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Enhancing the Third-Order Nonlinear Optical Properties of Porphyrins and Molecular Wires

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ENHANCING THE THIRD-ORDER NONLINEAR OPTICAL PROPERTIES OF PORPHYRINS AND MOLECULAR WIRES

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Virginia Commonwealth University.

by

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Abstract

ENHANCING THE THIRD-ORDER NONLINEAR OPTICAL PROPERTIES OF
PORPHYRINS AND MOLECULAR WIRES

By Jonathan Leslie Humphrey, Ph.D.

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Virginia Commonwealth University.

Virginia Commonwealth University, 2006

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The third-order nonlinear optical (NLO) properties of indium tin oxide (ITO) thin films, Fe$^{3+}$, Mn$^{3+}$, and Co$^{2+}$ 5,10,15,20-tetrakis-(4-hydroxytetraphenyl)porphyrin (TPP) films, and a series of ethynyl-linked azobenzene oligomers were investigated using degenerate four wave mixing (DFWM) with 100 fs laser pulses. To measure the NLO of ITO thin films, A DFWM method for measuring thin films on thick substrates was refined for the characterization of films less than 100 nm thick and applied to ITO films ~25 nm thick. It was found that the third-order nonlinear susceptibility of ITO, $\chi^{(3)}_{ITO}$, is purely electronic.
at 900 - 1300 nm (11000 – 7700 cm$^{-1}$) and has a value of $(2.16 \pm 0.18) \times 10^{-18}$ m$^2$ V$^{-2}$. The $\chi^{(3)}_{\text{ITO}}$ value reaches $(3.36 \pm 0.28) \times 10^{-18}$ m$^2$ V$^{-2}$ at 1500 nm (6700 cm$^{-1}$) due to two-photon absorption by free carriers (electrons). Ultrafast electron relaxation was also observed. The $\sim 100$ fs lifetime of this process could reflect electron scattering in the conduction band. This DFWM method was also used to investigate the two-photon properties of $\sim 500$ nm thick electropolymerized films of Fe$^{3+}$, Mn$^{3+}$, and Co$^{2+}$ TPP in the near-IR spectral region. Metalloporphyrins with strong charge transfer (CT) transitions in the linear absorption spectra also show enhanced two-photon absorption. (Metalloporphyrin two-photon absorption cross section, $\delta$, increases $>10$ times over that for the metal free porphyrin.) This effect was attributed to a two-photon induced charge transfer between the metal ion’s d orbitals and the $\pi$-system of the porphyrin. Correlation of one- and two-photon absorption properties of transition metal porphyrins suggests a new and simple approach to improve organic materials for photonic applications. Finally, a series of oligomers consisting of ethynyl-linked azobenzene units was prepared using Pd-catalyzed cross coupling. The linear and nonlinear optical properties of the oligomers were investigated. The molecular second hyperpolarizability, $\chi$, followed the power law $\gamma \approx n^{2.12 \pm 0.05}$ (n is number of repeat units) for unusually large molecular lengths. The exceptional exciton delocalization length exceeds 360 conjugated bonds (>49 nm) and is attributed to the rigidity of the conjugated backbone.
1. Introduction to Nonlinear Optical Effects and Nonlinear Optical Materials

1.1 Nonlinear Optical (NLO) effects and material design

The development and commercial availability of powerful pulsed lasers has made technologies based on nonlinear optical processes a reality. These technologies depend on third-order optical properties like the intensity dependent refractive index, \( n_2 \), and the two-photon absorption cross-section, \( \delta \). Telecommunications, information technology, and medicine would receive a tremendous benefit from technologies like two-photon microscopy, optical switching, 3-D data storage, and PDT that take advantage of these intensity dependent processes. While the lasers required to induce these effects are well developed, materials that meet the specifications required for technical applications have not yet been developed. The promise of these processes has motivated decades of research into developing materials with enhanced third-order nonlinear optical properties. While significant progress has been made, further refinement of our understanding of the structure-property relationship of these materials and continued research into the fundamental electronic properties that result in a particular \( \delta \) or \( n_2 \) value are required to realize the potential of nonlinear optical technologies.
Nonlinear optical effects are induced by intense pulsed lasers. The strong oscillating electric field of the laser changes the polarization of the molecule. This change in polarization as a function of the electric field, when the electric field is not too big, is typically expressed in an expanded power series as

$$ P(\omega) = P_0 + \chi^{(1)}(\omega) \cdot E(\omega) + \chi^{(2)}(\omega; \omega_1, \omega_2) \cdot E(\omega_1) E(\omega_2) + \chi^{(3)}(\omega; \omega_1, \omega_2, \omega_3) \cdot E(\omega_1) E(\omega_2) E(\omega_3) + \ldots $$ (1)

where $P$ is the electric dipole polarization ($P_0$ represents any permanent polarization), $E(\omega_i)$ is an electric field with frequency $\omega_i$, and the $\chi^{(n)}$ terms correspond to tensors of order $(n + 1)$. These $\chi^{(n)}$ terms describe the nonlinear susceptibility of the bulk material. The property of a material that is relevant to optical computing, two-photon microscopy, and other applications is described by the $\chi^{(3)}$ term. The $\chi^{(3)}$ term is a complex tensor quantity that fully describes the third-order nonlinearity of a system. The real component of the susceptibility is related to nonlinear refraction. As such, a large $\text{Re} \chi^{(3)}$ value is required to make an optical switch. The imaginary component is associated with two-photon absorption. A large number of studies have been performed on this property as it is required for two-photon microscopy and photodynamic therapy.

The bulk properties described by $\chi^{(3)}$ are useful in potential applications, but developing and improving nonlinear optical materials requires the origins of nonlinear behavior at the molecular level to be understood. The molecular nonlinearity is described by $\gamma$, the molecular hyperpolarizability, and it is related to $\chi^{(3)}$ by

$$ \gamma = \frac{\chi^{(3)}}{Nf^4} $$ (2)
where $N$ is the molecular number density and $f$ is the local field factor, $(n^2 + 2)/3$, and $n$ is the refractive index. Like $\chi^{(3)}$, $\gamma$ is a complex quantity with real and imaginary components. By choosing to optimize a particular component, a molecule can be tailored for use in a desired application. Models describing the nonlinearity of a particular system have been developed to aid in optimizing the nonlinearity of molecular systems.

The description of molecular nonlinearity that has proven most useful in the design of nonlinear materials is the Sum Over States (SOS) approach. This theory is based on the perturbation expansion of the Stark energy of the molecule as a function of the electronic field.$^2$ The SOS approach offers the advantage of including specific optical frequencies in the expression. This offers several advantages, the most important of which is the ability to determine which states are most important to the nonlinear response of a molecule.$^2$

Following the work of Orr and Ward,$^3$ several groups determined that there are three terms that dominate the third-order nonlinear response of a molecule.$^4$ These terms can be expressed as

$$\gamma \propto \frac{M_{01}^2 |\Delta \mu|^2}{(\omega_{01} - \omega - i\Gamma_{01})^3} - \frac{M_{01}^4}{(\omega_{01} - \omega - i\Gamma_{01})^3} + \frac{M_{01}^2 M_{12}^2}{(\omega_{02} - 2\omega - i\Gamma_{02})}$$

(3)

where $\Delta \mu = \mu_{11} - \mu_{00}$ is dipole moment difference between the first excited and the ground state, $M_{01}$ and $M_{12}$ are the transition dipole moments for $0 \rightarrow 1$ and $1 \rightarrow 2$ transitions, $\omega$ is frequency used in the experiment, $\omega_{01}$ and $\omega_{02}$ are frequencies derived from the excited state energies ($\omega_{01} = E_{01}/\hbar$ and $\omega_{02} = E_{02}/\hbar$), and $\Gamma_{01}$ and $\Gamma_{02}$ are dephasing parameters that account for the linewidths. This model has been used to predict molecular properties that will enhance nonlinear response.$^4$ Molecules designed on the results of this model have
shown improved nonlinearity. The model has also been used to rationalize the appearance of unusual nonlinear properties, particularly a negative real component of $\gamma$, and determine the nature of a state responsible for a given nonlinearity.

The first term in eq. 3 is related to the strength of the one photon dipole moment of a molecule and is typically referred to as the dipole, or D, term. The third term is related to two photon absorption and is called the TP term. In order for a molecule to have strong nonlinear properties, alterations must be made that result in the D and TP terms increasing faster than the second, or negative (N) term. Garito was the first to predict that maximizing the first and third terms in eq. 3 by increasing the transition dipole moments would lead to molecules with enhanced nonlinearity. The first experimental verification of Garito’s hypothesis was carried out by Marder and coworkers. They confirmed Garito’s prediction by modifying polarized carotenoids with different length polyene chains and donor groups to increase the transition dipole moments. Measurements of $\gamma$ were performed using Third Harmonic Generation (THG). The carotenoid with the longest conjugation length and

Figure 1. Schematic energy level diagram showing the three states that determine a molecule’s nonlinear response.
strongest donor group was found to have the highest nonlinearity. This particular molecule had a $\gamma_{max}$ 35 times larger than unmodified beta-carotene. These two strategies for increasing nonlinearity, adding donor-acceptor groups and lengthening the conjugation, have been applied to a number of different conjugated systems, including porphyrins and porphyrin-based materials.

1.2 Porphyrrins – molecular structure and properties

The biological importance of porphyrins, particularly in photosynthesis and oxygen transport, have resulted in decades of research on this class of compounds. The basic molecular structure of the porphine macrocycle is shown in Figure 1. Four pyrrole rings are connected via methine bridges to form a flat, conjugated macrocycle with 18 π electrons. Extensive modification to this basic structure can be made by adding substituents to various parts of the macrocycle or inserting a metal ion into the core. Tremendous variations in the electrical and chemical properties of a particular porphyrin can be achieved through these structural modifications. An example of this is the dependence of a metalloporphyrin’s redox potential on the identity and oxidation state of the central metal ion. The effects of various metal ions and substituents on the electronic properties of the porphyrin macrocycle are plainly evident as color changes.
Figure 2: The porphine macrocycle and the configurational interaction that results in the creation of the B and Q bands of the absorption spectrum.

The optical properties of porphyrins have been extensively examined. The absorption spectrum of a porphyrin is characterized by two distinctive features. Porphyrins have a very strong absorption peak in the UV, usually referred to as the Soret or B band, and weaker bands, called the Q bands, in the visible region. The energies and intensities of these bands are explained by Gouterman’s four orbital model (Figure 2). In this model, the two highest occupied orbitals and the two lowest unoccupied orbitals mix through configuration interaction (CI) and form two new states. A strongly allowed, higher energy state corresponds to the Soret band while a weakly allowed, lower energy state is associated with the Q bands. The presence of hydrogen atoms on two of the central nitrogen atoms in the free base porphyrin breaks the degeneracy of the x and y components of the transition dipole moment, resulting in two Q bands, Q_x and Q_y. The other two Q bands are vibronic transitions of the Q_x and Q_y transitions.

The electronic properties of the porphyrin macrocycle are altered by the introduction of a metal ion into the ring. The central metal makes the x and y component of the Q bands degenerate, reducing the number of Q bands to two. The presence of the metal can also
shift the energies of the transitions and result in the appearance of additional peaks in the absorption spectrum. For Fe\textsuperscript{3+}, Mn\textsuperscript{3+}, and Pb\textsuperscript{2+} porphyrins, the long wavelength bands are the result of charge transfer interactions between the metal and the macrocycle. These important effects will be discussed in more detail in Section 1.6.

The large $\pi$ network and synthetic flexibility of the macrocycle have made porphyrins an attractive target for use in a number of advanced materials.\textsuperscript{9-11} A significant effort has been made over the past two to three years to improve the two-photon absorption (TPA) cross-section, $\delta$, of the porphyrin macrocycle with the aim of using porphyrin-based photosensitizers in two-photon photodynamic therapy (PDT). PDT is a treatment strategy for cancer and other diseases that uses light to generate cytotoxic singlet oxygen. TPA is a nonlinear optical process that will make this treatment option safer for the patient and allow the use of PDT to expand to a number of different types of cancer.

1.3 The NLO properties of the porphyrin macrocycle

Porphyrins have recently become central to the development of new nonlinear materials. The porphyrin macrocycle is a synthetically flexible chromophore with an extended $\pi$-electron network. Interest in porphyrins is largely a product of their use in photodynamic therapy. A porphyrin based photosensitizer, Photofrin, is currently approved for use in treating cancer of the esophagus by photodynamic therapy. Following an injection of the drug, a fiber optic cable is used to irradiate the cancer with intense UV radiation. This light generates singlet oxygen via one-photon absorption by the photosensitizer. Subsequent relaxation to the triplet state allows the excitation energy to be transferred to oxygen and
generate cytotoxic singlet oxygen. As two-photon absorption requires the use of lower energy near-IR wavelengths that are less damaging to the treatment site and are able to penetrate more deeply into the tissue, porphyrins with sufficient TPA cross-sections for use as two-photon PDT photosensitizers is a highly active research area.

The two-photon absorptivity of the basic porphyrin unit has been thoroughly investigated by Rebane’s group.\textsuperscript{12-16} By measuring the two photon absorptivity of free base and zinc porphyrins using two photon fluorescence over a range of wavelengths, they were able to identify the electronic features of the macrocycle that determine its two-photon cross section. The two-photon response was found to differ in the two wavelength ranges that were investigated. At longer wavelengths, those that are twice as long as the Q band region of the linear absorption spectrum, the two-photon absorptivity was found to be small (1-10 GM) and largely resulted from relaxation of the two-photon symmetry forbidden transition into the ungerade Q bands. The second wavelength region used in their experiments was approximately twice the wavelength of the Soret band. As half of the experimental wavelength approaches the Soret region, it is also in the vicinity of the lowest energy Q band. The near-resonant one-photon state results in a resonance enhancement of the two-photon absorptivity. This enhancement was further improved by the presence of two-photon allowed gerade states in the same spectral region.

Like linear conjugated molecules, the two-photon absorptivity of a porphyrin can be enhanced by the addition of electron donating or accepting substituents. Following on the work of Marder,\textsuperscript{17} Rebane modified the porphyrin macrocycle with strong electron acceptors. In particular, tetraazaporphyrins (Figure 3), which showed higher intrinsic two-
photon absorption than the unmodified porphyrin, were symmetrically modified with \( t \)-butyl, bromophenyl, and nitrophenyl substituents at the \textit{meta} position of the porphyrin ring. The two-photon cross section was found to increase linearly with the Hammett constant of the substituent. The nitrophenyl modified compound showed the largest cross section, \( \delta = 1600 \text{ GM} \), at \( \sim 725 \text{ nm} \). This large \( \delta \) value is a consequence of three enhancement mechanisms, near one-photon resonance enhancement, the presence of allowed gerade states, and the effect of strong electron accepting substituents, acting together to result in a compound with a large two-photon cross section.

Figure 3: Modified tetraazaporphyrin studied by Rebane

Efforts to improve the \( \delta \) of the porphyrin macrocycle by systematically modifying the type of substituent and where that substituent is placed on the ring have also been made. Shen et. al. modified the substituents at the \textit{meso} position of the macrocycle.\(^{18}\) They modified their base compound, 4-hydroxy tetra-phenyl porphyrin (4-OH TPP), by replacing the OH groups with a strong electron donor, pyrrolidinyl, and by linking the TPP core to four triphenylamine groups, which are also strong electro donors, via an acyl bridge (Figure 4A). The addition of pyrrolidinyl resulted in \( \delta = 40 \text{ GM} \) compared to \( \delta = 20 \text{ GM} \) for TPP. The larger intramolecular charge transfer introduced by the conjugated acyl bridge-
triphenylamine groups resulted in a further increase to 45 GM. This value was improved to 157 GM by incorporating the compound into a polyether sulfone film. This enhancement was attributed to the increase in planarity induced by the rigid polymer matrix.

Figure 4: A) TPP with different donor strength substituents B) TPP-PEP dyad

Modifications to the $\beta$ position have also been used to modify the nonlinear optical properties of the porphyrin macrocycle. Pagani and coworkers combined a tetra-phenyl porphyrin (TPP) core with an electron-deficient pyridine linked to an electron donating pyrrole by an ethylene unit. This pyridine-ethylene-pyrrole (PEP) unit was coupled to the TPP macrocycle at the $\beta$ position by an ethylene unit (Figure 4B). Evidence for the electronic coupling of the macrocycle with the PEP fragment is provided by the UV/vis spectrum of the complex. The sharp Soret band of TPP is significantly broadened and a long tail extending over the entire Q band region of the spectrum is also present. As these features are not due to features from the TPP and PEP spectra, these perturbations to the TPP spectrum indicates that there is significant electronic coupling between the TPP macrocycle and the PEP fragment.
The coupling between TPP and PEP results in an enhanced $\delta$ value. The TPP-PEP dyad has a $\delta = 56 \pm 8$ GM measured by Z-scan at 800 nm using 150 fs pulses compared to $\delta = 16 \pm 4$ GM found for TPP. A three-fold enhancement is observed with the introduction of a Cu$^{2+}$ ion into the core of the PEP-modified macrocycle. The use of metal ions is an effective but poorly understood method to enhance the TPA cross section of porphyrin based materials. This approach is discussed in Section 1.5.

1.4 Extension of the conjugation length of the porphyrin macrocycle.

While porphyrin polymers consisting of directly meso-linked macrocycles were not found to demonstrate significantly improved nonlinear properties over the monomer, Anderson found that the [diagram]

Figure 5: Anderson’s butadiyne linked porphyrin oligomer repeat unit.

inclusion of a butadiyne linker between the porphyrins results in significantly higher $\gamma$ values (Figure 5). For the monomer, $\chi^{(3)}_{xxxx}$ was found to be $0.0050 \times 10^{-17}$ m$^2$ V$^{-2}$ with a $\gamma$ value of $0.0063 \times 10^{-45}$ m$^5$ V$^{-2}$ using Degenerate Four Wave Mixing at 1064 nm with a pulse duration of 50 ps. The dimer had $\chi^{(3)}_{xxxx} = 0.23 \times 10^{-17}$ m$^2$ V$^{-2}$ and $\gamma/N = 0.24 \times 10^{-45}$ m$^5$ V$^{-2}$, while the pentamer had a $\chi^{(3)}_{xxxx} = 0.73 \times 10^{-17}$ m$^2$ V$^{-2}$ and $\gamma/N = 0.62 \times 10^{-45}$ m$^5$ V$^{-2}$.
This increase on going from the monomer, to the dimer, to a pentamer shows that the
nonlinear optical properties of porphyrins can be dramatically increased by incorporating
the chromophore into a conjugated network.

The different nonlinear values of the directly linked and butadiyne linked porphyrin
polymers is a result of the conjugation that exists between the macrocycles in the presence
of a butadiyne linker. When directly connected, the hydrogen atoms bonded to the
macrocycle prevent the units from achieving a coplanar geometry. In the absence of this
coplanarity, there is no significant orbital overlap. The result is essentially a chain of
chemically bonded but electronically isolated porphyrin macrocycles. The insertion of the
butadiyne linker provides a conjugated and sterically compact unit to separate the
macrocycles and allow significant orbital overlap over the entire structure. The result is a
tremendous enhancement in the nonlinearity of the molecule.

The molecular origin of the enhanced nonlinearity observed in the butadiyne linked
porphyrin oligomers has been determined.22 By fitting the TPA spectrum of porphyrin
dimers with a three-state model, Anderson, Rebane et al. were able to determine several
important parameters that govern the nonlinear response. While a number of parameters
increased upon dimerization, the most significant improvement came in the oscillator
strength of the second excited state transition dipole. This value increased by an order of
magnitude on going from the monomer to the dimer. This factor is a direct consequence of
increasing the conjugation length of the oligomer.

Recent work has directly addressed the relationship between orbital overlap in a
porphyrin oligomer and the two-photon absorption cross section. Ahn et al. systematically
varied the angle between *meso-meso* linked porphyrin oligomers using tethers with varying lengths, coordination to a central metal ion, and host-guest chemistry.\textsuperscript{20} In the absence of a tether, a *meso-meso* linked dimer with a dihedral angle of 90° had a $\delta < 100$ GM. The shortest tether reduced the dihedral angle to 36° and $\delta = 7500$ GM. The same trend was observed with the other techniques used to reduce the dihedral angle. Extremely large $\delta$ values were achieved by preparing porphyrin tapes. A tetramer of these planar structures had one of the largest $\delta$ values recorded, 93,600 GM. These results unambiguously show that the increased orbital overlap of planar conjugated oligomers results in enhanced two-photon absorption.

