in pentane (25 mL), and the undissolved solid was removed by filtration. The pentane solution was washed with saturated aq. NH₄Cl and dried over MgSO₄. After the solvent was removed, purification by column chromatography (silica gel, CH₂Cl₂/hexanes 1:1) gave **88** (0.87 g, 85%) as an orange oil. *R*_f = 0.84 (CH₂Cl₂/hexanes 1:1); IR (CDCl₃, film) 2942, 2865, 2156 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.46 (AB q, *J* = 8.4 Hz, 2H), 7.40 (AB q, *J* = 8.4 Hz, 2H), 2.07 (s, 3H), 1.97 (s, 3H), 1.14 (s, 21H); ¹³C NMR (75.5 MHz, CDCl₃, APT) δ 139.2, 132.4, 131.5, 126.7, 124.9, 121.6, 118.9 (q, *J* = 320 Hz, CF₃), 106.6, 95.9, 94.1, 81.8, 21.2, 18.9, 18.8, 11.7; EIMS *m/z* 484.2 (M⁺, 18.8), 441.1 ([M - *i*-Pr]⁺, 100); HRMS (EI) calcd. for C₂₄H₃₁F₃O₃SSi (M⁺) 484.6536, found 484.1715.

4-Methyl-1-(4-triisopropylsilylethynyl-phenyl)-3-[(4-triisopropylsilylethynyl-phenyl)-ethynyl]-pent-3-en-1-yne 89.



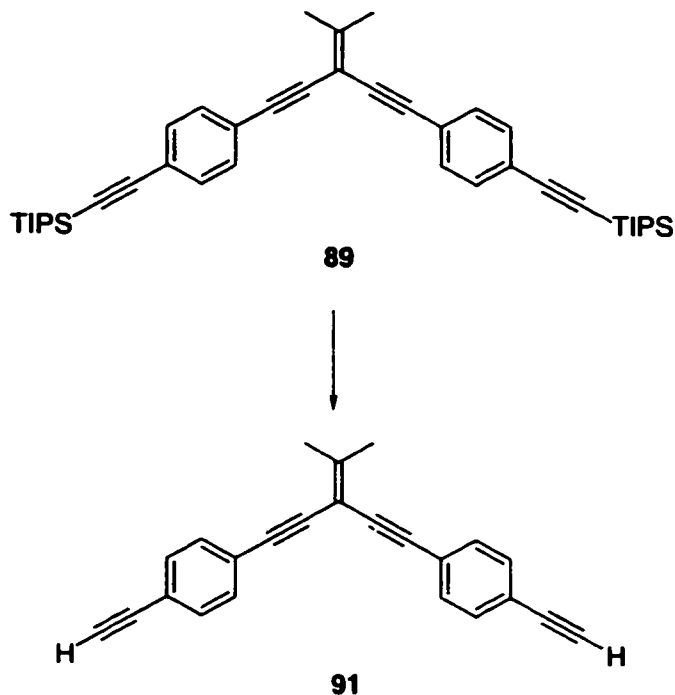
Diisopropyl amine (0.39 g, 3.9 mmol) was added to a stirred solution of **88** (0.63 g, 1.3 mmol), **86** (0.37 g, 1.3 mmol), CuI (25 mg, 0.13 mmol), and PdCl₂(PPh₃)₂ (49 mg, 0.07 mmol) in degassed THF (30 mL) under a nitrogen atmosphere. The mixture was stirred at rt for 4 h. The solution was then diluted with diethyl ether (25 mL). The resulting solution was washed with sat. NH₄Cl solution and dried over MgSO₄. The solvent was removed and purification by column chromatography (silica gel, CH₂Cl₂/hexanes 1:10) gave **89** (0.78 g, 97%) as an orange oil. Crystallization from CH₂Cl₂/MeOH gave an orange solid. Mp = 92-96 °C; *R*_f = 0.43 (CH₂Cl₂/hexanes 1:10); IR (CDCl₃, film) 2942, 2865, 2152 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.40 (br s, 8H), 2.14 (s, 6H), 1.11 (s, 42H); ¹³C NMR (126 MHz, CDCl₃) δ 155.3, 131.9, 131.3, 123.3, 123.2, 106.8, 101.3, 92.7, 91.1, 88.1, 23.0, 18.7, 11.4; HRMS (EI) calcd. for C₄₂H₅₆Si₂ (M⁺) 616.3920, found 616.3917. Anal. calcd. for C₄₂H₅₆Si₂: C, 81.75; H, 9.15. found: C, 81.93; H, 9.23.

Dimer 90.



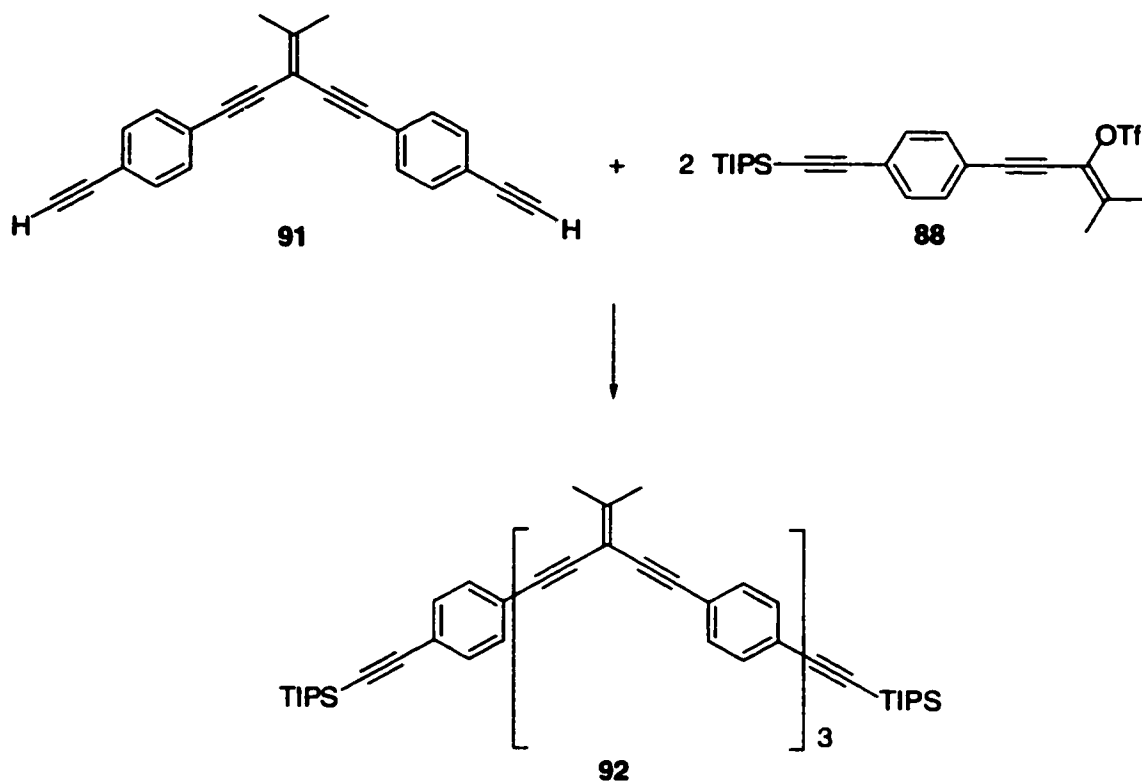
Diisopropylamine (0.08 g, 0.84 mmol) was added to a stirred solution of **88** (0.14 g, 0.280 mmol), **79a** (18 mg, 0.14 mmol), CuI (5.7 mg, 0.03 mmol) and PdCl₂(PPh₃)₂ (7.1 mg, 0.01 mmol) in degassed THF (30 mL) under nitrogen atmosphere. The mixture was stirred at rt for 2 h. Then the solution was then diluted with diethyl ether (25 mL). The resulting solution was washed with saturated aq. NH₄Cl and dried over MgSO₄. After the solvent was removed, purification by column chromatography (silica gel, CH₂Cl₂/hexanes 1:7) gave **90** (41.8 mg, 38%) as an orange oil. Crystalization from CH₂Cl₂/MeOH gave an orange solid. Mp = 142-146 °C; *R_f* = 0.60 (CH₂Cl₂/hexanes 1:3); UV-Vis (CHCl₃) 310 (94400), 328 (92500), 350 (21800) nm; IR (CDCl₃, film) 2942, 2864, 2153 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.42 (s, 4H), 7.40 (br s, 8H), 2.14 (s, 12H), 1.11 (s, 42H); ¹³C NMR (75.5 MHz, CDCl₃, APT) δ 155.3, 131.9, 131.4, 131.3, 123.3, 123.2, 123.1, 106.8, 101.3, 92.7, 91.2, 91.1, 88.1 (1 *sp* C is not observed), 23.0 (1 *sp*³ C is not observed), 18.7, 11.3; EIMS *m/z* 751.4 ([M - *i*-Pr]⁺, 72.3); ESIMS (CDCl₃, AgOTf added) calcd. for C₅₆H₆₆AgSi₂ ([M + Ag]⁺) 903.2, found 903.4.

4-Methyl-1-(4-ethynyl-phenyl)-3-[(4-ethynyl-phenyl)-ethynyl]-pent-3-en-1-yne 91.



To solution of **89** (0.20 g, 0.32 mmol) in wet THF (25 mL) at -10 °C was added dropwise a 1M solution of tetrabutylammonium fluoride (0.64 mL, 0.64 mmol in THF). The solution was then diluted with diethyl ether. After the solvent was removed, purification by column chromatography (silica gel, CH₂Cl₂/hexanes 1:1) of the residue afforded **91** (26 mg, 27%) as an unstable orange liquid. $R_f = 0.68$ (hexanes); IR (CDCl₃, film) 2927, 2865, 2152 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.42 (s, 8H), 3.14 (s, 2H), 2.14 (s, 6H); EIMS m/z 304.1 (M⁺, 100); HRMS (EI) calcd. for C₂₄H₁₆ (M⁺) 304.1252, found 304.1248.

