



Synthesis of new electron donors and acceptors based on ethylenedioxythienylpolyenes  
by Edward Scott Tarter

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in  
Chemistry

Montana State University

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Abstract:

The continuing advancement of frequency agile laser weapons has fueled the development of new optical power limiters that can provide protection for the eyes or optical sensors over the entire visible region of the spectrum. Organic chromophores with non-linear optical properties are one class of optical power limiters currently under study that show considerable promise.

In this research, a new class of organic chromophores incorporating the 3,4-ethylenedioxythiophene unit and containing strong electron-withdrawing tricyanovinyl groups have been synthesized. These chromophores operate via a reverse saturable absorption mechanism and can be incorporated into dendrons and dendrimers where they function as  $\pi$ -electron acceptors or donors.

The absorption characteristics of these new chromophores were examined in solution to assess their potential to function as optical power limiters.

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APPROVAL

of a thesis submitted by

Edward Scott Tarter

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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## ABSTRACT

The continuing advancement of frequency agile laser weapons has fueled the development of new optical power limiters that can provide protection for the eyes or optical sensors over the entire visible region of the spectrum. Organic chromophores with non-linear optical properties are one class of optical power limiters currently under study that show considerable promise.

In this research, a new class of organic chromophores incorporating the 3,4-ethylenedioxythiophene unit and containing strong electron-withdrawing tricyanovinyl groups have been synthesized. These chromophores operate via a reverse saturable absorption mechanism and can be incorporated into dendrons and dendrimers where they function as  $\pi$ -electron acceptors or donors.

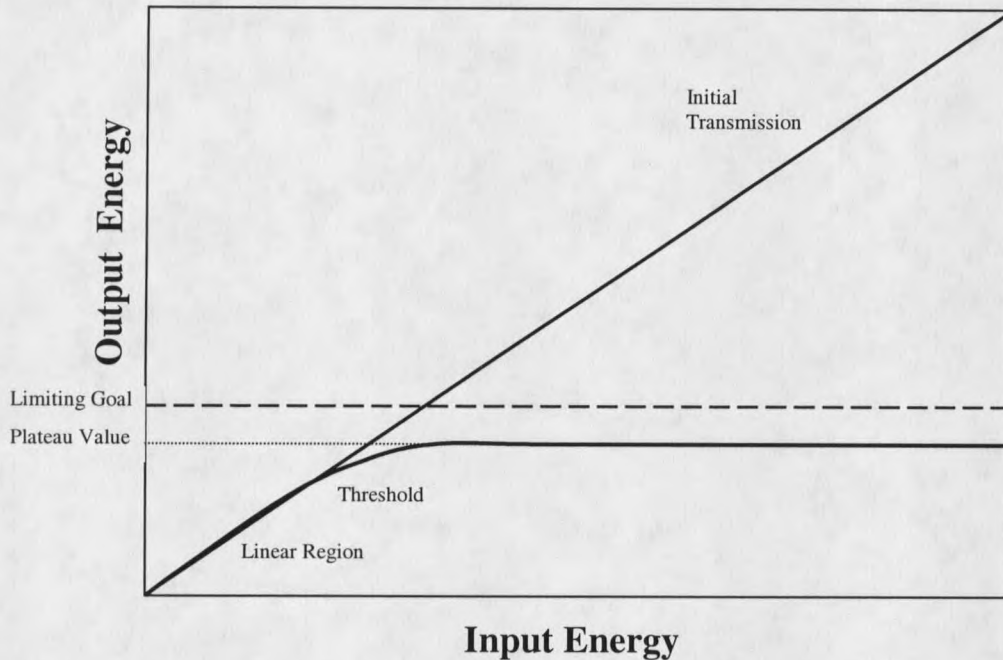
The absorption characteristics of these new chromophores were examined in solution to assess their potential to function as optical power limiters.

## CHAPTER 1

## INTRODUCTION

Over the years, laser weapons technology has made considerable progress. Lasers that are small and relatively inexpensive have been developed that can cause permanent damage to the human eye and/or optical sensors from a distance of up to six miles.<sup>1</sup> These weapons bear obvious military applications which makes the development of some sort of protection from these weapons imperative, particularly if the lasers become frequency agile. Although there have been many unsuccessful attempts to develop a form of protection against laser weapons whose operating frequency may not be known, the design of new organic optical power limiters (OPLs) which exhibit nonlinear effects is showing considerable progress.<sup>2</sup>

An optical power limiter is simply a device that has the ability to attenuate high level optical signals to maintain the output below a certain critical level, while allowing high transmittance for low level signals. Therefore, an optical limiting device for protection against laser weapons must absorb high intensity radiation that would be harmful to the eye or an optical sensor, and be transparent to harmless, low-level radiation. The characteristics of an ideal optical limiter are shown in Figure 1.

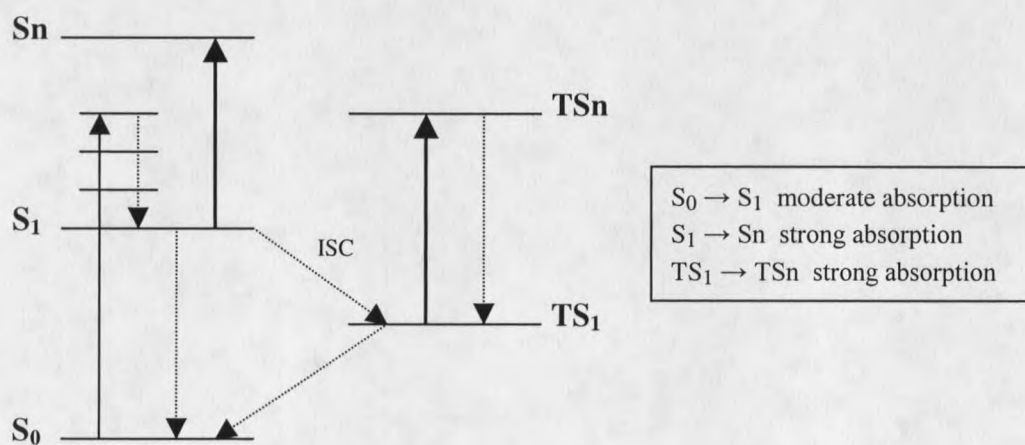


**Figure 1:** Characteristics of an ideal optical power limiter.

As Figure 1 illustrates, an ideal optical power limiter must meet several criteria. First, the material should allow high linear transmittance under ordinary ambient conditions as illustrated by the linear region of the curve. As the input energy reaches a set (and preferably variable) threshold level, the power limiter turns on and effectively keeps the output energy below this level. It is important that the threshold level is below the point at which damage to the eye or optical sensor will occur. To protect against tunable lasers that can fire short and high-intensity bursts of radiation, the limiter must also have a fast response time (picoseconds or faster), and be able to cover as much of the visible region of the spectrum as possible. Finally, the optical limiting material must be resilient enough to withstand high enough levels of radiation before damage to the limiter itself occurs.

At the present time, some of the most promising types of optical power limiters involve the use of organic chromophores. These chromophores can operate via two different mechanisms: reverse saturable absorption, and two-photon absorption.

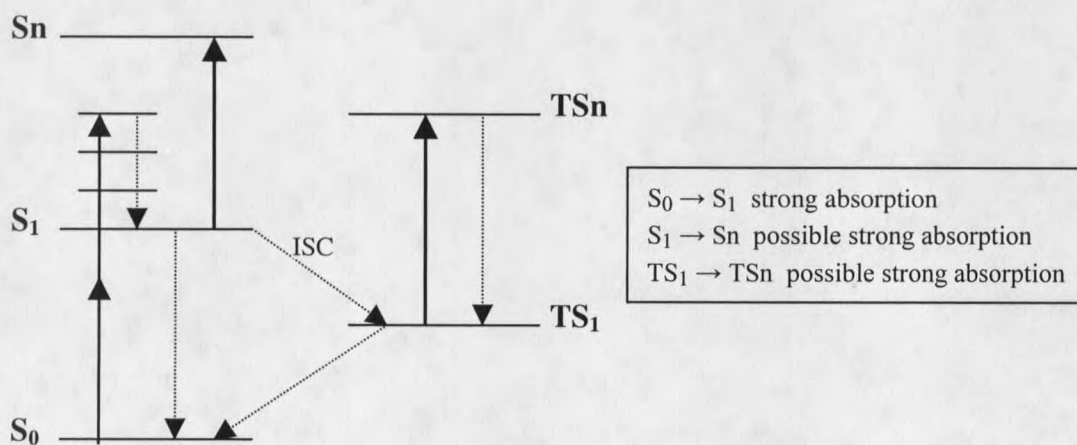
Figure 2 illustrates the pathway for reverse saturable absorption (RSA). In this mechanism, the ground state to first excited state transition ( $S_0 \rightarrow S_1$ ) provides weak to moderate absorption. This allows low intensity radiation to pass unabated. The electrons at  $S_1$  can decay back to  $S_0$  directly via fluorescence, or to a transient state at  $TS_1$  which is obtained through intersystem crossing. This transient state can be a triplet or a photogenerated charge state. As the intensity of the radiation increases, the electron population of the first excited state at  $S_1$  or  $TS_1$  increases. This allows for a second transition to higher electronic states at  $S_n$  or  $TS_n$ . If the  $S_1 \rightarrow S_n$  and  $TS_1 \rightarrow TS_n$  transitions provide strong absorption, the incident radiation will be attenuated and optical limiting is possible. Some materials that have been previously studied as RSAs include indantrones<sup>3</sup>, phthalocyanins<sup>4</sup>, porphyrins<sup>5</sup>, and fullerenes<sup>6</sup>.



**Figure 2:** Mechanism for Reverse Saturable Absorption (RSA).

The two-photon absorption (TPA) mechanism for optical power limiting is illustrated in Figure 3. TPA occurs when two photons strike the chromophore simultaneously and promote a ground-state electron to an excited state. This mechanism generally occurs at twice the excitation energy in which a single photon would be absorbed. Because the probability of two photons striking the molecule simultaneously is very small at low intensities of radiation, this low level radiation can pass through unabated. At high intensities of radiation however, this probability increases dramatically for molecules with large two-photon cross-sections, and the material becomes an effective optical limiter.

Chromophores exhibiting RSA and TPA behavior have been the focus of the C. Spangler research group for some time. It is important to note that many of the best chromophores currently under study are capable of functioning by either of the above mechanisms. This is very beneficial because one mechanism may occur at one region of the spectrum, while the other mechanism occurs at a different region. This allows for a much broader coverage of the entire visible range of the spectrum.



**Figure 3:** Mechanism for two-photon absorption (TPA).

## CHAPTER 2

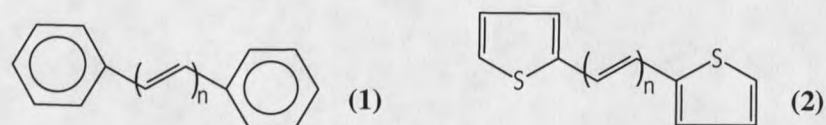
## HISTORICAL SECTION

For the past 20 years, the chemical and electronic properties of polyenes have been a growing topic of interest. One of the primary motivations for studying these materials was the electroactive and nonlinear optical effects that were observed upon chemical or electrochemical doping to form polaron and bipolaron states, particularly in  $\pi$ -conjugated polymers. Much of the modeling efforts focused on increasing the magnitude of the nonlinear optical response of organic chromophores. Through many detailed structure-property relationship studies, an understanding of how changes in chromophore structure affects third-order optical nonlinearity began to emerge. In general, these studies have focused on manipulation of the effective conjugation length of the  $\pi$ -electron framework, and the addition of donor and acceptor substituents to affect the overall electron density distribution.

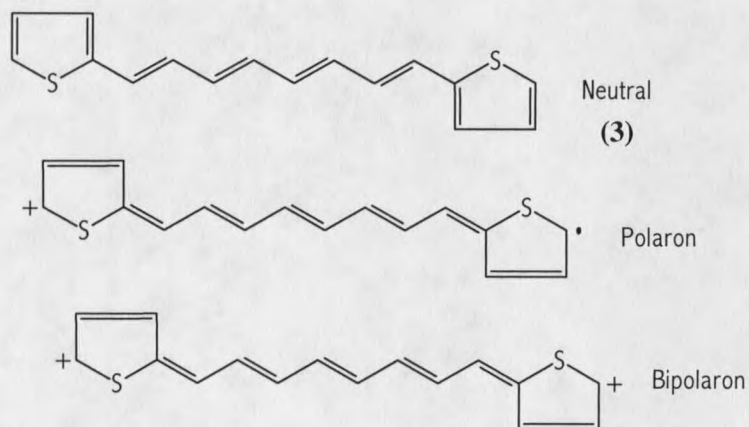
In recent years, the C. Spangler research group has been utilizing these developments in structure-property relationships to synthesize and study organic chromophores that operate by RSA or TPA mechanisms for use in optical power limiting applications. Much of this research has been focused around  $\alpha,\omega$ -diphenyl- and  $\alpha,\omega$ -dithienylpolyenes with varying numbers of conjugated double bonds as illustrated in Figure 4. These molecules can exhibit RSA behavior by forming polaron-like radical cations and bipolaron-like dications through successive one-electron transfers upon photoexcitation similar to those observed by oxidative doping in solution with strong



oxidizing agents such as  $\text{SbCl}_5$ .<sup>7-12</sup> These polaronic and bipolaronic states for an  $\alpha,\omega$ -dithienylpolyene are shown in Figure 5.