While linking chromophores with conjugated units to create longer conjugation pathways is an effective way to amplify molecular hyperpolarizability, this mechanism is of limited utility. The effect typically saturates after the addition of several monomer units.\textsuperscript{23} Rather than increasing in a supralinear fashion, additional units only increase $\gamma$ linearly. While the measured $\gamma$ value will continue to rise, $\gamma$ per repeat unit will eventually reach a constant value that does not change with additional monomer units. The length at which this saturation occurs is a function of the system under investigation.

The porphyrin oligomers discussed above show saturation of the length dependence around the hexamer. To further enhance the nonlinearity of the chain, Anderson et al. used the coordination of a central zinc atom to generate a self-assembled system that resulted a nine-fold increase in the nonlinearity over the isolated chain.\textsuperscript{24} The system was constructed by coordinating a zinc atom placed in the center of the porphyrin macrocycle to a linear bidentate ligand. The enhanced nonlinearity of the resulting two stranded porphyrin
complex was a consequence of the increased planarity of the system. The bidentate ligand forces the chains to adopt a cofacial geometry. This results in a planar system for both chains. The increased planarity of the oligomer results in greater conjugation and, hence, higher nonlinear values.

1.5 The use of metal ions to enhance third-order nonlinear optical properties

In his work on porphyrin oligomers, Anderson noted that the addition of metal ions into the core of the porphyrin macrocycle (Figure 5) enhanced the nonlinearity of the oligomers. The inclusion of a Pb$^{2+}$ ion in a butadiyne linked porphyrin polymer increased the $|\gamma_{xxx}|$ per repeat unit 12 times over the free base polymer when measured at 1064 nm.$^{25}$ It was suggested that the metal enhances the nonlinearity by increasing the excited transition dipole moments. This proposal was based on the strong charge transfer band in linear absorption spectrum of the Pb$^{2+}$ complex, but no detailed studies have been performed to support this assertion. The significant improvement offered by the inclusion of a metal into the electronic framework of the conjugated system suggests that the rich electronic variability of metal ions may offer an additional route to improve nonlinear materials.

The incorporation of metals into nonlinear materials remains a relatively unexplored research area. One system that has been investigated is the nonlinear optical properties of metalloocene acetylide complexes. Charge transfer transitions were found to have a significant affect on the nonlinearity of Group 4 (Ti, Zr, and Hf) metalloocene acetylide complexes.$^{26}$ The Ti complex had the highest $\gamma$, $92 \times 10^{-36}$ esu, with the Zr and Hf complexes having $\gamma$ values from $50 - 60 \times 10^{-36}$ esu when measured by third harmonic
generation (THG) at 633 nm (laser wavelength of 1.9 μm). The authors attribute this trend to the closer correspondence in the energy of the Ti d orbitals to the alkynyl π orbitals than the energies of the Zr and Hf d orbitals. The closer energy results in greater overlap between the metal orbitals and the π system. This larger π system results in larger nonlinear coefficients.

The effects of metal ions on the nonlinearity of azo dyes have also been investigated. Wu et al. used a wavelength of 647 nm for their study. At this wavelength, all of the compounds studied had a negative Re γ. Materials with negative nonlinear refractions defocus the intense laser light that pass through them. This is a useful property that could be used in sensor protection. Wu attributes the negative hyperpolarizability to the negative term of the SOS expression (Eq. 3). This is due in large part to the increase in the ground state dipole moment that occurs upon the addition of metal atom to the system. The mixing of the organic chromophore’s orbitals, in this case an azo compound, and the metal d orbitals creates a strong charge transfer transition. This strong dipole moment raises Re γ from \(-2.3 \times 10^{-32}\) esu to \(-2.9 \times 10^{-29}\) esu with the addition of a Co\(^{2+}\) ion. Interaction between the π orbitals of the organic chromophore and the d orbitals of the metal ion clearly result in an enhanced nonlinearity.

Porphyrrins readily coordinate a variety metals into the core of the macrocycle. Given the large numbers of ions that have been inserted into porphyrrins, virtually the entire periodic table, a variety of interactions between the metal ion and the porphyrin macrocycle have been observed. While nonlinear optical studies have been performed on porphyrin systems with metal ions in the core, the role of the metals in these systems was largely
structural.\textsuperscript{27,28} These systems frequently incorporate zinc into the macrocycle. As Zn\textsuperscript{2+} is a d\textsuperscript{10} ion, the π orbitals of the macrocycle and the metal d orbitals do not interact. As such, the effect of the metal on the electronics of the systems is largely inconsequential. However, the inclusion of metals with incomplete orbitals allows mixing of the metal and macrocycle electron densities,\textsuperscript{8,29} resulting in modified nonlinear properties like those discussed below. Despite this impact, few detailed studies on the effect of metals on the nonlinear optical properties of porphyrin macrocycles have been performed. Those that have been undertaken only used a single wavelength in their experiments.\textsuperscript{25,30}

While useful, single wavelength experiments offer little direct insight into the states important to the nonlinear properties of a molecule. For a three level system, the SOS expression shows that both one and two photon states are important in the nonlinear response. While information about the one photon state can be gained by using linear spectroscopy (UV/vis, fluorescence, Raman), the properties of the two-photon states are more difficult to probe. The dramatic effect of the metal ion on the electronic properties of the macrocycle can be seen in the electronic absorption spectrum of various metalloporphyrins (Figure 6).\textsuperscript{8} Because of their importance in photochemistry and photobiology, electric dipole allowed one-photon transitions have been extensively studied and are relatively well understood.\textsuperscript{8,31,32} The shifts in the energies of the Soret and Q bands are the result of interactions between the metal and porphyrin orbitals. The blue shift of the
Figure 6: A) Electronic absorption spectra of H₂ (---), Zn²⁺ (----), and Co²⁺ (-----) 4-OH TPP. B: Electronic absorption spectra Fe³⁺ (---), Mn³⁺ (----), and Pb²⁺ (-----) 4-OH TPP.

The > 480 nm spectral region in both figures has been multiplied by 5. Porphyrins in B have important charge transfer (LMCT) one-photon transitions.

visible bands of the Co²⁺ spectrum results from the interaction of the empty \( e_g(\pi^*) \) orbitals of the macrocycle with the filled \( nd_m \) metal orbitals. The additional bands in the Fe³⁺ and Mn³⁺ porphyrins are the result of ligand to metal charge transfer transitions. The energy of the singly valent \( d_n \) orbital lies between the porphyrin orbitals, thereby introducing additional transitions (Figure 6B). In contrast, two-photon states have only been examined for metal-free or Zn²⁺ porphyrins.\textsuperscript{16,33-35} Given the dramatic enhancement in nonlinear properties observed upon the insertion of metals into nonlinear materials, investigations of the two-photon states of metalloporphyrins could provide more detailed information on the types of interactions between metals and organic chromophores that result in enhanced nonlinear properties.
1.6 Measuring the $\chi^{(3)}$ properties of metalloporphyrins

A number of spectroscopic techniques have been developed to measure the $\chi^{(3)}$ properties of molecules and materials.\textsuperscript{36} The most widely used technique is Z-scan.\textsuperscript{37} This experiment is fairly simple as it only requires the sample to be translated through the focus of a pulsed laser beam. The sample translated through the focus of the beam. When the sample is far from the focus, the beam intensity is too low to induce nonlinear optical effects, but the intensity increases as the sample approaches the focus and nonlinear effects can be observed.

Z-scan allows Re $\chi^{(3)}$ and Im $\chi^{(3)}$ to be directly measured in a single experiment.\textsuperscript{37} Re $\chi^{(3)}$ is measured by placing an aperture in front of the diode used to measure the intensity of the pulsed beam after it passes through the sample. This technique is referred to as closed-aperture Z-scan. Im $\chi^{(3)}$ is measured by performing open-aperture Z-scan. As the name suggests, no aperture is placed in front of the detecting diode. By placing a beam splitter after the sample, both of these experiments can be performed in a single scan.

While this technique has been used to measure the $\chi^{(3)}$ of metalloporphyrins,\textsuperscript{30} there are difficulties associated with using this technique to measure the relatively small nonlinearities of metalloporphyrins. While the $\chi^{(3)}$ values of most solvents are small, the large numbers of these molecules in a sample solution results in a strong nonlinear response from the solvent as well as the solute. While this problem can be overcome by increasing the concentration of the solution until its signal is much larger than the solvent, a limited solubility in suitable solvents or aggregation induced by the high concentration can complicate performing and interpreting the experiments. Solvent contributions can be
eliminated by measuring thin films of a particular material, but the substrate used to support the film will introduce unwanted contributions to the nonlinear response as well.

Solvent and substrate contributions can be eliminated completely by measuring fluorescence from the material of interest. Two-photon-induced fluorescence (TPF) can be used to measure $\text{Im} \chi^{(3)}$. This technique allows the two-photon absorption cross section, $\delta$, of a molecule to be measured free from solvent contributions. Like Z-scan, TPF only requires a single beam to induce the nonlinear optical effect. The value of $\delta$ is determined by comparing the molecule’s TPF intensity to that of a material with a known $\delta$ value. To ensure that the same conditions are used to measure both samples, a beam splitter is used to produce two beams to allow the unknown and reference materials to be measured simultaneously.

The use of TPF to measure the nonlinear optical properties of metalloporphyrins is limited to those systems that have strong emission. Porphyrins with Zn$^{2+}$ ions have strong emission and can be studied using TPF. Other metalloporphyrins have strong emission, but this limitation prevents possible trends in the dependence of the nonlinear response on the properties of the ion from being thoroughly investigated.

The optimal technique for measuring the nonlinear optical properties of metalloporphyrins would have the versatility of Z-scan with the ability to eliminate contributions to the nonlinear response from the substrate offered by TPF. Degenerate Four Wave Mixing (DFWM) is a third nonlinear optical spectroscopy that offers both of these advantages. DFWM does not require an emissive sample, and, while the solvent or substrate will contribute to the nonlinear response in a similar manner as that seen in Z-
scan, the experiment can be modified to allow thin films to be measured in the absence of contributions from the substrate. DFWM also allows the temporal evolution of the nonlinear response to be measured, (the time dependence offers insight into the origin of the nonlinear response) and, while DFWM measures $|\chi^{(3)}|$, the Re $\chi^{(3)}$ and Im $\chi^{(3)}$ components can be determined by modeling a $\chi^{(3)}$ spectrum.

DFWM is a more demanding experimental technique than Z-scan or TPF. In a DFWM experiment, three beams are overlapped in the sample. Additionally, the pulsed nature of the laser used in these experiments requires that all three of the pulses arrive simultaneously. While adding complexity, this allows the temporal dependence of the nonlinear response to be probed by delaying the arrival of one of the pulses. Despite this experimental complexity, we selected DFWM to measure the nonlinear properties of metalloporphyrins. We also chose to measure metalloporphyrins films to take advantage of DFWM’s ability to eliminate the contribution of the substrate. A nonlinear optical device would require a solid-state material, so measuring thin films also allows us to determine if the nonlinear optical properties of a molecule are modified when it’s incorporated into a film.

1.7 Research Overview

This dissertation describes two research projects aimed at expanding the tools available to improve the nonlinear optical properties of porphyrins and other organic materials. The work addresses the saturation of the nonlinear enhancement of $\chi^{(3)}$ and $\gamma$ as the conjugation length is increased and the role of metal ions in enhancing the nonlinear optical properties of porphyrins. The role of charge transfer transitions in the two-photon properties of
metalloporphyrins is investigated by measuring electropolymerized films of the porphyrins using degenerate four wave mixing (DFWM). The DFWM spectrometer and the preparation of the electropolymerized films are discussed in Chapter 2. To measure the porphyrin films, we used a variation of the DFWM experiment that allows thin films supported by thick substrates to be measured without contributions from the thick substrate. To demonstrate the effectiveness of this experimental approach, we measured the nonlinear optical properties of indium tin oxide (ITO) films that are ~20 nm thick in the near-IR spectral region. We found that \( \chi^{(3)}_{\text{ITO}} = (2.16 \pm 0.18) \times 10^{-18} \text{ m}^2 \text{ V}^{-2} \) at 900 - 1300 nm (11000 – 7700 cm\(^{-1}\)), but two-photon absorption by the free carriers, which are electrons in ITO, at 1500 nm (6700 cm\(^{-1}\)) results in an enhanced \( \chi^{(3)}_{\text{ITO}} \) value of \( (3.36 \pm 0.28) \times 10^{-18} \text{ m}^2 \text{ V}^{-2} \). A detailed description of the DFWM thin film experiment and the nonlinear optical properties of the ITO is given in Chapter 3. A detailed study on the nonlinear optical properties of Fe\(^{3+}\) TPP is given in Chapter 4 with these results compared to those of Mn\(^{3+}\) and Co\(^{2+}\) TPP discussed in Chapter 5. These results show that a two-photon charge transfer transition enhances the two-photon cross section of the porphyrin macrocycle by an order of magnitude. The two-photon peak is assigned to the \( d_{x^2} \rightarrow \pi^* \) transition. The enhancement is larger with Mn\(^{3+}\) ions than in systems with the Fe\(^{3+}\) ion. This difference is due to a stronger one-photon charge transition dipole moment in the Mn\(^{3+}\) porphyrin. This dependence on the one-photon charge transfer transition dipole moment also accounts for an absence of a two-photon peak in the Co\(^{2+}\) spectrum. The problem of conjugation length saturation is addressed by a polymer repeat unit that couples azobenzene units through an ethynyl linkage. The rigidity of the structure and lack on hydrogen atoms on the azo and
ethyl vinyl units creates a highly planar backbone that has an unusually long conjugation length. The $\gamma$ values obey an empirical power law of $\gamma \propto n^{2.12 \pm 0.05}$ (n is number of repeat units) through the longest oligomer, $n = 36$, measured in the study. This exceptionally long effective conjugation length of at least 360 conjugated bonds (>49 nm) is likely due to the rigidity of the conjugated backbone. These results are discussed in detail in Chapter 6. Finally, a summary of each project is presented in Chapter 7.
2. DFWM Spectroscopy and Electropolymerized Film Preparation

2.1 Degenerate four wave mixing (DFWM) spectroscopy

Degenerate four wave mixing (DFWM) experiments were performed using ultrafast laser pulses. The 0.8 mJ 120 fs pulses were provided by a regeneratively amplified Ti:Sapphire laser system (Spectra Physics). This system could be tuned to perform experiments from 760 – 840 nm. An optical parametric amplifier (OPA TOPAS, Quantronix) was used to perform experiments at wavelengths longer than 840 nm. The pulses generated by the OPA were also 120 fs FWHM, and a maximum pulse energy of 0.24 mJ was obtained at 1200 nm. The power output of the OPA was optimized by adjusting the direction of the direction of the input laser pulse using the knobs of an external mirror mount.

A schematic of the DFWM spectrometer is given in Figure 7. The three pulses needed for the four wave mixing experiment are generated by using beam splitters (BS1 and BS2). Beam intensities were attenuated using neutral density filters. All three beams were s polarized in the DFWM experiments. Distortions to this polarization induced by the
multiple reflections used to manipulate the beams were corrected by having the laser pulses pass through a polarizer prior to illuminating the sample.

Figure 7. Schematic of the DFWM spectrometer.

The DFWM experiments were performed using the forward-box beam geometry (Figure 8). In this geometry, the three laser pulses (the dashed arrows in Figure 8) form three corners of a square with the signal pulse (the solid arrow in Figure 8) completing the square. The overlap of the laser pulses in the sample material that is necessary for observation of the signal pulse was achieved using an \( f = 25 \text{ cm} \) lens with a 5 cm diameter. The laser pulses were aligned in the square geometry and passed through the lens. By placing the sample at the focal length of the lens, the beams intersected at the sample to provide the required beam overlap. The overlap was optimized by adjusting the path of each individual beam with the knobs on the mirror mount.

In addition to spatial overlap, the laser pulses must also arrive at the sample simultaneously. For this to occur, each laser pulse must travel the same distance. This dependence on distance allows the temporal overlap to be optimized by adjusting the path length of each pulse. This was accomplished by placing a pair of mirrors on translational
stages as indicated in Figure 7. The translational stages of pulses 1 and 3 were adjusted manually while the translational stage of pulse 2 was computer controlled. When DFWM signals could not be observed using the PMT or photodiode detectors, beam alignment was achieved using a ZnS window. The use of this material allowed the spatial and temporal overlap of the laser pulses to be observed visually.

Figure 8. Beam geometry used in the DFWM mixing experiments. The laser pulses are indicated by dotted arrows. The signal pulse is shown as a solid arrow.

By using an $f = 15$ cm lens, the illuminated sample area was imaged to the photodetector (GaInAs photodiode for experiments at $\lambda > 920$ nm, and a PMT for experiments at $\lambda < 920$ nm). A metal screen blocked all beams except the signal beam, which passed through an iris diaphragm. By translating the micrometer-mounted screen, signals 4 and 6 could be measured without realignment of the optical beams or changing the position of the sample and/or the photodiode. The time dependence of nonlinear signals was measured by lengthening the path of beam 2. This was accomplished by using the computer controlled delay line. Photodiode and PMT signals were gated and integrated with boxcar signal
averagers and digitized by a 16 bit ADC card in a personal computer. Lab View software was used to collect the signal and control the delay line. Several thousand data points were collected at a rate of a 1000 data points per second and averaged for each measurement. The synchronization of the laser pulse generation and the boxcar averagers are shown in Figure 9.

Figure 9. Schematic of the electronics used to sync laser pulse generation and the collection and processing of the DFWM signal.

The intensity of the signal generated in a DFWM experiment has a cubic dependence on the total excitation energy.\textsuperscript{36} As such, the DFWM signal should have a cubic intensity dependence. All DFWM experiments were performed at an intensity that was in this cubic
intensity dependence region. An appropriate intensity was determined by varying the
intensity of the laser pulse using neutral density filters. A plot of the signal intensity as a
function of laser pulse intensity was used to determine the minimum excitation energy
needed to ensure that the observed signals correlated to the nonlinear optical properties of
the sample. A typical plot used to confirm that the experiments were being performed with
the correct laser intensity is shown in Figure 10.

![Graph](image)

**Figure 10. Typical graph of the intensity dependence of the DFWM signal.**

Both of the axis are in a log scale. The slope of the line is 3, which indicates that the
intensity dependence is cubic for the range of excitation energies used in the experiment.

### 2.2 Preparation of the electopolymerized porphyrin films

The electopolymerized porphyrin films were prepared by applying a potential to a ~1 mM solution of a porphyrin with 0.1 M of tetra-butyl ammonium perchlorate as a
supporting electrolyte. Indium tin oxide (ITO) coated glass slides were used as one of the
electrodes. Prior to use in film preparation, the ITO slides were ultrasonically cleaned in
water for five minutes. This was followed by an additional five minutes in isopropanol, which was followed by five minutes in acetone. The slide was dried with a stream of nitrogen gas and placed in an oven for at least 15 minutes prior to film preparation.