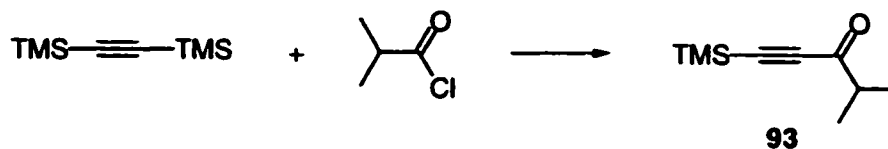
Trimer 92.



Diisopropylamine (1.08 mL, 7.6 mmol) was added to a stirred solution of **88** (0.12 g, 0.24 mmol), **91** from **90** (74 mg, 0.12 mmol), CuI (19 mg, 0.01 mmol) and PdCl₂(PPh₃)₂ (70 mg, 0.01 mmol) in degassed THF (30 mL) under nitrogen atmosphere. The solution was then stirred at rt for 4 h. Then the solution was then diluted with diethyl ether (25 mL). The resulting solution was washed with saturated aq. NH₄Cl and dried over MgSO₄. After the solvent was removed, column chromatography (silica gel, CH₂Cl₂/hexanes 1:3) gave **92** (11 mg, 9%) as an orange oil. Crystallization from CH₂Cl₂/MeOH gave an orange solid. Mp = 127-128 °C; *R_f* = 0.39 (CH₂Cl₂/hexanes 1:3); UV-Vis (CHCl₃) 310 (122000), 328 (129000), 350 (47800) nm; IR (CDCl₃, film) 2924, 2863, 2153 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.42 (br s, 8H), 7.40 (br s, 8H), 2.14 (br s, 18H), 1.11 (s, 42H); ¹³C NMR (126 MHz,

CDCl₃, APT) δ 155.24, 155.20, 131.9, 131.4, 131.3, 123.3, 123.2, 123.1 (2 *Ar*-C are not observed), 106.8, 101.3 (1 *sp*²-C is not observed), 92.7, 91.2, 91.1, 88.10, 88.06 (2 *sp*-C are not observed), 23.0 (2 *sp*³-C are not observed), 18.7, 11.4; ESIMS (CDCl₃, AgOTf added) calcd. for C₇₀H₇₆Ag Si₂ ([M + Ag]⁺) 1081, found 1081.

4-Methyl-1-trimethylsilyl-pent-1-yn-3-one **93**.⁸⁵



1,2-Bis-(trimethylsilyl)-acetylene (4.9 g, 29 mmol) and *iso*-butyryl chloride (3.1 g, 29 mmol) in CH₂Cl₂ (100 mL) were placed in a flask at 0 °C under nitrogen atmosphere. Aluminium chloride (3.9 g, 29 mmol) was added all at once. The solution immediately became colored. After 3 h stirring at 0-5 °C, The solution was poured into a mixture of 10% HCl soln (50 mL) and ice (50 mL). The aqueous layer was then extracted with diethyl ether (4 × 50 mL) and the combined organic phases were washed with saturated aq. NaHCO₃, followed by brine and then dried over MgSO₄. Removal of solvent and vacuum distillation gave **93** (4.2 g, 86%) as a yellow oil. *R*_f = 0.49 (CH₂Cl₂/hexanes 1:3); ¹H NMR (300 MHz, CDCl₃) δ 2.62 (sept, *J* = 6.9 Hz, 1H), 1.17 (d, *J* = 6.9 Hz, 6H), 0.22 (s, 9H).

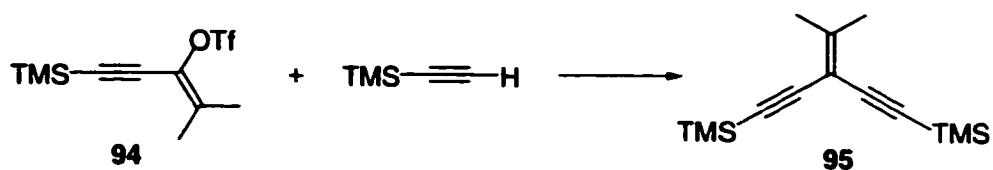
Trifluoro-methanesulfonic acid 2-methyl-1-[(trimethylsilyl)-ethynyl]-propenyl ester **94.**⁷²



To a solution of **93** (1.7 g, 10 mmol) and 2,6-(di-*tert*-butyl)-4-methyl-pyridine (2.7 g, 13 mmol) in CH₂Cl₂ (30 mL) under a nitrogen atmosphere at 0 °C was added dropwise triflic anhydride (4.2 g, 15 mmol). The reaction mixture was stirred at rt for 4 h. The solvent was removed and the residue was extracted by pentane (25 mL). The undissolved solid was removed by filtration. The pentane solution was then washed with saturated aq. NH₄Cl and dried over MgSO₄. After the solvent was removed, purification by column chromatography (silica gel, CH₂Cl₂/hexanes, 1:3) gave **94** (2.14 g, 69%) as a yellow oil. *R*_f = 0.60 (CH₂Cl₂/hexanes 1:3); ¹H NMR (300 MHz, CDCl₃) δ 1.96 (s, 3H), 1.89 (s, 3H), 0.19 (s, 9H).

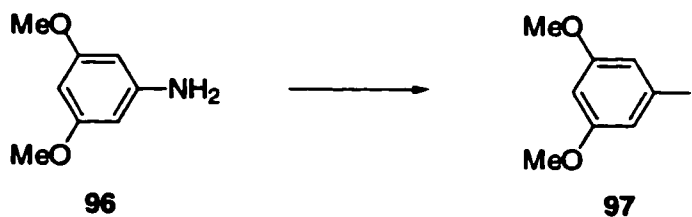
4-Methyl-1-trimethylsilyl-3-trimethylsilylethynyl-pent-3-en-1-yne

95.⁷²



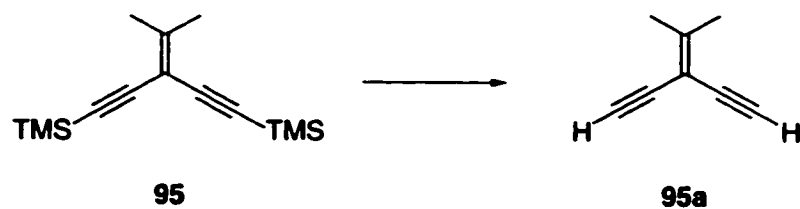
Diisopropyl amine (2.2 mL, 16 mmol) was added to a stirred solution of **94** (1.6 g, 5.2 mmol), trimethylsilylacetylene (0.67 g, 6.8 mmol), CuI (95 mg, 0.50 mmol) and PdCl₂(PPh₃)₂ (0.18 g, 0.26 mmol) in degassed THF (30 mL) under a nitrogen atmosphere. The solution was stirred at rt for 4 h. The solution was then diluted with diethyl ether, washed with saturated aq. NH₄Cl and dried over MgSO₄. After the solvent was removed, purification by column chromatography (silica gel, hexanes) gave **95** (0.570 g, 45%) as a yellow oil. *R*_f = 0.40 (hexanes); ¹H NMR (300 MHz, CDCl₃) δ 2.00 (s, 6H), 0.18 (s, 18H).

3,5-Dimethoxyiodobenzene **97**.⁹³



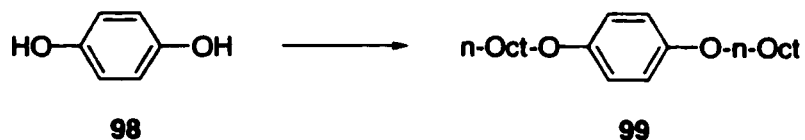
96 (2.25 g, 14.7 mmol) was diazotized in the usual manner using sodium nitrite (1.11 g, 16.2 mol) in water (5 mL) and hydrochloric acid (7 mL) in water (100 mL). The addition of sodium nitrite was discontinued when nitrous acid was present in excess as indicated by starch-iodide paper. After 10 min, a solution of potassium iodide (24.9 g, 0.15 mol) in water (30 mL) was added with stirring and the mixture was allowed to stir overnight. It was then made basic with sat'd sodium hydroxide. The resulting solution was extracted with diethylether (25 mL), which was then dried over MgSO_4 . After the solvent was removed, purification by column chromatography (silica gel, hexanes) gave **97** (0.52 g, 13%) as a colorless solid. Mp = 74-75 °C (lit mp = 74.3-74.6 °C⁹³); R_f = 0.27 (CH_2Cl_2 /hexanes 1:3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 6.84 (d, J = 2.4 Hz, 2H), 6.39 (t, J = 2.4 Hz, 1H), 3.74 (s, 6H).

3-Ethynyl-4-methyl-pent-3-en-1-yne 95a.⁷²



To a solution of **95** (0.21 g, 0.84 mmol) in THF/ MeOH (1:1, 30 mL) was added potassium carbonate (10 mg, 0.07 mmol). The solution was stirred at rt for 30 min. The solution was extracted with ether (50 mL), washed with water (50 mL), and dried over MgSO₄. The solvent was removed under vacuo with low temperature, the resulting saturated solution was used in the next reaction directly without further purification.

