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The Functionalization of Thermally Stable Third-Order NLO Chromophores

James Richard Sawyer
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THE FUNCTIONALIZATION OF THERMALLY STABLE
THIRD-ORDER NLO CHROMOPHORES

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

By

JAMES R. SAWYER
B.S., Otterbein College, 1997

2001
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ABSTRACT


There is a need to functionalize NLO chromophore systems to incorporate them into polymeric matrices by covalent attachment. The functionalization of a series of NLO chromophores based on the N,N-diphenyl-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenyl]amine structure has been investigated. All the chromophores were synthesized from the intermediate chromophore N-phenyl-N-[4-(4-bromophenyl)phenyl]-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenyl]amine which was prepared by a six-step process. Bromination of fluorene yielded 2,7-dibromo-fluorene which could be converted to 2,7-dibromo-9,9-diethylfluorene by alkylation with ethyl iodide in DMSO. Reaction of 2,7-dibromo-9,9-diethylfluorene with one equivalent of butyl lithium followed by reaction with DMF provides 2-bromo-7-formyl-9,9-diethylfluorene. Condensation of 2-bromo-7-formyl-9,9-diethylfluorene and 2-aminobenzenethiol in DMSO results in the formation of 7-(2-benzothiazolyl)-2-bromo-9,9-diethylfluorene. The palladium catalyzed reaction of 7-(2-benzothiazolyl)-2-bromo-9,9-diethylfluorene with aniline afforded N-phenyl-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenyl]amine which was subjected to a second palladium catalyzed reaction with 4,4’-dibromobiphenyl to yield N-phenyl-N-[4-(4-bromophenyl)phenyl]-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenyl]amine. Further reactions have yielded a series of thermally stable NLO chromophores in which the functional group is located in the para position to the amine nitrogen.
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DEDICATION

To my wife, Jenn, who is always there to support me and all my crazy dreams. Without your understanding this would not have been possible. To my parents who always supported me through the years and gave me the guidance I needed to learn how to succeed. Thanks for all your patience and love.
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INTRODUCTION

Photonics is the analog of electronics in which a photon rather than an electron is used to transmit, store, process, and acquire information.\textsuperscript{1,2} The use of photonics offers several advantages over electronics. The most important advantage is the increase in speed as photons travel much faster than electrons. In the case of optical computing, photonic switching can take place at femtosecond speeds, which is several orders of magnitude faster than any electronic process.\textsuperscript{3} Other advantages include the ability to use 3-dimensional connectivity in photonics circuits to produce smaller optical chips, the absence of interference from electrical and magnetic sources, and complete compatibility with existing fiber optic networks. Additional applications of photonics are also found in the area of eye and sensor protection from unwanted laser radiation.

The level of research interest in photonics technology is evident in that over 9,800 articles on the subject of nonlinear optics have been published since 1990.\textsuperscript{4} Nonlinear optics is an essential element in the development of applications and devices for photonics technology. Examples of potential uses involving nonlinear optical phenomena include optical switching at junctions of electronic and photonic circuits, and frequency conversion, such as frequency doubling for high-density optical data storage or image analysis. Research to develop new nonlinear optical materials is currently being carried out in academic, industrial, and government laboratories worldwide. Incidentally, Japanese research efforts in this area are more than double those in the U.S.\textsuperscript{5}
HISTORICAL

Nonlinear Optical Materials

In reality almost any material can exhibit nonlinear optical properties, however, the intensity of the light source required to elicit these effects varies over several orders of magnitude. Nonlinear optical (NLO) materials can be classified as being either molecular materials or bulk materials. Molecular materials are made up of chemically bonded molecular units that interact in the bulk through weak van der Waals interactions and dipolar forces. For molecular materials, the optical nonlinearity is principally a function of the molecular structure. Examples of molecular materials include organic crystals and polymers. For bulk materials, the optical nonlinearity is determined by the electronic characteristic of the bulk medium. Examples of bulk materials include quantum well structures and most inorganic systems. Within the last 10 years molecular materials have emerged as an important class of NLO materials.

Molecular materials, particularly organic structures, offer several advantages over bulk materials. The two most important advantages of organic systems are that they provide flexibility to tailor their molecular structure through organic synthesis, and the ability to use molecular engineering to maximize the optical nonlinearity. Additionally, organic materials offer the potential of significant cost savings, improved thermal stability, and superior processibility in comparison to inorganic systems. The scope of the discussion in this thesis is limited to the case of organic systems.
**Linear Optical Response**

The optical response of a medium is based on the interaction between light and the molecular material. When the oscillating electromagnetic field of light propagates through the medium it exercises a polarizing force on the electrons of the medium. Since the inner electrons are more tightly bound to the nucleus, the major polarizing effect will be on the valence electrons of the system. Organic molecules are generally viewed as being nonmagnetic, nonconducting, and having their electrons tightly bound. The interaction and propagation characteristics of light with the medium are described by Maxwell’s equation.\(^\text{10}\) For organic systems the interaction with light is usually viewed within the framework of a dielectric subjected to an electric field.\(^\text{3,11}\) This approach is often referred to as the dipole approximation since the charge distribution induced in the molecule by the field is conveniently approximated by that of an induced dipole. The induced dipole moment (\(\mu_{\text{ind}}\)) is given by:

\[
\mu_{\text{ind}} = -er
\]

where \(e\) is the electronic charge and \(r\) is the field induced displacement. The induced dipole moment gives the bulk polarization (\(P\)) as defined by:

\[
P = -Ne\text{r}
\]

where \(N\) is the electron density of the medium. When the strength of the applied field is relatively low, the bulk polarization will be linear with respect to the applied field. The linear polarization can be expressed in terms of the linear or first-order susceptibility (\(\chi^{(1)}\)) such that:

\[
P = \chi^{(1)} \cdot E
\]
where $E$ is the applied electric field. The linear susceptibility is a dimensionless constant that is independent of the field strength and typically has a value of unity.\textsuperscript{12} The linear susceptibility is related to the dielectric constant ($\varepsilon$) and the refractive index ($n$) by the equation:

$$\varepsilon = n^2 = 1 + 4\pi\chi^{(1)}.$$ 

In the study of the optical properties of matter, $\chi^{(1)}$ is the most important property.\textsuperscript{13}

**Optical Nonlinearity in Organic Systems**

When an intense externally applied field interacts with the medium, the relation between the radiation field and the polarization is no longer linear. If the strength of the externally applied field is comparable with the atomic fields of the material ($\sim 10^8$ V/cm), the electric field that is created can disrupt the internal electric field of the atoms within the material. The result being that the laser radiation and the material modify one another.\textsuperscript{13,14} The polarization response (including the permanent polarization) of the medium can now be expressed as a power series expansion of the form\textsuperscript{15}:

$$P = P_0 + \chi^{(1)}E + \chi^{(2)}EE + \chi^{(3)}EEE + \ldots$$

where $\chi^{(1)}$ is the previously mentioned linear susceptibility, $\chi^{(2)}$ is the second-order nonlinear susceptibility, and $\chi^{(3)}$ is the third-order nonlinear susceptibilities of the bulk material.\textsuperscript{3} The magnitude of $\chi^{(2)}$ and $\chi^{(3)}$ respectively, describe the strength of the second-order and third-order processes. Higher order terms are also possible, however; they are extremely difficult to observe and are of little consequence from a materials perspective. An analogous equation described by the field-dependent molecular dipole moment expansion can be generated for the individual molecules of the material to give the microscopic polarization:
\[ \mu = \mu_0 + \alpha \cdot E + \beta \cdot EE + \gamma \cdot EEE + \ldots \]

where \( \alpha, \beta, \) and \( \gamma \) are, respectively, the polarizability, the first hyperpolarizability, and the second hyperpolarizability. They are a measure of the responsivity of the molecule to the applied field.

An alternate way of viewing the bulk polarization is to view the electric field as a sinusoidal oscillation:

\[ E(\mathbf{z},t) = E(0) \cos(\omega t - k\mathbf{z}) \]

Where \( \mathbf{z} \) represents direction in space, \( t \) represents time, \( \omega \) is the oscillation frequency, and \( k \) is the propagation vector.\(^3\) The combination of this equation with the proper trigonometric identities for \( \cos^2 \theta \) and \( \cos^3 \theta \) allows the polarization equation to become:

\[
P = \chi^{(1)} E_0 \cos(\omega t - k\mathbf{z}) + \chi^{(2)} E_0^2 [1 + \cos(2\omega t - 2k\mathbf{z})] \\
+ \chi^{(3)} E_0^3 [\cos(\omega t - k\mathbf{z}) + \cos(3\omega t - 3k\mathbf{z})]
\]

From this equation it can be seen that the second-order process produces a frequency contribution that is independent of the field, and a contribution at \( 2\omega \). The third order process on the other hand gives contributions at \( \omega \) and \( 3\omega \). The net result being that the even-order and the odd-order processes give rise to distinct types of nonlinear optical responses.\(^3\) The third-order susceptibility is a complex quantity and consists of a real and an imaginary part. Third-order optical processes arise from a combination of nonresonant effects that are regarded as the real part of \( \chi^{(3)} \) and resonant effects that are regarded as the imaginary part of \( \chi^{(3)} \). Examples of third-order processes include self-action, degenerate four-wave mixing, and two-photon absorption. Most \( \chi^{(3)} \) processes are classified as being either resonant or nonresonant, but some processes are best viewed as a combination of both.\(^3\) The focus of this research is based on the third-order process of
two-photon absorption for use in eye and sensor protection, therefore, the current discussion will be limited to this area.