The assembly used to prepare the porphyrin films is shown in Figure 11. Once the apparatus was assembled, nitrogen was bubbled through the solution for 15 minutes prior to application of the potential. A potentiostat was used to apply the potential to the solution. The thickness of the film was controlled by varying the amount of time the potential was applied to the solution and changing the concentration of porphyrin in the solution. Thick films could be prepared using a concentrated solution (1 mM) with a relatively short application of the potential (~15 minutes), while using a more dilute porphyrin concentration (100 µM) allowed for greater control of the film thickness by applying the potential for different lengths of time. Following film generation, the films were rinsed with acetonitrile and dried with a stream of nitrogen gas. The films were characterized using UV/vis absorption, Raman spectroscopy, and step profilometry. They were stored in the dark at ambient conditions.
1 mM solution of the hydroxyphenyl porphyrin with 0.1M TBAP, acetonitrile, +1.5 V potential for 30 min

Figure 11. Apparatus used to prepare the porphyrin films. A schematic of the porphyrin film on the ITO coated glass slide is also shown.
3. Optical Susceptibilities of Indium Tin Oxide (ITO) Thin Films\textsuperscript{40}

3.1 The electrical and optical properties of indium tin oxide

Indium tin oxide (ITO) is a conductive material that transmits visible light but reflects infra-red radiation.\textsuperscript{41} A number of techniques have been used to grow nanometer to micrometer thick films of ITO on transparent substrates.\textsuperscript{42-44} This processability has allowed the unique combination of electrical and optical properties of ITO to be applied to solar cells, heat-reflecting mirrors, and antireflective coatings.\textsuperscript{45} Layers of functionalized materials can be added to ITO thin films by physical (i.e., spin-coating or vapor deposition) or chemical (i.e., electropolymerization of porphyrins) methods.\textsuperscript{46-51} This versatility has resulted in ITO being used to prepare electroluminescent devices, flat panel displays, and light emitting diodes (LEDs).\textsuperscript{52-56}

The electrical and optical properties that have made ITO useful in a broad array of technologies are a consequence of the relative energies of the valence and conduction
bands. ITO is a highly degenerate n-type, wide band gap (3.5-4.3 eV) semiconductor with an electrical resistivity of $2-4 \times 10^{-4}$ $\Omega$ cm$^3$. The low resistivity is the result of a degeneracy created during film formation by oxygen vacancies and substitutional tin dopants. As a result, the Fermi level is above the conduction band edge. This ordering results in a conductive material with a carrier concentration in the range of $10^{20}$ to $10^{21}$ cm$^{-3}$. These free carriers are responsible for the transition of ITO from a transparent to reflective material.

ITO's shift from a transparent to reflective material occurs over a broad range of wavelengths. The free carrier absorption reaches a maximum when the transmission, $T$, and the reflectance, $R$, have the same value. This spectral feature is called the plasma frequency, $\omega_p$. The plasma frequency of ITO is usually found in the near-IR. The value of $\omega_p$ is determined by the conditions used to generate the film. A simple Drude model describes free carrier effects on the optical and electric properties of ITO. According to this model, $\omega_p$ depends on the concentration of free carriers, $N$:

$$\omega_p^2 = \frac{Ne^2}{\varepsilon_0 \varepsilon_r m_e^* c^2}$$

where $e$ is the electron charge, $\varepsilon_0$ and $\varepsilon_r$ are the dielectric constants of the medium and free space, respectively, $m_e^*$ is the effective mass of the charge carrier, and $c$ is the speed of light.

The inherent presence of free electrons in the crystal lattice of ITO could make it useful in the development of photonic devices. We recently characterized the two-photon absorption and nonlinear refraction properties of electropolymerized metalloporphyrin
films on ITO substrates.\textsuperscript{6,61} Many photonic devices are based on nonlinear optical effects,\textsuperscript{36} yet the nonlinear optical properties of ITO films have not been characterized to date. The physical mechanisms that give rise to nonlinear optical effects are similar to those that contribute to “simpler” optical properties like absorbance, reflectance, and transmittance.\textsuperscript{36} Nonlinear susceptibilities, which describe the efficiency of processes such as two-photon absorption and nonlinear refraction, depend on the properties of the ground and excited states.\textsuperscript{36} In this paper, we analyze the third-order nonlinear optical susceptibility, $\chi^{(3)}_{\text{ITO}}$, of ITO films in a near-IR wavelength region important for telecommunications and consider contributions of the plasma frequency and free electron absorption to the nonlinear spectra.

3.2 Materials

ITO/glass slides (ITO coated Corning 1737 aluminosilicate glass) were purchased from Delta Technologies. The glass substrate was 0.7 mm thick, and the ITO films had a reported resistance of 100 $\Omega\cdot\square$. The thickness of the ITO film, \textasciitilde 20 - 30 nm, was determined using Atomic Force Microscopy (Nanoscope IIIA multi-mode, Digital Instruments). The tapping mode of the AFM was used to measure the ITO film. The ITO coated glass slide was cleaned with water, isopropanol, and acetone by sonication in an ultrasonic cleaner for five minutes in each solvent. The slide was dried with a stream of nitrogen. In addition to ITO coated substrates, glass substrates from which the ITO layer was removed were also studied. The ITO layer was removed by placing the coated slide in an aqueous solution of 20\% HCl and 5\% HNO$_3$ for ten minutes. A 1 mm thick silica
window (purchased from Thorlabs) was used as a reference in the DFWM experiments. The transmittance and reflectance spectra were measured with a PerkinElmer Lambda 950 UV-Vis-NIR spectrometer.

3.3 Degenerate Four Wave Mixing (DFWM) spectroscopy.

The “forward box” DFWM geometry has been described previously. A femtosecond optical parametric amplifier (OPA TOPAS, Quantronix/Light Conversion) was used to generate pulses for excitation at 900 – 1500 nm (11000 – 6700 cm⁻¹). The OPA was pumped by a regeneratively amplified Ti:Sapphire laser system (Spitfire, Spectra Physics). In a four wave mixing experiment, the overlap of three laser beams with intensities I₁, I₂, and I₃ in the sample gives rise to a signal beam, I₄. Beams I₁ - I₄ were s polarized in the experiments reported here. Signal I₄ is proportional to the square of the material’s third-order nonlinear susceptibility, \(\chi^{(3)}\),

\[ I₄ = \left(\chi^{(3)}\right)^2 \frac{l^2}{n^2} I₁I₂I₃ \]  

(5)

where \(l\) is the thickness of the material and \(n\) is the refractive index. According to Eq. (5), the DFWM signal should have a cubic intensity dependence. This dependence was verified in all of the experiments. The typical excitation intensity used in DFWM experiments (\(I₁ + I₂ + I₃\)) was 14.5 GW cm⁻².

3.4 DFWM spectroscopy of thin supported films.

In DFWM studies of thin films on thick substrates, the optical signal contains contributions from both the film and the substrate. These contributions can be separated using a method based on the different phase-matching conditions of the thin film and thick
substrate.\textsuperscript{39,63-65} As shown in Figure 12, the phase-matched signal, \( I_4 \), propagates in a direction that satisfies geometric (phase-matching) conditions defined as \( k_1 + k_2 = k_3 + k_4 \), where \( k_i \) are the wave vectors of the corresponding optical beams (\( k_4 \) is a wave vector of an optical signal, \( k_1 - k_3 \) are the wave vectors of laser beams).\textsuperscript{39} Signals that do not satisfy the phase-matching conditions, \( I_5 \) and \( I_6 \), are also generated during the experiment. The propagation direction of these beams is indicated in Figure 12. The intensity of these additional signals relative to that of the fully phase-matched signal, \( I_4 \), depends on the thickness of the material as described below.

![Figure 12. Experimental geometry for DFWM measurements that are based on different phase-matching conditions for substrates and thin films](image)

Strokhendl et al showed that the intensities of \( I_4, I_5, \) and \( I_6 \) can be determined by solving the Maxwell’s equations for these signals.\textsuperscript{39} According to this model, the intensity of the non phase-matched signals, \( I_6 \) and \( I_5 \), can be expressed as:

\[
I_5 = I_6 = F(\chi^{(3)})^2 \frac{l^2}{n^4} I_1 I_2 I_3
\]  
(6)
This expression is identical to that of Eq. (5), except that the phase-matching effects are described by the inclusion of factor $F$. Factor $F$ is

$$F = \left( \frac{\sin(x)}{x} \right)^2 \quad \text{where} \quad x = \frac{\theta^2 \omega l}{2nc}$$

(7)

$\theta$ is the angle between the optical beams, $\omega$ is the optical frequency used in the experiment, and $c$ is the speed of light. The magnitude of $F$ is largely determined by the thickness, $l$. Films of nm - $\mu$m thickness will have $F \approx 1$, but thicker materials, such as those used as substrates, will have $F \ll 1$.

Strokhendl et al have applied this method to the study 10 $\mu$m thick C$_{60}$ films on 1 mm thick CaF$_2$ substrates and 3.1 $\mu$m thick C$_{70}$ films on 1.49 mm thick fused silica substrates.$^{39,63-65}$ They showed that for the 3.1 - 10 $\mu$m thick films, $F = 1$, and $F = 0$ for the 1 - 1.49 mm thick substrates. The substrate’s contribution to the $I_0$ signal did not need to be considered because its phase-mismatched signal amplitude was $\approx 1\%$ of the film’s phase-mismatched signal amplitude.$^{39}$

Greater attention must be given to the substrate’s phase-mismatched signals when very thin films are studied. The ITO films measured in this study are 20 - 30 nm thick. Here we show that a careful analysis of the dependence of $F$ on the angle, $\theta$, and laser frequency, $\omega$, allows the model described by Eq. (6) to be applied to the study of such films.
Figure 13. A: Factor $F$ calculated using Eq. (7) for a 20 nm thick film (---, $\theta = 2.7^\circ$ or $3.2^\circ$, lines overlap) and for a 0.7 mm thick substrate (---, $\theta = 2.7^\circ$ and - - - - - , $\theta = 3.2^\circ$).

B: Experimental (symbols) and calculated (lines) $F$ values for 0.7 mm thick silica substrates. Angles used in the experiments: $\theta = 3.2^\circ$ (■) and $\theta = 2.7^\circ$ (○).

The dependence of factor $F$ on the laser wavelength is illustrated by the plot shown in Figure 13A. The $F$ values were calculated using Eq. (7). The 20 - 30 nm thick ITO films have an $F = 1$ and the 0.7 mm glass substrate has $F \ll 1$ from 350 - 1600 nm (28500 - 6250 cm$^{-1}$). When $\theta = 2.7^\circ$, the plots in Figure 13A indicate that $F < 0.015$ from 900 - 1200 nm (11000 - 8300 cm$^{-1}$). An angle of $\theta = 3.2^\circ$ will provide the same reduction in the glass substrate signal for measurements at 1200 - 1500 nm (8300 - 6700 cm$^{-1}$).

A comparison of Eqs. (6) and (7) shows that the value of factor $F$ can be determined experimentally by taking the ratio of the amplitudes of $I_6$ and $I_4$:

$$F = \frac{I_6}{I_4} \tag{8}$$
Experimental results are shown in Figure 13B. The agreement between the calculated and experimental $F$ values confirms that Eq. (7) accurately describes the intensity of the phase-mismatched DFWM signals of thick substrates. Because $F$ depends on both the beam angle and laser wavelength, Eq. (7) can be used to select an angle that will provide the optimal reduction of the glass substrate’s phase-mismatched DFWM signals over a particular spectral region. As shown in Figure 13B, optimal reduction of the substrate signal in the spectral region of our studies on 20 nm thick ITO films is provided by angles of $\theta = 3.2^\circ$ (the wavelength range $1200 - 1500$ nm) and $\theta = 2.7^\circ$ (at $900 - 1200$ nm).

3.5 Optical spectra

The ITO films used in our study had an optical transmittance of $85 - 90\%$ and reflectance of $\sim 10\%$ at $400 - 2500$ nm ($25000 - 4000$ cm$^{-1}$). Figure 14 shows the absorbance ($A$), transmittance ($T$) and reflectance ($R$) spectra of the film. (Absorbance values were obtained from $A + T + R = 1$.) The spectra in Figure 14 are similar to those reported for 40 nm thick ITO films.$^{58}$ In particular, the plasma frequency, $\omega_p$, defined by the condition $T = R$, does not occur in this wavelength range. $\omega_p \approx 2500$ cm$^{-1}$ (4000 nm) is expected for the ITO films studied here based on reported spectra.$^{57,58}$
Figure 14: Typical Transmission, $T$, (—), reflectance, $R$, (—), and absorption, $A$, (---) spectrum of the ITO films used in the DFWM experiments.

3.6 Determination of the $\chi^{(3)}$ spectrum

As described in Section 3.3, we measured phase-mismatched DFWM signals to determine $\chi^{(3)}_{\text{ITO}}$. Measurements were performed using beam angles of $\theta = 3.2^\circ$ and $\theta = 2.7^\circ$. The use of two angles allows the nonlinear susceptibility of the ITO thin films to be characterized over a broad wavelength range. The $\chi^{(3)}_{\text{ITO}}$ values were determined by comparing the amplitudes of the phase-mismatched DFWM signal of the ITO thin film, $I_6^\text{ITO}$, and the phase-matched signal of the silica reference, $I_4^\text{silica}$.

$$\left| \chi^{(3)}_{\text{ITO}} \right| = \left| \chi^{(3)}_{\text{silica}} \right| \sqrt{\frac{I_6^\text{ITO}}{I_4^\text{silica}} \frac{l_{\text{silica}}}{l_{\text{ITO}}} \frac{n_{\text{ITO}}^2}{n_{\text{silica}}^2}}$$  \hspace{1cm} (9)
with $n_{\text{ITO}} = 2.0^{57}$, $l_{\text{ITO}} = 20$ nm, $n_{\text{silica}} = 1.46$, $l_{\text{silica}} = 1.0$ mm, and $\chi^{(3)}_{\text{silica}} = 2.04 \times 10^{-22}$ m$^2$V$^{-2}$ (1.46×10$^{-14}$ esu). The $\chi^{(3)}_{\text{ITO}}$ spectra are shown in Figure 15. The $I_0^{\text{ITO}}$ signals used to generate the $\chi^{(3)}$ spectra shown in Figures 10A and 10B may have contributions from the glass substrate. Because of the interference between the ITO film signal with that of the glass substrate, separation of the substrate’s contribution to the ITO film signal needs to be carefully considered. To perform this analysis, contributions to the $\chi^{(3)}_{\text{ITO}}$ spectra from the glass substrate are indicated as solid lines in Figures 10A and 10B (calculated using Eq. (7)).

The data in Figure 15A show that the small contributions from the substrate allow the $\chi^{(3)}$ values found at $\lambda > 1200$ nm ($< 8300$ cm$^{-1}$) with $\theta = 3.2^\circ$ to be attributed to the ITO film. At $\lambda < 1200$ nm ($> 8300$ cm$^{-1}$) there is a significant contribution from the glass substrate. This contribution prevents the susceptibility values determined at these wavelengths from being unambiguously assigned to the ITO film. The substrate signal is actually larger than the signal from the ITO coated slide at $\lambda < 1000$ nm ($<10000$ cm$^{-1}$). This could be the result of destructive interference between the film and substrate signals (the extent of the interference depends on the phase difference between the two components). Therefore, only $\chi^{(3)}_{\text{ITO}}$ values measured at $\lambda > 1200$ nm ($> 8300$ cm$^{-1}$) with $\theta = 3.2^\circ$ are used in the analysis of the nonlinear optical properties of ITO.
Figure 15: $\chi^{(3)}_{\text{ITO}}$ spectra measured with $\theta = 3.2^\circ$ (A) and $\theta = 2.7^\circ$ (B).

The contributions from the substrate to the $\chi^{(3)}_{\text{ITO}}$ values are indicated by the solid lines. The solid lines are plots of Eq. 7 that are normalized to the $\chi^{(3)}_{\text{ITO}}$ values based on the amplitudes of the phase-mismatched signals for the glass substrate and the ITO film.

The region between 900 - 1100 nm (11000 – 9000 cm$^{-1}$) is better characterized using $\theta = 2.7^\circ$ (Figure 15B). Under these conditions, the susceptibility spectrum only reflects the properties of the ITO film.

3.7 Analysis of the ITO $\chi^{(3)}$ spectrum
The composite $\chi^{(3)}_{\text{ITO}}$ spectrum is shown in Figure 16. The spectrum only includes susceptibilities measured at wavelengths where $I_0^{\text{ITO}}$ was at least two times larger than $I_0^{\text{glass}}$. The ITO film has an essentially constant nonlinear susceptibility from 900 - 1300 nm (11000 - 7700 cm$^{-1}$) with the value of $\chi^{(3)}_{\text{ITO}} = (2.16 \pm 0.18) \times 10^{-18}$ m$^2$ V$^{-2}$. The $\chi^{(3)}_{\text{ITO}}$ begins to increase around 1300 nm (7700 cm$^{-1}$) and reaches $\chi^{(3)}_{\text{ITO}} = (3.36 \pm 0.28) \times 10^{-18}$ m$^2$ V$^{-2}$ at 1500 nm (6700 cm$^{-1}$). The mechanism of nonlinear polarizability can be determined by comparing the $\chi^{(3)}_{\text{ITO}}$ spectrum to the linear absorption spectrum. This analysis allows both one- and two-photon absorption effect to be considered.

First, we consider if one-photon absorption has significant contributions to the $\chi^{(3)}_{\text{ITO}}$ spectrum. There is weak one-photon absorption over the entire spectral region used in the DFWM experiments (Figure 14). This absorption increases from 0.015 at 1150 nm (8700 cm$^{-1}$) to 0.022 at 1500 nm (6700 cm$^{-1}$). This gradual rise is different from the sharp increase at 1300 nm (7700 cm$^{-1}$) observed in the $\chi^{(3)}_{\text{ITO}}$ spectrum. This difference suggests that one-photon effects do not make significant contributions to the nonlinear polarization of ITO from 900 – 1500 nm (11000 – 6700 cm$^{-1}$).

Two-photon absorption, which is a third-order nonlinear process, could also contribute to the $\chi^{(3)}_{\text{ITO}}$ spectrum. To evaluate contributions from two-photon absorption, the $\chi^{(3)}_{\text{ITO}}$ spectrum must be compared to the absorption spectrum at two times higher energy (for example, a two-photon transition to a state at 750 nm would require the absorption of two 1500 nm photons). This type of comparison is shown in Figure 16. The $\chi^{(3)}_{\text{ITO}}$ and absorption spectra have similar features when compared in this manner. The sharp
increase in absorption at 650 nm (15400 cm\(^{-1}\)) is similar to the increase in the nonlinear susceptibility at 1300 nm (7700 cm\(^{-1}\)). The spectra are also similar in that both the absorption and the \(\chi^{(3)}_\text{ITO}\) values are essentially constant at lower energies. These similarities suggest that two-photon absorption contributes to the nonlinear susceptibility of the ITO films in the near-IR.

![Graph showing \(\chi^{(3)}_\text{ITO}\) and absorption spectra for ITO films.](image)

**Figure 16: Comparison of \(\chi^{(3)}_\text{ITO}\) (■) and absorption (—) spectra for ITO films.**

Two-photon absorption effects are considered here by showing the linear absorption spectrum (top scale) at twice the energy of the DFWM experiment (bottom scale).

The above analysis allows the different regions of the \(\chi^{(3)}_\text{ITO}\) spectrum to be attributed to a particular nonlinear polarization mechanism. We attribute the 900 – 1300 nm (11000 – 7700 cm\(^{-1}\)) region of the spectrum to nonresonant polarization. This polarization is most likely due to free electrons in the conduction band. The ultrafast time response discussed below supports this assignment. The increase in \(\chi^{(3)}_\text{ITO}\) at \(\lambda > 1300\) nm (7700 cm\(^{-1}\)) is attributed to two-photon absorption by the bulk plasmon. (Measurements of ITO prepared under various conditions have shown that the surface plasmon appears at much lower
energies,\(^59\) therefore there is likely no significant contribution from the surface plasmon in the \(\chi^{(3)}_{\text{ITO}}\) spectrum.)

The \(\chi^{(3)}_{\text{ITO}}\) values found here are comparable to the nonlinear susceptibilities found for other semiconductor thin films. For example, a 55 nm thick film of ZnO microcrystallites was found to have \(\chi^{(3)}\) values ranging from \(1.4 \times 10^{-16} - 1.4 \times 10^{-14}\) m\(^2\) V\(^{-2}\) (1 \(\times\) 10\(^{-8}\) - 1 \(\times\) 10\(^{-6}\) esu) when the excitation was at or near the exciton band-edge.\(^{67}\) A \(\chi^{(3)}\) value of 1.8 \(\times\) 10\(^{-16}\) m\(^2\) V\(^{-2}\) (1.3 \(\times\) 10\(^{-8}\) esu) was determined for an 80 nm thick amorphous VO\(_2\) films at 532 nm (18800 cm\(^{-1}\)).\(^{68}\) Third-harmonic generation with the laser energy tuned to the absorption edge (~365 nm) gave \(\chi^{(3)} = 3.8 \times 10^{-18}\) m\(^2\) V\(^{-2}\) (2.7 \(\times\) 10\(^{-11}\) esu) for GaN films on sapphire substrates.\(^{69}\)

The nonlinear optical properties of organic thin films have also been investigated. The \(\chi^{(3)}\) spectrum of C\(_{70}\) was measured from 740 – 1600 nm (13500 – 6250 cm\(^{-1}\)) using DFWM with femtosecond pulses.\(^{64}\) The \(\chi^{(3)}\) values ranged from \(2.37 \times 10^{-20}\) m\(^2\) V\(^{-2}\) (1.7 \(\times\) 10\(^{-12}\) esu) at 1500 nm to \(\sim\) 7 \(\times\) 10\(^{-20}\) m\(^2\) V\(^{-2}\) (5 \(\times\) 10\(^{-12}\) esu) at 1000 nm. For an electopolymerized film of Mn(III)-5,10,15,20-tetrakis-(4-hydroxytetraphenyl)porphyrins (Mn\(^{3+}\) TPP), we reported \(\chi^{(3)} = 1.36 \times 10^{-19}\) m\(^2\) V\(^{-2}\) at 1200 nm.\(^{61}\) At the telecommunication wavelength of 1500 nm (6700 cm\(^{-1}\)), the optical nonlinearity of ITO is about 150 times bigger than that of the C\(_{70}\) film and about 25 bigger than that of the Mn\(^{3+}\) TPP electopolymerized film.