1,4-Dioctyloxybenzene **99**.⁹⁵



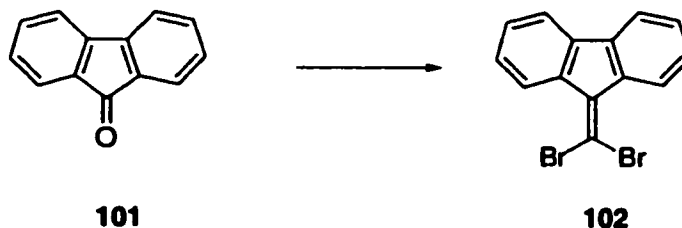
Potassium carbonate (30 g, 0.22 mol) and 1-octyl iodide (48 g, 0.20 mol) were added to a solution of **98** (9.8 g, 89 mmol) in acetone (80 mL). This mixture was refluxed under a nitrogen atmosphere for 3 days, after which time additional potassium carbonate (8.3 g, 0.06 mol) was added. The hot mixture was then filtered to remove insolubles. Evaporation of the solvent yielded a brown solid which was recrystallized twice from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to yield **99** (10.8 g, 36%) as a colorless solid. Mp = 55-56 °C (lit mp = 56-56.5 °C⁹⁵); R_f = 0.67 ($\text{CH}_2\text{Cl}_2/\text{hexanes}$ 1:1); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 6.80 (s, 4H), 3.38 (t, J = 6.6 Hz, 4H), 1.74 (quint, J = 6.6 Hz, 4H), 1.45-1.27 (m, 20H), 0.87 (t, J = 6.9 Hz, 6H).

1,4-Dioctyloxy-2,5-diiodobenzene **100**.⁹⁵



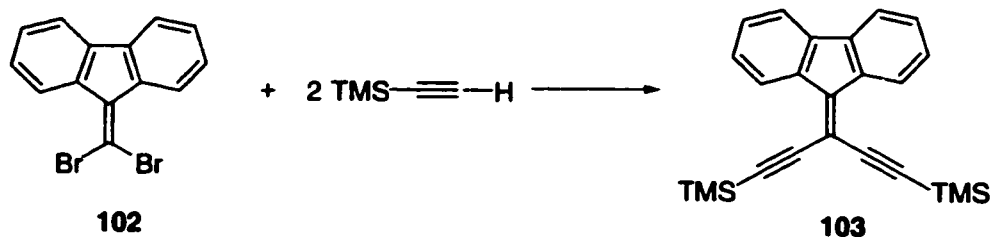
Compound **99** (4.0 g, 12 mmol), KIO_3 (1.0 g, 4.8 mmol), and I_2 (3.3 g, 13 mmol) were combined in acetic acid (150 mL), H_2SO_4 (2 mL) and H_2O (20 mL). The mixture was refluxed for 6 h and then 20% aq. $\text{Na}_2\text{S}_2\text{O}_4$ was added until the brown color disappeared. Diethyl ether (200 mL) was added, the resulting solution washed with saturated aq. NH_4Cl and dried over MgSO_4 . After the solvent was removed, purification by column chromatography (silica gel, hexanes) gave **100** (4.0 g, 57%) as a colorless solid. Mp = 52-52.5 °C (lit mp = 52-53 °C⁹⁵); R_f = 0.87 (hexanes); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.15 (s, 2H), 3.91 (t, J = 6.6 Hz, 4H), 1.78 (quint, J = 6.6 Hz, 4H), 1.50-1.30 (m, 20H), 0.87 (t, J = 6.9 Hz, 6H).

9-Dibromomethylene-9H-fluorene **102**.⁹⁶



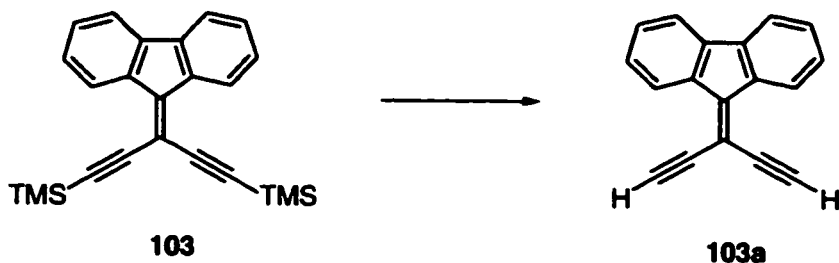
To a solution of PPh_3 (29 g, 0.11 mol) in anhydrous benzene (100 mL) was added CBr_4 (17 g, 0.05 mol). After stirring at rt for 30 min, **101** (9.0 g, 0.05 mol) was added and the mixture was stirred for 15 h at rt. The precipitate was removed from the solution by filtration. Removal of the solvent under reduced pressure and column chromatography (silica gel, hexanes) yielded **102** (6.4 g, 38%) as a light-yellow solid. $\text{Mp} = 129\text{-}131\text{ }^\circ\text{C}$ (lit mp = $131\text{-}132\text{ }^\circ\text{C}$ ⁹⁶); $R_f = 0.49$ (hexanes); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.60 (d, $J = 8.1$ Hz, 2H), 7.63 (d, $J = 8.1$ Hz, 2H), 7.40 (t, $J = 7.0$ Hz, 2H), 7.30 (t, $J = 7.0$ Hz, 2H).

9-[3-Trimethylsilyl-1-trimethylsilylethynyl-prop-2-ynylidene]-9H-fluorene **103.⁹⁷**



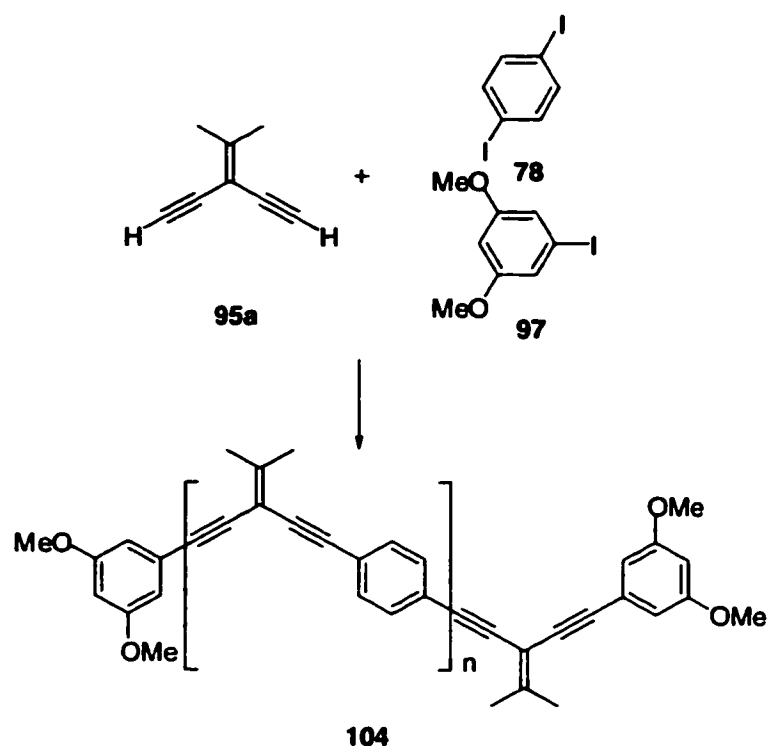
To solution of triethylamine (10 mL), compound **102** (0.20 g, 0.60 mmol) and trimethylsilylacetylene (0.14 g, 3.5 mmol) in degassed benzene (30 mL) was added PdCl₂(PPh₃)₂ (21 mg, 0.03 mmol) and CuI (11 mg, 0.06 mmol). The mixture was stirred at 70 °C for 24 h. The solvent and other volatile impurities were removed under reduced pressure. Purification by recrystallization (CH₂Cl₂/MeOH) gave **103** (0.120 g, 55%) as an orange solid. Mp = 131-132 °C (lit mp = 132-133 °C⁹⁷); R_f = 0.67 (CH₂Cl₂/hexanes 1:3); ¹H NMR (300 MHz, CDCl₃) δ 8.65 (d, *J* = 7.8 Hz, 2H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.34 (dt, *J* = 7.5 Hz, *J* = 1.2 Hz, 2H), 7.23 (dt, *J* = 7.5 Hz, *J* = 1.2 Hz, 2H), 0.33 (s, 18H).

9-(1-Ethynyl-prop-2-ynylidene)-9H-fluorene 103a.



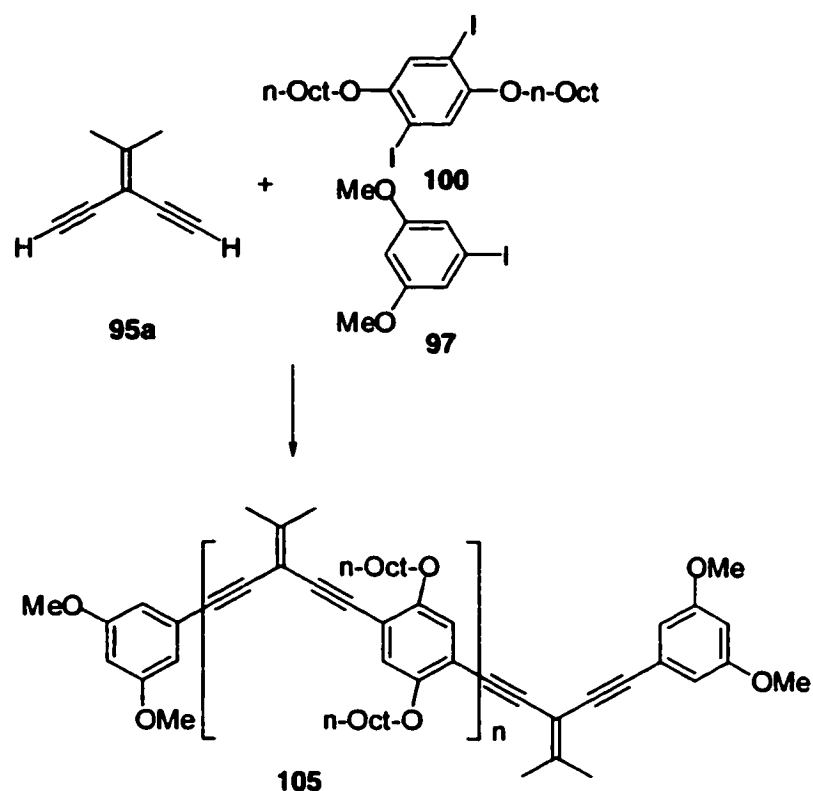
To a solution of **103** (1.0 g, 2.7 mmol) in THF/MeOH (1:1, 30 mL) was added potassium carbonate (10 mg, 0.07 mmol). The solution was then stirred at rt for 30 min. The solution was extracted with ether (50 mL), washed with water (50 mL), and dried over MgSO₄. After removal of solvent, the product was used in the next reaction directly without any further purification.