**Two-Photon Absorption**

The nonlinear process of two-photon absorption was theoretically predicted by Göppert-Mayer in 1931\(^\text{16}\) and experimentally confirmed by Peticolas in 1967.\(^\text{17}\) Two-photon absorption occurs when the material possesses an electronic excited state at a level equal to twice the input beam’s frequency \(\omega\). It is a resonant nonlinear optical process that involves the imaginary part of \(\chi^{(3)}\). This can be seen in the equation for the resulting polarization of the bulk material\(^\text{18}\):

\[
P_i(\omega) = \text{Im} \left[ \chi^{(3)}_{iik} (-\omega, \omega; \omega, -\omega) \right] E_i(\omega) E_k(\omega) |^2
\]

where \(i\) and \(k\) refer to the coordinate system, \(E_i\) and \(E_k\) are the components of the applied electric field, \(\omega\) is the frequency of the incident beam, and \(\text{Im}\) represents the imaginary part of \(\chi^{(3)}\). A process that involves the imaginary part of \(\chi^{(3)}\) implies a dampening of the wave in the medium as a result of the exchange of energy between the medium and the applied optical field.\(^\text{3}\)

The general mechanism of two-photon absorption is illustrated in Figure 1.\(^\text{19}\) Initially, an intense laser pulse is applied to the material resulting in the simultaneous absorption of two photons by the molecules to reach an excited state. Once the molecule has been promoted to the excited state, it can undergo a nonradiative decay to a lower singlet excited state (identified in Figure 1 as the emitting state) followed by emission of a single photon at a higher frequency, \(\omega_1\), to return to the ground state. The overall process allows the two-photon absorbing organic molecule to absorb infrared (IR) radiation and to emit radiation in the visible (vis) range.
Additional processes that can occur once the molecule has reached an excited state include the possibility of additional photon absorption and the possibility of intersystem crossing to reach transient states.\textsuperscript{20}

As previously mentioned, the intensity of the incident beam decreases due to an interaction with the nonlinear optical medium. The intensity of the incident beam propagating through the material can be expressed in terms of the linear absorption coefficient ($\alpha$) and the two-photon absorption coefficient ($\beta$) as:

$$\frac{\delta I}{\delta z} = -(\alpha I + \beta I^2)$$

in which $z$ is the direction of propagation.\textsuperscript{21} Although it is not obvious from this equation, as the value of $\beta$ increases the intensity of the transmitted radiation will decrease. The two-photon absorption coefficient can be expressed in terms of the molecular two-photon cross-section ($\sigma_2$) in the equation:

$$\beta = \sigma_2 N_0$$

where $N_0$ is the molecular density of the material.\textsuperscript{21} The two-photon cross-section can be expressed in terms of Planck’s constant ($h$), the frequency of the incident light ($\nu$), the index of refraction ($n$), the speed of light in a vacuum ($c$), the number of absorbing molecules ($N$), and the imaginary part of $\chi^{(3)}$ in the equation:
\[ \sigma_2 = \left( \frac{8\pi^2 \nu}{n^2 c^2 N} \right) \cdot \text{Im}(\chi^3). \]

Multiplication of \( \sigma_2 \) by the energy of the incident photon generates a new expression \( \sigma'_2 \) which gives a precise and reproducible coefficient of the material’s two-photon activity.

**Design of Third-Order Nonlinear Optical Chromophores**

Recent developments in the synthesis of new nonlinear optical dyes with large two-photon cross-sections have given rise to several applications that were thought to be unattainable just a few years ago.\(^{11}\) These applications include two-photon upconverted lasing,\(^{22}\) three-dimensional optical data storage,\(^{23}\) photodynamic therapy,\(^{24}\) multiphoton confocal microscopy,\(^{25}\) and two-photon optical power limiting.\(^{26}\) The applications of this technology that are of the greatest interest to the Air Force are the development of two-photon technology as a material for optical power limiting and as an imaging tool for the nondestructive evaluation (NDE) of aircraft coatings.\(^{27}\)

With these interests in mind, a research program to develop structure-property relationships for a number of organic molecules in order to develop two-photon dyes with the necessary solubility, photostability, and enhanced nonlinear properties was undertaken. The design concept for the chromophores is based on the effective molecular two-photon absorption cross-section, as measured by the value of \( \sigma'_2 \).\(^{27}\) The structures that have been proposed for study are classified as Type I and Type II chromophores and are generally illustrated in Figures 2 and 3.\(^{27}\)

Type I chromophores are of the form of an electron rich thiophene core that is symmetrically flanked on either side by a heterocyclic \( \pi \) acceptor or \( \pi \) donor group, typically a benzothiazole or diphenylamine. Type II chromophores are composed of a polarizable \( \pi \) electron bridge that is flanked on one side by a \( \pi \) electron donor and of the
other side by a heterocyclic $\pi$ electron acceptor. The key design problem that had to be addressed, was the ability to maintain the two-photon absorption peak at 800 nm while increasing the two-photon cross-section of the chromophores. Two-photon absorbing molecules depend on absorption in the 600 – 800 nm range in order to give rise to optical power limiting effects in the visible range.$^{20}$

Through analysis of the two-photon cross-sections of these chromophores, a set of general guidelines has been developed to aid in designing new chromophores with increased two-photon activity.$^{20}$ These guidelines seek to:

1. Increase the planarity of the chromophore
2. Change the identity of the polarizable $\pi$ electron bridge
3. Extend the conjugation length of the chromophore
4. Change the identity of the heterocyclic acceptor group
5. Increase the $\pi$ donor strength

Through systematic modification of the structural elements of the chromophores, an understanding of the third-order susceptibility and how to improve two-photon activity has been achieved.

Experimental measurements of the two-photon activity have shown that Type II chromophores typically give superior cross-sectional measurements. The two
The current research has been focused solely on Type II chromophores and the remaining discussion will be limited to these asymmetric materials. It should be noted that all optical measurements reported in this thesis were made in THF solution and a wavelength of 800 nm. The chromophores all exhibit a linear absorption in the range of 400 nm, but no absorption in the 500-850 nm range, which indicates that upon irradiation there should be no linear absorption induced fluorescence emission.\textsuperscript{27} Valid comparison of the two-photon absorption of different chromophores can only be achieved if the individual two-photon absorption peaks are at approximately the same wavelength.

\textbf{The Polarizable $\pi$ Bridge}

The importance of the polarizable $\pi$ bridge can be seen by examination of a series of two-photon chromophores that have been synthesized in which the central bridge has been varied. The different core molecules investigated were 2,6-naphthyl, 4,4’-biphenyl, 2,7-fluorene, and 7,7’-bifluorene,\textsuperscript{27,28} which are illustrated in Figure 5.
The initial step in the synthesis of N,N-diphenyl-N-[4-[4-[2-(4-pyridyl)ethenyl]phenyl]phenyl]amine (1a) and N,N-diphenyl-N-[7-[2-(4-pyridyl)ethenyl]-9,9-diethyl-2-fluorenyl]amine (1b) was the palladium-catalyzed monosubstitution of 4,4’-dibromobiphenyl (2a) and 2,7-dibromo-9,9-diethylfluorene (2b), with the lithium salt of diphenylamine (3) to give N,N-diphenyl-N-[4-(4-bromophenyl)phenyl]amine (4a) and N,N-diphenyl-N-[2-[7-bromo-9,9-diethyl]fluorenyl]amine (4b) respectively. The compound 6-bromo-N,N-diphenyl-2-naphthylamine (4c) was synthesized by a condensation reaction of 2-bromo-6-hydroxy-naphthalene (5) with aniline (6), followed by arylation with iodobenzene (7). Compounds 4a, 4b, and 4c, were then reacted with 4-vinylpyridine under Heck conditions to give compounds 1a, 1b, and N,N-diphenyl-N-[6-[2-(4-pyridyl)ethenyl]-2-naphthyl]amine (1c).
Compound 4b could then be converted to the tri-n-butyltin derivative (4b') and coupled to 7-bromo-9,9-diethyl-2-[2-(4-pyridyl)ethenyl]fluorene (8) via a palladium catalyzed Stille reaction to give N,N-diphenyl-N-[7-[7-[2-(4-pyridyl)ethenyl]-9,9-diethyl-2-fluoren-2-yl]-9,9-diethyl-2-fluorenyl]amine (1d).

Compounds 1a, 1b, 1c, and 1d, differ only in the identity of the polarizable π bridge. Examination of the structures shows that in each case a diphenylamine is present as the π-electron donor and a vinylpyridine is present as the π-electron acceptor.
Since the only difference between the compounds is the polarizable bridge, is it logical to assume that any difference in the third-order optical properties is due solely to the $\pi$ bridge. Results of the two-photon measurements are listed in Table 1.27

**Table 1.** Two-Photon Absorption Characteristics of Compounds 1a, 1b, 1c, and 1d in THF at a wavelength of 800 nm.

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\beta$</th>
<th>$\alpha_2'$ (x 10^{-48} cm$^4$ sec cm$^4$ sec mol$^{-1}$)</th>
<th>$\alpha_2'MW$ (x 10^{-50} cm$^4$ sec mol$^{-1}$ ph molecule g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>367 (485)</td>
<td>1.9</td>
<td>39.0</td>
<td>9.2</td>
</tr>
<tr>
<td>1b</td>
<td>388 (488)</td>
<td>4.7</td>
<td>97.0</td>
<td>19.7</td>
</tr>
<tr>
<td>1c</td>
<td>388 (488)</td>
<td>3.3</td>
<td>68.4</td>
<td>17.2</td>
</tr>
<tr>
<td>1d</td>
<td>383.5 (492)</td>
<td>3.8</td>
<td>79.4</td>
<td>11.1</td>
</tr>
</tbody>
</table>

Comparison of chromophores 1a and 1b illustrates the importance of the planarity of the core molecule. While both compounds have the same conjugation length, the biphenyl bridge in 1a is less planar due to the absence of the bridging methylene group that is found in compound 1b. The difference in planarity results in a 248% increase in the experimentally determined two-photon cross-section.27 Comparison of 1b with 1c shows that fluorene is also superior to naphthalene as a $\pi$ bridge. Analysis of this result
would indicate that the difference is due to the greater conjugation length of the fluorene molecule compared to naphthalene as both structures are highly planar. Comparison of 

**1b** with **1d** shows that despite the increase in conjugation length due to the additional fluorene molecule the two-photon cross-section decreases. This it postulated to be due to a decrease in the effective conjugation length due to the loss of planarity by rotation of the adjoining fluorene.27

In addition to the identity of the polarizable \( \pi \) bridge, the identity of the alkyl pendant side chains has been found to have an unexpected influence on the two-photon cross-section.27 Evaluation of cross-sections of N,N-diphenyl-N-[7-[2-(4-pyridyl)ethenyl]-9,9-diethyl-2-fluorenyl]amine (**1b**), N,N-diphenyl-N-[7-[2-(4-pyridyl)ethenyl]-9,9-di-\( n \)-hexyl-2-fluorenyl]amine (**1e**), and N,N-diphenyl-N-[7-[2-(4-pyridyl)ethenyl]-9,9-di-\( n \)-decyl-2-fluorenyl]amine (**1f**), shows that the two-photon cross-section increases as the chain length increases.