\textbf{3.8 Polarization relaxation in ITO thin films}
Several DFWM kinetics are shown in Figures 12A - C. The ultrafast nonlinear response supports our assignment of the major nonlinear mechanism to nonresonant electronic polarization of free carriers (electrons) in the ITO conduction band. In addition, each of the kinetics has a slower component which increases in amplitude at longer wavelengths. Deconvolution assuming a Gaussian laser pulse shape was used to analyze this data.\textsuperscript{70} When single exponential relaxation was assumed, deconvolution yielded lifetimes of $\tau_{\text{DFWM}} = 53$ fs at 1200 nm (8300 cm$^{-1}$), 84 fs at 1300 (7700 cm$^{-1}$) and 1450 nm (6900 cm$^{-1}$), and 130 fs at 1500 nm (6700 cm$^{-1}$).

![Figure 17: Phase-mismatched DFWM kinetics at 1200 nm (□, A), 1300 nm (○, B), and 1500 nm (■, C).](image)

A Gaussian function representing a 110 fs laser pulse is shown for comparison in each plot. A solid line represents fitting (deconvolution) results obtained assuming a Gaussian laser pulse shape and a single exponential decay. D: Lifetimes of the exponential component from 1125 – 1500 nm (●).
The DFWM signal, as expressed by Eq. (5), is proportional to the square of the material’s $\chi^{(3)}$ value. Therefore, the lifetime that describes a material’s relaxation is $\tau = 2 \tau_{DFWM}$. The lifetimes determined using this approach are summarized in Figure 16D.

Several mechanisms could contribute to the femtosecond relaxation observed in the kinetics shown in Figure 17. The tail in the DFWM kinetics could be due to electron scattering in the ITO conduction band. The Drude free electron model used to describe the electrical and optical properties of ITO thin films relates the plasma frequency, $\omega_p$, to the electron scattering time, $\tau$:

$$\omega_p = \sqrt{\frac{1}{R\varepsilon_0 c^2 \tau}}$$

where $R$ is the electrical resistance of the material and the other parameters were defined above. A lifetime of 162 fs (the average for the 1270 – 1450 nm kinetics) gives a $\lambda_p = 4166$ nm (2400 cm$^{-1}$). As described above, $\lambda_p > 2500$ nm ($< 4000$ cm$^{-1}$) for the ITO thin films studied here, and the estimated $\lambda_p = 4000$ nm (2500 cm$^{-1}$) is in good agreement with published values for ITO films of similar thickness. Thus, the results are consistent with an assignment of the tail in the DFWM kinetics to electron scattering.

The wavelength dependence of the lifetime $\tau$, particularly the increase at 1500 nm (Figure 17D), suggests that additional mechanisms may contribute to the femtosecond relaxation in the DFWM kinetics. More detailed studies are required to establish these mechanisms. In molecular systems, one- and two-photon absorption gives rise to tails in DFWM kinetics similar to those in Figure 17. If the increase in $\chi^{(3)}_{ITO}$ at 1500 nm in
Figure 5 is attributed to two-photon absorption, then the longer lifetime at 1500 nm could be related to the relaxation of two-photon states.

3.9 Summary

We have measured the nonlinear susceptibility spectrum of supported ITO films by using a DFWM technique based on the different phase-matching properties of thin films and thick substrates. The nonlinear response at 900 - 1300 nm (11000 – 7700 cm\(^{-1}\)) is attributed to non-resonant polarization of conduction band electrons. The \(\chi^{(3)}_{\text{ITO}}\) values increase at \(\lambda > 1300\) nm (7700 cm\(^{-1}\)). Comparison of \(\chi^{(3)}_{\text{ITO}}\) and absorption spectra suggests that the enhancement may be due to a two-photon process. The DFWM kinetics have a femtosecond component at all of the wavelengths measured in our experiments. The lifetimes determined by deconvolution are consistent with the decay being due to electron scattering.
4. Charge Transfer States Determine the Nonlinear Optical Properties of Fe$^{3+}$ Porphyrin Films in the near-IR Spectral Region$^6$

4.1 Introduction

Organic materials are actively explored for third-order nonlinear optical applications such as ultrafast all-optical switching, optical memory, optical power limiting, 3D microfabrication, photodynamic therapy, and fluorescence microscopy. The chemist’s goal in this work is to design molecules and materials with high nonlinear coefficients and develop models that can predict these characteristics from the molecular structure.$^{72,73}$ The efficiency of processes related to two photon absorption is described by the imaginary part of the material’s third order nonlinear susceptibility, $\chi^{(3)}$, and molecular second hyperpolarizability, $\gamma$. Nonlinear refraction is described by the real part of coefficients $\chi^{(3)}$ and $\gamma$.

Recently, third order nonlinear properties of porphyrins, porphyrin polymers, and porphyrin coordination compounds have been extensively studied.$^{13,15,21,28,30,74,81}$ This is related, in part, to wide porphyrin use in photomedicine and molecular photonics.$^{82}$ Many important questions about porphyrin third-order nonlinear properties remain to be
addressed. In this chapter, we consider the role of charge transfer (CT) states in determining transition metal porphyrin third-order nonlinear optical properties. We study Fe(III)Cl tetrakis(4-hydroxyphenyl)porphyrin (1), because of the importance of iron porphyrin CT states in photochemistry and photobiology. CT states can be described as involving electron transfer from the porphyrin macrocycle to the metal d orbitals. \[ \chi^{(3)} \]

![Figure 18. 5,10,15,20-tetrakis-(4-hydroxyphenyl)-porphyrin Fe^{3+}Cl (Fe^{3+} TPP)](image)

To learn about electronic states giving rise to nonlinear effects, experiments at different wavelengths are necessary; we carried out such studies at 760-1350 nm - in the near-IR wavelength region important for telecommunications. Two photon absorption spectra (Im $\chi^{(3)}$) spectra were already reported for several porphyrins. In contrast, previous nonresonant DFWM or z-scan studies that allow determination of both Re $\chi^{(3)}$ and Im $\chi^{(3)}$ components were only carried out at a single wavelength. Thus, this paper appears to be the first report of porphyrin Re $\chi^{(3)}$ and Im $\chi^{(3)}$ spectra in the near IR.

We use femtosecond degenerate four wave mixing (DFWM) to study porphyrin third-order nonlinear spectra. While more complex than other experimental methods, DFWM experiments yield $\chi^{(3)}$(-$\omega_1$, $\omega_2$, $\omega_3$) tensor components important for all-optical information.
processing applications. DFWM experiments also allowed the examination of the time
dependence of nonlinear signals.

Both one-photon and two-photon transitions are important for third-order nonlinear
effects; therefore $\chi^{(3)}$ spectra yield properties of two-photon states that cannot be observed
using linear spectroscopy. For a molecule with a center of symmetry (D$_{4h}$ symmetry for 1)
a change in parity between the initial and final states is required for an electric dipole
allowed one-photon transition. In contrast, two-photon transitions are allowed between
states of the same parity. Using quantum chemical methods, two photon $\pi\pi^*$ states for
metal-free, Zn$^{2+}$, and Mg$^{2+}$ porphyrins were found at 30000 - 33000 cm$^{-1}$.$^{34,35,68,84}$ Two-
photon fluorescence experiments found metal-free porphyrin two photon states at similar
energy.$^{13,16}$ In contrast, we find that much lower energy two-photon states are important
for Fe$^{3+}$ porphyrins. Fe$^{3+}$ porphyrin film third order nonlinear susceptibility is enhanced at
least several times due to the charge transfer states.

We investigated porphyrin thin films prepared by electrochemical polymerization.$^{49,50,85}$
Such simple preparation methods afforded films of high optical quality, transparent in
near-IR, and stable for a long time in air.

4.2 Materials

Tetrakis(4-hydroxyphenyl)porphyrin Fe$^{3+}$Cl (Porphyrin Systems, Germany), analytical
grade organic solvents (Aldrich), and electrochemical grade terabutylammonium
perchlorate (TBAP, Fluka) were all used as received. 1737 aluminosilicate glass substrates
with and without conductive ITO layer (In$_2$[Sn]O$_x$, resistance 100 $\Omega$/) were from Delta
Technologies.
4.3 Porphyrin film preparation and characterization

ITO slides were ultrasonically cleansed in demineralized water, isopropanol, and acetone, dried with a stream of nitrogen, and placed in an oven for a minimum of 15 minutes prior to film preparation. Porphyrins were dissolved (0.5 mM) in acetonitrile with 0.1M TBAP as a supporting electrolyte. Nitrogen was bubbled through the solution for 15 minutes prior to the application of the potential and throughout the film growing process. Porphyrin films on conductive ITO substrates were deposited in cyclic voltammetry and controlled potential experiments; both methods appeared to yield films with the same absorption spectra. For cyclic voltammetry, a conventional three-electrode system consisting of a platinum-working electrode, a platinum wire counter electrode and an Ag/AgNO₃ reference electrode were used. When a two-electrode setup was utilized, a fixed potential (above 500 mV vs. ferocene/ferrocenium) was applied to platinum wire and ITO substrate electrodes. The film was grown for about 30 minutes. The coated substrates were rinsed in acetonitrile and dried with a stream of nitrogen. UV/vis spectra were recorded with an HP-8452A spectrometer. Resonance Raman spectra were acquired with 532 nm excitation (10 mW). SPEX model 1870 0.5 m spectrograph and Princeton Instruments 1340×400 CCD cooled with liquid nitrogen were used. Porphyrin film thickness was determined with a step profilometer. The films were stored in the dark at room temperature; their optical characteristics did not change for several months.
Figure 19. Schematics of an optical setup for thin film DFWM measurements.

A: Arrangement of laser beams (1, 2, and 3) and signal beam (4, 5, 6) propagation directions. B: Top and side view showing sample, lens used for imaging, screen, and photodetector. Numbers denote optical paths of respective beams.

4.4 Degenerate Four Wave Mixing (DFWM)

A regeneratively amplified Ti:Sapphire laser system (Spectra Physics) provided 120 fs, 0.8 mJ pulses at 760 – 840 nm. Experiments at longer wavelength were carried out with excitation from an optical parametric amplifier (OPA TOPAS, Quantamix). Pulses generated by OPA were also 120 fs FWHM, maximal pulse energy (at 1200 nm) was 0.24 mJ. The spectrometer for nonlinear optical experiments was described previously.62 A modified optical scheme for near-collinear beam geometry DFWM experiments is shown in Figure 19 (angle $\Theta = 4.1^\circ$). In DFWM experiments on supported thin film samples it is necessary to separate a thin film optical signal from a substrate signal. As explained bellow, the optical setup shown in Figure 19 allows the contribution of the thick substrate
to be separated from the thin film signal by taking advantage of different phase-matching properties of the thin film and thick substrate.\textsuperscript{39} By using a large (75 mm diameter) f = 15 cm lens, we imaged the illuminated sample area to the photodetector (GaInAs photodiode for experiments at $\lambda > 920$ nm, and a PMT for experiments at $\lambda < 920$ nm). A metal screen blocked all beams except the signal beam, which passed through an iris diaphragm. By translating the micrometer-mounted screen, signals 4, 5, and 6 could be measured without realigning the optical beams or changing the sample or photodiode position. The time dependence of nonlinear signals was measured by making the optical path of beam 3 longer with a computer controlled delay line.

In DFWM experiments, three laser beams overlap in the sample as shown in Figure 19. When all three laser pulses (1, 2, 3) reached the sample simultaneously, the signal pulse 4 was generated. Beam 4 propagated in the direction satisfying strict geometric conditions (the phase matching conditions can be defined as $k_1 + k_2 = k_3 + k_4$, where $k_i$ are wave vectors of corresponding optical beams i). When the sample being investigated consisted of thick substrate and thin film, however, additional signal beams (5 and 6 in Figure 19) could be observed.\textsuperscript{39} Optical signals 5 and 6 propagate in directions shown in Figure 19. The power of the phase mismatched signals 5 and 6 was reduced by a factor $F = [\sin(x)/x]^2$, where $x = \Delta k l/2$ and $l$ is thickness of the medium in which the nonlinear signal is generated.\textsuperscript{39} When the angles $\Theta$ are small, $\Delta k$ can be calculated as $\Delta k = 2\pi\Theta^2/(n \lambda)$, where $n$ is a refractive index and $\lambda$ is wavelength. For a glass substrate $F = 0.011$ (glass = 0.7 mm) and therefore beams 5 and 6 have only negligible contribution from the glass. In
contrast, for a thin porphyrin film $F \approx 1$ ($p_{porphyrin} = 500$ nm). Therefore, only the thin film nonlinear properties were reflected in non-phase matched signals 5 and 6.

All experiments were performed using laser beams of vertical polarization (s-polarization), therefore results reflect values of $\chi^{(3)}_{1111}(-\omega,\omega,\omega,-\omega)$ tensor component. The energy of laser pulses for beams 1-3 was 5-15 $\mu$J, intensity of respective beams was 1-10 GW/cm$^2$. DFWM signals ($I_{\text{signal}}$) had cubic dependence on the excitation intensity, $I_{\text{Laser}}$:

$$I_{\text{signal}} \propto I_{\text{Laser}}^{3+0.1}.$$  

4.5 Preparation, absorption spectra, and electrochemical properties of the porphyrin films.

In acetonitrile solution, Fe(II)/Fe(III) redox couple was reversible; potential was 620 mV vs. ferrocene/ferrocenium. The oxidation and reduction peaks were unchanged in the initial scan when an ITO slide was used as the working electrode. With repetitive scanning, both reduction and oxidation peaks shifted to higher potentials (see cyclic voltammetry data shown in Appendix 1). The oxidation and reduction waves also increased in amplitude with each scan. These characteristics indicate that a conductive porphyrin polymer film was growing on the ITO electrode$^{50,85}$ The polymerized film was not soluble in acetonitrile. The properties of the porphyrin films were investigated with resonance Raman and UV-Vis absorption spectroscopy. Resonance Raman data (Figure 20A) allows the oxidation and spin state of the porphyrin to be determined. The bands at 600 – 1600 cm$^{-1}$ correspond to in-plane porphyrin skeletal modes$^{1,86,87}$ In particular, frequencies of $\nu_4$ (1360 cm$^{-1}$, polarized), $\nu_{19}$ (1513 cm$^{-1}$, anomalously polarized) and $\nu_2$ (1547 cm$^{-1}$, polarized) bands in Figure 20A are characteristic of high-spin, Fe$^{3+}$ tetrphenyl
porphyrins. These results indicate that the electrochemical polymerization of film formation does not alter the properties of the central metal ion. This result is consistent with the mechanism proposed in the literature – tetrakis(p-hydroxyphenyl)porphyrin polymerization occurs by forming bonds between the hydroxyphenyl substituents, while the porphyrin macrocycle and metal remain unaffected.

Figure 20. A: Resonance Raman spectrum of porphyrin film measured with 532 nm excitation. Band assignments are based on variation of band intensities in the polarized Raman spectra.¹ B: Electronic absorption spectra for 1 in acetonitrile solution (—) and for the porphyrin film (—–).

In agreement with assignment from the Raman spectrum, the electronic absorption spectrum of porphyrin 1 in acetonitrile solution (Figure 20B) is typical of high spin Fe³⁺ porphyrins. While the intense Soret band and less intense Q bands characteristic of all porphyrins are present, a low energy CT transition \((a_{1u}(\pi), a_{2u}(\pi) \rightarrow e_g(d_{yz}, d_{zx}))\) result in the addition of two peaks at 660 and 700 nm. In comparison to other Fe³⁺ porphyrins, the
hydroxyl groups induce a red shift of CT bands. In addition, the oscillator strength of the purely electronic Q(0,0) band is reduced in comparison to the porphyrin in solution, and this band is almost completely obscured by a shoulder of the nearby Q(0,1) band. A similar reduction in Q(0,0) band intensity was observed for tetrakis(\(\rho\)-methoxyphenyl)porphyrins Fe\(^{3+}\)Cl,\(^{88}\) which suggests that electron donating substituents on the phenyl rings reduce Q(0,0) band intensity.

Changes in the film spectrum are consistent with observations of similar systems.\(^{50}\) The Soret band is red-shifted by approximately 20 nm and considerably broadened, while the Q(0,1) band broadening is significant enough to completely obscure the Q(0,0) band. The CT bands show a slight shift to the blue. Additionally, the Soret band intensity is reduced and the CT band intensities have increased. The red-shift and weakening of Soret band could be attributed to excitonic coupling between adjacent porphyrin molecules. The degree of dipole-dipole interaction is largely a function of transition dipole moment. As the transition dipoles of the Q bands are approximately twenty times smaller than that of the Soret band, the energies of these transitions are largely unchanged in the film spectrum. The significant band broadening observed in the film spectrum can also be a consequence of inhomogeneity associated with irregular orientations of neighboring molecules.

4.6 The \(\chi^{(3)}\) properties of the ITO substrate

The porphyrin film was generated by electropolymerization on a glass substrate coated with an ITO layer; therefore we first examine glass and ITO nonlinear properties. Figure 21A shows the DFWM kinetics for a silica reference and a glass substrate measured at position “4” (Figure 18). Silica is a convenient reference material for measurements with
femtosecond pulses because its third-order nonlinear susceptibility $\chi^{(3)}_{\text{silica}} = 2.04 \times 10^{-22}$ m$^2$V$^{-2}$ (1.46×10$^{-14}$ esu) is independent of the wavelength and laser pulsewidth.\textsuperscript{66} The unknown third-order nonlinear susceptibility for glass, $\chi^{(3)}_{\text{glass}}$, is obtained from the amplitudes of the DFWM signals, $I_{\text{silica}}$ and $I_{\text{glass}}$, by using the following equation (correct in the case of a nonabsorbing sample):\textsuperscript{36}

$$|\chi^{(3)}_{\text{glass}}| = |\chi^{(3)}_{\text{silica}}| \sqrt{\frac{I_{\text{glass}}}{I_{\text{silica}}} \frac{l_{\text{silica}}}{l_{\text{glass}}} \frac{n_{\text{glass}}^2}{n_{\text{silica}}^2}}.$$  \hspace{1cm} (11)

where $l_{\text{silica}} = 1.0$ mm and $l_{\text{glass}} = 0.7$ mm are the optical path lengths in the two media, $n_{\text{silica}} = 1.46$ and $n_{\text{glass}} = 1.53$ are the linear refractive indices. Calculation yields $|\chi^{(3)}_{\text{glass}}| = 1.5 \times 10^{-22}$ m$^2$V$^{-2}$ (1.1×10$^{-14}$ esu). $\chi^{(3)}_{\text{silica}}$ is usually assumed to be real and positive because near-IR wavelengths are very far from one-, two-, and three-photon resonances for this material. Electronic states for glass are at similar energies as those for silica, therefore we assume that $\chi^{(3)}_{\text{glass}}$ also has only real and positive component, Re $\chi^{(3)}_{\text{glass}} = |\chi^{(3)}_{\text{glass}}| = 1.5 \times 10^{-22}$ m$^2$V$^{-2}$. 
Figure 21. DFWM kinetics measured at 1137 nm (8795 cm⁻¹).

A: signals measured at position “4” (Scheme I) for silica reference (■—■), glass substrate (●—●), and ITO/glass (▲—▲). B: signals measured at position “6” for glass substrate (●—●) and ITO/glass (■—■). Inset: ITO film nonlinear spectrum calculated from measurements at “6” position.