Polymer 104.



Diisopropylamine (0.11 mL, 0.75 mmol) was added to a stirred solution of **95a** from **95** (62 mg, 0.25 mmol), **78** (79 mg, 0.24 mmol), **97** (5.3 mg, 0.020 mmol), CuI (4.8 mg, 0.025 mmol) and PdCl₂(PPh₃)₂ (8.4 mg, 0.012 mmol) in degassed THF (30 mL) under nitrogen atmosphere at rt. The solution was stirred under nitrogen atmosphere for 2 days. The solution was diluted by addition of CH₂Cl₂ (25 mL). The resulting solution was washed with saturated aq. NH₄Cl, EDTA soln, and dried over MgSO₄. After the solvent was removed, precipitation from hexanes/CH₂Cl₂ gave **104** (14 mg, 29%) as a dark-brown insoluble solid. Partial characterization: UV-Vis (CHCl₃) 310, 328, 350 nm IR (CDCl₃, film) 2925, 2848, 2201, 1587 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.64 (d, *J* = 6.3 Hz, 4H), 7.42 (s, 12H), 7.19 (d, *J* = 7.8 Hz, 4H), 2.14 (s, 24H); ¹³C NMR (126 MHz, CDCl₃, APT) δ 155.3, 137.4, 132.9, 131.3, 123.0, 101.3, 93.9, 91.1, 88.0, 23.0.

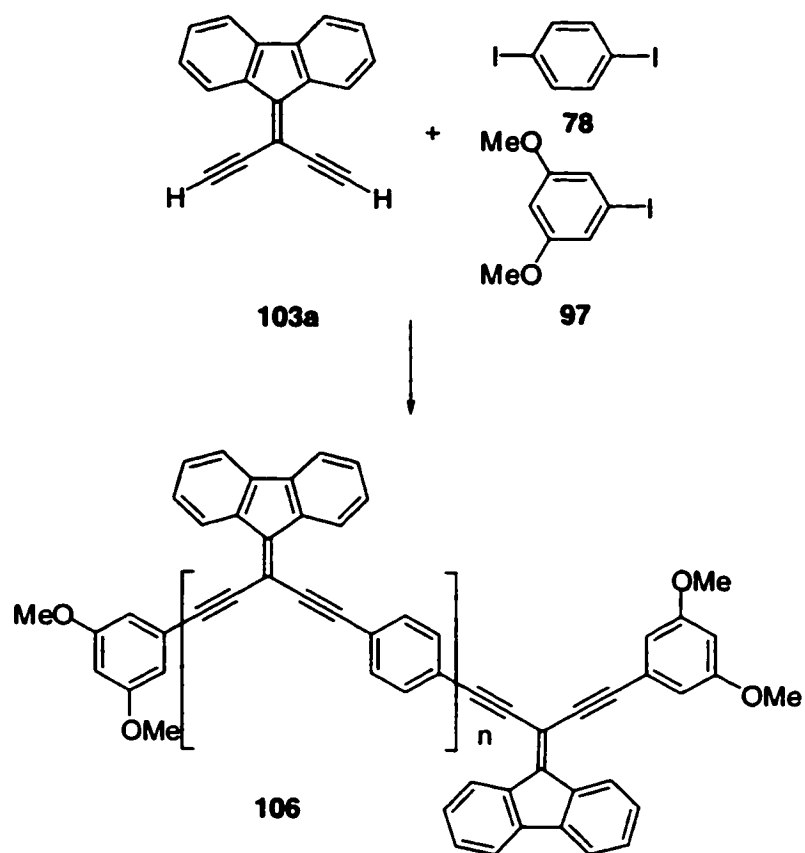
Polymer 105.



Diisopropylamine (0.35 mL, 2.5 mmol) was added to a stirred solution of **95a** from **95** (0.21 g, 0.84 mmol), **100** (0.47 g, 0.81 mmol), **97** (18 mg, 0.067 mmol), CuI (16 mg, 0.08 mmol) and PdCl₂(PPh₃)₂ (29 mg, 0.042 mmol) in degassed THF (30 mL) under nitrogen atmosphere at rt. The solution was stirred under nitrogen atmosphere for 2 days. The solution was diluted by addition of CH₂Cl₂ (25 mL). The resulting solution was washed with saturated aq. NH₄Cl, EDTA soln, and dried over MgSO₄. After the solvent was removed, precipitation from MeOH/CH₂Cl₂ gave **55** (0.17 g, 47%) as a dark-brown solid. UV-Vis (CHCl₃) 293, 371 nm; IR (CDCl₃, film) 2925, 2854, 2201, 1587 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.92 (br d, 20H), 6.89 (d, 4H), 6.42 (s, 2H), 3.95 (d, 40H), 3.77 (s, 12H), 2.17 (d, 23H), 2.11 (s, 66H), 1.76 (br s, 40H), 1.45 (br s, 40H), 1.24 (br s, 160H), 0.85 (br s, 60H); ¹³C NMR (126 MHz, CDCl₃, APT) δ 160.5, 154.9, 153.5, 124.9, 116.3, 116.2, 116.1, 114.0, 113.8, 113.6,

113.4, 109.4, 109.3, 102.1, 101.3, 92.0, 91.9, 91.1, 90.8, 88.8, 87.8, 69.51, 69.47, 55.5,
31.9, 29.5, 29.3, 26.1, 23.2, 23.1, 23.0, 22.7, 14.1.

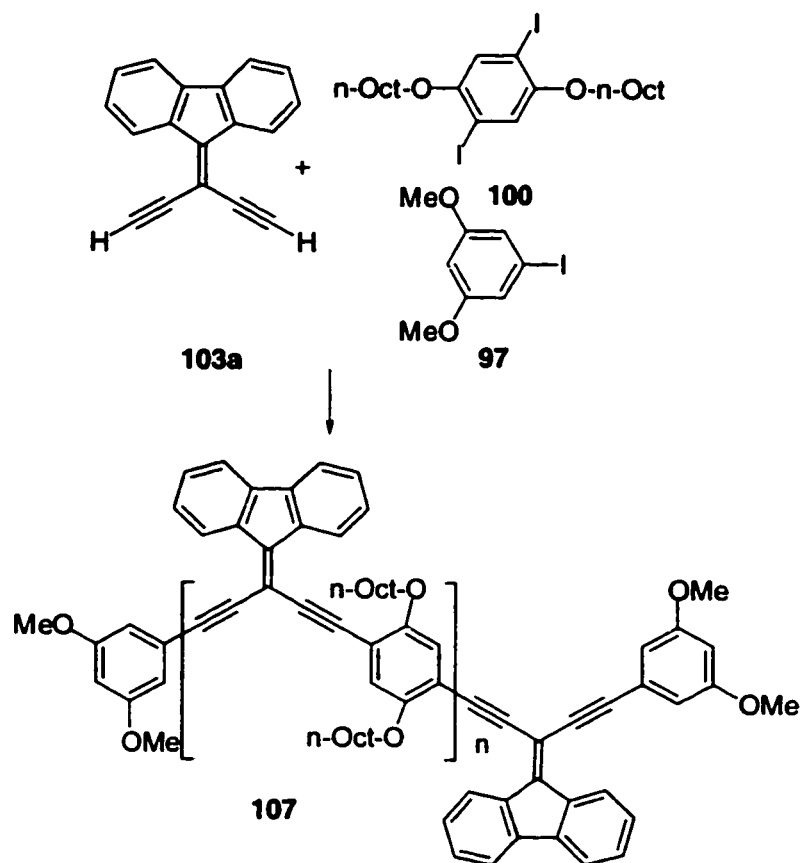
Polymer 106.



Diisopropylamine (0.58 mL, 4.1 mmol) was added to a stirred solution of **103a** from **103** (0.52 g, 1.4 mmol), 1,4-diodobenzene **78** (0.43 g, 1.3 mmol), **97** (29 mg, 0.11 mmol), CuI (26 mg, 0.14 mmol) and PdCl₂(PPh₃)₂ (49 mg, 0.070 mmol) in degassed THF (30 mL) under nitrogen atmosphere at rt. The solution was stirred under a nitrogen atmosphere for 2 days. Then the solution was diluted by addition of CH₂Cl₂ (25 mL). The resulting solution was washed with saturated aq. NH₄Cl, EDTA soln, and dried over MgSO₄. After the solvent was removed, purification by size exclusion chromatography (S-X8 bio-beads, toluene) gave **106** (28.5 mg, 7%) as a dark-brown insoluble solid. Partial characterization: UV-Vis (CHCl₃) 228, 401 nm; IR (CDCl₃,

film) 3056, 2923, 2852, 2185 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 8.63 (m, 9H), 7.70 (m, 21H), 7.35 (m, 27H).

