Synthesis of dendrons and dendrimers incorporating diphenylamino-N-ethyl-N-hydroxyethylaminodiphenylpolyenes for photonic applications

by Kimba Lee Ashworth

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

Abstract:

With the recent advances in laser technology, a need for protection from their potential damage is imperative. This problem requires the development of new optical power limiting materials to offer protection for eyes and optical sensors.

In this research, diphenylamino-N-ethyl-N-hydroxyethylamino-diphenylpolyene chromophores with up to three double bonds have been synthesized and incorporated into dendrons and generation-0 dendrimers. The convergent dendrimer synthesis was successfully used in the conversion of chromophores to dendrons and dendrimers.

The chromophores were also tested for their photoluminescence for organic light emitting diode and hole transport materials. The evaluation of the dendrons and dendrimers for these applications is currently being carried out in other collaborating laboratories.

The absorption characteristics of the three chromophores and their respective dendrons and dendrimers were examined to assess their optical power limiting performance. ll three chromophores and their dendrons and dendrimers form stable, highly absorbing bipolaronic charge states showing promise for reverse saturable absorption optical power limiting. The possibility also exists that these materials will show optical power limiting by two photon absorption. The compounds are currently being evaluated as bimechanistic optical limiting materials operating by both reverse saturable absorption and two photon absorption.

SYNTHESIS OF DENDRONS AND DENDRIMERS INCORPORATING DIPHENYLAMINO-N-ETHYL-N-HYDROXYETHYLAMINODIPHENYLPOLYENES FOR PHOTONIC APPLICATIONS

by

Kimba Lee Ashworth

A thesis submitted in partial fulfillment
of the requirements for the degree

of

Master of Science

in

Chemistry

MONTANA STATE UNIVERSITY
Bozeman, Montana

June 2000

APPROVAL

of a thesis submitted by

Kimba Ashworth

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 6/12/00
(Signature) Date

Approved for the Department of Chemistry and Biochemistry

Eric Grimsrud Eric Grimsrud 6/13/00
(Signature) Date

Approved for the College of Graduate Studies

Bruce McLeod Bruce R. McLeod 6-26-00
(Signature) Date

STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a master's degree at Montana State University, I agree that the Library shall make it available to borrowers under rules of the Library.

If I have indicated my intention to copyright this thesis by including a copyright notice page, copying is allowable only for scholarly purposes, consistent with "fair use" as prescribed in the U.S. Copyright Law. Requests for permission for extended quotation form of reproduction of this thesis in whole or in parts may be granted only by the copyright holder.

Signature Kimba Ashworth

Date 6-5-00

ACKNOWLEDGEMENTS

I am so grateful to my advisor, Dr. Charles Spangler, for his guidance, patience, and friendship through this journey of graduate school. I would like to thank the Spangler Group for their friendship and helpful discussions involving my project.

I would also like to thank the members of my committee, Dr. Lee Spangler and Dr. Mary Cloninger, for reviewing my thesis.

I would like to acknowledge The Graduate School and The Department of Chemistry for their financial assistance. Partial support of this research by the Air Force Office of Scientific Research under grants F49620-96-1-0440 and F49620-97-0413 is gratefully acknowledged. Partial support is also acknowledged from Technical Management Concepts, Inc, Contract #TMC-97-5405-0018-02.

Thank you to my parents for their continual support and encouragement. And finally, I would like to thank my son, Brian Ray, for his sacrifices that allowed me to continue my education for this degree.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Figure Page

Figure Page

LIST OF SCHEMES

Scheme Page

ABSTRACT

With the recent advances in laser technology, a need for protection from their potential damage is imperative. This problem requires the development of new optical power limiting materials to offer protection for eyes and optical sensors.

In this research, diphenylamino-N-ethyl-N-hydroxyethylamino-diphenylpolyene chromophores with up to three double bonds have been synthesized and incorporated into dendrons and generation-0 dendrimers. The convergent dendrimer synthesis was successfully used in the conversion of chromophores to dendrons and dendrimers.

The chromophores were also tested for their photoluminescence for organic light emitting diode and hole transport materials. The evaluation of the dendrons and dendrimers for these applications is currently being carried out in other collaborating laboratories.

The absorption characteristics of the three chromophores and their respective dendrons and dendrimers were examined to assess their optical power limiting performance. All three chromophores and their dendrons and dendrimers form stable, highly absorbing bipolaronic charge states showing promise for reverse saturable absorption optical power limiting. The possibility also exists that these materials will show optical power limiting by two photon absorption. The compounds are currently being evaluated as bimechanistic optical limiting materials operating by both reverse saturable absorption and two photon absorption.

CHAPTER 1

INTRODUCTION

With the recent advances in laser technology, a need for protection from their potential damage is imperative. Military needs include protection for eyes and optical sensors against lasers with a wide range of wavelengths and response times. Norinco, Inc. (PRC) has already marketed a portable laser system capable of inflicting damage from up to six miles away.[1] The design of new optical power limiting (OPL) materials has become a progressing field in answer to this need for laser protection.

Optical power limiting is demonstrated when a material can limit the transmittance or output of energy at high energy input. Figure 1 shows a general graph of this process. There are some important parameters to be considered when designing effective optical power limiters for laser protection. The material should transmit light under ambient conditions allowing the eye or sensor to function normally, as indicated by the linear region of the curve, but then the material absorbs most of the intense laser light when needed. The limit goal value is the maximum energy that the eye or sensor can withstand without damage, so the plateau value is set below the limit goal to ensure protection.

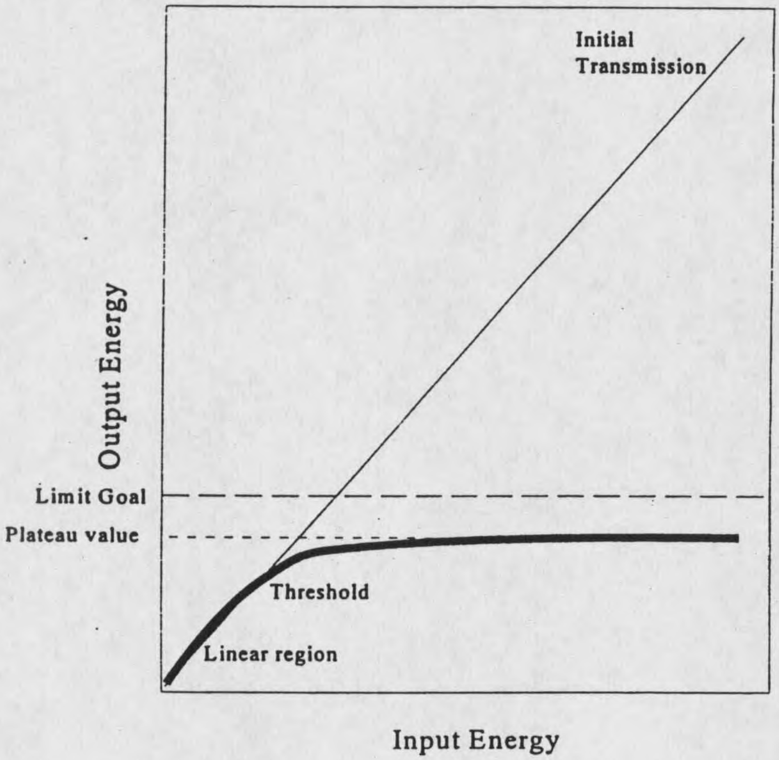


Figure 1. Optical Power Limiting Curve

There is a need to protect against different types of lasers, different wavelengths and different pulse durations. If optical power limiting materials are to be used as a defense, they must be designed to respond quickly and protect a wide frequency range of the spectrum. There are different types of optical power limiting materials being researched at the current time, including reverse saturable absorbers, two photon absorbers, photorefractive materials, photochromic materials and sacrificial materials. Organic materials that exhibit either reverse saturable absorption

(RSA) or two photon absorption (TPA) have the most potential for being effective optical power limiters in laser defense.

Simple forms of schematic energy level diagrams have been presented to represent the pathways giving rise to optical power limiting via either RSA or TPA. Figure 2 illustrates the pathway for RSA. After the S_0 to S_1 transition, then either S_1 to S_n or intersystem crossing (ISC) to another transient state (TS) can occur. The transient states could be triplet, or photogenerated charge states. If the absorptions for S_1 to S_n or TS_1 to TS_n are strong then optical limiting is possible.

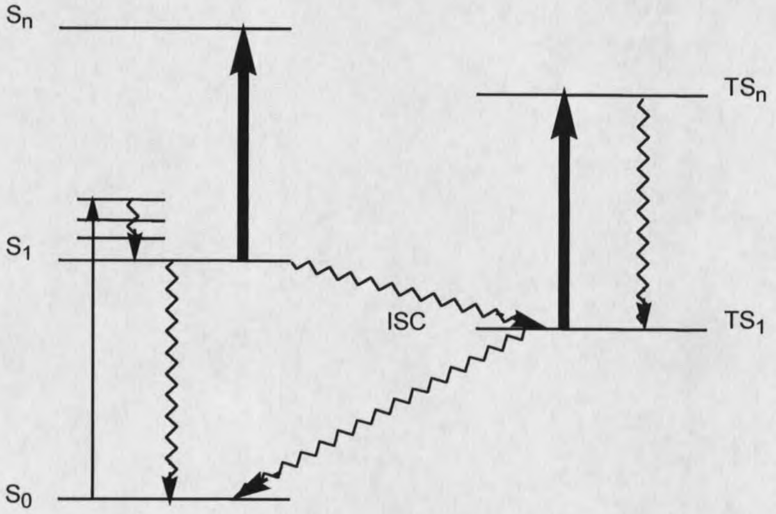


Figure 2. Energy Level Diagram for RSA Optical Power Limiting

There are a variety of materials that have been studied as reverse saturable absorbers, including indanthrones[2], phthalocyanins[3], porphyrins[4], and fullerenes[5]. These materials have RSA behavior based on formation of triplet states resulting from intersystem crossing from the first excited state that has been populated by laser irradiation. The Spangler research group has been studying the RSA behavior of organic chromophores that upon oxidative doping form polaron-like radical-cations and bipolaron-like dications as stable, highly absorbing transient states.[6] These chromophores have transient state absorption cross-sections which are larger than the ground state absorption cross-section. Therefore, as the intensity of the laser irradiation increases, it might be possible for the transient state (TS) transitions via intersystem crossing to become dominant, allowing more light to be absorbed.

Two photon absorbing chromophores have also been a focus of the research in the Spangler group. Figure 3 represents the pathway of TPA. Two photons at half the energy of the excitation wavelength are simultaneously absorbed, populating the S_1 or S_2 levels giving access to the excited state manifold.

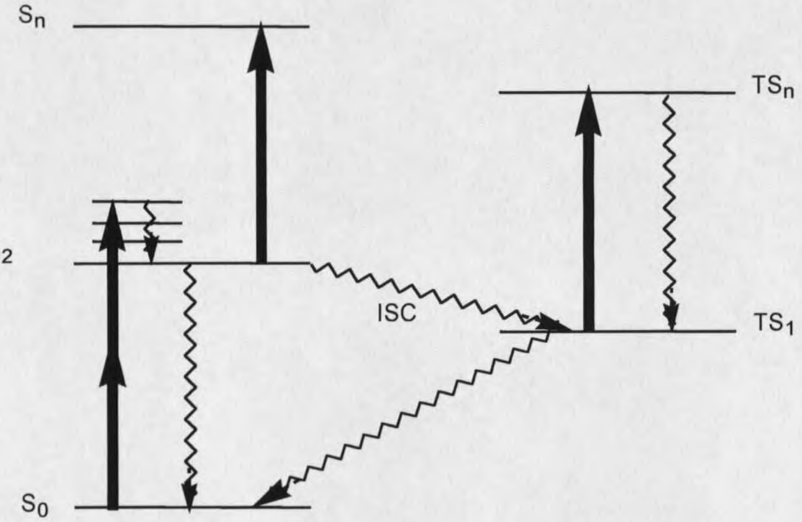


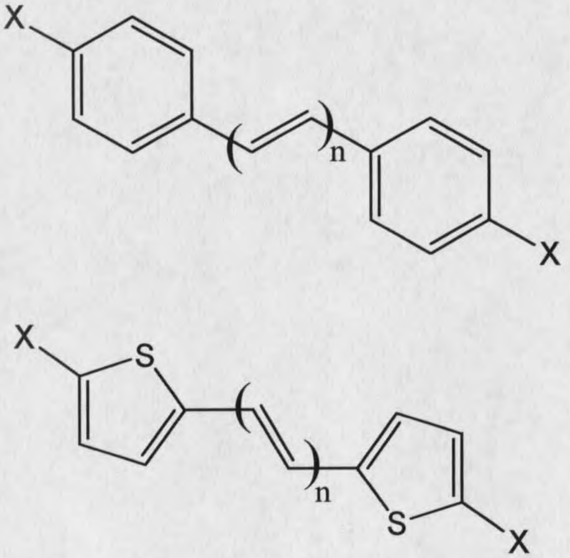
Figure 3. Energy Level Diagram for TPA behavior.

CHAPTER 2

HISTORICAL SECTION

Design of RSA and TPA Chromophores

The Spangler research group has been synthesizing and studying optical power limiting chromophores that operate by RSA or TPA for the past few years, specifically α,ω-dithienyl- and α,ω-diphenylpolyenes with up to ten double bonds.[6-11] Figure 4 shows the general structures for these chromophores.



(1)

n = 1 - 10

X = R_2N, RS, RO, H

(2)

Figure 4. α,ω-Diphenyl- and α,ω-Dithienylpolyenes.

As the number of double bonds increases, the absorptions are red-shifted and the shift in oscillator strength correlates to the electron-donating ability of the substituent groups. The Spangler group has created an extensive library of chromophores with their absorption characteristics to use as a reference when designing nonlinear optical systems, specifically optical power limiting chromophores.

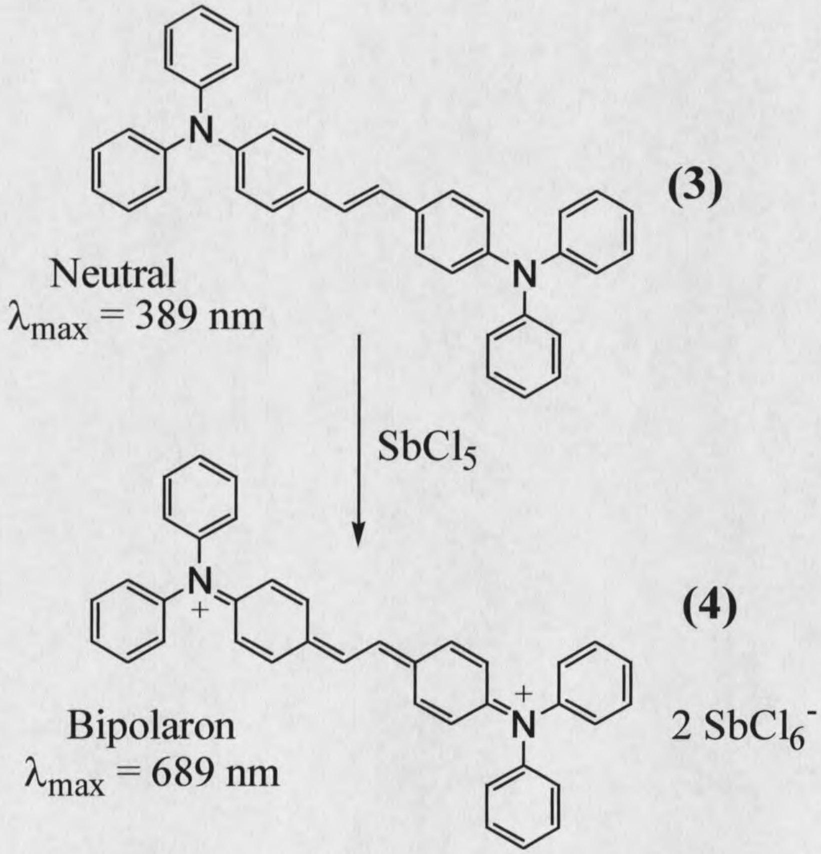


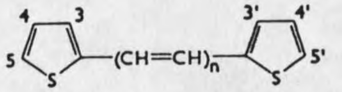
Figure 5. Formation of Bipolaron in Bis-(diphenylamino)-stilbene.

These chromophores exhibit RSA behavior by the formation of stable highly absorbing charge states as the transient species. The neutral and charge state forms of a bis-(diphenylamino)-stilbene chromophore are shown in Figure 5.

Listed in Table 1[6] are the λ_{max} for several dithienylpolyenes and their polaron-like radical cations and bipolaron-like dications. This shows how varying conjugation length and substituents can change absorption characteristics. In almost all cases the polaronic and bipolaronic charge states absorb more strongly than the S_0 to S_1 process indicating the possibility for optical power limiting by the reverse saturable absorption mechanism.

The ability to tune the absorption characteristics of both the neutral and charge state of a chromophore is an important aspect of designing optical power limiting materials. Using the information from structure property relationship studies, tuning the wavelength response of a chromophore is possible. The ideal OPL material for eye protection would have neutral absorption below 400 nm affording the sample little or no color, and then charge state absorptions between 400-700 nm. If these charge states can be photoinduced on the ns or ps time scale, they would be effective OPL materials.

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



Substituents	n	λ_{max} π-π* (nm)[a]	λ_{max} P (+ •) (nm)	λ_{max} BP (+ +) (nm)
none	5	416, 443	705, 797, 1084	653, 713
none	6	432, 461	760, 853, 1154	713, 776
5,5′-(Me)$_2$	5	425, 450	[808][b]	660, 710
5,5′-(Me)$_2$	6	441, 469	888, 1167, 1580	720, 776
3,3′-(Me)$_2$	5	422, 449	[795][b]	650, 699
3,3′-(Me)$_2$	6	440, 469	881, 1154, 1574	713, 769
5,5′-(OMe)$_2$	3	398, 420	[731, 1076][b]	520, (545)[d]
5,5′-(OMe)$_2$	4	416, 442	806, 1103, 1299	577, (605)[d]
5,5′-(SMe)$_2$	3	404	792, 1009, 1240	610, (643)[d]
5,5′-(SMe)$_2$	4	422, 444	859, 1114, 1348	663, (702)[d]
5,5′-(SMe)$_2$	5	434, 460	*c*	717, (775)[d]
5,5′-(SMe)$_2$	6	451, 478	*c*	773, (835)[d]
5,5′-(SC$_{10}$H$_{21}$)$_2$	7	462, 493	*c*	834, (905)[d]
5,5′-(SC$_{10}$H$_{21}$)$_2$	8	475, 507	*c*	884, (970)[d]
3,4,3′,4′-(Bu)$_4$	3	422, 399, 380	*c*	593, 655
3,4,3′,4′-(Bu)$_4$	4	443, 418, 396	*c*	600, 661
3,4,3′,4′-(Bu)$_4$	5	462, 435, 412	*c*	679, 715
3,4,3′,4′-(Bu)$_4$	6	480, 450, 426	*c*	719, 809
3,4,3′,4′-(Bu)$_4$	7	496, 464, 439	*c*	790, 849
3,4,3′,4′-(Bu)$_4$	8	510, 477, 450	*c*	855, 914
3,4,3′,4′-(Bu)$_4$	9	521, 489, 461	*c*	892, 971
3,4,3′,4′-(Bu)$_4$	10	534, 499, 471	*c*	950, 1022
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

[a] CH$_2$Cl$_2$ solution. [b] Absorption spectra decay to BP (+ +) very fast; only unambiguous assignable absorption. [c] Not observed on spectrometer scanning time scale. [d] Absorptions 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. Sienicki, ed.), copyright CRC Press, Boca Raton, Florida.