Next, we analyze the ITO nonlinear properties. The ITO signal 4 amplitude is very similar to glass signal 4 amplitude (Figure 21A), and determination of ITO’s nonlinear properties from measurement at position “4” is difficult. As described in Section 4.4, it is convenient to determine thin film nonlinear susceptibility of ITO, \( \chi^{(3)}_{\text{ITO}} \), from the phase-mismatched signal, \( I_{\text{ITO}} \) (measured at position “6”, Figure 18). As evident from Figure 21B, ITO’s signal “6” is significantly larger than the glass substrate’s signal. To calculate \( \chi^{(3)}_{\text{ITO}} \) according to a formula similar to Eq. (11), we would need to know the thickness of the ITO layer. Our several attempts to measure this thickness were not successful, therefore we only report \((\text{I}_{\text{ITO}}/\text{I}_{\text{silica}})^{0.5} = 0.11\) at 1137 nm. The ratio of susceptibilities is then \( |\chi^{(3)}_{\text{ITO}}/\chi^{(3)}_{\text{silica}}| = (\text{I}_{\text{ITO}}^{0.5}/\text{I}_{\text{silica}}^{0.5})(\text{I}_{\text{silica}}^{0.5}/\text{I}_{\text{ITO}}^{0.5})= 0.21 \text{I}_{\text{silica}}/\text{I}_{\text{ITO}} \). The inset in Figure
21B shows the \((I_{\text{ITO}}/I_{\text{silica}})^{0.5}\) spectrum at 920 – 1210 nm. Over this wavelength range, the ratio is approximately constant. Based on this result, we assume that \(\chi^{(3)}_{\text{ITO}}\) value does not change in the wavelength range of this study. From the analysis of the porphyrin film \(\chi^{(3)}_{\text{film}}\) spectrum, \(\chi^{(3)}_{\text{ITO}}\) was estimated to be \(-2 \times 10^{-20}\) m\(^2\)V\(^{-2}\) (see Section 4.6).

Figure 22. A: 1137 nm DFWM kinetics measured at position “6” for the porphyrin film (---) and the glass substrate (-----). B: Third order nonlinear susceptibility spectrum (---) at 760 – 1350 nm. For comparison, the linear absorption spectrum (----) of the porphyrin film is also shown.

4.7 The \(\chi^{(3)}\) properties of the porphyrin film

The DFWM kinetics measured at 1137 nm for a Fe\(^{3+}\) TPP film electropolymerized on a glass/ITO substrate are shown in Figure 22A. Both the porphyrin and ITO thin films contribute to this non-phase matched signal, but an analysis developed in Section 4.4 allows these contributions to be separated. In particular, the intensity of the porphyrin film
signal at 1137 nm is less than that of the ITO film (Figure 22B). This reduction is due to the interference between the ITO and porphyrin signals (a similar effect was reported for thermally evaporated fullerene C\textsubscript{60} films on CaF\textsubscript{2} substrates).\textsuperscript{39} The calculation for the \( \chi^{(3)} \)\textsubscript{film} is based on formula similar to Eq.\textsuperscript{(11)}, but the porphyrin film signal, \( I_{\text{porphyrin}} \), is compared to silica reference signal, \( I_{\text{silica}} \):

\[
\left| \chi^{(3)} \text{film} \right| = \left| \chi^{(3)} \text{silica} \right| \sqrt{\frac{I_{\text{porphyrin}}}{I_{\text{silica}}} \frac{I_{\text{silica}} n^2_{\text{porphyrin}}}{I_{\text{porphyrin}} n^2_{\text{silica}}}} \tag{12}
\]

Because \( n_{\text{porphyrin}} = 2.6 \)\textsuperscript{78} and \( I_{\text{porphyrin}} = 500 \) nm, \( \chi^{(3)} \)\textsubscript{film} = \( 8.0 \times 10^{-20} \) m\textsuperscript{2}V\textsuperscript{-2} (5.7\times10\textsuperscript{-12} esu) at 1137 nm.

In addition to the amplitudes, it is also important to consider the kinetics of the DFWM experiment. If excited states are formed following irradiation, much can be learned about the properties of the excited states and intermolecular interactions from these kinetics. On the other hand, for some nonlinear optical applications it is desirable to avoid formation of excited states, as absorption leads to attenuation of optical beams and can induce photochemical damage to the material. As evident from Figure 22A (also Figures 16A and B), all kinetics have FWHM \( \approx 125 \) fs, which is equal to the autocorrelation function width of the laser pulse. The DFWM kinetics of the porphyrin film shown in Figure 22A decay to \(<1%\) of initial amplitude in about 200 fs, which suggests that nonlinearities are purely electronic and nonresonant. Different results were obtained for Zn\textsuperscript{2+} porphyrin polymer films in experiments with ps pulses at 1064 nm, where residual amplitudes were significant.\textsuperscript{78} The use of lower energy (but higher peak power) fs pulses in our
experiments allows better characterization of porphyrin polymer films by eliminating resonant and thermal effects.

Signals at the “4” and “6” positions were measured between 760 – 1350 nm. Figure 22B shows the $\chi^{(3)}_{\text{film}}$ spectrum obtained from the measurements taken at position “6”. Because the signal amplitude of ITO is approximately constant in this wavelength range (inset in Figure 21B), the spectral features are due to the Fe$^{3+}$TPP film. The peak at $\sim$8700 cm$^{-1}$ ($\sim$1150 nm) is in the wavelength region with no one-photon absorption (the one-photon absorption spectrum is also shown in Figure 22B). The peak at 8700 cm$^{-1}$ may be related to a two-photon process. An analysis developed in Section 3.9 allows Re $\gamma$ and Im $\gamma$ of the Fe$^{3+}$TPP film to be determined. This analysis supports the assignment of the peak at 8700 cm$^{-1}$ to a two-photon absorption process.

Higher than third-order nonlinear optical effects (such as three photon absorption) have been observed for organic molecules at high excitation intensities, but we do not consider that higher order processes contribute significantly the nonlinear spectrum in Figure 22B.$^{90}$ DFWM signals had cubic dependence on the excitation intensity, which is characteristic of $\chi^{(3)}$ process. Higher order processes (for example, three photon absorption is described by $\chi^{(5)}$ nonlinear susceptibility) should have higher-order intensity dependence in DFWM experiments. In addition, absorption to the Soret band with the maximum at 436 nm (22936 cm$^{-1}$) cannot be achieved with three 8700 cm$^{-1}$ photons. Because the selection rules for one- and three-photon transitions are the same, three-photon transition energies usually well-match linear absorption peaks.$^{91}$ Therefore, we do not consider higher order processes when analyzing spectrum in Figure 22B.
Next, we consider the increase in $\chi^{(3)}_{\text{film}}$ values at $>11000$ cm$^{-1}$ (Figure 22B). The CT absorption band of Fe$^{3+}$TPP has a maximum at 14300 cm$^{-1}$ and a FWHM of 1020 cm$^{-1}$. Weak absorption can be observed down to 12500 cm$^{-1}$. Therefore, the larger $\chi^{(3)}_{\text{film}}$ values in this spectral region are related to resonance enhancement with this state. Rebane and coworkers have found that the two-photon absorption of metal-free porphyrins at $\sim 12500$ cm$^{-1}$ is enhanced due to: 1) near-resonance with the longest wavelength absorption band (Q(0,0) band in the case of metal-free porphyrins) and 2) two-photon (g symmetry) states at $\sim 26000$ cm$^{-1}$. Similar two-photon state energies for metal-free porphyrins were also predicted in computational experiments.\textsuperscript{34,35,68,84} We cannot rule out that $\chi^{(3)}_{\text{film}}$ at $>11000$ cm$^{-1}$ has contributions from similar two-photon states, however modeling shows that $\chi^{(3)}_{\text{film}}$ values in this spectral region can be well-approximated by only considering the resonant contribution from the CT state.

4.8 Porphyrin interactions in the electopolymerized film.

Electrosynthesis was previously used to prepare porphyrin films for electrochemical and optical studies.\textsuperscript{49,50,85} Murray and coworkers proposed that the formation of hydroxyphenyl porphyrin films is analogous to the electropolymerization of phenol.\textsuperscript{50} Starting from this assumption, Savenije et al. have investigated the mechanism of Zn$^{2+}$ tetrakis($p$-hydroxyphenyl)porphyrin film formation and proposed that an ether bond forms between adjacent porphyrins at the meta carbon of the phenyl ring.\textsuperscript{85} These workers also determined that the porphyrin macrocycle is not affected by the polymerization process. Our studies support this conclusion. The porphyrin film does not dissolve in acetonitrile, whereas porphyrin monomers are highly soluble in this solvent. From resonance Raman
and electronic absorption spectra (Figure 20) we find that iron porphyrin oxidation and spin states do not change during polymerization. Absorption bands broaden and shift significantly, indicating electronic interactions between the porphyrins; however, the Raman and UV-Vis data indicate that the porphyrin macrocycle is not affected by polymerization. While the porphyrins are linked by covalent bonds, DFWM data indicate that electronic coupling between adjacent porphyrins is not strong. It is well-known that phenyl groups substituted at porphyrin meso-positions form a dihedral angle with the porphyrin plane (≈60° in solution). This geometry reduces electronic coupling between porphyrins connected through meta phenyl linkages. The increase in electronic coupling is expected to yield large hyperpolarizability values, and electropolymerization of porphyrins with different linkers that do not include the phenyl groups may yield films with higher nonlinear susceptibilities. The current films provide an opportunity to investigate the effects of CT states on the nonlinear optical properties of TPP.

4.9 Real and imaginary components of $\chi^{(3)}$

The goal in this section is to separate porphyrin two-photon absorption ($\text{Im } \chi^{(3)}$) and nonlinear refraction ($\text{Re } \chi^{(3)}$) contributions to the spectrum shown in Figure 22B. We also take the Re $\chi^{(3)}$ of the ITO layer into account. We start by using a sum-over-states description for the molecular second hyperpolarizability. The general sum-over-states model is simplified by assuming that three states (ground state, one-photon and two-photon states) are required to describe the second hyperpolarizability of the porphyrin, $\kappa_{\text{porphyrin}}$. In this case, $\kappa_{\text{porphyrin}}$ is expressed as the sum of three terms, $\kappa_1$, $\kappa_2$, and $\kappa_3$.
\[ \gamma_{\text{porphyrin}} \propto \frac{M_{01}^2 \Delta \mu^2}{(\omega_1 - \omega - i\Gamma_1)^3} - \frac{M_{01}^4}{(\omega_2 - \omega - i\Gamma_2)^3} + \frac{M_{01}^2 M_{12}^2}{(\omega_2 - 2\omega - i\Gamma_2)(\omega_2 - 2\omega - 2i\Gamma_2)} = \gamma_I + \gamma_{II} + \gamma_{III} \quad (13) \]

Where \( \Delta \mu = \mu_{11} - \mu_{00} \) is dipole moment difference between the first excited and the ground state, \( M_{01} \) and \( M_{12} \) are the transition dipole moments for 0→1 and 1→2 transitions, \( \omega \) is frequency used in the experiment, \( \omega_1 \) and \( \omega_2 \) are frequencies derived from the excited state energies \( E_1 \) and \( E_2 \) (\( \omega_1 = E_1/\hbar \) and \( \omega_2 = E_2/\hbar \); \( \hbar \) is reduced Planck’s constant), and \( \Gamma_1 \) and \( \Gamma_2 \) are dephasing parameters that account for the linewidths. Porphyrin dipole moments in the ground and excited states are similar (typical porphyrin Stokes shifts are only several nm), and \( \Delta \mu \) is much smaller than \( M_{01} \) and \( M_{12} \). Therefore, in the first approximation \( \gamma \) can be neglected in the analysis and only \( \gamma_I \) and \( \gamma_{II} \) terms will be considered. Term \( \gamma_{III} \) describes resonant one-photon contribution to third-order nonlinearity. \( \gamma_{II} \) describes two-photon absorption (see inset in Figure 4). \( M_{01} \) can be obtained by integrating porphyrin absorption spectrum in the CT band region:

\[ M_{01} = \frac{1500(\hbar c)^2 \ln 10}{\pi N_A E_i} \int \alpha(\nu) d\nu \quad (14) \]

where \( N_A \) is Avogadro’s number, \( \alpha(\nu) \) is the extinction coefficient, \( c \) is the speed of light, and \( \nu \) is the wavenumber. Calculation yields \( M_{01} = 1.3 \text{ D} \) (4.3×10⁻²⁹ cm in SI units). \( M_{12} \) describes transition between the excited one-photon state and a two-photon state, and could be estimated using formula similar to Eq. (14) if excited state absorption extinction coefficients were known. In the visible spectral range, porphyrin excited state extinction coefficients have similar values as the ground state extinction coefficients.¹²,⁹³ We are not aware of Fe³⁺ TPP excited state extinction coefficient measurements at 1000 – 1500 nm
and will treat $M_{12}$ as an adjustable parameter in the analysis. The second unknown parameter in Eq. (13) is the energy of the two-photon state, $E_2$, $E_1 = 14300$ cm$^{-1}$ corresponds to the CT band in the linear absorption spectrum. For $\Gamma_1$ and $\Gamma_2$ we use 900 cm$^{-1}$, similar to the width of the CT absorption band. A bandwidth of this order corresponds to the electronic dephasing time of 10 fs ($T_2 = \hbar/\Gamma_0$), which is typical for porphyrins.$^{94}$

Assuming a random orientation of the porphyrins in the electropolymerized film, $\chi^{(3)}_{\text{porphyrin}}$ is related to $\gamma_{\text{porphyrin}}$ as:

$$\chi^{(3)}_{\text{porphyrin}} = Nf^4 \gamma_{\text{porphyrin}}$$

where $f$ is the local field factor, $f = (n^2 + 2)/3$; $f = 2.0$ based on $n = 2.0$ (refractive index value was determined for a spin-cast porphyrin polymer film$^{78}$). From Beer's law, molecular number density $N = 1000$ A $N_A/(\varepsilon l_{\text{porphyrin}})$, where $A$ is absorption at the maximum of the Q(0,1) band. $N = 6.2 \times 10^{26}$ molecules m$^{-3}$ based on $A = 0.64$ and $\varepsilon = 1.25 \times 10^4$ mol$^{-1}$ cm$^{-1}$ a 700 nm. Finally, total nonlinear susceptibility $\chi^{(3)}_{\text{film}}$ is:

$$\chi^{(3)}_{\text{film}} = \text{Re}(Nf^4 \gamma_{\text{porphyrin}} + \chi^{(3)}_{\text{MO}}) + iNf^4 \text{Im}(\gamma_{\text{porphyrin}})$$

(16)
Figure 23. The real (— —) and imaginary (———) components of the third-order nonlinear susceptibility (——) of the Fe$^{3+}$ TPP film.

The right axis shows the corresponding $\gamma_{\text{porphyrin}}$ values. Inset: Energy levels used in the simulation. The arrows illustrate $\gamma_{\text{II}}$ and $\gamma_{\text{III}}$ processes contributing to the third order nonlinearity (see Eq. (13)).

Eqs. (13) and (16) were used to simulate the experimental $\chi^{(3)}_{\text{film}}$ spectrum. The results of the simulation, the real, imaginary, and absolute values of $\chi^{(3)}_{\text{film}}$, are shown in Figure 23. The transition dipole moment $M_{12}$ was found to be 4.2 D. This value is similar to that of $M_{01}$. A value of $E_2 = 17400$ cm$^{-1}$ was determined for the two-photon state. The presence of a two-photon state is suggested by the $\chi^{(3)}_{\text{film}}$ spectrum. Variation of the other fitting parameters does not change the $E_2$ value. $\text{Re} \chi^{(3)}_{\text{ITO}}$ was found to be $-2 \times 10^{-20}$ m$^2$ V$^{-2}$.

4.10 Two-photon absorption in the Fe$^{3+}$ TPP film
From the $\text{Im } \gamma_{\text{porphyrin}}$ value, we can calculate the two-photon absorption cross section, $\delta$, using ($\varepsilon_0$ is electric constant):\textsuperscript{73}

$$\delta(\omega) = \frac{6\pi^2 \hbar}{\varepsilon_0 \hbar^2 \lambda^2} f^4 \text{Im } \gamma(-\omega, \omega, \omega, -\omega)$$

(17)

![Graph showing laser frequency and absorption spectrum](image)

**Figure 24.** Linear absorption spectrum (---) and two photon absorption spectrum (----) for Fe(III) porphyrin film ($\delta$ is reported in GM; 1 GM = $1 \times 10^{-50}$ m$^4$s).

The one- and two-photon absorption spectra are compared in Figure 24. The frequency axis of the two-photon spectrum (top axis) is divided by 2 because the energies of two photons are added in a two-photon transition. This graph can be used to evaluate two-photon absorption when laser frequency is tuned between 6000 - 11000 cm$^{-1}$ (1660 - 900 nm). This graph shows that the two-photon absorption band overlaps the weak Q(0,0) band in the one-photon spectrum (also see Figure 20).
We first consider if the two-photon absorption is enhanced due to overlap with Q(0,0) band. Because metal porphyrins have D_{4h} symmetry, the electronic ground state of the porphyrin g parity. One-photon absorption corresponds to an allowed electronic transition from a g parity ground state to a u parity excited state. Two-photon absorption is allowed for an electronic transition from the g parity ground state to an excited state with g parity. Therefore, two-photon absorption to the Q(0,0) band is not allowed for TPP. However, phenyl rotation or intramolecular interactions can reduce the molecule’s symmetry and make two-photon absorption to the Q band a weakly allowed process. Kruk et al. have proposed that this effect is more significant for the Q(0,1) band because this band has contributions from molecular vibrations. This reduction in symmetry changes the parity of vibrational wavefunctions.\textsuperscript{16} We observe strong two-photon absorption at energies close to the purely electronic Q(0,0) band region but not in the vibrational/electronic Q(0,1) band spectral region. Therefore, symmetry changes due to molecular distortions are not the origin of the peak in the \( \chi^{(3)}_{\text{film}} \) spectrum, and different origin of the two-photon absorption peak should be considered.

Next, we consider if the \( \pi\pi^* \) two-photon states of the porphyrin macrocycle could explain the peak in \( \chi^{(3)}_{\text{film}} \) spectrum. Two-photon states for several porphyrins have been investigated at different levels of theory.\textsuperscript{34,35,68,84} Calculations have not been performed on Fe\textsuperscript{3+} porphyrins. The lowest energy two-photon states of Metal-free,\textsuperscript{34,68} Zn\textsuperscript{2+},\textsuperscript{84} and Mg\textsuperscript{2+}\textsuperscript{35} were found at 30000 - 33000 cm\textsuperscript{-1}. This places these allowed transitions in the Soret region of the spectrum. Electronic interaction between adjacent porphyrin macrocycles can lower the energies of the two-photon states, but these interactions also
lead to significant changes in the one-photon spectrum. The one-photon spectrum of the Fe$^{3+}$ TPP film is similar to the spectrum of 1 in solution (Figure 20). Based on this similarity, it is unlikely that the energy of $\pi\pi^*$ two-photon states could go from $\sim$30000 cm$^{-1}$ to 17400 cm$^{-1}$.

The two-photon spectrum of 1 is different from that of a metal-free porphyrin (as well from spectra of other metal-free tetrapyrrloic compounds).$^{15}$ Overlap with the Q(0,0) band and transitions to a $\pi\pi^*$ two-photon state cannot explain this difference, we speculate that 17400 cm$^{-1}$ state is likely to be a charge transfer state. It would be interesting to examine such assignment in calculations. An alternative explanation would involve intermolecular charge transfer and excimer formation.

Karotki et al. have found that $\delta = 1 - 6$ GM for a metal-free tetraphenyl porphyrin from 1100 - 1400 nm.$^{15}$ In the zero-frequency (low energy) limit, similar $\delta$ value can be extrapolated for 1 (Figures 14 and 15). In the near-IR region, the $\delta$ of 1 is significantly higher ($\delta_{\text{max}} = 82$ GM at 1150 nm) than a metal-free porphyrin. We attribute this enhancement to resonance with a two-photon CT state. Several molecular design strategies have been developed increase the two-photon absorption cross section of the porphyrin macrocycle. These approaches include substitution with donor/acceptor groups,$^{13}$ porphyrin self-assembly,$^{27}$ as well as a more general use of donor and acceptor motifs.$^{17,95}$ Data for 1 demonstrates that transition metal two-photon states can also be important in optimizing $\delta$ values in organic materials.