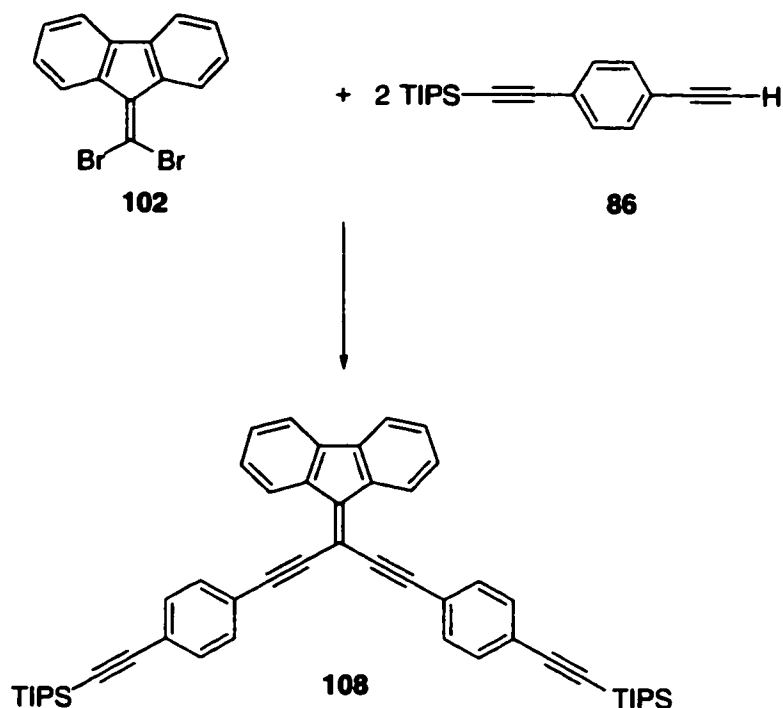
Polymer 107.



Diisopropylamine (1.14 mL, 8.10 mmol) was added to a stirred solution of **103a** from **103** (1.00 g, 2.70 mmol), **100** (1.52 g, 2.59 mmol), **97** (58 mg, 0.22 mmol), CuI (51 mg, 0.27 mmol) and PdCl₂(PPh₃)₂ (95 mg, 0.14 mmol) in degassed THF (30 mL) under nitrogen atmosphere at rt. The solution was stirred under nitrogen atmosphere for 2 days. The solution was diluted by the addition of CH₂Cl₂ (25 mL). The resulting solution was washed with saturated aq. NH₄Cl, EDTA soln, and dried over MgSO₄. After the solvent was removed, purification by size exclusion chromatography (S-X8 bio-beads, toluene) gave **107** (1.22 g, 82%) as a dark-brown solid. UV-Vis (CHCl₃) 273, 445 nm; IR (CD₂Cl₂, film) 3058, 2924, 2853, 2180, 1597, 1530 cm⁻¹; ¹H NMR

(300 MHz, CD₂Cl₂) δ 8.97 (d, 48H), 7.69 (br s, 48H), 7.36 (s, 48H), 7.28 (s, 48H), 7.17 (s, 46H), 6.82 (s, 4H), 6.55 (s, 2H), 4.12 (br s, 92H), 3.83 (s, 12H), 1.86 (br s, 92H), 1.44 (br s, 92H), 1.13 (br s, 368H), 0.76 (br s, 138H); ¹³C NMR (75.5 MHz, CD₂Cl₂, APT) δ 161.3, 154.4, 145.5, 140.6, 137.7, 130.1, 128.0, 126.2, 119.9, 117.4, 114.7, 109.9, 101.5, 95.6, 94.7, 70.3, 55.9, 32.2, 29.8, 29.6, 26.4, 23.0, 14.2.

9-[3-(4-Triisopropylsilylethynyl-phenyl)-1-[(4-triisopropylsilylethynyl-phenyl)-ethynyl]-prop-2-ynylidene]-9H-fluorene **108.**



Diisopropylamine (0.44 mL, 3.2 mmol) was added to a stirred solution of **102** (0.18 g, 0.53 mmol), **86** (0.30 g, 1.1 mmol), CuI (10 mg, 0.05 mmol) and PdCl₂(PPh₃)₂ (18 mg, 0.03 mmol) in degassed THF (25 mL) under nitrogen atmosphere. The solution was stirred at rt overnight. The solution was then diluted by addition of diethyl ether (25 mL). The resulting solution was washed with saturated aq. NH₄Cl and dried over MgSO₄. After the solvent was removed, purification by column chromatography (silica gel, hexanes) gave **108** (89.0 mg, 23%) as an orange oil. Crystalization from CH₂Cl₂/MeOH gave an orange solid. Mp = 81-82 °C; R_f = 0.38 (CH₂Cl₂/hexanes 1:7); UV-Vis (CHCl₃) 332 (45400), 408 (43100) nm; IR (CD₂Cl₂, film) 2923, 2853, 2153 cm⁻¹; ¹H NMR (300 MHz, CD₂Cl₂) δ 8.69 (d, *J* = 3.5 Hz, 2H), 7.72 (d, *J* = 3.3 Hz,

2H), 7.63 (d, $J = 8.4$ Hz, 4H), 7.54 (d, $J = 8.4$ Hz, 4H), 7.42 (td, $J = 7.5$ Hz, 1.2 Hz, 2H), 7.34 (td, $J = 7.5$ Hz, 1.2 Hz, 2H), 1.16 (s, 42H); ^{13}C NMR (126 MHz, CD_2Cl_2 , APT) δ 145.9, 140.7, 137.6, 132.5, 131.9, 130.3, 128.0, 125.8, 124.7, 122.8, 120.1, 106.8, 101, 97.9, 94.2, 90.6, 18.8, 11.7; HRMS (EI) calcd. for $\text{C}_{52}\text{H}_{58}\text{Si}_2$ (M^+) 738.4077, found 738.4087. Anal. calcd. for $\text{C}_{52}\text{H}_{58}\text{Si}_2$: C, 84.49; H, 7.91. found: C, 83.99; H, 7.97.

V. References and Notes

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VI. APPENDIX

CHEN	FREQUENCY	PPM	INTEGR
1	376.062	1.167	10.6
2	366.939	1.232	11.8
3	66.896	0.729	63.7

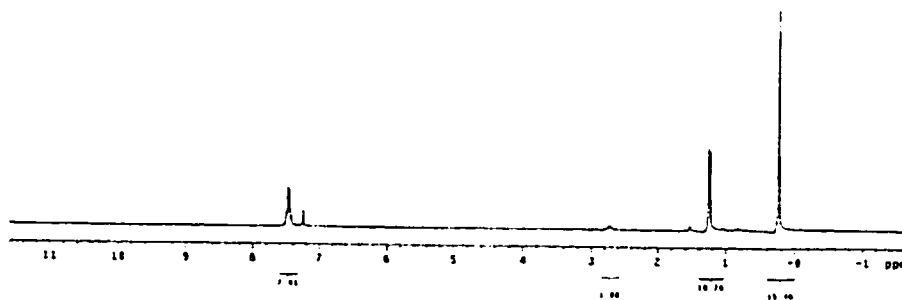
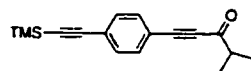


Figure 18: The ^1H -NMR spectrum of compound 80.

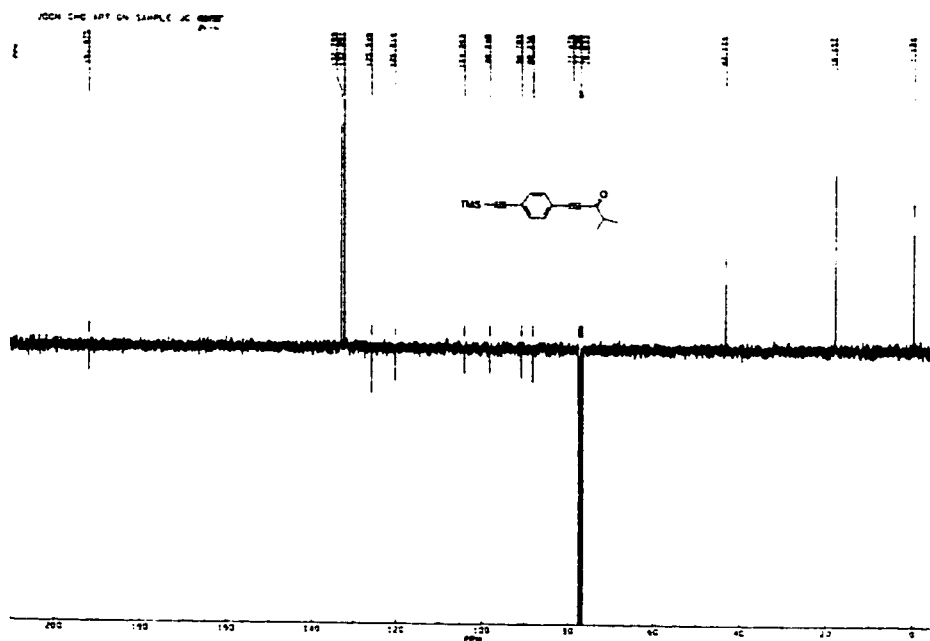


Figure 19: The ^{13}C -NMR spectrum of compound 80.