Research has been directed towards increasing the efficiency of photo-generated charge state formation in conjugated molecules. Sariciftci[12] and coworkers demonstrated photoinduced electron transfer between a conducting polymer and an electron acceptor, specifically C_{60}. They proposed the following mechanism:

$D + A \rightarrow {}^{1,3}D^* + A$	Donor excited
${}^{1,3}D^* + A \rightarrow {}^{1,3}(D{-}{-}{-}A)^*$	Excitation is delocalized over donor-acceptor complex
${}^{1,3}(D{-}{-}{-}A)^* \rightarrow {}^{1,3}(D^{\delta+}{-}{-}{-}A^{\delta-})^*$	Charge transfer initiated
${}^{1,3}(D^{\delta+}{-}{-}{-}A^{\delta-})^* \rightarrow {}^{1,3}(D^{+\circ}{-}{-}{-}A^{-\circ})$	Charged D(+) and A(-) begin to form
${}^{1,3}(D^{+\circ}{-}{-}{-}A^{-\circ}) \rightarrow D(+_\circ) + A(-_\circ)$	Polarons are formed

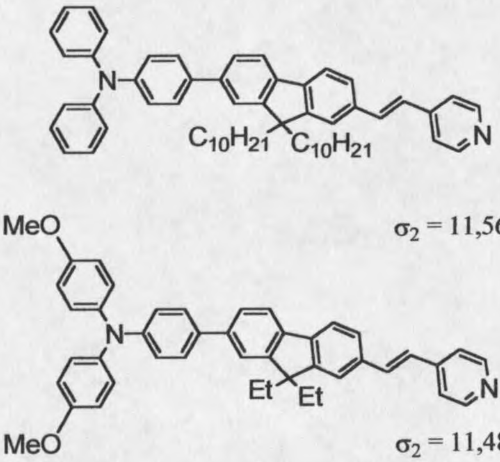
1 and 3 represent singlet or triplet states

In this mechanism the donor and acceptor can have a guest-host relationship or be covalently attached to the same molecule. Pumping the acceptor can lead to the same excited states, so reverse saturable absorption can be achieved by either photo-induced electron transfer or photo-induced hole transfer. Several different acceptor molecules such as C_{60} and TCNQ derivatives have been tested with donor chromophores for photo-induced transfer. Designing an OPL system by this method should offer control of the affected optical region by individually controlling chromophore identity, conjugation length, substituent effects, acceptor identity, and the donor/acceptor ratio.

Designing efficient TPA chromophores is also being studied. Two photon cross-sections are related to the Im component of third-order nonlinear optical response:

$$\sigma_2 = \frac{8\pi^2 h\nu}{n^2c^2N}\,\mathrm{Im}[\chi^{(3)}]$$

where h=Planck's constant, ν=frequency of incident light, n=index of refraction, c=speed of light in vacuum and N=number of absorbing molecules.[13]



(5)

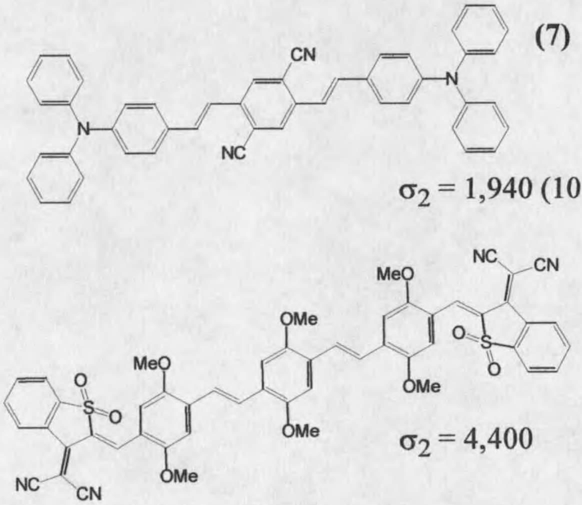
σ_2 = 11,560 (10^{-50} cm^4s/photon)

(6)

σ_2 = 11,480

Figure 6. Chromophores with Enhanced TPA Cross-sections (Reinhardt).

In addition to the Spangler group, two other groups have also been studying structure property relationships in order to increase the two photon cross-sections. Reinhardt and coworkers at Wright Labs (AFRL) have designed a series of molecules for comparison of their TPA cross-sections and discovered some structural properties that increase TPA cross-sections.[14] By designing a chromophore with a high degree of polarizability, extended conjugation length, and maximum planarity, the TPA cross-section can be optimized. The best TPA chromophores from this design study are illustrated in Figure 6. Another group at the University of Arizona, Perry, Marder and coworkers, has also discovered parameters for the design of enhanced TPA chromophores.[15] Originally they showed that bis-(di-n-butylamino)-E-stilbene had a TPA cross-section 20 times that of E-stilbene. They expanded on this experimental result to show that by increasing conjugation length and the extent of charge transfer, the TPA cross-section is enhanced. The extent of charge transfer can be increased by symmetrically adding donor and acceptor groups to the molecule. Either D-A-D or A-D-A motifs can be used. Examples of both are shown in Figure 7.



(7)

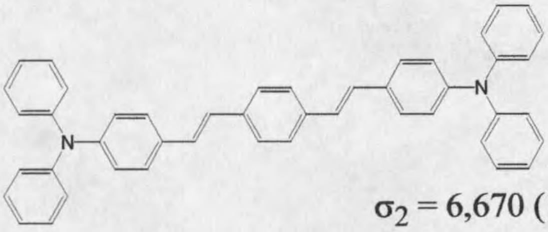
$\sigma_2 = 1{,}940\ (10^{-50}\text{cm}^4\text{s/photon})$

(8)

$\sigma_2 = 4{,}400$

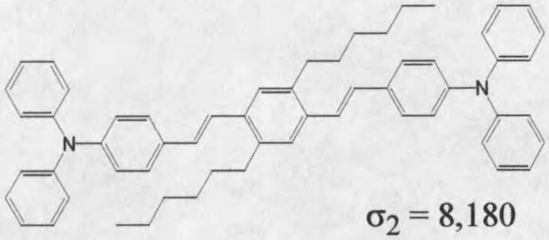
Figure 7. Chromophores with D-A-D and A-D-A Motifs.

The Spangler group, in collaboration with Science Applications International Corporation and the Materials Directorate at Wright Laboratories (MLPJ) (WPAFB, OH), has shown that α,ω-dithienylpolyenes have enhanced two photon absorption states that provide optical limiting.[16] The Spangler group has also designed new TPA chromophores in collaboration with Laser Photonics Technology. Two examples of chromophores developed with large two photon cross-sections for 10 ns pulses are shown in Figure 8.



(9)

$\sigma_2 = 6{,}670\ (10^{-50}\mathrm{cm}^4\mathrm{s/photon})$



(10)

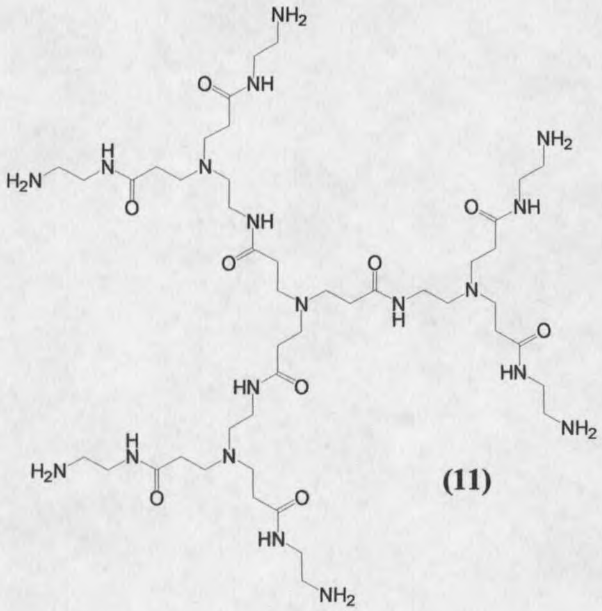
$\sigma_2 = 8{,}180$

Figure 8. Chromophores with Enhanced TPA Cross-sections (Spangler).

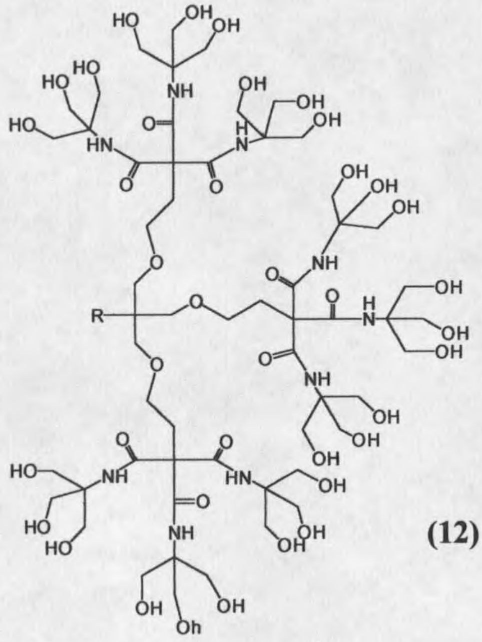
Design and Synthesis of Dendrimers

With the increasing number of applications for organic molecules in materials science, the need for processible and functional polymers has increased. The ability to control the molecular architecture of macromolecules has been achieved with a new class of hyperbranched molecules called dendrimers.[17,18,19]

In the 1980's Tomalia[20] and Newkome[21] published different approaches to highly branched starburst **11** and arboral **12** structures as illustrated in Figure 9.



(11)



(12)

Figure 9. Tomalia's and Newkome's Original Dendrimers

These original structures were prepared by the traditional divergent methodology which involves the addition of a polyfunctional monomer to a central core. Tomalia used methyl acrylate and ammonia, followed by amidation of the resulting esters with excesses of ethylenediamine. Repetition of the two steps leads to higher generations (Figure 10).

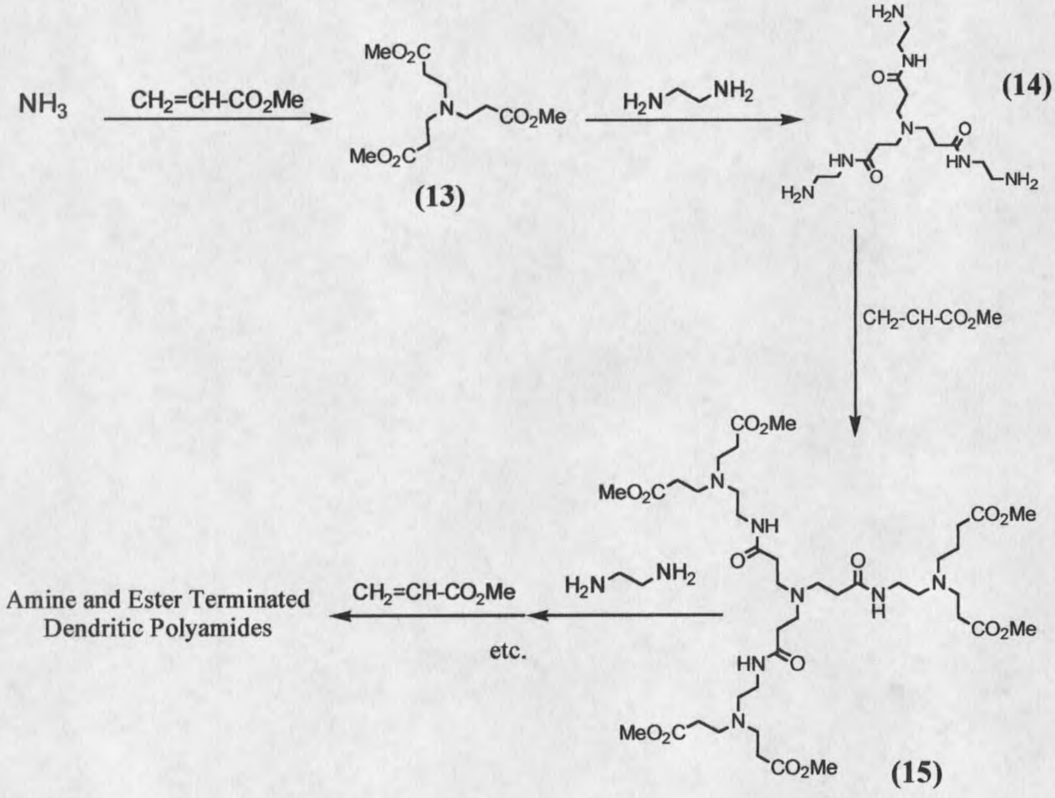


Figure 10. Tomalia's Starburst Synthesis.

A number of potential problems arise from synthesis of dendrimers with this divergent approach. With the rapid increase in the number of reactive groups at the surface of the dendrimer, any incomplete reaction of the terminal groups leads to imperfections in the next generation. Also, extreme excess amounts of reagents are required in the reactions of higher generations causing difficulty in purification. Using a convergent method of dendrimer synthesis potentially answers these particular problems.

Convergent synthesis of dendrimers starts with what will eventually be the periphery of the molecule and growth occurs from the outside-in with the reaction of only a limited number of reactive sites. The starting material **(16)** contains the eventual surface functionality (phenyl) and a reactive functional group (CH_2-Br). It is reacted with a monomer **(17)** with at least two coupling sites and a protected functional group (CH_2-OH) that can be converted to the reactive group to continue the growth. These successive reactions create wedges that are referred to as dendrons **(18)**. The dendrons are eventually coupled to a polyfunctional core **(21)** to provide the final dendritic macromolecule **(22)**. Each successive generation of dendron is purified before the next reaction, which allows for production of controlled monodisperse dendritic macromolecules. Fréchet and Hawker[17] synthesized a family of dendritic polyether macromolecules using 3,5-dihydroxybenzyl alcohol **(17)** as the monomer unit. This synthesis is illustrated in Figure 11. One problem with the convergent method of dendrimer synthesis is the increasing steric crowding around the core during attachment as the size of the dendron increases.

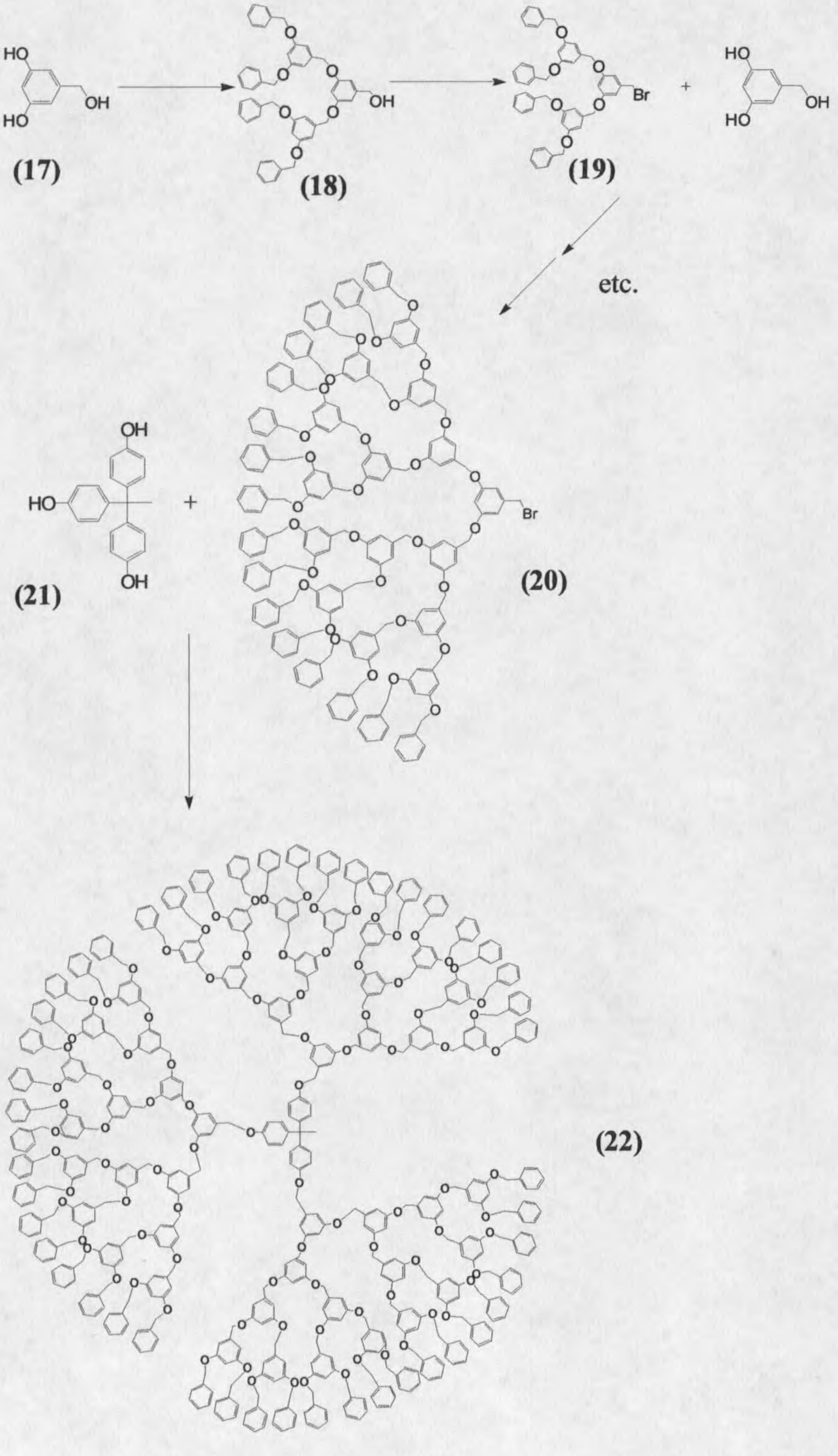


Figure 11. Fréchet Convergent Dendrimer Synthesis

CHAPTER 3

RATIONALE FOR PROPOSED RESEARCH

As mentioned earlier, the Spangler group has synthesized many α,ω-dithienyl- and α,ω-diphenylpolyenes for optical power limiting. The bis-(diphenylamino)diphenylpolyene series (Figure 12) with up to three double bonds showed preliminary success as both RSA and TPA chromophores[22].

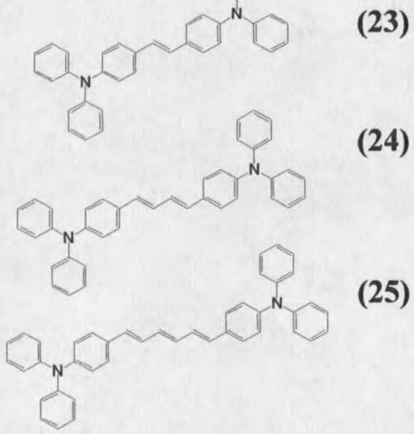
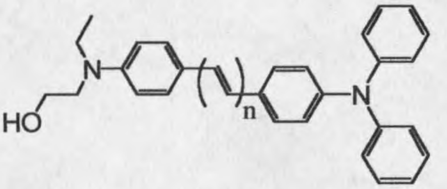


Figure 12. Bis-(diphenylamino)diphenylpolyenes.

As of now, one of the major limitations in designing OPL materials is generating broad band coverage. A possible solution is to design optical limiting chromophores that can protect via two mutually supportive mechanisms. Since the chromophores

23, **24**, and **25** have shown OPL behavior via either RSA or TPA, they are currently being viewed as candidates for this possible solution.

Because of the processing advantages to using polymers for device applications, chromophores needed to be functionalized for polymer attachment. This turned out to be nontrivial for this series **(23-25)**. The proposed solution was to modify the chromophore by replacing a diphenylamino group on one end with an N-ethyl, N-hydroxyethyl amino group (Figure 13). This modification would allow for chromophore attachment to polymers.



n=1 **(26)**
n=2 **(27)**
n=3 **(28)**

Figure 13. Chromophores Modified for Polymer Attachment.

The Spangler group traditionally synthesized pendant polymers by attaching chromophores to a PMMA backbone. Over the past few years the group proposed synthesizing dendrons and dendrimers with chromophores around the periphery as an alternative to pendant structures. Dendrimers were preferred rather than conventional pendant polymers because the dendrimer can be loaded with a much higher concentration of chromophore. Also, PMMA is often damaged from laser testing, so another form of polymer is required for OPL device application. The synthetic approach to the dendrimers will also allow for the incorporation of electron-accepting chromophores for photo-induced charge state formation. This approach is illustrated in Figure 14.

The focus of the research is to synthesize dendrimers with the diphenyl-polyenes **26-28** as the surface groups. It is predicted that these compounds will have optical power limiting properties with the possibility of bimechanistic OPL via both RSA and TPA.

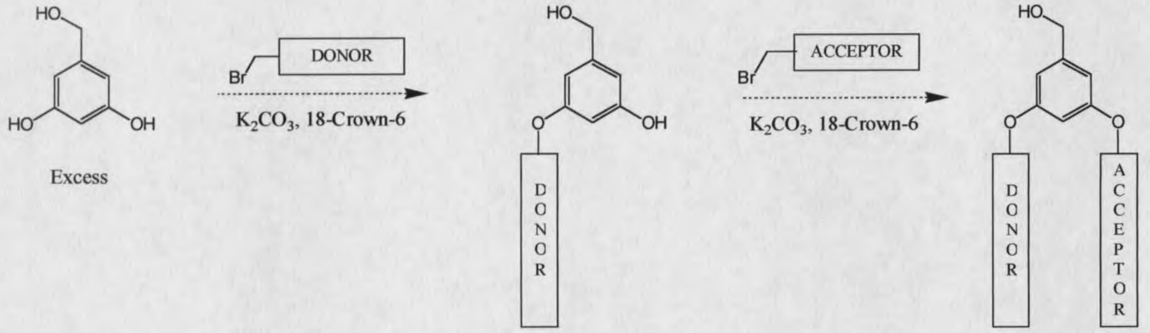


Figure 14. Synthesis of Dendron Incorporating both Donor and Acceptor Chromophores

CHAPTER 4

RESULTS AND DISCUSSION

Proposed Synthesis of Functionalized Chromophores

Synthesis of appropriately functionalized chromophores can be envisioned by the following disconnections. (Figure 15)

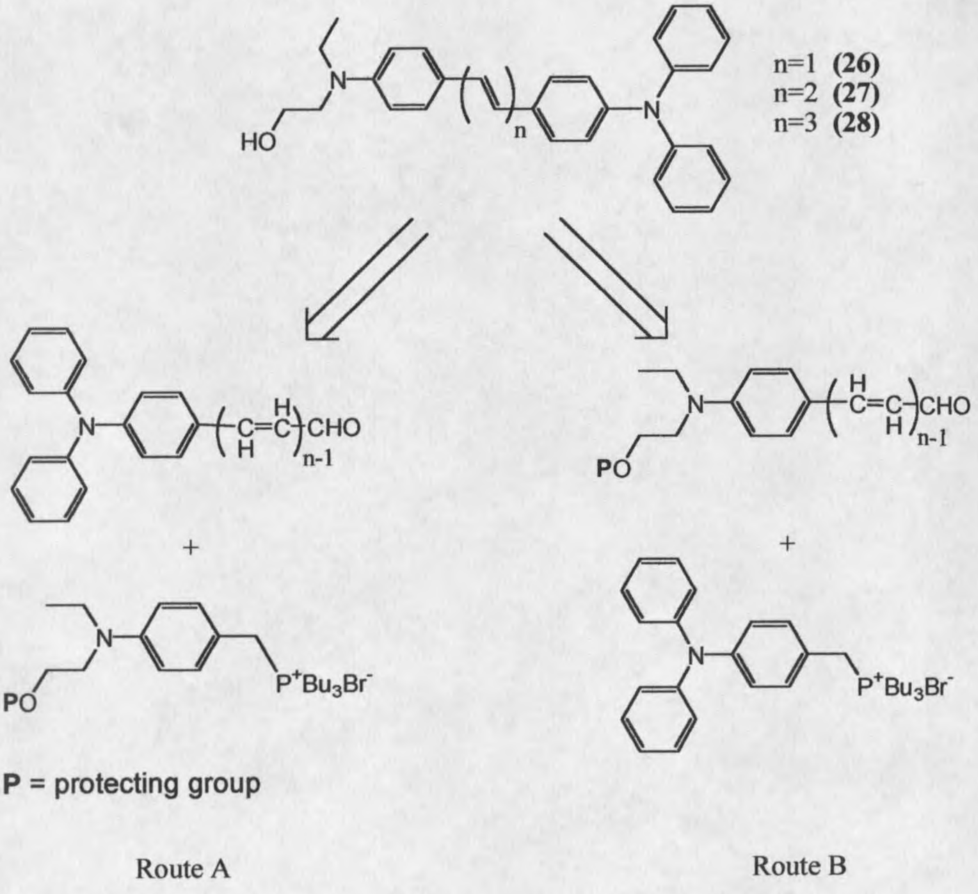
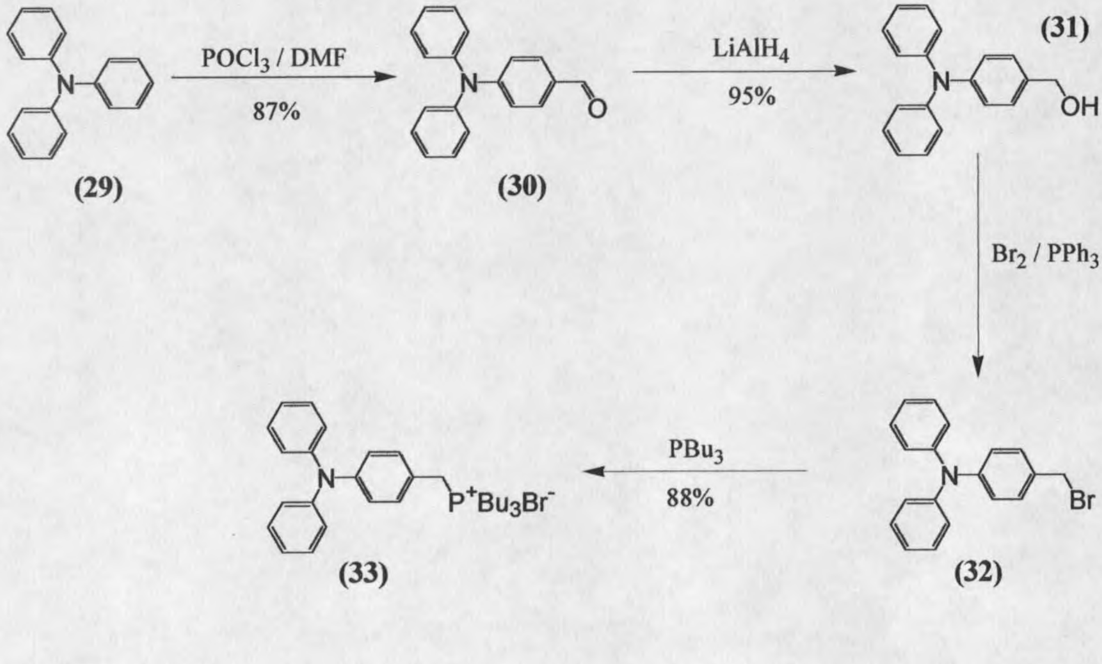


Figure 15. Retrosynthesis of Functionalized Chromophores

It was decided to pursue Route B to avoid the complication of incorporating the Wittig salt and protected alcohol in the same moiety.

The important intermediate 4-diphenylaminobenzyl tributylphosphonium bromide was synthesized as illustrated in Scheme1. Triphenylamine (Aldrich) was formylated with the Vilsmeier-Haack reaction in 87% yield. The aldehyde was reduced with LAH to the alcohol, bromination with bromine and triphenylphosphine was followed by heating with tributylphosphine for 16 hours. The desired Wittig salt was obtained as a white solid in high yield (88%). The crude bromide **32** was not purified due to its relative instability.

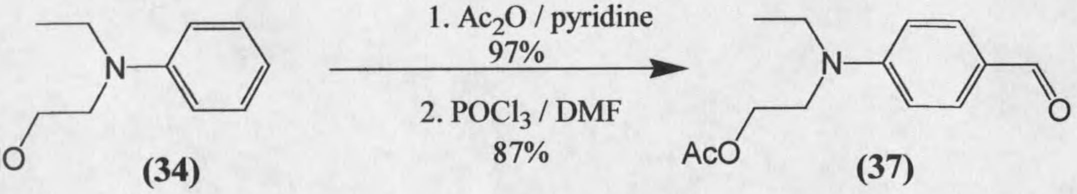
Scheme 1. Synthesis of 4-Diphenylamino benzyl tributylphosphonium bromide.



Synthesis of Diphenylamino-N-ethyl-N-hydroxyethylaminodiphenylpolyene Chromophores

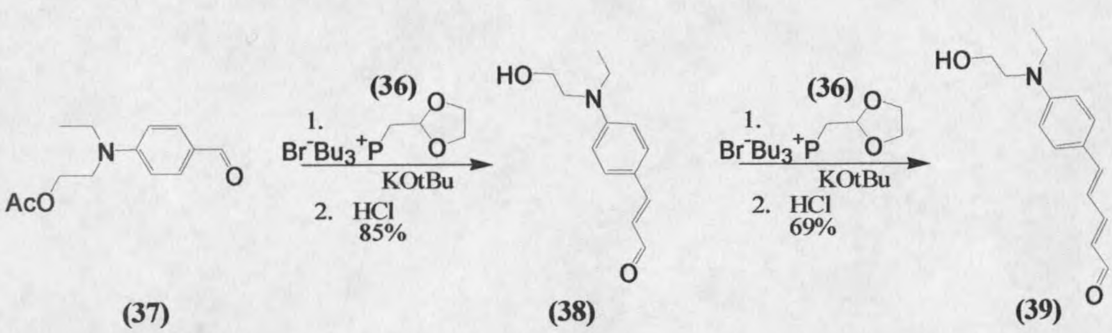
The diphenylamino-N-ethyl-N-hydroxyethylaminodiphenylpolyenes were synthesized starting with a molecule prefunctionalized with a hydroxyl group for dendrimer synthesis. Commercially available N-ethyl-N-hydroxyethyl aniline (Aldrich) was first reacted with acetic anhydride in pyridine to protect the hydroxyl functionality for the acidic Vilsmeier-Haack reaction. This procedure is shown in Scheme 2. This aldehyde is ready for coupling to the Wittig salt to make the chromophore with an ethene bridge.

Scheme 2. Synthesis of 4-[N-ethyl-N-(2'-acetoxyethyl)amino]benzaldehyde



In order to make the chromophores with butadiene and hexatriene bridges, the conjugation of the aldehyde is extended as shown in Scheme 3. The Spangler et al. oxopropenylation methodology[23] was followed. A highly reactive phosphonium salt incorporating an acetal that can be converted to an aldehyde upon hydrolysis was used. The acetal formation was monitored by NMR spectroscopy. The reaction was continued until all of the starting aldehyde was consumed because separation of starting and extended aldehydes is extremely difficult. Once the acetal was obtained, it was immediately dissolved in THF and hydrolyzed with 3M HCl. Finally, the solution was neutralized with Na_2CO_3 to deprotonate the amine for organic extraction. The aldehyde **38** was obtained as a dark orange solid in 85% yield. The extension reaction was repeated for extended aldehyde **39**, which was obtained as a dark red solid in 69% yield.

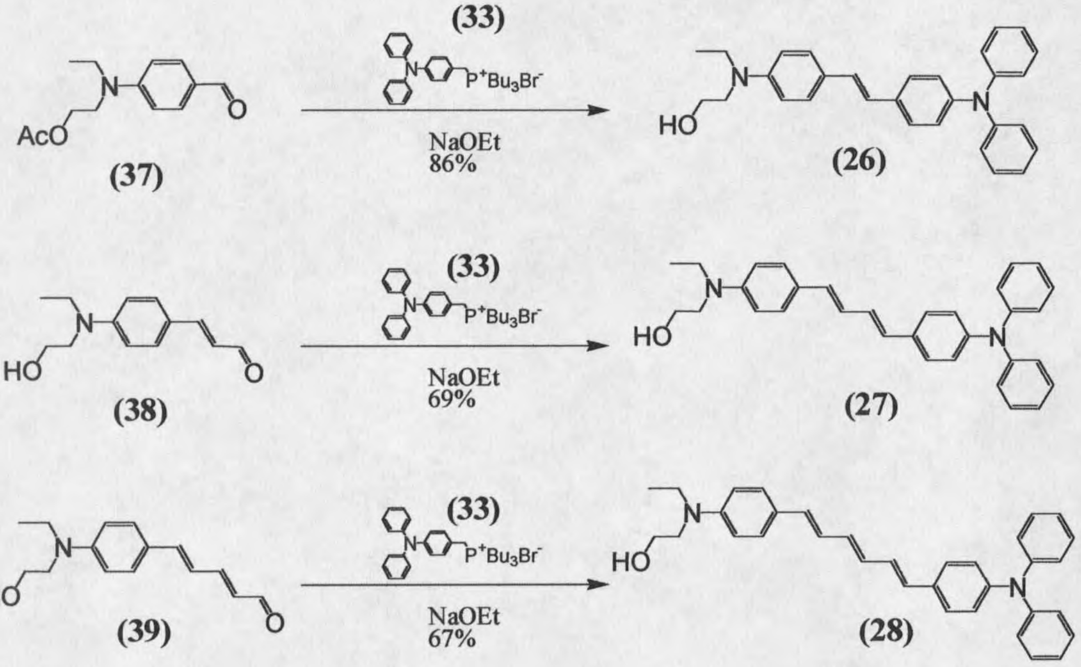
Scheme 3. Conjugation Extension of Aldehydes



(37) (38) (39)

α-Diphenylamino-ω-N-ethyl-N-(2'-hydroxyethyl)aminodiphenylpolyenes **26**, **27**, and **28** were synthesized from aldehydes **37**, **38** and **39** by Wittig reactions with yields of 86%, 69%, and 67% respectively. The reactions are illustrated in Scheme 4.

Scheme 4. Wittig Reactions

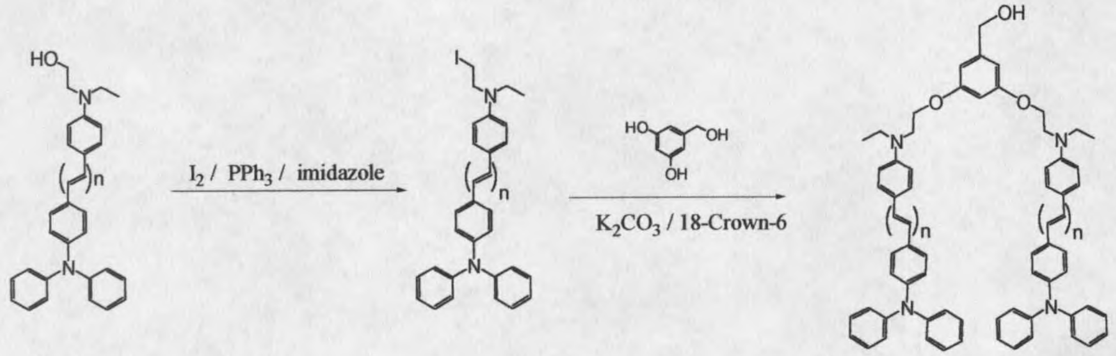


Synthesis of Dendrons

The three chromophores, **26**, **27**, and **28**, whose syntheses are outlined in the previous section, were converted to dendrons for convergent dendrimer synthesis (Scheme 5). First, the hydroxy functionality was converted to an iodide followed by condensation with 3,5-dihydroxybenzyl alcohol according to the methodology developed by the Fréchet group.[17]

Bromination of the chromophores was first tried with both Br_2 / PPh_3 and PBr_3 giving considerably lower yields than the iodination. The reaction of the chromophores with iodine in the presence of triphenylphosphine and imidazole successfully converted the hydroxyl group to an iodide. The timing of the reaction was critical. The reaction was complete in 10-15 minutes and longer than 30 minutes would lead to degradation of the product. The n=3 chromophore **(28)** was especially vulnerable to degradation so a lower yield was accepted with the ability to recover about 20% of the hydroxy-functionalized chromophore. The crude iodide products were purified by filtering through a silica plug to afford iodides **40**, **41**, and **42** in 80%, 90%, and 52% yields.

Scheme 5. Synthesis of Dendrons



26, n = 1
27, n = 2
28, n = 3

n	Compound #	
1	**40**	80%
2	**41**	90%
3	**42**	52%

n	Compound #	
1	**43**	38%
2	**44**	63%
3	**45**	29%

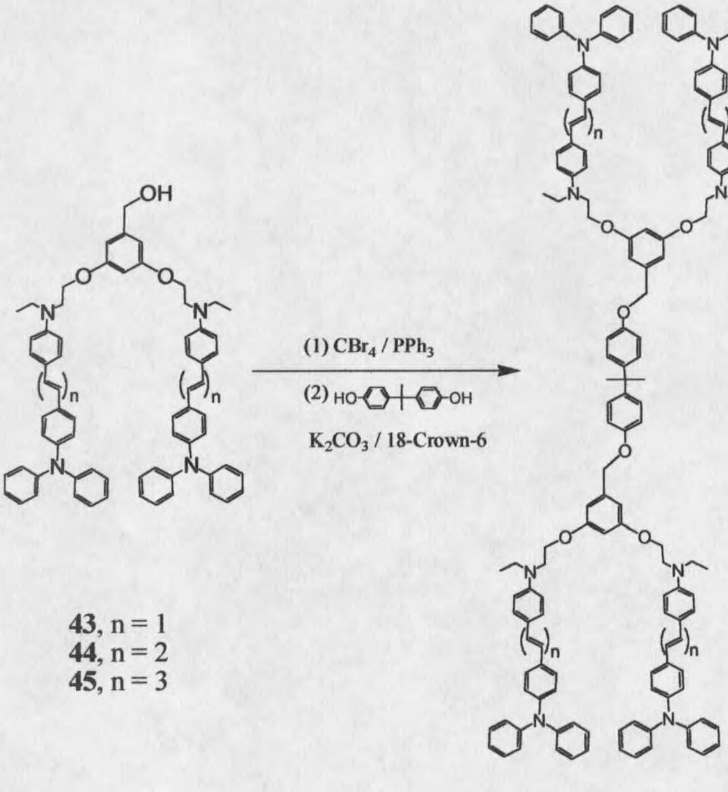
The iodides were then reacted with 3,5-dihydroxybenzyl alcohol, potassium carbonate, and 18-crown-6, under an atmosphere of nitrogen. A considerable amount of elimination product was recovered from initial refluxing for 48 hours. In the attempt to select for the substitution reaction, the mixture was stirred at room temperature for 48 hours before refluxing for 48 hours. This procedure did improve the yield of dendron by 10%. The dendrons **43**, **44**, and **45**, were isolated in 38%, 63%, and 29% yields as solids after column chromatography.

Synthesis of Dendrimers

Model generation-0 dendrimers were synthesized in order to offer comparison of the optical properties of chromophores, dendrons, and dendrimers. The convergent dendrimer synthesis requires that the dendrons be activated by bromination and then coupled to a polyfunctional core. Bisphenol-A was chosen as the core to give the G-0 dendrimer with four chromophore moieties on the surface. Scheme 6 illustrates the conversion of dendrons to dendrimers.

The dendrons **43**, **44**, and **45** were first brominated with tetrabromomethane and triphenylphosphine. Excess CBr_4 and PPh_3 were removed by column chromatography and then the dendron bromides were used immediately in the coupling to the bisphenol-A core. The bromides were refluxed in acetone with bisphenol-A, potassium carbonate, and 18-crown-6 under nitrogen for 48 hours. After purification by column chromatography, the dendrimers **46**, **47**, and **48** were obtained as solids in 66%, 58%, and 59% yields.

Scheme 6. Synthesis of Generation-0 Dendrimers



43, n = 1
44, n = 2
45, n = 3

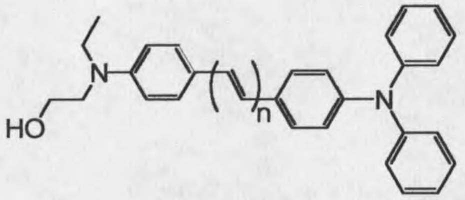
n	Compound #	
1	**46**	66%
2	**47**	58%
3	**48**	59%

UV-VIS Spectra of Chromophores, Dendrons, and Dendrimers

UV-VIS spectroscopy was used to examine the absorption characteristics of the chromophores, dendrons, and dendrimers. Determination of any changes in the absorption characteristics between a chromophore and its respective dendron and dendrimer was important. If the UV-VIS spectra are comparable, then the assumption is made that the chromophores behave independently even though attached to a core molecule.

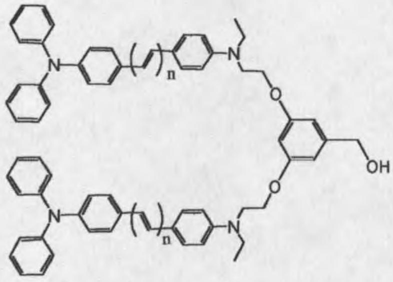
The chromophores, dendrons, and dendrimers were tested in solutions of methylene chloride and oxidatively doped with $SbCl_5$. All compounds formed stable bipolaronic dications in solution with absorbances in the range of 550-675 nm. The UV-VIS absorptions for both neutral and oxidized species are displayed in Tables 2, 3, and 4. The comparative spectra for the three chromophores and their dendron and dendrimer counterparts are shown in Figures 15-23.

Table 2. Bipolaron Formation in Functionalized Diphenyl Polyenes



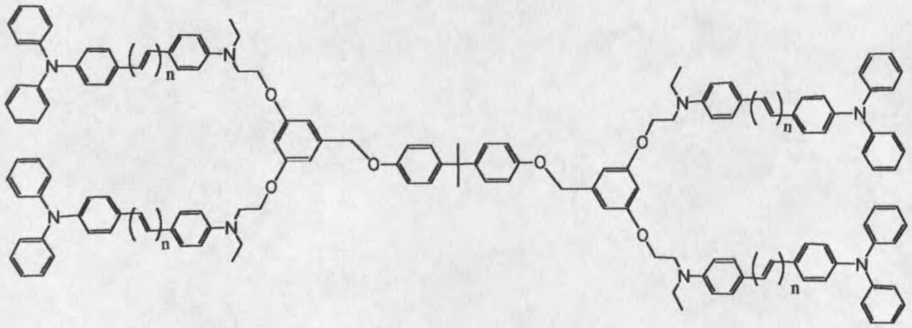
n	λ_{max} neutral (nm)	λ_{max} bipolaron (nm)	ε_{max} neutral ($M^{-1}cm^{-1}$)
1	380	590	54,300
2	399	626	69,800
3	417	670	92,500

Table 3. Bipolaron Formation in Dendrons



n	λ_{max} neutral (nm)	λ_{max} bipolaron (nm)	ε_{max} neutral ($M^{-1}cm^{-1}$)
1	382	593	106,200
2	399	630	135,600
3	418	665	157,900

Table 4. Bipolaron Formation in Dendrimers



n	λ_{max} neutral (nm)	λ_{max} bipolaron (nm)	ε_{max} neutral ($M^{-1}cm^{-1}$)
1	381	590	184,600
2	399	630	272,200
3	418	662	337,800

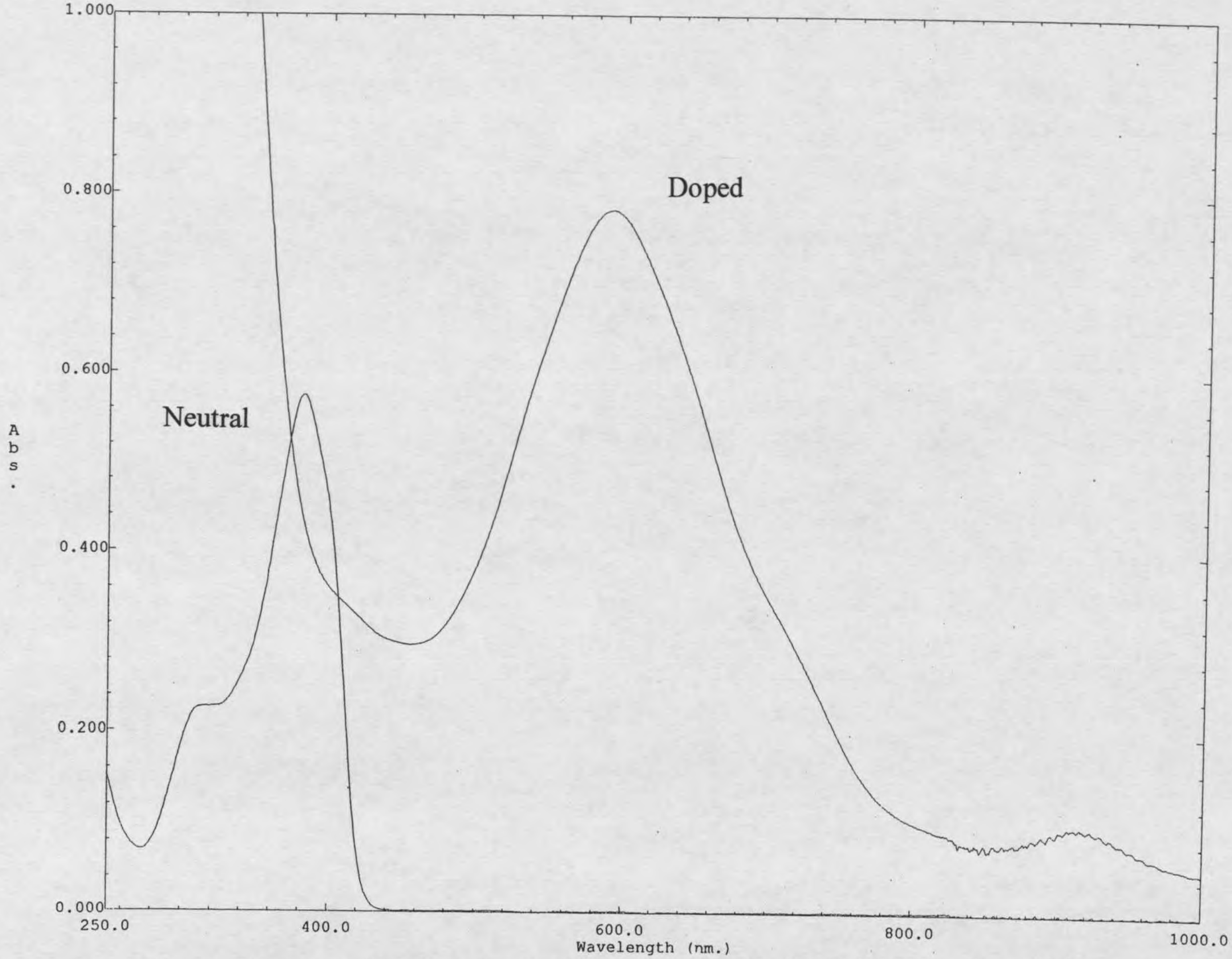


Figure 16. Absorption Spectra for Neutral and Doped n=1 Chromophore (26)

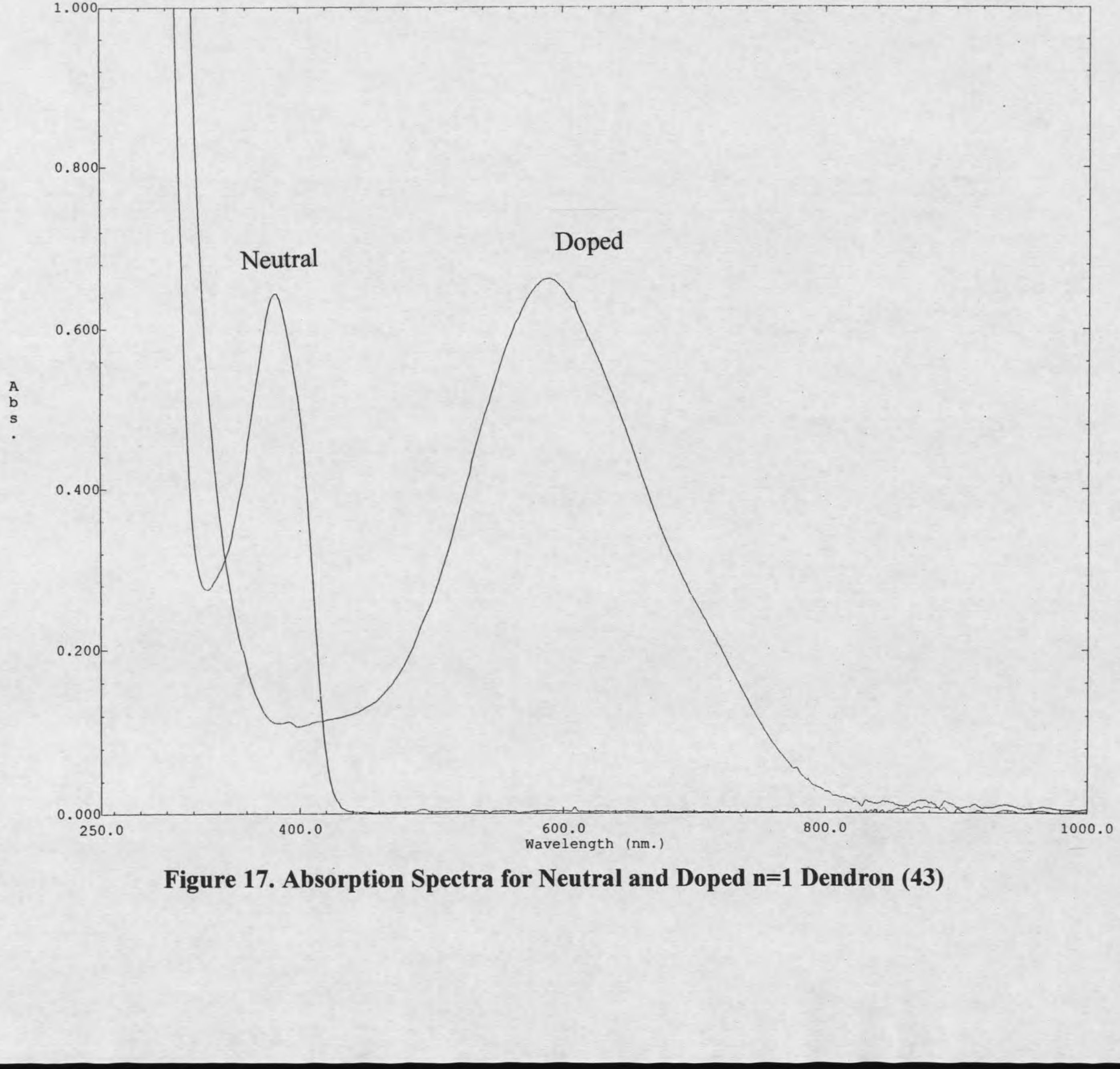


Figure 17. Absorption Spectra for Neutral and Doped n=1 Dendron (43)

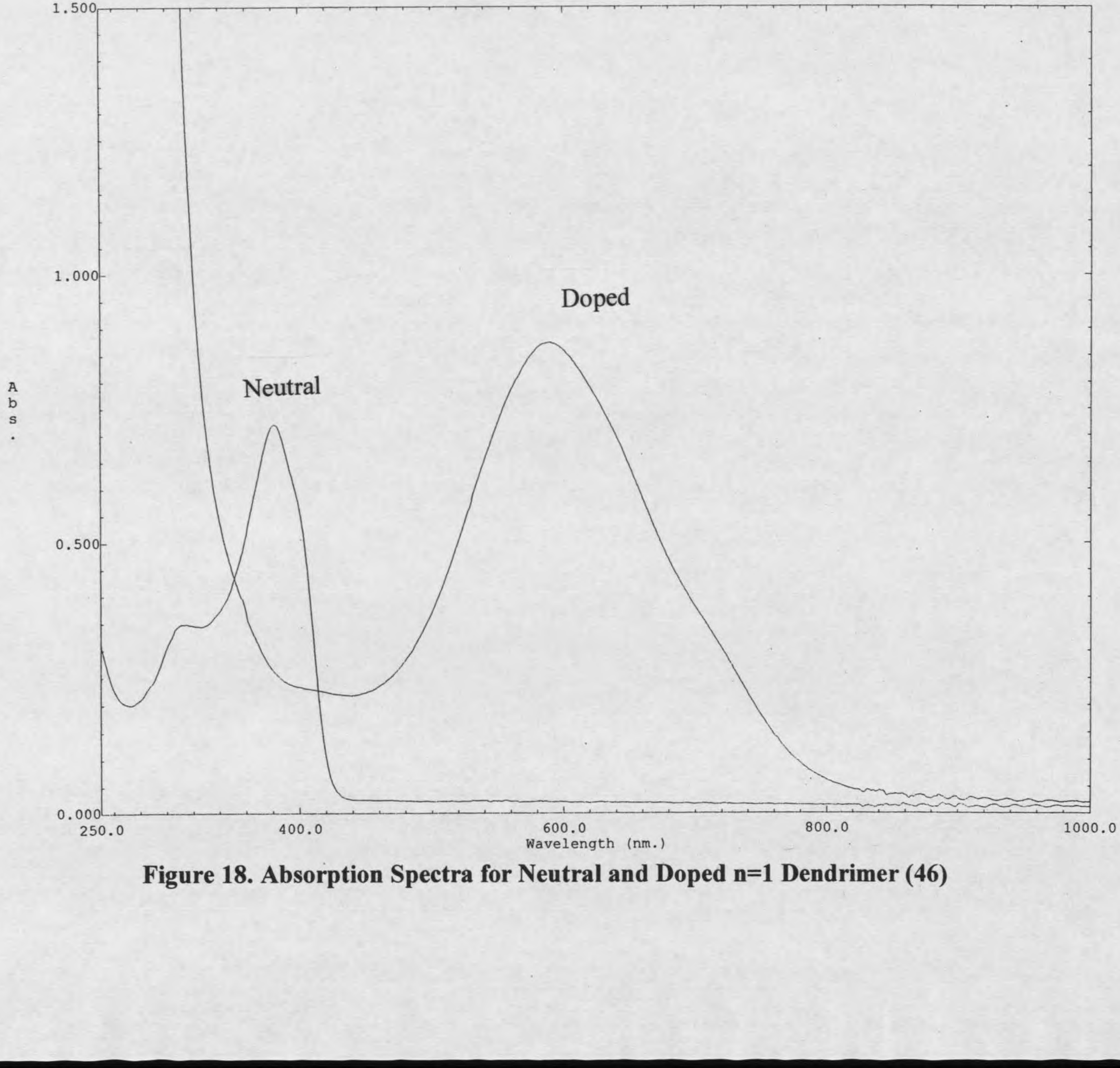


Figure 18. Absorption Spectra for Neutral and Doped n=1 Dendrimer (46)

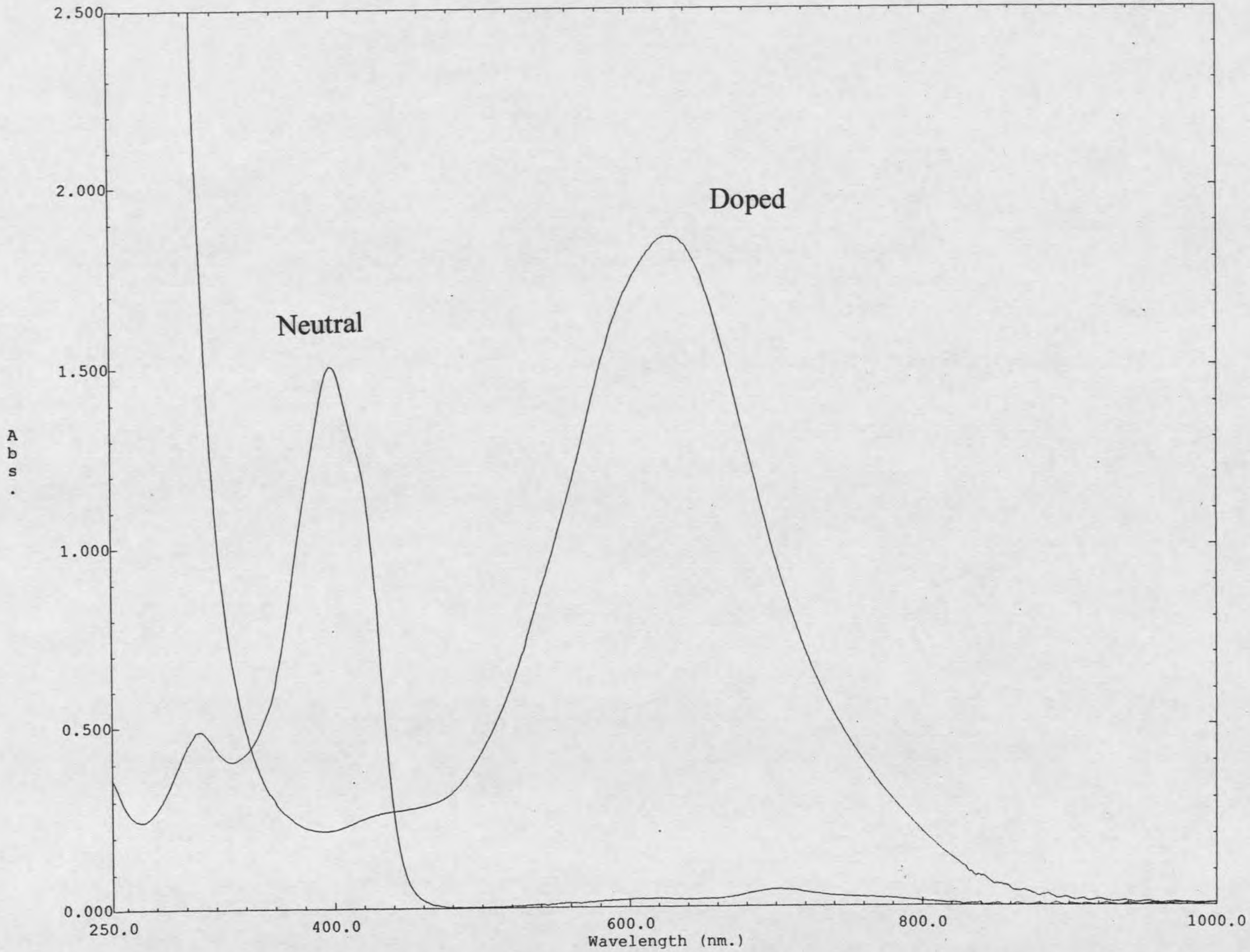


Figure 19. Absorption Spectra for Neutral and Doped n=2 Chromophore (27)

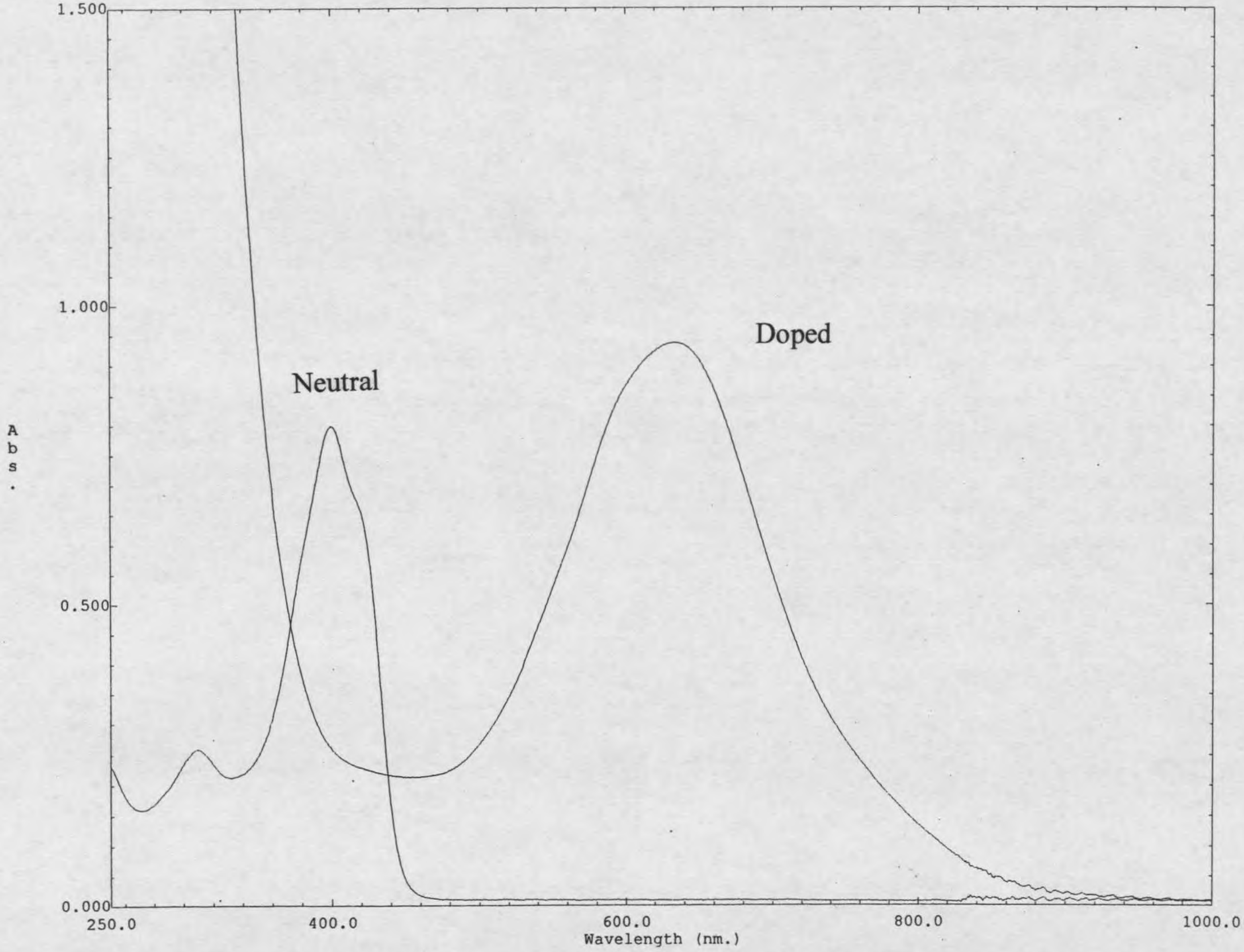


Figure 20. Absorption Spectra for Neutral and Doped n=2 Dendron (44)

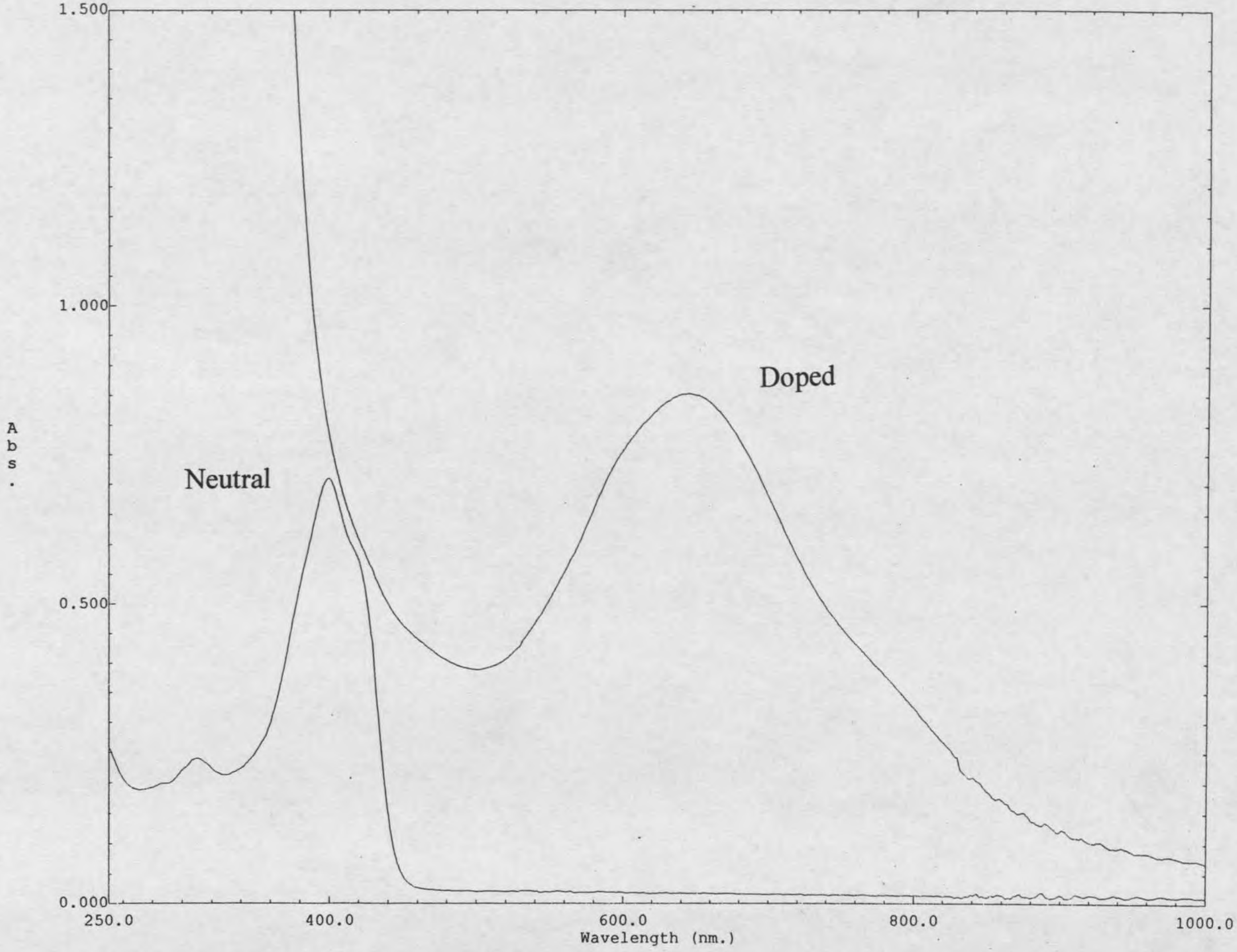


Figure 21. Absorption Spectra for Neutral and Doped n=2 Dendrimer (47)

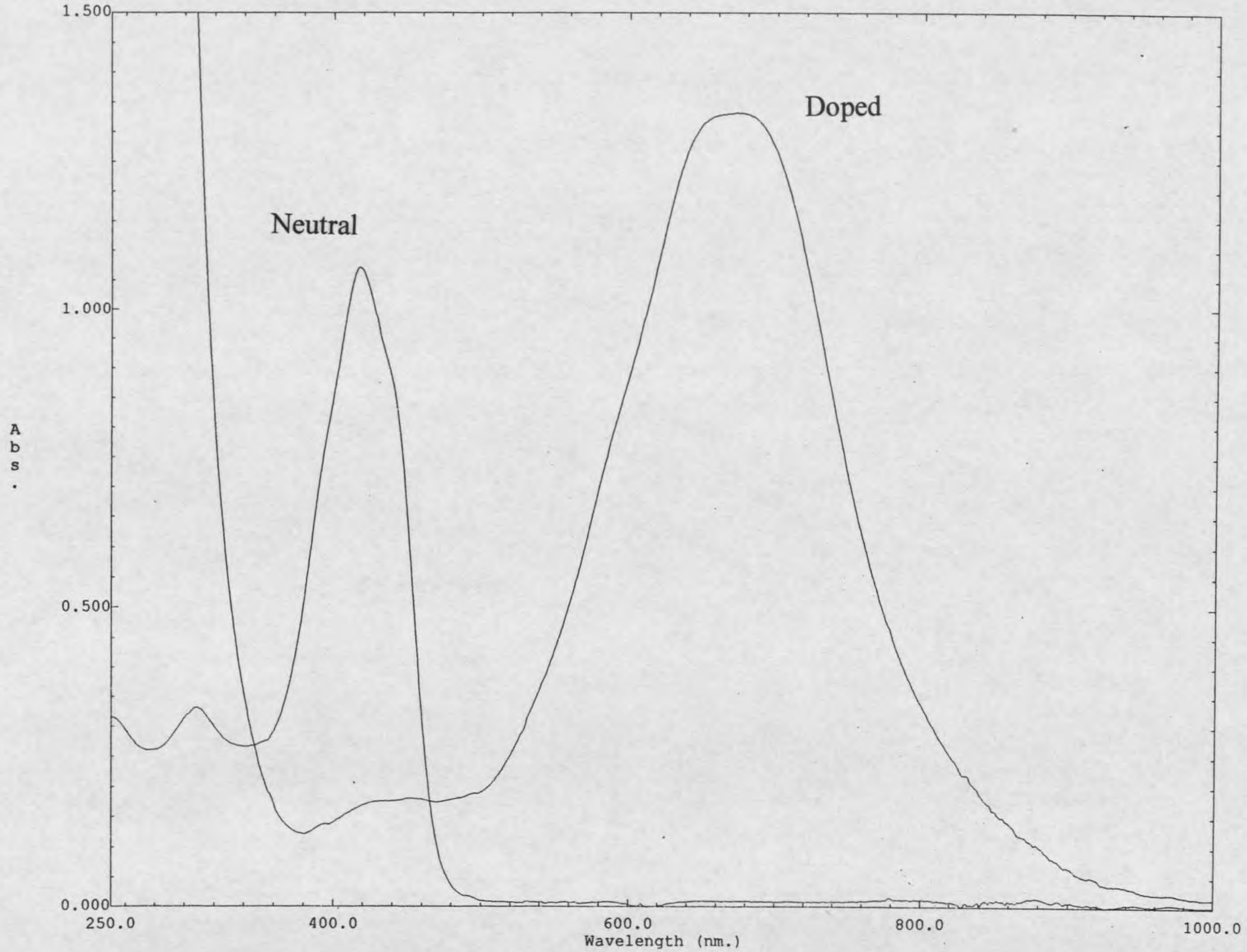


Figure 22. Absorption Spectra for Neutral and Doped n=3 Chromophore (28)

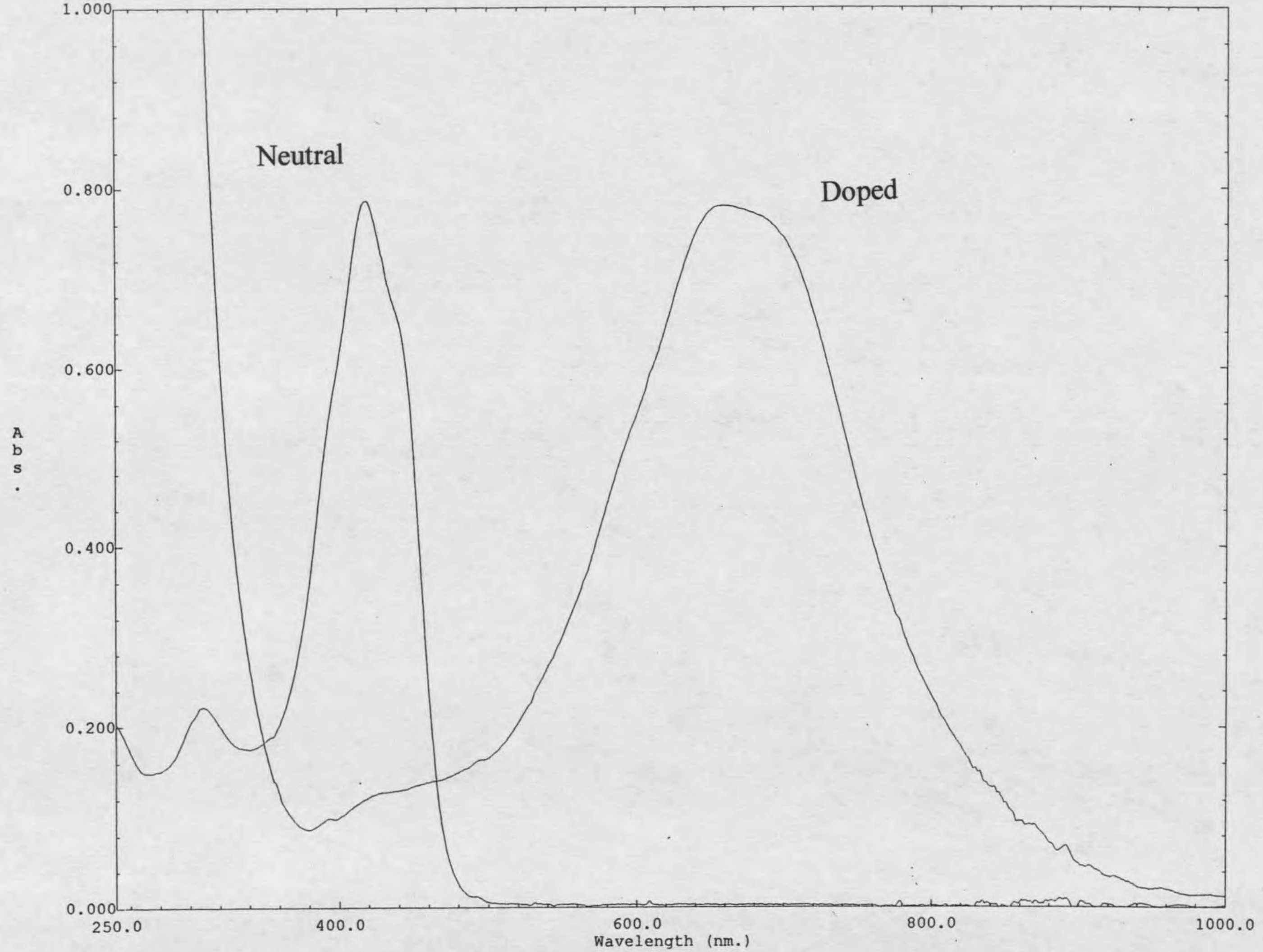


Figure 23. Absorption Spectra for Neutral and Doped n=3 Dendron (45)

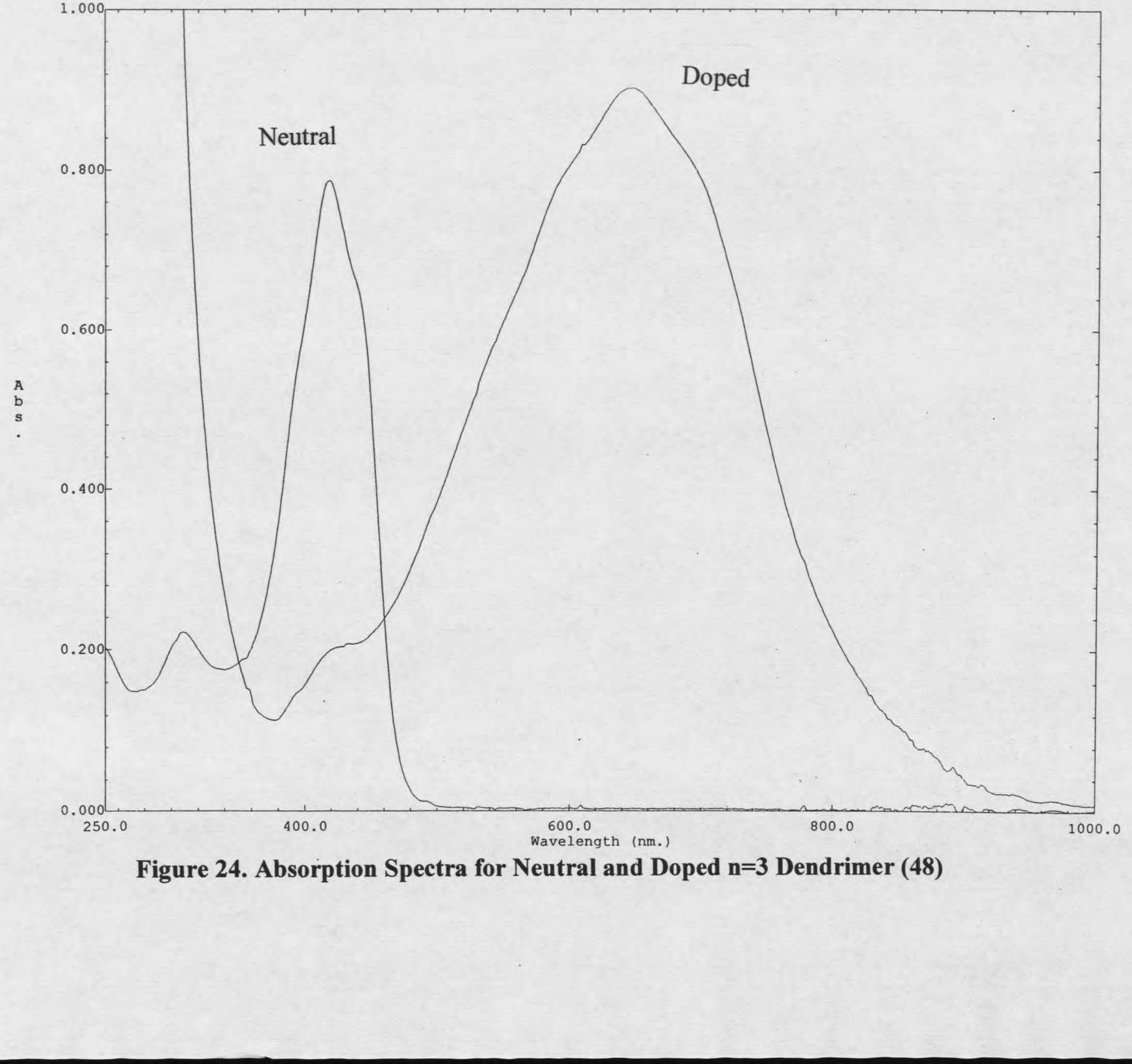


Figure 24. Absorption Spectra for Neutral and Doped n=3 Dendrimer (48)

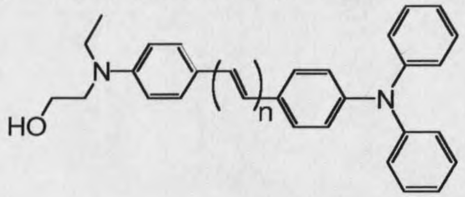
The absorption maxima for each chromophore and its corresponding dendron and dendrimer are the same within 1 nm, and the bipolaron maxima of each chromophore and its dendron and dendrimer are within 10 nm of one another. Each bipolaron displays enhanced absorption indicating that these materials may exhibit optical limiting via RSA.

Because the absorption spectra of each chromophore and its respective dendron and dendrimer are so similar, it is concluded that the chromophore moieties are behaving independently during oxidative doping.

Photoluminescence Studies for OLEDs

During the synthesis of these materials, it was discovered that they might be useful in new organic light emitting diodes (OLEDs) as either hole-transport or emitter components. Similar to optical limiting, OLEDs require the formation of charge states by electron and hole injection. One complication in OLEDs is that the charge generation and transport must be balanced in order to have an efficient device. The used of dendrimers in this application could also answer this problem by incorporating the electron acceptor and donor into the same dendrimer. Preliminary characterization studies of the chromophores and their respective dendrons and dendrimers have begun with Prof. Linda Sapochak and her research group at the University of Nevada-Las Vegas. The three chromophores were evaluated for their photoluminescence properties in comparison to Alq as a standard. The absorbance, photoluminescence and quantum efficiency of the chromophores are shown in Table 5.

Table 5. Photoluminescence Data for Diphenylamino-N-ethyl-N-hydroxyethylaminodiphenyl Polyenes



n	Absorbance (nm)	Photoluminescence (nm)	Quantum Efficiency vs. Alq
1	382	450	4.05
2	401	489	3.04
3	421	541	0.95

Both n=1 and n=2 chromophores have relatively good luminescence efficiency and might be good blue and blue/green emitters. Further testing of the dendrons and dendrimers incorporating these chromophores is in progress.

CHAPTER 5

CONCLUSIONS

Chromophores, dendrons and dendrimers incorporating functionalized diphenylaminodiphenyl polyenes with up to three double bonds were synthesized. The convergent dendrimer synthesis was successfully used to convert functionalized chromophores to dendrons and G-0 dendrimers.

All three chromophores and their corresponding dendrons and dendrimers can be oxidized in solution with $SbCl_5$ to form stable bipolarons which exhibit absorption characteristics favorable to RSA optical power limiting. The chromophores, dendrons and dendrimers described in this project are currently being tested as optical power limiters in collaboration with Prof. Lee Spangler's group (Montana State University) and Scientific Materials Corp. (Bozeman, MT).

The three chromophores and their dendron and dendrimer counterparts are candidates for showing OPL behavior via TPA. Two-photon measurements will be conducted in collaboration with Laser Photonics Technology, Inc. (Amherst, NY). If these materials display OPL by TPA, then they will be candidates for bimechanistic OPL materials.

The model chromophores displayed encouraging photoluminescence results for use in OLEDs. The dendrons and dendrimers are also being evaluated for photoluminescent behavior in collaboration with Prof. Linda Sapochak's group (University of Nevada-Las Vegas).

CHAPTER 6

EXPERIMENTAL SECTION

General

Proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were recorded on Bruker AM-250, DRX-250 (250 MHz) or AM-300, DRX-300 (300 MHz) spectrometers. All NMR spectra were determined as solutions in $CDCl_3$ and shifts were reported as parts-per-million (ppm) relative to tetramethylsilane (TMS). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and dd = doublet of doublets. All *J* values are reported in Hertz (Hz).

The optical absorption spectra were obtained as solutions in CH_2Cl_2 in a 1 cm path length quartz cell using a Shimadzu UV-3101 PC UV-VIS-IR spectrophotometer.

The compounds of interest were oxidatively doped for preliminary RSA absorption evaluation. 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 the case of the chromophores, an excess of dopant was added. The dendrons and dendrimers showed signs of instability in the presence of excess dopant, so the smallest possible drop was added to the 3 mL solutions.

The low resolution and high resolution/accurate mass analyses, using electron ionization (EI) were performed on a VG 70E-HF double focusing magnetic mass spectrometer (Micromass Instruments; Manchester, UK) operating at a mass resolution of 1500 and 10,000 respectively. All EI spectra were obtained at 70eV and an acceleration potential of 6000 volts. The fast atom bombardment (FAB) spectra were obtained on a VG 70E-HF double focusing magnetic mass spectrometer operating at a mass resolution of 2000 and an ion acceleration potential of 6000 volts. FAB spectra were obtained by using glycerol and 3-nitrobenzylalcohol as a matrix.

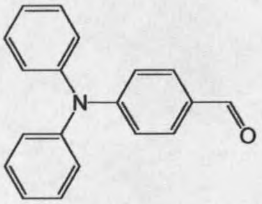
All thermal data including melting points (m.p.), glass transition temperatures (Tg), and decomposition temperatures was recorded on a TA Instruments DSC 2920 differential scanning calorimeter.

Column chromatography was performed using Whatman 70-230 mesh, 60A silica gel. Preparative thin layer chromatography was on a 1mm thick silica gel plate manufactured by Merck.

The following abbreviations are used throughout this experimental section: milliliter (mL), gram (g), molar (M), millimol (mmol), sodium carbonate ($NaCO_3$), magnesium sulfate ($MgSO_4$), sodium ethoxide (NaOEt), ethanol (EtOH), N,N-dimethylformamide (DMF), tetrahydrofuran (THF), ethyl ether (Et_2O), ethyl acetate (EtOAc), acetonitrile (CH_3CN), dichloromethane (CH_2Cl_2), phosphorus oxychloride ($POCl_3$), hydrochloric acid (HCl), triphenylphosphine (PPh_3), potassium carbonate (K_2CO_3), antimony pentachloride ($SbCl_5$), lithium aluminum hydride (LAH), potassium t-butoxide (KOtBu), 1,2-dichloroethane ($ClCH_2CH_2Cl$), sodium hydroxide

(NaOH), tetrabromomethane (CBr_4). All of the above solvents and reagents were obtained from Fisher Scientific and Aldrich Chemical Companies and used as received.

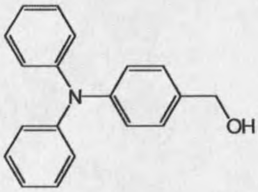
Synthetic Procedures



Triphenylamine-4-carbaldehyde (30)

A mixture of triphenylamine (50.0 g, 204 mmol) and DMF (32mL, 29.8 g, 408 mmol) in 250 mL $ClCH_2CH_2Cl$ was cooled to 0°C, and $POCl_3$ (30.5 mL, 50.1 g, 330 mmol) was added dropwise. The mixture was heated to reflux for 3 hours and then cooled to room temperature. The mixture was poured into 200 mL ice water and neutralized with Na_2CO_3. The reaction mixture was extracted with CH_2Cl_2 (3 X 200 mL); combined extracts were washed with water (2 X 150 mL), washed with brine (1 X 150 mL), dried ($MgSO_4$), and solvent evaporated. Recrystallization from EtOH afforded triphenylamine 4-carbaldehyde **30** (48.8 g, 87%) as yellow solid.

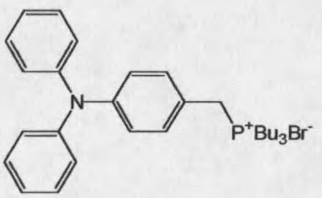
m.p. 133.4°C (lit[24] 132-133.5°C); ^{1}H NMR: 6.99 (2H, d, *J*=8.7 Hz), 7.14 (6H, m), 7.32 (4H,m), 7.65 (2H, d, *J*=8.7 Hz, 2.0 Hz), 9.79 (1H, s, CHO); λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 359 (25,600); m/z found 273.



Preparation of 4-hydroxymethyl triphenylamine (31)

A solution of LAH (2.85 g, 75 mmol) in dry THF stirred under nitrogen at room temperature. Triphenylamine-4-carbaldehyde **30** (41 g, 150 mmol) was dissolved in dry THF and added to the solution dropwise. The mixture was stirred at room temperature for 4 hours and then cooled to 0°C. Water was added dropwise to quench the excess LAH and then HCl was added to adjust pH to 4-5. The mixture was extracted with Et_2O (3 X 200 mL); combined extracts were washed with water (3 X 100 mL), dried ($MgSO_4$), and solvent evaporated to yield a white solid. The solid was dissolved in a minimum amount of EtOAc and then precipitated in hexanes to afford pure triphenylamine 4-hydroxymethyl **31** (39.1 g, 95%).

m.p. 103.1°C; ^{1}H NMR: 1.57 (1H, s, OH), 4.62 (2H, s, C$\underline{H}_2$-OH), 7.02 (8H,m), 7.22 (6H, m); λ_{max}/nm (ε_{max}/dm^3 mol^{-1}cm^{-1}) 304 (26,300); m/z found 275.



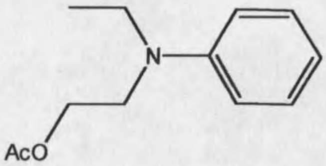
4-Diphenylaminobenzyl tributylphosphonium bromide (33)

To a solution of PPh_3 (40.0 g, 156 mmol) in 350 mL Et_2O, bromine (8.0 mL, 25.0 g, 156 mmol) was added dropwise. The mixture stirred at room temperature for 15 min. 4-Hydroxymethyltriphenylamine **31** (39.0 g, 142 mmol) dissolved in Et_2O was added to the mixture and allowed to stir for 2 hours. The mixture was filtered and solvent evaporated.

^{1}H NMR: 4.48 (2H, s, CH_2-Br), 7.03 (8H, m), 7.24 (6H, m)

The crude bromide **(32)** was carried forward to the next reaction without further purification. To a solution of this bromide dissolved in toluene, tributylphosphine (39.0 mL, 31.6 g, 156 mmol) was added dropwise under nitrogen. The mixture was heated at 100°C for 12 hours and then the solvent was evaporated. The solid was dissolved in the minimum amount of CH_2Cl_2 and precipitated in Et_2O to give product **33** (67.5 g, 88%) as a white solid.

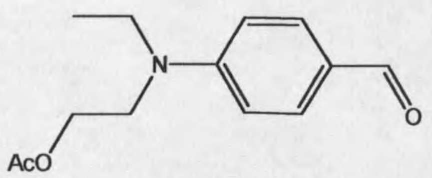
m.p. 152.6°C ^{1}H NMR: 0.92 (9H, t, *J*=6.5 Hz, $BuCH_3$), 1.45 (12H, m, CH_2), 2.41 (6H, m, P-CH_2), 4.10 (2H, d, *J*=14.5 Hz, Ph-$C\underline{H}_2$-P), 7.03 (8H, m), 7.24 (6H, m); λ_{max}/nm (ε_{max}/dm^3 mol^{-1}cm^{-1}) 304 (23,800).



N-2-actoxyethyl-N-ethyl aniline (35)

A solution of commercially available N-ethyl-N-hydroxyethyl aniline **34** (20 g, 121 mmol), acetic anhydride (68 g, 666 mmol), and pyridine (86 g, 1.09 mol) was stirred at room temperature for 12 hours. The solution was cooled to 0° C; 100 mL of H_2O was added and stirred for 1hour. The reaction mixture was extracted with ether (3 X 200 mL). The combined extracts were dried ($MgSO_4$) and solvent evaporated. Excess pyridine was removed by flash chromatography on 150g silica, eluting with CH_2Cl_2. The product was obtained as a tan liquid (24.35 g, 97%).

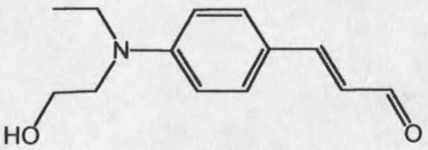
^{1}H NMR: 1.17 (3H, t, *J*=7.0 Hz, CH_3), 2.05 (3H, s, AcCH_3), 3.41 (2H, q, *J*=7.0 Hz, N-C$\underline{H_2}$-CH_3), 3.55 (2H, t, *J*=6.5 Hz, N-C$\underline{H_2}$-CH_2-O), 4.23 (2H, t, *J*=6.5 Hz, CH_2-0), 6.68 (1H, d, *J*=7.3 Hz, aromatic H), 6.73 (2H, d, *J*=8.5 Hz, aromatic H), 7.22 (2H, m, aromatic H); λ_{max}/nm (ε_{max}/dm^3 mol^{-1}cm^{-1}) 260 (15,000); HRMS (EI$^+$) calc. for $C_{12}H_{17}NO_2$ 207.1259, found 207.1268.



4-[N-ethyl-N-(2'-acetoxyethyl)amino]benzaldehyde (37)

A mixture of **35** (24 g, 115 mmol) and DMF (18 mL, 16.9 g, 231 mmol) in 150 mL $ClCH_2CH_2Cl$ was cooled to 0°C, and $POCl_3$ (17 mL, 28.4 g, 185 mmol) was added dropwise. The mixture was heated to reflux for 3 hours and then cooled to room temperature. The mixture was poured into 200 mL ice water and neutralized with Na_2CO_3. The reaction mixture was extracted with CH_2Cl_2 (3 X 200 mL); combined extracts were washed with H_20 (2 X 150 mL), washed with brine (1 X 150 mL), dried ($MgSO_4$), and solvent evaporated. Chromatography on 200 g silica, eluting with CH_2Cl_2-EtOAc (4:1) gave **37** (23.7 g, 87%) as yellow liquid.

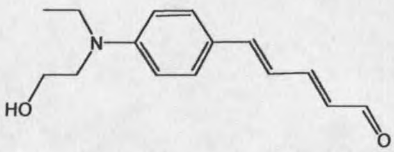
^{1}H NMR: 1.18 (3H, t, *J*=7.1 Hz, CH_3), 2.00 (3H, s, $AcCH_3$), 3.46 (2H, q, *J*=7.1 Hz, $C\underline{H}_2$-CH_3), 3.61 (2H,t, *J*=6.3 Hz, N-$C\underline{H}_2$-CH_2-O), 4.22 (2H, *J*=6.3 Hz, CH_2-$C\underline{H}_2$-O), 6.73 (2H, d, *J*=8.9 Hz, aromatic H), 7.69 (2H, d, *J*=8.9 Hz, aromatic H), 9.69 (1H, s, CHO); λ_{max}/nm (ε_{max}/dm^3 mol^{-1}cm^{-1}) 337 (31,500); HRMS (EI$^+$) calc. for $C_{13}H_{17}NO_3$ 235.1208, found 235.1210.



3-[4’-(N-ethyl-N-2”-hydroxyethyl)aminophenyl]-2-propenal (38)

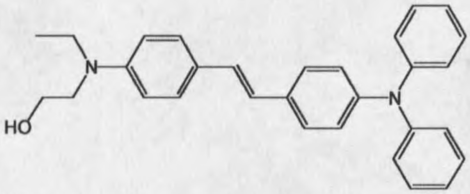
KOtBu (96 mL, 96 mmol, 1M soln in THF) was added dropwise to a solution of aldehyde **37** (15 g, 64 mmol) and (1,3-dioxalane-2-ylmethyl) tributylphosphonium bromide **36** (77 mL, 77 mmol, 1 M soln in THF) in 100 mL dry THF. The mixture stirred at room temperature for 2 hours. The reaction mixture was poured into 400 mL ice water and stirred 30 min, extracted with Et_2O (3 X 200 mL), combined extracts were dried ($MgSO_4$), and solvent evaporated. The crude mixture was checked by NMR to ensure complete reaction of starting material. The mixture was redissolved in 100 mL THF and stirred with 250 mL 3M HCl for 3 hours. The reaction mixture was neutralized with Na_2CO_3, extracted with Et_2O (3 X 200 mL), combined extracts were dried ($MgSO_4$) and solvent evaporated. Chromatography on 200 g silica, eluting with CH_2Cl_2-EtOAc (3:1) gave the extended aldehyde **38** (11.9 g, 85%) as a dark orange solid.

m.p. 61.4°C; ^{1}H NMR: 1.19 (3H, t, *J*=7.1 Hz, CH_3), 3.49 (2H, q, *J*=7.1 Hz, $C\underline{H}_2$-CH_3), 3.54 (2H,t, *J*=5.8 Hz, N-$C\underline{H}_2$-CH_2-O), 3.83 (2H, t, *J*=5.8 Hz, CH_2-$C\underline{H}_2$-O), 6.51 (1H, dd, *J*=7.9 Hz, 15.7 Hz, vinyl H), 6.77 (2H, d, *J*=8.8 Hz, aromatic H), 7.34 (1H, d, *J*=15.7 Hz, vinyl H), 7.43 (2H, d, *J*=8.8 Hz, aromatic H), 9.57 (1H, d, *J*=7.9 Hz, CHO); λ_{max}/nm (ε_{max}/dm^3 mol^{-1}cm^{-1}) 386 (42,600); HRMS (EI$^+$) calc. for $C_{13}H_{17}NO_2$ 219.1259, found 219.1256.



5-[4'-(N-ethyl-N-2"-hydroxyethyl)amino phenyl]-2,4-pentadienal (39)

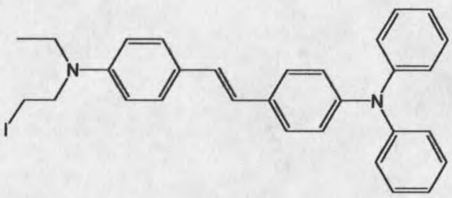
KOtBu (35 mL, 35 mmol, 1M soln in THF) was added dropwise to a solution of aldehyde **38** (5.0 g, 23 mmol) and (1,3-dioxalane-2-ylmethyl) tributylphosphonium bromide **36** (28 mL, 28 mmol, 1 M soln in THF) in 50 mL dry THF. Mixture stirred at room temperature for 2 hours. The reaction mixture was poured into 200 mL ice water and stirred for 30 minutes, extracted with Et_2O (3 X 100 mL), combined extracts dried ($MgSO_4$), and solvent evaporated. The crude product was checked by NMR to ensure complete reaction of starting material. The mixture was redissolved in 50 mL THF and stirred with 150 mL 3M HCl for 3 hours. The mixture was neutralized with Na_2CO_3, extracted with Et_2O (3 X 100 mL), combined extracts were dried ($MgSO_4$) and solvent evaporated. Chromatography on 150 g silica, eluting with CH_2Cl_2-EtOAc (3:1) afforded extended aldehyde **39** (3.9 g, 69%) as a dark red solid. m.p. 102.2°C; ^{1}H NMR: 1.20 (3H, t, *J*=7.0 Hz, CH_3), 3.50 (2H, q, *J*=7.0 Hz, $C\underline{H}_2$-CH_3), 3.53 (2H,t, *J*=5.4 Hz, N-$C\underline{H}_2$-CH_2-O), 3.82 (2H,t, *J*=5.4 Hz, CH_2-$C\underline{H}_2$-O), 6.18 (1H, dd, *J*=8.0 Hz, 15.0 Hz, vinyl H), 6.84 (2H, m, aromatic H), 6.93 (1H, d, *J*=15.0 Hz, vinyl H), 7.23 (2H, m, vinyl H), 7.40 (2H, m. aromatic H), 9.55 (1H, d, *J*=8.0 Hz, CHO); λ_{max}/nm (ε_{max}/dm^3 mol^{-1}cm^{-1}) 416 (43,300); HRMS (EI$^+$) calc. for $C_{15}H_{19}NO_2$ 245.1416, found 245.1415.



4-Diphenylamino-4'- (N-ethyl, N-2"-hydroxyethyl)amino stilbene (26)

To a solution of **37** (4.17 g, 18 mmol) and **33** (11.5 g, 22 mmol) in 100 mL of EtOH, NaOEt (27 mL, 27 mmol, 1 M soln in ethanol) was added dropwise. The mixture was heated to reflux for 4 hours and then solvent was evaporated. Chromatography on 100 g silica, eluting with CH_2Cl_2 afforded product **26** (6.65 g, 86%) as a pale yellow solid. An analytical sample was further purified by recrystallization from EtOH.

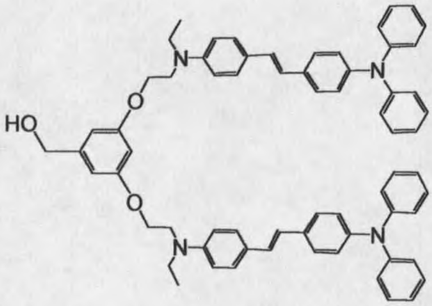
m.p. 116.3°C; ^{1}H NMR: 1.16 (3H, t, *J*=7.0 Hz, CH_3), 1.54 (1H, s, OH), 3.43 (2H, q, *J*=7.0, N-$\underline{CH_2}$-CH_3), 3.47 (2H, t, *J*=5.6, N-$\underline{CH_2}$-CH_2-OH), 3.78 (2H, t, *J*=5.6, CH_2-OH), 6.73 (2H, d, *J*=8.7 Hz, aromatic H), 6.83 (1H, d, *J*=16.3 Hz, vinyl H), 6.92 (1H, d, *J*=16.3 Hz, vinyl H), 7.00 (4H, m, aromatic H), 7.08 (4H, m, aromatic H), 7.23 (4H, m, aromatic H), 7.34 (4H, dd, *J*=8.7 Hz, 8.2 Hz, aromatic H); ^{13}C NMR: 12.49, 46.22, 53.04, 60.58, 113.23, 123.24, 124.54, 124.69, 126.75, 127.34, 127.66, 128.09, 129.71, 133.10, 146.98, 147.94, 148.16; λ_{max}/nm (ε_{max}/dm^3 mol^{-1}cm^{-1}) 381 (54,300); m/z found 434; (Anal. Calc. for $C_{30}H_{30}N_2O$: C, 82.91; H, 6.96; N, 6.45. Found: C, 82.58; H, 6.85; N, 6.28)



4-Diphenylamino-4'- (N-ethyl, N-2"-iodoethyl)amino stilbene (40)

To a solution of PPh_3 (3.62g, 13.8 mmol) and imidazole (0.94g, 13.8 mmol) dissolved in CH_3CN-Et_2O (1:3), iodine (3.51g, 13.8 mmol) was added slowly. The mixture stirred at room temperature for 1 hour. Compound **26** (2.0 g, 4.6 mmol) was dissolved in solvent mixture CH_3CN-Et_2O (1:3) and added to reaction mixture. The reaction was stirred at room temperature for 15 min. The mixture was passed through a silica plug (50 g) eluting with 5% EtOAc in hexanes and solvent evaporated to afford **40** (2.0 g, 80%) as a pale yellow powder. The product was utilized in the preparation of **43** without further purification.

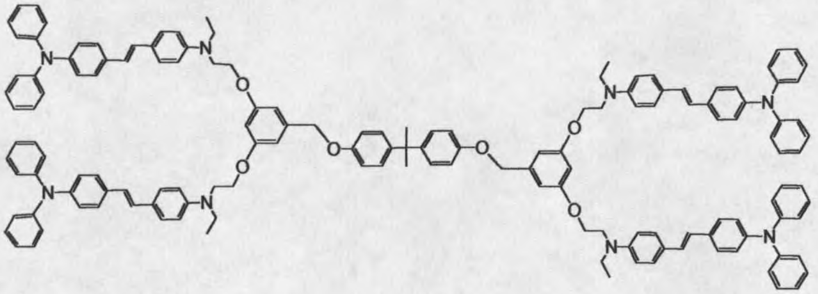
^{1}H NMR: 1.21 (3H, t, *J*=7.0 Hz, CH_3), 3.21 (2H, t, *J*=8.2, CH_2-I), 3.42 (2H, q, *J*=7.0, N-$C\underline{H}_2$-CH_3), 3.67 (2H, t, *J*=8.2, N-$C\underline{H}_2$-CH_2-I), 6.65 (2H, m), 7.02 (10H, m), 7.28 (8H, m).



3,5-Bis- [4'-diphenylamino-4"-(N-ethyl, N-ethyleneoxy)aminostilbene] benzyl alcohol (43)

Compound **40** (1.97 g, 3.6 mmol) was dissolved in dioxane. K_2CO_3 (0.57 g, 4.1 mmol), 3,5-dihydroxybenzyl alcohol (0.23 g, 1.7 mmol), and 18-Crown-6 (0.09 g, 0.3 mmol) were added to the reaction mixture and stirred under nitrogen at room temperature for 48 hours. The mixture was then heated to reflux for 48 hours. The solvent was evaporated and the mixture was partitioned between CH_2Cl_2 (50 mL) and H_2O (50 mL). The mixture was extracted with CH_2Cl_2 (3 X 100 mL), dried ($MgSO_4$), and the solvent was evaporated. Chromatography on 50 g silica eluting with CH_2Cl_2 afforded **43** (0.61g, 38%) as a pale yellow solid.

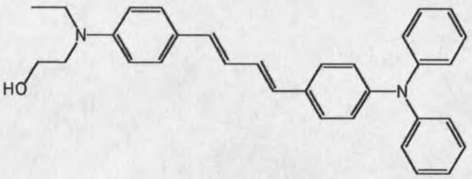
Tg 65.25°C; decomp. T 308°C; ^{1}H NMR: 1.19 (6H, t, *J*=7.0 Hz, CH_3), 1.57 (1H, s, OH), 3.47 (4H, q, *J*=7.0, N-$C\underline{H}_2$-CH_3), 3.71 (4H, t, *J*=5.7, N-$C\underline{H}_2$-CH_2-OPh), 4.08 (4H, t, *J*=5.7, CH_2-OPh), 4.58 (2H, d, *J*=5.2, CH_2-OH), 6.33 (1H, s, aromatic H) 6.49 (2H, s, aromatic H), 6.68 (4H, d, *J*=8.7 Hz, aromatic H), 6.82 (2H, d, *J*=16.5 Hz, vinyl H), 6.92 (2H, d, *J*=16.5 Hz, vinyl H), 7.01 (8H, m, aromatic H), 7.08 (8H, d, *J*=7.6 Hz, aromatic H), 7.23 (8H, m, aromatic H), 7.34 (8H, dd, *J*=8.7 Hz, 7.6 Hz, aromatic H); ^{13}C NMR: 12.80, 46.17, 50.08, 65.64, 98.82, 100.86, 105.79, 112.28, 123.12, 124.24, 124.60, 126.16, 127.21, 127.65, 128.08, 129.61, 133.12, 143.88, 146.88, 147.37, 148.11, 160.52; λ_{max}/nm (ε_{max}/dm^3 mol^{-1}cm^{-1}) 382 (106,200); MS (FAB) found m/z 974; (Anal. Calc. for $C_{67}H_{64}N_4O_3$: C, 82.68; H, 6.63; N, 5.76. Found: C, 82.65; H, 6.59; N, 5.58)



Generation-0 Dendrimer (46)

CBr_4 (0.82 g, 2.5 mmol) and PPh_3 (0.65 g, 2.5 mmol) were added to a solution of **43** (1.20 g, 1.2 mmol) in the minimum amount of dry THF (40 mL). The mixture was stirred under nitrogen at room temperature for 45 minutes. Water (50 mL) was added and the mixture was extracted with CH_2Cl_2 (3 X 100 mL). The combined extracts were dried ($MgSO_4$) and solvent evaporated. Chromatography over silica eluting with hexanes-CH_2Cl_2 (1:1) gave brominated dendron (0.78 g, 61%). The product was used without further purification. A mixture of the brominated dendron (0.74 g, 0.6 mmol), bisphenol-A (Aldrich) (0.08 g, 0.3 mmol), K_2CO_3 (0.12 g, 0.8 mmol) and 18-Crown-6 (0.02 g, 0.06 mmol) in dry acetone (50 mL) was stirred at room temperature under nitrogen for 48 hours. The reaction was heated to reflux for 48 hours. The mixture was cooled and evaporated to dryness. The residue was partitioned between CH_2Cl_2 (50 mL) and water (50 mL). The mixture was extracted with CH_2Cl_2 (3 X 100 mL) and the combined extracts were dried ($MgSO_4$) and solvent evaporated. The crude product was purified by column chromatography over silica, eluting with hexanes- CH_2Cl_2 (1:2) to yield compound 46 (0.48 g, 66%).

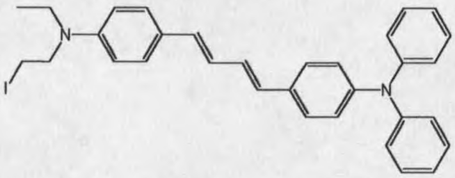
Tg 93.9°C; decomp. T 310°C; ^{1}H NMR: 1.20 (12H, t, *J*=6.8 Hz, CH_3), 1.62 (6H, s, CH_3), 3.47 (8H, q, *J*=6.8, N-C$\underline{H}_2$-CH_3), 3.71 (8H, t, *J*=5.5, N-C$\underline{H}_2$-CH_2-OPh), 4.09 (8H, t, *J*=5.5, CH_2-OPh), 4.91 (4H, s, CH_2-OPh), 6.37 (2H, s, aromatic H) 6.56 (4H, s, aromatic H), 6.70 (8H, d, *J*=7.5 Hz, aromatic H), 6.87 (12H, m, 8 vinyl H and 4 aromatic H), 7.02 (16H, m, aromatic H), 7.10 (20H, m, aromatic H), 7.24 (16H, m, aromatic H), 7.37 (16H, m, aromatic H); ^{13}C NMR: 12.80, 31.46, 42.12, 46.16, 50.06, 65.97, 70.28, 101.09, 106.49, 112.30, 114.61, 123.14, 124.23, 124.61, 126.17, 127.24, 127.69, 128.15, 129.63, 133.14, 140.19, 143.85, 146.87, 147.38, 148.12, 156.98, 160.49; λ_{max}/nm (ε_{max}/dm^3 mol^{-1}cm^{-1}) 382 (184,600); MS (FAB) found m/z 2138. (Anal. Calc. for $C_{149}H_{140}N_8O_6$: C, 83.67; H, 6.60; N, 5.24. Found: C, 83.24; H, 6.59; N, 4.83)



4'-Diphenylamino-4"-(N-ethyl-N-2'"-hydroxyethyl)amino-1,4-diphenyl-1, 3-butadiene (27)

To a solution of **38** (13.5 g, 62 mmol) and **33** (40.2 g, 74 mmol) in 150 mL of EtOH, NaOEt (93 mL, 93 mmol, 1 M soln in EtOH) was added dropwise. The mixture was heated to reflux for 12 hours and then solvent was evaporated. Chromatography on 200 g silica, eluting with CH_2Cl_2 afforded product **27** (19.5 g, 69%) as a yellow-gold solid. An analytical sample was further purified by recrystallization from EtOH.

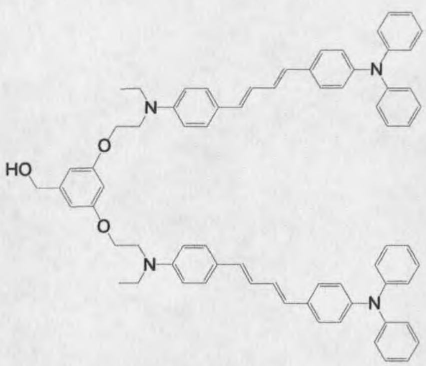
m.p. 155.8°C; ^{1}H NMR: 1.15 (3H, t, *J*=7.0 Hz, CH_3), 1.70 (1H, s, OH), 3.42 (2H, q, *J*=7.0 Hz, N-C$\underline{H}_2$-CH_3), 3.47 (2H, t, *J*=5.7 Hz, N-C$\underline{H}_2$-CH_2-OH), 3.78 (2H, t, *J*=5.7 Hz, CH_2-OH), 6.52 (2H, m, aromatic H), 6.79 (4H, m, vinyl H), 7.00 (4H, m, aromatic H), 7.08 (4H, m, aromatic H), 7.26 (8H, m, aromatic H); ^{13}C NMR: 12.39, 46.19, 52.98, 60.60, 113.19. 123.31. 124.20. 124.79. 126.08. 127.38. 128.05. 128.98. 129.67. 130.46. 132.54. 132.63. 147.220. 148.03; λ_{max}/nm (ε_{max}/dm^3 mol^{-1}cm^{-1}) 399 (69,800); MS found m/z 460; (Anal. Calc. for $C_{32}H_{32}N_2O$: C, 83.44; H, 7.00; N, 6.08. Found: C, 83.02; H, 6.92; N, 6.02)



4’-Diphenylamino-4”-(N-ethyl-N-2’”-iodoethyl)amino-1,4-diphenyl-1, 3-butadiene (41)

To a solution of PPh_3 (4.28 g, 16.3 mmol) and imidazole (1.11 g, 16.3 mmol) dissolved in CH_3CN-Et_2O (1:3), iodine (4.14 g, 16.3 mmol) was added slowly. The mixture stirred at room temperature for 1 hour. Compound **27** (2.5 g, 5.4 mmol) was dissolved in solvent mixture CH_3CN-Et_2O (1:3) and added to reaction mixture. The reaction was stirred at room temperature for 15 min. The mixture was passed through a silica plug (50 g) eluting with 5% EtOAc in hexanes and solvent evaporated to afford **41** (2.80 g, 90%) as a yellow powder. The crude iodide was utilized in the preparation of **44** without further purification.

^{1}H NMR: 1.19 (3H, t, *J*=7.0 Hz, CH_3), 3.20 (2H, t, *J*=5.7 Hz, CH_2 –I), 3.41 (2H q, *J*=7.0 Hz, N-$C\underline{H}_2$-CH_3), 3,67 (2H, t, J=5.7 Hz, N-$C\underline{H}_2$-CH_2 -I), 6.57 (2H, m, aromatic H), 6.79 (4H, m, vinyl H), 7.00 (4H, m, aromatic H), 7.08 (4H, m, aromatic H), 7.26 (8H, m, aromatic H).

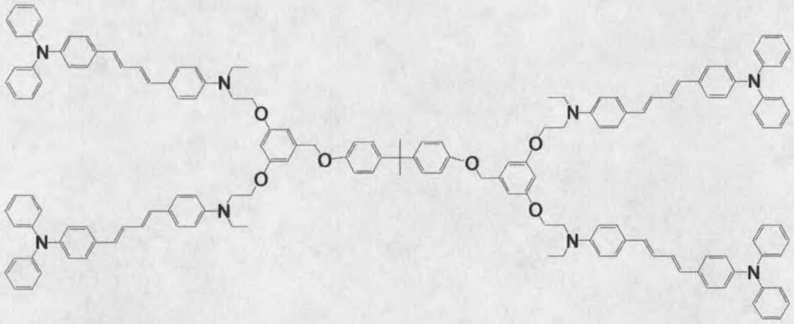


3,5-Bis-[4"-diphenylamino-4"'-(N-ethyl-N-ethyleneoxy)amino-1',4'-diphenyl-1',3'-butadiene] benzyl alcohol (44)

Compound **41** (2.00 g, 3.5 mmol) was dissolved in dioxane. K_2CO_3 (0.58g, 4.2 mmol), 3,5-dihydroxybenzylalcohol (0.24 g, 1.7 mmol), and 18-Crown-6 (0.09 g, 0.3 mmol) were added to the reaction mixture and stirred under nitrogen at room temperature for 48 hours. The mixture was then heated to reflux for 48 hours. The solvent was evaporated and the residue was partitioned between CH_2Cl_2 (50 mL) and H_2O (50 mL). The mixture was extracted with CH_2Cl_2 (3 X 100 mL). The combined extracts were dried ($MgSO_4$), and the solvent was evaporated. Chromatography on 75g silica eluting with CH_2Cl_2 afforded **44** (1.08 g, 63%) as a yellow solid.

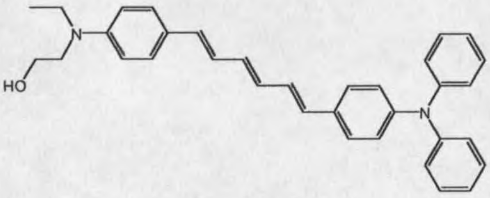
Tg 79.8°C; decomp T 306°C; ^{1}H NMR: 1.18 (6H, t, *J*=6.7 Hz, CH_3), 3.46 (4H, q, *J*=6.7, N-C$\underline{H}_2$-CH_3), 3.70 (4H, t, *J*=5.7, N-C$\underline{H}_2$-CH_2-OPh), 4.08 (4H, t, *J*=5.7, CH_2-OPh), 4.57 (2H, d, *J*=5.2, CH_2-OH), 6.31 (1H, s, aromatic H) 6.47 (2H, s, aromatic H), 6.53 (4H, m, aromatic H), 6.77 (8H, m, vinyl H), 6.98 (8H, m, aromatic H), 7.07 (8H, m, aromatic H), 7.25 (16H, m, aromatic H); ^{13}C NMR: 12.77, 46.16, 50.05, 65.61, 100.84, 105.80, 112.26, 123.27, 124.20, 124.75, 125.78, 126.10, 127.33, 128.11, 129.03, 129.64, 130.22, 132.64, 143.89, 147.15, 148.01, 160.49; λ_{max}/nm

(ε_{max}/dm^3 mol^{-1}cm^{-1}) 399 (135,600); MS (FAB) found m/z 1025. (Anal. Calc. for $C_{71}H_{68}N_4O_3$: C, 80.93; H, 7.57; N, 6.19. Found: C, 80.81; H, 7.53; N, 5.72)



Generation-0 Dendrimer (47)

CBr_4 (0.97 g, 2.9 mmol) and PPh_3 (0.77 g, 2.9 mmol) were added to a solution of **44** (1.50 g, 1.5 mmol) in the minimum amount of dry THF (50 mL). The mixture was stirred under nitrogen at room temperature for 30 minutes. Water (50 mL) was added and the mixture was extracted with CH_2Cl_2 (3 X 100 mL). The combined extracts were dried ($MgSO_4$) and solvent evaporated. Chromatography over silica eluting with hexanes-CH_2Cl_2 (1:1) gave brominated dendron (1.15 g, 72%). The product was used without further purification. A mixture of the brominated dendron (1.15 g, 1.1 mmol), bisphenol-A (Aldrich) (0.12 g, 0.6 mmol), K_2CO_3 (0.19 g, 1.4 mmol) and 18-Crown-6 (0.03 g, 0.1 mmol) in dry acetone (50 mL) was stirred at room temperature under nitrogen for 48 hours. Then the reaction was heated to reflux for 48 hours. The mixture was cooled and evaporated to dryness. The residue was partitioned between CH_2Cl_2 (50 mL) and water (50 mL). The mixture was extracted with CH_2Cl_2 (3 X 100 mL) and the combined extracts were dried ($MgSO_4$) and solvent evaporated. The crude product was purified by column chromatography over silica, eluting with hexanes- CH_2Cl_2 (1:2) to yield compound **47** (0.72 g, 58%). Tg 95.7°C; decomp. T 310°C; ^{1}H NMR: 1.17 (12H, t, *J*=6.6 Hz, CH_3), 1.58 (6H, s, CH_3), 3.44 (8H, q, *J*=6.6, N-C$\underline{H}_2$-CH_3), 3.68 (8H, t, *J*=5.7, N-C$\underline{H}_2$-CH_2-OPh), 4.07 (8H, t, *J*=5.7 Hz, CH_2-OPh), 4.87 (4H, s, CH_2-OPh), 6.28 (2H, s, aromatic H) 6.49 (4H, s, aromatic H), 6.54 (8H, m), 6.80 (20H, m, 16 vinyl H and 4 aromatic H), 6.99 (16H, m, aromatic H), 7.08 (20H, m, aromatic H), 7.25 (32H, m, aromatic H); ^{13}C NMR: 12.79, 31.46, 42.12, 46.14, 50.02, 65.95, 70.26, 101.07, 106.49, 111.94, 112.28, 114.61, 123.28, 124.23, 124.76, 125.76, 126.11, 127.34, 128.15, 129.08, 129.66, 130.22, 132.69, 140.19, 143.85, 147.15, 147.42, 148.03, 156.97, 160.48; λ_{max}/nm (ε_{max}/dm^3 mol^{-1}cm^{-1}) 399 (272,157); MS (FAB) found m/z 2243. (Anal. Calc. for $C_{157}H_{148}N_8O_6$: C, 84.07; H, 6.65; N, 4.99. Found: C, 84.27; H, 6.68; N, 4.62)

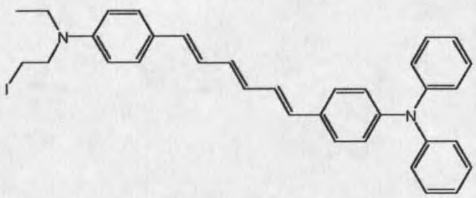


4'-Diphenylamino-4"-(N-ethyl-N-2'"-hydroxyethyl)amino-1,6-diphenyl-1, 3,5-hexatriene (28)

To a solution of **39** (5.0g, 20.0 mmol) and **33** (13.2 g, 24.0 mmol) in 100 mL of EtOH, NaOEt (31 mL, 31 mmol, 1 M soln in ethanol) was added dropwise. The mixture was heated to reflux for 4 hours and then the solvent was evaporated.

Chromatography on 100 g silica, eluting with CH_2Cl_2 afforded product **28** (6.69 g, 67%) as an orange solid.

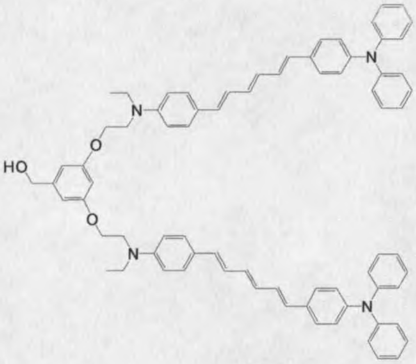
m.p. 137.4°C; ^{1}H NMR: 1.15 (3H, t, *J*=7.0 Hz, CH_3), 3.47 (4H, m), 3.79 (2H, t, *J*=5.5 Hz, CH_2-OH), 6.47 (4H, m, 2 vinyl H, 2 aromatic H), 6.71 (4H, m, vinyl H), 7.00 (4H, m, aromatic H), 7.08 (4H, m, aromatic H), 7.24 (8H, m, aromatic H); 13C NMR: 12.38, 46.10, 52.90, 60.68, 113.07, 123.36, 124.04, 124.84, 125.80, 127.47, 128.09, 128.48, 129.66, 131.27, 132.39, 132.81, 134.03, 147.38, 147.95; λ_{max}/nm (ε_{max}/dm^3 mol^{-1}cm^{-1}) 417 (92,500); MS found m/z 486; (Anal. Calc. for $C_{34}H_{34}N_2O$: C, 83.91; H, 7.04; N, 5.76. Found: C, 83.94; H, 6.92; N, 5.82)



4'-Diphenylamino-4"-(N-ethyl-N-2'"-iodoxyethyl)amino-1,6-diphenyl-1, 3,5-hexatriene (42)

To a solution of PPh_3 (1.63 g, 6.2 mmol) and imidazole (0.42 g, 6.2 mmol) dissolved in CH_3CN-Et_2O (1:3), iodine (1.57 g, 6.2 mmol) was added slowly. The mixture stirred at room temperature for 1 hour. Compound **28** (1.5 g, 3.1 mmol) was dissolved in solvent mixture CH_3CN-Et_2O (1:3) and added to reaction mixture. The reaction was stirred at room temperature for 15 min. The mixture was passed through a silica plug (50 g) eluting with 5% EtOAc in hexanes and solvent evaporated to afford **42** (0.96 g, 52%) as an orange powder. The crude iodide was used in the preparation of **45** without further purification.

^{1}H NMR: 1.18 (3H, *J*=7.0 Hz, CH_3), 3.20 (2H, t, *J*=5.5 Hz, CH_2-I), 3.41 (2H, q, *J*=7.0 Hz, N-$C\underline{H_2}$-CH_3), 3.67 (2H, t, *J*=5.5 Hz, N-$C\underline{H_2}$-CH_2-I), 6.48 (4H, m) 6.71 (4H, m) 7.00 (4H, m), 7.08 (4H, m), 7.26 (8H, m).

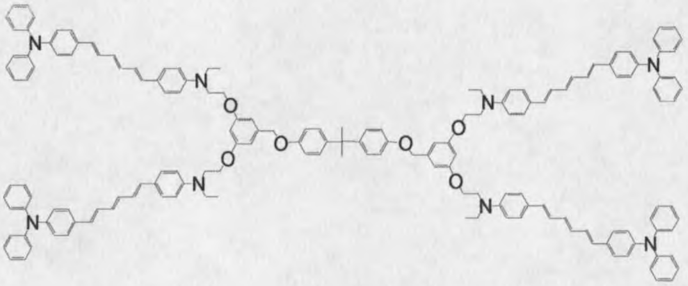


3,5-Bis-[4"-diphenylamino-4'"-(N-ethyl-N-ethyleneoxy)amino-1', 6'-diphenyl-1',3',5'-hexatriene] benzyl alcohol (45)

Compound **42** (1.59 g, 2.7 mmol) was dissolved in dioxane. K_2CO_3 (0.46 g, 3.3 mmol), 3,5-dihydroxybenzyl alcohol (0.19 g, 1.3mmol), and 18-Crown-6 (0.07 g, 0.26 mmol) were added to the reaction mixture and stirred under nitrogen at room temperature for 48 hours. The mixture was then heated to reflux for 48 hours. The solvent was evaporated and the residue was partitioned between CH_2Cl_2 (50 mL) and H_2O (50 mL). The mixture was extracted with CH_2Cl_2 (3 X 100 mL). The combined extracts were dried ($MgSO_4$), and the solvent was evaporated. Chromatography on 50 g silica eluting with CH_2Cl_2 afforded **45** (0.41 g, 29%) as an orange solid.

Tg 72.5°C; decomp. T 240°C; ^{1}H NMR: 1.18 (6H, t, *J*=6.8 Hz, CH_3), 3.46 (4H, q, *J*=6.8 Hz, N-$C\underline{H_2}$-CH_3), 3.69 (4H, t, *J*=5.5 Hz, N-$C\underline{H_2}$-CH_2-OPh), 4.08 (4H, t, *J*=5.5

Hz, CH_2-OPh), 4.57 (2H, d, *J*=5.6 Hz, CH_2-OH), 6.29 (1H, s, aromatic H), 6.47 (10H, m, 4 vinyl H, 6 aromatic H), 6.74 (8H, m, vinyl H), 7.00 (8H, m, aromatic H), 7.07 (8H, m, aromatic H), 7.25 (16H, m, aromatic H); ^{13}C NMR: 12.74, 46.13, 50.03, 65.05, 65.94, 100.82, 105.78, 112.21, 123.34, 124.04, 124.82, 125.52, 127.44, 128.15, 128.50, 129.64, 131.14, 132.87, 134.09, 143.87, 147.34, 147.91, 160.44; λ_{max}/nm (ε_{max}/dm^3 mol^{-1}cm^{-1}) 418 (157,900); MS (FAB) found m/z 1076. (Anal. Calc. for $C_{75}H_{72}N_4O_3$: C, 83.61; H, 6.78; N, 4.96. Found: C, 83.46; H, 7.07; N, 4.77)



Generation-0 Dendrimer (48)

CBr_4 (0.46 g, 1.4 mmol) and PPh_3 (0.36 g, 1.4 mmol) were added to a solution of **45** (0.75 g, 0.7 mmol) in the minimum amount of dry THF (25 mL). The mixture was stirred under nitrogen at room temperature for 30 minutes. Water (25 mL) was added and the mixture was extracted with CH_2Cl_2 (3 X 50 mL). The combined extracts were dried ($MgSO_4$) and solvent evaporated. Chromatography over silica eluting with hexanes-CH_2Cl_2 (1:1) gave brominated dendron (0.41 g, 52%). The product was used without further purification. A mixture of the brominated dendron (0.41 g, 0.4 mmol), bisphenol-A (Aldrich) (0.04 g, 0.2 mmol), K_2CO_3 (0.06 g, 0.4 mmol) and 18-Crown-6 (0.01 g, 0.03 mmol) in dry acetone (25 mL) was stirred at room temperature under nitrogen for 48 hours. Then the reaction was heated to reflux for 48 hours. The mixture was cooled and evaporated to dryness. The residue was partitioned between CH_2Cl_2 (25 mL) and water (25 mL). The mixture was extracted with CH_2Cl_2 (3 X 50 mL) and the combined extracts were dried ($MgSO_4$) and solvent evaporated. The crude product was purified by column chromatography over silica, eluting with hexanes- CH_2Cl_2 (1:2) to yield compound **48** (0.23 g, 59%).

Tg 88.5°C; decomp T 210°C; ^{1}H NMR: 1.17 (12H, t, *J*=6.8 Hz, CH_3), 1.59 (6H, s, CH_3), 3.43 (8H, q, *J*=6.8 Hz, N-C$\underline{H_2}$-CH_3), 3.68 (8H, t, *J*=5.7, N-C$\underline{H_2}$-CH_2-OPh), 4.06 (8H, t, *J*=5.7, CH_2-OPh), 4.88 (4H, s, CH_2-OPh), 6.31 (2H, s, aromatic H) 6.48 (20H, m, 8 vinyl H and 12 aromatic H), 6.73 (20H, m), 7.00 (20H, m), 7.07 (16H, m, aromatic H), 7.25 (32H, m, aromatic H); ^{13}C NMR: 12.79, 31.47, 42.13, 46.15, 50.03, 65.94, 70.26, 101.07, 106.52, 112.27, 114.62, 115.14, 123.38, 124.07, 124.85, 125.56, 126.09, 126.75, 127.49, 128.18, 128.22, 128.55, 129.69, 130.17, 130.90, 131.19, 131.94, 132.43, 132.98, 134.15, 140.21, 143.86, 147.36, 147.97, 156.97, 160.46; λ_{max}/nm (ε_{max}/dm^3 mol^{-1}cm^{-1}) 418 (337,800). (Anal. Calc. for $C_{165}H_{156}N_8O_6$: C, 83.43; H, 6.70; N, 4.71. Found: C, 81.42; H, 7.38; N, 3.76)

REFERENCES

1. Reuters News Service, Chicago Tribune, Sect. 1, May 4, 1995, p. 4.
2. R. C. Hoffman, K. A. Stetyick, R. S. Potember and D. G. McLean, *J. Opt. Soc. Am. B Opt. Phys.* 1989, **6**, 772.
3. J. S. Shirk, R. G. S. Pong, G. J. Bartoli, and A. W. Snow, *Appl. Phys. Lett.*, 1993, **63**, 1880.
4. W. Su and T. M. Cooper, *Chem. Mater.* 1998, **10**, 1212.
5. Y.-P. Sun, J. E. Riggs and B. Liu, *Chem Mater.* 1997, **9**, 1268.
6. C. Spangler and M. He, in *Handbook of Organic Conductive Molecules and Polymers: Vol. 2. Conductive Polymers: Synthesis and Electrical Properties*, ed. H. S. Nalwa, John Wiley & Sons Ltd., Chichester, 1997, pp. 389-414.
7. C. W. Spangler, R. K. McCoy, A. A. Dembek, L. S. Sapochak and B. C. Gates, *J. Chem Soc., Perkin Trans. 1*, 1989, 151.
8. C. W. Spangler, P.-K. Liu. A. A. Dembek and K. O. Havelka, *J. Chem. Soc., Perkin Trans. 1*, 1991, 799.
9. C. W. Spangler, P.-K. Liu. and K. O. Havelka, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1207.
10. C. W. Spangler and P.-K. Liu., *J. Chem. Soc., Perkin Trans. 2*, 1992, 1959.
11. C. W. Spangler and M. Q. He, *J. Chem. Soc., Perkin Trans. 1*, 1995, 715.
12. N. S. Sariciftci and A. J. Heeger, in *Handbook of Organic Conductive Molecules and Polymers: Vol. 2. Conductive Polymers: Vol. 1. Charge-Transfer Salts,*

Fullerenes and Photoconductors, ed. H. S. Nalwa, John Wiley & Sons Ltd., Chichester, 1997, pp. 414-455.

13. C. W. Spangler, *J. Mater. Chem.*, 1999, **9**, 2013-2020.
14. B. A. Reinhardt, L. L. Brott, S. J. Clarson, A. G. Dillard, J. C. Bhatt, R. Kannan, L. Yuan, G. S. He and P. N. Prasad, *Chem. Mater.* 1998, **10**, 1863.
15. M. Albota, D. Beljonne, J.-L.Bredas, J. E. Ehrlich, J.-Y. Fu, A. A. Heikal, S. E. Hess, T. Kogej, M. D. Levin, S. R. Marder, D. McCord-Maughon, J. W. Perry, H. Rockel, M. Rumi, G. Subramanian, W. W. Webb, X.-L. Wu and C. Xu, *Science*, 1998, **281**, 1653.
16. L. V. Natarajan, R. L. Sutherland, L. A. Sowards, N. Tang, P. A. Fleitz, T. Cooper and C. W. Spangler, *Proc. SPIE*, 1997, **3146**, 31.
17. C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1990, **112**, 7638.
18. O. A. Matthews, A. N. Shipway, J. F. Stoddart, *Prog. Polym. Sci.*, 1998, **23**, 1.
19. A. W. Bosman, H. M. Janssen, E. W. Meijer, *Chem. Rev.*, 1999, **99**, 1665.
20. D. A. Tomalia, H. Baker, J. R. Dewald, M. Hall, G. Kallas, S. Martin, J. Roech, J. Ryder, P. Smith, *Polym. J.*, 1985, **17**, 117.
21. G. R. Newkome, Z.-Q. Yao, G. R. Baker, V. K. Gupta, *J. Org. Chem.* 1985, **50**, 2003.
22. B. Reeves, E. H. Elandaloussi, unpublished results (to be submitted, *J. Chem. Perkin Trans. 1*).
23. C. W. Spangler and R. McCoy, *Synth. Comm.*, 1988, **18(1)**, 51.

24. T. N. Baker III, W. P. Doherty Jr., W. S. Kelley, W. Newmeyer, J. E. Rogers Jr. R. E. Spalding, R. I. Walter, *J. Org. Chem.,*1965, **30**, 3714