4.11 Nonlinear refraction in Fe$^{3+}$ TPP films
The real component of the nonlinear susceptibility, $\text{Re } \chi^{(3)}(-\omega, \omega, \omega, -\omega)$, that is measured in the DFWM experiment is related to optical switching and other applications based on changes in the nonlinear index of refraction. This paper appears to be the first report of the $\text{Re } \chi^{(3)}(-\omega, \omega, \omega, -\omega)$ spectrum of TPP in the near-IR spectral region. Previous nonresonant studies were carried out at a single wavelength of 1064 nm$^{21,24,77,78}$ or ~800 nm.$^{28,30}$

As shown in Figure 19, the Fe$^{3+}$ TPP film has a negative $\text{Re } \chi^{(3)}_{\text{film}}$ over a broad spectral range. The molecular hyperpolarizability is $\gamma_{\text{porphyrin}} = -5 \times 10^{-48}$ m$^2$V$^{-2}$ at 9000 – 13000 cm$^{-1}$. According to Eq. (11), $\text{Re } \gamma_{\text{porphyrin}}$ is negative when the photon energy is higher than $E_2/2$ ($2\hbar\omega > E_2$). Organic materials for nonlinear optics that have a $\text{Re } \chi^{(3)} < 0$ are not common$^{96}$, but this property is potentially important because laser light is defocused in these materials. This defocusing protects the material from optical damage (in contrast, materials with positive $\text{Re } \chi^{(3)}$ focus light).

Metal-free and Zn$^{2+}$ porphyrins also have negative $\text{Re } \gamma$ values at 1064 nm$^{21,77}$ and 800 nm.$^{30}$ This sign was accounted for by invoking contributions from two-photon states. Because the two-photon absorption spectrum of metal-free TPP is different from Fe$^{3+}$ TPP (see previous section), different two-photon states must be relevant for metal-free and Zn$^{2+}$ porphyrin $\chi^{(3)}$ frequency dispersion in the near-IR spectral range. Detailed studies of other organic materials have shown that more than three states could be required to explain $\chi^{(3)}$ frequency dispersion.$^{97}$ Measurements of $\chi^{(3)}$ spectra for other porphyrins would show if this is the case for tetrapyrrolic compounds.
4.12 Conclusions

We report detailed femtosecond DFWM studies on electropolymerized Fe$^{3+}$ TPP films, and we find that the frequency dependence of $\chi^{(3)}_{\text{film}}$ and $\gamma_{\text{porphyrin}}$ in near-IR are well described by a three-level model. An increase in the nonlinear coefficients at $\sim$800 nm is attributed to the near-resonance enhancement in the CT band; these characteristics are similar to other porphyrins. In addition, a two-photon state at 17400 cm$^{-1}$ was identified. This type of transition has not been observed for metal-free tetrapyrrolic compounds; therefore it is attributed to CT transitions. Due to the resonance with the two-photon state, $\chi^{(3)}_{\text{film}}$ increased more than 10 times when compared to values in the long-wavelength limit. The time response of the third-order nonlinearity in porphyrin films is faster than 120 fs.
5. Charge Transfer Enhances Two-Photon Absorption in Transition Metal Porphyrins$^{61}$

Porphyrin-based materials are promising for applications that require strong two-photon absorption$^{24,27,91}$ like fluorescence microscopy, photodynamic therapy using two-photon excitation, 3D microfabrication, and sensor protection$^{24,27,91}$. Enhancement of the optical properties that determine the efficiency of two-photon absorption (molecular second hyperpolarizability, $\gamma$ and two-photon absorption cross-section, $\delta$) has been achieved through modifications to the $\pi$-network of the porphyrin macrocycle$^{24,27,91}$. In this report, we consider the effect of transition metal ions on the $\gamma$ and $\delta$ values of the porphyrin macrocycle.$^{25,30}$ We show that metalloporphyrins with strong charge transfer (CT) transitions in their one-photon absorption spectra have $\delta$ values that are an order of magnitude larger than those of the free base porphyrin. We attribute this effect to CT transitions between the metal ion’s $d$ orbitals and the $\pi$–system of the porphyrin.
Electro-polymerized thin films of Fe$^{3+}$, Mn$^{3+}$, and Co$^{2+}$ 5,10,15,20-tetra-kis-(4-hydroxytetraphenyl)porphyrins (TPP) were studied. Because these metalloporphyrins have low emission yields, degenerate four wave mixing (DFMW) experiments with 100 fs laser pulses were used to determine $\gamma$ and $\delta$. Details of the film preparation and optical studies are discussed in the 3.6 and 3.7.

![Figure 25. A) One-photon absorption spectrum of Mn$^{3+}$ (---), Fe$^{3+}$ (--), and Co$^{2+}$ (----) TPP. B) Molecular orbital diagram for Mn$^{3+}$ and Fe$^{3+}$ TPP. Metal orbitals are shown in red. Adapted from references 11-13](image)

The absorption spectra of Fe$^{3+}$, Mn$^{3+}$, and Co$^{2+}$ TPP are shown in Figure 25A. Gouterman’s four orbital model ($a_{1u}, a_{2u}$ HOMO and $e_g$ LUMO, Figure 25B) qualitatively explains the origin of the porphyrin’s B and Q bands. For Fe$^{3+}$ and Mn$^{3+}$ TPP, mixing of the metal $d$ and macrocycle $\pi$–orbitals leads to additional peaks in the absorption spectrum. For Fe$^{3+}$ TPP, these CT transitions involve the $\pi (a_{1u}, a_{2u})$ orbitals of the macrocycle and the metal ion’s $d_\pi$ orbitals ($\pi \rightarrow d_\pi$). For Mn$^{3+}$ TPP, the CT bands include the $\pi (b_{2u}) \rightarrow d_\pi (\lambda_{max} = 482 \text{ nm})$ and $\pi (a_{1u}, a_{2u}) \rightarrow d_\sigma (\lambda_{max} = 638 \text{ nm})$ transitions. These CT transitions are allowed as they occur between electronic states of opposite symmetry ($g \rightarrow u$). The absence of similar CT bands in the Co$^{2+}$ TPP absorption spectrum suggests that
the mixing of the Co$^{2+}$ ion's $d$ orbitals with the macrocycle's $\pi$-system is less efficient. This difference in the mixing of the metal ion and macrocycle orbitals allows the role of these interactions on the two-photon absorption spectrum to be investigated by comparing the nonlinear optical properties of Co$^{2+}$ TPP and Mn$^{3+}$/Fe$^{3+}$ TPP.

The metalloporphyrin's $\gamma$ spectra are shown in Figure 26. Peaks are observed in the near-IR region of the $\gamma$ spectra at $\sim$1150 nm for Fe$^{3+}$ TPP and $\sim$1250 nm for Mn$^{3+}$ TPP. The Co$^{2+}$ TPP $\gamma$ spectrum does not have this feature. The molecular orbital model shown in Figure 25B suggests that the peaks in the $\gamma$ spectra could be related to two-photon transitions between metal $d$ and macrocycle $\pi^*$ orbitals. As both orbitals have $g$ symmetry, two-photon transitions are allowed. In contrast, one-photon transitions between these orbitals are forbidden and are not seen in the absorption spectra in Figure 25A.
The solid lines are fitting results according to Eq. 18. The two-photon component (Im $\gamma$, ---) is also shown.

A sum-over-states model was used to estimate the two-photon state energies and dipole moments. A three-state model (ground, one- and two-photon excited states) was previously applied to porphyrin materials: $^{21}$

$$\gamma \propto \frac{M_{01}^4}{(\omega_1 - \omega - i\Gamma)^3} + \frac{M_{01}^2 M_{12}^2}{(\omega_1 - \omega - i\Gamma)^2 (\omega_2 - 2\omega - i\Gamma)}$$ (18)

where $M_{01}$ and $M_{12}$ are the transition dipole moments for the $0\rightarrow1$ and $1\rightarrow2$ transitions, $\omega$ is the experimental frequency, $\omega_1$ and $\omega_2$ are frequencies derived from the excited state energies $E_1$ and $E_2$ ($\omega_1=E_1/h$ and $\omega_2=E_2/h$; $h$ is the reduced Planck’s constant). Parameter $\Gamma$ accounts for the linewidths. Analysis of the $\gamma$ spectra yields the $M_{12}$, $E_2$, and $\Gamma$ values (Table 1; $E_1$ and $M_{01}$ were obtained from absorption spectra in Figure 25A). As suggested by the $\gamma$ spectra in Figure 26, the Fe$^{3+}$ TPP two-photon state has a higher energy than that of Mn$^{3+}$ TPP. Both porphyrins have $M_{12}$ values of 4.2 Debye (D).
Table 1. Linear and nonlinear spectroscopic properties of the metalloporphyrin films.

<table>
<thead>
<tr>
<th></th>
<th>$M_{01}$,a (D)</th>
<th>$M_{12}$,b (D)</th>
<th>$E_1$,a (cm$^{-1}$)</th>
<th>$E_2$,b (cm$^{-1}$)</th>
<th>$\Gamma$,a (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$^{3+}$</td>
<td>3.85</td>
<td>4.2</td>
<td>15686</td>
<td>16050</td>
<td>1150</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>1.3</td>
<td>4.2</td>
<td>14300</td>
<td>17400</td>
<td>900</td>
</tr>
</tbody>
</table>

a) The errors are ± 3.5% in these values, b) ± 10% error.

To determine the effect of the metalloporphyrin two-photon states on the two-photon absorption cross-section, $\delta$, we consider the imaginary component of hyperpolarizability, $\text{Im} \gamma$. The cross-section $\delta$ can be obtained from

$$\delta = \frac{6 \pi^2 \hbar}{\varepsilon_0 n^2 \lambda^4} \text{Im} \gamma \quad (19)$$

where $\varepsilon_0$ is the electric constant, $n$ is the index of refraction, and $\lambda$ is the wavelength. Application of Eq. (19) to the $\text{Im} \gamma$ data yields $\delta_{\text{max}} = 82$ GM for Fe$^{3+}$ TPP and $\delta_{\text{max}} = 164$ GM for Mn$^{3+}$ TPP (Figure 26; 1 GM = 1×10$^{-50}$ cm$^4$s$^{-1}$). The difference in $\delta_{\text{max}}$ values can be attributed to the increase in the transition dipole moment, $M_{01}$, of Mn$^{3+}$ TPP over that of Fe$^{3+}$ TPP. For metal-free TPP, $\delta < 10$ GM in the spectral range of our experiments. Therefore, Mn$^{3+}$ and Fe$^{3+}$ ions enhance two-photon absorption intensity of TPP by at least an order of magnitude.
Figure 27. One- (→) and two-photon (←) spectra of Mn$^{3+}$ TPP (black) and Fe$^{3+}$ TPP (red).

A comparison of the one- and two-photon spectra (Figure 27, the energy scale in the upper axis reflects a two photon process) offers further support for the assignment of the two-photon absorption bands (dashed lines) to intramolecular charge transfer. The two-photon transitions do not originate in the π network of the macrocycle, as they are not allowed by the selection rules. If the selection rules for the two photon processes are relaxed due to symmetry breaking from distortion of the macrocycle in the solid state, two-photon absorption would be stronger into the vibronic Q(0,1) band than into the purely electronic Q(0,0) band.\textsuperscript{15,15} Our results show the opposite trend: two-photon absorption is stronger into the region of the Q(0,0) band than into that of the Q(0,1) band. Additionally, the porphyrin macrocycle’s two-photon states were predicted to have much higher energies than those observed in our experiments.\textsuperscript{34,35,68,84}

Shifts in the energies of the two-photon states, $E_2$, suggest which molecular orbitals give rise to the two-photon CT transitions. For Fe$^{3+}$ and Mn$^{3+}$ TPP, the metal $d_{xy}$, $d_{yz}$, and $d_{z^2}$ orbitals are in the HOMO/LUMO gap of the macrocycle’s π orbitals. The Fe$^{3+}$ ion’s $d_{xy}$
orbital is very close in energy to the $a_{1u}, a_{2u}$ orbitals, and the Fe$^{3+}$ TPP two-photon state energy determined in our experiments is very close in energy to the Q(0,0) state. This suggests involvement of the $d_{xy}$ orbital in the two-photon transition, $d_{xy} \rightarrow \pi^*$. For the Mn$^{3+}$ ion, the $d_{xy}$ orbital is at a higher energy than the macrocycle’s $a_{1u}, a_{2u}$ orbitals. If the two-photon transition originates from the $d_{xy}$ orbital, the Mn$^{3+}$ TPP state will be at a lower energy than that observed for Fe$^{3+}$ TPP. The experimental results agree with this prediction (Table 2 and Figure 27). Definite assignment of the molecular orbitals involved in the two-photon transition will require quantum chemical computations to determine the molecular excited states. These studies are difficult for transition metal complexes with an unfilled d electron shells.

While the Co$^{2+}$ $d_{xy}$ orbital is at an energy similar to those of the Mn$^{3+}$ and Fe$^{3+}$ ions, we did not observe CT transitions in Co$^{2+}$ TPP $\gamma$ spectra. The much weaker transition dipole moment, $M_{01}$, of this metalloporphyrin could account for this result. While the CT absorption bands have $\varepsilon = 2300$ M$^{-1}$ cm$^{-1}$ for Fe$^{3+}$ TPP and $\varepsilon = 10000$ M$^{-1}$ cm$^{-1}$ for Mn$^{3+}$ TPP, the corresponding extinction coefficient of Co$^{2+}$ TPP was only $\varepsilon \approx 75$ M$^{-1}$ cm$^{-1}$. The small $\varepsilon$ value implies that the $M_{01}$ of Co$^{2+}$ TPP is too small to promote amplification of the two-photon processes. The two-photon absorption enhancement in linear conjugated oligomers is also dependent on $M_{01}$.

In summary, Fe$^{3+}$ and Mn$^{3+}$ ions enhance the second hyperpolarizability, $\chi$ and two-photon absorption cross-section, $\delta$, of transition metal porphyrins by at least an order of magnitude. The enhancement is dependent on the one-photon transition dipole moment. A
two-photon $d_{xy} \rightarrow \pi^*$ charge transfer transition was observed for Fe$^{3+}$ and Mn$^{3+}$ tetraphenyl porphyrins for the first time. The order of magnitude enhancement induced by this transition suggests a new approach to enhance the nonlinear optical properties of porphyrin materials.
6. Second Hyperpolarizability of Ethynyl Linked Azobenzene Molecular Wires

Optical switching, \textsuperscript{103} optical limiting, \textsuperscript{104} 3-D microfabrication and two-photon microscopy\textsuperscript{28} all require materials with a large third-order optical nonlinearity. Conjugated organic materials have long been a focus of this research due to their extended \( \pi \) network and synthetic flexibility. An important structure-function parameter of these materials is the increase in second hyperpolarizability, \( \gamma \), upon extension of the conjugated backbone. In conjugated oligomers, the evolution of \( \gamma \) is often described using a power law, \( \gamma = \gamma_m n^\alpha \), where \( \gamma_m \) is the second hyperpolarizability of the monomer unit, \( n \) is the number of repeat units, and \( \alpha \) is a constant. The scaling behavior of conjugated systems have been studied experimentally and theoretically.\textsuperscript{105} The resultant power laws typically apply to the first several members of an oligomer series. As more repeat units are added, the power law enhancement of \( \gamma (\alpha > 1) \) saturates, and \( \gamma / n \) becomes independent of \( n \) (\( \alpha = 1 \)) because of the existence of the proper thermodynamic limit.\textsuperscript{105} For one-dimensional molecular wires, the saturation length is typically reached after about 60 conjugated bonds, which correspond to molecular lengths of \(<10 \text{ nm} \).\textsuperscript{23,106,107}
One-dimensional molecular wires are essentially extended π networks of widely studied chromophores like stilbene (PPV) or tolane (PPE).\textsuperscript{108} In this letter, we describe the effect of incorporating another widely studied chromophore, azobenzene, into extended molecular wires. For conjugated azo oligomers, nonlinear enhancement of γ is observed at unprecedented molecular lengths.

![Figure 28: Structure of the azobenzene-ethynyl repeat unit](image)

To determine the length dependence of the second hyperpolarizability, a series of oligomers were synthesized using Pd-catalyzed cross coupling.\textsuperscript{109} Alkoxy groups have been added to the azobenzene units to improve the solubility of the oligomers. A complete synthetic scheme is available in Appendix 2. The resulting oligomers have a rigid conjugated backbone that is essential for nonlinear optical applications.
**Figure 29:** UV/vis spectra and linear extinction coefficients for oligomers $n=4$ (—), $n=9$ (——), $n=27$ (—), and $n=36$ (——).

The absorption spectra of the oligomers are shown in Figure 29. The absorption spectra indicate strong electronic coupling between azobenzene chromophores. As was previously reported for other poly azo compounds,$^{10,11}$ the extinction coefficient increases linearly upon elongation of the conjugated backbone. The oligomers also show a bathochromic (red) shift as more repeat units are added. For example, $\lambda_{\text{max}}=460$ nm for $n=9$, $\lambda_{\text{max}}=487$ nm for $n=27$, and $\lambda_{\text{max}}=496$ nm for $n=36$. The evolution of the bathochromic shift with increasing conjugation length can also be described by a power law; for the azo oligomers $\lambda_{\text{max}}=n^{0.053\pm0.001}$. Typically, $\lambda_{\text{max}}$ increases linearly with $n$. $^{112}$ The smaller exponent for the azo oligomers is a consequence of the unusually small bathochromic shift (36 nm over 27 repeat units). The small bathochromic shift ensures the optical transparency that is required for nonresonant nonlinear optical applications, and suggests that the energies of the electronic excited states do not vary significantly over the range of our oligomers.

There is no evidence for saturation of the bathochromatic shift for oligomers $n<36$. This contrasts with a series of phenylethynyl oligomers, where the red-shift was found to saturate after approximately 27 repeat units.$^{113}$ Due to the close structural similarity between phenylethynyl oligomers and the azo oligomers studied here, the extension of the effective conjugation length most likely results from inclusion of the azo functionality in the conjugated backbone.

The $\gamma$ values were determined using degenerate four wave mixing (DFWM) at 780 nm with 100 fs laser pulses.$^{62}$ The oligomers were studied in THF solutions and neat THF was
used as a reference ($\chi^{(3)}_{\text{THF}}=1.4\times10^{-22}$ m$^2$V$^{-2}$).\textsuperscript{62,112} The length dependence of the second hyperpolarizability for oligomers $n=1$-150 is summarized in Figure 30.

To determine oligomer second hyperpolarizability, $\chi$, we used a method described in the literature.\textsuperscript{36} Briefly, a comparison of solution and solvent $\chi^{(3)}$ yields

$$|\chi^{(3)}_{\text{solution}}| = \sqrt{\frac{I_{\text{solution}}}{I_{\text{THF}}}} \times |\chi^{(3)}_{\text{THF}}|$$  

(20)

where $I_{\text{solution}}$ and $I_{\text{THF}}$ are DFWM signals measured for solution and THF reference. This $|\chi^{(3)}_{\text{solution}}|$ value is used in equation (21) to find $|\gamma|

$$|\gamma| = \frac{|\chi^{(3)}_{\text{solution}}| - |\chi^{(3)}_{\text{THF}}|}{Nf^4}$$  

(21)

where $N$ is the number molecular density (measured in molecules per cm$^3$), $f = (n^2 + 2)/3$ (n is refractive index, n = 1.407 for THF), and $\chi^{(3)}_{\text{THF}} = 1.4\times10^{-22}$ m$^2$ V$^{-2}$.\textsuperscript{62,112}

To confirm this approach, $|\chi^{(3)}_{\text{solution}}|$ concentration dependence was measured and analyzed using equation (22)

$$|\chi^{(3)}_{\text{solution}}| = \left( |f^4 N_{\text{solute}} \Re \gamma_{\text{solute}} + \chi^{(3)}_{\text{solute}}|^2 + |f^4 N_{\text{solute}} \Im \gamma_{\text{solute}}|^2 \right)^{1/2}$$  

(22)

The representative concentration dependence data for the $n = 27$ oligomer is shown in Figure 30. Nonlinear least squares fitting using equation (22) yields $\gamma = (2.4\pm0.2)\times10^{-46}$ m$^5$V$^{-2}$ and $\Im \gamma = 0.0\pm0.0$ m$^5$V$^{-2}$. This result is in good agreement with the values obtained using Eqs. (20) and (21) ($|\gamma| = (2.31\pm0.19)\times10^{-46}$ m$^5$V$^{-2}$).
Figure 30. Nonlinear susceptibility $\chi^{(3)}$ concentration dependence for oligomer $n=27$ (THF solution).