Compounds **1e** and **1f** can be synthesized using the reaction scheme outlined for **1b**.

Results of the two-photon measurements for **1b**, **1e**, and **1f** are listed in Table 2.27
Table 2. Two-Photon Absorption Characteristics of Compounds 1b, 1e, and 1f in THF at a wavelength of 800 nm.

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>$\lambda_{max}$ (nm)</th>
<th>$\beta$ (cm/GW at 0.02 mol/L)</th>
<th>$\sigma_2^+$ (x 10$^{-48}$ cm$^2$ sec cm$^4$ mol e/Upconv. Em.)</th>
<th>$\sigma_2^+/MW$ (x 10$^{-50}$ cm$^4$ sec mol e/ph molecule g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1b</td>
<td>388 (488)</td>
<td>4.7</td>
<td>97.0</td>
<td>19.7</td>
</tr>
<tr>
<td>1e</td>
<td>389 (494)</td>
<td>5.1</td>
<td>106.1</td>
<td>17.5</td>
</tr>
<tr>
<td>1f</td>
<td>390 (492)</td>
<td>5.6</td>
<td>115.6</td>
<td>16.1</td>
</tr>
</tbody>
</table>

The two-photon cross-section is increased by approximately 19% in going from ethyl pendant groups to decyl pendant groups. It is postulated that the additional steric hindrance of the larger alkyl groups increases the two-photon activity by inhibiting aggregate, and possibly eximer, formation.$^{27}$

The $\pi$ Electron Donor

The $\pi$ donor groups that have been incorporated into the chromophores include thiophene, diphenylamine, and substituted derivatives of diphenylamine.$^{27}$ A quantitative comparison of the donor effects can be achieved by evaluation of N,N-diphenyl-N-[6-(4-pyridyl)-2-naphthyl]amine (9a) and 2-[7-(4-pyridyl)-9,9-di-n-decyl-2-fluorenyl]thiophene (9b). Chromophore 9a was synthesized in a three-step sequence starting from compound 5. Compound 5 was condensed with 6 to give N-phenyl-N-[6-bromo-2-naphthyl]amine (10), which was then reacted under Stille conditions with (4-pyridyl)-tri-n-butyltin (11) to give N-phenyl-N-[6-(4-pyridyl)-2-naphthyl]amine (12). The synthesis was completed by a copper catalyzed arylation with 7. Compound 9b was synthesized by a two-step reaction sequence of consecutive Stille mono-coupling reactions of 2,7-dibromo-9,9-di-n-decylfluorene (13) with 11, and then with (2-thiophenyl)-tri-n-butyltin (14).
Comparison of the experimental measurement of the two-photon cross-sections in given in Table 3.27

| Table 3. Two-Photon Absorption Characteristics of Compounds 9a and 9b in THF at a wavelength of 800 nm. |
|-------------------------------------------------|-----------------|------------------|------------------|------------------|
| Chromophore | $\lambda_{\max}$ (nm) | $\beta$ | $\sigma_2'$ ($\times 10^{-48}$ cm$^4$ sec ph molecule) | $\sigma_2'MW$ ($\times 10^{-50}$ cm$^4$ sec mole g) |
| 9a | 347 (453) | 0.6 | 12.9 | 3.5 |
| 9b | 345 (410) | 0.06 | 1.31 | 0.2 |
Comparison of \(9a\) and \(9b\) on the basis of the polarizable \(\pi\) bridge would give the expectation that \(9b\) would have superior third-order optical properties, however, the optical measurements show that \(9a\) possesses a larger \(\sigma^2\) value. Inspection of the remaining molecular structure indicates that both compounds contain a 4-pyridine acceptor group, but different \(\pi\) donor groups. The conclusion can thus be drawn that the diphenylamine has a greater ability than thiophene to push electron density toward the acceptor group, and is a better \(\pi\) donor group for third-order optical applications.\(^{27}\)

Additional enhancement of the two-photon properties can be achieved by attachment of electron donating groups on the aromatic rings of the diphenylamine. This can be seen in the series of chromophores \(1b\), N,N-di-(3-hydroxy)phenyl-N-[7-[2-(4-pyridyl)ethenyl]-9,9-diethyl-2-fluorenyl]amine (\(9c\)), and N,N-di-(3-methoxy)phenyl-N-[7-[2-(4-pyridyl)ethenyl]-9,9-diethyl-2-fluorenyl]amine (\(9d\)).\(^{27}\) Compound \(9c\) was prepared by a reaction sequence analogous to \(1b\). Synthesis of \(9d\) was accomplished via a Heck reaction followed by a palladium catalyzed amination reaction. Two-photon measurements are reported in Table 4.

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
2b & \quad \text{Pd(OAc)}_2, \text{P(o-tolyl)}_3 \
& \quad \text{Toluene, } 90^\circ C \\
\text{Br} & \quad \text{N} \\
8 & \quad \text{Pd(dba)}_2, \text{P(o-tolyl)}_3 \
& \quad \text{Toluene, } 90^\circ C
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{O} & \quad \text{N} \\
OCH_3 & \quad \text{N} \\
\text{CH}_3\text{O} & \quad \text{N} \\
\text{OCH}_3 & \quad \text{N}
\end{align*}
\]
Table 4. Two-Photon Absorption Characteristics of Compounds 1b, 9c, and 9d in THF at a wavelength of 800 nm.

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\beta$</th>
<th>$\sigma_2^\prime (x 10^{-48})$</th>
<th>$\sigma_2^\prime$/MW ($x 10^{-50}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1b</td>
<td>388 (488)</td>
<td>4.7</td>
<td>97</td>
<td>19.7</td>
</tr>
<tr>
<td>9c</td>
<td>392 (500)</td>
<td>5</td>
<td>103</td>
<td>19.6</td>
</tr>
<tr>
<td>9d</td>
<td>386 (488)</td>
<td>5.6</td>
<td>114.8</td>
<td>20.8</td>
</tr>
</tbody>
</table>

The measurements indicate that the increase in the $\sigma_2^\prime$ value is due to the increased electron density on the diphenylamino group. The observed effect was somewhat unexpected as the hydroxy and methoxy are both not able to contribute through a resonance mechanism. It should also be noted that the increase in going from hydroxy to
methoxy is postulated to be due to a lower tendency of the methoxy to form aggregates due to the lack of hydrogen bonding ability.\textsuperscript{27}

The $\pi$ Electron Acceptor

Correlation of the third-order absorptivity with the identity of the $\pi$ acceptor group has been made on the basis of a series of diphenylaminofluorene based molecules in which the $\pi$ acceptor group was varied.\textsuperscript{29} The acceptor groups that have been investigated are 2-(4-pyridyl)ethenyl, 2-benzothiazolyl, benzoyl, 2-benzoazolyl, 2-quinoxalinyl, 2-(N-phenyl)benzimidazolyl, and 2-(4,5-diphenylimidazolyl).\textsuperscript{29} The synthesis of compounds $1b$ and $1f$ which utilize the 2-(4-pyridyl)ethenyl acceptor group was described in the previous section. Initially $2b$ was monoformylated to give 2-bromo-7-formyl-9,9-diethylfluorene ($15$), which was subsequently reacted with 2-aminothiophenol ($16$)\textsuperscript{30} to give 7-(2-benzothiazolyl)-2-bromo-9,9-diethylfluorene ($17$). Reaction of $17$ with diphenylamine ($3b$) under copper catalyzed conditions gave N,N-diphenyl-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenyl]amine ($18a$). The compounds N,N-diphenyl-N-[7-benzoyl-9,9-diethyl-2-fluorenyl]amine ($18b$), N,N-diphenyl-N-[7-(2-benzoazolyl)-9,9-diethyl-2-fluorenyl]amine ($18c$), and N,N-diphenyl-N-[7-(2-quinoxalinyl)-9,9-diethyl-2-fluorenyl]amine ($18d$) were all synthesized in reactions from the key intermediate $4b$. The final two chromophores that were investigated, N,N-diphenyl-N-[7-[2-(N-phenyl)imidazolyl]-9,9-di-$n$-decyl-2-fluorenyl]amine ($18e$) and N,N-diphenyl-N-[7-[2-(4,5-diphenyl)imidazolyl]-9,9-di-$n$-decyl-2-fluorenyl]amine ($18f$), were both synthesized via reactions from the intermediate N,N-diphenyl-N-[7-bromo-9,9-di-$n$-decyl-2-fluorenyl]amine ($4d$). The optical properties of this series of compounds are reported in Table 5.\textsuperscript{29}
1. \( n\)-BuLi, THF, -78°C
2. DMF/THF

\( \text{Cu, } \text{K}_2\text{CO}_3 \) 18-crown-6

1. \( n\)-BuLi, THF, -78°C
2. PhCN
3. \( \text{H}_3\text{O}^+ \)

1. \( n\)-BuLi, THF, -78°C
2. \( \text{Bu}_3\text{SnCl, THF} \)
3. \( \text{PdCl}_2(\text{PPh}_3)_2 \) 18-crown-6

1. \( n\)-BuLi, THF, -50°C
2. \( \text{Bu}_3\text{SnCl, THF} \)
3. \( \text{PdCl}_2(\text{PPh}_3)_2 \)
Table 5. Two-Photon Absorption Characteristics of Compounds 1b, 1f, 18a, 18b, 18c, 18d, 18e, and 18f in THF at a wavelength of 800 nm.

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>( \lambda_{max} ) (nm)</th>
<th>Linear Abs. ( \beta ) cm/GW at 0.02 mol/L</th>
<th>( \alpha_2' \times 10^{-48} ) cm(^4) sec/phon molecule</th>
<th>( \alpha_2'/MW \times 10^{-50} ) cm(^4) sec mole/phon molecule g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1b</td>
<td>388 (488)</td>
<td>4.7</td>
<td>97.0</td>
<td>19.7</td>
</tr>
<tr>
<td>1f</td>
<td>390 (492)</td>
<td>5.6</td>
<td>115.6</td>
<td>16.1</td>
</tr>
<tr>
<td>18a</td>
<td>391.5 (479)</td>
<td>4.7</td>
<td>97.7</td>
<td>17.6</td>
</tr>
<tr>
<td>18b</td>
<td>386 (490)</td>
<td>4.1</td>
<td>84.5</td>
<td>17.1</td>
</tr>
<tr>
<td>18c</td>
<td>389 (488)</td>
<td>1.1</td>
<td>22.7</td>
<td>4.5</td>
</tr>
<tr>
<td>18d</td>
<td>402.5 (552)</td>
<td>1.9</td>
<td>39.2</td>
<td>7.6</td>
</tr>
<tr>
<td>18e</td>
<td>370 (439)</td>
<td>3.3</td>
<td>67.1</td>
<td>8.3</td>
</tr>
<tr>
<td>18f</td>
<td>384 (449)</td>
<td>0.2</td>
<td>3.9</td>
<td>0.4</td>
</tr>
</tbody>
</table>

**18f**

1. \( n \)-BuLi, THF, -78°C
2. DMF/THF

\( \text{Cu(OAc)}_2 \)

EtOH

\( \text{NH}_4\text{O}_2\text{CH}_3 \)
Analysis of the $\sigma^2$ values for the series of chromophores shows that the largest values were obtained for $1b$, $1f$, $18a$, and $18b$. Analysis of $1b$, $18a$, and $18b$ indicates that, under the current conditions, the ability to accept charge from the diphenyl amino group follows the order: 2-(4-pyridyl)ethenyl $\approx$ 2-benzothiazolyl $>$ benzoyl. The effect of the alkyl side chains of the core molecule is evident here from the enhanced $\sigma^2$ values observed for $1f$. The di-$n$-decyl analog of $18a$ has been synthesized$^{31}$, however; no direct comparison of the two-photon cross-sections can be made as the optical measurements were made using a different technique. An additional interesting comparison can be made between the 2-benzothiazolyl derivative $18a$ and the 2-(N-phenyl)benzimidazolyl derivative $18e$. In symmetrical Type I chromophores the 2-(N-phenyl)benzimidazole group produces superior third-order optical properties, however, in the Type II series despite the difference in the pendant side chains, $18a$ shows better optical properties than $18e$.$^{32,33}$

The third-order optical properties of $1b$ and $18a$ suggest that both the 2-(4-pyridyl)ethenyl and 2-benzothiazolyl are potential acceptor groups for two-photon materials. Comparison of the compounds on the basis of physical properties shows that $18a$ offers greater chemical, thermal, and photochemical stability than $1b$. After repeated exposure to nanosecond laser radiation, $18a$ was shown to be optically intact, but solutions of $1b$ and $1f$ were both shown to darken over time when subjected to the same conditions.$^{29}$ Evaluation of the effects of the $\pi$ donor, the $\pi$ bridge, and the $\pi$ acceptor on the two-photon activity, has led to the current research being focused on chromophores based on the N,N-diphenyl-N-[7-(2-benzothiazolyl)-9,9-dialkyl-2-fluorenyl]amine framework.
Synthesis of Two-Photon Chromophores

The third-order nonlinear optical chromophores are highly aromatic systems that are synthesized by several reactions. The following discussion will be limited to the topics of aryl-aryl bond formation reactions, aromatic amination reactions, and functionalization reactions of aromatic systems. The reactions covered will be limited to those that the current research has either utilized or considered for the synthesis of the two-photon chromophores.

Aryl-Aryl Bond Forming Reactions

The formation of aryl-aryl bonds is a synthetic challenge that has in large part been overcome through the development of the Ullmann reaction\textsuperscript{34}, and several palladium- and nickel-catalyzed catalytic cross-coupling reactions. Of the latter, we are primarily concerned with the Stille reaction, which involves the use of organotin reagents, and the Suzuki reaction, which utilizes organoboron reagents. A review of catalytic cross-coupling reactions has been published.\textsuperscript{35}

The Ullmann reaction is the oldest of the aryl coupling reactions that is commonly used in synthesis today. The reaction is named after Fritz Ullmann who, in 1903, discovered that aromatic halides when heated in the presence of a copper(I) catalyst, provide the corresponding symmetrical biaryl molecule.\textsuperscript{34,36} The reaction can be seen in the coupling of two equivalents of iodobenzene 7 to yield biphenyl 7'.

\[
\text{Cu, K}_2\text{CO}_3 \quad \text{Xylene, 180}^\circ\text{C} \quad \text{Cu, K}_2\text{CO}_3 \quad \text{Xylene, 180}^\circ\text{C}
\]

The reaction is generally carried out using iodides, but bromides, chlorides, and thiocyanates have also been used. The Ullmann reaction can be run in either an
intermolecular or an intramolecular fashion, and has been used to synthesize both symmetrical and unsymmetrical biaryl compounds.\textsuperscript{37} The effects of the substituents on the aromatic ring follow the general reactivity trends for aromatic nucleophilic substitution with a few exceptions. The nitro group is found to be highly activating due to electronic effects, but only when in the ortho position.\textsuperscript{38} Also, the substituents COOH and SO$_2$NH$_2$ are found to be completely deactivating as they cause side reactions.\textsuperscript{39} The mechanism is not definitively known, but it is most commonly viewed as being a two-step process in which the halide group of one molecule is substituted to form the organocopper species which then reacts with a second molecule of aryl halide.

The major disadvantages of the Ullmann reaction are that it requires equimolar equivalents of copper and that the reaction temperatures commonly used are quite high. Several modifications of the Ullmann reaction have appeared since 1903. These include the use of an activated copper powder which can improve product yields\textsuperscript{40}, a low temperature analog that uses zerovalent nickel complexes in place of copper\textsuperscript{41}, and a catalytic alternative that uses Pd(OAc)$_2$ as a catalyst with base and isopropanol.\textsuperscript{42}

Aryl-aryl bonds can also be formed using a family of aromatic cross-coupling reactions that rely on use of catalytic amounts of palladium or nickel catalyst, that are commonly used in modern syntheses. These reactions include the Kharasch reaction which uses aryl Grignard reagents, the Negishi reaction which uses arylzinc reagents, the Stille reaction which uses arylstannanes, and the Suzuki reaction which uses arylboronic
acids. As previously mentioned the current discussion will only be concerned with the Stille reaction and the Suzuki reaction.

The Stille reaction, named in recognition of the mechanistic and synthetic studies completed by John K. Stille, began to be used for the formation of aryl-aryl bonds shortly after it was first published in 1978. Advantages of the Stille reaction include no air or moisture sensitivity, reactions occur under neutral conditions, and compatibility with numerous functional groups. In addition, organotin reagents are stable to both air and moisture, and can be easily purified. The major disadvantage of the Stille reaction is that the organotin compounds are highly toxic. This toxicity, combined with the difficulty of removing the organotin compounds from the reaction have greatly hindered the use of the Stille reaction in industrial applications. An example of the Stille reaction is the reaction of (4-methylphenyl)tri-\textit{n}-butylstannane (19) and 1-bromo-4-nitrobenzene (20).

The general mechanism of the Stille reaction, as well as the other catalytic reactions is illustrated in Figure 5.
The initial step is the in situ generation of the catalytically active metal(0) species from the metal(II) catalyst. Once the metal(0) species has been generated, the reaction can be viewed as a three-step cycle that consists of an oxidative addition, a transmetallation, and a reductive elimination. Studies have shown that the transmetallation is often the rate-determining step in the catalytic cycle.

The most common leaving groups that are used in this reaction are halides, most commonly bromides and iodides, and triflates. Recently, a method for the Stille coupling of aryl chlorides has been developed. Analysis of the substituents on the aromatic rings of the halide or triflate, have shown the trend that electron-withdrawing groups in the para position tend to accelerate the rate of reaction, and that steric hindrance at the ortho position to the coupling site can drastically reduce the rate of reaction. A modified version of the Stille reaction has been published in which the reaction rate has been accelerated by selection of alternative ligands on the metal catalyst.
The second catalytic cross-coupling of interest is the Suzuki reaction, named for the pioneering work of Akira Suzuki.\textsuperscript{47} The reaction mechanism follows the same catalytic cycle as illustrated for the Stille reaction, but with aryl organoboron reagents rather than the organotin reagents. The most common organoboron reagents that have been used are the boronic acids as they are commercially available, inert and thermally stable to air and moisture, and thus can be handled without special precautions.\textsuperscript{48} An example of this reaction is the combination of phenylboronic acid (21) with 20.

\[
\begin{align*}
\text{B(OH)}_2 & \quad + \quad \text{NO}_2^- \\
& \quad \text{Br} \quad \rightarrow \quad \text{NO}_2
\end{align*}
\]

The most commonly employed leaving groups are bromides, iodides, and triflates. Recently new catalysts have been developed that allow for the reaction to be carried out with aromatic chlorides.\textsuperscript{49} The effects of the substituents of the aromatic rings are analogous to those observed in the Stille reaction. The Suzuki reaction offers the same advantages that were seen in the Stille, but with the additional benefit that neither the organoboron reagent nor the byproducts are toxic as in the case of the organotin compounds. The Suzuki reaction can be tuned by selection of the base, the palladium catalyst, and the solvent.\textsuperscript{48}

In both the Stille and the Suzuki reactions, the potential exists for side reactions that cause the reactions to be ineffective\textsuperscript{44,48}, but will not be covered in this discussion.

**Aromatic Amination Reactions**

Selection of the aryl amine functionality as the donor group of the chromophores has made aromatic amination reactions extremely important in the synthesis of third-order nonlinear optical molecules. The two most important reactions that will be
discussed are a version of the Ullmann reaction previously discussed, and the more recently developed palladium catalyzed aromatic amination reaction.

The Ullmann reaction not only encompasses the copper-catalyzed formation of biaryls, but also the analogous condensation reaction of nucleophiles such as diphenylamine 3b, with aromatic halides.\(^\text{36}\) An example is the reaction of aniline \(6\) with two equivalents of 4-iodotoluene (22) to give the triarylamine product.\(^\text{50}\)

\[
\begin{align*}
\text{NH}_2 & \quad \text{I} \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

The general discussion given for the Ullmann biaryl synthesis is also applicable here. It should be noted that the low temperature variation using zerovalent nickel complexes has not been found to be applicable to this case. To overcome the harshness of the reaction procedures using crown ethers\(^\text{51}\) and hydrolytically stable coordinating ligands\(^\text{50}\) have been utilized with some success.

Aromatic amines have more recently been catalyzed using a palladium catalyzed reaction that is commonly associated with the independent work of Buchwald and Hartwig.\(^\text{52}\) The first N-arylation of this type was reported by Migita in 1983\(^\text{53}\), and has since been modified and shown to be a highly useful synthetic reaction. The current research has utilized the procedure for triarylamine synthesis published by Marder and coworkers.\(^\text{54}\) An example of this method is the reaction of aniline with 1-bromo-4-\(n\)-butylbenzene (23) in the presence of Pd\(_2\)(dba)\(_3\), DPPF, and NaO-\(t\)-Bu.
Bromides are the most commonly used leaving groups, but iodides, chlorides, and triflates have also been shown to be compatible. The most recent work has focused on the development of improved catalyst systems and applying the methodology to generate improved synthetic techniques.

**Functionalization Reactions**

Functionalization of any of the aforementioned chromophores will allow them to be incorporated into the matrix of a second material. The three functional derivatives considered for investigation in this research are the formyl group, the vinyl group, and the hydroxy group.

Formylation of aromatic rings can be done through a number of synthetic procedures. These procedures include the Vilsmeier-Haack reaction, and the Gatterman reaction. An effective formylation procedure involving an aromatic halide is a two-step reaction utilizing a halogen-metal exchange of the halide with the lithium reagent, followed by a substitution reaction with DMF to generate the aldehyde product.
Incorporation of a vinyl group can be accomplished by several procedures. The first of these is via a Stille reaction of the aromatic bromide with tri-n-butyl ethenylstannane. The optimized conditions for this reaction are reported to be the use of toluene as a solvent and tetrakis(triphenylphosphine)palladium(0) as a catalyst at a temperature of 100°C. The substituent effects that were discussed previously for the Stille reaction are also valid for the current example. Observations have shown that the presence of an amine function in the para position to the bromide is highly deactivating and in some cases prevents the synthesis of the vinyl product. Other more involved procedures that could be used to synthesize the vinyl group include dehydration of a secondary alcohol or a Wittig reaction involving an aldehyde.

Functionalization can also be accomplished by reduction of an aldehyde to give the corresponding primary alcohol. By using sodium borohydride, selective reduction of the aldehyde functionality can be achieved in the presence of many other functional groups.

The objectives of the current research were to: 1) synthesize a series of two-photon chromophores functionalized at the para position to the amine nitrogen, and 2) to have the two-photon cross-sections measured for comparison with previously synthesized chromophores.
EXPERIMENTAL

Instrumentation and Chemicals

Starting materials were purchased from Aldrich Chemical Company or Lancaster Chemicals, unless details of the preparation are given. All commercial reagents were used without further purification. All butyl lithium reactions were run in THF that had been distilled from sodium after the characteristic blue color of sodium diphenyl ketyl generated in situ was found to persist. Melting points were taken using an Electrothermal capillary melting point apparatus equipped with a thermocouple, and are reported uncorrected. Nuclear magnetic resonance (NMR) spectra were obtained using a Bruker AC200 spectrometer ($^1$H and $^{13}$C). Chemical shifts ($\delta$) refer to the signal of trimethylsilane (TMS). A Perkin Elmer 1600 Series FTIR using KBr pellets was used to record the infrared spectra (IR). Elemental analysis and mass spectrometry (MS) were performed by Materials Laboratory Sample Analysis (MLSA) at Wright Patterson Air Force Base. Additional analysis of some compounds was done by gas chromatography with mass spectral detection using a Hewlett-Packard 5900 GC/MS.

2,7-dibromofluorene (24)

A solution of fluorene (157.5 g, 0.95 mol) and iodine (2.69 g, 0.011 mol) in methylene chloride (1 L) was mechanically stirred at room temperature until complete dissolution. A solution of bromine (100 mL, 1.941 mol) in methylene chloride (150 mL) was added dropwise over a period of 3 h to yield a deep red solution. The mixture was allowed to stir for 15 min after which a sodium bisulfite solution (8 g NaHSO$_3$, 250 mL
H2O) and the reaction was allowed to stir overnight. Addition of the bisulfite solution caused the mixture to change from red in color to pink, before finally becoming colorless. The methylene chloride was removed by distillation during which H2O was added to the solution (4 x 200 mL). The distillation was stopped when the temperature of the solution reached 100°C. The mixture was cooled to 40°C using a water bath. The product was collected by vacuum filtration, washed with water (3 L), and air dried overnight. The precipitate was slurried in ethanol (1000 mL) and refluxed for 3 hours. The slurry was cooled to room temperature, the product was recollected by vacuum filtration, and washed with water (3 L) to afford 24 (306.2 g, 99%) as white crystals: m.p. 164-166°C; IR (KBr) cm⁻¹ 2919 (aliphatic C-H), 1453 and 1397 (Ar-C=C), 813 (C-H out of plane); ¹H NMR δ 3.82 (s, 2H, CH₂), 7.62-7.85 (m, 6H, Ar-H); mass spectrum, m/z (relative intensity) 326, 324, 322 (M⁺, 9.5, 19.4, 10.7). Anal. Calcd. for C₁₃H₈Br₂: C, 48.19; H, 2.49; Br, 49.32. Found: C, 48.09; H, 2.53; Br, 49.54.

2,7-dibromo-9,9-diethylfluorene (25)

A solution of 2,7-dibromofluorene (101.1 g, 0.312 mol), potassium hydroxide (75.45 g, 1.3 mol), and potassium iodide (5.42 g, 0.03 mmol) in dimethysulfoxide (180 mL) was cooled to 10°C in an ice bath. Ethyl bromide (65 mL) was added dropwise over a period of 1.5 h while maintaining the reaction temperature below 15°C. The resulting purple solution was allowed to stir for 16 h and was then poured into water (3 L) at which time the purple color disappeared. The water mixture was stirred for 2 h and then collected by vacuum filtration. The product was recrystallized from hexanes (700 mL, charcoal, MgSO₄) to yield 25 (103.3 g, 87.1%) as beige colored crystals: m.p. 157-158°C; IR (KBr) cm⁻¹ 3071 (Ar-C-H), 1572 and 1449 (Ar-C=C), 2959, 2916, and 2871 (aliphatic
C-H), 814 (C-H out of plane); $^1$H NMR δ 0.31 (t, 6H, -CH$_3$), 2.00 (q, 4H, CH$_2$), 7.44-7.5 (m, 6H, Ar-H); mass spectrum, m/z (relative intensity) 382, 380, 378 (M$^+$, 18.6, 41.8, 19.7). Anal. Calcd. for C$_{17}$H$_{16}$Br$_2$: C, 53.72; H, 4.24; Br, 42.04. Found: C, 53.82; H, 4.19; Br, 41.97.

2-bromo-7-formyl-9,9-diethylfluorene (26)

To a mechanically stirred solution of 2,7-dibromo-9,9-diethylfluorene (60.0 g, 0.158 mol) in dry THF (375 mL) that had been cooled to –77$^\circ$C was added a solution of $n$-butyllithium in hexanes (1.6M, 100 mL). The rate of addition was controlled in order to maintain the temperature of the reaction mixture below –70$^\circ$C. The yellow reaction mixture was allowed to stir for 15 minutes and a solution of dimethylformamide (22.5 mL) in THF (20 mL) was added over 30 minutes. The solution was stirred for 2 h after which it was allowed to warm to 5$^\circ$C. A solution of hydrochloric acid (15 mL) in water (25 mL) was added, and the solution was allowed to stir overnight at room temperature. The mixture was diluted with toluene (200 mL), washed with a saturated sodium bicarbonate solution (3 x 50 mL), and the organic phase was separated. The aqueous layer was extracted with additional toluene (100 mL) which was separated and combined with the organic phase. The organic phase was dried with MgSO$_4$, filtered, and evaporated. The crude product was recrystallized from heptane to afford 26 (44.54 g, 85.5%) as white crystals: m.p. 127-129$^\circ$C; IR (KBr) cm$^{-1}$ 3063 (Ar-C-H), 2961, 2926, and 2871 (aliphatic C-H), 1604 and 1454 (Ar-C=C), 2804 and 2744 (aldehydic C-H), 1688 (C=O), 812 (C-H out of plane); $^1$H NMR δ 0.34 (t, 6H, CH$_3$), 2.04 (q, 4H, CH$_2$), 7.51-7.86 (m, 6H, Ar-H), 10.07 (s, 1H, CHO); mass spectrum, m/z (relative intensity)
7-(2-benzothiazolyl)-2-bromo-9,9-diethylfluorene (27)

In a 250 mL 3-necked flask equipped with a distillation head, a mixture of 2-bromo-7-formyl-9,9-diethylfluorene (43.00 g, 0.131 mol), and 2-aminothiophenol (16.38 g, 14 mL, 0.136 mol) in DMSO (60 mL) was heated to 160°C for 1.5 h. The reaction mixture was poured in small portions, with vigorous stirring, into a solution containing sodium chloride (60 g), water (250 mL), and crushed ice (600 g). The resulting mixture was stirred overnight, collected by vacuum filtration, and washed with water (4 L). The product was refluxed in ethanol (500 mL) for 5 h, collected by vacuum filtration, and purified by silica gel column chromatography (heptane;toluene) to afford (46.45 g, 81.9%) as yellow crystals: m.p. 136-138°C; IR (KBr) cm⁻¹ 3059 (Ar-C-H), 2962, 2921, and 2874 (aliphatic C-H), 1454 (Ar-C=C); ¹H NMR δ 0.34 (t, 6H, CH₃), 2.05 (q, 4H, CH₂), 7.37-8.10 (m, 10H, Ar-H); mass spectrum, m/z (relative intensity) 435, 433 (M⁺, 94.4, 100). Anal. Calcd. for C₂₄H₂₀BrNS: C, 66.36; H, 4.64; Br, 18.39; N, 3.22; S, 7.38. Found: C, 66.52; H, 4.39; Br, 18.61; N, 4.13; S, 7.28.

N-phenyl-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenyl]amine (28)

To a 1000 mL 3-necked flask equipped with a Dean-Stark condenser and maintained under a dry N₂ atmosphere was added 2-benzothiazolyl-7-bromo-9,9-diethylfluorene (41.24 g, 0.92 mol), aniline (20 mL, 0.22 mol), and toluene (325 mL). The mixture was heated to reflux and maintained for 2 h to remove all moisture from the system. After cooling to room temperature, bis(dibenzylideneacetone)palladium (Pd(dba)₂) (1.116 g, 1.94 mmol), bis(diphenylphosphino)ferrocene (DPPF) (0.996 g, 1.80
mmol), and sodium tert-butoxide (13.95 g, 0.146 mol) were added to the solution which was then stirred at 100°C for 16 h. After cooling, the organic layer was washed with H2O, dried over MgSO4, filtered, and concentrated. The product was purified by silica gel column chromatography (toluene) and recrystallized (toluene:heptane, 98:2) to afford 28 (37.39 g, 88.2%) of yellow crystals: m.p. 174-175°C; IR (KBr) cm⁻¹ 3397 and 3276 (N-H), 3081 (Ar-C-H), 2962, 2917, and 2873 (aliphatic C-H), 1595, 1497, and 1458 (Ar-C=C), 1315 (C-N); ¹H NMR δ 0.34 (t, 6H, CH3), 2.05 (q, 4H, CH2), 4.50 (s, 1H, NH), 7.37-8.10 (m, 15H, ArH); mass spectrum, m/z (relative intensity) 446 (M⁺, 100). Anal. Calcd. for C₃₀H₂₆N₂S: C, 80.68; H, 5.87; N, 6.27; S, 7.18. Found: C, 80.33; H, 5.84; N, 6.26; S, 7.17.

N-phenyl-N-[4-(4-bromophenyl)phenyl]-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenyl]amine (29)

To a solution of N-phenyl-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenyl]amine (6.7 g, 15.0 mmol), 4,4’-dibromobiphenyl (9.4 g, 30.2 mmol), and toluene (50 mL), from which the moisture had been removed by the procedure used for 28, and under a dry N₂ atmosphere, was added bis(dibenzylideneacetone)palladium (Pd(dba)₂) (0.170 g, 0.30 mmol), bis(diphenylphosphino)ferrocene (DPPF) (0.155g, 0.28 mmol), and sodium tert-butoxide (2.20g, 23.0 mmol). The solution was stirred at 105°C for 14 h. After cooling, the organic layer was washed with H₂O, dried over MgSO₄, filtered, and concentrated.. The product was purified by silica gel column chromatography using gradient elution (heptane:((50:50)heptane:toluene):toluene) to afford 29 (6.44g, 82.1%) of yellow crystals. m.p. 216-217°C; IR (KBr) cm⁻¹ 3031 (Ar-C-H), 2961, 2921, and 2873 (aliphatic C-H), 1595, 1481, and 1460 (Ar-C=C), 1280 (C-N); ¹H NMR δ 0.34 (t, 6H, CH3), 2.05 (q, 4H, CH₂), 7.37-8.10 (m, 33H, ArH); mass spectrum, m/z (relative intensity) 678, 676
(M+, 92.3, 100). Anal. Calcd. for C$_{42}$H$_{33}$BrN$_2$S: C, 74.43; H, 4.91; Br, 11.79; N, 4.13; S, 4.73. Found: C, 74.85; H, 5.03; Br, 12.07; N, 3.73; S, 4.64.

**Ethenyl-tri-\textit{n}-butyltin**

To a solution of ethenylmagnesium chloride (1.6 M, 100 mL) was added a mixture of tri-\textit{n}-butyltin chloride (49 mL, 0.144 mol) in THF (40 mL) dropwise so as to maintain the temperature of the reaction below 60°C. Once the addition was complete the reaction was heated to 80°C and stirred for 16 h. The mixture was distilled to remove the THF which was replaced with heptane (40 mL). The solution was cooled to room temperature, and the MgCl$_2$ salts were removed by vacuum filtration using a Buchner funnel, with the solution collected directly into a single-necked flask and the heptane was evaporated. Vacuum distillation of the reaction mixture yielded the product (44.21 g, 46.8%) as a colorless liquid: m/z (relative intensity) 291, 289, 287 (M$^+$, 44.1, 33.8, 19.41).

**N-phenyl-N-[4-(4-ethenylphenyl)phenyl]-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenyl]amine (30)**

To a dry solution of 2-benzothiazolyl-7-(N-bromobiphenyl-N-phenylamino)-9,9-diethylfluorene (3.0 g, 4.43 mmol) and toluene (20 mL) under nitrogen atmosphere was added tetrakis(triphenylphosphino)palladium (Pd(PPh$_3$)$_4$) (0.102 g, 0.10 mmol), tri-\textit{n}-butyl(ethenyl)tin (1.4 mL, 4.78 mmol), and a few crystals of 2,6-di-\textit{tert}-butyl-4-methylphenol. The solution was refluxed for 14 h. After cooling, an aqueous solution of potassium fluoride was added and the reaction mixture was stirred for 1 h. The solution was dried with MgSO$_4$, filtered, and concentrated. The product was purified by silica gel column chromatography (92:8 hexanes/ethyl acetate) to afford 30 (1.59 g, 58%) as yellow crystals. m.p. 158-161°C; IR (KBr) cm$^{-1}$ 3030 (Ar-C-H), 2961 and 2922
(aliphatic C-H), 1597, 1492, and 1459 (Ar-C=C), 1279 (C-N); \textsuperscript{1}H NMR δ 0.34 (t, 6H, CH\textsubscript{3}), 2.05 (q, 4H, CH\textsubscript{2}), 6.36 (d, 1H, -CH=CH\textsubscript{2}), 6.58 (d, 1H, -CH=CH\textsubscript{2}), 6.8 (m, 1H, -CH=CH\textsubscript{2}), 7.37-8.10 (m, 33H, Ar-H); mass spectrum, m/z (relative intensity) 624 (M\textsuperscript{+}, 100). Anal. Calcd. for C\textsubscript{44}H\textsubscript{36}N\textsubscript{2}S: C, 84.58; H, 5.81; N, 4.48; S, 5.13. Found: C, 84.19; H, 5.77; N, 4.66; S, 5.38.

**N-phenyl-N-[4-(4-formylphenyl)phenyl]-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenyl]amine (31)**

To a mechanically stirred solution of N-phenyl-N-[4-(4-bromophenyl)phenyl]-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenyl]amine (6.48 g, 0.0098 mol) in THF (100 mL) that had been cooled to –77°C was added a solution of \textit{n}-butyllithium in hexanes (1.6M, 13.75 mL). The rate of addition was controlled in order to maintain the temperature of the reaction mixture below –70°C. The yellow reaction mixture was allowed to stir for 15 min and a solution of dimethylformamide (2.75 mL) in THF (2.5 mL) was added over 15 min. The solution was stirred for 2 h after which it was allowed to warm to 5°C. A solution of hydrochloric acid (2 mL) in water (4 mL) was added and the solution was allowed to stir overnight at room temperature. The mixture was diluted with toluene (60 mL) and washed with a saturated sodium bicarbonate solution (3 x 15 mL) and the organic phase was separated. The aqueous layer was extracted with additional toluene (40 mL) which was separated and combined with the organic phase. The organic was then combined with MgSO\textsubscript{4}, filtered, and evaporated. The crude product was purified by silica gel column chromatography (toluene; 90:10 toluene:ethylacetate), and recrystallized from toluene/heptane to afford 31 (5.35 g, 89.4%) as yellow crystals: m.p. 219-221°C; IR (KBr) cm\textsuperscript{-1} 3032 (Ar-C-H), 2961 and 2921 (aliphatic C-H), 1595, 1490, and 1459 (Ar-C=C), 2805 and 2754 (aldehydic C-H),
1699 (C=O), 1281 (C-N); 'H NMR δ 0.34 (t, 6H, CH₃), 2.04 (q, 4H, CH₂), 7.51-7.86 (m, 33H, Ar-H), 10.07 (s, 1H, CHO); mass spectrum, m/z (relative intensity) 626 (M⁺, 100).

Anal. Calcd. for C₄₃H₃₄N₂OS: C, 82.40; H, 5.47; N, 4.47; O, 2.55; S, 5.12. Found: C, ; H, ; N, ; O, ; S, .

N-phenyl-N-[4-(4-hydroxymethylphenyl)phenyl]-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenyl]amine (32)

To a solution of N-phenyl-N-[4-(4-formylphenyl)phenyl]-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenyl]amine (2.5g, 0.004 mol) in ethanol (20.0 mL) was added THF (44 mL) until the solid was completely dissolved. The solution was placed in an ice bath and cooled to 3°C. Sodium borohydride (0.10 g, 0.003 mol) was then added in small portions over a period of 10 min. The solution was left in the ice bath and allowed to stir for 16 h, gradually warming to room temperature. The solution was blown dry under nitrogen over a period of 4 h, after which water (50 mL) was added. Acetic acid (0.4g, 0.007mol) was the added dropwise to destroy the excess NaBH₄ and the reaction was allowed to stir for 20 min. The product was collected by vacuum filtration to afford 32 (2.50g, 99.7%) as yellow crystals: m.p. 213-215°C; IR (KBr) cm⁻¹ 3030 (Ar-C-H), 2961, 2922, and 2873 (aliphatic C-H), 1598, 1493, 1460, and 1431 (Ar-C=C), 3402 (O-H), 1280 (C-N); 'H NMR δ 0.3.34 (t, 6H, CH₃), 2.04 (q, 4H, CH₂), 4.75 (s, 2H, CH₂OH), 7.51-7.86 (m, 33H, Ar-H); mass spectrum, m/z (relative intensity) 626 (M⁺, 100). Anal. Calcd. for C₄₃H₃₆N₂OS: C, 82.13; H, 5.77; N, 4.45; O, 2.54; S, 5.10. Found: C, ; H, ; N, ; O, ; S, .
RESULTS AND DISCUSSION

2,7-dibromofluorene

The compound 24 was prepared by the electrophilic aromatic substitution of fluorene using bromine and a catalytic amount of iodine.

Evidence of dibromination can clearly be seen in the mass spectrum in which the three distinct peaks at m/z 322, 324, and 326 (M, M+2, M+4) are found in the characteristic intensity ratio. The infrared spectrum (Figure 7) of 24 shows absorptions for the aromatic C-H stretch at 3031 cm\(^{-1}\), the aliphatic C-H stretch at 2919 cm\(^{-1}\), the aromatic C=C stretch at 1453 and 1397 cm\(^{-1}\), and the out-of-plane C-H stretch at 813 cm\(^{-1}\). As expected the \(^1\)H NMR spectrum (Figure 8) displayed a singlet at 3.817 \(\delta\) corresponding to the two methylene hydrogens and a multiplet between 7.62-7.85 \(\delta\) corresponding to the six aromatic hydrogens.

2,7-dibromo-9,9-diethylfluorene

The alkylation of 24 was accomplished by a nucleophilic substitution reaction employing potassium hydroxide, potassium iodide, and ethyl bromide, with dimethylsulfoxide used as the solvent to yield 25.
The mass spectrum again shows the characteristic peak pattern for a dibrominated compound with the peaks at m/z 378, 380, and 382 (M, M+2, M+4). The infrared spectrum (Figure 9) shows absorptions for the aromatic C-H stretch at 3071 cm\(^{-1}\), the aliphatic C-H stretch at 2959, 2916, and 2871 cm\(^{-1}\), the aromatic C=C stretch at 1572 and 1449 cm\(^{-1}\), and the out-of-plane C-H stretch at 814 cm\(^{-1}\). The \(^1\)H NMR spectrum (Figure 10) exhibits a triplet at 0.31 \(\delta\) corresponding to the six methyl hydrogens, a quartet at 2.00 \(\delta\) corresponding to the four methylene hydrogens, and a multiplet between 7.44-7.50 \(\delta\) corresponding to the six aromatic hydrogens of 25.

2-bromo-7-formyl-9,9-diethylfluorene

The synthesis of compound 26 was accomplished by a two-step process involving a halogen-metal exchange reaction of 25 with \(n\)-butyllithium followed by substitution of the resulting organolithium with dimethylformamide, using THF as a solvent.

The mass spectrum shows the peaks at m/z 328 and 330 (M, M+2) in the characteristic pattern of a monobrominated compound. The infrared spectrum (Figure 11) of 26 exhibits absorptions for the aromatic C-H stretch at 3063 cm\(^{-1}\), the aliphatic C-H stretch at 2961, 2626, and 2871 cm\(^{-1}\), the aldehydic C-H stretch at 2804 and 2744 cm\(^{-1}\), the aldehyde carbonyl stretch at 1688 cm\(^{-1}\), and the aromatic C=C stretch at 1604 and 1454 cm\(^{-1}\).
cm\(^{-1}\). The \(^1\)H NMR spectrum (Figure 12) exhibits a triplet at 0.34 \(\delta\) corresponding to the six methyl hydrogens, a quartet at 2.04 \(\delta\) corresponding to the four methylene protons, a multiplet between 7.51-7.86 \(\delta\) corresponding to the six aromatic hydrogens, and singlet at 10.07 \(\delta\) corresponding to the hydrogen of the aldehyde.

7-(2-benzothiazolyl)-2-bromo-9,9-diethylfluorene

The synthesis of 27 was accomplished by reaction of 26 with 2-aminothiophenol in dimethysulfoxide.

\[
\begin{align*}
\text{Br} & \quad \text{CHO} & \quad \text{NH}_2 & \quad \text{S} \\
\text{26} & \quad \text{DMSO} & \quad \text{27}
\end{align*}
\]

The only deviation from the literature procedure was that the product was worked up by pouring the reaction mixture into a slurry of ice, water, and sodium chloride in order to isolate to product as a solid material. Analysis of the mass spectrum shows the peaks at m/z at 433 and 435 (M, M+2) in the characteristic pattern of a monobrominated compound. The infrared spectrum (Figure 13) of 27 shows absorption for the aromatic C-H stretch at 3059 cm\(^{-1}\), the aliphatic C-H stretch at 2962, 2921, and 2874 cm\(^{-1}\), and the aromatic C=C stretch at 1454 cm\(^{-1}\). The \(^1\)H NMR spectrum (Figure 14) exhibits a triplet at 0.34 \(\delta\) corresponding to the six methyl hydrogens, a quartet at 2.05 \(\delta\) corresponding to the four methylene hydrogens, and a multiplet between 7.37-8.10 \(\delta\) corresponding to the ten aromatic hydrogens.
N-phenyl-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenlyl]amine

The synthesis of compound 28 was accomplished by the palladium catalyzed amination reaction of 27 using aniline, Pd(dba)$_2$, DPPF, NaO-$t$-Bu, and toluene as the solvent.

Analysis of the mass spectrum reveals a molecular ion peak at m/z 446 (M) corresponding to compound 28. The infrared spectrum (Figure 15) exhibits absorptions for the N-H stretch at 3397 and 3276 cm$^{-1}$, the aromatic C-H stretch at 3081 cm$^{-1}$, the aliphatic C-H stretch at 2962, 2917, and 2873 cm$^{-1}$, aromatic C=C stretch at 1595, 1497, and 1458 cm$^{-1}$, and the C-N stretch at 1315 cm$^{-1}$. The $^1$H NMR spectrum (Figure 16) exhibits a triplet at 0.34 $\delta$ corresponding to the six methyl protons, a quartet at 2.05 $\delta$ corresponding to the four methylene protons, a singlet at 4.5 $\delta$ corresponding to the amine hydrogen, and a multiplet between 7.37-8.10 $\delta$ corresponding to the fifteen aromatic hydrogens.
**N-phenyl-N-[4-(4-bromophenyl)phenyl]-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenyl]amine**

The synthesis of compound 29 was accomplished by a palladium catalyzed monoamination of 4,4′-dibromobiphenyl using 28, Pd(dba)$_2$, DPPF, NaO-t-Bu, and toluene as the solvent. Analysis of the mass spectrum shows peaks at m/z 676 and 678 (M, M+2) with a pattern that is characteristic of a monobrominated compound. The infrared spectrum (Figure 17) exhibits absorptions for the aromatic C-H stretch at 3031 cm$^{-1}$, the aliphatic C-H stretch at 2961, 2921, and 2873 cm$^{-1}$, the aromatic C=C stretch at 1595, 1481, and 1460 cm$^{-1}$, and the C-N stretch at 1280 cm$^{-1}$. The $^1$H NMR spectrum (Figure 18) exhibits a triplet at 0.34 $\delta$ corresponding to the six methyl protons, a quartet at 2.05 $\delta$ corresponding to the four methylene protons, and a multiplet between 7.37-8.10 $\delta$ corresponding to the thirty-three aromatic hydrogens.
N-phenyl-N-[4-(4-ethenylphenyl)phenyl]-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenyl]amine

The synthesis of 30 was accomplished via a Stille coupling reaction of 29 with ethenyl-tri-n-butyltin, tetrakis(triphenylphosphino)palladium, and toluene as the solvent.

Analysis of the mass spectrum shows the molecular ion peak to occur at m/z 624 (M) which corresponds to compound 30. The infrared spectrum (Figure 19) exhibits absorptions for the aromatic C-H stretch at 3030 cm⁻¹, the aliphatic C-H stretch at 2961 and 2922 cm⁻¹, the aromatic C=C stretch at 1597, 1492, and 1459 cm⁻¹, and the C-N stretch at 1279 cm⁻¹. The ¹H NMR spectrum (Figure 20) exhibits a triplet at 0.34 δ corresponding to the six methyl protons, a quartet at 2.05 δ corresponding to the four methylene protons, two doublets at 6.36 δ and 6.58 δ and a multiplet at 6.8 δ corresponding to the ethenyl hydrogens, and a multiplet between 7.37-8.10 δ corresponding to the thirty-three aromatic hydrogens.
N-phenyl-N-[4-(4-formylphenyl)phenyl]-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenyl]amine

The synthesis of compound 31 was accomplished by a two-step process involving a halogen-metal exchange reaction of 29 with n-butyllithium followed by substitution of the resulting organolithium with dimethylformamide, using THF as a solvent.

![Chemical Structure]

Analysis of the mass spectrum exhibits a molecular ion peak at m/z 626 (M) corresponding to compound 31. The infrared spectrum (Figure 21) of 31 exhibits absorptions for the aromatic C-H stretch at 3032 cm\(^{-1}\), the aliphatic C-H stretch at 2961 and 2921 cm\(^{-1}\), the aromatic C=C stretch at 1595, 1490, and 1459 cm\(^{-1}\), the aldehydic C-H stretch at 2805 and 2754 cm\(^{-1}\), the aldehyde carbonyl stretch at 1699 cm\(^{-1}\), the aromatic C=C stretch at 1604 and 1454 cm\(^{-1}\), and the C-N stretch at 1281 cm\(^{-1}\). The \(^1\)H NMR spectrum (Figure 22) exhibits a triplet at 0.34 \(\delta\) corresponding to the six methyl hydrogens, a quartet at 2.04 \(\delta\) corresponding to the four methylene protons, a multiplet
between 7.51-7.86 δ corresponding to the thirty-three aromatic hydrogens, and singlet at 10.07 δ corresponding to the hydrogen of the aldehyde.

**N-phenyl-N-[4-(4-hydroxymethylphenyl)phenyl]-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenyl]amine**

The synthesis of 32 was accomplished by reduction of 31 using sodium borohydride in a solvent system of methanol and THF.

![Chemical Structures](image)

The infrared spectrum (**Figure 23**) of 32 exhibits absorptions for the O-H stretch at 3402 cm⁻¹, the aromatic C-H stretch at 3030 cm⁻¹, the aliphatic C-H stretch at 2961, 2922, and 2873 cm⁻¹, the aromatic C=C stretch at 1460 and 1430 cm⁻¹, and the C-N stretch at 1280 cm⁻¹. The ¹H NMR spectrum (**Figure 24**) exhibits a triplet at 0.34 δ corresponding to the six methyl hydrogens, a quartet at 2.04 δ corresponding to the four methylene protons, a singlet at 4.75 d corresponding to the methylene of the hydroxymethyl group and a multiplet between 7.51-7.86 δ corresponding to the thirty-three aromatic hydrogens.
Conclusions and Future Work

- Functionalization of third-order nonlinear-optical chromophores will allow them to be incorporated in a host matrix. The focus of this research has been to functionalize a series of chromophores such that they can be covalently attached using sol gel technology or incorporated into a siloxane matrix through hydrosilylation.

- Three new functionalized chromophores, \( \text{N-phenyl-N-[4-(4-ethenylphenyl)phenyl]-N-[7-(2-benothiazolyl)-9,9-diethyl-2-fluorenyl]amine (30)} \), \( \text{N-phenyl-N-[4-(4-formylphenyl)phenyl]-N-[7-(2-benothiazolyl)-9,9-diethyl-2-fluorenyl]amine (31)} \), and \( \text{N-phenyl-N-[4-(4-hydroxymethylphenyl)phenyl]-N-[7-(2-benothiazolyl)-9,9-diethyl-2-fluorenyl]amine (32)} \), have been successfully synthesized and characterized.

- Elemental analysis of \( \text{N-phenyl-N-[4-(4-hydroxymethylphenyl)phenyl]-N-[7-(2-benothiazolyl)-9,9-diethyl-2-fluorenyl]amine (32)} \) was not completed.

- Two new unfunctionalized chromophores, \( \text{N-phenyl-N-[4-(phenyl)phenyl]-N-[7-(2-benothiazolyl)-9,9-diethyl-2-fluorenyl]amine (35)} \) and \( \text{N-phenyl-N-[7-(2-benothiazolyl)-9,9-diethyl-2-fluorenyl]-N-[4-(4-[N-phenyl-N-[7-(2-benothiazolyl)-9,9-diethyl-2-fluorenyl]amino]phenyl)phenyl]amine (36)} \), were also synthesized and characterized.

- Measurement of the two-photon absorption, \( \sigma_2 \) and \( \sigma_2' \), will be carried out at SUNY Buffalo.
Figure 7. IR spectrum of 2,7-Dibromofluorene (24).

Figure 8. $^1$H NMR spectrum of 2,7-Dibromofluorene (24).
Figure 9. IR spectrum of 2,7-dibromo-9,9-diethylfluorene (25).

Figure 10. IR spectrum of 2,7-dibromo-9,9-diethylfluorene (25).
Figure 11. IR spectrum of 2-bromo-7-formyl-9,9-diethylfluorene (26).

Figure 12. $^1$H NMR spectrum of 2-bromo-7-formyl-9,9-diethylfluorene (26).
Figure 13. IR spectrum of 7-(2-benzothiazolyl)-2-bromo-9,9-diethylfluorene (27).

Figure 14. $^1$H NMR spectrum of 7-(2-benzothiazolyl)-2-bromo-9,9-diethylfluorene (27).
Figure 15. IR spectrum of N-phenyl-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenly]amine (28).

Figure 16. $^1$H NMR Spectrum of N-phenyl-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenly]amine (28).
Figure 17. IR Spectrum of N-phenyl-N-[4-(4-bromophenyl)phenyl]-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenyl]amine (29).

Figure 18. $^1$H NMR Spectrum of N-phenyl-N-[4-(4-bromophenyl)phenyl]-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenyl]amine (29).
Figure 19. IR Spectrum of N-phenyl-N-[4-(4-ethenylphenyl)phenyl]-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenyl]amine (30).

Figure 20. $^1$H NMR Spectrum of N-phenyl-N-[4-(4-ethenylphenyl)phenyl]-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenyl]amine (30).
Figure 21. IR spectrum of N-phenyl-N-[4-(4-formylphenyl)phenyl]-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenyl]amine (31).

Figure 22. $^1$H NMR spectrum of N-phenyl-N-[4-(4-formylphenyl)phenyl]-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenyl]amine (31).
Figure 23. IR spectrum of N-phenyl-N-[4-(4-hydroxymethylphenyl)phenyl]-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenyl]amine (32).

Figure 24. $^1$H NMR spectrum of N-phenyl-N-[4-(4-hydroxymethylphenyl)phenyl]-N-[7-(2-benzothiazolyl)-9,9-diethyl-2-fluorenyl]amine (32).
APPENDIX

The following pages contain images of a poster entitled “Functionalization of Thermally Stable NLO Chromophores” presented at the American Chemical Society Meeting (Organic Division and Sci-Mix Poster sessions) held in San Diego, CA in April, 2001.
Two-Photon Absorption (TPA)

- Third-order nonlinear response coupled with the electronic and vibrational resonances yields phenomena such as two-photon absorption. (First predicted in 1931 - Goppert-Mayer)
- Two-photon absorption is described at the molecular level as an absorption cross section $\sigma_2$.

$$\sigma_2 = \frac{\text{rate of energy absorption in ground state}}{\text{incident energy flux}}$$
Landmarks of Two-Photon Technology

- 1931: Theoretical Prediction of 2-Photon Abs.
- 1961: 2 PA Observed Experimentally in CaF$_2$:Eu$^{3+}$
- 1967: Multi-photon Spectroscopy
- 1972: 2 Photon LSCM Invented
- 1980: 2 Photon Pumped Cavity Lasing Hollow fiber & Doped Polymer Rod APSS Synthesized 3800 G-M (800 nm)
- 1990: 2-Photon Stimulated Emission in Polymer Waveguides (DCM-PMMA)
- 1993: 2-Photon Stimulated Emission in Polymer Waveguides (DCM-PMMA)
- 1995: BDBAS Synthesized 17,700 G-M (600 nm)
- 1996: Synthesis & Characterization AF-50 19,350 G-M (800 nm)
- 1997: Synthesis & Characterization AF-50 19,350 G-M (800 nm)

Upconverted Fluorescence Emission for Selected Chromophores

- 1 (453)
- 2 (465)
- 3 (475)
- 4 (488)
- 5 benzene (476)
- 5a THF (492)
- 6 (521)
- 7 (500)
- 8 benzene (463)
- 8a THF (491)
**Potential for Two-Photon Technology**

- 2-Photon Photocuring
  - Low Energy Cure
- Microfabrication
- New Molecular Structures
  - 2-Photon Pumped Upconverted Lasing
    - Blue Light From a Plastic Laser
- Photodynamic Therapy
  - Noninvasive Cancer Treatment
- 2-Photon Confocal Microscopy
  - NDE of Paint
- 3D Optical Data Storage
  - 1000 CDs in 1 cm³

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**DAGSI* Project Objectives**

The objective of this program is the design and implementation of advanced optical composites for Air Force and Ohio Industry applications. An optical composite is defined as any system where solid materials are incorporated into polymer hosts to integrate the optical performance characteristic of both materials. Advanced optical composites for protecting eyes and sensors from laser radiation are of particular interest to the Hardened Materials Branch in the Materials Directorate/AFRL. In industry, there are a wide variety of applications for advanced optical composites including imaging, printing, fiber optics and solid state lasers. The research of the DAGSI project is intended to overcome current shortfalls in materials performance by the synergistic design of compatible chromophore/matrix combinations.

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**Synthetic Objectives**

- Develop derivatization chemistry to enable the incorporation of highly active two-photon AFX chromophores into suitable matrix materials via catalytic hydrosilylation (advanced optical composites)
- Sol-gel process (two-photon responsive aircraft coating)
**Basic Chromophore Component Synthesis**

1. \[ \text{C}_2\text{H}_5\text{Br}, \text{KOH} \rightarrow \text{Br}_2, \text{CH}_2\text{Cl}_2/\text{I}_2 \rightarrow \text{Yield: 99\% m.p. 159-166\°C} \]

2. \[ \text{Yield: 85\% m.p. 156-158\°C} \]

3. \[ \text{Yield: 78\% m.p. 128-130\°C} \]

4. \[ \text{Yield: 74\% m.p. 133-136\°C} \]

**Phenol Substituted Chromophore**

1. \[ \text{Phenol: N-H + CH}_2\text{Br} \rightarrow \text{K}_2\text{CO}_3, \text{DMF} \rightarrow \text{Yield: 88\% m.p. 51-54\°C} \]

2. \[ \text{Phenol: N-H + OCH}_2\text{C}_6\text{H}_5 \rightarrow \text{Pd(dba)_2}, \text{dpf}, \text{NaOBut, Toluene} \rightarrow \text{Yield: 83\% m.p. 246-247\°C} \]

3. \[ \text{Phenol: N-S + OCH}_2\text{C}_6\text{H}_5 \rightarrow \text{Pyridine-HCl} \rightarrow \text{Yield: 87\% m.p. 181-183\°C} \]
**Phenol Facilitated Pendent Attachment**

\[
\text{Phenol Facilitated Pendent Attachment}
\]

\[
\text{Nucleophilic Substitution Substrate}
\]

**Bromo Substituted Chromophore Synthesis**

\[
\text{Bromo Substituted Chromophore Synthesis}
\]

\[
\text{Yield: 88% m.p. 174-175°}
\]
Vinyl Chromophore Synthesis

- The bromine is deactivated for a Stille coupling reaction by the conjugated electron-donating nitrogen.
- The vinyl, bromo, and reduced products cannot be separated by chromatography.
- The vinyl substituent may be introduced by 1) a Wittig reaction, 2) an alkyne reduction, or 3) a dehydration.

Summary of Functional Chromophores

<table>
<thead>
<tr>
<th>Chromophores</th>
<th>Functionalization - X</th>
<th>Application</th>
<th>Status</th>
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<tbody>
<tr>
<td>-H</td>
<td>Parent Compound, High Two Photon Cross Section</td>
<td>Done, Multigram Synthesis Available</td>
<td></td>
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<tr>
<td>-OH</td>
<td>Reactive Linkage Introduced</td>
<td>Done, I. Kuhr MS Thesis, August, 2000</td>
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<tr>
<td>-OCH_2_CH_2_Br</td>
<td>Alkylation Reagent</td>
<td>Done, Characterized M. Matuszewski</td>
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<td>-OCH_3_C_6_H_4_CH_2_=_CH_2_ (p)</td>
<td>Silylation Reactant</td>
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<td>-C_4_H_4_Br_ (p)</td>
<td>Alternative Linkage</td>
<td>In Progress, J. Sawyer</td>
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<tr>
<td>-C_4_H_4_C_6_H_4_Br_ (p)</td>
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<tr>
<td>-C_4_H_4_CHO_ (p)</td>
<td>Silylation, Vinyl Precursor</td>
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<tr>
<td>-C_4_H_4_CHO_ (m)</td>
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<td>-C_4_H_4_C_6_H_4_CH_2_=_CH_2_</td>
<td>Multichromophore clusters</td>
<td>In Progress J. Sawyer</td>
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VITA

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