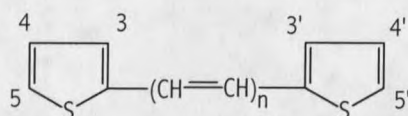
**Figure 4:**  $\alpha,\omega$ -diphenylpolyene and  $\alpha,\omega$ -dithienylpolyene where “n” represents any number of conjugated double bonds.



**Figure 5:** Structures for neutral, polaronic, and bipolaronic states of a typical  $\alpha,\omega$ -dithienylpolyene.

UV-Vis spectroscopy provides an excellent tool for studying the electronic structure of these conjugated polyenes. By observing the UV-Vis absorption characteristics of the neutral and oxidatively doped polyenes, the molecules can be fine-tuned synthetically by varying the conjugation length and by adding substituents to obtain

varying degrees of absorption in different regions of the spectrum. Table 1 shows the absorption characteristics of some neutral and charged-state dithienylpolyenes with varying conjugation lengths and attached substituent groups. As indicated in the table, the polaronic and bipolaronic charge states tend to absorb much more strongly and at longer wavelengths than the neutral  $S_0 \rightarrow S_1$  transitions. This is exactly what is needed for optical limiting. If these charge states can be photoinduced on a rapid enough time scale, then effective optical power limiting using these materials may be possible.

**Table 1:** P(+•) and BP(++ ) formation in dithienylpolyenes.

Substituent	n	$\lambda_{\max} \pi-\pi^*$ (nm) <sup>a</sup>	$\lambda_{\max} P(+\bullet)$ (nm)	$\lambda_{\max} BP(++)$ (nm)
None	5	<u>416</u> , 443	<u>705</u> , 797, 1084	653, <u>713</u>
None	6	<u>432</u> , 461	<u>760</u> , 853, 1154	713, <u>776</u>
5,5'-(Me) <sub>2</sub>	5	<u>425</u> , 450	[808] <sup>b</sup>	660, <u>710</u>
5,5'-(Me) <sub>2</sub>	6	<u>441</u> , 469	<u>888</u> , 1167, 1580	720, <u>776</u>
3,3'-(Me) <sub>2</sub>	5	<u>422</u> , 449	[795] <sup>b</sup>	650, <u>699</u>
3,3'-(Me) <sub>2</sub>	6	<u>440</u> , 469	<u>881</u> , 1154, 1574	713, <u>769</u>
5,5'-(OMe) <sub>2</sub>	3	<u>398</u> , 420	[731, 1076] <sup>b</sup>	<u>520</u> , (545) <sup>d</sup>
5,5'-(OMe) <sub>2</sub>	4	<u>416</u> , 444	<u>806</u> , 1103, 1299	<u>577</u> , (605) <sup>d</sup>
5,5'-(SMe) <sub>2</sub>	3	<u>404</u>	<u>792</u> , 1009, 1240	610, (643) <sup>d</sup>
5,5'-(SMe) <sub>2</sub>	4	<u>422</u> , 444	<u>859</u> , 1114, 1348	663, (702) <sup>d</sup>
5,5'-(SMe) <sub>2</sub>	5	<u>434</u> , 460	— <sup>c</sup>	717, (775) <sup>d</sup>
5,5'-(SMe) <sub>2</sub>	6	<u>451</u> , 478	— <sup>c</sup>	773, (835) <sup>d</sup>
5,5'-(SC <sub>10</sub> H <sub>21</sub> ) <sub>2</sub>	7	<u>462</u> , 494	— <sup>c</sup>	834, (905) <sup>d</sup>
5,5'-(SC <sub>10</sub> H <sub>21</sub> ) <sub>2</sub>	8	<u>475</u> , 507	— <sup>c</sup>	884, (970) <sup>d</sup>
3,4,3',4'-(Bu) <sub>4</sub>	3	422, <u>399</u> , 380	— <sup>c</sup>	593, <u>655</u>
3,4,3',4'-(Bu) <sub>4</sub>	4	443, <u>418</u> , 396	— <sup>c</sup>	600, <u>661</u>
3,4,3',4'-(Bu) <sub>4</sub>	5	462, <u>435</u> , 412	— <sup>c</sup>	679, <u>715</u>
3,4,3',4'-(Bu) <sub>4</sub>	6	480, <u>450</u> , 426	— <sup>c</sup>	<u>719</u> , 809
3,4,3',4'-(Bu) <sub>4</sub>	7	496, <u>464</u> , 439	— <sup>c</sup>	<u>790</u> , <u>849</u>
3,4,3',4'-(Bu) <sub>4</sub>	8	510, <u>477</u> , 450	— <sup>c</sup>	855, <u>914</u>
3,4,3',4'-(Bu) <sub>4</sub>	9	521, <u>489</u> , 461	— <sup>c</sup>	892, <u>971</u>
3,4,3',4'-(Bu) <sub>4</sub>	10	534, <u>499</u> , 471	— <sup>c</sup>	950, <u>1022</u>
3,4,3',4'-(Bu) <sub>4</sub> ; 5,5'-(BuS) <sub>2</sub>	3	424	— <sup>c</sup>	643
3,4,3',4'-(Bu) <sub>4</sub> ; 5,5'-(BuS) <sub>2</sub>	4	439	— <sup>c</sup>	657
3,4,3',4'-(Bu) <sub>4</sub> ; 5,5'-(BuS) <sub>2</sub>	5	451	— <sup>c</sup>	705
3,4,3',4'-(Bu) <sub>4</sub> ; 5,5'-(BuS) <sub>2</sub>	6	466	— <sup>c</sup>	754
3,4,3',4'-(Bu) <sub>4</sub> ; 5,5'-(BuS) <sub>2</sub>	7	476	— <sup>c</sup>	801
3,4,3',4'-(Bu) <sub>4</sub> ; 5,5'-(BuS) <sub>2</sub>	8	488	— <sup>c</sup>	849

Note: Underlined peaks represent peaks of maximum absorption.

<sup>a</sup> CH<sub>2</sub>Cl<sub>2</sub> solution

<sup>b</sup> Absorption spectra decay to BP(++ ) very fast; only unambiguous assignable absorption.

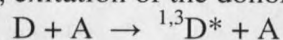
<sup>c</sup> Not observed on spectrometer scanning time scale.

<sup>d</sup> Absorption shown in parentheses represents shoulders.

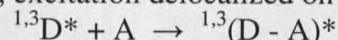
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Adding substituent groups to the polyene molecules not only provides a way of altering the  $\lambda_{\text{max}}$ , but can also increase the efficiency of the charge state formation and provide stabilization to prevent premature decay back to the neutral state. Of particular interest is the idea of using electron donating and accepting groups for increased efficiency of photogenerated charge state formation. Sariciftci and Heeger<sup>13</sup> have demonstrated that photoinduced electron transfer can occur between a conducting polymer and an acceptor molecule such as C<sub>60</sub>. The mechanism they proposed is as follows:

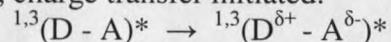
Step 1, excitation of the donor:



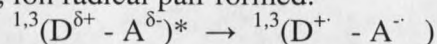
Step 2, excitation delocalized on donor-acceptor complex:



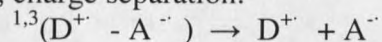
Step 3, charge transfer initiated:



Step 4, ion radical pair formed:



Step 5, charge separation:



1 and 3 represent singlet or triplet states, respectively.

The donor and acceptor moieties can be covalently attached to the same molecule, or they can exist as separate entities in solution. Because the same photogenerated charged state can be obtained by pumping the acceptor molecule instead of the donor, RSA behavior can be obtained from either photoinduced electron transfer or photoinduced hole transfer.

Designing optical power limiters that operate by a TPA mechanism is still a relatively new but promising field of study. Two-photon cross sections are related to the **Im** component of the third-order nonlinear optical response as indicated in the following equation:

$$\sigma^2 = \frac{8\pi^2 h\nu}{n^2 c^2 N} \text{Im}[\chi^{(3)}]$$

Where  $\sigma^2$  = two-photon cross-section,  $h$  = Planck's constant,  $\nu$  = frequency of incident radiation,  $n$  = index of refraction,  $c$  = speed of light, and  $N$  = number of absorbing molecules.

Bruce Reinhardt and coworkers at the Air Force Research Laboratories at WPAFB have designed and studied several molecules that exhibit strong TPA behavior.<sup>14</sup> During these studies, they developed the following set of design parameters for increasing the molecular two-photon cross-sections:

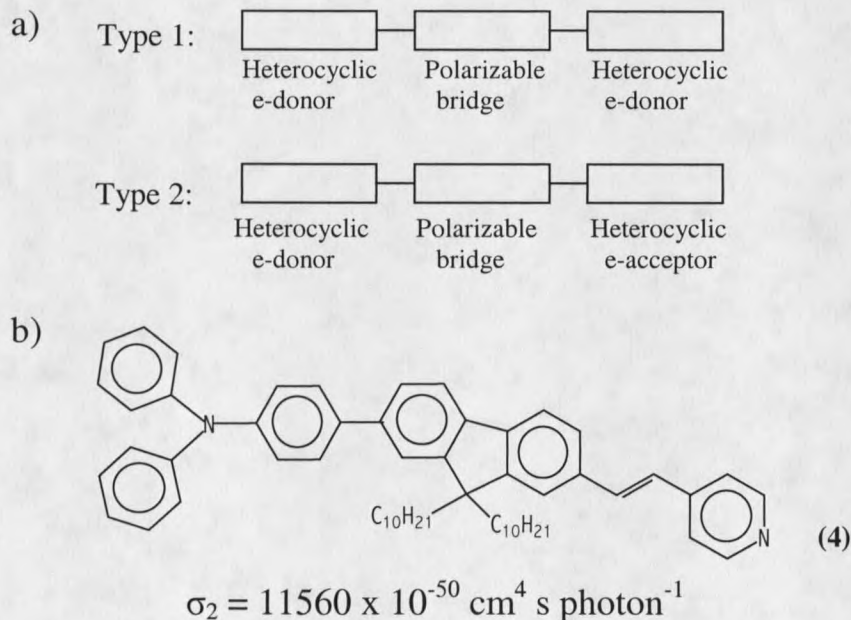
- (1) Extend the conjugation length
- (2) Change the identity of the conjugation bridge
- (3) Increase the  $\pi$ -donor strength
- (4) Increase the planarity of the chromophore

The Reinhardt group based their observations on two primary types of TPA chromophores which can be represented schematically as shown in Figure 6, which also illustrates one of the best compounds to come out of their studies.

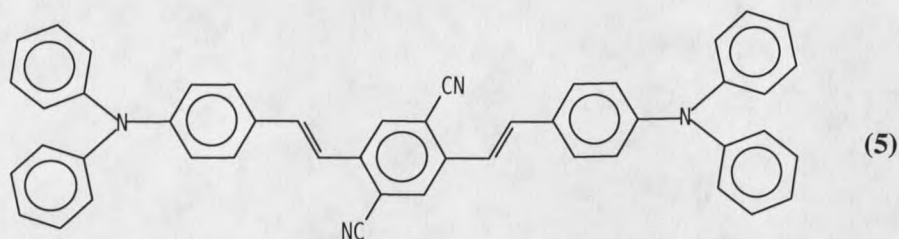
Marder and Perry's research group at the University of Arizona has also been studying TPA chromophore design and have identified parameters similar to those

reported by the Reinhardt group.<sup>15</sup> However, based on their observations of the effects of strong electron donor substitution on stilbene derivatives, they designed their chromophores with a donor-acceptor-donor or acceptor-donor-acceptor motifs. Figure 7 shows two of their chromophores which utilize this electron donating/accepting design.

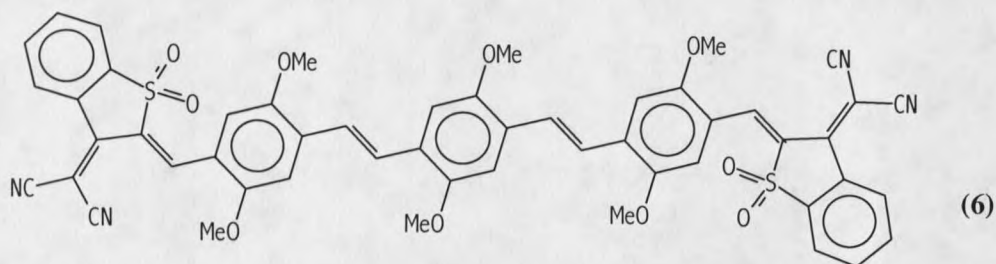
It should be noted that nanosecond laser pulses create a greater population in the excited state which can give rise to increased excited state absorption compared to either picosecond or femtosecond pulses. Therefore, the “effective” cross-sections observed for nanosecond pulses are larger than for shorter pulse durations. The cross-section shown in Figure 6 is for 8 nanosecond laser pulses, while those in Figure 7 are for picosecond pulses.



**Figure 6:** a) Two types of structural motifs for efficient two-photon absorption proposed by the Reinhardt research group. b) One of the Reinhardt group’s best TPA chromophores for nanosecond laser pulses.



$$\sigma_2 = 1940 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1}$$

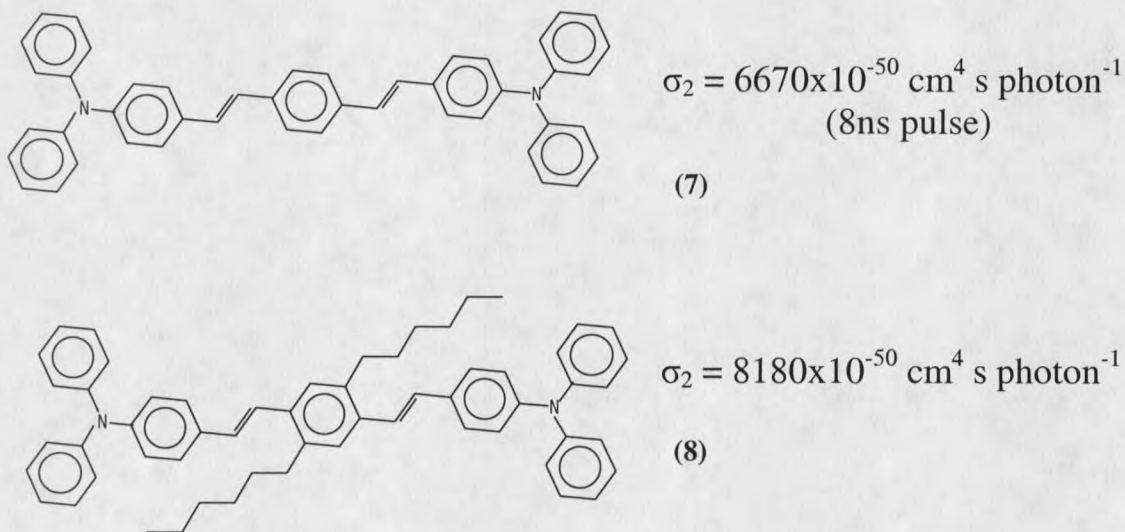


$$\sigma_2 = 4400 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1}$$

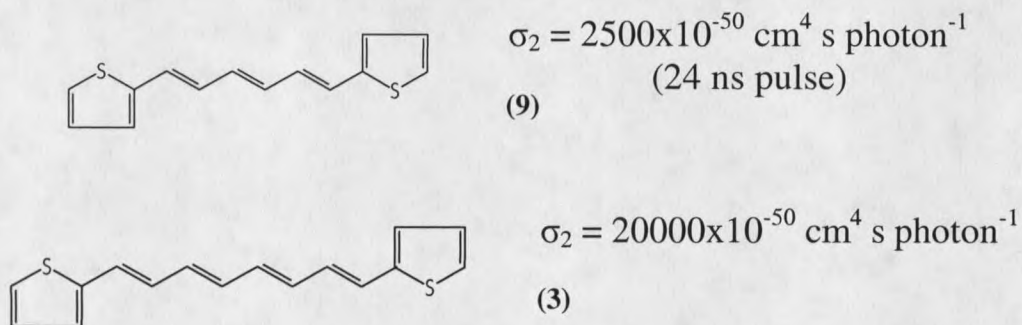
**Figure 7:** Examples of donor-acceptor-donor and acceptor-donor-acceptor TPA chromophores designed by the Marder and Perry research group for picosecond laser pulses.

During recent years, the C. Spangler research group has designed several new TPA chromophores as part of a collaboration with scientists at Laser Photonics Technology Inc. (Amherst, NY). Two examples of these chromophores for limiting of nanosecond laser pulses are shown in Figure 8. In collaboration with Science Applications International Corp. and the Materials Directorate at Wright Laboratories (MLPJ) (WPAFB, OH), the Spangler group has also shown via fluorescent studies that  $\alpha,\omega$ -dithienylpolyenes have large two-photon cross-sections for nanosecond laser pulses. Therefore, these polyenes have the ability to function as bimechanistic optical power

limiters utilizing both RSA and TPA mechanisms.<sup>12</sup> Figure 9 shows the two-photon cross-sections for two  $\alpha,\omega$ -dithienylpolyenes with different conjugation lengths.



**Figure 8:** Two chromophores designed by the C. Spangler group which possess large two-photon cross sections for nanosecond pulses.



**Figure 9:** Two-photon cross sections for two  $\alpha,\omega$ -dithienylpolyenes with different conjugation lengths.

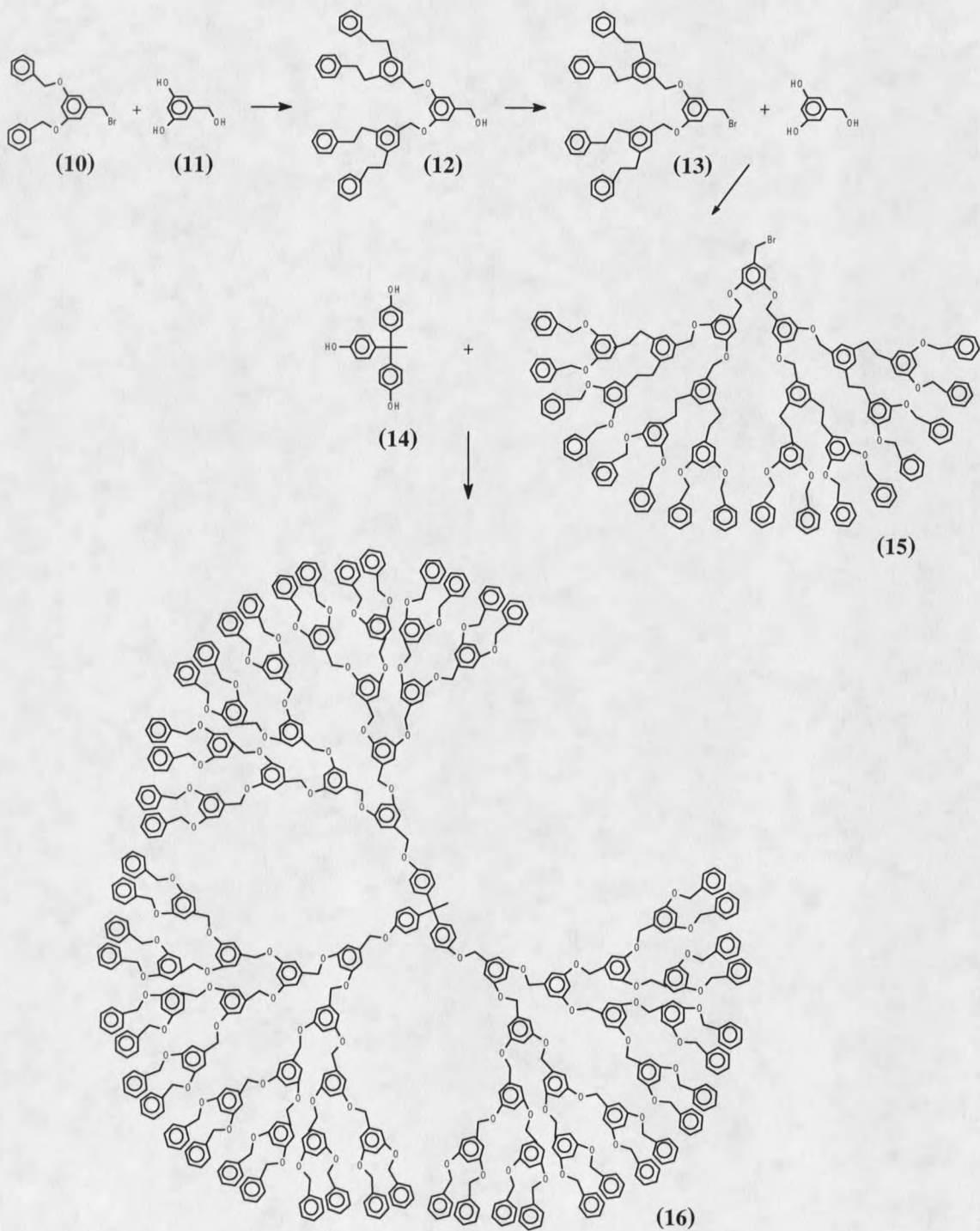


The L. Spangler group (MSU), in collaboration with the C. Spangler group, has recently shown that bis-(diphenylamino)diphenylpolyenes with one, two, and three double bonds form polaronic charge states when irradiated in the presence of  $C_{60}$  in solution.<sup>16</sup> In these studies, optically pumping the  $C_{60}$  at 532nm forms  $C_{60}$  triplet, which then accepts an electron from the donor polyenes. Since the experiment was carried out in solution, the electron transfer process is diffusion-limited to the microsecond time scale. In order to get more efficient and faster electron transfer, it would be desirable to have both the donor and acceptor groups covalently attached to the same structure.

An excellent way of incorporating both donor and acceptor groups into one organic chromophore is through the use of dendrimer design. Dendrimers are highly branched, three-dimensional, monodisperse macromolecules that contain a large number of chain ends at the surface. An example of a typical dendrimer synthesized using a convergent methodology by Fréchet and Hawker<sup>17</sup> is illustrated in Scheme 1.

Dendrimer synthesis utilizing convergent methodology, as opposed to divergent methodology, starts at the outside of the molecule and works towards the core. The starting material (**10**), which contains the surface functionality and a reactive functional group, is coupled to a monomer unit (**11**) which contains two or more coupling sites and a protected functional group. This forms a derivatized moiety identified as a dendron (**12**). The individual dendrons can then be deprotected and attached directly to a core molecule (**16**) to form a first generation dendrimer; or, they can be further coupled to another monomer unit to produce higher generation dendrimers (**17**). Although in theory this process can be carried out as many times as one likes to form higher and higher

generations of dendrimers, solubility and steric crowding around the core molecule do pose practical limitations.

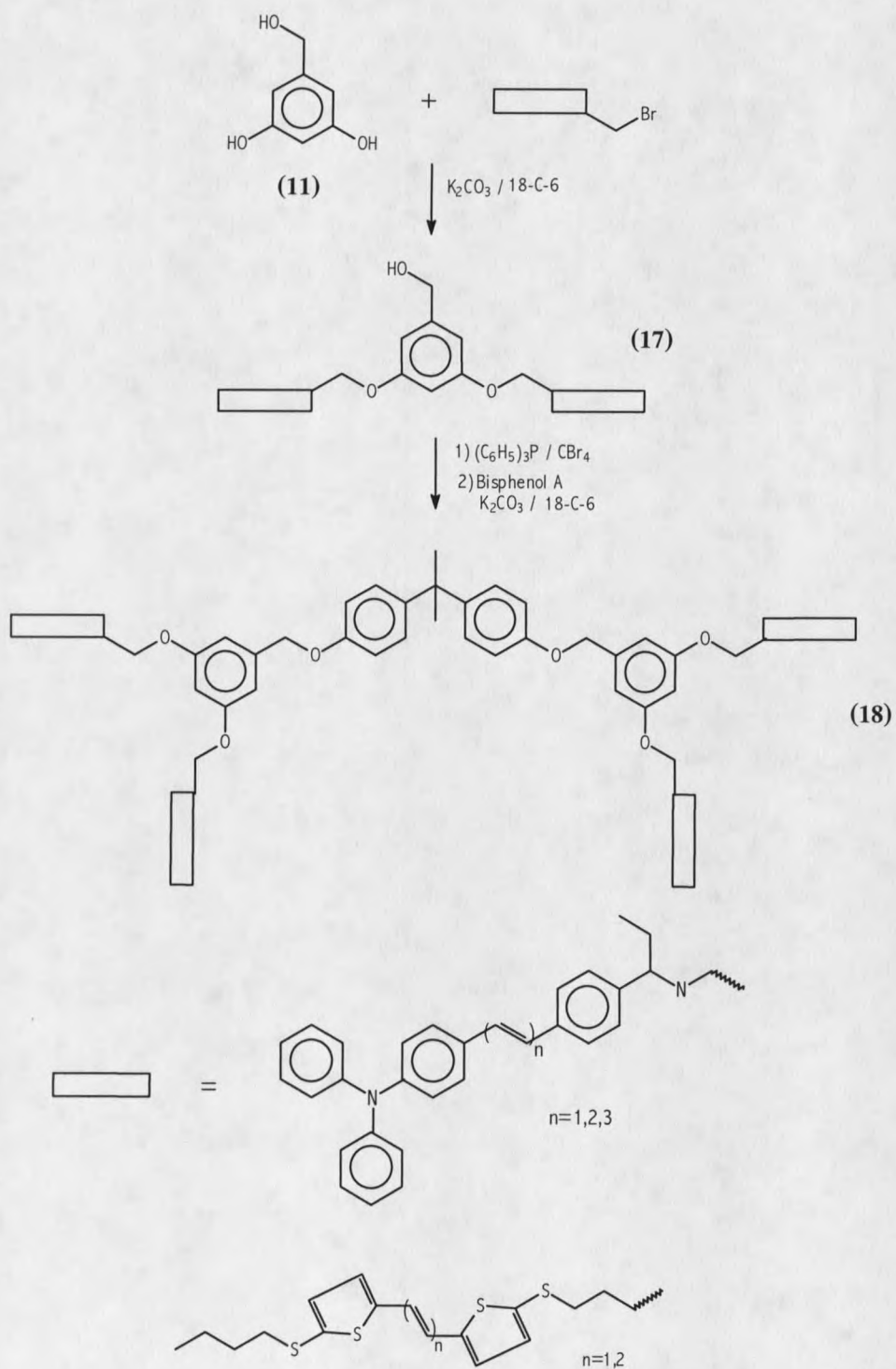


**Scheme 1:** Fréchet convergent dendrimer synthesis.

Some of the advantages of using surface functionalized dendrimers for RSA optical limiters are as follows:

- The percentage incorporation of active species is high.
- Both donor and acceptor species can be incorporated into the dendrimer readily in an almost infinitely variable D/A ratio.
- The distance and rotational flexibility between donor and acceptor moieties can be controlled by varying spacer group length and identity.
- The relative closeness of the donor and acceptor moieties allows for fast and efficient electron transfer, thus aiding in the formation of highly absorbing polaron and bipolaron charge states.

Dendrimers incorporating organic chromophores have been one of the primary foci of the C. Spangler group in their quest to develop efficient optical power limiters. Spangler et. al. has recently shown fast, efficient electron transfer between donor chromophores which have been incorporated into dendrons based on 3,5-dihydroxybenzyl alcohol, and into dendrimers formed by coupling these dendrons to a core molecule such as bisphenol-A, as shown in Scheme 2.<sup>18</sup> In these cases, the electron acceptor was C<sub>60</sub>, and the system was optically pumped at 532 nm as described previously. However, there are many limitations with using C<sub>60</sub> as an electron acceptor as will be described in Chapter 3. These limitations have prompted a search for new acceptors that are processible and can be readily derivatized for attachment to dendrons such as 3,5-dihydroxybenzyl alcohol.



**Scheme 2:** Example of a first generation dendrimer utilizing donor chromophores synthesized by the C.Spangler research group.

## CHAPTER 3

## RATIONAL FOR PROPOSED RESEARCH

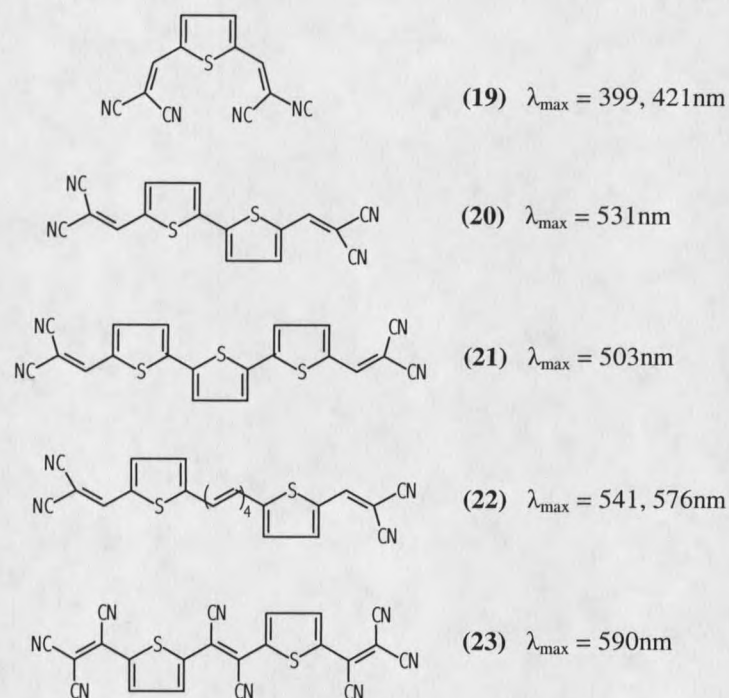
As previously mentioned in Chapter 2, the C. Spangler research group has focused considerable effort synthesizing dendrons and dendrimers with photonic-active chromophores that can function as efficient optical power limiters. These chromophores can exhibit large two-photon cross-sections, or function as RSAs through the photogeneration of highly absorbing charge states via an electron transfer from donor to acceptor substituents.

Although a number of good donor chromophores have been synthesized and studied in the Spangler group, all of the electron transfer studies have centered around  $C_{60}$  as the electron acceptor. Although  $C_{60}$  is a good electron acceptor, it has a number of other drawbacks that fuels the need to find better alternatives. One of the biggest problems with  $C_{60}$  is its lack of solubility in most common organic solvents with the exception of toluene and o-dichlorobenzene. It is also relatively difficult to functionalize the molecule with a reactive tether group to allow for covalent attachment to produce dendrons and dendrimers. Once the molecules are functionalized, the derivatized  $C_{60}$  moieties are generally even less soluble than  $C_{60}$  itself and often lose some of their electron accepting ability. Finally, it is difficult to "fine-tune" the absorption characteristics of any derivatized  $C_{60}$  materials to obtain absorption in the regions of the spectrum necessary for optical limiting of frequency-agile lasers.

In general, substituents that are recognized as strong electron withdrawing groups in electrophilic aromatic substitution reactions tend to have a similar effect in electron-transfer processes. Some of the early electron acceptors that have been proposed as alternatives to  $C_{60}$  have focused on the tricyanovinyl and dicyanovinyl groups as shown below:



Shown in Figure 10, are a group of preliminary model electron acceptors and their peak absorption wavelengths that were synthesized by Hu Li at Scientific Materials Corp. These acceptors utilize both dicyanovinyl and tricyanovinyl groups attached to thiophene moieties.



**Figure 10:** Some electron acceptor molecules and their peak absorption wavelengths that utilize dicyanovinyl and tricyanovinyl groups.

Although these acceptor molecules do show promise, the extinction coefficients as measured through UV/VIS spectroscopy are higher than desired for use as effective optical limiters. This tends to make the molecules function as saturable absorbers instead of as reverse saturable absorbers. Also, we would like to shift the absorption characteristics of the molecules farther towards the red region of the spectrum in order to provide the necessary coverage of the entire visible region.

The purpose of the research, therefore, is to design new electron acceptor chromophores based on the thiophene moiety and utilizing tricyanovinyl functional groups near the termini of the molecule to help bipolaron formation and stabilization. To improve the reactivity of the thiophene unit towards nucleophilic substitution reactions,



3,4-ethylenedioxythiophene (EDOT) was also utilized in chromophore design. Because no electron donor chromophores have yet been designed based on the EDOT moiety, some EDOT based polyenes have also been synthesized and tested for their potential to function as electron donors in organic chromophores. The thiophene and EDOT moieties were chosen because:

- The sulfur heteroatom helps stabilize the polaron and/or bipolaron.
- It's relatively easy to add a tether group to the ring structure to allow attachment of the chromophore to dendrons.
- Substituted thiophenes tend to have limited wavelength coverage.
- The electrons in thiophene and EDOT are much more available to nucleophilic substitution reactions than the electrons in phenyl rings.

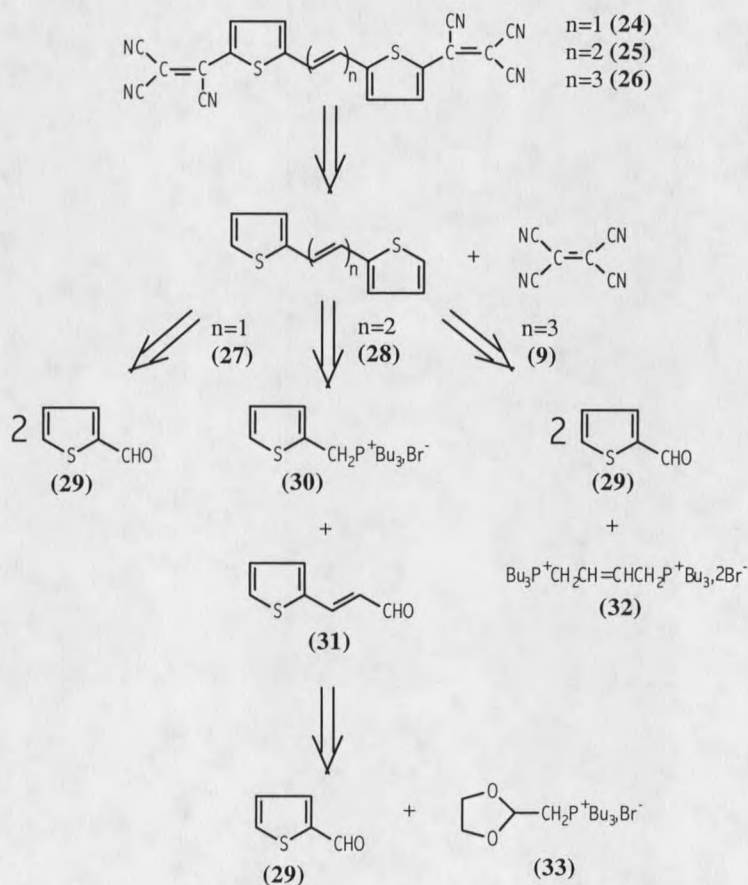
If these acceptor and donor chromophores exhibit the necessary characteristics, they can later be incorporated into dendrons and dendrimers to function as optical power limiters.

## CHAPTER 4

## RESULTS AND DISCUSSION

Proposed Synthesis of Bis-(tricyanovinyl-thienyl)polyenes for use as Electron-Accepting Chromophores

The first electron acceptor target molecules incorporating the thiophene and tricyanovinyl moieties that were studied can be analyzed retrosynthetically as follows in Scheme 3.

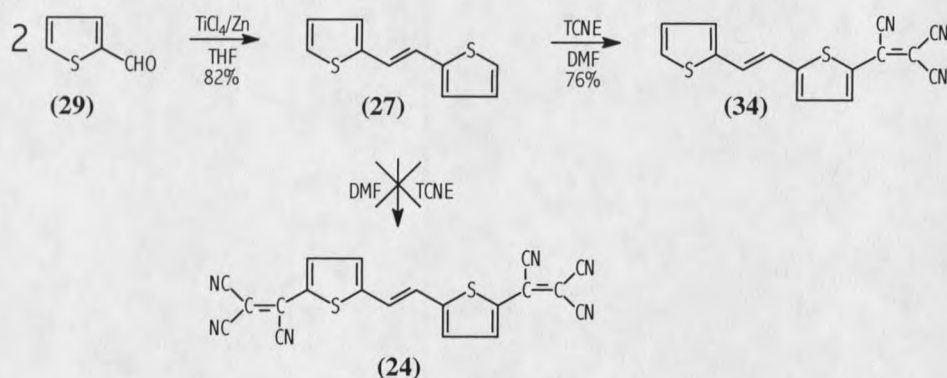


**Scheme 3:** Retrosynthesis of some Bis-(tricyanovinyl-thienyl) polyenes with varying numbers of conjugated double bonds.

Attempted Synthesis of 1,2-Bis-(5'-tricyanovinyl-2'-thienyl)ethene

The synthetic route to 1,2-bis-(5'-tricyanovinyl-2'-thienyl)ethene (**24**) is shown in Scheme 4. The intermediate 1,2-bis-(2'-thienyl)ethene (**27**) was synthesized from two equivalents of thiophene-2-carboxaldehyde (**29**) via a McMurry coupling reaction using  $\text{TiCl}_4$  and Zn. After extraction and purification by column chromatography, the resulting product (**27**) was reacted with tetracyanoethylene in DMF to give the target molecule; however, only the mono-substituted product, 1-[2'-(5'-tricyanovinyl)thienyl]-2-[2''-thienyl]ethene (**34**) was obtained. Even with a large excess of TCNE and long reflux times, the desired di-substituted product was not achieved in any practical yield. Heating the reaction mixture over  $100^\circ\text{C}$  for any length of time resulted in a number of byproducts visible by thin layer chromatography that are very hard to separate in the purification process. The best yields were obtained by heating the reaction to  $90^\circ\text{C}$  for approximately four hours.

Because only the mono-substituted product could be obtained, and because of its relatively poor solubility, the syntheses of the longer chain chromophores with  $n=2$  and  $n=3$  double bonds were not attempted.



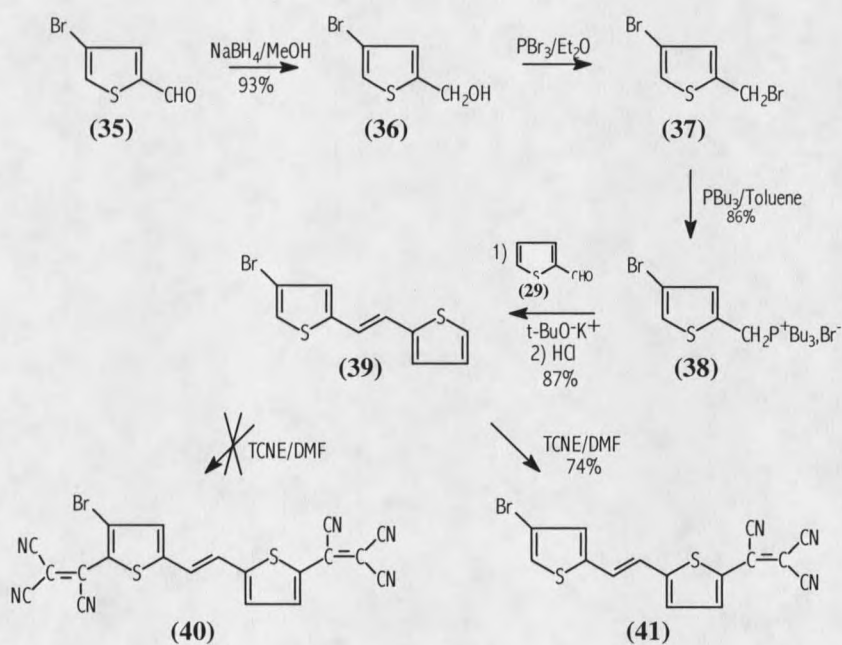
**Scheme 4:** Synthesis of 1-[2'-(5'-tricyanovinyl)thienyl]-2-[2''-thienyl]ethene.

Attempted Synthesis of Functionalized 1,2-Bis-(5'-tricyanovinyl-2'-thienyl)ethene Chromophore

In order to attach an electron-accepting chromophore to a dendron, there must be a reactive tether group present on the acceptor. Therefore, to allow for future tether group attachment, the synthesis of 1-[2'-(4'-bromo-5'-tricyanovinyl)thienyl]-2-[2''-(5'-tricyanovinyl)thienyl]ethene (**40**) was attempted as illustrated in Scheme 5.

To synthesize the Wittig salt intermediate (**38**), 4-bromo-2-thiophenecarboxaldehyde (**35**) was first reduced to the alcohol (**36**) with  $\text{NaBH}_4$ . The alcohol was then converted to the bromide (**37**) using phosphorus tribromide in ether. This bromide intermediate was not purified and was used immediately in the next step of the synthesis without removal of the solvent to avoid decomposition. Finally, the bromide was converted into the Wittig salt intermediate by refluxing with tri-*n*-butylphosphine in toluene to give white crystals of (**38**) which can be removed by

filtration, and purified by recrystallizing from ethyl acetate. The Wittig salt was then coupled with thiophene-2-carboxaldehyde (**29**) through a Wittig condensation reaction to give (**39**). After isolation and recrystallization from 95% ethanol, (**39**) was refluxed with a large excess of TCNE in DMF but again gave only the mono-substituted product, 1-[2'-(4'-bromo)thienyl]-2-[2''-(5''-tricyanovinyl)thienyl]ethene (**41**). As before, because of the lack of sufficient yield of di-substituted product, the synthesis of longer chain polyenes of this molecule was not attempted.

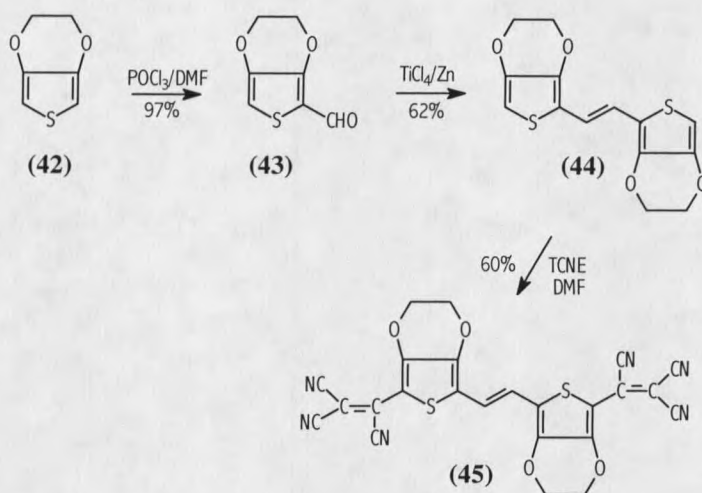


**Scheme 5:** Synthesis of 1-[2'-(4'-bromothiienyl)]-2-[2''-(5''-tricyanovinyl)]ethene.

Synthesis of 1,2-Bis-(5'-tricyanovinyl-3',4'-ethylenedioxy-2'-thienyl)ethene Electron-Accepting Chromophores

In order to increase the reactivity of the thiophene ring towards nucleophilic substitution by TCNE, the electron rich 3,4-ethylenedioxythiophene (EDOT) was incorporated in place of the thiophene. This was done in order to obtain the di-substituted product with the tricyanovinyl groups on both ends of the chromophore. Scheme 6 illustrates the synthesis of bis-(tricyanovinyl-EDOT)ethylene (**45**).

Commercially available 3,4-ethylenedioxythiophene (**42**) (Aldrich) was converted to the aldehyde (**43**) via a Vilsmeier-Haack reaction with  $\text{POCl}_3$  and DMF. The aldehyde is easily purified by recrystallizing from ethanol and then can be self-coupled by a McMurry coupling reaction which forms the ethene bridge between the two EDOT molecules to give (**44**). This intermediate was then reacted with three equivalents of TCNE in DMF to give the desired disubstituted chromophore. After heating the reaction to  $90^\circ\text{C}$  for twelve hours, the product was retrieved by allowing the solution to cool to room temperature and then vacuum filtering the resulting precipitate. The filter cake was washed thoroughly with methylene chloride to remove any remaining DMF, and then placed in a Soxhlet extractor and extracted with methylene chloride for 24 hours. Because of the poor solubility of this molecule, longer chain polyene versions with butadiene and hexatriene bridges were not synthesized, as solubility tends to decrease as the conjugation length increases.

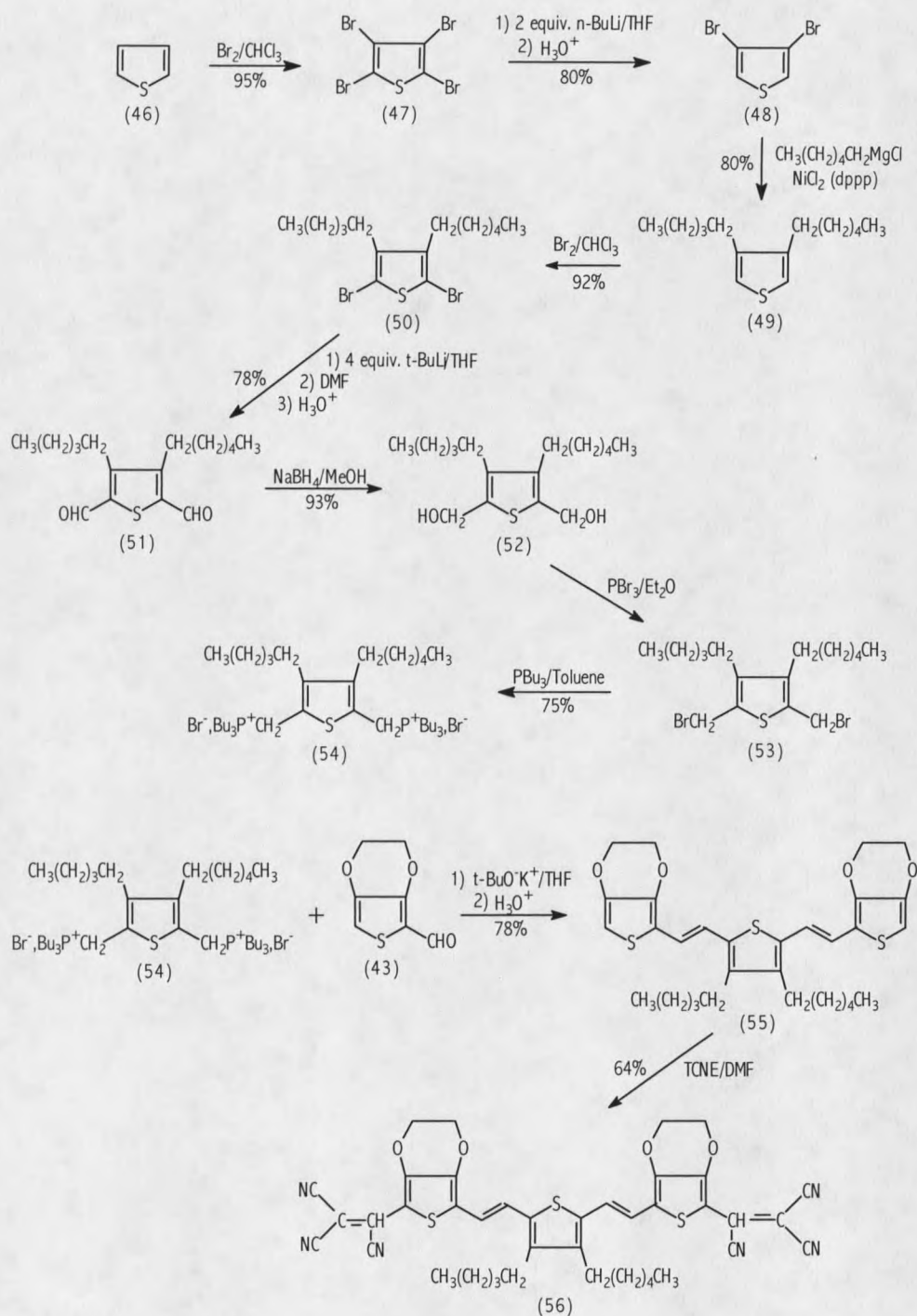


**Scheme 6:** Synthesis of 1,2-bis-(5'-tricyanovinyl-EDOT)ethylene.

In order to improve the solubility of the di-substituted tricyanovinyl polyene, it was decided to incorporate alkyl chains within the molecule. Scheme 7 illustrates the ten step synthesis of 3,4-dihexyl-2,5-bis[(5'-tricyanovinyl-3',4'-ethylenedioxy-2'-thienyl)] thiophene (**56**). The thiophene starting material (**46**) was converted to 2,3,4,5-tetrabromothiophene (**47**) using liquid bromine in chloroform. The bromine molecules in the 2 and 5 positions were then removed with two equivalents of *n*-butyllithium to give (**48**), and then the bromines in the 3 and 4 positions were replaced with hexyl groups using hexylmagnesium chloride in ether to give (**49**). Both (**48**) and (**49**) are high boiling liquids that can be purified by vacuum distillation in high yield. This nickel catalyzed coupling reaction of the Grignard reagent and the aromatic bromide had to be done in dry diethyl ether. Attempts to run the reaction in dry tetrahydrofuran resulted in very poor yields.

Next, the 2 and 5 positions on the thiophene ring were rebrominated as before and then converted to aldehyde functionalities with four equivalents of *t*-butyllithium and DMF giving the di-aldehyde product (**51**). This product was purified by column chromatography and then converted to the bis-Wittig salt by reduction of the aldehyde groups with NaBH<sub>4</sub> to the alcohols (**52**), followed by conversion of the CH<sub>2</sub>OH groups to CH<sub>2</sub>Br (**53**) with phosphorus tribromide, and finally reacting this product with tri-*n*-butylphosphine in toluene to give the bis-Wittig salt intermediate (**54**). The bis-Wittig salt was then coupled to two equivalents of 3,4-ethylenedioxythiophene-2-carboxaldehyde (**43**) forming the two ethene bridges in (**55**). Finally, (**55**) was reacted with TCNE in DMF to give the desired di-substituted product (**56**). The solubility of the final product was sufficient enough to allow purification of small amounts (< 100mg) via column chromatography. Larger quantities are best purified using a Soxhlet extractor as was done for (**45**).





**Scheme 7:** Synthesis of 3,4-dihexyl-2,5-bis[(5'-tricyanovinyl-3',4'-ethylenedioxy-2'-thienyl)]thiophene.

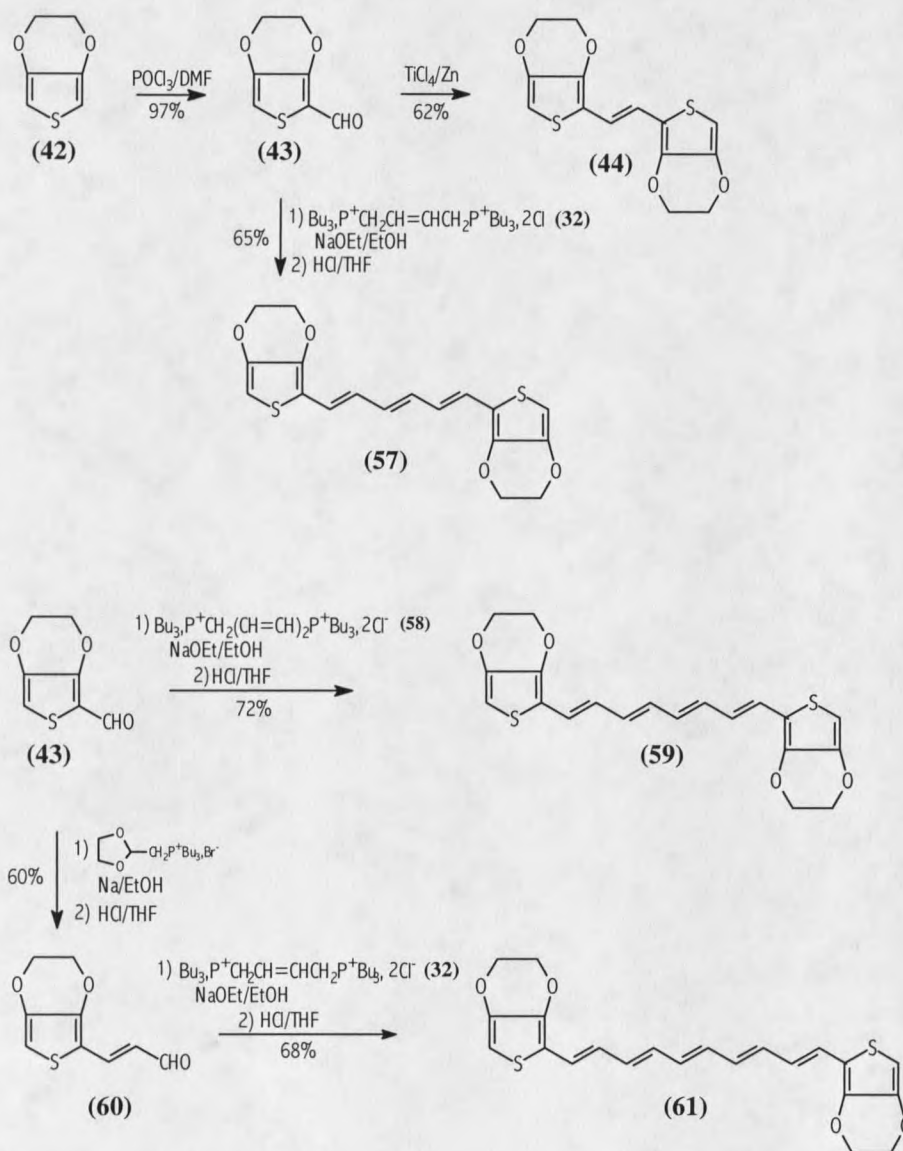
Synthesis of  $\alpha,\omega$ -Bis-(ethylenedioxythienyl)polyenes for use as Electron-Donating Chromophores.

A series of bis-(ethylenedioxythienyl)polyenes with varying numbers of conjugated double bonds was synthesized as illustrated in Scheme 8 to determine their absorption characteristics and evaluate their electron-donating capabilities.

The synthesis of the first polyene with  $n=1$  double bond (**44**) has already been described. The synthesis of 1,6-bis-(3',4'-ethylenedioxy-2'-thienyl)-1,3,5-hexatriene (**57**) with  $n=3$  double bonds was performed via a Wittig condensation reaction by refluxing (**43**) with the bis-Wittig salt (**32**) in ethanol in the presence of sodium ethoxide. The resulting orange crystals were then purified by recrystallizing from ethanol and toluene. The synthesis of 1,8-bis-(3',4'-ethylenedioxy-2'-thienyl)-1,3,5,7-octatetraene (**59**) with  $n=4$  double bonds was performed in the same manner, but the longer chain bis-Wittig salt (**58**) was used. This product consisted of flaky orange/brown crystals that recrystallized well from ethyl acetate.

To synthesize 1,10-bis-(3',4'-ethylenedioxy-2'-thienyl)-1,3,5,7,9-decapentaene (**61**) with  $n=5$  double bonds, the aldehyde (**43**) first had to be extended to 3-(3',4'-ethylenedioxy-2'-thienyl)-2-propenal (**60**) via Wittig methodology using Spangler et al.'s oxopropenylation methodology.<sup>19</sup> This oxopropenylation reaction should be followed via NMR to insure that no starting material remains, otherwise, it is very hard to remove in the purification process. The extended aldehyde (**60**) may be purified by column chromatography or by recrystallizing from ethyl acetate, and then refluxed with the bis-Wittig salt (**32**) in ethanol in the presence of sodium ethoxide to give the desired

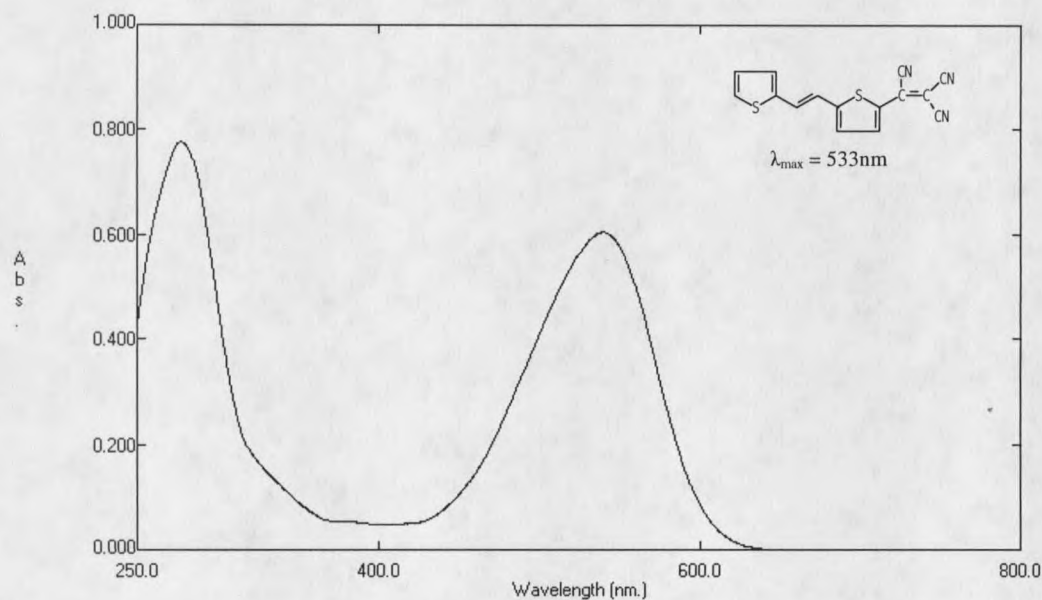
product **(61)**. This product consisted of brown crystals that were recrystallized from ethyl acetate.



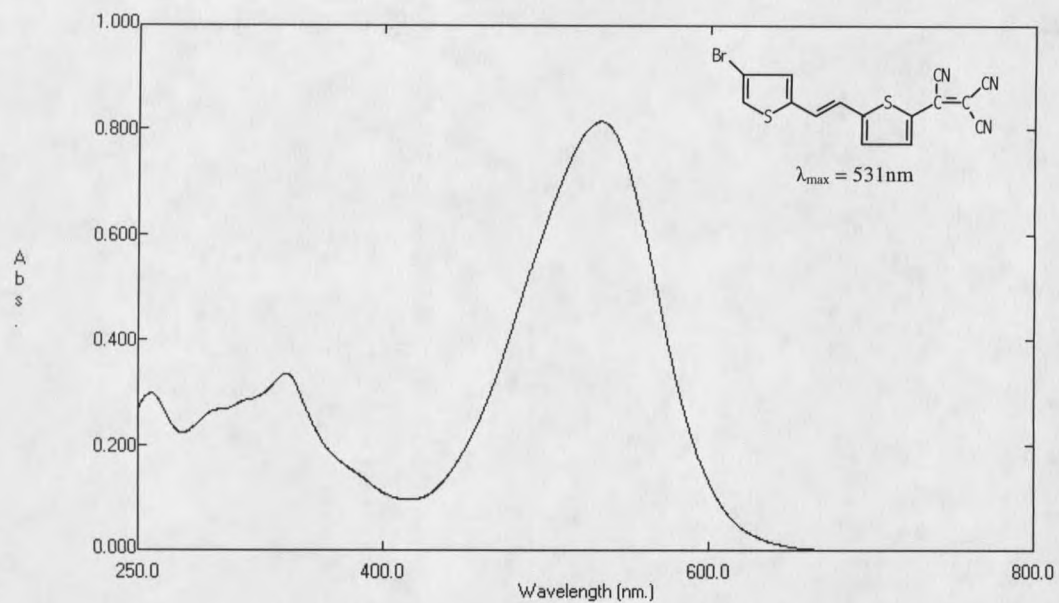
**Scheme 8:** Synthesis of some Bis-(3,4-ethylenedioxythienyl) polyenes with  $n=1, 3, 4,$  and  $5$  double bonds.

### UV/VIS Spectra Characteristics of the Chromophores

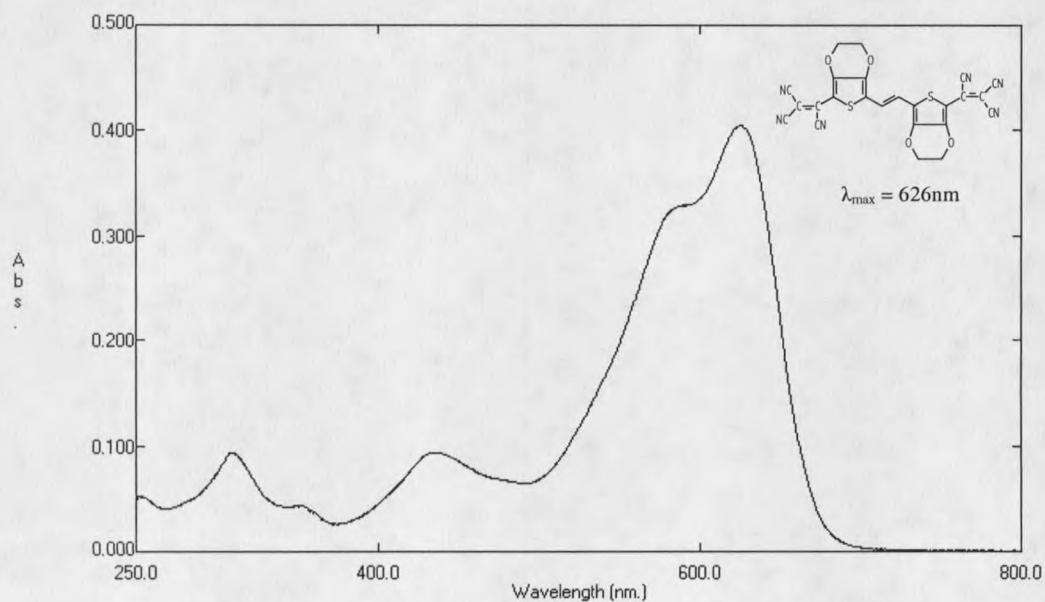
UV/VIS spectroscopy was used to analyze the absorption characteristics of all the chromophores that were synthesized. Both the acceptor and donor chromophores were tested in solutions of methylene chloride. While the acceptors were only tested in their neutral state to determine the wavelength of peak absorption and the extinction coefficient, the donors were tested in the neutral state and after oxidatively doping with  $\text{SbCl}_5$  to form the bipolaron. However, because of the instability of the bipolaronic charged state, the extinction coefficient of this state could not be accurately determined. Figures 11 through 18 show the absorption characteristics of each chromophore. Table 2 gives a summary of the wavelengths of maximum absorption for the neutral and charged states, and also gives the extinction coefficients for all chromophores tested.



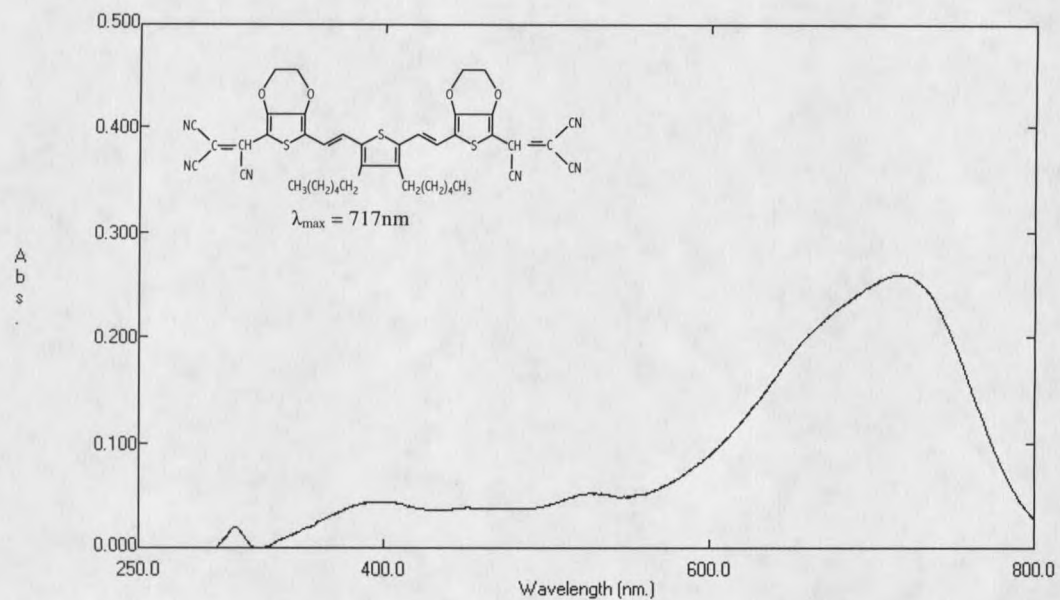
**Figure 11:** Absorption spectra for neutral Chromophore (34).



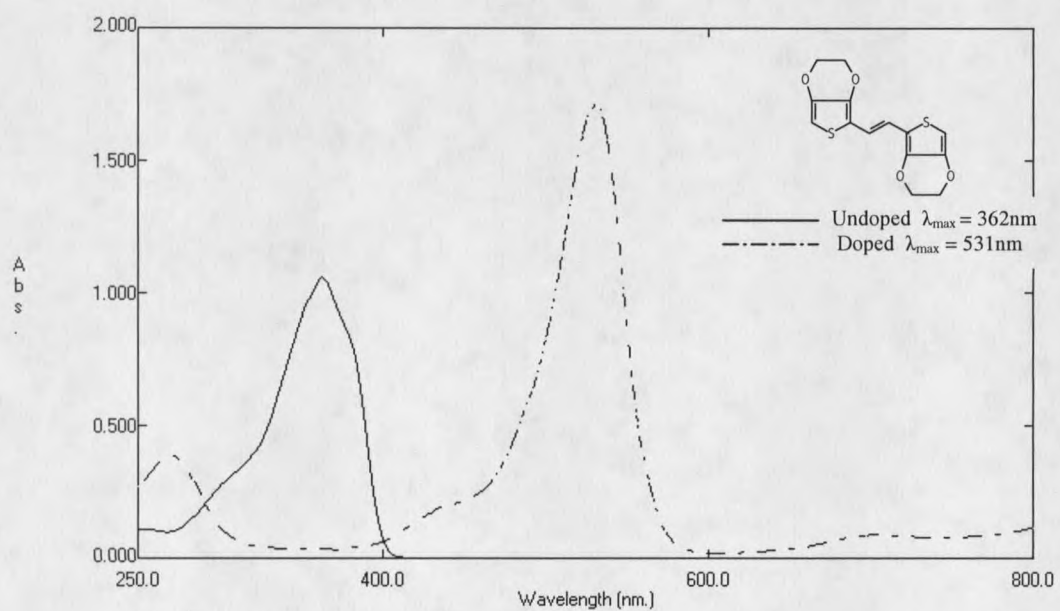
**Figure 12:** Absorption spectra for neutral Chromophore (41).



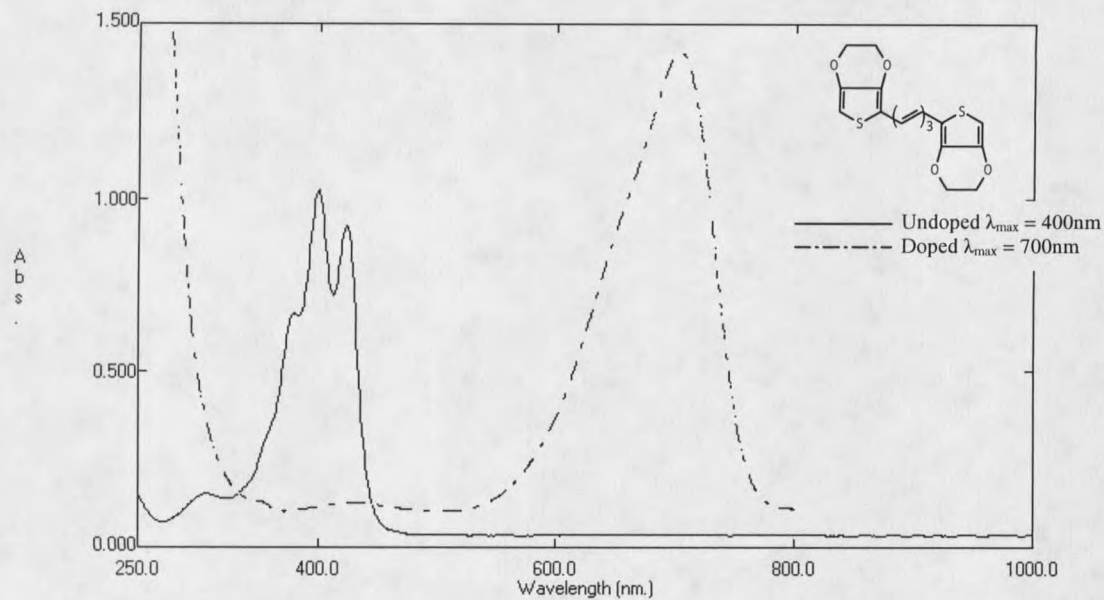
**Figure 13:** Absorption spectra for neutral Chromophore (45).



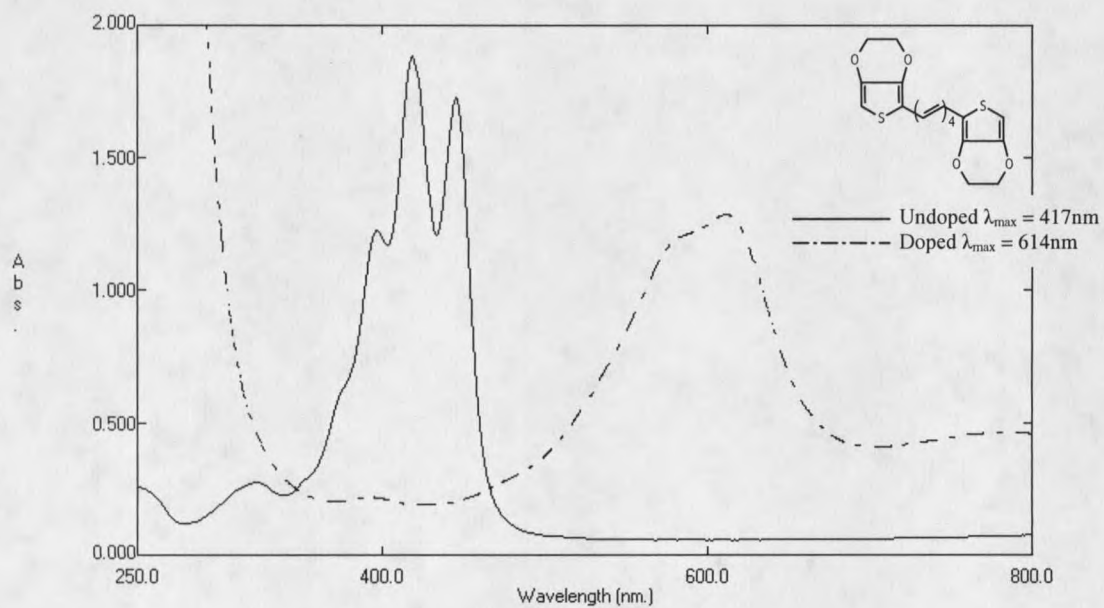
**Figure 14:** Absorption spectra for neutral Chromophore (56).



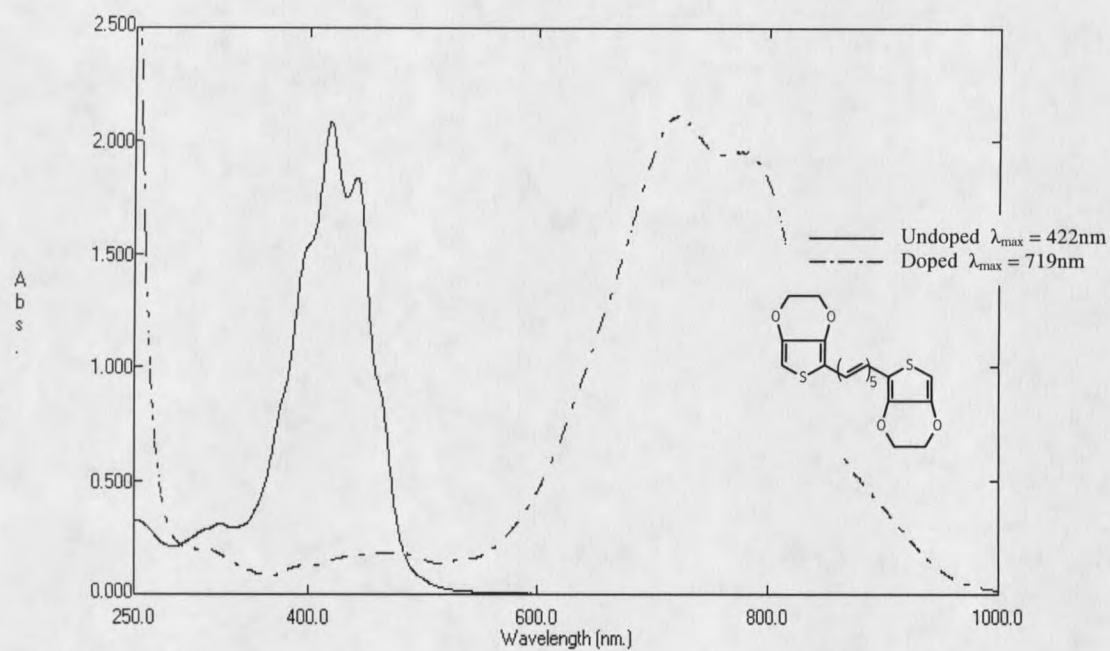
**Figure 15:** Absorption spectra for neutral and doped Chromophore (44).



**Figure 16:** Absorption spectra for neutral and doped Chromophore (57).



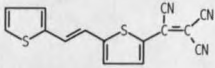
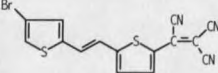
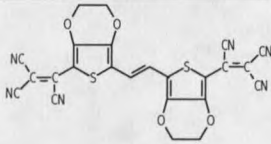
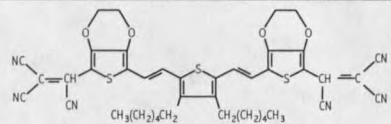
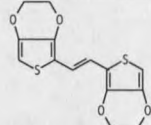
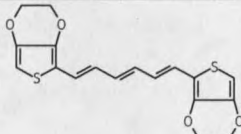
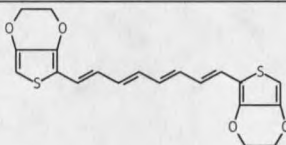
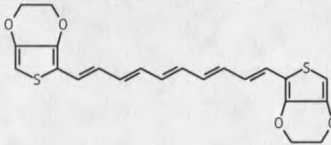
**Figure 17:** Absorption spectra for neutral and doped Chromophore (59).



**Figure 18:** Absorption spectra for neutral and doped Chromophore (61).



**Table 2:** Wavelengths of maximum absorption and extinction coefficients for each chromophore.

Chromophore	$\lambda_{\max}$ neutral (nm)	$\lambda_{\max}$ bipolaron (nm)	$\epsilon_{\max}$ neutral ( $M^{-1} cm^{-1}$ )
	539	*	35500
	533	*	30300
	626	*	20800
	717	*	24600
	362	531	51600
	400	700	76200
	417	614	81800
	422	721	85100

\* Not measured

## CHAPTER 5

## CONCLUSIONS

Electron-accepting chromophores based on bis-thienylpolyene structures incorporating tricyanovinyl groups have been synthesized. Although it is relatively easy to synthesize the mono-substituted chromophores, the di-substituted chromophores incorporating a tricyanovinyl group on each end of the molecule are more difficult to prepare. However, by substituting the electron-rich EDOT moiety in place of the thiophene unit, the disubstitution process is more facile. The first examples of these new acceptor chromophores, bis-(tricyanovinyl-EDOT)ethylene (**45**) and 3,4-dihexyl-2,5-bis[(5'-tricyanovinyl-3',4'-ethylenedioxy-2'-thienyl)] thiophene (**56**), display strong absorption bands at ca. 626 nm and 717 nm respectively. This is farther into the red region of the spectrum than any of the other acceptors that have been tested to date. This indicates that these new materials may be useful for optical pumping of the reverse saturable absorption process in the red region of the visible spectrum.

Donor chromophores based on the bis-(EDOT)polyenes containing varying numbers of conjugated double bonds were also synthesized. UV/VIS spectroscopy showed that the peak absorption wavelength and extinction coefficient of these chromophores increases as the number of conjugated double bonds increases. Although these molecules do form bipolaronic charged states in solution when oxidatively doped with  $\text{SbCl}_5$ , this charged state is not stable -- probably due to the instability of the positive charges on the terminal  $\alpha$ -positions of the thiophene ring. Therefore, in order for these

chromophores to function as reverse saturable absorbers in optical power limiters, electron-donating groups or another blocking group would need to be incorporated onto the ends of the molecule.

## CHAPTER 6

## EXPERIMENTAL SECTION

General

Proton ( $^1\text{H}$ ) and carbon ( $^{13}\text{C}$ ) nuclear magnetic resonance (NMR) spectra for the following compounds were recorded on Bruker AM-250, DRX-250 (250MHz) or AM-300, DRX-300 (300 MHz) spectrometers. All chemical shifts are reported as parts-per-million (ppm) relative to tetramethylsilane (TMS). Peak multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and dd = doublet of doublets.  $J$  coupling values are reported in Hertz (Hz).  $^{13}\text{C}$  NMR could not be obtained on the tricyano-substituted compounds due to their very poor solubility.

Low resolution mass analysis using electron impact ionization was performed on a VG 70E-HF double focusing magnetic mass spectrometer (Micromass Instruments; Manchester, UK) operating at a mass resolution of 1500.

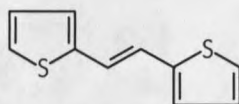
Optical absorption spectra were recorded on a Shimadzu UV-3101 PC UV-VIS-IR spectrometer. The compounds were analyzed as solutions in  $\text{CH}_2\text{Cl}_2$  in a quartz cuvette with a 1 cm path length.

Melting points for all compounds were recorded using a TA Instruments DSC 2920 differential scanning calorimeter (DSC) and are uncorrected.

All column chromatography was performed using Whatman 70-230 mesh, 60A silica gel. Thin layer chromatography (TLC) was performed using Selecto Scientific 200 micron Silica Gel 60.

The following abbreviations are used throughout this section: ethanol (EtOH), chloroform (CHCl<sub>3</sub>), diethyl ether (Et<sub>2</sub>O), dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), methanol (MeOH), tetrahydrofuran (THF), ethyl acetate (EtOAc), tetracyanoethylene (TCNE), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), magnesium sulfate (MgSO<sub>4</sub>), N,N-Dimethylformamide (DMF), lithium aluminum hydride (LAH), sodium borohydride (NaBH<sub>4</sub>), sodium hydroxide (NaOH), sodium chloride (NaCl), hydrochloric acid (HCl), and 3,4-ethylenedioxythiophene (EDOT). All of these chemicals were obtained from either Fisher Scientific or Aldrich Chemical Companies and were used as received. When completely anhydrous THF was required, the solvent was freshly distilled from a mixture containing sodium metal and benzophenone.

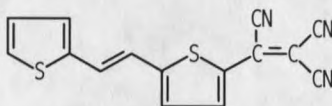
### Synthetic Procedures



#### **1,2-Bis-(2'-thienyl)ethene (27)**

TiCl<sub>4</sub> (15.7 mL, 0.143 mol) was added dropwise to 300 mL dry THF at 0° C under N<sub>2</sub>. Powdered Zn (18.6g, 0.285 mol) was added slowly to the mixture which was then heated to reflux for 30 minutes. After recooling to 0° C, thiophene-2-carboxaldehyde (**29**) (6.7 mL, 0.0713 mol) was added dropwise, and the reaction mixture

was again heated to reflux for 2.5 hours, cooled to room temperature, and poured into 500 mL water. The product was extracted with  $\text{CHCl}_3$  (4 X 100 mL), washed with water (3 X 50 mL), and dried with  $\text{MgSO}_4$ . After filtration to remove the  $\text{MgSO}_4$ , the solvent was removed by roto-evaporation and the residue was purified through a silica column eluting with  $\text{CH}_2\text{Cl}_2$ . The dark yellow solid was then recrystallized from EtOH yielding bright yellow crystals of **(27)** (5.21g, 76%). mp: 131-133°C;  $^1\text{H}$  NMR: 6.97 (dd, 2H,  $J=5$  Hz,  $J=3.5$  Hz aromatic H), 7.02 (d, 2H,  $J=3.5$ Hz, aromatic H), 7.04 (s, 2H, CH=CH), 7.16 (d, 2H,  $J=5$  Hz, aromatic H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 121.5, 124.3, 126.0, 127.6, 142.4; (LRMS( $\text{EI}^+$ ) calc. for  $\text{C}_{10}\text{H}_8\text{S}_2$  192.3, found 192.3).

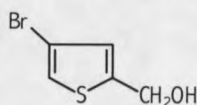


### 1-[2'-(5'-tricyanovinyl)thienyl]-2-[2''-thienyl]ethene (**34**)

TCNE (2.7g, 21.1 mmol) was added to a solution of **(27)** (1.84g, 9.57mmol) in 150 mL DMF. The mixture was heated to 90° C for 4 hours, then cooled to room temperature and poured into 300 mL cold water. The product was extracted with  $\text{CH}_2\text{Cl}_2$  (4 X 100 mL), washed with water (3 X 50 mL), and dried with  $\text{MgSO}_4$ . After filtration, the solvent was removed by roto-evaporation and the remaining black sludge was purified through a silica column, eluting with  $\text{CH}_2\text{Cl}_2$ . The final product consisted of glittery black crystals of **(34)** (2.08g, 74%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 7.03 (d, 1H,  $J=16$  Hz, CH=CH), 7.07 (dd, 1H,  $J=4.5$  Hz,  $J=3.5$  Hz, aromatic H), 7.21 (d, 1H,  $J=3.5$  Hz, aromatic H), 7.25 (d, 1H,  $J=3.5$  Hz, aromatic H), 7.39 (d, 1H,  $J=4.5$  Hz, aromatic H),

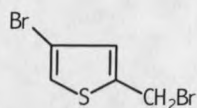
7.44 (d, 1H,  $J=16$  Hz, CH=CH), 7.96 (d, 1H,  $J=4.5$  Hz, aromatic H);  $\lambda_{\max}/\text{nm}$  ( $\epsilon_{\max}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) 539 (35500); (Anal. Calc. for  $\text{C}_{15}\text{H}_7\text{N}_3\text{S}_2$ : C 61.4%, H 2.41%, N 14.33%.

Found: C 61.22%, H 2.46%, N 13.84%).



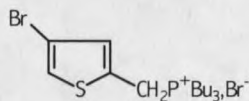
#### 4-Bromo-2-hydroxymethylthiophene (36)

A solution of  $\text{NaBH}_4$  (0.412g, 0.0117mol) in MeOH (10 mL) and NaOH (20%, 4.0 mL) was added dropwise to a solution of (35) (5.0g, 0.023mol) dissolved in 30 mL THF and 30 mL MeOH at room temperature. The mixture was stirred at room temperature for 2.5 hours and then poured into 100 mL water. The product was extracted with EtOAc (3 X 100 mL), washed with water (1 X 25 mL) and with NaCl brine (2 X 25 mL), and dried with  $\text{MgSO}_4$ . After filtration, the solvent was removed under vacuum and the product was purified through a silica column, eluting with 70%  $\text{CH}_2\text{Cl}_2$  and 30% EtOAc. The final product consisted of a yellow oil of (37) (4.08g, 93%).  $^1\text{H NMR}$ : 1.91 (s, 1H, OH), 4.80 (s, 2H,  $\text{CH}_2$ ), 6.89 (s, 1H, aromatic H), 7.18 (s, 1H, aromatic H); (Anal. Calc. for  $\text{C}_5\text{H}_5\text{OBrS}$ : C 31.1%, H 2.61%. Found: C 30.87%, H 2.67%).



### 2-Bromomethyl-4-bromothiophene (37)

A solution of **(36)** (4.50g, 0.0233mol) in 25 mL dry THF was added dropwise to a solution of phosphorus tribromide (2.21 mL, 0.0116 mol) in 200 mL dry THF under  $N_2$  at  $0^\circ C$ . After addition was complete, the mixture was allowed to rise to room temperature and stirred for an additional six hours. The solution was then neutralized with concentrated  $Na_2CO_3$  and the product was extracted with  $Et_2O$  (4 X 100 mL), washed with NaCl brine (3 X 50 mL), and dried with  $MgSO_4$ . After the  $MgSO_4$  was removed by filtration, approximately half of the solvent was removed by roto-evaporation and the crude product was carried into the next step of the synthesis immediately and without removal of the remainder of the solvent to prevent product decomposition.

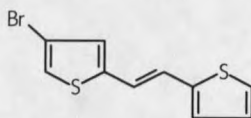


### (4-Bromo-2-thienyl)methyltributylphosphonium bromide (38)

To a solution of **(37)** in approximately 300 mL  $Et_2O/THF$  at room temperature under  $N_2$ , there was added tributylphosphine (5.82 mL, 0.0233mol) dropwise. The mixture was stirred for 36 hours. The reaction mixture was then allowed to sit at  $0^\circ C$  for a couple of hours and the resulting white precipitate was removed by vacuum filtration. The crystals were washed thoroughly with cold  $Et_2O$  to remove any traces of tributylphosphine and then recrystallized from  $EtOAc$  giving the pure Wittig salt **(38)**

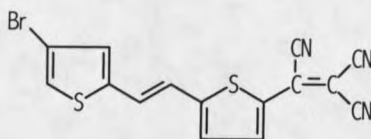


(8.0g, 75%). mp: 154-155.5°C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 0.92 (t, 9H,  $J=6.5$  Hz,  $\text{CH}_3$ ), 1.47 (m, 12H,  $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$ ), 2.43 (m, 6H, P- $\text{CH}_2\text{-CH}_2$ ), 4.76 (d, 2H,  $J=14.5$  Hz, ring-P- $\text{CH}_2$ ), 7.15 (s, 1H, aromatic H), 7.26 (s, 1H, aromatic H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 13.4, 18.6, 19.0, 23.8, 23.8, 23.9, 24.0, 123.6, 132.2; (Anal. Calc. for  $\text{C}_{17}\text{H}_{31}\text{PBr}_2$ : C 44.55%, H 6.82%. Found: C 44.51%, H 7.07%).



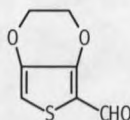
### 1-[2'-(4'-Bromo)thienyl]-2-[2''-thienyl]ethene (**39**)

Potassium *t*-butoxide (8.2 mL, 8.2 mmol, 1 M soln in THF) was added dropwise to a solution of aldehyde (**29**) (0.55 g, 4.9 mmol) and the Wittig salt (**38**) (2.5g, 5.4 mmol) in 150 mL dry THF under  $\text{N}_2$ . The solution was stirred at room temperature for 4 hours and then poured into 200 mL cold water. The solution was then acidified with 3M HCl and allowed to stand for several hours. The resulting yellow precipitate was removed by vacuum filtration and recrystallized from MeOH to give pure (**39**) (1.16 g, 87%). mp: 102.5-104°C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 6.47 (d, 1H,  $J=12$  Hz,  $\text{CH}=\text{CH}$ ), 6.63 (d, 1H,  $J=12$  Hz  $\text{CH}=\text{CH}$ ), 6.90-7.04 (m, 4H, aromatic H), 7.19 (d, 1H,  $J=5$  Hz, aromatic H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 120.0, 121.1, 122.7, 125.0, 126.8, 127.8; (Anal. Calc. for  $\text{C}_{10}\text{H}_7\text{BrS}_2$ : C 44.28%, H 2.60%. Found: C 44.01%, H 2.47%).



### 1-[2'-(4'-Bromo)thienyl]-2-[2''-(5''-tricyanovinyl)thienyl]ethene (**41**)

To a solution of TCNE (0.113g, 0.885mmol) in 10 mL DMF, was added a solution of (**39**) (0.20g, 0.738 mmol) in 20 mL DMF with stirring. The mixture was heated to 90°C for 4 hours and then poured into 200 mL cold water. The product was extracted with CH<sub>2</sub>Cl<sub>2</sub> (4 X 75 mL), washed with water (3 X 25 mL), and dried with MgSO<sub>4</sub>. The MgSO<sub>4</sub> was removed by filtration, and the solvent was removed by roto-evaporation. Purification was accomplished through a silica column, eluting with CH<sub>2</sub>Cl<sub>2</sub> to give (**41**) (0.20g, 74%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 6.92 (d, 1H, *J*=16 Hz, CH=CH), 7.03 (d, 1H, *J*=16 Hz, CH=CH), 7.07 (d, 1H, *J*=4.5 Hz, aromatic H), 7.08 (d, 1H, *J*=4.5 Hz, aromatic H), 7.20 (s, 1H, aromatic H), 7.36 (s, 1H, aromatic H); λ<sub>max</sub>/nm (ε<sub>max</sub>/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) 533 (30300); (Anal. Calc. for C<sub>15</sub>H<sub>6</sub>N<sub>3</sub>BrS<sub>2</sub>: C 48.39%, H 1.63%, N 11.29%. Found: C 48.96%, H 2.03%, N 10.78%).



### 3,4-Ethylenedioxy-2-thiophenecarboxaldehyde (**43**)

3,4-Ethylenedioxythiophene (**42**) (10.0g, 0.0703mol) and dry DMF (7.20 mL, 0.0985 mol) were added to 60 mL 1,2-dichloroethane and cooled to 0° C. POCl<sub>3</sub> (7.87 mL, 0.0844 mol) was added dropwise and the solution was allowed to rise slowly to



