The line is a fit to equation (22) with Re $\gamma = 2.4\times10^{-46}$ m$^5$V$^{-2}$ and Im $\gamma = 0$ m$^5$V$^{-2}$.

Previously, we have shown that, for oligomer $n=55$, the third-order nonlinearity is electronic, and we have determined the two-photon absorption coefficient and a nonlinear change in the index of refraction for this compound.\textsuperscript{62}
Figure 31: The second molecular hyperpolarizability, $\gamma$, increases according to the power law $\gamma = n^{2.12 \pm 0.05}$ for azo oligomers $n=2-36$.

As shown in Figure 31, for oligomers $n = 2 - 36$, the hyperpolarizability $\gamma$ data could be described using a power law of $\gamma = \gamma_0 n^{2.12 \pm 0.05}$ m$^2$V$^{-2}$. The small $\gamma$ increase for the monomer $n=1$ can be attributed to the end group contribution, while $n=55$ and $n=150$ oligomers deviate from this power law due to the expected saturation effects.$^{23,106,107}$ The most important finding of this study is the exceptional range of molecular lengths, $n = 2 - 36$, that show a stronger than quadratic increase in $\gamma$ (and bathochromic absorption shifts). The molecular length in this series of oligomers reaches $\approx 49$ nm, and the longest oligomer consists of $>360$ conjugated bonds. This is a significant improvement over the scaling behavior of other molecular wires. For instance, poly(triacetylene) oligomers and oligothiienylthienylenes both showed saturation around 60 conjugated bonds.$^{23,106,107}$
This corresponds to an effective conjugation length of 7.5 nm for the poly(triacetylene) series.\textsuperscript{23}

The increasing azo oligomer length from $n = 1$ to $n = 36$ leads to $>2000$ times amplification of $\gamma$. Calculated per repeat unit, hyperpolarizability increases $\approx 27$ times when comparing $n = 1$ and $n = 36$ oligomers: $\gamma_{36}/36 = 127 \times 10^{-49}$ m$^5$V$^{-2}$, while $\gamma_1 = 4.7 \times 10^{-49}$ m$^5$V$^{-2}$. The estimated $\gamma_m = 2 \times 10^{-49}$ m$^5$V$^{-2}$ is typical for small organic molecules, including DRI azo dyes that are often used in photonics applications.\textsuperscript{62}

The extraordinarily long effective conjugation length of the azo oligomer could be a result of the rigid structure of the backbone. The oligomers do not have obvious points of conformational flexibility. Cis-trans isomerization around the azo bond of azobenzene moieties is a widely studied process that could potentially have an influence on the $\pi$ network.\textsuperscript{114} We see no evidence of this isomerization in the linear absorption spectra of the oligomers. The same observation was made for other conjugated polymers with azobenzene in the backbone.\textsuperscript{115} Phenyl group rotation could also break conjugation. While the phenyl groups can rotate at room temperature in PPE,\textsuperscript{116} the influence of the azo group on the threshold for phenyl ring rotation, and hence its impact on conjugation, is not known. Our results suggest that the azo group enhances conjugation through the backbone.

The length dependence of hyperpolarizability $\gamma$ was studied experimentally and theoretically for several organic compounds in order to determine the value of exponent $\alpha$ and the molecular length at which $\gamma$ approaches its thermodynamic limit (at the thermodynamic limit, properties begin to scale linearly with an increase in molecular size).\textsuperscript{23,105-107,117} Theoretical studies have shown that the saturation length of the
hyperpolarizability is directly related to the exciton coherence size in conjugated oligomers. Therefore, the exciton delocalization length in the conjugated ethynyl-linked azobenzene oligomers is exceptionally large, and these oligomers exhibit molecular wire characteristics at molecular lengths up to 50 nm. The values of exponent $a$ predicted in theoretical studies are higher ($a = 3 - 5$) than that observed for our oligomers. However, exponent $a = 2.12 \pm 0.05$ is similar to values found for other conjugated oligomers: $a = 2.5$ for polyenes, $a = 2.46-2.64$ for poly(triacetylenes), and $a = 2.4$ for oligothiophenylenevinylene. The similarity of the exponent $a$ value found here to those describing other conjugated systems is somewhat unexpected given the much smaller linear absorption bathochromic shifts for the azo oligomers. This result suggests that the extent of electron delocalization could be different in the electronic states that define the linear and nonlinear optical properties of azo oligomers.

Figure 32: DFWM kinetics for $n=27$ oligomer solution in THF (concentration 317 $\mu$M, ■) and for THF reference (▲).
Polarizations of all optical beams used in experiment were vertical. The solid lines are Gaussian fits to the data with widths (FWHM) equal to 128 fs.

Next, we consider if direct excitation into excited states contributes to the nonresonant hyperpolarizability \( \gamma \). The DFWM experiments were carried out different excitation intensities (the optical signals had an expected cubic dependence on the excitation intensity) and at different oligomer concentrations. A representative DFWM kinetics trace for the \( n=27 \) oligomer and the THF reference is shown in Figure 32. The THF reference and oligomer solution data can be fitted with a Gaussian function having the same width (full width at half magnitude, FWHM = 128 fs). In the case of resonant excitation, which could occur by one-photon or two-photon absorption leading to excited state formation, DFWM kinetics would have a different, slower decaying, temporal profile.\(^{62} \) The ultrafast, excitation pulse limited, DFWM kinetics indicate that resonant processes do not contribute to the DFWM signals.

No one-photon absorption is expected at 780 nm based on the oligomer linear absorption spectra. The DFWM kinetics in Figure 32 indicate that two photon absorption at 780 nm is also negligible (the same conclusion is obtained from the excitation intensity dependence and concentration dependence studies, see Appendix 3). Similar results were obtained in open-aperture Z-scan experiments on symmetric azobenzene compounds.\(^{118} \) The Z-scan experiments directly probe two-photon absorption.\(^{118} \) For symmetric azobenzene compounds, the two-photon cross sections vary by less than 20 % at 730 - 1000 nm.\(^ {118} \)

The absence of excited state decay tails in the DFWM signals also indicates that two-photon absorption is forbidden (in the dipole approximation) into the azo oligomer
electronic excited states with one photon absorption at 390 nm. Different one and two photon absorption properties indicate that the symmetries of the oligomer frontier orbitals are determined by the symmetry of the conjugated backbone. The conjugated ethynyl azobenzene backbone has $C_{2v}$ symmetry, and its electronic states will have either $g$ or $u$ symmetry. Two photon absorption is only allowed between states with the same parity ($g \rightarrow g$ or $u \rightarrow u$), while one photon absorption can only occur between states with the opposite symmetry ($g \rightarrow u$). Therefore, although absorption at 390 nm is strong in the one photon spectrum (extinction coefficient $\sim 10^4$ Lmol$^{-1}$cm$^{-1}$), absorption of two 780 nm photons is not allowed by the selection rules. This is consistent with our finding that for all of the oligomers the real component of $\chi$, Re $\chi$, is much larger than the imaginary component, Im $\chi$. As Re $\gamma$ reflects nonlinear refraction and Im $\gamma$ can be related to two-photon absorption, theazo oligomers studied here primarily have refractive nonlinearities at 780 nm. As such, resonance effects do not contribute to the quadratic enhancement of $\gamma$.

In summary, we have found that the rigid conjugated backbone of ethynyl linked azobenzenes results in an exceptionally long effective conjugation length of more than 36 repeat units (49 nm). This result suggests that the incorporation of azo functional groups and alkynyl linkages into organic optical materials may result in dramatically improved performance in nonlinear optical applications.
7. Summary

The potential of applications that take advantage of third-order nonlinear optical processes has resulted in efforts to optimize the nonlinear index of refraction, $n_2$, or two-photon absorption cross section, $\delta$, of organic molecules and materials. A number of strategies to increase the nonlinear response of these materials have been developed as a result of this research. Extension of the conjugation length, the addition of electron donating and/or accepting groups, and the arrangement of electron rich or deficient groups in a conjugated system are well-developed approaches to developing organic materials with large nonlinear optical coefficients.$^{17,95}$ Recently, additional approaches like supramolecular assembly,$^{24,27,28}$ aggregation,$^{119}$ and the use of metal ions$^{25}$ have been introduced as means to amplify $n_2$ or $\delta$. The projects discussed in this dissertation aid in the continuing development of these approaches to the design of nonlinear optical materials. The work on azobenzene molecular wires discussed in Chapter 5 contributes to the established strategy of extending the conjugation length to enhance the response of nonlinear materials, and Chapters 3 and 4 offer new insight into how metal ions can be incorporated into the design paradigms developed in the last decade.
The application of nonlinear technologies to telecommunications or computing will require solid state materials. This presents an experimental difficulty to organic materials as these materials are usually incorporated into device components as thin films supported on thick substrates. The work in Chapter 2 describes an experimental technique that can be used to overcome this limitation. This chapter describes how a standard degenerate four wave mixing (DFWM) experiment can be modified to measure the nonlinear optical properties of thin films on thick substrates. The modified DFWM experiment is based on the difference in the phase-matching properties of thin films and thick substrates. Only a single DFWM signal is fully phase-matched for the substrate, but, because the phase-matching rules are relaxed for the thin film, there are multiple phase-matched signals for the thin film. Because the substrate contributions to these signals are very small, the nonlinear optical properties of the thin film can be determined from them. Careful selection of the beam angle allows for optimal reduction of the glass substrate signal for experiments performed at a particular wavelength. The experiment is described in greater detail in section 3.4.

Our refinement of this method allowed the third-order susceptibility, $\chi^{(3)}$, of indium tin oxide (ITO), an important material in a number of optical technologies, to be measured in the near-IR region of the spectrum that is used in telecommunications. This is the first report of $\chi^{(3)}$ for ITO. The nonlinear response was found to be nonresonant from 900 – 1300 nm (Figure 16) with a value of $\chi^{(3)}_{\text{ITO}} = (2.16 \pm 0.18) \times 10^{-18} \text{ m}^2 \text{ V}^{-2}$. A resonant enhancement begins to appear around 1350 nm with an increase of $\chi^{(3)}_{\text{ITO}} = (3.36 \pm 0.28) \times 10^{-18} \text{ m}^2 \text{ V}^{-2}$ at 1500 nm. By comparing the $\chi^{(3)}_{\text{ITO}}$ data to the absorption spectrum of ITO
at the laser wavelength used in the DFWM experiment (one-photon enhancement) and at
wavelengths twice as energetic as the laser photons (two-photon enhancement), it was
determined that the enhancement was due to two-photon resonance with the plasmons of
ITO (Figure 16).

Relaxation dynamics were also observed in the DFWM data (Figures 12 A – C).
Deconvolution of a Gaussian pulse with single exponential decay yielded lifetimes of \( \tau = 106 \ \text{fs at 1200 nm}, \ 168 \ \text{fs at 1300 – 1450 nm}, \) and \( 260 \ \text{fs at 1500 nm} \) (Figure 17 D). The
origin of these decay dynamics is ambiguous. The lifetime of the decay is consistent with
an electron scattering mechanism, but the relaxation dynamics could also be due to
relaxation of a two-photon absorption induced excited state. Additional experiments are
needed to definitely assign the decay to a specific mechanism.

This modified DFWM experiment was also used to determine the second
hyperpolarizability, \( \gamma \), and \( \delta \) of electopolymerized metalloporphyrin films. The aim of the
experiment was to not only determine if a particular metal ion enhanced the nonlinear
response of the system but to establish the mechanism and origin of that enhancement. The
use of DFWM allowed non-emissive thin films to be studied on thick substrates, and
performing the experiments over a broad range of wavelengths, 900 – 1300 nm, provided
insight into how the metal ion amplifies the nonlinear optical response of the porphyrin
macrocycle.

Electro polymerized films were prepared by applying a potential to a solution containing
the porphyrin of interest and a supporting electrolyte (tetra-butyl ammonium perchlorate)
with an ITO slide as one of the electrodes. Films of Fe\(^{3+}\) 5,10,15,20-tetrakis-(4-
hydroxyphenyl)-porphyrin (TPP), Mn$^{3+}$ TPP, and Co$^{2+}$ TPP were prepared. These metal ions were selected for their adjacency in the periodic table and the variety of metal ion/porphyrin macrocycle interactions that are manifested in the UV/vis absorption spectrum of each system. The films were measured using the modified DFWM experiment.

The results of the DFWM experiments on these systems are shown in Figure 26. The peak observed in the Fe$^{3+}$ TPP and Mn$^{3+}$ TPP films was attributed to a charge transfer two-photon absorption. The $\delta$ values observed at the highest intensity of these peaks (Fe$^{3+}$ TPP = 80 GM and Mn$^{3+}$ TPP = 150 GM) are an order of magnitude larger than $\delta$ values that have been reported for metal-free TPP. No peak was seen in the Co$^{2+}$ TPP spectrum. Because two-photon transitions must occur between states that have the same symmetry ($g \rightarrow g$ or $u \rightarrow u$), the two-photon peak was assigned to a metal-to-ligand charge transfer transition. The observation of the charge transfer peak in two systems allowed the origin of the peak to be determined by comparing the shifts and relative energies of the two-photon peaks to the spectral features of the one-photon absorption spectrum. This analysis led to an assignment of $d_{xy} \rightarrow \pi^*$ for the two-photon charge transfer transition.

The absence of a two-photon resonance in the Co$^{2+}$ TPP film was found to be due to the difference in interactions between the orbitals of the metal ion and the porphyrin macrocycle. Both Fe$^{3+}$ TPP and Mn$^{3+}$ TPP have strong charge transfer transitions in the one-photon absorption spectrum. The molar absorptivities, $\varepsilon$, of these transitions are much larger for these metalloporphyrins ($\varepsilon_{\text{Mn}^{3+}\text{TPP}} = 10,000$ M$^{-1}$ cm$^{-1}$ and $\varepsilon_{\text{Fe}^{3+}\text{TPP}} = 2,300$ M$^{-1}$ cm$^{-1}$) than Co$^{2+}$ TPP ($\varepsilon = 75$ M$^{-1}$ cm$^{-1}$). This correlation between peaks in the one-photon...
spectrum and peaks in the two-photon spectrum provide a screening process for the
selection of metal ions to enhance $\delta$ in porphyrin-based nonlinear optical materials. The
presence of charge transfer bands in the one-photon spectrum appears to indicate enhanced
two-photon properties.

The experiments on electropolymerized porphyrin films provided a principle to aid in the
use of metal ions in the development of novel porphyrin-based nonlinear optical materials.
Chapter 5 describes a study that explores how the incorporation of an azo linkage into a
conjugated system affects the nonlinear optical response. While the use of azo groups had
been explored in the development of nonlinear optical materials, the azo group was
incorporated into the material by attaching it in a side chain to the polymer backbone.$^{120,121}$

Our work is the first to incorporate the azo linkage into the conjugated polymer backbone.
The azo linkage was incorporated into a conjugated oligomeric system by linking
azobenzene units with ethynyl groups. The structure of the repeat unit is shown in Figure
28. A series of oligomers were prepared and the nonlinear optical properties were
measured using DFWM.

The most dramatic effect of incorporating the azo group into the polymer backbone can
be seen in the effective conjugation length (ECL). The ECL was determined from the
absorption spectra of the azobenzene oligomers (Figure 29). The $\lambda_{\text{max}}$ shifts to longer
wavelengths as additional repeat units are added to the chain up to the longest oligomer, n
= 36, prepared for this study. Poly(phenylethynylene) (PPE) has an effective conjugation
length of 27 repeat units.$^{113}$ This is a typical ECL for conjugated organic systems. The
similar structures of the azobenzene oligomers and PPE (PPE consists of benzene rings
linked by ethynyl groups) suggests that the dramatic increase in the effective conjugation length can be attributed to the incorporation of the azo group into the conjugated backbone. The unusually long ECL of the azobenzene molecular wires can also be seen from the evolution of the $\gamma$ values with elongation of the conjugated backbone (Figure 31). The empirical power law derived from the DFWM experiments, $\gamma \propto n^{2.12 \pm 0.05}$, applies to all of the oligomers that were prepared. As the supralinear increase in $\gamma$ values with increasing conjugation length typically saturates around 60 conjugated bonds,\textsuperscript{23,106,107} the persistence of the increase up to $\sim 350$ bonds points to the remarkable effect of the azo group in modifying the conjugation of the backbone. The lack of saturation after several repeat units has a dramatic effect on increasing the $\gamma$ values of the oligomers. The second hyperpolarizability increases by a factor of more than 2000 on going from the monomer to the $n = 36$ oligomer.

The remarkably long conjugation length of the azobenzene molecular wires was attributed to the rigidity of the backbone. There are no bonds for that allow for conformational changes to occur. This prevents conjugation along the backbone from being disrupted by changes in the structure of the oligomer. Additionally, the azo and ethynyl groups do not have hydrogen atoms. This reduction in steric bulk prevents distortion of the planarity of the conjugated backbone by steric repulsion of hydrogen atoms on different groups in the backbone.


(70) the software used to perform the deconvolution analysis can be found at [http://www.public.asu.edu/~laserlab/asufit/asufit.html](http://www.public.asu.edu/~laserlab/asufit/asufit.html)


APPENDIX 1: Cyclic voltammetry of Fe$^{3+}$ TPP on an ITO electrode

![Cyclic voltammetry graph](image)

Figure 33: Consecutive CV scans of Fe$^{3+}$ TPP with an ITO electrode.

The shift in the redox potential and increase in the current is evidence of film growth on the ITO electrode.
APPENDIX 2: Preparation of the Azobenzene Oligomers

All of the oligomers were prepared by Dr. Kimberly Lott.

Synthesis of Short \((n=1-4)\) Azobenzene Oligomers. Short \((n=1-4)\) oligomers were synthesized by controlled chain extension. 3-bromo-4-methoxyphenol (1) was reacted with the diazonium salt of 4-iodoaniline (2) (Figure 33) to provide an azobenzene with an iodine on the less hindered aromatic ring and a bromine at the more substituted aromatic ring. The iodine offers a more reactive site for the coupling reaction to take place. This product, 1-[4-bromo-2-hydroxy-5-methoxyphenylazo]-4-iodobenzene (3), was coupled to 4-ethynyl anisole to produce 4 in 55% yield.

Figure 34. The synthesis of 3 and 1-(4-bromo-5-methoxy-2-hexyloxyphenylazo)-4-(4-methoxyphenylethynyl)benzene (4).

A key intermediate to generating the oligomers was generated via selective reaction of the
iodo group in 3 upon treatment with (trimethylsilyl)acetylene, thus affording in high yield the precursor to compound 5. The trimethylsilyl group was easily removed to afford 5 (Figure 34).

Figure 35. The Synthesis of {4-bromo-2-hexyloxy-5-methoxyphenylazo}-4-ethynylbenzene (5).

Treatment of 5 with 1.1 mol-equiv of 4 was then used to produce dimer 6 by palladium-catalyzed cross coupling (Figure 35). The non-end-capped dimer 6 was purified on a silica gel flash column with chloroform as the eluent. Then compound 6 was end-capped with 4-ethynyl anisole to produce dimer 7 that was subjected to final purification by silica gel flash column chromatography using dichloromethane as eluent.
Figure 36. Convergent Synthesis of Oligomers 7-9.

The trimer (8) was then synthesized by coupling dimer 6 (n=2) with 1.0 equivalent of 5, thus producing a new 6 (n=3), and then subsequent end-capping with 4-ethynylanisole affords the desired trimer 8. Tetramer 9 was prepared by treating 6 (n=3, intermediate in the preparation of 8) with compound 5 followed by an end-capping reaction with 4-ethynylanisole.

