



Synthesis and charge state formation in dendrons and dendrimers incorporating dithienylpolyene moieties
by Berrak Ozer

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:

With the latest development in laser technology, protection of eye and sensors against hazardous applications is a challenging problem which requires development of new optical power limiting materials that can respond quickly and protect over a wide frequency range of the spectrum.

In this research, dithienylpolyenes with one and two double bonds have been synthesized with hydroxyl functional groups. The chromophores were converted to dendrons for convergent dendrimer synthesis by first converting the alcohol functionality to an iodide followed by condensation with 3,5-dihydroxybenzyl alcohol. Dendrons were coupled to Bisphenol A core yielding G-O dendrimers containing four photonic-active chromophores.

Absorbing characteristics of the chromophores, dendrons and model dendrimers were examined in solution. All three forms of the dithienylpolyenes formed highly absorbing bipolaronic dications in solution whose absorbance is in the range of 500-650 nm. The compounds are currently being evaluated as optical limiting materials operating by reverse saturable absorption from photogenerated bipolaronic states.

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**A thesis submitted in partial fulfillment
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Master of Science

in

Chemistry

**MONTANA STATE UNIVERSITY
Bozeman, Montana**

April 2000

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APPROVAL

of a thesis submitted by

Berrak Ozer

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,

Charles W. Spangler

Charles W. Spangler
(Signature)

4/12/00
Date

Approved for the Department of Chemistry and Biochemistry

Paul Grieco

Paul Grieco
(Signature)

4-12-00
Date

Approved for the College of Graduate Studies

Bruce McLeod

Bruce R. McLeod
(Signature)

4-14-00
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ABSTRACT

With the latest development in laser technology, protection of eye and sensors against hazardous applications is a challenging problem which requires development of new optical power limiting materials that can respond quickly and protect over a wide frequency range of the spectrum.

In this research, dithienylpolyenes with one and two double bonds have been synthesized with hydroxyl functional groups. The chromophores were converted to dendrons for convergent dendrimer synthesis by first converting the alcohol functionality to an iodide followed by condensation with 3,5-dihydroxybenzyl alcohol. Dendrons were coupled to Bisphenol A core yielding G-0 dendrimers containing four photonic-active chromophores.

Absorbing characteristics of the chromophores, dendrons and model dendrimers were examined in solution. All three forms of the dithienylpolyenes formed highly absorbing bipolaronic dications in solution whose absorbance is in the range of 500-650 nm. The compounds are currently being evaluated as optical limiting materials operating by reverse saturable absorption from photogenerated bipolaronic states.

CHAPTER 1

INTRODUCTION

Latest improvements in laser technology have led to the production of advanced lasers that are inexpensive, small and can operate at different wavelengths. Lasers, which have become part of our everyday lives, also emerged as destructive weapons that can damage eye and optical sensors.¹ With increasing usage of lasers in hazardous applications involving wavelengths that can damage the human eye, there is a need for materials that can respond quickly and be frequency agile. As a result, the design and synthesis of new optical power limiting materials is emerging as a highly attractive frontier.

During the last few years our research group has been focused on designing new organic chromophores that function as optical power limiters (OPLs). These materials should transmit light under ambient conditions, but absorb most of intense laser light when needed. An optical limiter is a device that can attenuate optical signals to hold the output below a given level, but maintain a high transmittance for low level signals. For many applications, including protection of optical sensors from laser-induced damage, it is desirable for an optical limiter to have high linear transmittance. The output of what is often referred to as an ideal optical limiter is shown in Figure 1. E_L is the energy at which limiting begins and E_D is the energy at which the limiting device is damaged. The limiter should have a high linear transmittance, a variable and potentially low limiting threshold

(the input corresponding to the breaking point in the curve), a fast response (picoseconds or faster) and a broadband response (e.g. the entire visible spectrum).² In most cases, the limiting does not occur with a sharp threshold as indicated in Figure 1, but changes from high to low transmittance gradually.

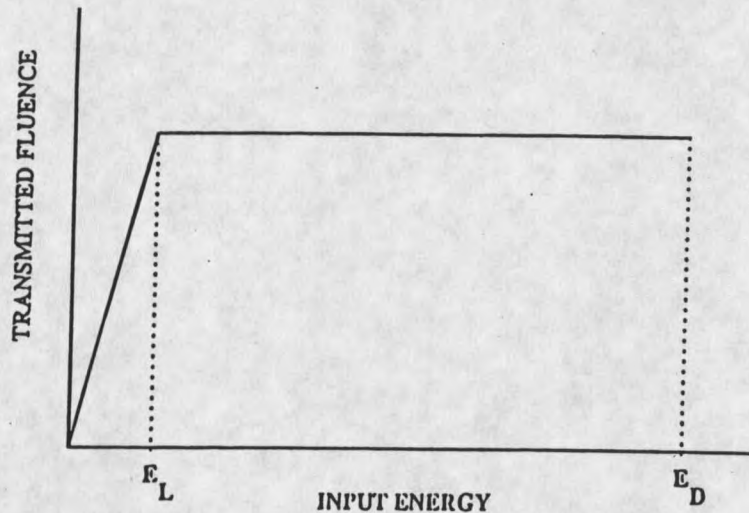


Figure 1. The Output Energy of an Ideal Optical Limiting Device as a Function of the Input Energy

There are two important approaches to the design of materials for optical power limiting, one of which is to design chromophores with large two-photon cross-sections that give access to highly absorbing transient excited states. This mechanism is called optical power limiting by two-photon absorption. The other approach is reverse saturable absorption (RSA) which derives limiting capability from the photo-generation of highly absorbing charge states.³ At the current time, reverse saturable absorption plays the dominant role in designing new smart passive limiters. The first definitive observation of nonlinear effects was conducted by Franken, et al⁴ in 1961, and reverse saturable

absorbance described for solutions in anthracene in 1974.⁵ Since then indanthones⁶, metal cluster compounds⁷, porphyrins⁸, phthalocyanines^{9,10,11}, and fullerenes^{12,13} have been examined and characterized as reverse saturable absorbers.

Reverse saturable absorber chromophores become more strongly absorbing as the incident energy is increased. Chromophores can exhibit reverse saturable absorption when an excited state, which is populated by optical excitation, has an absorption cross section which is larger than the ground-state absorption cross-section over a certain spectral range.

Figure 2 illustrates the energy level diagram for reverse saturable absorber chromophore. First, the S_0 to S_1 transition occurs. As the intensity of the laser irradiation increases, the S_1 to S_n or the S_1 to another transient state (TS) transitions via intersystem crossing become dominant, and more light is absorbed. The identity of the transient excited states could be triplet or charged states, such as polaronic radical-ions or bipolaronic dications, resulting from electron transfer pathways.

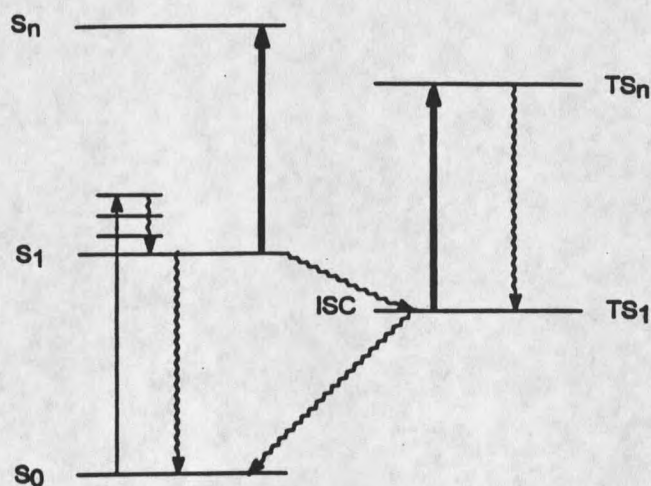


Figure 2. Energy Level Diagram for RSA Chromophore Behavior

CHAPTER 2

HISTORICAL SECTION

Synthesis of Dithienylpolyenes

There were very few literature reports of the synthesis of dithienylpolyenes with more than two double bonds until this class of polyenes were synthesized by Spangler et al. in 1991.¹⁴ α,ω -Dithienylpolyenes were synthesized from appropriately substituted 2-thienyl or 3-thienyl carbaldehydes or propenals by condensation with either bis-Wittig reagents or bis-phosphonate esters (Horner-Emmons-Wadsworth modifications) containing one or two double bonds. These reactions are illustrated in Figure 3.

Dithienylpolyenes containing mesomerically interactive substituent groups can be oxidatively doped with SbCl_5 in solution to give stabilized bipolaron-like charge states. The problem with the synthesis of dithienylpolyenes which contain more than six double bonds is their increasing insolubility.¹⁵ In order to study the bipolaron formation of dithienyl polyenes with more than six double bonds, a long chain alkylthio group was incorporated in the 5-position of each thiophene ring which allowed the synthesis of dithienyl polyenes containing up to ten double bonds, as outlined in Figure 4.¹⁶

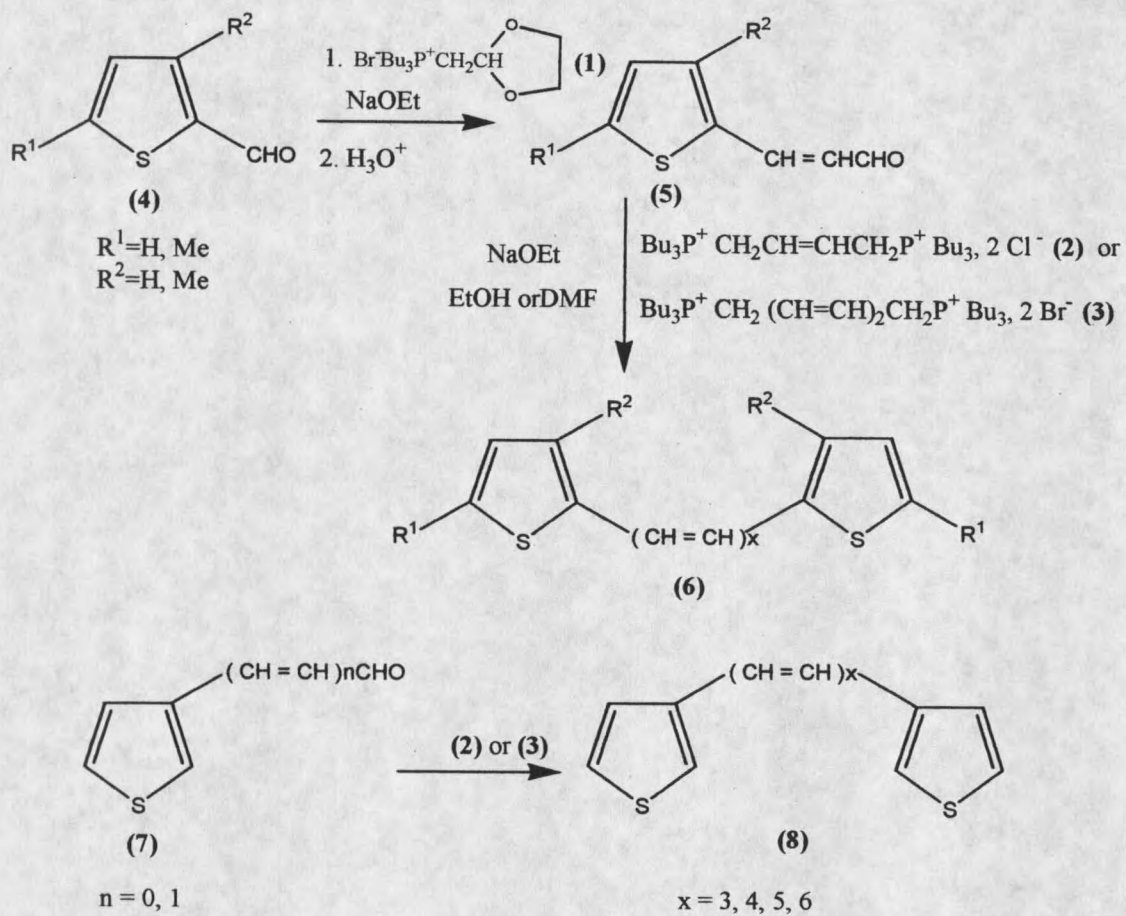


Figure 3. Synthesis of Dithienylpolyenes

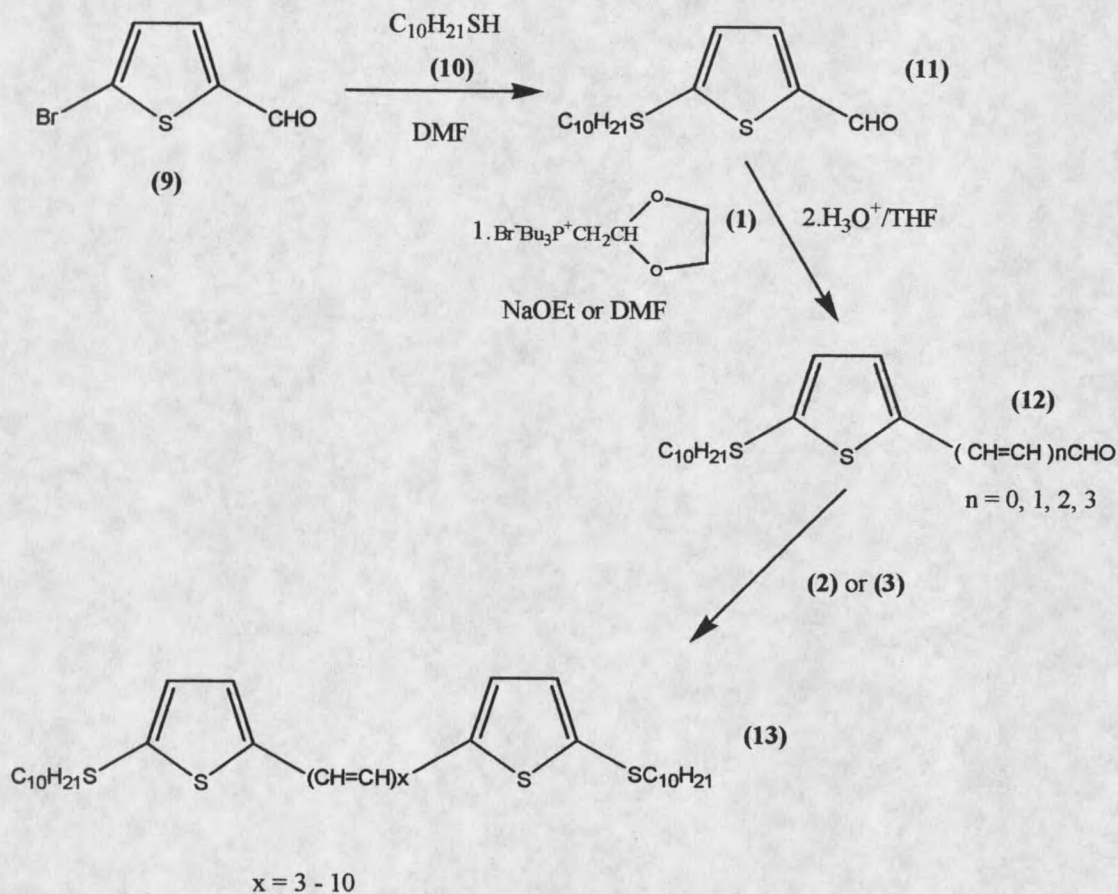


Figure 4. Synthesis of Dithienylpolyenes Incorporating Solubilizing Substituents

Although dithienyl polyenes substituted with long chain alkyl thio groups had increased solubility and additional resonance stabilization of bipolaronic charge states provided by the substituent and the ring sulfur atoms, measurement of their photonic properties, such as their third-order nonlinearities by third harmonic generation (THG) still proved difficult for the longer conjugation lengths.¹⁷ Therefore, further synthetic modifications was necessary to increase the solubility of longer polyenes.

Spangler and He^{18,19} synthesized a series of 3,4-dibutylthienyl end-capped polyenes that are extremely soluble in a wide variety of solvents, including hexane. Bipolarons formed from this series are exceptionally stable, and have been obtained up to the decamer level as illustrated in Figure 5.

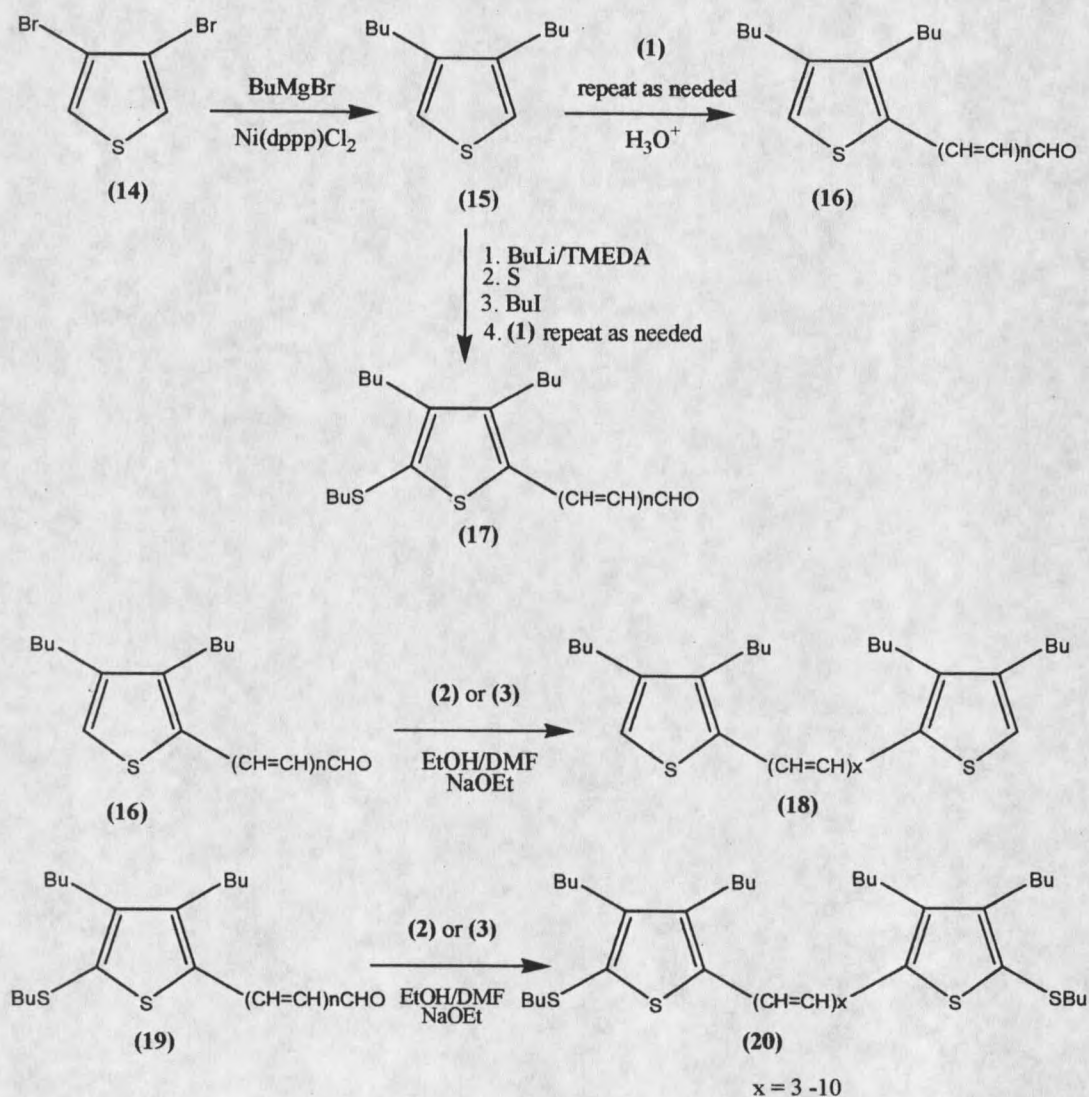
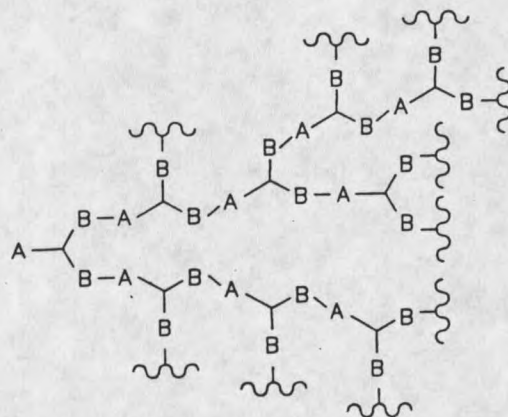


Figure 5. Synthesis of Dithienylpolyenes Incorporating Butylthio Groups

Design and Synthesis of Dendrimers

The synthesis of polymers with highly controlled molecular architectures has gained increased importance due to the rising demand for specialty polymers that possess novel properties that may prove useful in a variety of technological applications.²⁰ Dendritic macromolecules are characterized by entanglement-free hyperbranched structures that contain a very large number of chain ends at the periphery (surface) of the macromolecules.

From a historical perspective, progress towards the design of macromolecules with hyperbranched architecture could be classified in three general eras.²¹ The first period was from the late 1860's to the early 1940's, when branched structures were considered as being responsible for insoluble and intractable materials formed in polymerization reactions. The early 1940's to the late 1970's define the second period, in which branched structures were considered primarily from a theoretical perspective. Kuhn²² published the first report of the use of statistical methods for analysis of a polymer problem in 1930. Equations were derived for molecular weight distributions of degraded cellulose. After that, mathematical analysis of polymer properties and interactions flourished, and P. J. Flory has profoundly affected the design of linear and non-linear polymer chemistry, for which he received the Nobel Prize for Chemistry in 1974. During 1941 and 1942, Flory^{23,24,25,26} demonstrated theoretical and experimental evidence for the appearance of branched-chain, three-dimensional macromolecules resulting from AB_2 repeat units. (Figure 6)



(21)

Figure 6. Branched Polymer Architecture as Demonstrated by Flory by the Assembly of AB_2 -type Monomers

The modern era of cascade or dendrimer chemistry started when Vogtle²⁷ used repetition of similar and complimentary synthetic steps for the preparation of many new and exciting materials. Cascade synthesis meant reaction sequences that could be carried out repeatedly, whereby a functional group is made to react in such a way as to appear twice in the subsequent molecule.

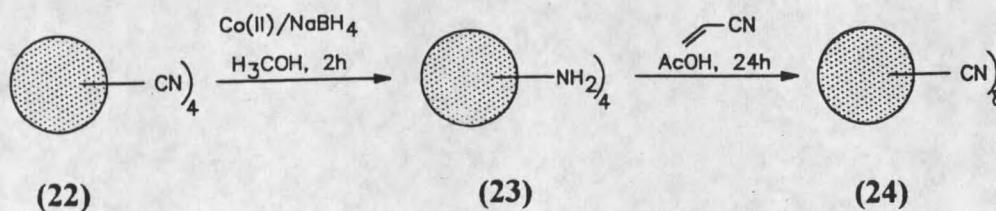
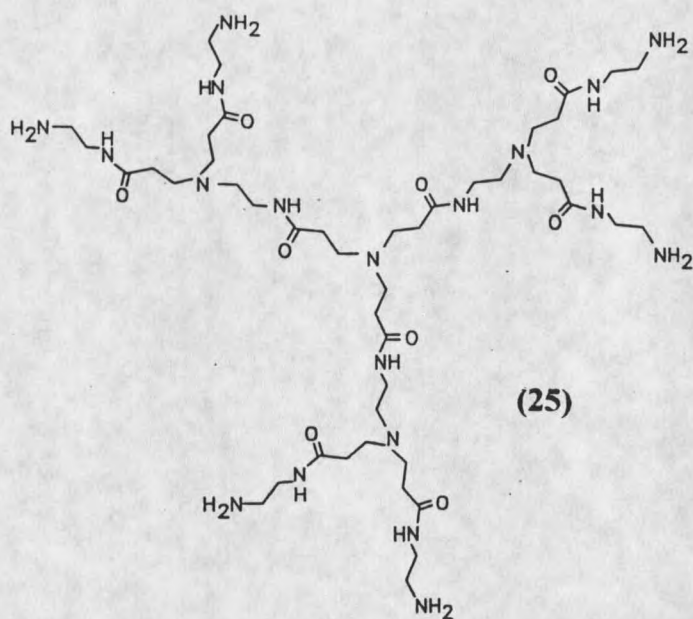


Figure 7. The Concept of "Cascade" or "Repeating" Synthesis

In the mid 1980's, Tomalia²⁸ and Newkome²⁹ published different approaches to highly branched starburst and arborol structures as illustrated in Figure 8.

General Construction

1 → 2 N-Branching (Tomalia)



1 → 3 C-Branching (Newkome)

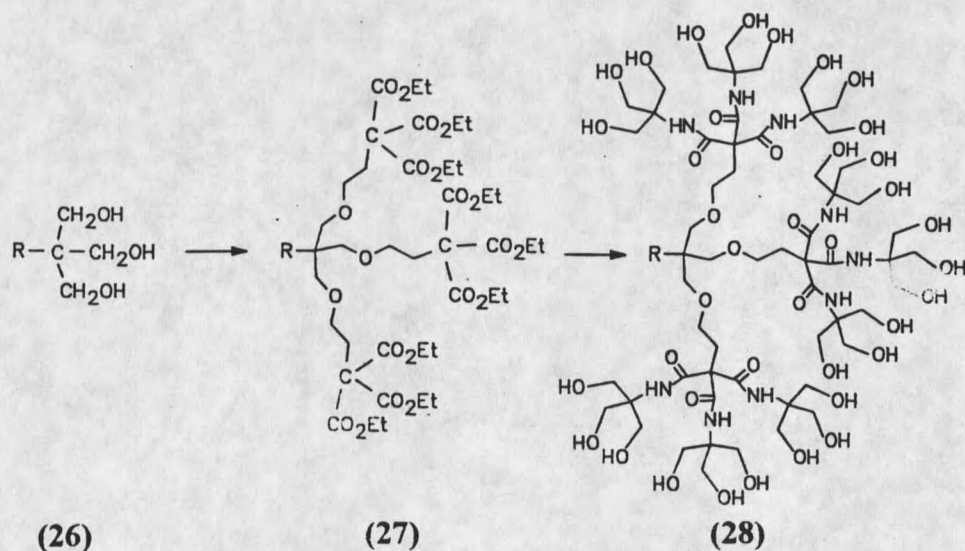


Figure 8. Tomalia et al.'s and Newkome et al.'s Original Dendrimer Motifs

These approaches all rely on the traditional divergent methodology which involves the addition of a polyfunctional monomer to a central core containing two or more coupling sites. This is followed by sequential addition-modification steps with outward growth from the central core and with the formation of an increasingly large number of identical chain ends at the outer boundaries of the polymer.

Tomalia's synthesis of the starburst dendrimer involves the initial reaction of methyl acrylate and ammonia, followed by exhaustive amidation of the resulting esters with large excesses of ethylenediamine to afford the next generation of reactive amine groups. Repetition of the two-step procedure leads to subsequent generations. (Figure 9)

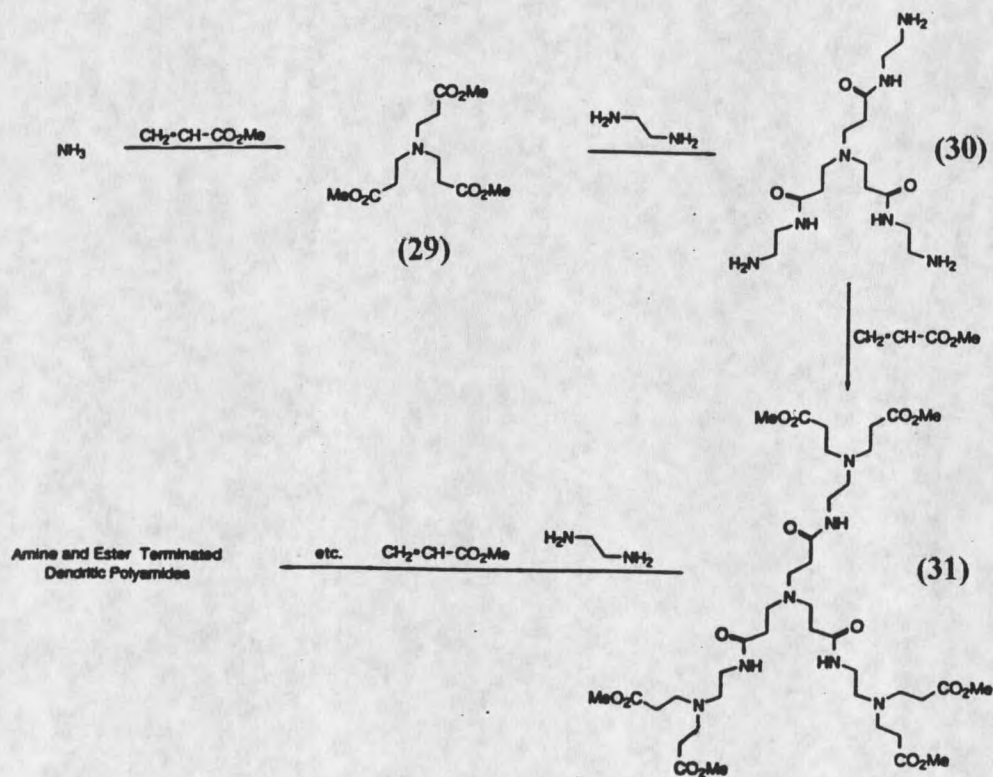


Figure 9. Synthesis of the Starburst Dendrimer

The rapid increases in the number of reactive groups at the chain ends of the growing molecule cause potential problems as growth is pursued. Any incomplete reaction of the terminal groups would lead to imperfections or failure sequences in the next generation. Also, extremely large excess amounts of reagents are required in latter stages of growth in order to prevent side reactions and to force reactions to completion which eventually leads to difficulties in purification. Starburst® dendrimers currently marketed by Dendritech Inc. and sold through Aldrich Chemical Co. are not perfect monodisperse macromolecules, but rather, dendrimers with mixtures of incomplete structures.

The convergent mode of dendritic construction is another strategy where branched polymeric arms (dendrons) are synthesized from the outside-in. In 1990, Frechet and Hawker³⁰ described the synthesis of dendritic polyether macromolecules based on 3,5-dihydroxybenzyl alcohol as the monomer unit using a novel convergent methodology. Convergent approach has two significant differences when compared to the starburst approach.³¹ First, growth begins at the outer surface of the molecule and then several dendritic fragments are attached to a polyfunctional core. Second, each generation-growth step requires limited number of reactions instead of an increasingly larger number of reactions for divergent approach.

Frechet et al.³⁰ demonstrated the convergent synthesis in a simplified scheme where the starting material **32** which contains what will eventually constitute surface functionality of the dendritic macromolecule as well as a reactive functional group (fp), condensed with monomer **33**. The monomer itself has at least two coupling sites(c) and a

protected functional group (fp). After coupling, fp is activated to fr to give **34** and the process is continued by successive repetitions, for example until the dendritic wedge, **35**, is obtained. Dendrimer **35** has a single reactive group fr at its focal point and may be coupled to a polyfunctional core such as **36** to provide the final dendritic macromolecule **37** which has 64 functional groups as illustrated in Figure 10.

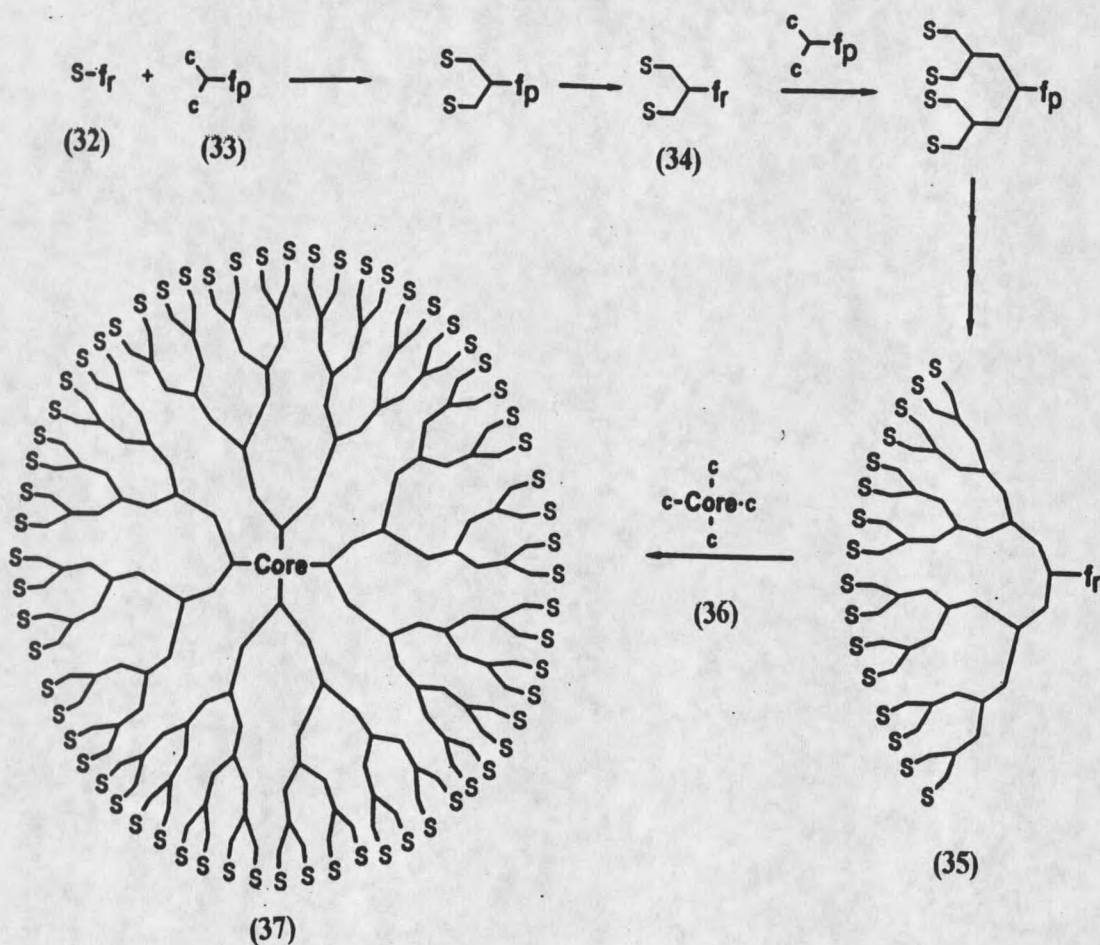


Figure 10. Convergent Methodology for Dendrimer Synthesis

One significant problem with convergent dendrimer design is the increase of steric crowding about the core during attachment as the size of the monodendron increases.

Doping Studies of Conjugated Materials

Generating highly absorbing model charge states that are necessary for an effective reverse saturable absorbing mechanism can be accomplished through a process called chemical doping.

Doping requires the addition of extra electrons or the generation of positive charges or "holes". This can be done chemically or electrochemically. For this research, discussion will be limited to oxidative and reductive doping. In oxidative doping, an oxidizing agent is introduced to the polymer in either solution or gas phase. Electrons could then be removed from the polymer forming positive polarons or positive bipolarons. In the same manner, negative polarons and negative bipolarons can be formed by reductive doping. (Figure 11)

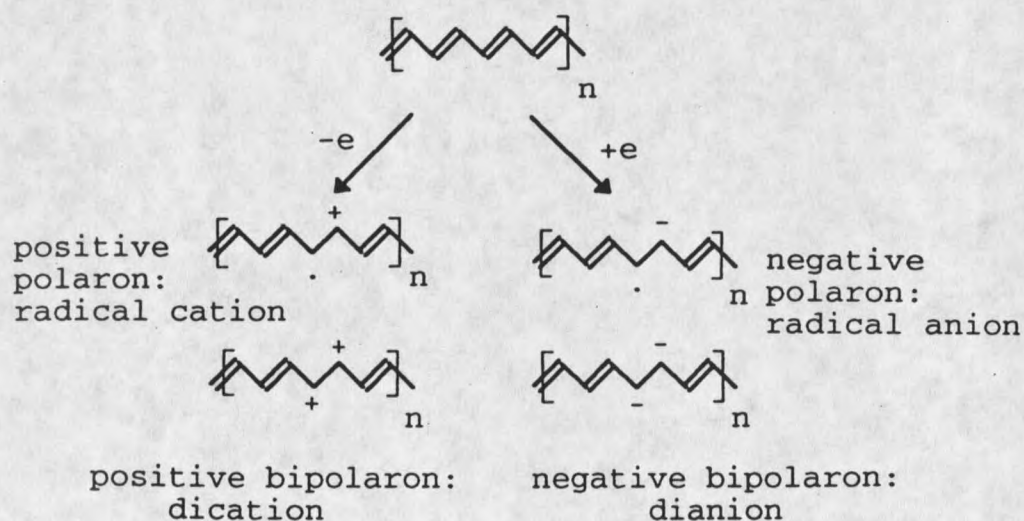


Figure 11. Generation of Polarons and Bipolarons

UV-Vis spectroscopy is the ideal tool for examining the electronic structure of polyenes. Energy absorbed in the ultraviolet and visible regions of the spectrum produces changes in the electronic energy of the molecule, affecting only the valence electrons in the highest occupied molecular orbital (HOMO). It is the non-bonding and the π electrons that are responsible for most of the absorption in the UV-VIS region. The position of the absorption band will depend on the amount of energy it takes to promote an electron in the ground state (S_0) to the first excited state (S_1), and the probability of the transition is determined by the change in the electronic structure when the molecule is in the excited state.³² The π - π^* transitions that characterize the conjugated materials will have extremely intense absorption bands. Those bands red shift with the increasing length of conjugation.

Over the past years, Spangler et al.³³ synthesized diphenyl and dithienylpolyenes and studied their oxidative doping behaviors. Doping studies were carried out in methylene chloride solutions and $SbCl_5$ was used as doping reagent. In some oxidative doping studies of diphenylpolyenes, an absorption band is observed, then it is rapidly replaced by a second absorption. This can be interpreted as oxidation of polyene to a polaron-like cation, followed by rapid oxidation to a stable bipolaron-like dication via two successful 1-electron oxidations. However in most cases, when excess doping reagent is used only a stable bipolaron-like dication is observed. (Figure 12)

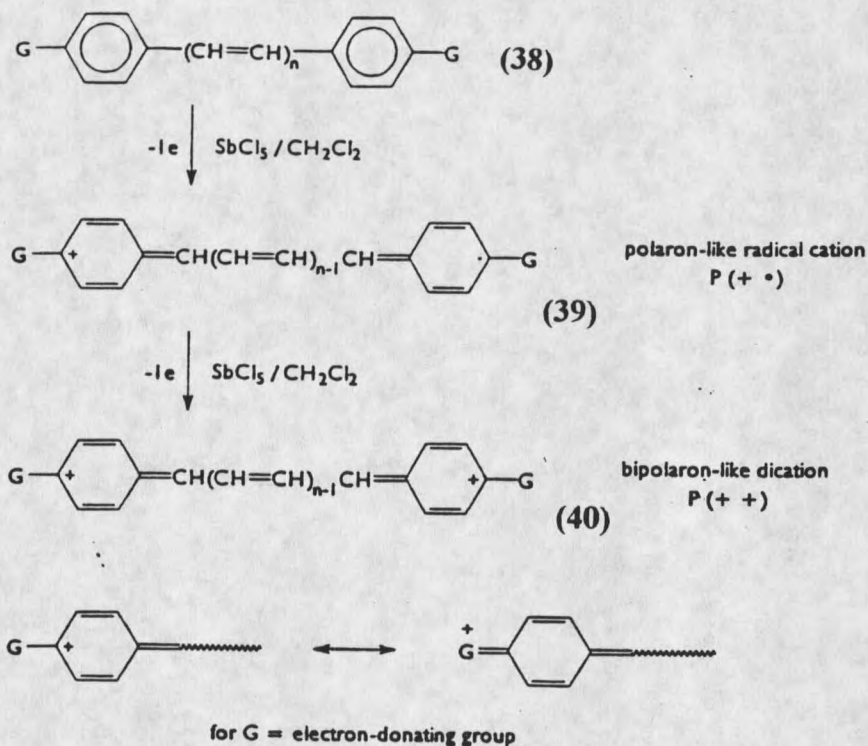
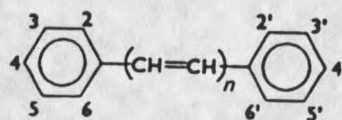


Figure 12. Oxidative Doping of Diphenylpolyenes

The dications formed in the oxidative doping are found to be greatly stabilized by addition of electron-donating substituents. This stabilization parallels totally the electron-releasing ability of the substituents: $R_2N > RO > R > \text{halogen} > H > CN$. The absorption characteristics of polaronic and bipolaronic charge states for a variety of substituted diphenylpolyenes are summarized in Table 1.

Table 1. P (+•) and BP (++) Formation in Diphenylpolyenes



Substituents	<i>n</i>	$\lambda_{\max}\pi-\pi^*(\text{nm})^a$	$\lambda_{\max}P(+\cdot)(\text{nm})$	$\lambda_{\max}BP(++)(\text{nm})$
None	5	374, 394, 418	[717] ^b	612, 564
None	6	393, 414, 438	[770] ^b	615, 685
4,4'-(OMe) ₂	4	370, 390, 413	740, 927, 1113	593, 647, 700
4,4'-(OMe) ₂	5	388, 410, 435	797, 1073, 1200	627, 692, 755
4,4'-(OMe) ₂	6	402, 426, 452	853, 1175, 1300	680, 741, 818
4,4'-(NMe ₂) ₂	4	425	c	613, 667, 723
4,4'-(NMe ₂) ₂	5	445, 470	c	646, 713, 773
4,4'-(NMe ₂) ₂	6	458, 485	c	700, 748, 833
4,4'-(F) ₂	5	380, 398, 427	[720] ^b	567, 615
4,4'-(F) ₂	6	398, 408, 438	[733, 1123] ^b	687, 727
4,4'-(Cl) ₂	5	385, 405, 430	[727] ^b	567, 622
4,4'-(Cl) ₂	6	400, 422, 450	787, 1120, 1240	630, 687
4,4'-(Br) ₂	5	381, 401, 431	740, 1033, 1127	587, 640
4,4'-(Br) ₂	6	396, 419, 446	780, 1113, 1273	640, 693
4,4'-(SMe) ₂	3	385, 403	592, 743	733, 815
4,4'-(SMe) ₂	4	400, 422	808, 985, 1217	777, 869
4,4'-(SMe) ₂	5	417, 443	855, 1083, 1338	823, 920
4,4'-(SMe) ₂	6	433, 461	904, 1189, 1400	864, 966

^aCH₂Cl₂ solution.

^bAbsorption spectra decay to BP (++) very fast; only unambiguous assignable absorption.

^cNot observed on spectrometer scanning time scale.

Note: Peaks in italic represent maximum absorption.

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From these results, it can be concluded that the longer polyenes display larger red shifts upon doping, which correlates with longer delocalization length. One disadvantage of the diphenylpolyenes as potential optical limiting materials is that they become very insoluble as the chain length increases that makes model doping studies difficult in solution.

Another important series of compounds are the dithienylpolyenes synthesized by Spangler et al.^{14,16,34} Polaron and bipolaron formation in these series via oxidative doping is similar to diphenylpolyenes. However, dithienylpolyene bipolarons are more

stable over time because the heteroatom in the ring can provide additional resonance stabilization of the polaronic and bipolaronic charge delocalization. This is illustrated in Figure 13.

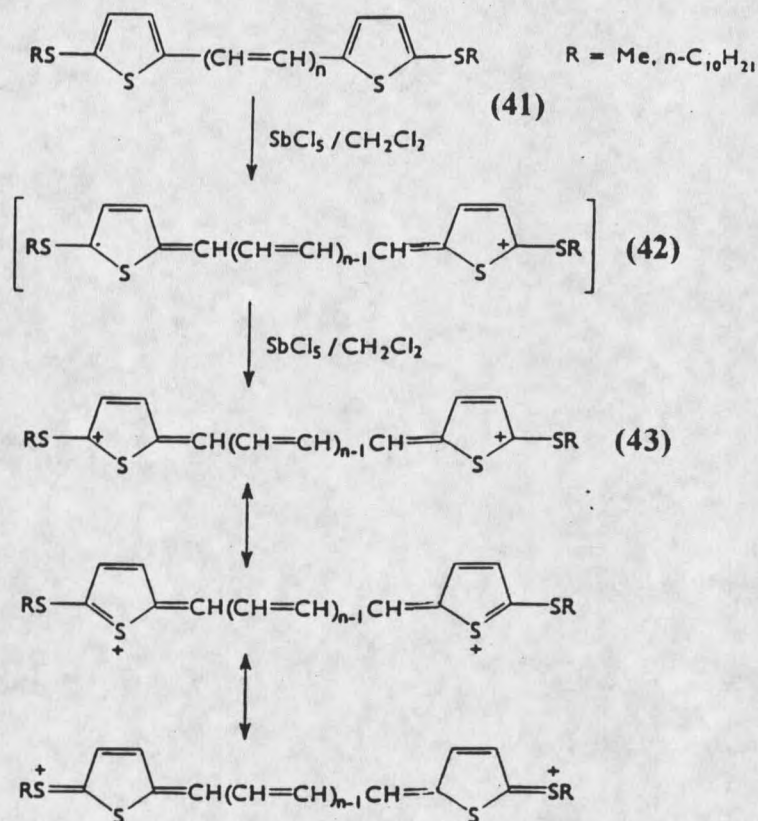
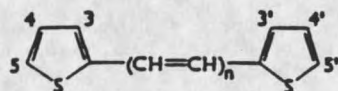


Figure 13. Resonance Stabilization of Dithienylpolyene Bipolarons Stabilized by Alkylthio Substituents

Incorporation of the alkyl groups on the thiophene ring increases the solubility of the thiophenepolyenes. Based on these characteristics, Spangler et al.³⁵ have synthesized series of dithienylpolyenes whose absorption characteristics for both the neutral and oxidatively doped species are listed in Table 2.

Table 2. P (+•) and BP (++) Formation in Dithienylpolyenes



Substituents	n	$\lambda_{\max} \pi-\pi^*$ (nm) ^a	$\lambda_{\max} P (+\bullet)$ (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) ₂	5	<u>425</u> , 450	[808] ^b	660, <u>710</u>
5,5'-(Me) ₂	6	<u>441</u> , 469	<u>888</u> , 1167, 1580	720, <u>776</u>
3,3'-(Me) ₂	5	<u>422</u> , 449	[795] ^b	650, <u>699</u>
3,3'-(Me) ₂	6	<u>440</u> , 469	<u>881</u> , 1154, 1574	713, <u>769</u>
5,5'-(OMe) ₂	3	<u>398</u> , 420	[731, 1076] ^b	<u>520</u> , (545) ^d
5,5'-(OMe) ₂	4	<u>416</u> , 442	<u>806</u> , 1103, 1299	<u>577</u> , (605) ^d
5,5'-(SMe) ₂	3	404	<u>792</u> , 1009, 1240	610, (643) ^d
5,5'-(SMe) ₂	4	<u>422</u> , 444	<u>859</u> , 1114, 1348	663, (702) ^d
5,5'-(SMe) ₂	5	<u>434</u> , 460	c	717, (775) ^d
5,5'-(SMe) ₂	6	<u>451</u> , 478	c	773, (835) ^d
5,5'-(SC ₁₀ H ₂₁) ₂	7	<u>462</u> , 493	c	834, (905) ^d
5,5'-(SC ₁₀ H ₂₁) ₂	8	<u>475</u> , 507	c	884, (970) ^d
3,4,3',4'-(Bu) ₄	3	422, <u>399</u> , 380	c	593, <u>655</u>
3,4,3',4'-(Bu) ₄	4	443, <u>418</u> , 396	c	600, <u>661</u>
3,4,3',4'-(Bu) ₄	5	462, <u>435</u> , 412	c	679, <u>715</u>
3,4,3',4'-(Bu) ₄	6	480, <u>450</u> , 426	c	<u>719</u> , 809
3,4,3',4'-(Bu) ₄	7	496, <u>464</u> , 439	c	790, <u>849</u>
3,4,3',4'-(Bu) ₄	8	510, <u>477</u> , 450	c	855, <u>914</u>
3,4,3',4'-(Bu) ₄	9	521, <u>489</u> , 461	c	892, <u>971</u>
3,4,3',4'-(Bu) ₄	10	534, <u>499</u> , 471	c	950, <u>1022</u>
3,4,3',4'-(Bu) ₄ ; 5,5'-(BuS) ₂	3	424	c	643
3,4,3',4'-(Bu) ₄ ; 5,5'-(BuS) ₂	4	439	c	657
3,4,3',4'-(Bu) ₄ ; 5,5'-(BuS) ₂	5	451	c	705
3,4,3',4'-(Bu) ₄ ; 5,5'-(BuS) ₂	6	466	c	754
3,4,3',4'-(Bu) ₄ ; 5,5'-(BuS) ₂	7	476	c	801
3,4,3',4'-(Bu) ₄ ; 5,5'-(BuS) ₂	8	488	c	849

^aCH₂Cl₂ solution. ^bAbsorption spectra decay to BP (++) very fast; only unambiguous assignable absorption. ^cNot observed on spectrometer scanning time scale. ^dAbsorptions shown in parentheses represent shoulders. Note: Underlined peaks represent peaks of maximum absorption. Portions of this table are reprinted with permission from *Molecular Electronics and Molecular Electronic Devices*, Vol. III (K. Siemicki, ed.), copyright CRC Press, Boca Raton, Florida.

It was concluded from these studies that dithienylpolyenes form very stable bipolarons compared to diphenylpolyenes, and that the absorption characteristics of the charge states can be 'fine-tuned'. It was also found that as the number of double bonds increases, absorption bands of both polaron and bipolaron species red shift to longer wavelengths in the UV-VIS spectrum.

CHAPTER 3

RATIONALE FOR PROPOSED RESEARCH

A few years ago, Spangler et al. synthesized dithienylhexatriene and demonstrated optical limiting for dithienylpolyenes covalently attached as pendant groups to a PMMA backbone.³⁶ In collaboration with Laser Photonics Technology, Inc., optical limiting properties of the polymer in solution, C₆₀ in solution, and a mixture of polymer with C₆₀ in solution were examined. Upon irradiation with a 532 nm source, polymer with C₆₀ showed better optical limiting behavior than polymer and C₆₀ alone. But it was not clear whether the two individual limiting effects were additive, or whether charge state formation and limiting by polaronic or bipolaronic charge state had been observed.

During the past few years, it has been shown with sub-picosecond (180 fs) fluorescence studies that dithienylpolyenes have two-photon absorption states that can provide optical limiting.^{36,37} In almost all examples of dithienylpolyene chromophores, polaronic and bipolaronic charge states absorbed more strongly than the neutral species. Since dithienylpolyenes have significant two-photon cross sections¹⁵, and are proved to be good reverse saturable absorbers, they may be considered to behave as bimechanistic optical power limiters (RSA and TPA), albeit in different spectral regions

Over the past few years Spangler group has proposed synthesizing dendrons and dendrimers with photonic-active chromophores that might have optical limiting

capabilities via acceptor-assisted photogeneration of the highly absorbing charge states. Dendrimers were preferred rather than more conventional pendant polymers because a higher percentage of photonic-active groups can be incorporated without phase separation and chromophore-chromophore interaction that can lead to peak broadening and tailing resulting in increased absorption losses and loss of ambient transparency. Another reason for selecting dendrimers is that while using PMMA with incorporated optical power limiting chromophores is acceptable for testing purposes, high power laser pulses can damage PMMA. Therefore, a new approach for actual device design has been pursued which involves the application of surface-functionalized dendrimers. In this proposed model, RSA-OPL chromophores will be arranged on the globular mono-disperse macromolecular surface. This synthetic approach will also allow the covalent incorporation of electron-accepting chromophores which is necessary for photo-generated charge state formation by both inter-and intra-molecular electron transfer. This approach is illustrated below in Figure 14.

The original goal of the research, therefore was to design and synthesize new dendritic macromolecules incorporating dithienylpolyenes as surface groups. We predict that these compounds to have unique nonlinear optical and charge transfer and optical limiting properties.

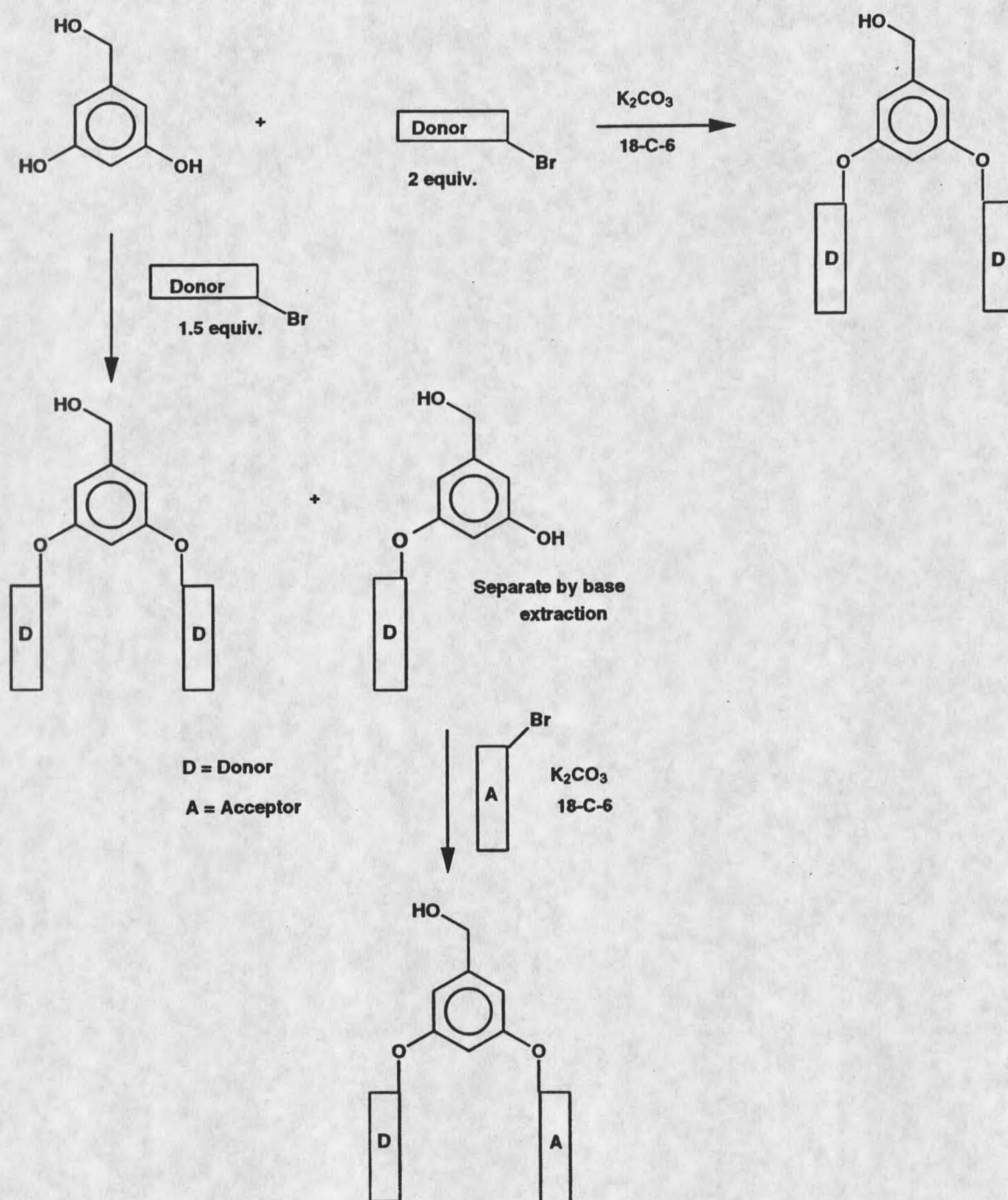


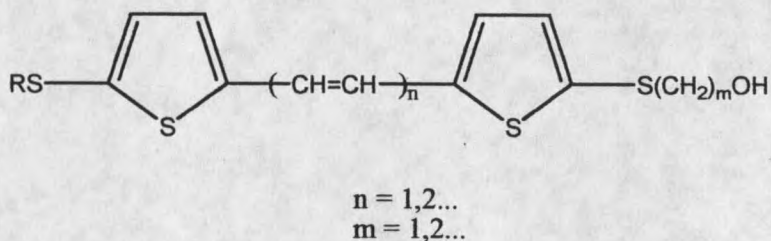
Figure 14. Formation of Typical Surface-functionalized Dendrimer with Donor and Acceptor Groups

CHAPTER 4

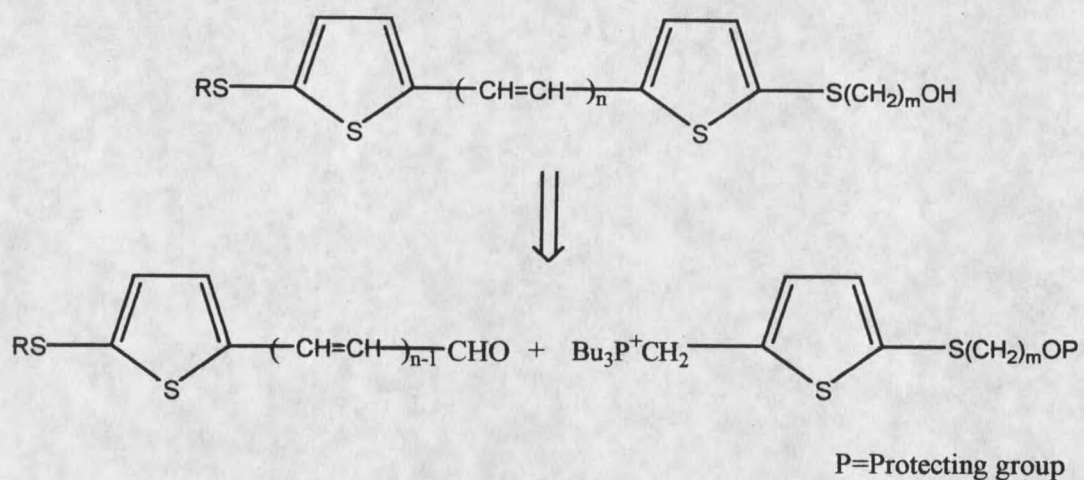
RESULTS AND DISCUSSION

Retro-Synthetic Analysis of Asymmetrically Substituted Dithienylpolyenes

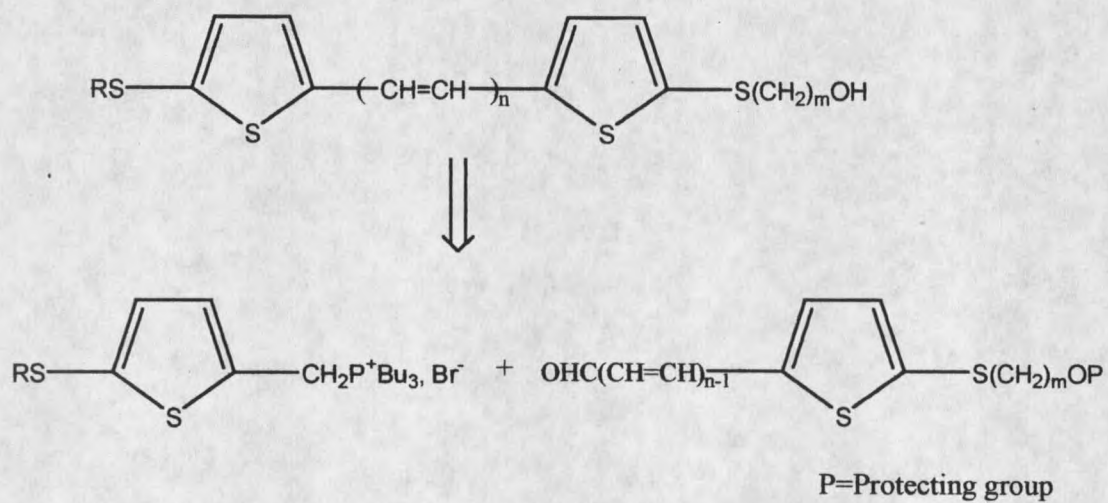
Previous synthesis of dithienylpolyenes involved mostly symmetric structures. The polyenes required for dendron synthesis and subsequent coupling to a central core are, by necessity, asymmetric structures. In order to stabilize the incipient polaronic or bipolaronic charge state formation, donor groups are required. Alkylthio groups have previously been shown to stabilize charge state formation, and with the necessity of having a reactive tether group for dendron attachment, the following polyene targets were formulated.



Most extended polyene synthesis rely on Wittig methodology, therefore, retrosynthetic analysis of the target structure can be outlined as follows:



Route 1



Route 2

It was decided to pursue Route 2, since similar methodology had been employed in previous synthesis of the symmetric dithienylpolyenes. The chromophores synthesized by this route could then be attached to 3,5-dihydroxybenzyl alcohol to form the dendrons as illustrated previously in Figure 14.

Synthesis of the Thienyl Wittig Salt

The critical intermediate thienyl Wittig salt was synthesized by the series of reactions described in Scheme 1. A butylthio substituent was introduced by lithiation of thiophene (Aldrich) followed by the reaction with sulfur powder and iodobutane. A formyl group was then introduced to the substituted thiophene by Vilsmeier-Haack reaction in 95% yield. The aldehyde was then reduced to the corresponding alcohol by using NaBH_4 as reducing agent. 2-Bromomethyl-5-butylthiophene was synthesized by reacting the alcohol with PBr_3 , to be carried over to the next step immediately, without the removal of the solvent to prevent product decomposition. After vigorous stirring with tributylphosphine for 48 hours, the desired Wittig salt was obtained as white solid in good yield (73%).

Synthesis of Dithienyl Chromophores Functionalized for Dendron Attachment

Functionalized dithienylpolyenes were required in order to attach them to 3,5-dihydroxybenzyl alcohol to form the dendrons for convergent dendrimer synthesis. The dithienylpolyenes were designed to incorporate butylthio groups at one terminus both for

solubility and stabilization of either polaronic or bipolaronic charge states. The other terminus had an alkylthio substituent terminated with an OH group for attachment to 3,5-dihydroxybenzyl alcohol. Ideally, the functionalized tether group should be as short as possible therefore the first chromophore that was synthesized had a hydroxy methyl group. 1-(5''-Butylthio-2''-thienyl)-2-(2'-thienyl) ethene was successfully prepared by using the Wittig approach. The reaction was carried out at room temperature overnight to give pure product after column chromatography in 97% yield. A formyl group was then attached to dithienylpolyene by Vilsmeier-Haack reaction. The resulting aldehyde was then reduced to give the hydroxymethyl chromophore as a yellow solid in 91% yield. However this end group proved to be quiet difficult to convert to a stable CH_2X ($\text{X}=\text{Halogen}$) for dendron attachment by Frechet methodology.^{39,40} Several attempts were made to convert the OH group to Br. First, the chromophore was treated with tetrabromomethane and triphenylphosphine and stirred under nitrogen for two hours. After removal of the solvent NMR revealed that there was no trace of the desired product. The second attempt was to react the chromophore with phosphorus tribromide in ether. Analysis of the yellow solid that resulted from the reaction showed only the starting material. Either the thienyl alcohol was totally unreactive under the standard reaction conditions, or, which is more likely, the $-\text{CH}_2\text{Br}$ product is extremely unstable to hydrolysis. These procedures are described in Scheme 2.

Next, an attempt was made to synthesize a chromophore containing $(\text{CH}_2)_2\text{OH}$ tether group. As illustrated in Scheme 3, thiophene was lithiated, followed by reaction with sulfur powder and 2-(2'-Iodoethoxy) tetrahydro-2H-pyran. The tetrahyropyranyl

protecting group hydrolyzed upon aqueous work-up and 2-(2'-hydroxyethylthio) thiophene was obtained. The -OH functionality reacted with acetic anhydride in order to protect the hydroxyl group. A formyl group was then introduced to the thiophene ring via the Vilsmeier-Haack reaction. Reaction of aldehyde **56** with Wittig salt **48** gave an elimination product of the desired compound. The targeted dithienylpolyene was not obtained due to the too strong basic character of potassium tert-butoxide, and the possible anchimeric assistance of the sulfur atom promoting elimination. These reactions are illustrated in Scheme 4. No further attempt has been made to pursue the synthesis of this chromophore.

Finally, a new chromophore containing a $(\text{CH}_2)_3\text{OH}$ tether group was synthesized successfully and proved to be stable to both conversion to halide and attachment to 3,5-dihydroxybenzyl alcohol to provide a stable dendron. Schemes 5 and 6 describe the synthesis of aldehyde and extended counterpart which are then used to form the desired OPL chromophores. Hydroxypropylthio substituent was introduced by lithiation of the thiophene ring followed by reaction with sulfur powder and 2-(3'-Iodopropoxy) tetrahydro-2H-pyran. The crude product was purified by vacuum distillation, with attendant removal of the dihydropyranyl group. The resulting substituted thiophene was reacted with acetic anhydride as described above to protect the hydroxyl group as acetate. A formyl group was introduced via the Vilsmeier reaction. The aldehyde extension via Wittig methodology was accomplished via Spangler et al.'s oxopropanylation methodology.⁴¹ In order to obtain an extended aldehyde, a highly reactive phosphonium salt incorporating an acetal that can be converted to an aldehyde upon hydrolysis was

used. Acetal formation was monitored by NMR spectroscopy. Reaction was carried out until all the starting aldehyde was gone because it was almost impossible to separate the starting aldehyde from the extended product by column chromatography. Once the completely reacted acetal was obtained, it was immediately dissolved in THF and hydrolyzed with 3N HCl solution. The final product was obtained as a red liquid in 63% yield. Dithienylpolyenes **64** and **65** were then synthesized from either aldehyde or extended counterpart by Wittig reaction in yields of 85% and 96% respectively as shown in Scheme 7.

Synthesis of Dendrons

The two chromophores ($n=1$ and $n=2$) whose synthesis are outlined in the previous section, were converted to dendrons for convergent dendrimer synthesis by first converting the alcohol functionality to an iodide followed by condensation with 3,5-dihydroxybenzyl alcohol according to the methodology developed by the Fréchet group.^{39,40}

The reaction of the OH functionalized chromophores with a variety of halogenating agents was investigated. The use of tetrabromomethane in combination with triphenylphosphine gave poor yields. However, in a successful attempt the two chromophores **64** and **65** were reacted with iodine in the presence of triphenylphosphine and imidazole in order to convert the hydroxyl group into iodide. Both of the crude products were purified by column chromatography to give the desired compounds **66** and **67** in 95% and 96% yields. To obtain the dendrons, the iodides, 3,5-dihydroxybenzyl

alcohol, potassium carbonate and 18-Crown-6 as phase transfer agent were refluxed in 1,4-dioxane under vigorous stirring for 48 hours. It was found essential to maintain efficient stirring throughout the reaction in order to obtain a high rate of conversion. The reaction of **66** and 3,5-dihydroxybenzyl alcohol gave dendron **68**, which was isolated in 65% yield after column chromatography eluting with methylene chloride. The reaction of **67** and 3,5-dihydroxybenzyl alcohol under similar conditions yielded **69** in 76% yield after purification via column chromatography using methylene chloride as eluent. These reactions are illustrated in Scheme 8.

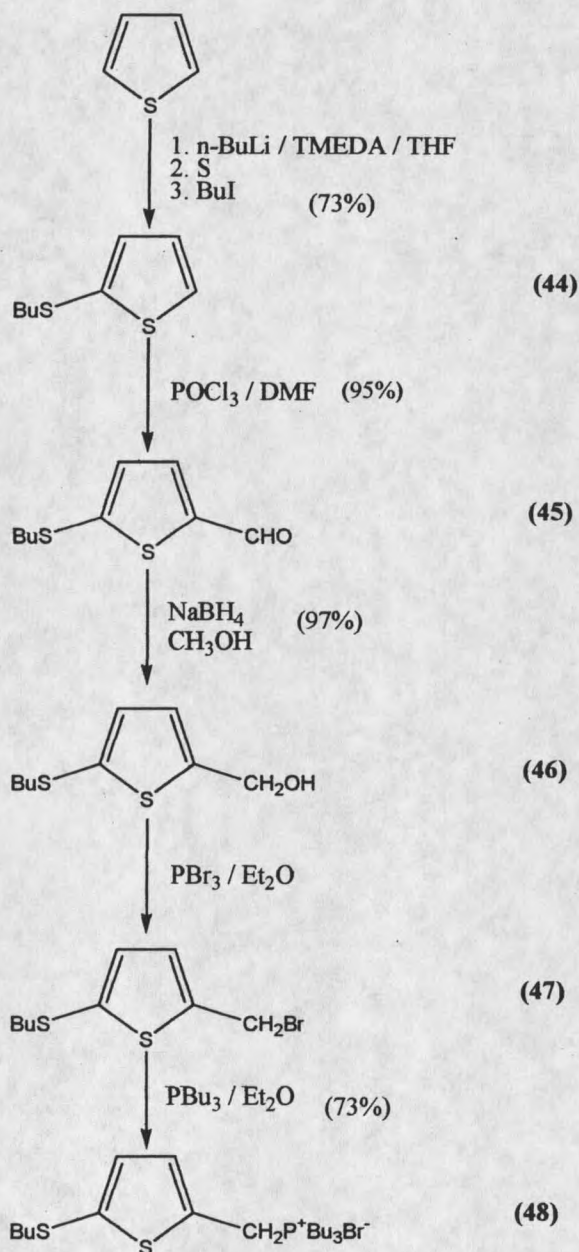
Synthesis of Dendrimers

Convergent approaches to dendrimer synthesis require that for each generation, the appropriate generation dendron be coupled to a central core molecule with two or more functionalities. In this project model G-0 dendrimers were prepared to examine and compare the photonic properties of the chromophores, dendrons, and dendrimers. G-0 dendrimers were synthesized by coupling the dendrons to bisphenol-A.

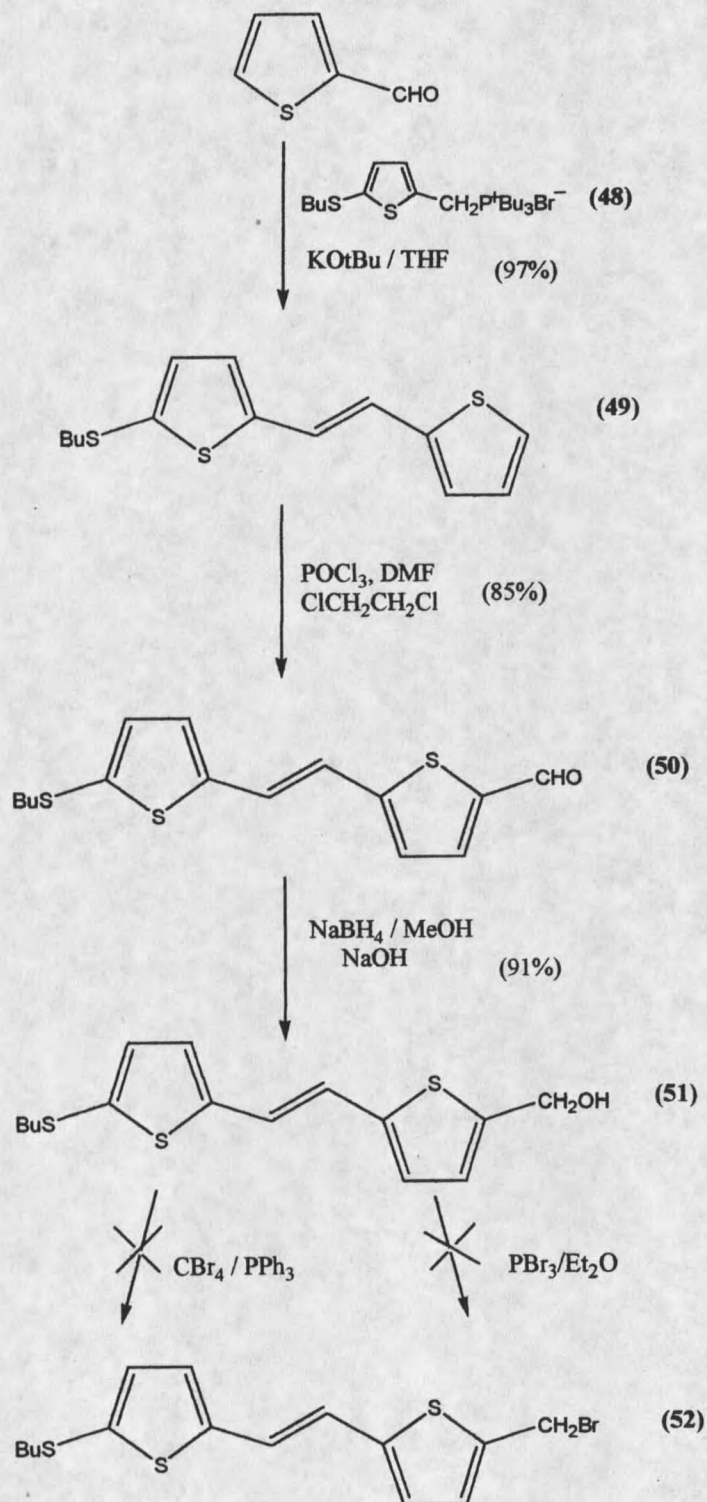
As illustrated in Scheme 9, dendrons **68** and **69** were converted to the corresponding bromides by standard methodology. In a typical reaction, a dendron was reacted with CBr_4 and triphenylphosphine in a minimum amount of dry THF under nitrogen for 20 minutes. Excess CBr_4 and triphenylphosphine were removed via column chromatography prior to dendron coupling to bisphenol-A core in order to avoid the formation of unwanted side products arising from possible reactions with CBr_4 . After bromides **70** and **71** were obtained, coupling to a polyfunctional core was carried out as

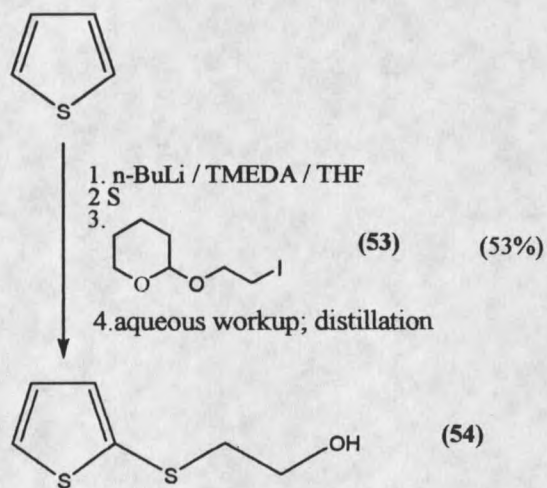
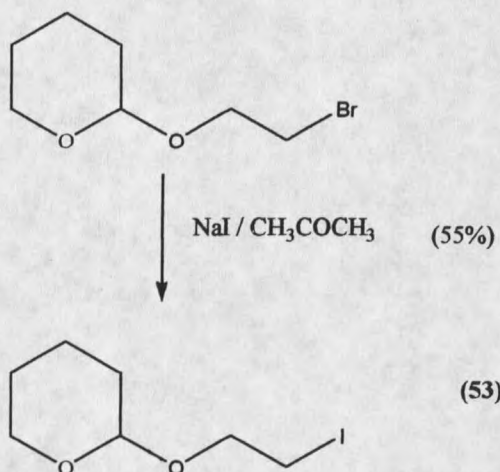
shown in Scheme 10. An acetone solution of dendron bromide was heated at reflux with the core molecule, bisphenol-A, in the presence of potassium carbonate and 18-Crown-6. After careful purification via column chromatography, pure G-0 dendrimers, **72** and **73**, were obtained as yellow gels in 97% and 88% yield respectively.

Scheme 1. Synthesis of (5-Butylthio-2-thienyl) tributylmethylphosphonium bromide

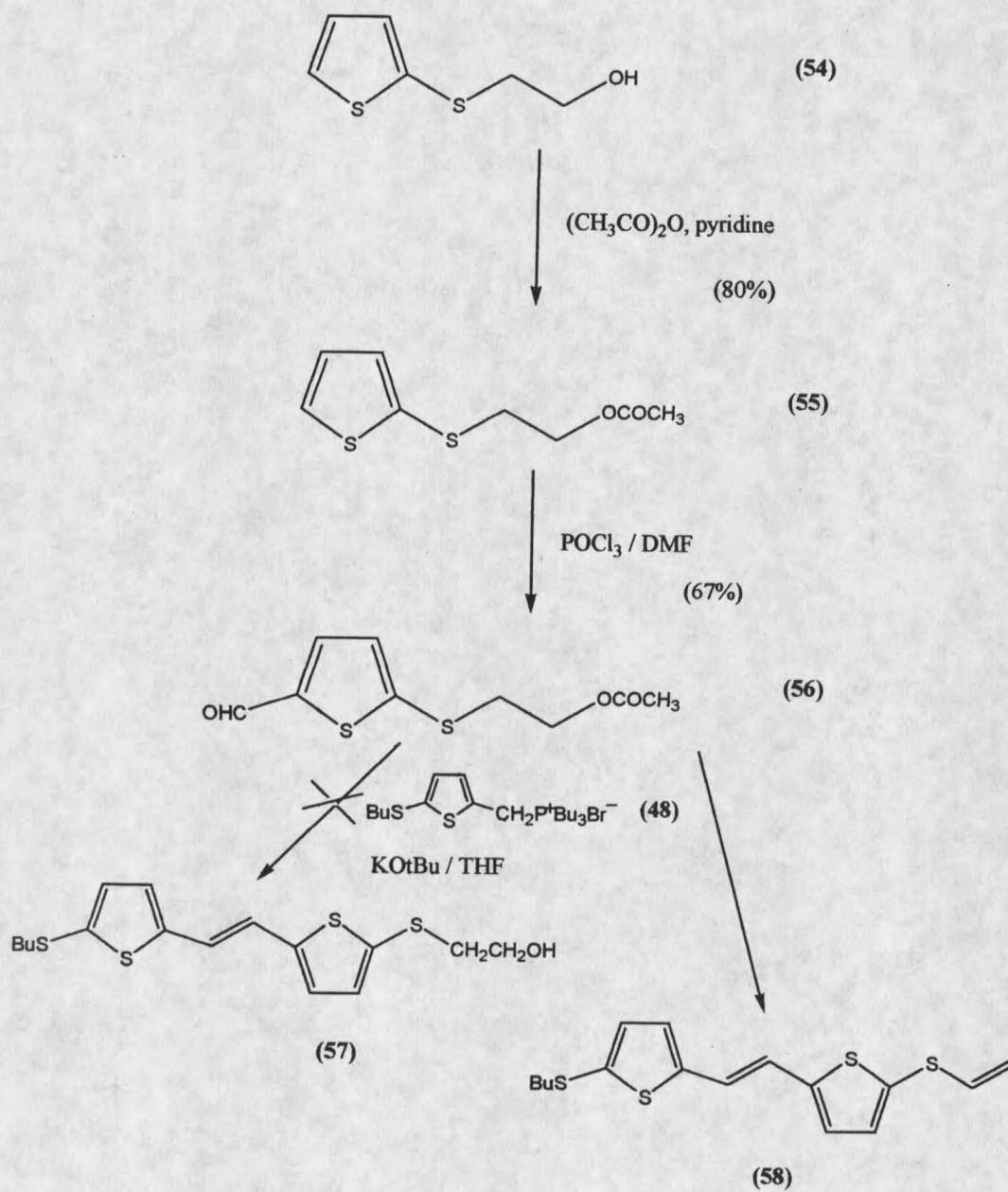


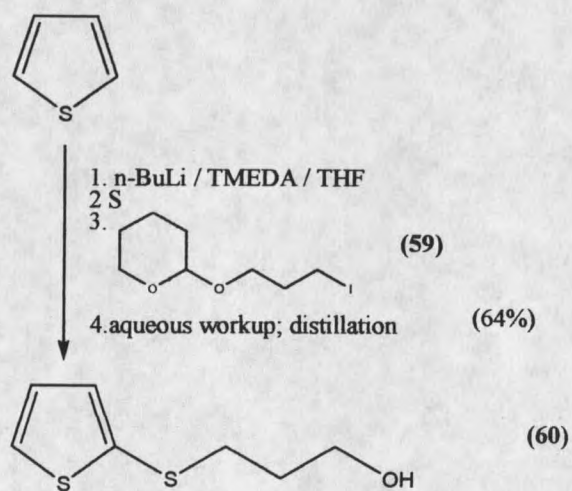
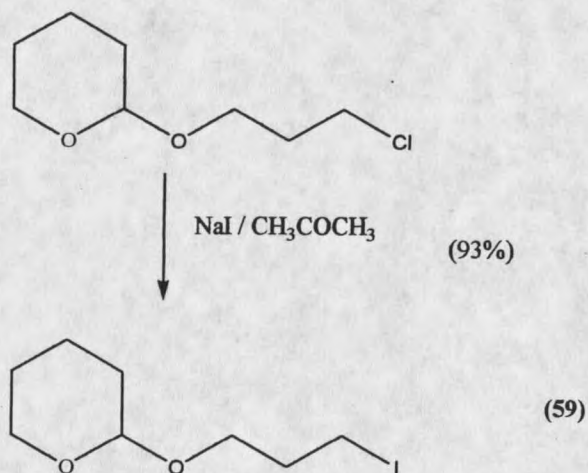
**Scheme 2. Attempted Synthesis of
1-(5''-Butylthio-2''-thienyl)-2-(5'-hydroxymethyl-2'-thienyl) ethene**



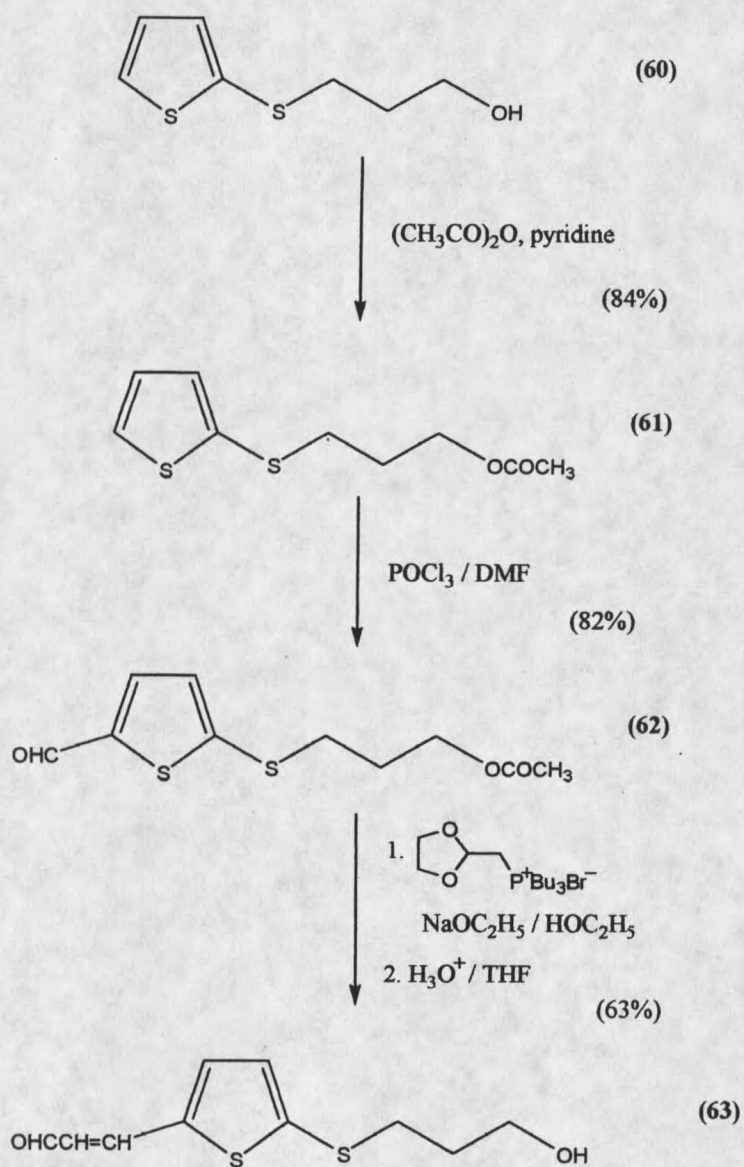
Scheme 3. Synthesis of 2-(2'-hydroxyethylthio) thiophene

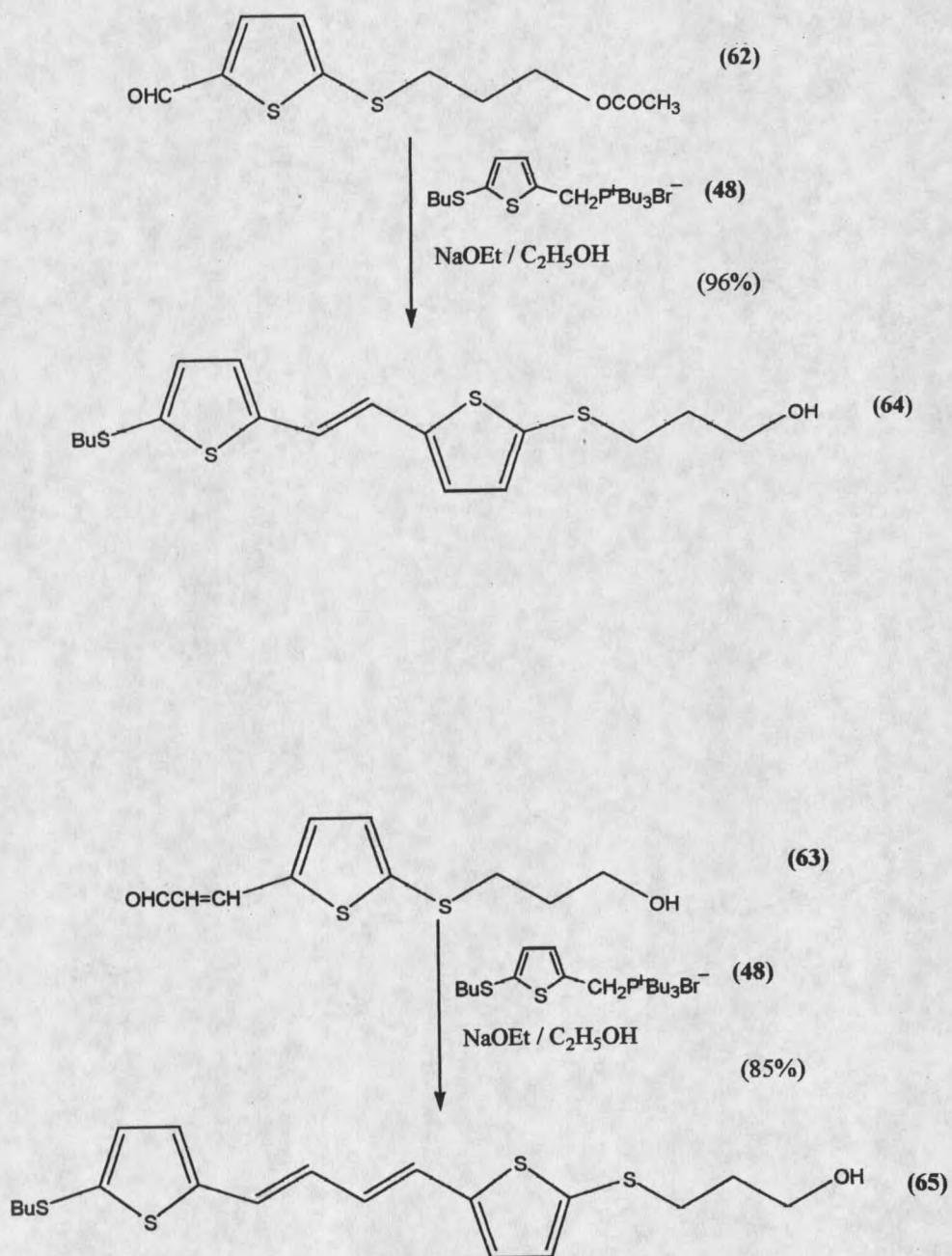
**Scheme 4. Attempted Synthesis of
2-[5'-Butylthio-2'-thienyl]-1-[5''-(2'''-hydroxyethyl)-2''-thienyl] ethene**

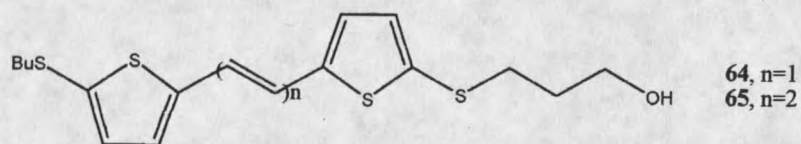
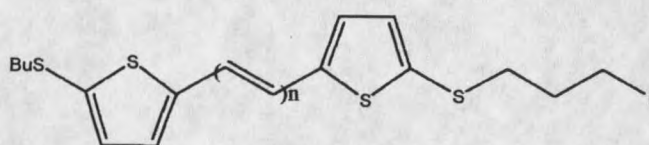


Scheme 5. Synthesis of 2-(3'-hydroxypropylthio)thiophene

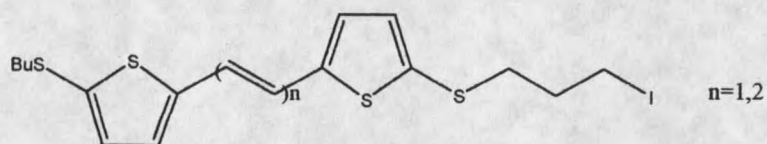
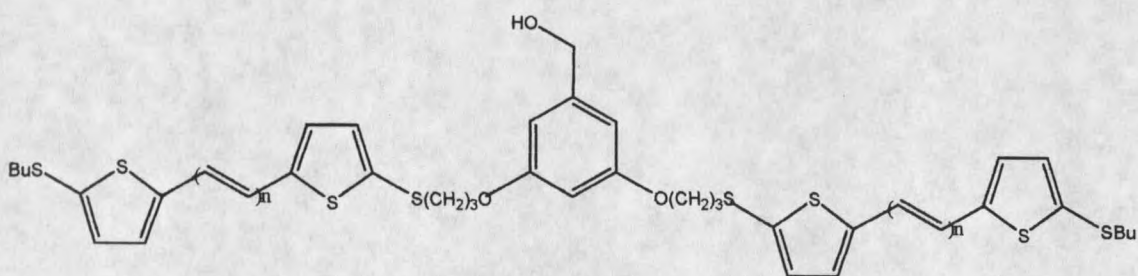
Scheme 6. Synthesis of 3-(5'-hydroxypropylthio-2'-thienyl)-2-propenal



Scheme 7. Synthesis of $n=1$ and $n=2$ Chromophores

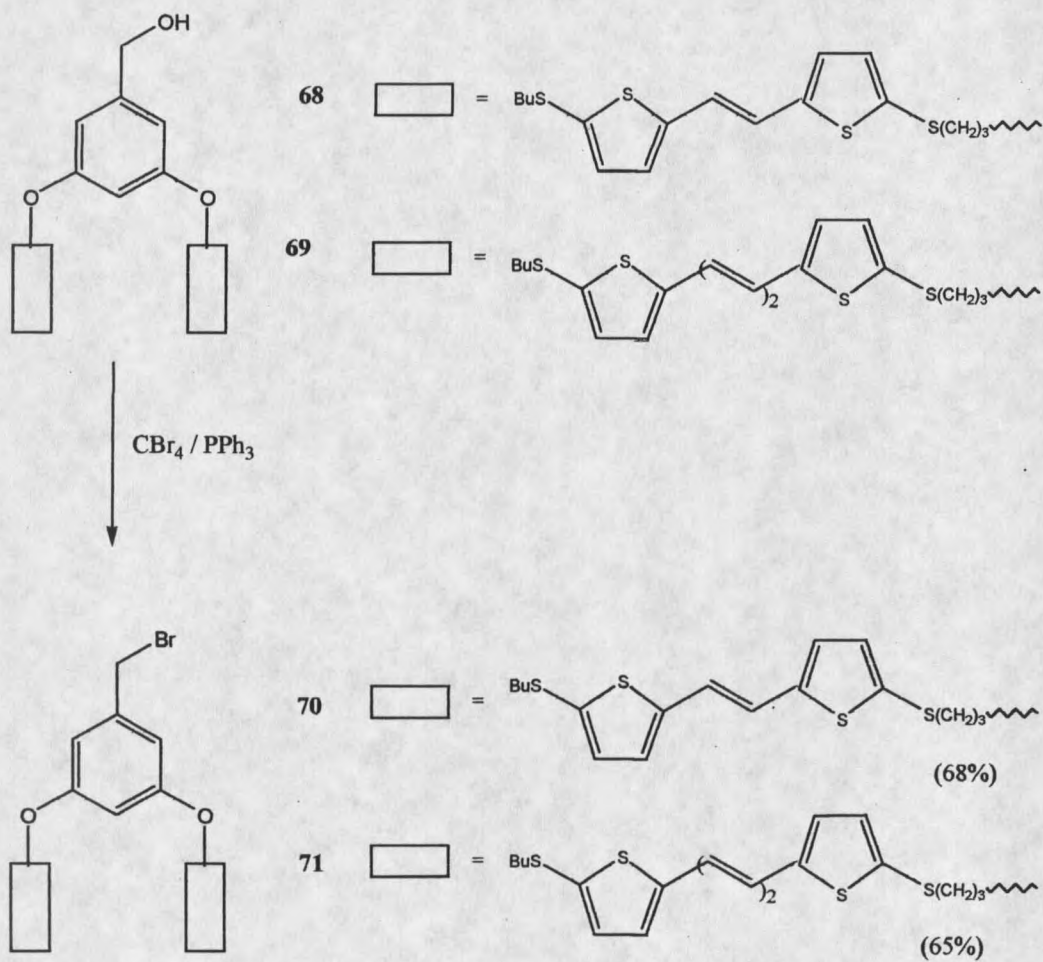
Scheme 8. Synthesis of $n=1$ and $n=2$ Dendrons
 $I_2 / PPh_3 / \text{imidazole}$


n	Compound #	Yield (%)
1	66	96%
2	67	95%

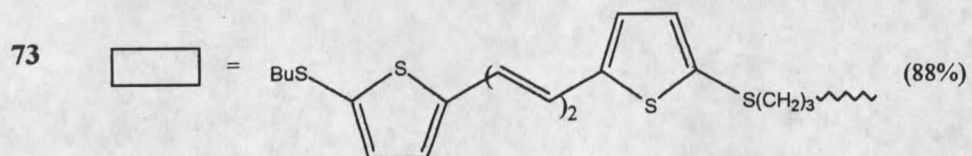
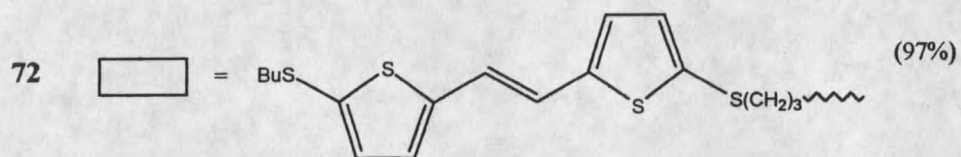
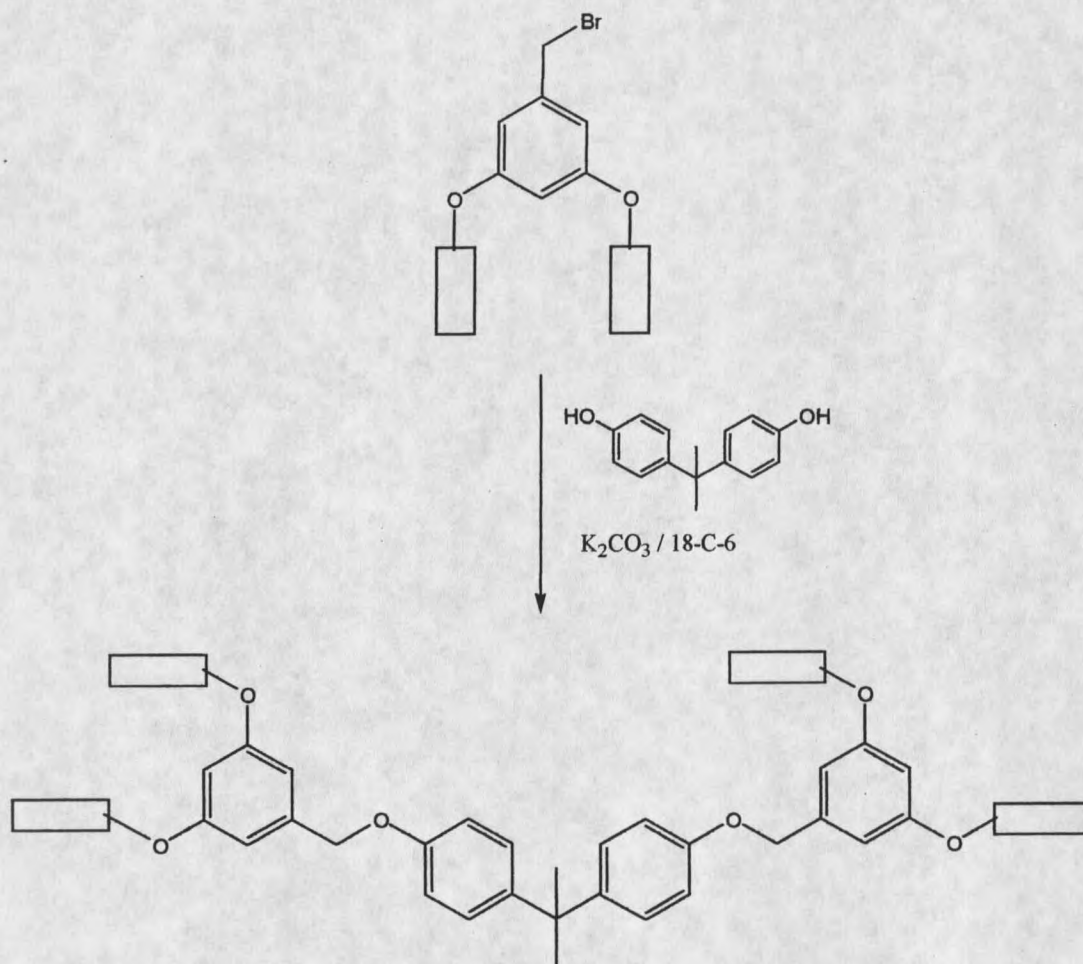

 $\text{HO-C}_6\text{H}_3\text{(OH)-CH}_2\text{OH} / K_2CO_3 / 18\text{-C-6}$


n	Compound #	Yield (%)
1	68	65%
2	69	76%

Scheme 9. Synthesis of n=1 and n=2 Dendritic Bromides

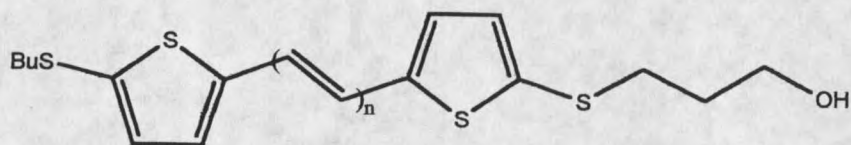


Scheme 10. Synthesis of n=1 and n=2 Dendrimers

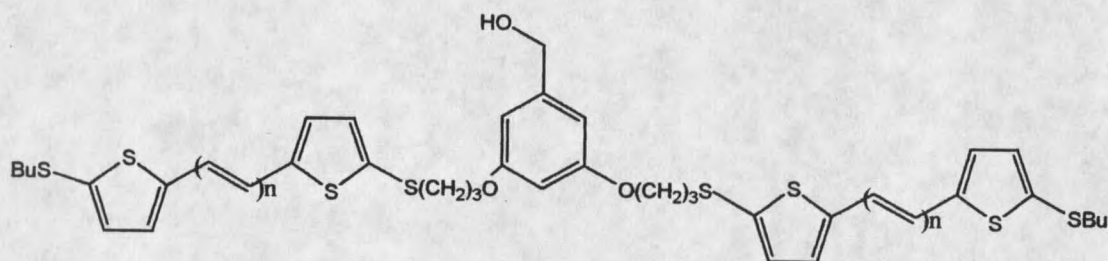


UV-VIS Spectra of Chromophores, Dendrons and Dendrimers

The attractive aspect of using dendrimers for photonic applications is the relatively high percentage of the moiety that is actually photonic-active. In this research, UV-VIS spectra was used to determine absorption characteristics of chromophores, dendrons and dendrimers. The absorption characteristics of the chromophores ($n=1$ and $n=2$), dendrons ($n=1$ and $n=2$) and dendrimers ($n=1$ and $n=2$) in solution were examined to determine if any significant changes occur upon incorporation of chromophores. The oxidative doping of the three species in solution with SbCl_5 was also examined. Oxidative doping was carried out in methylene chloride solution by careful addition of SbCl_5 to a 10^{-6}M to 10^{-5}M solution of chromophores, dendrons and dendrimers. In all cases, in order to ensure that the compounds were oxidized completely, an excess of dopant was utilized. The absorption changes were monitored by a Shimadzu UV-3101-PC UV-VIS-IR spectrophotometer during the doping process. The chromophores, dendrons and dendrimers all formed highly absorbing bipolaronic dications in solution whose absorbance was in the range of 500-650 nm. All of the bipolaron-like dications formed from the neutral forms of the dithienylpolyenes are extremely stable under ambient laboratory conditions. The UV-VIS-NIR absorptions for both neutral and oxidized species are displayed in the Tables 3, 4 and 5. The comparative spectra for the $n=1$ and $n=2$ chromophore, dendron and dendrimers are illustrated in Figures 15-20.

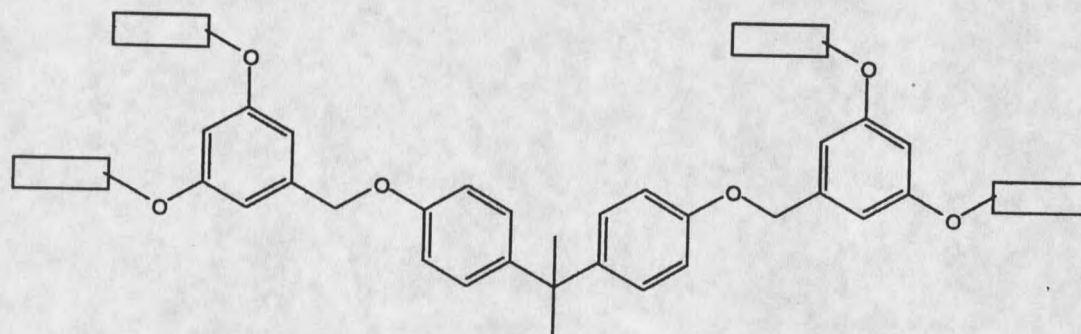
Table 3. Bipolaron Formation in Dithienyl Polyenes


n	λ_{\max} neutral (nm)	λ_{\max} bipolaron (nm)	ϵ_{\max} neutral ($M^{-1}cm^{-1}$)
1	372.5	569.5, 535.0	29,200
2	390.0	609.0, 571.5	45,100

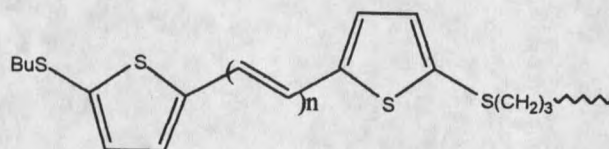
Table 4. Bipolaron Formation in Dithienyl Dendrons

n	λ_{\max} neutral (nm)	λ_{\max} bipolaron (nm)	ϵ_{\max} neutral ($M^{-1}cm^{-1}$)
1	373.0	569.0, 535.0	54,700
2	390.0	610.0, 572.0	86,800

Table 5. Bipolaron Formation in Dithienyl Dendrimers



 = Photonic active chromophore



n	λ_{\max} neutral (nm)	λ_{\max} bipolaron (nm)	ϵ_{\max} neutral ($M^{-1}cm^{-1}$)
1	373.0	573.5, 536.5	107,500
2	390.0	611.0, 571.0	194,900

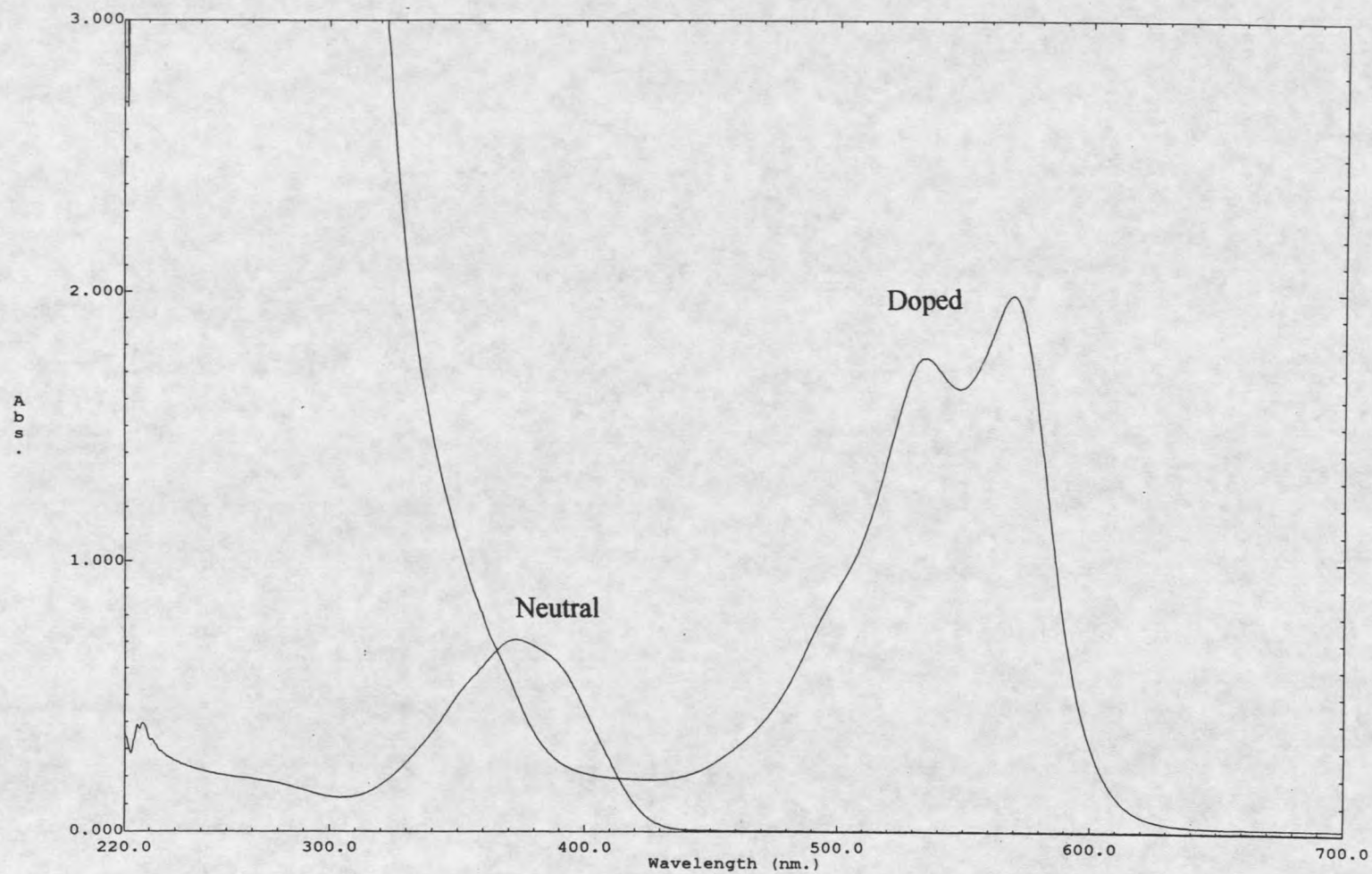


Figure 15. Absorption Spectra for Neutral and Doped n=1 Chromophore (64)

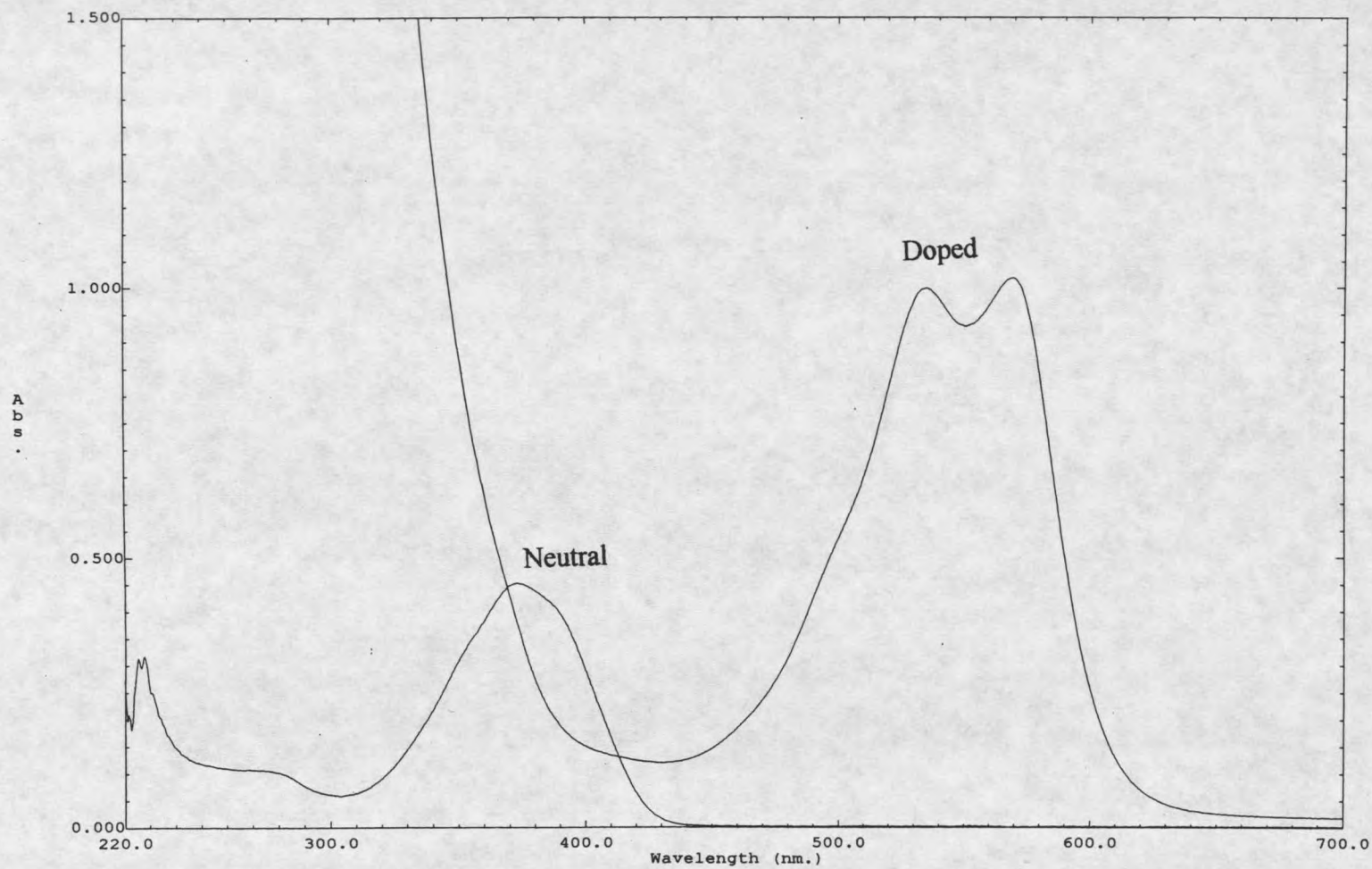


Figure 16. Absorption Spectra for Neutral and Doped n=1 Dendron (68)

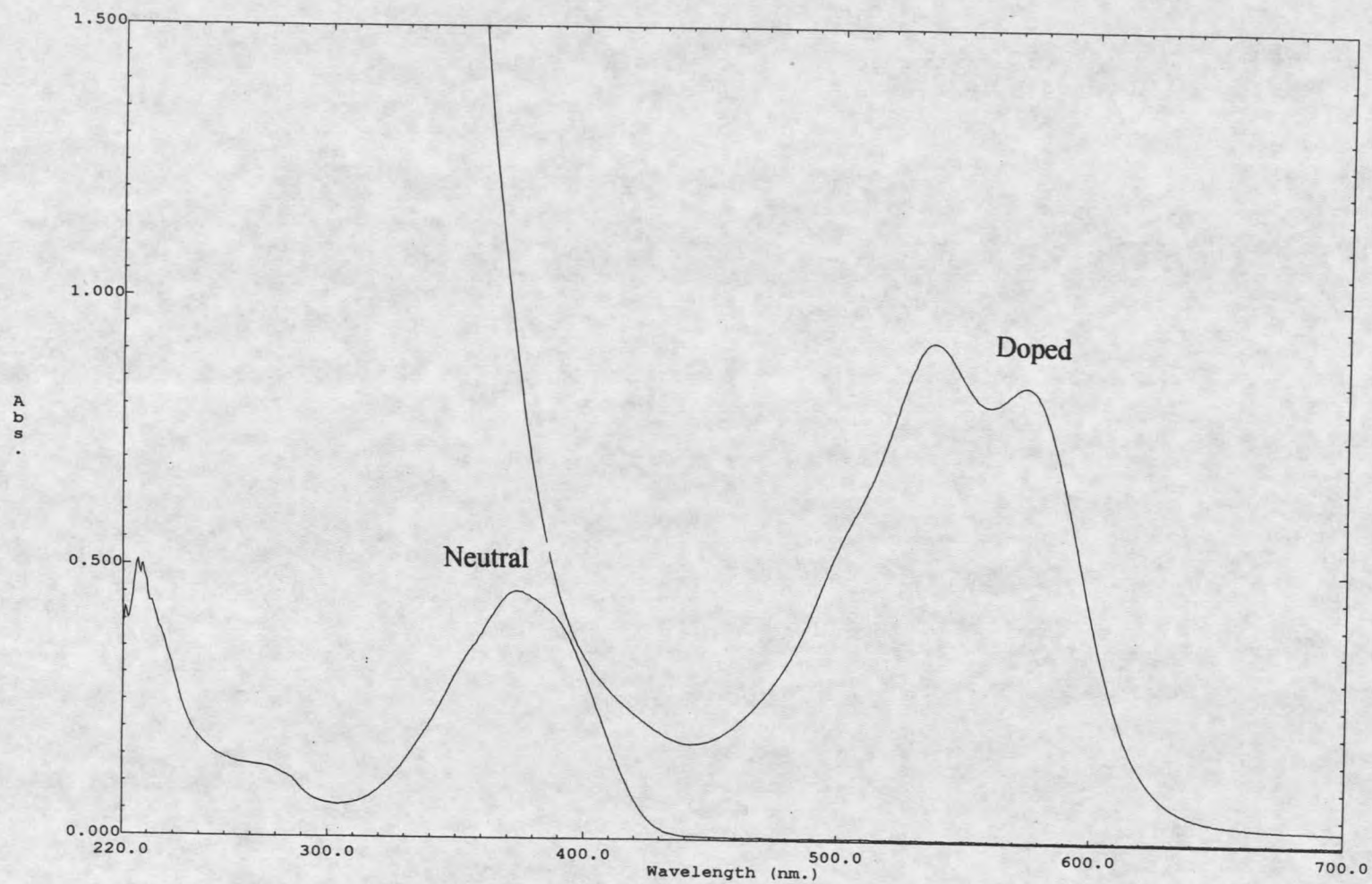


Figure 17. Absorption Spectra for Neutral and Doped n=1 Dendrimer (72)