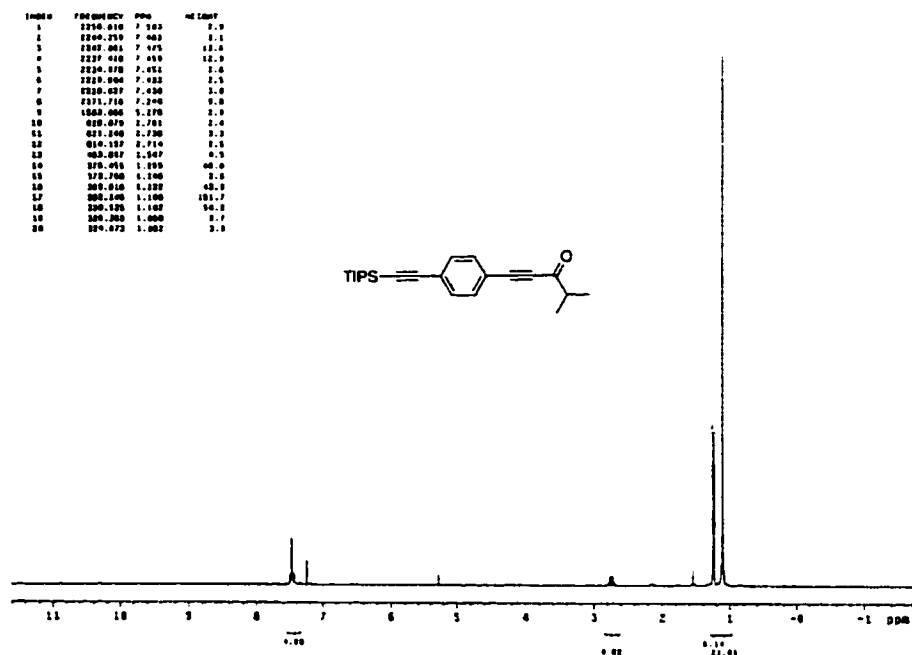


Figure 20: The ^1H -NMR spectrum of compound 87

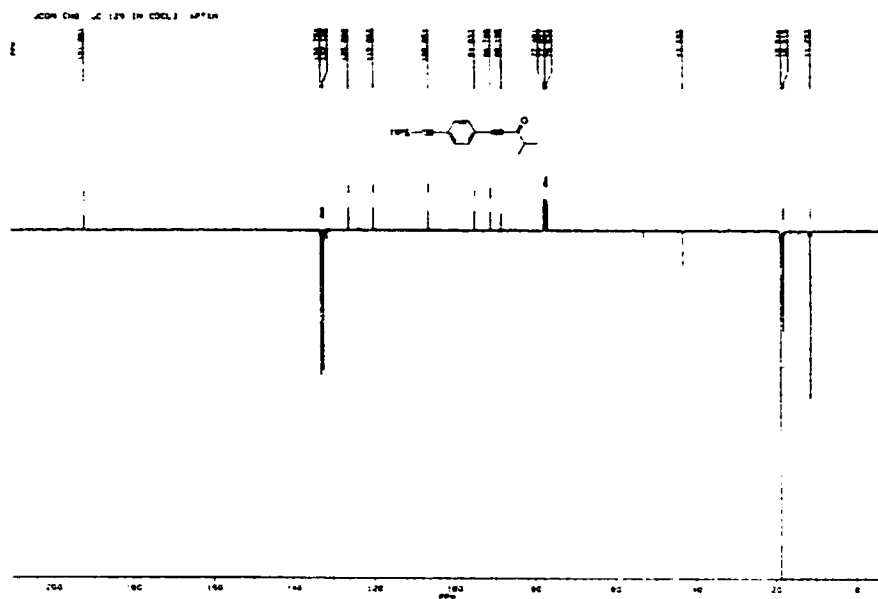


Figure 21: The ^{13}C -NMR spectrum of compound 87.

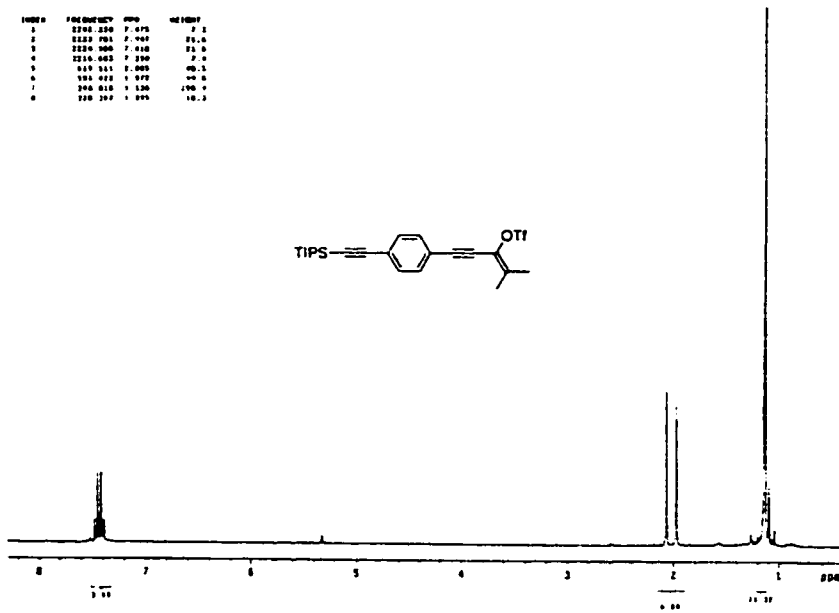


Figure 22: The ¹H-NMR spectrum of compound 88.

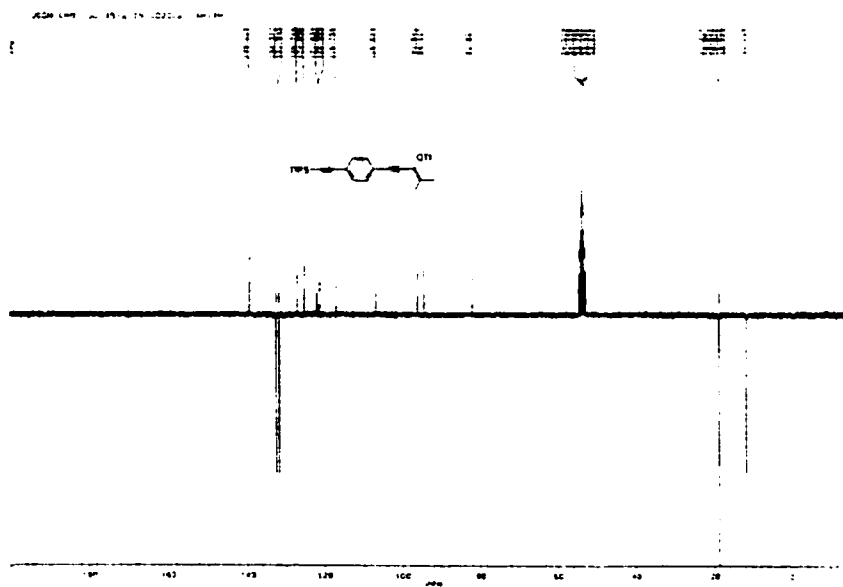


Figure 23: The ¹³C-NMR spectrum of compound 88.

INDEX	FREQUENCY	PPM	HEIGHT
1	2810.245	7.200	21.6
2	901.469	0.120	12.3
3	330.070	0.121	12.4

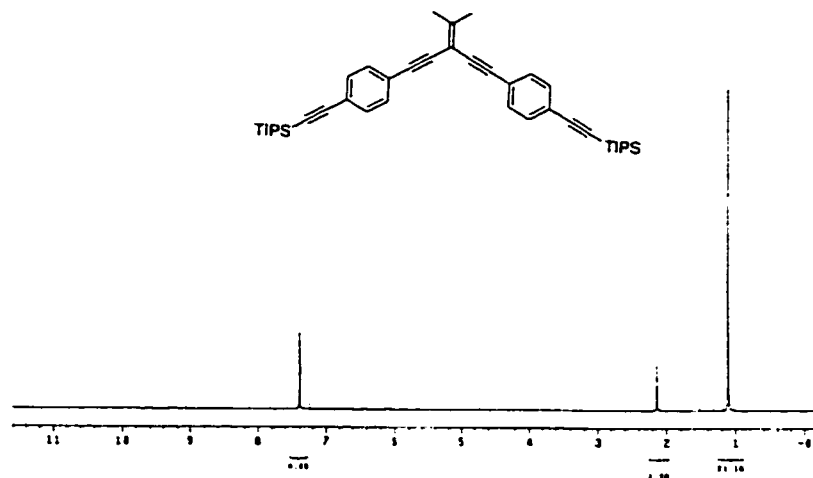


Figure 24: The ¹H-NMR spectrum of compound 89.

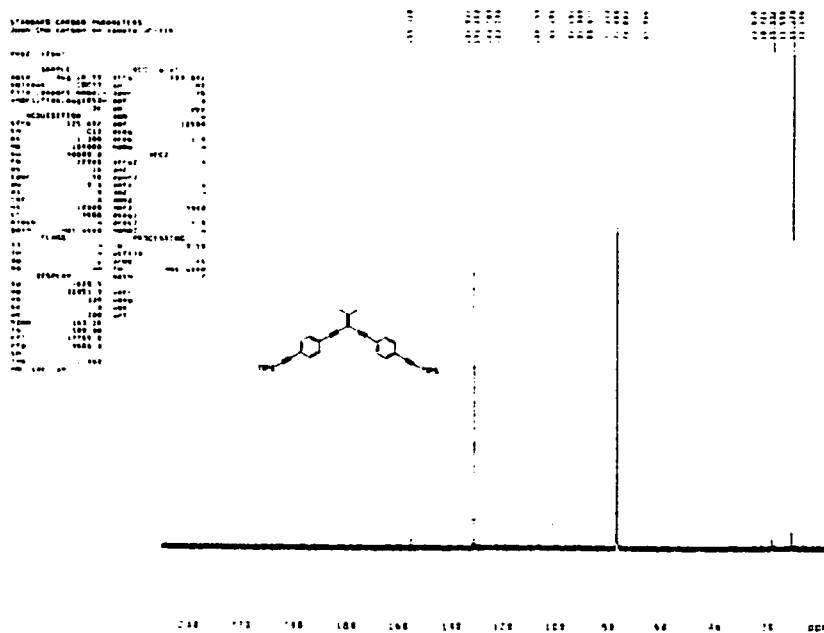


Figure 25: The ¹³C-NMR spectrum of compound 89.

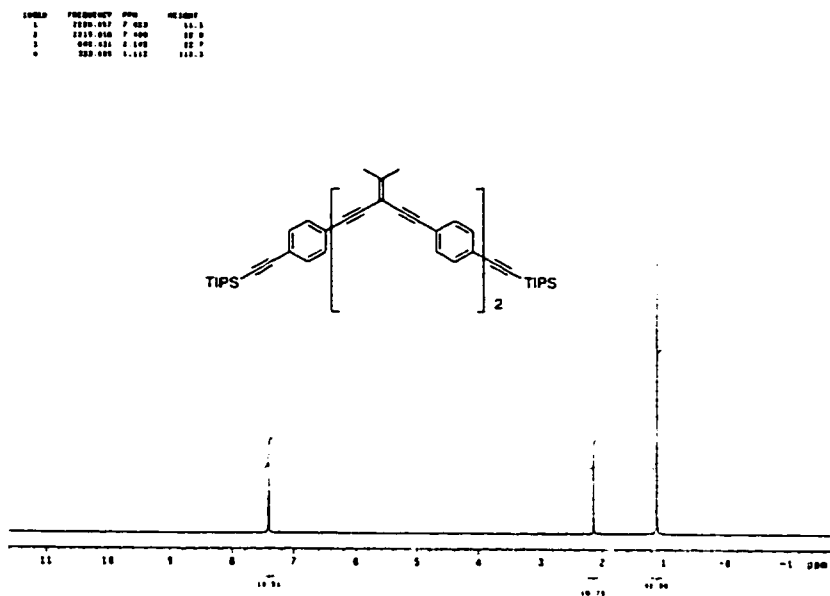


Figure 26: The ^1H -NMR spectrum of compound **90**.

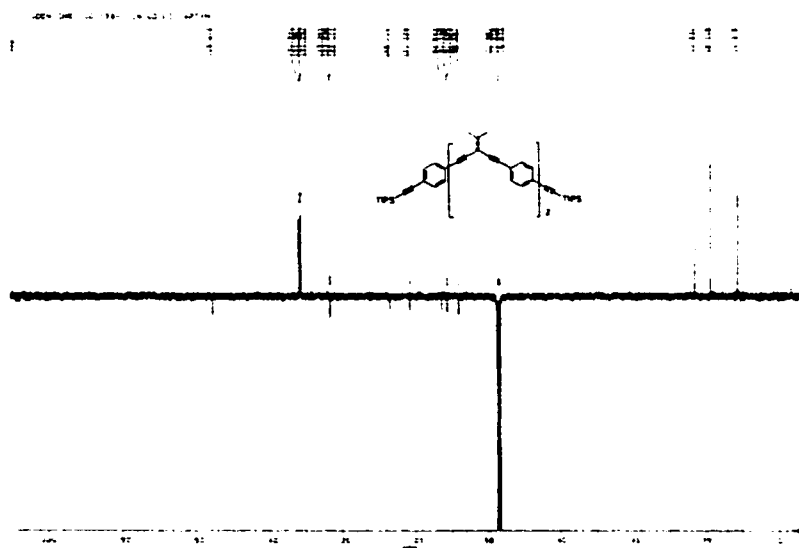


Figure 27: The ^{13}C -NMR spectrum of compound **90**.

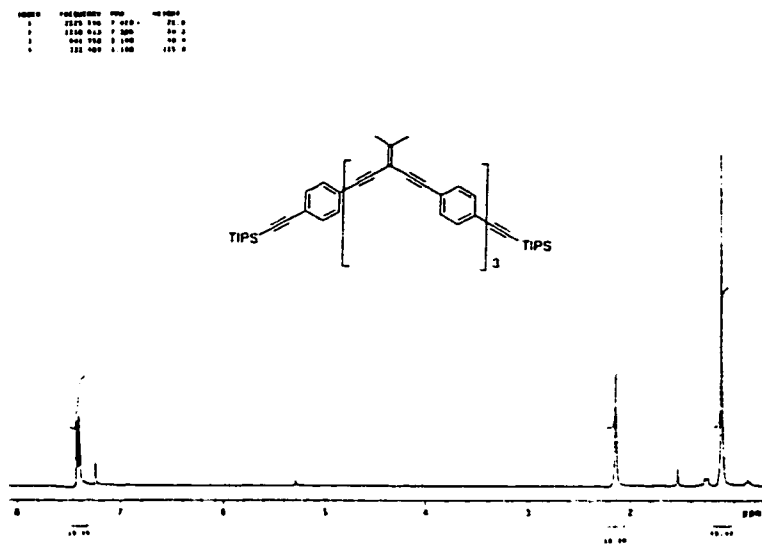


Figure 28: The ¹H-NMR spectrum of compound 92.

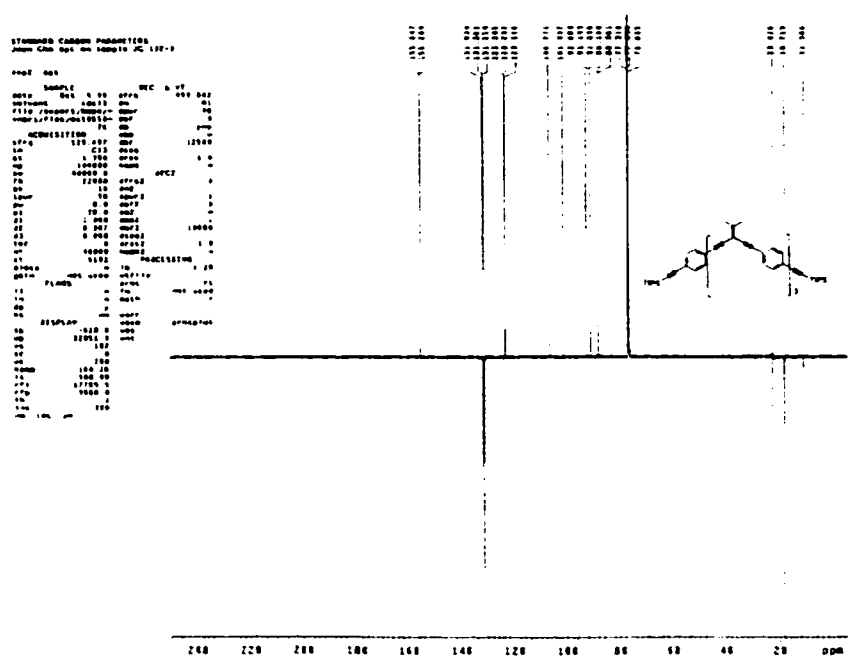


Figure 29: The ¹³C-NMR spectrum of compound 92.

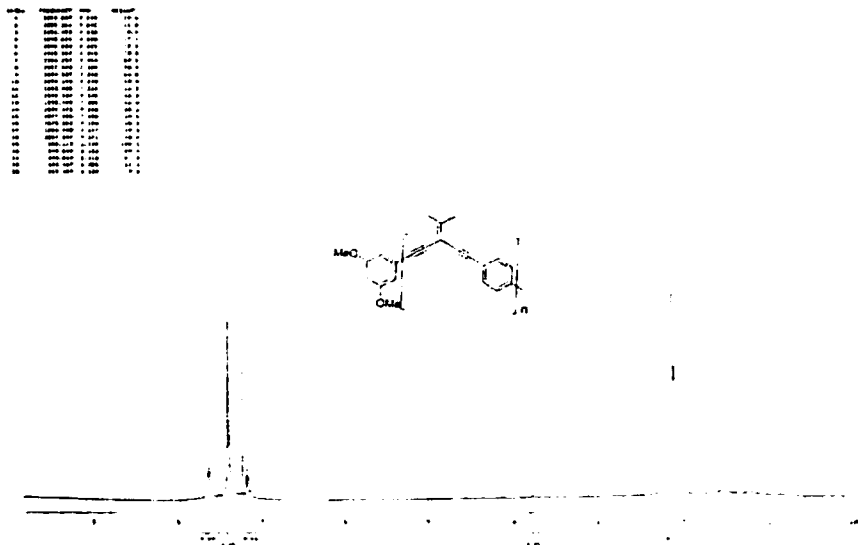


Figure 30: The $^1\text{H-NMR}$ spectrum of Polymer 104.



Figure 30: The $^{13}\text{C-NMR}$ spectrum of Polymer 104.

LINE#	FREQUENCY	PPM	HEIGHT	LINE#	FREQUENCY	PPM	HEIGHT
1	2982.603	11.818	0.3	46	322.858	0.874	1.7
2	2172.703	7.893	7.0	47	281.508	0.938	1.3
3	2171.530	7.829	18.0	48	256.258	0.803	18.0
4	2152.726	7.679	0.2	49	208.213	0.622	0.0
5	2079.210	6.931	0.3	50	95.319	0.184	0.3
6	2070.270	6.921	0.0	51	78.243	0.193	0.0
7	1879.173	6.901	0.1	52	62.230	0.185	0.1
8	2067.408	6.931	2.7	53	48.237	0.054	0.5
9	1769.169	6.022	1.1	54	19.926	0.018	0.0
10	1708.182	6.028	1.2				
11	1979.827	6.937	0.7				
12	1824.198	6.143	0.0				
13	1590.149	5.281	1.1				
14	1562.807	5.277	2.8				
15	1293.194	2.923	0.1				
16	1189.722	2.953	9.0				
17	1185.891	2.937	0.0				
18	1159.821	2.953	1.1				
19	1130.526	2.789	0.0				
20	1040.083	2.959	0.0				
21	727.198	2.029	0.0				
22	731.898	2.248	0.2				
23	698.298	2.291	0.2				
24	659.498	2.183	10.7				
25	840.170	2.194	12.0				
26	622.142	2.189	12.7				
27	619.130	2.082	0.1				
28	591.493	1.975	1.1				
29	569.133	1.874	0.7				
30	519.897	1.813	0.0				
31	519.178	1.769	1.6				
32	519.130	1.740	0.0				
33	463.828	1.537	1.2				
34	422.130	1.447	1.1				
35	389.839	1.418	0.2				
36	428.817	1.432	0.0				
37	379.859	1.298	21.0				
38	371.891	1.288	11.7				
39	328.134	1.099	2.6				

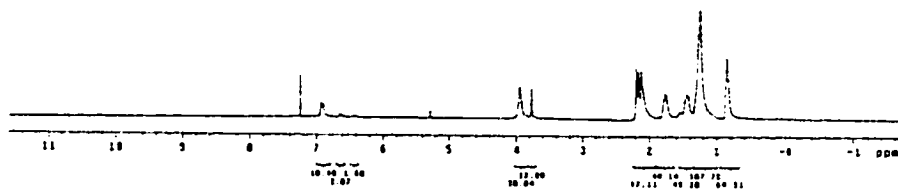
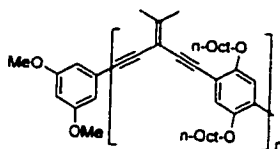


Figure 32: The ¹H-NMR spectrum of polymer 105.

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STANDARD CARBON PARAMETERS
2000 MHz Carbon on sample 800
PROB VIEW1
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P3: 12.00
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P11: 12.00
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P14: 12.00
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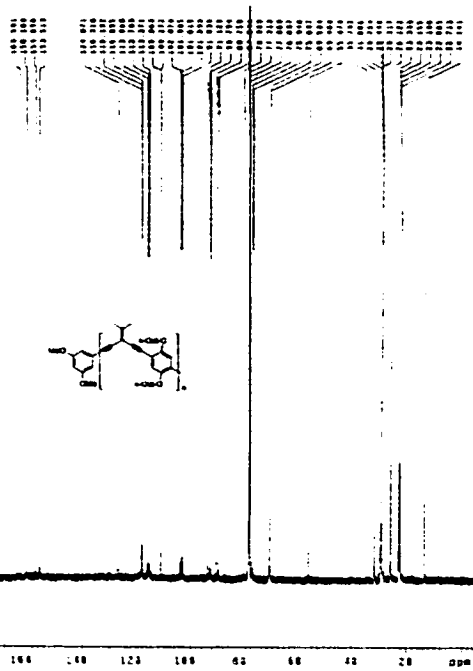


Figure 33: The ¹³C-NMR spectrum of polymer 105.

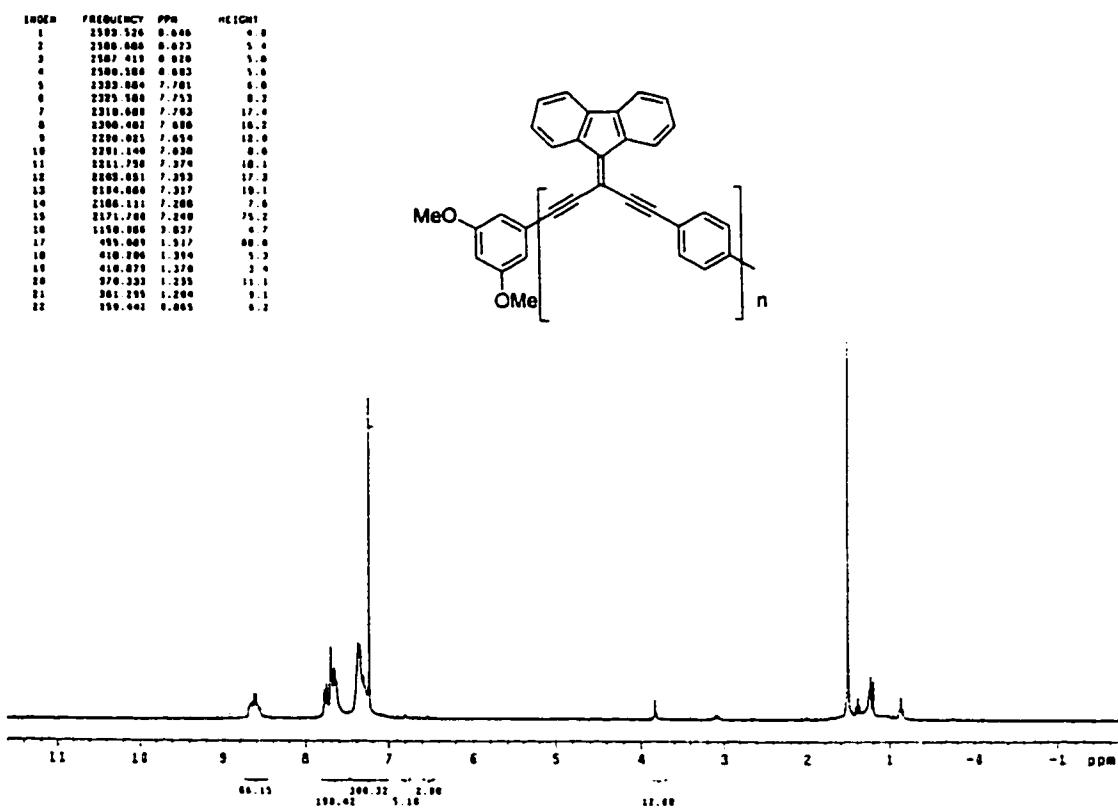


Figure 34: The ¹H-NMR spectrum of polymer 106.

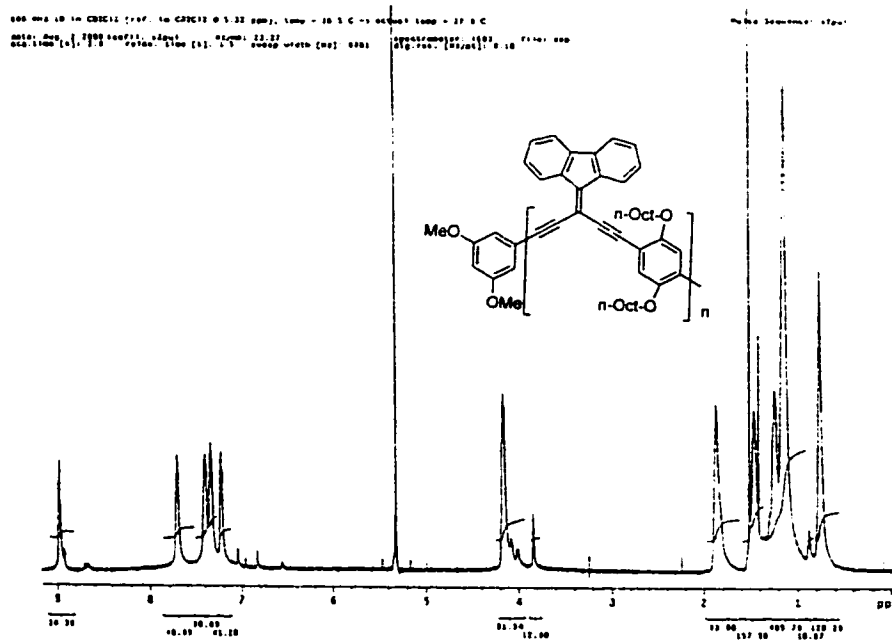


Figure 35: The ¹H-NMR spectrum of polymer 107.

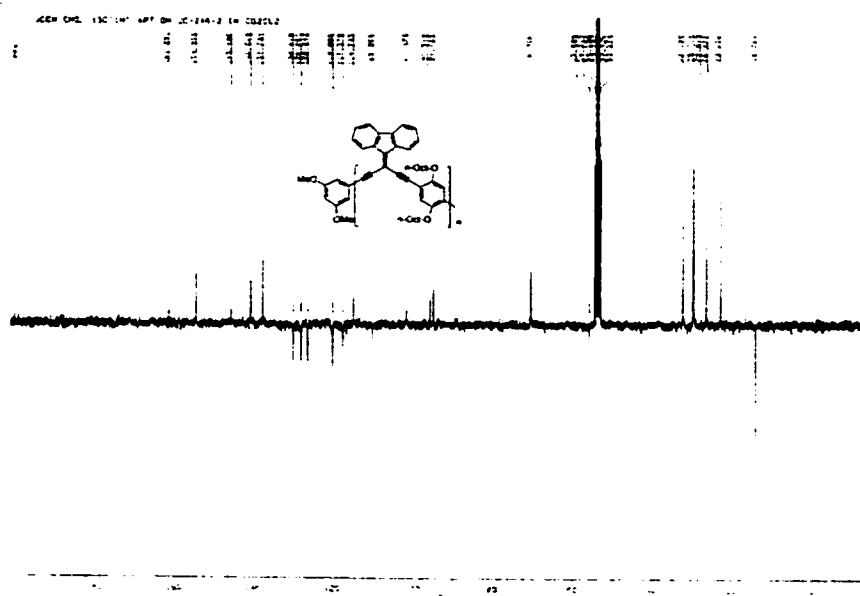


Figure 36: The ¹³C-NMR spectrum of polymer 107.