**Synthesis of Long (n=9, 27, 36) Azobenzene Oligomers.** Longer oligomers were synthesized by adding increasing amounts of a 4-ethynylanisole end-cap to a palladium cross-coupling polymerization reaction of 4’4-dibromo-2-methoxy-5-hexyloxy-azobenzene
and 4,4′-bis(ethynyl)-2-methoxy-5-hexyloxyazobenzene (Figure 31).

\[
\begin{align*}
\text{Br} & \quad \text{MeO} \\
\text{N} & \quad \text{N} \\
\text{MeO} & \quad \text{Br}
\end{align*}
\]

1 mole equiv.

\[
\begin{align*}
\text{H} & \quad \text{MeO} \\
\text{N} & \quad \text{N} \\
\text{MeO} & \quad \text{H}
\end{align*}
\]

1 mole equiv.

Pd(PPh3)2Cl2 (3 mol-%)
PPh3 (10 mol-%)
CuI (5 mol-%)
NET3 (0.4 M)
45 °C

\[
\begin{align*}
\text{H} & \quad \text{O}\text{Me} \\
\text{N} & \quad \text{N} \\
\text{MeO} & \quad \text{H}
\end{align*}
\]

(Varying Amount)

\[
\begin{align*}
\text{H} & \quad \text{O}\text{Me} \\
\text{N} & \quad \text{N} \\
\text{MeO} & \quad \text{H}
\end{align*}
\]

\(n = 9, 27, 36\)

**Figure 37. Divergent Synthesis of Larger Azobenzene Oligomers**

Increasing the mol-% of endcap produced smaller number average molecular weight \((M_n)\) oligomers. Molecular weights for the oligomers were determined using Gel Permeation Chromatography (GPC) and are reported relative to polystyrene standards.

**Detailed Experimental Procedures and Data**

**General Methods.** All manipulations of compounds and solvents were carried out using standard Schlenk techniques. Solvents were degassed and purified by distillation under nitrogen from standard drying agents. Infrared spectra were measured with Perkin Elmer 1750 FT-IR spectrometer, 1H NMR and 13C NMR measurements were performed using Bruker AC-200 MHz, Varian Mercury 300 MHz, or Varian Inova 400 MHz spectrometers. 1H NMR and 13C NMR chemical shifts are reported versus the respective
solvent residue peak (Solvent, $^1$H, $^{13}$C: CDCl$_3$, $\delta$ 7.25 ppm, $\delta$ 76.9 ppm; DMSO-d$_6$, $\delta$ 2.62 ppm, $\delta$ 36.9 ppm). The organic reagents were purchased from Aldrich Chemical Co. and used as received.

**Preparation of 4-{4-bromo-2-hydroxy-5-methoxyphenylazo}-1-iodobenzene.**

To prepare the diazonium salt, 4-iodoaniline (4.95 g, 23.0 mmol) was dissolved in HCl (5.5 mL conc. HCl in 35 mL water). The solution was cooled in an ice bath, and 7 mL of an aqueous solution of NaNO$_2$ (1.70 g, 24.6 mmol) was slowly added. For the coupling reaction, 3-bromo-4-methoxyphenol (4.59 g, 23.0 mmol) was dissolved in 10% NaOH (100 mL). The solution was cooled in an ice bath and the diazonium salt solution was added dropwise. After stirring at 0 °C for 2 h the mixture was acidified with HCl (37% aqueous) and the precipitate was collected by vacuum filtration. The crude product was purified by column chromatography (silica gel, CH$_2$Cl$_2$) and after removal of solvent afforded 3 as a dark orange solid (7.82 g, 79%). $^1$H NMR (CDCl$_3$): $\delta$ 7.80 (d, 2H), 7.72 (d, 2H), 7.41 (s, 1H), 7.29 (s, 1H), 3.96 (s, 3H).

**Preparation of {4-bromo-2-hexyloxy-5-methoxyphenylazo}-4-iodobenzene (3).**

A DMF (40 mL) solution containing 4-bromo-4'-iodo-2-hydroxy-5-methoxyoxyazobenzene (7.82 g, 18.0 mmol), hexyl iodide (2.65 mL, 18.0 mmol), and K$_2$CO$_3$ (7.46 g, 54.0 mmol) was heated to 40 °C. After 12 h the reaction was cooled to ambient temperature and diluted with ether (75 mL). The organic layer was washed with water (100 mL), saturated NH$_4$Cl (100 mL), dried over MgSO$_4$, and concentrated to dryness. The compound was triturated with cold pentane to afford bright red needles (8.92 g, 75%). $^1$H NMR (CDCl$_3$): $\delta$ 7.84 (d, $J$= 9 Hz, 2H), 7.67 (d, $J$= 8.7 Hz, 2H), 7.34 (s, 1H),
7.32 (s, 1H), 4.13 (t, J= 5.1 Hz, 2H), 3.92 (s, 3H), 1.84 (m), 1.62 (m), 1.36 (m), 0.91 (t, J= 5.1 Hz, 3H) ppm. $^{13}$C NMR (CDCl$_3$): δ 152.4, 152.1, 141.7, 138.6, 124.9, 120.8, 116.9, 116.8, 99.3, 97.9, 71.3, 56.9, 31.8, 29.5, 25.9, 22.9, 14.3.

**Preparation of 4-(4-bromo-2-hexyloxy-5-methoxyphenylazo)-1-(4-methoxyphenylethynyl)benzene (4).** A DMF/Et$_3$N (10 mL/ 2 mL) solution containing 3 (1.34 g, 2.6 mmol), 4-ethylalanisole (340 mg, 2.5 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (55 mg, 0.08 mmol), PPh$_3$ (68 mg, 0.26 mmol), and Cul (25 mg, 0.08 mmol) was heated to 50 °C for 5 h with stirring. The mixture was cooled to ambient temperature and then diluted with ether (50 mL). The organic layer was washed with water (75 mL x 3), dried over MgSO$_4$, and then concentrated to dryness. Purification by column chromatography (silica gel, 50:50 hexanes:CH$_2$Cl$_2$) and then removal of solvents afforded 4 as a dark red solid (1.36 g, 47%).

$^1$H NMR (CDCl$_3$): δ 7.92 (d, J= 6.3 Hz, 2H), 7.63 (d, J= 6.3 Hz, 2H), 7.49 (d, J= 6.9 Hz, 2H), 7.35 (s, 1H), 7.34 (s, 1H), 6.9 (d, J= 6.9 Hz, 2H), 4.14 (t, J= 5.1 Hz, 2H), 3.92 (s, 3H), 3.83 (s, 3H), 1.89 (m), 1.51 (m), 1.39 (m), 0.91 (t, J= 5.1 Hz, 3H) ppm. $^{13}$C NMR (CDCl$_3$): δ 160.1, 152.1, 150.8, 142.1, 133.4, 132.4, 131.5, 131.0, 130.9, 126.6, 123.4, 123.1, 120.9, 117.9, 116.5, 115.2, 114.3, 113.9, 99.4, 88.4, 71.5, 56.9, 55.6, 31.8, 29.5, 25.9, 22.8, 14.3.

**Preparation of {4-bromo-2-hexyloxy-5-methoxyphenylazo}-4-ethynylbenzene (5).** A DMF/Et$_3$N (16 mL/ 2 mL) solution containing 3 (1.92 g, 3.7 mmol), trimethylsilylacetylene (0.52 mL, 3.7 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (78 mg, 0.11 mmol), PPh$_3$ (97 mg, 0.37 mmol), Cul (35 mg, 0.18 mmol) was heated to 50 °C with stirring for a period of 5 h. The reaction was cooled to ambient temperature and diluted with ether (75 mL). The
organic layer was washed with water (75 mL x 3), dried with MgSO₄, and then concentrated to dryness. Purification by column chromatography (silica gel, hexanes:CH₂Cl₂, 1:1, v:v) afforded the TMS-protected product as a dark red solid (1.50 g, 83 %). ¹H NMR (CDCl₃): δ 7.87 (d, 2H), 7.60 (d, 2H), 7.34 (s, 1H), 7.32 (s, 1H), 4.16 (t, J= 6.6 Hz, 2H), 3.92 (s, 3H), 1.87 (m), 1.60 (m), 1.35 (m), 0.91 (t, J= 6.9 Hz, 3H), 0.28 (s, 9H). This entire sample was dissolved in CH₃OH/H₂O (50 mL/ 5 mL) and then with stirring at ambient temperature solid K₂CO₃ (1.28 g, 9.3 mmol) was added over a 5 min period. After 12 h of reaction the mixture was diluted with ether (75 mL), washed with H₂O (100 mL x 2), dried over MgSO₄, and then concentrated to dryness. The compound was purified by column chromatography (silica gel, 7:93, ethyl acetate:hexanes, v:v) to yield 5 as a red solid (1.2 g, 94%). ¹H NMR (CDCl₃): δ 7.86 (d, J= 9.0 Hz, 2H), 7.62 (d, J= 8.4 Hz, 2H), 7.34 (s, 1H), 7.31 (s, 1H), 4.12 (t, J= 6.3 Hz, 2H), 3.91 (s, 3H), 3.22 (s, 1H), 1.84 (m), 1.46 (m), 1.34 (m), 0.89 (t, J= 6.3 Hz, 3H); ¹³C NMR (CDCl₃): δ 152.7, 152.1, 150.8, 141.9, 133.2, 124.8, 123.2, 120.9, 116.9, 99.29, 83.6, 79.8, 71.8, 71.4, 56.9, 31.8, 29.5, 25.9, 22.9, 14.3.

Preparation of dimer 7. A DMF/Et₃N (4:1) solution containing 5 (0.10 g, 0.2 mmol), 4 (0.115 g, 0.2 mmol), Pd(PPh₃)₂Cl₂ (4.0 mg, 0.005 mmol), PPh₃ (5.0 mg, 0.02 mmol), and Cul (2.0 mg, 0.015 mmol) was heated to 45 °C with stirring for a period of 3.5 h. The mixture was diluted with ether (50 mL), washed with water (3 x 100 mL), dried with Na₂SO₄, and concentrated to dryness. Product 6 was subjected to a flash column chromatography (silica gel, CHCl₃) and the solvents removed. This product was then stirred in a solution of Et₃N (5 mL), Pd(PPh₃)₂Cl₂ (4 mg, 0.005 mmol), Cul (2 mg, 0.015
mmol). PPh₃ (5 mg, 0.02 mg), and 4-ethynyl anisole (30 mg, 0.2 mmol) was brought to
reflux. After 4 h the solution was cooled to ambient temperature and diluted with ether (50
mL), washed with water (3 x 100 mL), dried with Na₂SO₄ and concentrated to dryness.
Compound 7 was purified by a flash column chromatography (silica gel, CH₂Cl₂) to yield a
dark red solid. ¹H NMR (CDCl₃): δ 1H NMR (CDCl₃): δ 7.92 (d, J= 3.3, 2H), 7.91 (d, J=
3.3 Hz, 2H), 7.68 (d, J= 8.6 Hz, 2H), 7.64 (d, J= 9Hz, 2H), 7.52 (d, J= 3Hz, 4H), 7.35 (s,
1H), 7.34 (s, 1H), 7.33 (s, 1H), 7.33 (s, 1H), 6.92 (d, J= 3Hz, 4H), 4.15 (m, 4H), 3.93 (s,
3H), 3.92 (s, 3H), 3.85 (s, 3H), 1.89 (m, 4H), 1.53 (m, 4H), 1.37 (m, 8H), 0.92 (m, 6H).

Preparation of oligomers 8 and 9. In a similar manner to above compound 6 is
treated with 5 as the ethynyl reagent. This product can be end-capped with the 4-
ethynylanisole or used again in the coupling reaction with 5 to afford the tetrameric
compound (minus the endcap). In each case the trimer and tetramer is end-capped using a
DMF/Et₃N (4:1) solution containing the oligmer and 4-phenylethynylanisole. Reaction
time and workup of the reactions were similar to 7 above.

Oligomer 8: ¹H NMR (CDCl₃): δ 7.94 (d, J= 9.3 Hz, 6H), 7.67 (d, J= 8.1 Hz, 6H), 7.50 (d,
J= 6.6 Hz, 4H), 7.32 (s, 3H), 7.27 (s, 3H), 6.89 (d, J= 6.3 Hz, 4H), 4.18 (t, J= 9.3 Hz, 6H),
3.97 (s, 9H), 3.91 (s, 9H), 1.89 (m, 6H), 1.52 (m, 3H), 1.36 (m, i5H), 0.93 (t, J= 7.5 Hz,
9H).

Oligomer 9: ¹H NMR (CDCl₃): δ 7.94 (m, 8H), 7.64 (m, 4H), 7.51 (m, 8H), 7.37 (s, 4H),
7.31 (s, 4H), 6.90 (m, 4H), 4.17 (m, 8H), 3.96 (s, 12H), 3.89 (s, 6H), 1.89 (m), 1.65 (m),
1.43 (m), 0.919 (m, 12 H).

In-situ oligomerization of {4-bromo-2-methoxy-5-hexyloxypyrenylazo}-4.
bromobenzene and {4-ethynyl-2-methoxy-5-hexyloxyphenylazo}-4-ethynylbenzene. A
triethylamine (0.4 M) solution containing {4-bromo-2-methoxy-5-hexyloxyphenylazo}-4-
bromobenzene and {4-ethynyl-2-methoxy-5-hexyloxyphenylazo}-4-ethynylbenzene in a
one:one molar ratio, Pd(PPh₃)₂Cl₂ (3 mol-%), Cul (5 mol-%), PPh₃ (10 mol-%), and
varying amounts (10-20 mol-%) of 4-ethynyl anisole were heated to 60 °C. After the
reaction was complete, the mixture was cooled to ambient temperature, diluted with ether
(75 mL), washed with water (100 mL x 2), saturated NH₄Cl (100 mL), dried with MgSO₄
and concentrated to dryness. The higher molecular weight oligomers were precipitated
into cold CH₂Cl₂ (100 mL). Additional purification was done using flash column
chromatography (silica gel, 5:95, ethyl acetate:hexanes) if required.

**Gel Permeation Chromatography (GPC).** GPC data was collected on a Hewlett
Packard 1100 HPLC system employing a PL size-exclusion column (300 x 7.5 mm, 5µ
particle size) and polystyrene standards. The GPC analysis of the azobenzene oligomers is
shown in Figure S.1. (GPC data for oligomer n=55 was reported previously.⁶²) The
elution time decrease with a shortening of the oligomer.

![Figure 38. GPC traces of the azobenzene oligomers.](image-url)
APPENDIX 3: Degenerate Four Wave Mixing Experiments on the Azobenzene Oligomers

The DFWM setup was described previously. Each oligomer sample was dissolved in THF, centrifuged at 5000 rpm's for five minutes, filtered through a 0.5 μm PTFE filter, and transferred to a 1 mm path length cell. Solutions were magnetically stirred. Due to varying solubilities, different concentration ranges were measured for each oligomer. The tetramer and nonamer solutions were several mM, for n=27, the concentration was hundreds of μM, and n=36 was run at less than 100 μM.

The intensity dependence of the DFWM signal was determined prior to kinetics measurements. The expected cubic dependence was observed for all samples (Figure S.3). All kinetics runs were performed between 0.20 I_{max} and 0.25 I_{max} (Figure S.4). This corresponds to an excitation intensity of 12.6 GW/cm² (20 μJ and 100 fs laser pulses overlapped in an area of 1.13 mm²).

![Graph showing intensity dependence of oligomers](image)

**Figure 39.** Intensity dependence of oligomers n = 9 (2 mM, ○), n = 27 (317 μM, ▲), n = 36 (70.5 μM, ▼), and THF (■). All lines are fit to the intensity dependence I_{signal} \propto I_{excitation}^{3.0±0.1} (slope 3.0 ± 0.1).
Figure 40. Typical DFWM signals for $n=4$ (A, ■, 5.6 mM), $n=9$ (B, ■, 2 mM), $n=27$ (C, ■, 317 μM), $n=36$ (D, ■, 70.5 μM), and a THF reference for each experiment (▲). The solid lines are Gaussian fits to the data with a width (FWHM) of 130 fs.
APPENDIX 4: Photographs of the ultrafast laser system and the DFWM spectrometer

![Image of ultrafast laser system and OPA]

Figure 41: Ultrafast laser system.

The three lasers used to generate and amplify the ultrashort pulse and the OPA used to generate different wavelengths of the laser pulses are labeled.
Figure 42: Optics used to direct pulses from the OPA into the DFWM spectrometer.

The wavelength separator used to isolate the wavelength of interest is indicated in the figure. The mirror used to direct pulses into the transient absorption spectrometer (TA) is also labeled. This mirror must be removed prior to performing DFWM experiments.
Figure 43: Optics used to produce and direct the three laser pulses to the sample.
Figure 44: Detection of the DFWM signal.

The arrangement of the sample, imaging lens, and photodiode are shown. The metal screen used to select the DFWM signals has been removed for clarity. The screen is placed in front of the imaging lens during experiments.
APPENDIX 5: Start-up and shut-down procedures for the ultrafast laser system

Start-up

1. Safety lamp switch ON. Chiller 1 (Millennia/Tsunami/Spitfire) ON, set to 18 C.
2. Chiller 2 (Evolution X) ON, set to 20 C.
3. Millennia power supply key – ON.
4. Millennia remote control Power ON (keep pressed for 5 sec) wait for laser diode temperature to stabilize – about 5 min. (bar graph).
5. Evolution X – Power ON and key ON; wait for diode temperature to stabilize (~1 min, watch temperature interlock).
6. Millennia remote control Power ON and keep pressed for 5 sec, until an indicator lights up. Check Millennia power – 5 W; in Power (not Current) mode.
7. When power at 4.5 W (or other set value), open Millennia shutter.
8. Tsunami should be lasing at this time. Check: (1) wavelength (usually 800+/-1 nm) with Ocean Optics USB2000, (2) power (800 mW), (3) if needed, maximize diode indicator on 3955.
10. ! Check that both Spitfire Pockels Cells are off, block beam entrance to Spitfire!
11. Evolution X remote control power ON (hold for 5 seconds until indicator lights up).
12. Check Spitfire free lasing pulse train with 300 MHz scope (with Pockels cell 1 ON, Sync Out delay ON). Note time of pulse train.
13. Send seed pulse into Spitfire, check 2 dots, 2 stripes on a stretcher grating (IR viewer). If not clear, seed with CW, check 4 dots on a grating. Correct as necessary (this means wavelength has changed).
14. Check seed pulse timing with 300 MHz scope (should be ~60 ns from #12).
15. Check amplified pulse timing with 300 MHz scope – Pockels cell 2 ON. Correct timing as necessary.
16. Check mode quality, open shutters, check beam alignment – all beams should be centered in all pinholes.
17. Function generator ON, autocorrelator scope ON. Observe amplified pulse with the scope (blue 2nd harmonics intensity measurement with a photodiode), adjust compressor. Measure output power – 1W means 1mJ/pulse.
18. Experiment… If will not run experiment for i hour, Evolution and Millennia OFF (#5,6,9,10)
Shut-down

1. Move delay line and/or sample stage to 0 ps (making it possible to find signal next time)!
2. Oscilloscopes, function generator, photodiodes, shutter controller, PMT power supply – OFF.
3. 300 MHz amplifier, ESP300, ESP100, boxcar, pulse generators can be left ON.
4. !SDG II (amplifier electronics), 3955 (Tsunami electronics) are always ON!
5. Pockels cells 1 and 2 – OFF
6. Evolution X remote control OFF, key OFF, power OFF
7. !!! Important: Evolution power supply has to have wall power all the time (even when it is off - do not unplug power supply for any reason!. Second harmonics LBO crystal is kept at constant ~323F temperature; there is a special procedure to lower the temperature to 75F)!
8. Tsunami mode locking OFF, Ocean Optics OFF
9. Millennia shutter Close, remote control power OFF, key OFF (Millennia power supply stays ON all the time!)
10. Both Chillers OFF, safety lamp switch OFF
11. Power meter OFF
VITA

Jonathan Leslie Humphrey was born on May 4, 1976 in Victorville, California. He studied chemistry at The College of William and Mary where he conducted research in the lab of Dr. Kathleen Morgan. He graduated with a Bachelor of Science degree in Chemistry in May of 1998. After graduation, he worked at PPD, Inc. in Richmond, Virginia until August of 2000. He left PPD to join the Solgar Stability Group housed in the Wyeth Consumer Healthcare Pharmaceutical Research and Development Facility also in Richmond, Virginia. He is the author of five publications and has presented his research at several national meetings.

Publications:

Jonathan L. Humphrey and Darius Kuciauskas; Optical Susceptibilities of Supported Indium Tin Oxide (ITO) Thin Films, *J. Appl. Phys.*, accepted.


Presentations:

