ULTRAFAST STUDIES OF A PHOTOCHROMIC OXAZINE IN SOLUTION

By

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To My Family
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This dissertation is composed of two studies. Ultrafast studies of a photochromic oxazine are the main project of the dissertation. An independent study that describes the anisotropic behavior of the phenylene ethynylene dendrimers is also presented.

Photochromic molecules alter their structure and electronic properties upon excitation by optical light sources. The photogenerated form of the photochromic molecule can return to its original form either thermally or photodynamically. If the reverse reaction is thermal, the photochromic cycles of the molecules can be achieved simply turning on and off the light source. Photochromic molecules with the ability to restore the output level in each cycle are good candidates for molecular switches. The rate of switching cycles is an important property of the photochromic molecules that needs to be known for the implementation of the molecular switches.

In this study, we worked with a novel photochromic oxazine which exhibits photochromism by a ring opening reaction. The C-O bond cleavage in the ring opening reaction occurs very fast and has to be investigated by ultrafast spectroscopy. The ultrafast measurements are complemented with preliminary steady state experiments.
To explore the electronic properties of the states involved in the ring opening mechanism, the experiments are performed in the presence and the absence of benzophenone, a good triplet sensitizer, and also they are measured in solutions of different solvents (acetonitrile and hexane).

Two distinctive transient absorption bands are observed in the experiments. One of the bands, which is formed at around 505 nm, raises within 250 femtosecond (fs) and decays with 2.2 ps and 3.7 ps time constants. This band is assigned to a charge separated state. The second band, which is absorbing at around 440 nm, is attributed to the open form of the photochromic molecule. The open form of the molecule is produced indirectly from the charge separated state with 12.5 ps time constant and directly from first excited with 6.3 ps time constant and remains unchanged at least 650 ps. Although, the band belonging to a charge separated state appears and disappears within the rise time of the ring opened form, it was proved that this state does not make a significant contribution to the production of the open form of the photochromic oxazine.

The minor study that completes the dissertation is on the anisotropic behaviors of unsymmetrical phenylene ethynylene dendrimers. The unsymmetrical Phenylene Ethynylene denderimers we studied exhibited low excitation anisotropy values along the excitation spectra at room temperature and at 77K confirming energy transfer from the longer conjugated segments to shorter ones with different transition moments. The excitation anisotropy of these molecules at 77 K exhibited a complex behavior suggesting the presence of more than one electronic state contributing to the anisotropic behavior.
CHAPTER 1
INTRODUCTION

Outline of the Dissertation

The main scope of this work is to investigate the ring opening mechanism of a novel photochromic oxazine. We have conducted experimental studies to understand the electronic properties of the states involved in this mechanism. For this purpose the nature of the energy transfer mechanism between photochromic oxazine and benzopheneone is examined.

Chapter 1 is an introduction to photochromism and photochemical and photophysical processes that can be observed in a photochromic system. This chapter also includes a brief introduction to energy transfer mechanisms and the solvent-solute interactions. Additionally, the anisotropy phenomenon, that is used to characterize the absorbing and emitting state of the unsymmetrical phenylene ethynylene dendrimers, is introduced.

Chapter 2 focuses on the experimental methods which were used to study the dynamics of ring opening mechanism of the photochromic oxazine. It also explains the anisotropy measurement performed to elucidate the presence of multiple electronic states in unsymmetrical phenylene ethynylene (PE) dendrimers.

In Chapter 3, steady state and transient absorption data for the photochromic oxazine, and the data analysis methods and the results are presented. This chapter is complemented with supplementary data analysis results in Appendix B. The analysis results allowed us to build a kinetic model to explain the ring opening dynamics of the photochromic molecule.

Chapter 4 describes the steady state anisotropy of unsymmetrical phenylene ethynylene dendrimers at room and low temperature. The anisotropy experiments are supported with the steady state excitation and emission experiments which are performed at 298 K and 77 K.

Finally, Chapter 5 describes the conclusion and provides a perspective into future look.
History of Photochromism

Before 1900, few significant examples of photochromism were reported. The earliest contribution to the field was done by Fritzche in 1867.\textsuperscript{1} He observed that the orange color of the tetracene solution vanished in the daylight and it was regenerated in the dark. Later, ter Meer\textsuperscript{2} found that potassium salt of dinitroethane in the solid state changed color from yellow to red when it was moved from dark to daylight. Following these examples, Phipson\textsuperscript{3} reported that a painted gate post had a different color from day to night due to a zinc pigment in the paint.

Marckwald\textsuperscript{4} was the first scientist who recognized photochromism as a phenomenon and described it as a reversible color changing process in 1899. He called this light driven process “phototropy”. Although the term phototropy was used for a while, it was not a proper name since it had already been used by the biological sciences to describe the movement of the plant toward the light.\textsuperscript{4}

The real development in the area occurred after 1940. In the period from 1940 to 1960 many studies were done in the synthesis of new organic and inorganic molecules with photochromic properties.\textsuperscript{5} In this period Hirsberg and Fisher were the pioneers of the field.\textsuperscript{6-8} In 1950, Hirsberg introduced the term photochromism, which is derived from two Greek words photo (light) and chroma (color) to describe the phenomenon of changing color as a response to light. Then, in a few years, he proposed a chemical memory model based on a reversible change of photochromic compounds as a first study related to the potential applications of photochromism.\textsuperscript{8} After 1960 the field has shown a steady growth. Photochromic glasses became available in that era. Since then the research studies related to the photophysical and photochemical properties of photochromic molecules became very popular.\textsuperscript{5}
**Definition of Photochromism**

Photochromism is defined as the reversible transformation of a molecule induced by light in one or both directions between two forms of a molecule each absorbs in different spectral regions.⁹

\[
\begin{align*}
A \xrightarrow[kv_1]{h} B \\
A \xleftarrow[kv_2 or \Delta]{h} B
\end{align*}
\]  

(1-1)

Figure 1-1 describes a typical photochromic system. Before \( t_1 \), the molecules in the system are in the form of A. At \( t_1 \), the system is not perturbed yet by a light source. Then the system responds to the perturbation by changing from form A to form B of the photochromic molecules. During the time between \( t_1 \) and \( t_2 \) the concentration of molecules in B form increases. Then at \( t=t_2 \) the perturbation source is removed and the molecules in B form go back to the original form either thermally or photodynamically.

![Figure 1-1. Typical curve analysis for a photochromic system. Adapted from reference.⁹](image)

Upon the excitation of the system, photochromism can be observed in specific molecular systems with a mechanism of heterolytic and homolytic bond cleavage⁵, cis-trans isomerism⁵,¹⁰, tautomerism⁵,¹¹, hydrogen transfer⁵,¹², and cyclization of \( \pi \)-conjugated chromophores⁵,¹³. The kinetics of these mechanisms provides useful information for implementation of the applications of that system.
In an ideal photochromic system, the colorless form has as much as possible absorption in the ultraviolet (UV) spectrum, while the colored form has a wide range of absorption across the visible spectrum. Additionally, the response of the material to the UV irradiation should be quick, the fading rate of the colored form must be controllable and the material should be photostable for many coloration cycles.

Spiropyrans, spirooxazines, chromenes, fulgides and diarylethenes are five main classes of photochromic compounds. They show photochromism with a bond cleavage mechanism and they are widely studied because they can approach those ideal requirements (Table 1-1). Closed (colorless) and open (colored) forms of Spiropyrans, Spirooxazines, and Chromenes absorb in UV and visible region of the spectrum, respectively. The colored form of these molecules goes back to the colorless form either thermally or by the irradiation of light. On the other hand, the open form of Fulgides and Diarylethenes are colorless and absorb in UV region while the closed forms are colored and absorbs in visible region of the spectrum. For these molecules, the fading reaction occurs only in case of irradiation with another source of light.

In a photochromic reaction, in addition to changes in absorption spectra various physical properties of the photochromic material such as refractive index, dielectric constant, oxidation reduction potential, and geometrical structure can change. These changes allow the photochromic materials to have applications in various areas.

The application of photochromic materials in ophthalmics, plastic lenses for sunglasses is common although the fading rates of these materials are not as high as desired. Therefore, studies are still going on in order to develop better materials for these applications. Along with the practical applications of the photochromic compounds, there are many potential application
areas such as optic memories for data storage,\textsuperscript{45,48,49,51-53} optical switches,\textsuperscript{15,45,48} nonlinear device components,\textsuperscript{54} etc. Additionally, incorporation of the photochromic compounds into a polymer chain and their possible application areas are the focus of many research groups\textsuperscript{54,55}.

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<tr>
<td>Spirooxazines</td>
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<tr>
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<tr>
<td>Fulgides</td>
<td><img src="image7.png" alt="Fulgides" /></td>
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<tr>
<td>Diarylethenes</td>
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</table>

Photochromic compounds are used also in novelty printing successfully. Fulgides are the photochromic family which is used mostly in novelty printing due to the low temperature dependency of the fading rates.\textsuperscript{9,50} The items produced in this area are mostly toys and T-shirts.
Photochromic compounds can be used as molecular switches in data storage due to their ability of interchanging between two or more states. For a successful molecular switch, the compounds should meet the requirements such as thermal stability, fatigue resistance, high efficiency of photoreactions, high reaction rates in both direction of photochromic reaction, and solubility in polymer matrix. The potential of spiropyans, spirooxazines, spirooxazines, spirooxazines, diarylethenes, spirooxazines, fulgides for meeting these requirements is the subject of an active research area.

**Photochemical and Photophysical Processes Related to Photochromism**

The successful applications of the photochromic materials require the eliminations of the limitations of these materials. Understanding the reaction rates and the mechanisms of photochromic compounds is important for the innovation of the materials with desired properties for different applications. The knowledge of basics of photophysical and photochemical processes in general is helpful in characterization of the photochromic systems.

For an electronic transition to occur, a photon needs to be absorbed by the material that promotes the removal of an electron from an orbital of the ground state to an unoccupied orbital of the excited state. The excited state can go through various processes such as internal conversion, intersystem crossing, fluorescence, and phosphorescence. The electronic states and the possible transitions between these states are shown on a Jablonski diagram in Figure 1-2.

In most molecules, with a singlet ground state, absorption occurs from ground state to the available singlet states \( S_1 \) or \( S_n \) approximately in \( 10^{-15} \) s.\(^\ddagger\) Internal conversion (IC), and intersystem crossing (ISC) are non-radiative transitions between either states with the same spin.

\(^\ddagger\) This is the maximum interaction time available for absorption of a photon by a molecule. A blue light has a wavelength of the order of 4000 Å. The speed of light is \( 3 \times 10^{18} \) Å sec\(^{-1}\). So, the time required for this photon to pass a point is \( t = 4000 \) Å/\( 3 \times 10^{18} \) Å sec\(^{-1}\) (speed of light) and it is equal to time of order of \( 10^{-15} \).
multiplicity, or between two isoenergetic vibrational levels of electronic states with different spin multiplicity, respectively. Internal conversion occurs in $10^{-11}$-$10^{-9}$ s while intersystem crossing takes $10^{-10}$-$10^{-8}$ s. Fluorescence is a radiative transition usually from $S_1$ state to $S_0$ state (Kasha’s rule\textsuperscript{57}) occurring in most cases in a time scale of $10^{-10}$-$10^{-7}$ s. The triplet ($T_1$) state which is populated via intersystem crossing is de-excited by a radiative process that is called phosphorescence in $10^{-6}$-1 s.

Figure 1-2. Jablonski diagram

Not all the compounds absorb at every wavelength with the same efficiency. For a given compound, absorbance $A(\lambda)$ and transmittance $T(\lambda)$ describe the efficiency of the light absorption at a specific wavelength (Equation 1-2).

$$A(\lambda) = -\log T(\lambda)$$

(1-2)

where $T(\lambda) = \frac{I^0}{I^0}$, $I^0$ and $I^\lambda$ are the intensities of the light beams entering and leaving the absorbing medium, respectively.
Under low intensity conditions, absorbance of a sample follows the Beer-Lambert Law, where $\varepsilon(\lambda)$ is the molar absorption coefficient (L mol$^{-1}$ cm$^{-1}$), $c$ is the concentration of the sample (mol L$^{-1}$) and $l$ is the absorption path length (namely the thickness of absorbing medium) (cm).

$$A(\lambda) = \log \frac{I_0^0}{I_{\lambda}} = \varepsilon(\lambda)cl$$

(1-3)

The electronic transition upon the absorption of a photon is an instantaneous process. Due to the fact that atomic nuclei in molecules do not have time to change positions in this process, they are vertical transitions. This explanation is called the Franck-Condon principle. Due to the vertical transitions, the same transitions are involved in both absorption and emission which creates a symmetric absorption and emission spectra.

Generally, the emission can occur at longer wavelengths than the wavelengths at which the molecule absorbs. The molecule can be excited to higher vibrational levels within the S$_1$ state or to the higher electronic states. If the molecule is excited to the higher electronic states, it relaxes to the S$_1$ state via internal conversion. Thus, in most cases emission occurs from S$_1$ irrespective of excitation wavelengths. Therefore, the emission spectrum is the mirror image of S$_0$ $\rightarrow$ S$_1$ absorption. This is known as Kasha’s Rule. Additionally, emission wavelengths can be shifted to the longer wavelengths due to the stabilization of the excited state by the solvent.

**Solvent Effects on Absorption and Emission Spectra**

In literature, it is reported that solvent polarity has a strong effect in the photochromic reactions of the spiropyrans and the related molecules. In our study, we also observed spectral shifts on the absorption and the emission spectra of the photochromic oxazine in different solvents (Chapter 3).

Depending on the solvent properties, shifts in the absorption and emission spectra due to the stabilization of the excited state of the fluorophores are very easy to observe. These shifts are
called solvatochromic shifts since they are originated from the solvent-solute interactions, which are commonly described with the Van der Waals interactions or hydrogen bondings. Molecules which show solvatochromic shifts are called solvatochromic molecules. With the increasing solvent polarity positive solvatochromism is bathochromic (red) shift while negative solvatochromism is hypsochromic (blue) shift.\textsuperscript{58,63}

Polar molecules are more sensitive to changes on the polarity of the solvents, as compared to the nonpolar molecules. Following the excitation of polar molecules, the charge distribution within the molecule is reorganized. In polar solvents, the dipole moments in excited state ($\mu_e$) are larger than the dipole moments they have in ground state ($\mu_g$). After the reorientation of the solvent, this results in lowering the energy of excited state and emitting at longer wavelengths. Increasing solvent polarity makes this effect larger. In polar solvents, charge separated state has the lowest energy and emission mostly comes form that state. On the other hand, in nonpolar solvents, charge separation is not favorable and most of the emission comes from the locally excited, Franck-Condon state.\textsuperscript{58} The solvent polarity can lower the energy of the excited state and determine which state has the lowest energy.

**Energy transfer**

To characterize the electronic states which are involved in the ring opening mechanism of the photochromic oxazine, we conducted sensitization experiments using benzophenone (Chapter 3). Identifying the properties of the energy transfer between the photochromic oxazine and benzophenone helps describing the properties of the electronic states of the photochromic oxazine.

In sensitization experiments, the energy transfer occurs from excited sensitizer (donor) to quencher (acceptor). The energy transfer can occur between those species if the energy of the
excited sensitizer is higher than the energy of the excited quencher. Also, the energy transfer process should occur within the natural life time of the excited sensitizer.

Energy transfer can be classified in two main categories: radiative and non-radiative energy transfer. In radiative energy transfer, a photon emitted by a molecule, called the donor (D), is absorbed by another molecule, called the acceptor (A). Spectral overlap between the emission of the donor and the absorption of acceptor is the requirement for this sort of energy transfer. On the other hand, besides the spectral overlap non-radiative energy transfer depends on the short or long-range interactions between the molecules.

**Radiative Energy Transfer**

For the radiative energy transfer to occur the donor needs to be excited by absorption of a photon with a frequency that the acceptor molecule can not absorb. Then it emits another photon with a frequency that the acceptor can absorb. In this way, the excitation energy is transferred to the acceptor molecule by the absorption of the photon emitted by the donor as it is summarized at Equation 1-4.

\[
D + h\nu_1 \rightarrow D^* \quad (1-4a)
\]

\[
D^* \rightarrow D + h\nu_2 \quad (1-4b)
\]

\[
h\nu_2 + A \rightarrow A^* \quad (1-4c)
\]

The efficiency of the radiative energy transfer depends on the quantum yield of the donor, concentration of the acceptor, extinction coefficient of the acceptor at the emission wavelengths of the donor, and the overlap between the emission spectrum and the absorption spectrum of the acceptor. Radiative energy transfer is more probable when these factors have the highest value.
Non-Radiative Energy Transfer

In non-radiative energy transfer, the donor molecule interacts with the acceptor molecule, which occurs in the presence coupling between the electronic states of the donor and the acceptor. Non-radiative energy transfer can be explained with Fermi’s Golden rule\textsuperscript{65} which is formulated as

\[
\text{Probability} \ (D^* \rightarrow D \rightarrow A^*) = \frac{2\pi}{\hbar} \rho \left| \langle \Psi_i | H | \Psi_f \rangle \right|^2
\]

(1-5)

where \( \Psi_i \) and \( \Psi_f \) are the wave function of initial and final states respectively, \( \rho \) is the measure of density of the final states and it related to the overlap integral, and \( H \) defines the specific interaction related to the coupling of initial and final states. The interactions between the initial and the final states can be either a Coulombic or exchange interaction (Figure 1-3). Therefore \( H \) can be rewritten as, \( H = H_{\text{coulombic}} + H_{\text{exchange}} \).

Figure 1-3. Coulombic and exchange mechanism in non-radiative energy transfer. Adapted from the reference.\textsuperscript{65}
In the Coulombic interaction mechanism which is shown with dotted arrows in Figure 1-3, the energy transfer occurred at a distance in presence of coupling between the states of A* and D*. In order to determine the magnitude of the interaction, Förster introduced levels of coupling between the states of D* and A* as strong, weak, and very weak coupling based on the relative values of interaction energy (U), the electronic energy difference between D* and A* (ΔE), the absorption bandwidth (Δω) and the vibronic bandwidth (Δε) (Figure 1-4).58,63,65

\[ \Delta \omega \]  

\[ \Delta \epsilon \]  

\[ \Delta E \]

Figure 1-4. Representation of the electronic energy difference between D* and A* (ΔE), the absorption bandwidth (Δω) and the vibronic bandwidth (Δε).58

The Coulombic interaction can be described as strong coupling if the condition \( U \gg \Delta E, \) and \( U \gg \Delta \omega, \Delta \epsilon \) holds. Under this condition, all of the vibronic levels can be involved in the energy transfer process. In other words, the molecules are at resonance with each other. In the case of weak coupling, the interaction energy is larger than the vibronic bandwidth but smaller than the absorption bandwidth \( (U \gg \Delta E, \Delta \omega \gg U \gg \Delta \epsilon) \). Therefore the excitation energy is not delocalized; it is more localized as compared to the strong coupling. The coupling is called very weak if the interaction energy is lower than the absorption bandwidth as well as the vibronic bandwidth \( (U \ll \Delta \epsilon \ll \Delta \omega) \). In very weak coupling, the resonance between the states is restricted.58

For the Coloumbic interaction Förster61 showed that
\[ k_{ET}(\text{Coulombic}) = k^{\frac{k^2 D_0}{k^6 D}} J(e_A) \]  \hspace{1cm} (1-6)

where \( k \) is a constant related to the refractive index and concentration, \( k^2 \) accounts for the orientation factor of the transition dipoles. \( J(e_A) \) is the integrated overlap of the emission curve of the donor \((i_D)\) and the absorption curve of the acceptor \((e_A)\).

In contrast to Coulombic interaction, the exchange requires the physical contact of the interacting pairs by having the electron clouds of the interacting species overlapped in space. Dexter\textsuperscript{61} has worked on energy transfer by electron exchange and showed that

\[ k_{ET}(\text{exchange}) = KJ \exp(-2R_{DA} / L) \]  \hspace{1cm} (1-7)

where \( K \) takes the orbital interactions into account, \( J \) is the spectral overlap with the normalized extinction coefficient of acceptor. In this way the energy transfer rate constant is independent of absorption characteristics of the acceptor. \( R_{DA} \) and \( L \) are the donor acceptor separation and van der Waals radii, respectively.

**Selection Rules**

In the sensitization experiments using oxazine-benzophenone mixtures, determining the electronic properties of the quenched state of the benzophenone, and the dynamics of that state helps understanding the electronic properties of the sensitized state of the oxazine. In this sense, basic selection rules in energy transfer mechanisms give an idea about the possible states of oxazine that can be sensitized by the singlet or triplet state of the benzophenone.

**Singlet-singlet energy transfer**

Singlet-singlet energy transfer is the interaction between a singlet state of the donor and a singlet state of the acceptor as it is shown in Equation 1-8. These interactions can be either
Coulombic or exchange interactions since both are spin-allowed in singlet-singlet energy transfer.

\[ D^*(S_1) + A(S_0) \rightarrow D(S_0) + A^*(S_1) \]  \hspace{1cm} (1-8)

**Triplet-triplet energy transfer**

Triplet-triplet energy transfer occurs via the interaction of the excited donor in its triplet state and acceptor in its ground state and producing excited acceptor in its triplet state (Equation 1-9).

\[ D^*(T_1) + A(S_0) \rightarrow D(S_0) + A^*(T_1) \]  \hspace{1cm} (1-9)

Triplet-triplet energy transfer generally occurs by exchange mechanism. Therefore, the close interaction (10-15 \( \text{Å} \)) of donor and the acceptor is needed for efficient energy transfer.

**Triplet-singlet energy transfer**

In triplet-singlet energy transfer, the Coulombic and exchange mechanisms are both spin forbidden. Therefore, this type of energy transfer is slow. The relatively long lifetime of the triplet states of the donors compensate the low rate constant and make the energy transfer from the triplet state of the donor to the singlet state of the acceptor possible (Equation 1-10).

\[ D^*(T_1) + A(S_0) \rightarrow D(S_0) + A^*(S_1) \]  \hspace{1cm} (1-10)

**Singlet-triplet energy transfer**

Singlet-triplet energy transfer occurs rarely compared to the others. It is shown in Equation 1-11 as the excited singlet donor interacts with the ground-state singlet acceptor to produce an excited triplet acceptor.

\[ D^*(S_1) + A(S_0) \rightarrow D(S_0) + A^*(T_1) \]  \hspace{1cm} (1-11)

The energy transfer that causes the spin flipping can be enhanced by the spin-orbit coupling processes.
Fluorescence Anisotropy

The anisotropic behavior of the unsymmetrical phenylene ethynylene dendrimers are investigated at room temperature and 77 K as an independent project. Before the experimental results are discussed in Chapter 4, we introduce the basics of the anisotropy concept in detail.

In homogenous solutions, molecules are randomly oriented. When these molecules are exposed to linearly polarized light, the molecules with the transition moment oriented in the same direction with the polarization of light are more likely to be excited. Then, the molecules in the excited state will have a specific orientation and the light emitted is polarized to some extent. The extent of polarization of the emitted light is described by the term anisotropy ($r$) which is equal to

$$r = \frac{I_{II} - I_{\perp}}{I_{II} + 2I_{\perp}}$$

(1-12)

where $I_{II}$ and $I_{\perp}$ are the intensities of the detected light with the polarization parallel and perpendicular to the polarization of the excitation source, respectively. The molecules with zero anisotropy display nonpolarized emission. Anisotropy values provide information about the angle between the absorption and emission transition moments since the fundamental anisotropy, the anisotropy measured in the absence of any molecular motion; ($r_0$) can be calculated by using Equation 1-13.

$$r_0 = \frac{2}{5} \left( \frac{3\cos^2 \beta - 1}{2} \right)$$

(1-13)

where $\beta$ is the angle between the absorption and emission transition moments. Theoretically, for a randomly oriented samples in 3-dimension, $r_0$ is equal to -0.2 (minimum) and 0.4 (maximum) when $\beta=90^\circ$ and 0°, respectively.
For the molecules following the Kasha’s rule,\textsuperscript{57} emission is independent of the excitation wavelength and it comes from the lowest excited state regardless of the excitation wavelength. For this reason, the anisotropy does not change with the emission wavelength. However, the fundamental anisotropy changes with excitation wavelength since the absorption transition moment is oriented differently at each excitation wavelength that reach different electronic states causing the change in $\beta$ and consequently in anisotropy values.

Sometimes, more than one state can contribute to the observed anisotropy. In this case, the total anisotropy is calculated as

$$r_0(\lambda) = f_n(\lambda) r_{0n} + f_1(\lambda) r_{01}$$

(1-14)

where $f_n(\lambda)$ is the fractional contribution of the $n^{th}$ state to the total absorption at the wavelength $\lambda$, and $r_{0n}$ is the experimental (limiting) anisotropy of the mentioned state. For absorption from more than one state, $f_n(\lambda) + f_1(\lambda) = 1$, $A_n(\lambda) = f_n(\lambda) A(\lambda)$, $A_1(\lambda) = f_1(\lambda) A(\lambda)$ where $A(\lambda)$ is the total absorption and the $A_n(\lambda)$ and $A_1(\lambda)$ are individual absorptions of the $n^{th}$ and $1^{st}$ states, respectively. Excitation anisotropy could be used to resolve the overlapping electronic transitions. Constant and monotonic increase in excitation anisotropy values across an absorption band corresponds to a single transition under this band. On the other hand, complex behavior of the anisotropy across an absorption band results from the overlapping transitions.

For large molecules in which rotational depolarization is slow, the decrease in excitation anisotropy in a system containing donor-acceptor pairs can be evaluated as an evidence of energy transfer due to the loss of orientation during the transfer process.
CHAPTER 2
EXPERIMENTAL METHODS

This chapter describes the experimental methods employed to uncover the ring opening mechanism of a photochromic oxazine (Chapter 3) and steady state anisotropic behaviors of the pheylene ethylene dendrimers at room and low temperatures (Chapter 4). In this study, steady state absorption, emission and excitation spectroscopy as well as transient absorption spectroscopy were used.

Steady State Measurements

Absorption spectra were recorded on a Hewlett Packard diode array spectrophotometer (8452A). Emission and excitation spectra were measured with a Jobin-Yvon instrument (Fluorolog-3).

Steady State Anisotropy Experiments

The anisotropy \( r \) is defined as the normalization of the difference between the parallel and perpendicular polarized light intensities to the total intensity (Equation 2-1).

\[
\frac{I_{II} - I_{\perp}}{I_{II} + 2I_{\perp}}
\]  

(2-1)

Intensities used to calculate the anisotropy are measured using an instrument with the configuration illustrated in Figure 2-1. The polarizations are determined with respect to the polarization of the excitation light. The parallel polarized light has the same orientation as the excitation source while the perpendicular polarization oriented at a 90° angle with respect to the excitation source.

The fluorimeter used for the steady state experiments has an L-shape configuration (Figure 2-1) with a single detection channel. This single detection channel has different sensitivities for parallel and vertical polarizations of the emitted light. Consequently, the measured intensities of
the polarized light are not the true intensities of parallel and vertical intensities. In order to measure the actual intensities we need to take into account the sensitivity of the detection channel.

In our measurements, four combinations of excitation and emission polarizations ($I_{VV}$, $I_{VH}$, $I_{HH}$, $I_{HV}$) are used to eliminate the error which comes from the instrument’s sensitivity (Figure 2-2). The subscripts of the lights indicate the orientation of the excitation and emission polarizers. For example, $I_{HV}$ represents the intensity measured when the excitation and emission are polarized horizontally and vertically, respectively.

**Figure 2-1.** Schematic diagram for measurement of anisotropy experiments.\(^{63}\)

**Figure 2-2.** Schematic diagram for the measurement of A) $I_{VV}$ and $I_{VH}$  B) $I_{HH}$ and $I_{HV}$.\(^{63}\)
The sensitivity factors of the emission channel for the vertically and horizontally polarized components, \( S_V \) and \( S_H \) respectively, can be obtained from the measured intensities with different polarizations since the intensities, \( I_{VV} \), \( I_{VH} \), \( I_{HH} \), and \( I_{HV} \) are defined as:

\[
I_{VV} = kS_V I_H 
\]
(2-2a)

\[
I_{VH} = kS_H I_\perp 
\]
(2-2b)

\[
I_{HV} = kS_V I_\perp 
\]
(2-2c)

\[
I_{HH} = kS_H I_\perp 
\]
(2-2d)

where \( k \) is the proportionality factor to compensate for the instrumental factors other than polarization sensitivities and quantum yield of the molecule under study. By combining the Equations from 2-2a to 2-2d, one can get

\[
\frac{I_{VV}}{I_{VH}} = \frac{S_V}{S_H} \frac{I_H}{I_\perp} = G \frac{I_H}{I_\perp} 
\]
(2-3)

\[
\frac{I_{HV}}{I_{HH}} = \frac{S_V}{S_H} \frac{I_\perp}{I_\perp} = G 
\]
(2-4)

where \( G \) is called a grating factor and is used to correct the variations due to the polarizations in anisotropy experiments. The rearrangement of Equation 2.1 makes it clear how to involve the \( G \) factor in the anisotropy calculations (Equation 2-5).

\[
r = \frac{\frac{I_H}{I_\perp} - 1}{\frac{I_H}{I_\perp} + 2} = \frac{I_{VV} - GI_{VH}}{I_{VV} + 2GI_{VH}} 
\]
(2-5)

The anisotropy measurements of pheylene ethylene dendrimers were performed at 298 K and 77 K. 77 K is obtained by using a liquid nitrogen flow cryostat (Oxford Instruments) and all
of the samples for low temperature measurements are prepared in 2-Methyl tetrahydrofuran (2-MeTHF) which forms a clear glass at 77 K.

**Time-Resolved Measurements**

Compared to time-resolved measurements, steady state measurements are easier to perform and the instrumentation is simpler and less expensive. However, during the steady state measurements, the time and intensity averaging processes result in the lost of dynamic information of the system under investigation. Time-resolved measurements provide information to understand the excited state dynamics of photophysical, photochemical and photobiological processes.63

**Pump-probe Spectroscopy**

Pump-probe spectroscopy is a time-resolved spectroscopy to probe and characterize that electronic and structural properties of the transient states formed during the light initiated processes. Processes occurring in time scales as fast as femtosecond can be probed by these techniques. In a typical pump probe experiment in the femtosecond (fs) – pico-second (ps) regime, two ultrashort pulses are overlapped spatially and temporally on a sample. The pump pulse excites the sample at t=0. The optical changes induced in the sample upon the excitation are probed by the probe pulse which is delayed with respect to the pump pulse.

The effect of the pump pulse on the sample may be analyzed in two different ways: For example, Raman scattering spectroscopy,64 laser induced fluorescence62 and coherent anti-Stokes Raman spectroscopy (CARS)74 techniques can be used to detect new effects created in the sample by the probe itself before and after the action of pump pulse. Transient absorption technique allows one to compare the changes in probe pulse characteristics such as intensity, phase and wave vector after passing through the sample before and after the perturbation of the sample by the pump pulse.64
Ultrafast Transient Absorption Spectroscopy

By employing the transient absorption method, the changes in the absorption spectrum of a sample upon excitation by an ultrashort pulse can be observed and measured with respect to time. The general principle of this technique is shown in Figure 2-3.

At time t=0, the pump beam excites the sample. The probe beam crosses the sample at a time t= t+Δt where Δt is provided by an optical delay line. The detector which can be a photodiode or a CCD measures I₀(λ) and I(λ, Δt). The relation between I₀(λ) and I(λ, Δt) can be explained by the Beer-Lambert Law\(^5\) in Equation 2-6.

\[
I(\lambda, \Delta t) = I_0(\lambda)10^{-\varepsilon_\lambda N(\Delta t)l}
\]

where \(\varepsilon_\lambda\) is the extinction coefficient of the sample at wavelength \(\lambda\), \(N(\Delta t)\) is the population absorbing at time \(\Delta t\) at wavelength \(\lambda\) and in \(l\), the length of the sample excited.

Figure 2-3. Basic principle of transient absorption experiment. Figure is adapted from reference\(^6\)

The major goal of the transient absorption experiment is to measure the optical density of transient absorption, so called change in absorption, defined as:

\[
\Delta A(\lambda, \Delta t) = \log \frac{I_0(\lambda)}{I(\lambda, \Delta t)} = \varepsilon_\lambda N(\Delta t)l
\] (2-7)
In a transient absorption experiment, we observe signals as positive or negative changes in absorption. A positive $\Delta A$ displays a photoinduced absorption process, while a negative $\Delta A$ can be observed due to either ground state bleach or a stimulated emission process. All the possible transitions and the related changes in absorption spectra are shown in Figure 2-4.

When the sample is exposed to the excitation pulse, a certain number of molecules will be excited. In other words, the number of the molecules at the ground state will decrease. The ground state absorption in the presence of the pump beam will be lower than the absorption of the state in the absence of the pump beam. In this situation, a negative transient absorption signal called ground state bleach will be observed. The bleach signal should be expected instantaneously after the excitation at the steady state absorption wavelengths.

Figure 2-4. Scheme of certain signals in transient absorption measurement.

Photoinduced absorption (also called excited state absorption) will be observed if the molecules at the excited state are excited to a higher state by the probe pulse. This type of process will lead a positive change in absorption ($\Delta A$).
Another change of absorption can be observed at the steady state emission wavelengths. This signal will be detected in case of stimulated emission, which occurs if the probe pulse stimulates the molecules at the excited state to return back to the ground state. In this case, the detector is exposed to relatively more photons, which makes \( \Delta A \) negative.

Besides the general considerations of the technique, some practical aspects such as probe characteristics, detection systems and experimental tricks to avoid artifacts\textsuperscript{75} should be taken into consideration for an effective technique.

The probe can either be a monochromatic beam, or it can have a broad spectrum. In the former case, the researcher has to know where to detect the species created upon excitation in the sample and choose a probe wavelength accordingly. This kind of study leans on preliminary data which helps to estimate the active spectral domain of the species to be probed. On the other hand, in the latter case it is possible to detect the expected species in the sample after the excitation as well as unexpected ones since it allows recording transient absorption at different wavelengths simultaneously. If the spectral domain where the excited species are active is not known it is better to use a broad band probe where continuum generation is a possibility.\textsuperscript{64}

Continuum generation arises from the propagation of intense picosecond or femtosecond pulses through a condensed or gaseous media. The origin of this process is mainly governed by Self Phase Modulation (SPM).\textsuperscript{76,77} SPM appears when the strong laser beam produces a refractive index change in the medium and then the medium causes a phase change on the incoming beam as a response. In the case of a pulsed laser input, laser intensity varies in time that leads to a SPM in time. Since the derivative of the phase with respect to time gives the angular frequency of a wave, SPM also occurs as a modulation in the frequency domain. Thus, the process ends up with a self-induced spectral broadening.\textsuperscript{76}
The probe in a transient absorption experiment can be detected by a Charge Coupled Device (CCD) camera or photodiode, depending on the spectral properties of the probe beam. When simultaneous measurements at different wavelengths are necessary, the detector should be a CCD and the optical density is measured directly as a function of wavelength.

In a transient absorption experiment variables such pump and probe relative polarizations, group velocity dispersion (GVD) along the optical pathway, various noise sources such as ambient light or electronic noise need to be considered in order to avoid experimental artifacts in the data.\textsuperscript{78,79}

If the pump beam is polarized in a particular direction, the spatial distribution of the excited molecules will be anisotropic (See Introduction, Chapter 1). Spatial randomization can occur via reorientation of the molecules within the reorientation time. Thus, the dynamics observed are not only the reflections of lifetimes of the excited molecules but also their reorientation time. If the aim of the experiment does not include measuring the anisotropic behavior of the molecules, the angle between pump and probe should be set to 54.7°, the magic angle where fundamental anisotropy is equal to zero.

Generally, electromagnetic waves propagate at different group velocities in different media that creating group velocity dispersion (GVD). Accordingly, the probe frequencies traveling through the different optical components are not at the same speed due to GVD.\textsuperscript{78-80} In other words, in a supercontinuum probe, the blue wavelengths arrive at the sample later than the red wavelengths since for the media with normal dispersion, the index of refraction for blue wavelengths is higher than that for the red wavelengths. It is possible to get rid of this effect in the measured spectrum by correcting the collected data numerically. This method is practical in case of well known continuum dispersion.\textsuperscript{64,76}
In our experiments, the biggest chirp we observed between 343 nm and 500 nm was about 800 fs. Thus, chirp correction is not necessary for the data which has time steps larger than 800 fs. Only the data with time steps smaller than 800 fs were corrected numerically by using a home-made Labview program. This program calculates the dispersion of light in every medium which the light interact with.

The velocity of the light in different mediums at different wavelengths depends on the refractive index of the medium at that wavelength since \( v(\lambda) = \frac{c}{n(\lambda)} \). The chirp correction program uses the Sellmeier equation (Equation 2-8) which gives an empirical relation between the refractive index and the wavelength.

\[
n^2(\lambda) = 1 + \frac{B_1 \lambda^2}{\lambda^2 - C_1} + \frac{B_2 \lambda^2}{\lambda^2 - C_2} + \frac{B_3 \lambda^2}{\lambda^2 - C_3}
\]

(2-8)

where B and C are the Sellmeier coefficients determined experimentally. The chirp at different wavelengths per mm is calculated by the program for different media. Figure 2-5 shows the chirp per mm with respect to the energy (wavelength) of the light for water (See Appendix A for air, BK7, CaF₂, fused silica, and methyl alcohol).

![Figure 2-5. Chirp per mm with respect to the energy (wavelength) of the light for water.](image-url)
The ultrafast transient absorption apparatus used in this study consists of three major components: femtosecond laser source, pump-probe set up and detection system.

**Femtosecond Laser Source**

A commercially available ultrafast laser system composed of Millenia, Tusunami, Evolution, Spitfire and OPA from Spectra Physics (®) is used as the excitation source in experiments in this thesis work. The function of these individual elements is explained briefly.

**Millenia Vs®:** It is a high power, visible cw solid state laser providing 532 nm output with power range 2-10 W. It uses neodymium yttrium vanadate (Nd:YVO₄) as the solid state laser media. The diode pump light is absorbed by the Nd:YVO₄ crystals and emitted as the output at 1064 nm. 1064 nm goes through a frequency doubling process on a phase matched, temperature-tuned LBO crystal and 532 nm becomes the output of the laser.

**Tsunami®:** Tsunami® is a solid state laser which uses Titanium-doped sapphire as a lasing media. It is pumped by the Millenia output. Tsunami® delivers ~35 fs pulses with 82 MHz repetition rate. The output of the Tsunami® is centered at around 790 nm with approximately 35 nm bandwidth (FWHM) and used as the seed of regenerative amplifier.

**Evolution X®:** It is a diode-pumped laser which designed around a neodymium: yttrium lithium fluoride (Nd:YLF) laser head pumped by four AlGaAs laser diodes. It provides Q-switched pulses with average powers greater than 6W at 527 nm at repetition rates of 1 kHz.

**Regenerative Amplifier, Spitfire®:** It is an optical amplifier which has Ti:Sa crystal as the active laser medium and is pumped by Evolution X®. It uses a Chirped Pulse Amplification technique to amplify the ~35 fs pulses at 82MHz repetition rate leaving the Tsunami. The pulses entering the amplifier undergo first the process of stretching, then amplification and finally compression before they are released from the system. The system
produces pulses with energy in a single pulse reaching up to 1 mJ centered at 790 nm with pulse widths around 50 fs at 1 kHz repetition rate.

**Optical parametric amplifier (OPA):** It provides a wide range of wavelength options for the pump pulse. Many complex systems absorb at wavelengths that cannot be delivered by the fundamental Ti: Sapphire regenerative amplifier or through its direct frequency conversion with harmonic generation. These required wavelengths are supplied by the OPAs. The OPA does not operate with the same principle of a laser. While a conventional laser operates on population inversion OPA’s gain is driven by nonlinear processes as second harmonic generation (SHG), fourth harmonic generation (FHG), sum frequency mixing (SFM), difference frequency mixing (DFM) in which white light continuum is used as a seed and beta-barium borate (BBO) crystal as nonlinear medium. Pump (Spitfire® output) and seed beams are overlapped spatially and in time on BBO crystal and generate two types output beams: signal and idler. Energy conservation determines the frequency of the signal and idler as $\omega_{pump} = \omega_{signal} + \omega_{idler}$ or

$$\frac{1}{\lambda_{pump}} = \frac{1}{\lambda_{signal}} + \frac{1}{\lambda_{idler}}.$$ 

The wavelength for signal and idler outputs are in range of 1.1-1.6 µm and 1.6-3.0 µm, respectively. Either signal or the idler outputs of the OPA can be used depending on the purpose of usage in the experiments. The signal and idler can be separated easily by taking the advantage of that they have the different polarizations (Signal is horizontally and idler is vertically polarized).

In our experiments we used 320 nm as the excitation source in our transient absorption experiments since photochromic oxazine has a high extinction coefficient at this wavelength. The beam which has a spectral peak at 320 nm is generated as the FHG of the signal output of the OPA. The FHG of the signal is achieved using two BBO crystals. After the FHG crystal,
TLM 1 mirrors, which have a high reflectivity at 320 nm, were used for a high power output. The power of the generated beam at 320 nm was around 2.5 µJ after the generation and it decreases to ~600 nJ at the sample position.

**Experimental Set-up**

The schematic representation of the experimental transient absorption set-up is presented in Figure 2-6. ~ 400 µJ of the output of amplified laser is used by an optical parametric amplifier (OPA) and followed by forth harmonic generation to produce 2.5 µJ pump beam at 320 nm with 1 kHz repetition rate.

The pump beam generated in the OPA follows an optical path containing a telescope. The telescope is composed of two quartz (a lens concave with f=-50 mm and a convex lens with f=150 mm) lenses and it is used to decrease the spot size of the pump beam and collimate it. The decrease of the spot size is determined by the focal lengths of the used lenses. In our set up, after the telescope, the beam size is decreased to 1/3 of the original size since the focal lengths of the lenses used to build the telescope is has a ratio of 1/3 (50/150).

After the telescope, the collimated beam goes through an optical delay line consisting of two perpendicularly mounted mirrors on a computer controlled motorized translation stage (Model No: M-415 D6, Physik Instrumente) which is used to change the time delay between pump and probe. After the delay stage, the pump beam passes through a chopper wheel in order to compare the signal with and without the pump. Then, a parabolic mirror (Janos Technology, A8037-207, off axis mirror with reflected focal length of f=152.4 mm) focuses it into the sample where it is overlapped with the probe.

A small fraction of the amplified laser output (~4 µJ) is focused onto a 1.5 mm thick CaF₂ window (1” diameter PW-1006-CFUV from CVI laser) with a lens of 100 mm focal length in
order to generate the white light continuum. The CaF$_2$ is held in a homemade rotating cell to eliminate the intensity fluctuations. After generation, the white light continuum is recollimated by an off-axis parabolic mirror (Janos Technology, A8037-175, reflected effective focal length of $f=25.40$ mm) and split into two beams via a beam splitter (neutral density filter with optical density of 0.3) in order to compensate fluctuations of laser power. One of these beams (probe) is used for probing the perturbation in the sample by the pump beam. Thus, it is overlapped with the pump beam at the sample position. The other beam is used as a reference, and it passes through an unperturbed area of the sample. Measurements are performed at magic angle where pump and probe are linearly polarized at $54.7^\circ$ with respect to each other.

Figure 2-6. Schematic representation of transient absorption set-up.

The perturbation created by the pump in the sample will be completely measured as long as the size of the probe beam is equal to or smaller than the pump beam size. Otherwise, the probe beam detection would reflect perturbed as well as some unperturbed volumes of the
sample which will result in an insignificant change in absorption spectrum. Accordingly, during
the measurements the probe and the pump beams have the diameters of 124 µm and 140 µm,
respectively. The beam sizes are measured by using the knife-edge scanning method. After
the sample, probe and the reference beams are directed and focused on to the slit of the
spectrograph at two different heights and read by the charge coupled device (CCD) camera.

**Signal Detection System**

The CCD camera is attached to a spectrograph (Shamrock SR 303i) that separates light
into its component wavelengths combined with Andor iStar that is an optical spectral analyzer.
The spectrograph can be used for the wavelength range from 190 nm to 10 µm. The grating used
in our experiments had a line density 300 l/mm.

CCD is basically a silicon based semiconductor chip containing 256 rows and 1024
columns for spectrographic applications. These rows and columns compose a two dimensional
imaging area with 256x1024 pixels. In our experiments, the reference and probe beams
approximately had a width of 10 rows on CCD chip in a 280 nm window (from 350 nm to 630
nm). The images of probe and reference were apart from each other (~ 50 rows) (Figure 2-7).

![Figure 2-7. The image of probe and reference beams on CCD chip.](image)
If an image is projected onto the array, light falling onto the pixels produces the corresponding charge pattern on the arrays of the CCD by producing electrons on the pixels of the array. The created charge pattern is transferred from the chip to the shift register by a series of horizontal transparent electrodes that cover the array.

The shift register runs below the imaging area. It is parallel to the light collecting rows and it has the same number of pixels as rows of imaging area. However, it is masked to avoid light to fall on it. The shift register also has a series of electrodes which are parallel to the columns. They are used to transfer the produced charge patterns into the amplifier pixel by pixel. Then the output of the amplifier is converted into a binary number via an analog to digital converter (A/D).

The change in transmission read by CCD is recorded by the computer connected to the CCD as a function of wavelength at different time points by using a homemade labview program. Afterwards during the data processing, the change in transmission is converted to changes in absorption.

In steady state measurements, transmission (T), absorption (A) and the relationship between transmission and absorption are defined as:

\[
T(\lambda) = \frac{I(\lambda)}{I_0(\lambda)}
\]  

(2-9)

\[
A(\lambda) = \log \frac{I_0(\lambda)}{I(\lambda)} = \log \frac{1}{T(\lambda)} = -\log T(\lambda)
\]  

(2-10)

The data collected in our system is recorded as absolute values of change in transmission since the change in the probe beam spectral intensity is normalized to the reference beam intensity in order to compensate for the fluctuations of laser power as it is expressed in Equation 2-11.
\[
\frac{\Delta T}{T} = \frac{T_{\text{pump}} - T_{\text{nopump}}}{T_{\text{nopump}}} = \left( \frac{I_t}{I_0^{\text{ref}}} \right)_{\text{pump}} - \left( \frac{I_t}{I_0^{\text{ref}}} \right)_{\text{nopump}} = \frac{I_{t,\text{pump}}}{I_{t,\text{nopump}}} - 1 \quad (2-11)
\]

Then, by using the Equation 2.11, the change in absorption is defined as

\[
\Delta A = -\log \left( \frac{\Delta T}{T} + 1 \right)
\]  

(2-12)

The time resolved data presented in Chapter 3 are average of around 30-40 experiments. I collected the average of 30 laser shot at a single time point in each experiment that allows me to have data average of ~1000 laser shots at a single time step.

**Time Resolution of the Experiment**

The instrument response function (IRF) of the system is measured by taking advantage of coherent artifacts in the pure solvent due to the cross phase modulation\textsuperscript{86-88} of pump and probe beams. These coherent effects are observed in acetonitrile and hexane. Figure 2-8 shows the

![Graph showing the coherent artifact of hexane excited at 320 nm, probed at 355 nm.](image)

Figure 2-8. Coherent artifact of hexane excited at 320 nm, probed at 355 nm.
coherent artifact signal in hexane when the solvent is excited at 320 nm and probed at 355 nm. The temporal width of IRF at FWHM is measured as ~250 fs (Figure 2-8).

Data Analysis Methods

Transient Absorption data is an \(nxm\) matrix where the size of the matrix shows that the whole data is the composition of a set of \(m\) spectra each containing \(n\) successive delay times. Each spectrum can contain contributions from “\(p\)” components. Since each one of the “\(p\)” components has a specific extinction coefficient at different wavelengths, they exhibit characteristic spectral responses at those wavelengths. The spectral responses of all of the components can be represented by an \(nxp\) matrix which is called \(S\) here. Because of the excited state dynamics of the system, concentrations of the components can change from one spectrum to another. The concentration profiles of “\(p\)” components in each spectrum can be put in the form of a \(pxm\) matrix, \(C\). Since absorbance of a species at a specific wavelength can be written as the multiplication of the concentration and extinction coefficient of that species, transient absorption data can be explained as product of \(S\) and \(C\) matrices similarly in Equation 2-13 where \(D\) matrix represents the whole transient absorption data. \(^{89-91}\)

\[
D = SC
\]  

(2-13)

In the analysis of transient absorption data it is critical to estimate the number of components in the system which are spectrally distinguishable species. This task can be achieved by employing the Singular Value Decomposition (SVD) method in determining the rank of matrix \(D\). The rank of the data matrix provides a lower limit for the number of the components of the system. In this way, application of SVD gives the opportunity to determine the representative and optimum data for further analysis. \(^{89,90}\) SVD is a mathematical method which decomposes the \(nxm\) matrices into three matrices according to Equation 2-14.
None of the matrices provided by SVD have a chemical or physical meaning. U and V represent orthogonal matrices with size of $n \times m$ and $m \times m$ respectively. W is an $m \times m$ square diagonal matrix and it contains the singular values in decreasing order of magnitudes. The magnitude of these values is a measure of the contribution of the corresponding columns of matrices U and V to the reconstruction of original matrix D. The components have values close to zero do not make significant contribution to the total system. The components with the relatively higher singular values can be used to explain the system. Therefore, the minimum number of components which are required to explain the system can be determined according to the magnitude of the singular values. However, in the presence of noise it may not be easy to set a threshold that dissects the contribution of the components from the contribution of noise. In this case, evolving factor analysis methods (EFA) can be employed to find out the significant number of the components present in the system.\(^{89}\)

The basic idea of EFA is to follow the evolution of the singular values in time. It evaluates the rank of the gradually increasing submatrices formed by the addition of one row at a time. If the rows are added from the top of the matrix to the bottom, it is called forward EFA and elicits the appearance of the singular values with increasing time. What is more, the disappearance of a singular value with increasing time can be detected with backward EFA where the rows are added from bottom to the top.\(^{89,92}\) The significant singular values determined by the EFA are those singular values above the noise level defined by the pool of nonsignificant singular values.\(^{93,94}\) Significant singular values, which correspond to the components of the system, can be clearly seen by plotting the results of forward and backward EFA as it is shown in Figure 2.9.
The system in Figure 2-9 consists of three components which are represented by the singular values above the noise level, the shaded area of the plot in figure.

Figure 2-9. (——) Results of forward EFA , (— -) Results of backward EFA. Adapted from reference.89

Upon the application of EFA to the transient absorption data, size of the S (nxp) and C (pxm) matrices in Equation 2-13 is discovered. The number of significant values which are exhibited by the EFA is equal to the number of components (p) in the system. The number of components provided by the EFA is equal to the number of SVD components which have significant singular values. Consequently, U and V matrices will have the same dimensions as S and C, respectively. Also, they contain the same information with S and C. Therefore, Equation 2-13 and 2-14 can be combined as in Equation 2-15.

\[ SC = UWV^T \] (2-15)

If one examines Equation 2-15 closely, one finds that the columns of U and V matrices contain spectral and concentration information, respectively. These columns are mathematically independent vectors and they might not have a physical meaning. However, they are linear
combinations of the physically meaningful vectors that fit a certain kinetic model. In order to find out these vectors a rotation can be performed on U or V matrix by using a pxp rotation matrix. In this thesis work, the rotation is performed by employing an algorithm called Multivariate Curve Resolution- Alternating Least Squares (MCR-ALS) instead of finding a rotation matrix.

MCR-ALS is an iterative self-modeling method relying on the alternating least squares (ALS) algorithm. It provides information about the kinetic and spectral profiles of the system components. The resolution of the method depends on the correct estimation of number of the components contributing to the system and application of chemical and mathematical constrains. Therefore the output of the EFA can be a proper input for the MCR-ALS method as the initial estimation.

MCR-ALS method decomposes a data matrix $D$ ($n \times m$) containing the combined information about an evolving system, into the matrices which contain the pure spectral and kinetic profiles of the system components. The decomposition is described in Equation 2-16 where the columns of $C$ ($n \times p$) represent kinetic profiles and rows of $S^T$ ($p \times m$) describe the related spectral profiles of $p$ species. $E$ ($n \times m$) is the random perturbation matrix containing the residuals.

$$D = CS^T + E$$ (2-16)

Despite all the advantages, curve resolution methods including MCR-ALS do not deliver a single solution for the set of components whose linear combinations describe the original data. One can claim that the biggest drawback of using these methods is rotational ambiguities; however, this drawback can be eliminated by applying some constraints in spectral and concentration domain.
Applying the various constraints during the execution of a Matlab routine in which the MCR-ALS algorithms are written is not an easy task. Fortunately, a user-friendly graphical interface developed by Chemometrics Group, University of Barcelona is available online. The algorithm used during the process is summarized in the scheme in Figure 2-10. In this process,

Figure 2-10. Scheme of ALS algorithm.

first the number of the components in the experimental data matrix D is determined by means of SVD. Then, initial estimates of concentration or spectral profiles by using EFA method. After choosing suitable constraints, least-squares calculation is performed until convergence is
achieved. In other words, the process is repeated until one can get the lack of fit (LOF) under a selected threshold value. LOF is a measurement of goodness of the optimization process. It represents the difference between the original data D and the data created by the reconstruction from the CS$^T$ product obtained by MCR-ALS. The value of LOF is calculated according to the Equation 2-17 where $d_{ij}$ is an element of the input data and $e_{ij}$ is the difference between the input and the MCR-ALS reproduction.

$$LOF(\%) = 100 \sqrt{\frac{\sum_{i,j} e_{ij}^2}{\sum_{i,j} d_{ij}^2}}$$ (2-17)
CHAPTER 3
RING OPENING MECHANISM OF A NOVEL PHOTOCHROMIC OXAZINE

Photochromic compounds respond to optical stimulations by changing their structural and electrical properties. In a photochromic system, a new state is formed by light excitation. and this photogenerated state can return to the original state thermally or with exposure of another light source. Therefore, by simply turning optical input on and off, photochromic compounds can complete many successive switching cycles by altering and resetting an output property. Since they interchange between two states, these materials appear as possible constituents of the molecular switches. The design of molecular switches is a challenge of miniaturization in future nanotechnology. Design and synthesis of new photoresponsive materials with improved properties such as colorability, fatigue resistance, and photostability is the primary purpose of the recent studies in field.5,9,35,56,99,100

Spiropyans and spirooxazines are the most studied photochromic families as molecular switch candidates because of their reversible optical activity.5,9,27,101 These molecules present two heterocyclic parts linked together by a common Carbon atom with sp^3 hybridization. They absorb at the UV region. The excitation with UV light leads to the changes in the molecular structure and absorption spectra. Removal of the excitation source results in returning to the original structure (Chapter 1).9

The photochromic reaction mechanism and the reaction dynamics of spiropyans and spirooxazines were studied with time resolved resonance Raman Spectroscopy,14,34,102 laser flash photolysis,20,23,71,73,103-105 quenching experiments,106 and picosecond and femtosecond absorption spectroscopies21,36,37,107-110 by various research groups. These studies uncovered important facts about the mechanism and the dynamics of photochromic reaction of the spiropyans and spirooxazines.
In spiropyans and spirooxazines, the first step of ring opening mechanism, the C-O bond cleavage, occurs in picoseconds\textsuperscript{20,37,104,111} while the isomerization of the molecule from cis to trans form around the C=C double bond takes place in microseconds.\textsuperscript{17,18,22-24,112} For the nitrosubstituted spiropyans\textsuperscript{17,18,23,24,112} and spirooxazines,\textsuperscript{40} the triplet states play an important role in the ring opening mechanism of the molecules. On the other hand, triplet states do not participate in the ring opening mechanism of spiropyans\textsuperscript{16,19} and spiroxazines without nitro groups.\textsuperscript{26,36,113} The merocyanines (open form of the spiropyans and spirooxazines) of these molecules are directly formed from the singlet excited state. In the mentioned studies it is reported that the C-O bond cleavage occurs in 150-700 fs\textsuperscript{114} time period while the relaxation of cis-cisoid isomers to various merocyanine forms takes place in the time range from 50-100 ps to 1.3 -1.7 ns.\textsuperscript{109}

In recent years, there have been many trials of implementation of molecular switches\textsuperscript{115-123} by taking the advantage of reversible isomerization properties of spiropyans and the related molecules. However, in these trials researchers were facing two major problems. The thermal back reaction takes several minutes after the optical input is turned off. Additionally, the number of switching cycles that can be performed by the compound is limited.\textsuperscript{99} Improved materials with reversible optical isomerization properties similar to spiropyans but free from the limitations of spiropyans are needed for the realization of molecular switches in future technology.

Raymo and co-workers reported a newly synthesized molecular switch which displays photochromic properties based on photoinduced ring opening and thermal closing of an oxazine ring.\textsuperscript{99,100} Upon ultraviolet excitation, the oxazine ring opens and the photogenerated product is a chromophore which absorbs at around 440 nm. The original form of the molecule is fully recovered in 50 ns after the removal of excitation source. Furthermore, it is stated that this
photochromic oxazine can survive more than 3000 switching cycles without any evidence of decomposition. Although the absorption spectrum and the lifetime of the chromophore which is generated during the coloration process are well defined, still there are unanswered questions about the coloring mechanism; What is the rise time of the chromophore absorbing at 440 nm? Are there any intermediate states involved in the ring opening mechanism?

The goal of this study is to uncover the ring opening mechanism of the photochromic oxazine by employing Ultrafast Transient Absorption (TA) and Steady State techniques. Applying the same techniques, complementary quenching experiments are performed by using benzophenone which is known as a very good triplet sensitizer. The experimental results are analyzed using the methods Singular Value Decomposition (SVD), Evolving Factor Analysis (EFA), and Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS) methods. A kinetic model is proposed to explain the ring opening mechanism of the novel photochromic oxazine.

**Materials and Experimental Methods**

The novel photochromic oxazine is provided by Prof. Raymo (University of Miami). 4-nitroanisole and the model indoline in Figure 3.1 are two chromophoric fragments of the novel photochromic oxazine. Their properties are independent and the sum of their individual steady state absorption spectrum resembles to the steady state absorption spectra of the photochromic oxazine.

Sample solutions are prepared in HPLC grade acetonitrile and hexane from Fisher Scientific without further purification. Steady state measurements and transient absorption experiments are performed in 1 cm and 5 mm optical path length quartz cuvettes, respectively. The laser system, and transient absorption set up are described in detail in Chapter 2.
All of solutions used in sensitization experiments with benzophenone are deoxygenated since oxygen is a quencher of triplet state. To degas the solutions, argon is purged in to the solutions for 20 minutes. This procedure applied to the solutions of pure oxazine, pure benzophenone, and oxazine and benzophenone mixtures which are used both in steady state and time resolved experiments.

**Steady State Spectroscopy**

The steady state absorption spectrum of photochromic oxazine is shown in Figure 3-2. The first absorption band of the oxazine has a wide overlapping region with the first absorption band

![Normalized absorption spectra of oxazine (---), and 4-nitroanisole (—) in acetonitrile](image)
of the 4-nitroanisole (Figure 3-2). Approximate values for the energy differences between
ground state and the first excited state of oxazine, 4-nitroanisole and the model indoline and the
extinction coefficients of those compounds (at the absorption maximum) are listed in Table 3-1.

Table 3-1. Absorption wavelengths (λ) and molar extinction coefficients (ε) and energy
difference between S₀ and S₁ in acetonitrile.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Energy difference S₁-S₀ (kcal/mol)*</th>
<th>λ (nm)</th>
<th>ε (mM⁻¹ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>model indoline</td>
<td>95-110</td>
<td>281</td>
<td>3.9±0.2</td>
</tr>
<tr>
<td>4-nitroanisole</td>
<td>75-115</td>
<td>307</td>
<td>11.1±0.6</td>
</tr>
<tr>
<td>photochromic oxazine</td>
<td>70-110</td>
<td>316</td>
<td>11±0.6</td>
</tr>
</tbody>
</table>

*Calculated from the absorption spectra in reference.100

Oxazine in acetonitrile shows very weak emission between 330 and 600 nm (Figure 3-3)
upon the excitation at λ=320 nm. It is not easy to compare the steady state absorption and
emission spectra of the oxazine in acetonitrile since the emission spectrum has a low S/N ratio
because of very low counts in emission (Figure 3-3). In this case, we can not determine whether
absorption and emission presents the similar transitions or not. From the values given in Table
3.1 and Tomasulo et al.,100 we conclude that when we excite the oxazine at λ=320 nm, the
nitroanisole part of the molecule will be excited since the indoline part does not absorb at this
wavelength. On the other hand, there was no significant emission from 4-nitroanisole in
acetonitrile after the excitation at λ= 320 nm. These observations suggest that the emission of the
oxazine in acetonitrile is not originated from the nitroanisole part of the molecule and there is an
interaction between indoline and the niroanisole parts in excited state.

In the literature, it is stated that nitroaromatic molecules exhibit neither fluorescence nor
phosphorescence at any temperatures in any solvents.124-126 Takezaki and coworkers determined
the triplet life time of nitrobenzene in alkane, benzene, ethanol, and water between 400 and 900
ps using picosecond time-resolved transient grating method.126 Yip et. al reported that the
nitrobenzene in THF has a triplet state with a lifetime of 800 ps.127 Triplet lifetime of the
nitrophenyl esters was investigated by Mir et al. In their study, they determined that 4-nitroanisole forms a triplet state in water. However, they could not detect any triplet state of the 4-nitroanisole in acetonitrile and by considering the studies about the nitrobenzene they concluded that they could not observe the triplet state of 4-nitroanisole in acetonitrile with nanosecond spectroscopy because 4-nitroanisole has a triplet state with lifetime in picosecond time domain.\textsuperscript{124}

Figure 3-3. Normalized absorption spectrum (\textbf{--}), emission spectrum (\textbf{--}) of oxazine in acetonitrile($\lambda_{\text{exc}}=320$ nm).

Since it is known that 4-nitroanisole possesses a triplet state, it is possible that oxazine also has a similar type of triplet state. Sensitization experiments using benzophenone were performed in order to detect whether the triplet state of 4-nitroanisole and oxazine has any role in the ring opening mechanism. In these experiments, solutions of benzophenone and oxazine at various concentrations were investigated using steady state emission and transient absorption spectroscopy.

In steady state, addition of benzophenone to an oxazine solution in acetonitrile enhanced the emission intensity of the oxazine after excitation at $\lambda =320$ nm. Figure 3-4 shows the
comparison of emission spectrum of oxazine with and without benzophenone in solution. Additionally, we observed that the phosphorescence of benzophenone is quenched in the presence of oxazine. It seems that energy transfer occurs from the triplet state of the benzophenone to the oxazine. The energy of the triplet state of the benzophenone is reported as 69 kcal/mol\(^6\) and the emission of the oxazine enhanced in the presence of the benzophenone has a peak around 360 nm which means that the emissive state has energy around 79 kcal/mol. Since the emissive state is energetically higher than the triplet state of the benzophenone an energy transfer from triplet state of the benzophenone to oxazine is not possible. The quenching of the benzophenone phosphorescence is observed because of not the direct quenching of triplet state but the precursor of it.

![Emission spectra of oxazine and benzophenone](image)

Figure 3-4. Emission spectra of oxazine 4.6x10\(^{-5}\) M (---), and oxazine with benzophenone 3.26x10\(^{-7}\)M (---), 6.52x10\(^{-7}\)M (-----) in acetonitrile, \(\lambda_{exc}=320\) nm. Inset shows the same data in an expanded scale.

Häupl and coworkers studied two types of spiro[cyclohexadieneindoline] and observed an emissive state. They discovered that this emissive state exhibits a significant solvent effect since the peak of the emission band shifts to red with increasing polarity of the solvent. They concluded that this emission belongs to a charge separated state which is created in the excited state.
state of the photochromic molecules between the indoline, where the nitrogen act as the electron donor, and the aroylcyclohexadiene moiety, where the keto group is the acceptor.\textsuperscript{69,70}

In order to check the solvent sensitivity, we measure emission spectra of oxazine after the addition of benzophenone in acetonitrile and hexane. We collected the emission spectra of the mixtures upon the excitation at 320 nm and observed a red shift of about 10 nm in acetonitrile compared to the emission spectrum in hexane (Figure 3-5).

The spectral shifts can be due to specific fluorophore-solvent effects\textsuperscript{63} and charge separation in the excited state as Häupl and coworkers reported.\textsuperscript{63,69,70} If the shift in emission spectrum is observed due to the general fluorophore-solvent effects, the same amount of shift should be seen in the absorption spectrum of the molecule. However, in case of charge separation, the molecules have larger dipole moments in the excited state ($\mu_e$) than in the ground state ($\mu_g$). The more polar environment results in lowering the energy of excited state and emitting at longer wavelengths. In this case, the shift observed in emission spectrum would be more significant than the spectral shift occurred in absorption spectrum.

![Figure 3-5. Emission spectra of oxazine in hexane (-----) and in acetonitrile (---).](image)
In order to characterize the emissive state of the photochromic oxazine, the absorption spectra of the molecule in both solvents are also compared (Figure 3-6). The absorption spectrum was red shifted about 4nm in acetonitrile compared to the absorption spectrum in hexane. In this case, the shift in absorption spectra is less than the one observed in emission spectra implying that $\mu_e$ is larger than $\mu_g$.

![Figure 3-6. Absorption spectra of oxazine in hexane (——) and in acetonitrile (---).](image)

According to steady state spectroscopy results, we suspect that there is a charge separated state that forms following the excitation of oxazine at $\lambda=320$ nm. The emission of that state is enhanced in the presence of benzophenone. Since energetically, the energy transfer can not be from the triplet state, we propose that energy transfer occurs from singlet state of the benzophenone either to the singlet state state or to the charge separated state of the oxazine. The time resolved data will provide better understanding of ring opening mechanism by giving detailed information about the energy transfer from benzophenone to oxazine.

**Transient Absorption Spectroscopy**

Raymo et al. reported that the UV excitation of the photochromic oxazine induces the cleavage of C-O bond, and this bond cleavage produces the open form of the molecule (Figure 3-
They observed a strong absorption band at 440 nm in acetonitrile when the sample is excited at \( \lambda = 355 \) nm. This absorption band is very similar to the steady state absorption spectrum of p-nitrophenolate which is also a part of the open form of the oxazine (in the circle of red dots in Figure 3-7). Under these conditions, they concluded that upon the excitation at \( \lambda = 355 \) nm, the closed form of the oxazine goes to the open form, which contains p-nitrophenolate chromophore as an absorbing unit. Therefore the absorption band observed at 440 nm is attributed to the open form of the photochromic oxazine.\textsuperscript{99,100}

What is more, they observed that the species absorbing at 440 nm is generated within the 6 ns excitation pulse and goes back to the original form with a lifetime of 22 ns.\textsuperscript{99,100} In these conditions, the formation of the photogenerated state is not resolved. In order to monitor the ring opening mechanism a better time resolution is needed. In this thesis, the photogeneration process (ring opening mechanism) is examined via picosecond transient absorption spectroscopy which is the technique described in detail in Chapter 2.

![Figure 3-7. Structure of the open form of the photochromic oxazine.](image)

Picosecond transient absorption spectroscopy data of the photchromic oxazine in acetonitrile between -12 and 50 ps with 2 ps resolution collected after the excitation at \( \lambda = 320 \) nm is presented in a wavelength vs. time graph in Figure 3-8. Two regions are present with
positive changes in absorption spectrum which corresponds to photoinduced absorption. The color coding of the plot gives an idea about the intensity of the signal observed. The darkest red color corresponds to the strong photoinduced absorption, while the darkest blue color shows a lower negative signal value.

One of the absorption bands raises within 10 ps with a spectral peak around 440 nm. Changes in the dynamics were not detected until ~600 ps which was the farthest time delay that can be reached with our instrument. The shape of the photoinduced absorption band and the relative long lifetime leads to conclude that the absorbing species is the final product of ring opening process.

Figure 3-8. Transient absorption spectra of photochromic oxazine after excitation at \( \lambda \)=320 nm. with 2 ps time steps.

Upon excitation at \( \lambda \)= 320 nm another absorption band, which was not detected via nanosecond transient absorption spectroscopy, is observed. This band has a spectral maximum around 505 nm, and it rises and decays within 4 ps. Under these circumstances, 2 ps time...
resolution is not good enough to characterize the band in detail. Therefore, transient absorption spectra with higher time step resolution is collected and presented in Figure 3-9.

This previously unknown band rises within the IRF (250 fs, Chapter 2) and decays within 2 ps. Note that this time period is shorter than the rise time of the absorption band assigned to the open form of the oxazine. Accordingly, we suggest that the absorption band, peaking around 500 nm, belongs to an intermediate species in the ring opening mechanism of the oxazine. Time resolved sensitization experiments with benzophenone in acetonitrile provide a better understanding of the mechanism and the electronic properties of the species involved in the mechanism.

![Figure 3-9. Transient absorption spectra of photochromic oxazine after excitation at $\lambda=320$ nm.](image)

Polar molecules which contain both electron donating and electron withdrawing groups suffer from charge localizations on specific subunits that constitute the molecule. These charge localizations occur according to the ionization potentials (IP) of the subunits. In Poisson et al.’s study, the ionization potentials of p-nitronitroanisole, and indoline, which are the subunits of the photochromic oxazine studied in this thesis, are given as 8.9 eV, and 7.0 eV, respectively.\(^{31}\) Due
to the difference in IP’s of the subunits, charge separation on the excited state can occur throughout the molecule. In this case, the localization of positive charge on indoline subunit, and the negative charge would reside on anisole part of the molecule.

Raymo and coworkers collected the electrochemical absorption spectrum of a model indoline after oxidation to form the radical cation (Figure 3-10). Transient absorption spectrum of oxazine recorded at 800 fs shows the photoinduced absorption band 505 nm and matches well with the steady state absorption of the radical cation (Figure 3-11). This matching can be evaluated as the formation of the charge separated species in a few hundred femtoseconds after the excitation.

![Chemical structure of A) neutral B) radical cation form of the model indoline.](image)

Figure 3-10. Chemical structure of A) neutral B) radical cation form of the model indoline.

Additionally, the transient absorption spectra of the oxazine exhibit a solvent effect which supports the idea of the formation of a charge separated state. Transient absorption spectra of the oxazine in acetonitrile and hexane each recorded at 800 fs and compared in Figure 3-12. In hexane, the peak of the absorption band has shifted to 515 nm while it was observed at 505 nm in acetonitrile. Häupl et al. reported that very polar excited species are stabilized in polar solvents due to positive solvatochromism and observed red shifts in fluorescence spectra of spiroindolines and their merocyanine with increasing solvent polarity. As we mentioned before, this red shift follows the stabilization of the emissive excited state. This shift to an excited state with lower energy is responsible for a blue shift on excited state excitation energies. Therefore, it is reasonable to observe a red shift in transient absorption spectra with decreasing solvent polarity if the absorption band observed at 800 fs belongs to a charge separated state.
Figure 3-11. (---) Transient absorption spectrum of oxazine recorded at 800 fs in acetonitrile after excitation at $\lambda=320$ nm. (-) Steady state absorption of oxidized indoline in acetonitrile.

Figure 3-12. Transient absorption spectrum of oxazine recorded at 800 ps in acetonitrile (---) and in hexane (---) after excitation at $\lambda=320$ nm.

It was mentioned before that transient absorption experiments are performed in order to figure out if there is a triplet state involved in ring opening mechanism of the oxazine or not. For this purpose, the solutions with different ratios of benzophenone to oxazine in acetonitrile were
created. In the same way, oxazine with various concentrations has been added to the benzophenone in acetonitrile.

**Sensitization Experiments**

Transient absorption spectrum of 0.05 M benzopheneone is presented in Figure 3-13 part A. In the data, a strong photoinduced absorption (PIA) band is observed with a spectral peak around 523 nm. Close scrutiny of Figure 3-13 shows that between 0-15 ps there is a small blue shift of this PIA signal. Aloise et al investigated the triplet formation of benzophenone and showed that at early times PIA from a singlet state of benzophenone is observed, followed by the creation of the triplet state. This process occurs within c.a. 15 ps and leads to the strong triplet state absorption at 523 nm.

The data presented in Figure 3-13 part A does not contain any oxazine in it. The amount of oxazine in 0.05 M benzophenone in part C is higher than in part B. Part D shows the transient absorption data for 0.05 M benzophenone with highest amount of oxazine. Upon the addition of oxazine to the benzophenone solution, a PIA band with a spectral peak around 505 nm appears. As the amount of oxazine increasing in solution, the intensity of newly appeared peak increases while the intensity of PIA that belongs to the triplet state of the benzophenone decreases. On the other hand, once the triplet state of benzophenone is formed its intensity does not change anymore, which means that there is no interaction between the triplet state of the benzophenone and oxazine in solution. In essence, even though most of the absorption is from the BP the energy is quickly transferred to the oxazine creating the fast 505 nm band and decreasing the formation of benzophenone triplet state.

Figure 3-14 A shows the transient absorption spectrum of 1.95x10^{-4} M oxazine in acetonitrile. In the data, we observed two PIA bands. One of the bands has a spectral peak around 500 nm and it is detectable in early times. Following the decay of this band, another PIA
band peaking around 440 nm appears. This band was assigned to the open form of the oxazine in Tomasulo et. al.\textsuperscript{99,100}

![Transient absorption spectra](image)

Figure 3-13. Transient absorption spectra of A) 0.05 M benzophenone, 0.05 M benzophenone with oxazine with the ratio of oxazine/benzophenone B) 2.6/1000, C) 4/1000, D)5.2/1000 in acetonitrile with 1 ps time steps.

The change in transient absorption spectra of 1.95x10\textsuperscript{-4} M oxazine upon the addition of small amount of benzophenone is presented in Figure 3-14 in parts B, C, and D. Transient absorption intensity of PIA around 500 nm increases with the increasing amount of benzopheneone in the solution. However, a detectable change was not observed at the other PIA band of oxazine at 440 nm.

Overall, from steady state emission experiments and time resolved experiments we conclude that an energy transfer occurs from benzophenone to oxazine. Steady state and time resolved experiments show that the emission and photoinduced absorption intensity of newly formed state increases upon the addition of benzophenone in the oxazine solutions and this state
is the one primarily formed when oxazine is added to benzophenone. Due to the energetic of electronic states in each molecule, we inferred that the triplet state of benzophenone was not involved in the energy transfer mechanism and that the energy transfer occurred from the precursor singlet state of the benzophenone to either singlet state or directly to the charged separated state of the oxazine.

![Figure 3-14. Transient absorption spectra of A) 1.95x10^{-4} M oxazine, 1.95x10^{-4} M oxazine with benzophenone with the ratio of benzophenone/oxazine B) 2/100 C) 4/100 D) 6/100 in acetonitrile with 1 ps resolution.](image)

**Decomposition of Transient Absorption Spectra**

In time resolved experiments, the charge separated state and the open form of the oxazine have overlapping regions in their absorption spectra although the bands have different kinetics. This can be appreciated in Figure 3-15. It shows the transient absorption at 436 nm, where both states contribute to the signal. An initial peak forms and decays within a few picoseconds and a second component rises after the decay of that peak. The total transient absorption data needs to
be analyzed in a way that allows uncovering the individual dynamics of each state present in the system.

![Figure 3-15. Transient absorption of photochromic oxazine at 436 nm.](image)

It is not obvious in the total transient absorption spectrum that the charge separated state is a precursor of the open form or whether it is involved in a mechanism that competes with the formation of open form of the oxazine. Additionally, some other states which are not detectable in the total transient absorption spectrum might be formed during the ring opening process of the oxazine. Analysis methods which can provide information about kinetics of individual states and allow the construction of a kinetic model are needed. Singular Value Decomposition (SVD), Evolving Factor Analysis (EFA), and Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS) were used as analysis methods in order to get the required information for the construction of a kinetic model.

**Data Analysis Results**

The SVD analysis of the transient absorption data collected between 380 and 630 nm within 50 ps after the excitation of oxazine in acetonitrile at $\lambda = 320$ nm (Figure 3-14 A) gives two significant components that can explain the complete set of whole transient absorption data.
(Figure 3-16). The magnitude of first two singular values is distinguished from the third and following singular values whose magnitudes are close to zero.

![Figure 3-16. Singular values, result of SVD analysis.](image)

Figure 3-16 presents the first two spectral and temporal components of the oxazine in acetonitrile. Although these two SVD components reconstruct the data very well, they do not

![Figure 3-17. Spectral (A1, and A2) and temporal (B1, and B2) components of 1.95x10^-4 M oxazine in acetonitrile, result of SVD analysis.](image)
have a chemical or physical meaning. Components of the system with physical meaning (population, absorption states) need to be determined by using MCR-ALS which allows the rotation of these components, generating a new set of spectral and temporal components. Before applying the MCR-ALS algorithm, EFA can show how the components of the system evolve in time. This method provides an initial guess for the MCR-ALS.

Results of EFA method confirm that two significant components contribute to the transient absorption spectra (Figure 3-18). The dotted line on the Figure 3-18 is placed to set the noise level. Components contributing above that noise level are considered as the principle components. The temporal response of these two principle components are provided in Figure 3-19. They are used as initial guesses to determine the temporal and spectral profiles of the components using MCR-ALS.

![Figure 3-18. \(\text{---}\) Results of forward EFA, \(\text{---}\) Results of backward EFA of 1.95x10^{-4} M oxazine in acetonitrile](image)

arising from a charge separated state (Figure 3-20 A1). The temporal component corresponding to the 440 nm absorption band rises during 50 ps (Figure 3-20 B2), while the other component with absorption band around 500 nm rises within the instrument response function of \(\sim 250\) fs and decays very fast and goes to zero in 50 ps (Figure 3-20 B1).
Figure 3-19. The result from EFA used as initial guess for temporal profiles of 1.95x10^{-4} M oxazine in acetonitrile.

The MCR-ALS method gives two spectral components: one has an absorption band peaked around 440 nm which is assigned to the absorption of the open form of the oxazine (Figure 3-20 A2), the other one has an absorption peak around 500 nm which we assigned as the absorption

Figure 3-20. Spectral (A1-A2), and temporal components (B1-B2) of 1.95x10^{-4} M oxazine in acetonitrile, result of MCR-ALS analysis.
We reconstructed the transient absorption data evaluating \( D = CS^T \) (See Chapter 2) from the MCR-ALS components presented in Figure 3-20. Comparison of the experimental and reconstructed data is shown in Figure 3-21. The goodness of the optimization process is evaluated using the percent of lack of fit (LOF). The difference between the experimental data and the reconstructed data is also a measure of how well the experimental data is explained by the MCR-ALS analysis.

Data collected after the addition of benzophenone at various concentrations to a solution of oxazine in acetonitrile was also analyzed (SVD and EFA results can be seen in Appendix B). For
each ratio of concentrations, the data can be explained with two spectral/temporal components similar to the components found for the solution of pure oxazine in acetonitrile. The main difference observed in the analysis of each mixture is that the absorption band at around 500 nm increases with increased amount of benzophenone in the mixture. There is no change observed in the temporal components associated with each spectral band (Figure 3-22).

![Figure 3-22. A1-A2) Spectral components of 1.95x10^-4 M oxazine (---), 1.95x10^-4 M oxazine and benzophenone with the ratio of benzophenone/oxazine 2/100 (----), 4/100 (--), 6/100 (---) and B1-B2) corresponding temporal components for each solution.

The spectral and temporal components obtained from the analysis of each data solution are used to reconstruct the data in each case. (See Figure 3-23, Figure 3-24 and Figure 3-25). The residuals show no structure, an indication of good match between experiment and analysis. Additionally, the LOF values are calculated as 1.21 %, for 1.95x10^-4 M oxazine in acetonitrile and1.85 %, 1.60%, 2.74% for the solutions of 1.95x10^-4 M oxazine and benzophenone with the ratio of benzophenone/oxazine 2/100, 4/100, 6/100 respectively. Even though benzophenone is
added to the oxazine solution, the observed components belong to the oxazine, and none of the benzophenone components are observed in the analysis of data.

Figure 3-23.Experimental (---), reconstructed (--), reconstructed transient absorption data, and difference between experimental and reconstructed transient absorption data (---) of 1.95x10^{-4} M oxazine and benzophenone with the ratio of 2/100 in acetonitrile.

As benzophenone is added, this relative contribution from the band peaked around 500 nm increases meaning that sensitization from benzophenone occurs either directly to the charge separated state or to a state that is the precursor of this charge separated state. On the other hand, since the absorption band centered at 440 nm is not affected by the presence of benzophenone, we conclude that the charge separated state (or the precursor of the charge separated state) is not a precursor in the mechanism of ring opening in this oxazine.
In order to understand which state of benzophenone is being quenched in the presence of the oxazine, we measured the transient absorption of mixtures of various concentrations of oxazine and 0.05 M of benzophenone in acetonitrile. The experimental data is analyzed using the methods mentioned before and results are compared to the pure benzophenone data which is collected under the same experimental conditions.

While I was working on transient absorption experiments of benzophenone, Aloise et al. published a report investigating the intersystem crossing in benzophenone. In the agreement with their results, after the excitation at 320 nm we observe three active electronic states (See...
The first singlet state ($S_1$) of benzophenone is populated right after the excitation. Decay of $S_1$ state (~6.5 ps) leads the formation of an intermediate state (IS). This process is followed by the formation of the triplet state of the molecule in ~10 ps. Spectral and temporal signatures of these states (provided by the SVD, EFA, and MCR-ALS analysis) are presented in Figure 3-26. The SVD components before the application of MCR-ALS can be seen in Appendix B.

Figure 3-25: Experimental (---), reconstructed (-----) transient absorption data, and difference between experimental and reconstructed transient absorption data (-----) of $1.95 \times 10^{-4}$ M oxazine and benzophenone with the ratio of 6/100 in acetonitrile.

After oxazine is added to the benzophenone solution an additional absorption band appears around 500 nm (See Figure 3-13 B, C, D), similar to the absorption band of the charge separated state of the oxazine. However, the absorption band around 440 nm corresponding to the open
form of the oxazine was not detected. Additionally, the first excited singlet state of the benzophenone was not detectable in the transient absorption of the mixtures since it was quenched in the presence oxazine. Moreover, absorption intensity of triplet state of benzophenone decreased with the increasing amount of oxazine in solution, while its kinetic curve is not changed. (rise time of the triplet state is ~10 ps) (Figure 3-26).

Figure 3-26. A1-A3) Spectral, B1-B3) temporal components from transient absorption data of benzophene in acetonitrile. A1 and B1 belong to S1, A2 and B2 belong to an intermediate, and A3 and B3 belong to T1.

When the SVD, EFA, MCR-ALS methods are used for the analysis of the transient absorption data of the benzophene/oxazine mixtures, a component with an absorption peak around 500 nm appears. This component rises and decays within 2 ps. Since this component is not present in the benzophenone data we assign it to the oxazine. When the concentration of the
oxazine is increased in the mixture solution, the contribution comes from this new band increases (Figure 3-27) and the contributions of benzophenone components decrease. The relative contributions of each component (singular values) are presented in Table 3-2.

![Figure 3-27. Increase of the temporal component appeared upon the addition of oxazine into benzophenone, 0.05 M benzophenone and oxazine with the ratio of oxazine/benzophenone = 2.6/1000 (---), 4/1000 (--), and 5.2/1000 (—) in acetonitrile.](image)

**Table 3.2 Singul ar values of the electronic states of benzophenone in pure benzophenone and benzophenone and oxazine mixture solution.**

<table>
<thead>
<tr>
<th>Mixtures</th>
<th>Singular Values of T₁</th>
<th>Singular Values of S₁</th>
<th>IS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05 M benzophenone</td>
<td>1.2882</td>
<td>0.1045</td>
<td>0.0429</td>
</tr>
<tr>
<td>0.05 M benzophenone and oxazine</td>
<td>0.9911</td>
<td>0.0435</td>
<td>0.0341</td>
</tr>
<tr>
<td>with oxazine/benzophenone = 2.6/1000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05 M benzophenone and oxazine</td>
<td>0.8753</td>
<td>0.0391</td>
<td>0.0339</td>
</tr>
<tr>
<td>with oxazine/benzophenone = 4/1000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05 M benzophenone and oxazine</td>
<td>0.5268</td>
<td>0.0367</td>
<td>0.0010</td>
</tr>
<tr>
<td>with oxazine/benzophenone = 5.2/1000</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

This new band is similar in spectral and temporal response to the band observed for the charge separated state in oxazine. However, that new band is slightly red shifted and narrower compared to the component attributed to the charge separated state of oxazine (Figure 3-28).
These differences can be explained with the localization of the transferred energy on the nitroanisole part of the oxazine.

Figure 3-28. Comparison of spectral and temporal component for the charge separated state absorption band in pure oxazine (—) and mixture of 0.05 M benzophenone with 2.6x10^-4 M oxazine (—) in acetonitrile.

**Kinetic Model**

Following excitation at λ = 320 nm, the steady state spectra of oxazine shows small emission from an excited state sensitive to solvent polarity. The shift observed in the emission spectra in solvents with different polarities lead us to propose that the emission arises from a charge separated state. What is more, comparison of absorption spectrum of the oxidized model indoline with the transient absorption of the oxazine at 800 fs supports the idea about the formation of a charge separated state, with excited state absorption maximum at ca. 500 nm.

In the transient absorption experiments, in addition to the band assigned to the charge separated state, the band attributed to the open form of the oxazine is also observed. According to the results of time resolved experiments, the charge separated state forms within the instrument response function (~250 fs) and initially it decays fast (decays with 2.2 ps and 3.7 ps
time constants) and then it goes to zero within 50 ps. Open form of the molecule rises during 50 ps. What is more, in the sensitization experiments with benzophenone we observed that the change in absorption of the charge separated increases with the increasing concentration of the benzophenone, while the absorption of the open form of the molecule is not affected by the presence of benzophenone. Finally, the transient absorption data shows that the triplet state is not involved in the ring opening mechanism.

From the experimental results we conclude that the charge separation occurs in the excited state and it competes with the ring opening channel. In order to better understand the mechanism, we build a model based on the experimental results. The validity of the model is checked by fitting the temporal components of the transient absorption data of oxazine in acetonitrile. For this purpose, the number of the points in the temporal components is increased by interpolation. Then the interpolated data is fitted by using a home-made Matlab fitting program which calculates the populations of the state by numerically integrating the differential form of the kinetic equations.

While building the model (Figure 3-29), and considering the results of the sensitization experiments, we assume that the charge separated state and the open form are produced directly from the first excited singlet state (S_1), in addition we assume that charge separated does not contribute to the ring opening mechanism. Although looking at the temporal components it might suggest a 2 state model, the decay of the 1st component does not correspond to the rise of the 2nd component. The fitting trials showed that the charge separated state contributes indirectly to the ring opening. This process involves an intermediate state which is not observable in the transient
absorption experiments, but who influences the dynamics.

Figure 3-29. Energy level scheme of the photoisomerization of oxazine.

The suggested kinetic model and the temporal components of oxazine match very well (Figure 3-30). The rate constants provided by the fitting procedure are presented in Table 3-3. According to the fitting results one can conclude that that from the excited state there are two relaxation channels. The first one is the charge transfer from within the closed form of the oxazine from indoline part to the nitroanisole part of the molecule, which occurs in the excited state as it is known for the lactone form of rhodamines.129 Second channel is the C-O bond cleavage and isomerisation to the open form of the oxazine. What is more, the ring opening process occurs mostly from the $S_1$ state. The charge separated state contributes indirectly to the
ring opening mechanism, but this contribution is small compared to the reaction with rate constant of $k_6$.

![Graph showing temporal components](image)

Figure 3-30. Interpolated forms of temporal components belong to the charge separated state (o) and open form of the oxazine (o) and prediction of kinetic model for charge separated state (—), and the open form (——).

<table>
<thead>
<tr>
<th>n</th>
<th>$k_n$ (ps$^{-1}$)</th>
<th>$\tau_n$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>&lt;0.25</td>
</tr>
<tr>
<td>2</td>
<td>0.27</td>
<td>3.7</td>
</tr>
<tr>
<td>3</td>
<td>0.46</td>
<td>2.2</td>
</tr>
<tr>
<td>4</td>
<td>0.18</td>
<td>5.5</td>
</tr>
<tr>
<td>5</td>
<td>0.08</td>
<td>12.5</td>
</tr>
<tr>
<td>6</td>
<td>0.16</td>
<td>6.3</td>
</tr>
</tbody>
</table>
What is more, there are other kinetic models that we have tried in the process of finding the appropriate kinetic model for our system. These kinetic models and the fittings according to them are presented in Appendix C.
CHAPTER 4  
ANISOTROPY OF PHENYLENE ETHYNYLENE DENDRIMERS

Lately, researchers have an interest in developing artificial photosynthetic mimics to be used as the components of the photonic devices. In the natural photosynthetic process, the solar energy is absorbed by the chlorophyll molecules at all over the organism and transferred to the reaction center. In the reaction center, light energy is converted to the chemical energy. In this sense, dendrimers receive the attention as prospective photosynthetic mimics due to their structural, physical and energetic properties.\textsuperscript{130-135}

Dendrimers are highly branched treelike macromolecules.\textsuperscript{130} Dendrimers are characterized by their generation (branching points) number and the branching of the end groups\textsuperscript{136} and they can be divided into three structural units as core or focal moiety, branches, and the end groups placed on the periphery.

Symmetrical dendrimers with equivalent branches and good light harvesting properties have been reported by many groups.\textsuperscript{137-141} Peng et al.\textsuperscript{142} introduced unsymmetrical dendrimers with structurally unequivalent branches. The structural differences between the dendrimers with symmetrical and unsymmetrical branching are presented in Figure 4-1. Structural properties of the unsymmetrical dendrimers (Figure 4-1) allows shortcuts in the communication between the end groups and the core while in the symmetrical dendrimers, each sub-branch is involved in the communication of the periphery and the core. Additionally, in unsymmetrical dendrimers the number of absorbing units grows faster with increasing generation. For these reasons, it is claimed that the dendrimers with unsymmetrical branching can be better candidates to serve as light harvesting antennae and energy-transferring funnels.\textsuperscript{142}

In dendrimers, the efficient energy transfer from periphery to the core requires an energy gradient between the outside branches and the branches close to the center of the molecule. That
energy gradient can be created with branches with increasing length from periphery to the center of the molecule.\textsuperscript{142}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure41.png}
\caption{Model structures of monodendrons with A) symmetrical branches, and B) unsymmetrical branches}
\end{figure}

The positions of branching affect the nature of the excitation energy transfer mechanism. When the branching occurs at \textit{meta} positions, it breaks the $\pi$-conjugation between the segments of molecule, causing the localization of the excitation energy on individual segments.\textsuperscript{136,138,140,143} When the dendrimers include \textit{ortho} and \textit{para} branching, there are more the delocalized excitations throughout the conjugated segments. It is not easy to estimate the type of energy transfer mechanism in a conjugated molecule where the excitations are delocalized\textsuperscript{133} although it is known that the interactions between well separated segments, where the excitations localized, can occur through the Förster mechanism.\textsuperscript{139,144-147}

In unsymmetrical Phenylethynylene (PE) dendrimers, which are introduced by Peng and coworkers, the energy gradient is achieved by the \textit{ortho} and \textit{para} linkages of the phenylethynylneles, leading to segments of different conjugation lengths and broad absorption spectrum.\textsuperscript{142}
Fréchet and coworkers introduced a flexible dye sensitized dendrimer which contains poly(aryl ether) groups. The dyes in the scaffold are electronically separated from each other. The absorption spectrum of the dendrimer shows the characteristic absorption bands of the individual dyes. They claimed that the energy transfer from periphery to the center of the dendrimer occurs via stepwise Förster mechanism with efficiency higher than 97%.\(^\text{139}\)

Moore group prepared a series of rigid phenyl ethynylene (PE) dendrimers. In these extended dendrimers, the energy gradient was created with the increasing conjugation length from the periphery to the center of the dendrimer. This energy gradient leads to a unidirectional energy transfer toward the center of the dendrimer with the efficiency close to unity.\(^\text{136,138,140,148}\) Additionally, the energy transfer mechanisms of PE dendrimers are studied by other groups theoretically\(^\text{143,149,150}\) and experimentally.\(^\text{151,152}\) Mukamel and coworkers reported that the electron-hole pairs created during the excitation of PE dendrimers were localized within the segments connected by benzene rings substituted at the meta position.\(^\text{143}\) The energy funneling properties of PE dendrimer called nanostar was investigated by Kleiman and coworkers with femtosecond degenerate pump-probe spectroscopy.\(^\text{151}\) In that study, they determined that the excitation energy is localized on subunits and energy transfer occurs stepwise in subpicosecond time scale. They claimed that Förster theory can be used to explain the experimental energy transfer rates qualitatively. What is more, the combined experimental and theoretical studies performed in Martinez group showed that the meta substitution in symmetrical dendrimers breaks the conjugation at ground state but not at the excited state.\(^\text{149,153}\) The report from the Goodson group supported the existence of delocalized excited states in symmetrical compact PE dendrimers.\(^\text{152}\)
Melinger et al.\textsuperscript{154} investigated the photophysical properties of unsymmetrical PE monodendrons\textsuperscript{142} in solution by employing the techniques of steady state absorption and fluorescence spectroscopy, time-dependent fluorescence, and ultrafast degenerate pump-probe spectroscopy. The unsymmetrical dendritic structures examined exhibit broad absorption spectral range due to the different conjugation lengths of the different branches. They showed that the energy transfer from the PE backbone to a perylene trap attached to the center of the dendrimer is highly efficient (~90\%). They showed that the energy transfer can occur via a coupling through space mechanism (Förster energy transfer).

The unsymmetrical PE dendrimers, constituted from the \textit{ortho} and \textit{para} substituted PE units in various lengths, were synthesized by Peng and coworkers.\textsuperscript{142,155,156} The intramolecular interactions and the energy transfer mechanism in these unsymmetrical PE dendrimers have been investigated by the Kleiman Group.\textsuperscript{157} They employed steady state, ultrafast fluorescence, and transient absorption spectroscopy in order to determine extent of delocalization within the dendrimer. They observed that in unsymmetrical PE dendrimers the initial excitation is delocalized through the molecule. Within~400 fs after the excitation, some degree of localization is observed. When an ethynylene perylene (EPer) trap is added to the system, the excitation energy is transferred to the trap by a direct and a stepwise mechanism in a subpicosecond time scale.

The conjugation length of the segments determines the extent of localization on the segments and thus the number states involved in the energy transfer mechanism. Fluorescence anisotropy is a powerful method to investigate the interactions between segments and excitation energy transfer mechanism in dendritic structures.
Anisotropy measures the relative changes in the orientation of the absorption and the emission transition moments with respect to each other (See Chapter 2 for a detailed description). The transition moments for absorption and emission lie along the specific directions within a fluorophore. Fluorophores absorb the photons which has an electric vector that is oriented parallel to the transition moments. Emitted light also has an orientation axis in fluorophore. The maximum measured anisotropy depends on the relative angle between the absorption and emission transition moments.  

The measured anisotropies may be lower than the maximum theoretical values. Energy transfer between the fluorophores is a factor that causes the decrease in anisotropy values. Thus, fluorescence anisotropy contributes to discover the excitation energy transfer. For the molecules which follow the Kasha’s rule, the anisotropy does not change with the emission wavelength since they emit from the first excited state regardless of the excitation wavelength. On the other hand, the fundamental anisotropy changes with the excitation wavelength since the absorption dipole moment might be oriented differently at particular excitation wavelengths causing a change in the relative orientations of the transition moments. 

In this work, we try to elucidate the presence of multiple electronic states in unsymmetrical phenylene ethynylene (PE) dendrimers called 2G1-m-OH, 2G2-m-OH, and 2G2-m-per by investigating the different orientation of the absorption and emission transition dipole moments via anisotropy experiments at 298 K and 77 K. We characterize the absorbing and emitting state of the unsymmetrical PE dendrimers according to changes observed at the anisotropy values and differences in the excitation, and emission spectra when temperature is decreased from 298 K to 77K. The details of the anisotropy measurements are given in Chapter 2.
The dendrimers used here, 2G\textsubscript{1}-m-OH, 2G\textsubscript{2}-m-OH, and 2G\textsubscript{2}-m-per (Figure 4-2), were synthesized by Peng and coworkers. In the notation which is used to name the dendrimers, the letter “G” means generation, the number before the letter “G” displays the number of the arms around the focal point and the subscript shows the number of the generations. The letter “m” represents the position where the functional group is substituted to the phenyl ring at the focal point of the dendrons. For example, 2G\textsubscript{1}-m-OH means that two of the first generation phenylethynelene dendritic structures are attached to a phenyl ring which has a meta OH substitution.

Figure 4-2. Structures of PE dendrimers. A) 2G\textsubscript{1}-m-OH, B) 2G\textsubscript{2}-m-OH, C) 2G\textsubscript{2}-m-per.

In all experiments, samples were dissolved in 2-CH\textsubscript{3}THF and the optical densities were kept below 0.1 in order to prevent any aggregation or excimer formation. Absorption spectra of the samples were recorded on a Varian Cary 100 spectrophotometer while the emission and excitation spectra were measured with a Jobin-Yvon instrument (Fluorolog-3). A
liquid nitrogen flow cryostat (Oxford instruments) was used in low temperature experiments (77K).

2G₁-m-OH

Steady state excitation spectra of 2G₁-m-OH at 298 K and 77 K were collected between 300 nm and 400 nm after setting the detection wavelength to 420 nm. Emission spectrum was recorded in the spectral region from 350 nm to 550 nm upon the excitation at 302 nm and 310 nm at 298 K and 77 K, respectively. The spectra collected at 77 K have sharper bands instead of broad shoulders compared to the spectra collected at 298 K. Additionally, hidden bands under the broad excitation and emission bands collected at room temperature were uncovered with the low temperature measurements (Figure 4-3).

Figure 4-3. Excitation and emission spectra of 2G1-m-OH at A) 298 K, B) 77 K.
At room temperature, phenyl rings are free to rotate. The rotation of the phenyl rings leads to formation of the segments with different conjugated lengths. The presence of segments with different conjugation lengths cause the inhomogenous broadening in the excitation and the emission spectra. On the other hand, when the temperature decreases from 298 K to 77 K the rotation of the phenyl rings are limited. Thus, the segments probably become flatter at 77 K decrease the inhomogenity in the excitation and the emission spectra at that temperature.

The fluorescence bands of 2G$_1$-m-OH observed at 77K resembles to the main excitation bands at longer wavelengths where the branches with longer conjugation lengths absorb. This means that the emission comes mainly from the segments with the longest conjugation length. This observation suggests that if the molecule is excited even with shorter wavelengths, where the segments with shorter conjugation lengths absorb, the excitation is transferred to the segments with longer conjugation lengths.

The excitation anisotropy of 2G$_1$-m-OH detected at 420 nm at room temperature is measured between 300 nm and 405 nm. The overall anisotropy values are under 0.1 and they monotonically increase from 0.01 to 0.07 throughout the excitation bandwidth (Figure 4-4).

![Figure 4-4. Excitation spectrum (---), and excitation anisotropy (---) of 2G$_1$-m-OH at 298 K.](image-url)
At room temperature, thermal energy allows for the formation of the segments with a broad distribution of the conjugation lengths and these segments will have different orientations. Anisotropy values close to zero confirm that the excitation and the emission transition moments have different orientations. Anisotropy values at longer excitation wavelengths are relatively higher than at shorter wavelengths suggesting energy transfer from short conjugated segments to longer conjugated segments.

The excitation anisotropy of 2G\textsubscript{1}-m-OH at 77 K is presented in Figure 4-5. In contrast to room temperature results, at low temperature there are four distinct regions with different anisotropy values. Anisotropy values increase from 0.02 to 0.1 between 300 nm and 340 nm. In the region from 340 nm to 375 nm a relatively constant anisotropy values around 0.1 were observed. These values are increased to 0.25 in the spectral region between 375 nm and 400 nm while there is a sharp decrease after 400 nm where the excitation diminishes. The excitation spectrum at low temperature is also shaded with different colors corresponding to the spectral regions with different anisotropy values.

![Figure 4-5. Excitation spectrum (---), and excitation anisotropy (---) of 2G\textsubscript{1}-m-OH at 77 K.](image-url)
This complex behavior of the excitation anisotropy shows that there is more than one electronic state contributing to the total anisotropy. At room temperature, the phenyl rings can rotate freely around ethynylene bonds causing the delocalization of the excitations throughout the longer segments. On the other hand, these rotations are limited at low temperature that results in the localization of excitations on specific segments.

At low temperature, the anisotropy values in the region from 300 nm to 340 nm increases monotonically showing that there are at least two states contributing to the anisotropy in that region (shaded with two colors). The constant anisotropy values in the spectral region from 340 nm and 375 nm is because the anisotropy comes from a single state (the spectral region shaded with single color). The spectral region with increasing anisotropy values from 375 nm to 390 nm shows again the contribution from different states (shaded as intersection of two states). In the region \( \lambda > 390 \text{ nm} \) the molecule shows a constant anisotropy value of 0.25 since it is the contribution of only one state (blue shaded area).

The gradually increased anisotropies, from 0.02 to 0.25 between 300 nm 400 nm, show that the energy is transferred from the conjugated segments that absorb at shorter wavelengths to the ones with longer conjugation length and absorbing at longer wavelengths. The overall anisotropy (0.02-0.25) is smaller than the fundamental anisotropy value of 0.4, what is observed when the excitation and emission transition moments have the same orientations, suggesting that the excitation and emission transition moments of 2G\(_1\)-m-OH have different orientations. What is more, the sharp increase after 400 nm is observed due to the emission which comes from the segments with longest conjugation lengths.
2G₂-m-OH

The room temperature and low temperature excitation spectra of 2G₂-m-OH were collected after setting the detection wavelength to 450 nm. Emission spectrum was recorded upon the excitation at 320 nm, and at 375 nm at room temperature, and at 77 K respectively. The emission and excitation spectra are presented in Figure 4-6. In the low temperature excitation spectrum of 2G₂-m-OH, we observe new sharp bands hidden under the broad excitation band at room temperature. Additionally, the emission peaks becomes sharper and present better defined vibronic structure at 77 K compared to the spectral peaks observed at room temperature.

![Graph](image)

Figure 4-6. Excitation and emission spectra of 2G₂-m-OH at A) 298 K, B) 77 K.

2G₂-m-OH has a broader excitation spectrum than 2G₁-m-OH since in unsymmetrical dendritic structures the ortho linkages prevent the phenyl rings to have a planar geometry. In this way, segments with various conjugation lengths are created causing the inhomogenous
broadening in excitation spectra. Additionally, the conjugation lengths increase with the increasing generation due to the \textit{para} linkages which result in long conjugated segments. Longer conjugated segments shift the spectrum of 2G$_2$-m-OH compared to the red compared to 2G$_1$-m-OH.

On the other hand, at low temperature the featured bands suggest localization of excitation to some extent on different conjugated segments. What is more, the shape of the emission spectrum at low temperature resembles the excitation spectrum at longer wavelengths supporting that the emission comes from the segments with longer conjugation lengths, which absorb at longer wavelengths, suggesting the energy transfer from shorter conjugated segments. These observations are consistent with the results of experiments performed with 2G$_1$-m-OH. A red shift in the emission spectrum of 2G$_2$-m-OH at 77 K compared to the emission spectrum at 298 K was observed. This red shift shows that a more planar geometry was adopted by the phenyl rings at low temperature.

The anisotropy values of 2G$_2$-m-OH at room temperature, collected setting the detection wavelength to 450 nm is presented in Figure 4-7. It shows anisotropy values very close to zero (0.01-0.07) throughout the excitation wavelengths. We can evaluate the low anisotropy values as a result of multiple energy transfer steps between segments with different orientations.

At low temperature (77 K), the anisotropy vs. wavelength plot (Figure 4-8) exhibits three different spectral regions (roughly defined) with different anisotropy values. The region between 300 nm and 380 nm has constant anisotropy value around 0.01. The constant anisotropy values suggest that these anisotropy values are only from one state (shaded in magenta). The monotonic increase of the anisotropy from 0.01 to 0.04 in the spectral region between 380 and 420 nm shows that there are at least two electronic states contributing to the anisotropy of the system.
The spectral region corresponding to this anisotropic behavior marked as the intersection of two regions belongs to different electronic states which are represented with different colors (magenta and blue). After 420 nm, the anisotropy values show a sharp increase to 0.1 within the following 10 nm. Additionally, a sharp decrease was observed in the anisotropy values after 430 nm. Therefore we concluded that the anisotropy value at that region comes from single state (spectral region shaded in blue).

At room temperature the thermal energy allows the free rotation of the phenyl rings leading to the conjugated segments in various lengths. At low temperature, free rotation of the phenyl rings is limited causing the formation of longer conjugated segments. The shorter wavelengths show lower anisotropy values compared to the ones at longer wavelengths supporting the idea of the energy transfer from the segments with shorter conjugation lengths to the segments which shows longer conjugations. The overall anisotropy values are lower than 0.4 which is supposed to be observed when the excitation and the emission transition moments are oriented in parallel. In this case, lower anisotropy values shows that the excitation and emission transition moments have different orientations.

Figure 4-7. Excitation spectrum ( ), and excitation anisotropy ( ) of 2G2-m-OH at 298 K.
Figure 4-8. Excitation spectrum (—), and excitation anisotropy (—) of 2G2-m-OH at 77 K.

**2G2-m-per**

The excitation (detected at 550 nm) and emission spectra (after excitation at 325 nm) of 2G2-m-per are presented in Figure 4-9. Comparing the Figure 4-6 and Figure 4-9, I can conclude that 2G2-m-OH and 2G2-m-per have similar excitation spectra except the spectral region where wavelengths are greater than 425 nm. The excitation spectrum of 2G2-m-per from \( \lambda = 300 \) nm to \( \lambda = 425 \) nm is assigned to the backbone of the molecule. The rest of the spectrum belongs to the ethynlene perylene (EPer) part of the molecule, which is used as an energy acceptor here.\textsuperscript{157} Thus, the excitation spectrum of 2G2-m-per which contains the characteristics of both 2G2-m-OH and EPer suggest weak coupling in ground state between dendritic backbone and EPer.\textsuperscript{157}

At 77 K (Figure 4-9 B), the spectral region assigned to the excitation spectrum of the backbone presents additional, sharper transitions compared to the same spectral region at room temperature. The excitation spectrum in the region where ethynlene perylene absorbs is similar to the spectrum at room temperature in terms of number of the peaks although the vibronic bands become sharper at low temperature. Overall, as temperature is lowered the excitation and the emission spectra are red shifted.
Figure 4-9. Excitation and emission spectra of 2G2-m-OH at A) 298 K, B) 77 K.

The differences between the excitation spectrum of 2G2-m-per at 77 K and 298 K originates from different lengths of the conjugated segments at those temperatures. The results are similar to ones observed for 2G1-m-OH and 2G2-m-OH. At room temperature, phenyl rings are oriented in any direction while the EPer trap is almost flat. Thus, the orientation of the phenyl rings at various directions varies the conjugation lengths In this case, a broad featureless excitation is observed instead of having sharp and featured peaks due to the longer and more homogenously distributed conjugation lengths as in case of 77 K.

Figure 4-10 shows the excitation anisotropy of 2G2-m-per, detected at 550 nm (EPer emission) at room temperature. Two regions with distinctive anisotropies are observed in the anisotropy vs. wavelength plot. The wavelengths corresponding to excitation of the backbone ($\lambda < 425$ nm) exhibit anisotropy values around zero while the excitation in the region where EPer
can be excited directly ($\lambda>425$ nm) yields an anisotropy value of $\sim 0.1$. Excitations of perylene at wavelengths above 360 nm cause $S_0 \rightarrow S_1$ transition. In this spectral region it shows constant and positive anisotropy.$^{161}$

The low anisotropy values at short wavelengths (298 K) suggest that the excitations are depolarized due to the energy transfer process between the segments with different conjugation lengths which have orientation of the excitation and emission transition dipoles. The higher anisotropy values at longer wavelengths were observed due to the direct excitation of the EPer having relatively similarly oriented excitation and emission transition moments.

![Figure 4-10. Excitation spectrum (---), and excitation anisotropy (---) of 2G$_2$-m-per at 298 K.](image)

The results for low temperature (77 K) are presented in Figure 4-11. The low temperature excitation anisotropy has also two distinctive spectral regions. In the spectral region from 300 nm to 425 nm lower anisotropy values (0.06) were observed compared to the anisotropies (0.25) at wavelengths longer than 425 nm.

The lower anisotropies were observed due to the energy transfer from backbone to the EPer. Since there is an ethynyl group between backbone and perylene, the relative orientation between the two moieties can have different values and following energy transfer the
polarization is decreased. The higher anisotropy values at the wavelengths longer than $\lambda=425$ nm is because at these wavelengths the perylene can be excited directly and there is no energy transfer from EPer suggesting that the excitation energy transfer is unidirectional and it occurs only from backbone to EPer.

![Excitation spectrum and anisotropy.png](attachment:Excitation_spectrum_and_anisotropy.png)

Figure 4-11. Excitation spectrum (---), and excitation anisotropy (---) of 2G2-m-per at 77 K.

**Conclusion**

The phenyl rings which are free to rotate around the ethynylene bonds create the segments with various conjugation lengths. The variability in the conjugation lengths of the segments makes the excitation spectra of 2G1-m-OH, 2G2-m-OH, and 2G2-m-per broad at room temperature. Excitations are delocalized along these long conjugated segments at that temperature. On the other hand, the bands hidden under the broad excitation bands at room temperature were uncovered at 77 K. In other words, the inhomogeneity of the spectrum is broken since conjugated segments with similar lengths are produced due to the limited rotation of the phenyl rings at that temperature.

The results of the anisotropy experiments support the conclusions we reached with the steady state excitation and the emission experiments. The anisotropy measurements for 2G1-m-
OH, 2G$_2$-m-OH at room temperature confirm the delocalization of the excitations along the conjugated segments. At 298 K, 2G$_2$-m-per show very low anisotropy values at the excitation wavelengths where the backbone has absorption and higher anisotropies at the wavelengths where EPer can be directly excited. These two spectral regions with different anisotropy values suggest that the backbone and the EPer are weakly coupled and there are two states that contribute the total anisotropy of the system. Additionally, very low anisotropy values obtained after backbone excitation are due to strong coupling between the branches within the backbone and energy transfer from backbone to the EPer acceptor.

At 77 K, the complex anisotropic behavior of the molecules, 2G$_1$-m-OH, 2G$_2$-m-OH, and 2G$_2$-m-per, shows that the excitations are localized on segments with longer conjugation lengths. It also suggests that there is more than one state involved in the energy transfer mechanism for each molecule.

Overall, the low anisotropy values at shorter wavelengths and relatively higher anisotropies at longer wavelengths show that an energy transfer occurs from the segments with shorter conjugation lengths to the segments with longer conjugations with excitation and emission transition moments have different orientations.
CHAPTER 5
CONCLUSION AND PERSPECTIVE

Since Hirsberg proposed a chemical memory model based on photochromic properties of a spiropyran in 1956, a vast number of studies were performed searching the photochromic properties of the organic compounds. As a result of these studies the number of the potential applications of photochromic molecules has extended. For successful implementation of most of applications, properties such as achieving high number of fast switching cycles and recovering the output are required. These requirements directed the researchers into a search of materials possessing the required properties. For this purpose, design and synthesis of materials with desired properties has been developed.

In this dissertation, a novel photochromic oxazine with faster switching cycle and higher fatigue resistance was studied in detail. The photophysical characterization of the molecule was obtained by steady state and ultrafast transient absorption spectroscopy. The goal of this study was to answer some fundamental questions related to the ring opening mechanism of the photochromic oxazine, which represents the coloring reaction of the molecule. For instance, what is the rise time of the state that corresponds to the open form of the molecule? Are there any intermediate states involved in the ring opening mechanism? If any intermediates are observed, what are the electronic properties of the states corresponding to these intermediates?

Initial experimental results at steady state showed that a state with very weak emissive properties appears when the molecule is excited at the wavelength at which the molecule has the highest extinction coefficient. The emissive property of the state is enhanced upon the addition of benzophenone, a good triplet sensitizer. When the emission experiments were repeated in another solvent with different polarity, the peak of the emission band shifted. These preliminary observations lead us to ask the questions: Does the emission belongs to a triplet
state? Does this state have a charge separation property similar to the results presented in literature? Time resolved transient absorption experiments provided experimental results that helped us answer these questions.

In transient absorption experiments, we observed two bands one absorbing at around 500 nm, rises within the instrument response function (250 fs) and decays with 2.2 ps and 3.7 ps time constants. The intensity of this band increased in the presence of benzophenone. However, the lifetime of the band was short for a state with triplet properties. Therefore, we decided that the emission band at steady state is not a triplet state. Additionally, this band exhibits a solvent effect similar to the emission band observed at steady state. Moreover, the transient absorption band was very similar to the absorption of the radical cation form of the model indole for the photochromic oxazine. When the results are evaluated cumulatively, it is concluded that the state which shows emission at steady state and transient absorption at around 500 nm is a charge separated state.

A second transient absorption band is observed at around 440 nm which is indirectly from the charge separated state with 12.5 ps time constant and directly from first excited with 6.3 ps time constants. This band is attributed to the open form of the molecule since the shape and maximum of the band coincides with the absorption of open form of the molecule reported in literature. No changes were observed in the intensity and dynamics of this band upon the addition of the benzophenone. We concluded that the charge separated state does not make a significant contribution to the production of the open form of the photochromic oxazine.

In order to decide which states are involved in the energy transfer from benzophenone to the charge separated state of the oxazine, the transient absorption of benzophenone was compared to the transient absorption of mixtures of benzophenone and oxazine to it. The
comparison showed that once it is formed, there is no change in the intensity and the dynamics of the triplet state of the benzophenone which means that the triplet state of benzophenone does not involve in the energy transfer mechanism. The energy transfer occurs from the singlet state of the benzophenone to the charge separated state of the photochromic oxazine before the triplet state of benzophenone is formed.

The experimental results showed that the photochromic oxazine has very fast ring opening dynamics possessing one of the desired properties of photochromic molecules in solution. In future, these dynamics can be investigated in solid media since the applications can be implemented in solid medium. Additionally, the effect of the substituted groups in switching dynamics of the photochromic oxazine can be investigated in both solution and solid phase for the purpose of developing the rate of switching cycles. We hope that the discoveries we presented in this study will bring the attempts of finding the right photochromic material for the successful implementation of the photochromic molecules one step further.

In chapter 4, an independent project is presented. We investigated the presence of multiple electronic states and orientation of transition dipoles of these states in unsymmetrical PE dendrimers. For this purpose, we performed steady state anisotropy experiments at 298K and 77K.

At room temperature all of the unsymmetrical Phenylene Ethynylene dendrimers we studied exhibited low excitation anisotropy values along the excitation spectra. It is concluded that the low anisotropy values at room temperature were observed due to energy transfer form the longer conjugated segments to shorter ones with different transition moments.

The anisotropy vales at 77 K of the unsymmetrical PE dendrimers exhibited a complex behavior along with the excitation spectra of the molecules. This complex behavior led us to
conclude that there was more than one state contributing to the anisotropic behavior of the molecules.

Due to their structural, physical and energetic properties, dendrimers are proposed as light-harvesting component of the solar energy converters in addition to their potential applications in photonic devices. We hope that the observations related to anisotropic behavior of the unsymmetrical PE dendrimers open new possibilities of design and synthesis of new dendritic structures with good light harvesting properties.
APPENDIX A

The chirp correction is done after the data is collected. The front panel of the Labview program is given in Figure A-1. Before running the program the thickness of each medium that light interacts with should be known. These are needed to be into the boxes under the names of each material. If any of the materials are not present in your set up, put 0.00 mm as the thickness of that material.

Figure A-1. Front panel of the chirp correction program.
A part of the block diagram of the chirp correction program is given in Figure A-2. In that part of the program it can be seen what are the parameters needed to calculate the chirp and correct the data. There are two characteristic numbers which are called linear and quadratic factors for each material to be entered into the program. Linear and quadratic factors for air, BK7, CaF₂, fused silica, MeOH and water are already present in the program (Figure A-3).

Figure A-2. A part of the block diagram of the chirp correction program
In order to get the linear and the quadratic factors we used Sellmeier equation and the chirp per mm with respect to energy (wavelength) for air, BK7, CaF₂, fused silica, MeOH is calculated. Then this calculated data is fitted by using a quadratic equation. The resultant equations are given on the plots in Figures A-4, A-5, A-6, A-7, and A-8. The multiplier of $x$ is the linear term and the multiplier of $x^2$ is the quadratic term.
Figure A-4. Chirp per mm with respect to the energy (wavelength) of the light for air.

Figure A-5. Chirp per mm with respect to the energy (wavelength) of the light for BK7.
Figure A-6. Chirp per mm with respect to the energy (wavelength) of the light for CaF2.

Figure A-7. Chirp per mm with respect to the energy (wavelength) of the light for fused silica.
Figure A-8. Chirp per mm with respect to the energy (wavelength) of the light for MeOH.

$y = -33x + 23.4x^2$
APPENDIX B

The SVD components presented in this section does not have any physical meaning. They are linear combination of physically meaningful components.

Figure B-1. A1-A2) Spectral, and B1-B2) temporal components of $1.95 \times 10^{-4}$ M oxazine and benzophenone with the ratio of benzophenone/oxazine= 2/100 in acetonitrile, result of SVD analysis.

Figure B-2. A1-A2) Spectral, and B1-B2) temporal components of $1.95 \times 10^{-4}$ M oxazine and benzophenone with the ratio of benzophenone/oxazine= 4/100 in acetonitrile, result of SVD analysis.
Figure B-3. A1-A2) Spectral, and B1-B2) temporal components of 1.95x10^-4 M oxazine and benzophenone with the ratio of benzophenone/oxazine= 6/100 in acetonitrile, result of SVD analysis.

Figure B-4. (——) Results of forward EFA, (——) Results of backward EFA of 1.95x10^-4 M oxazine and benzophenone with the ratio of benzophenone/oxazine= 2/100 in acetonitrile.
Figure B-5. (■) Results of forward EFA, (◇) Results of backward EFA of 1.95x10^-4 M oxazine and benzophenone with the ratio of benzophenone/oxazine= 4/100 in acetonitrile.

Figure B-6. (■) Results of forward EFA, (◇) Results of backward EFA of 1.95x10^-4 M oxazine and benzophenone with the ratio of benzophenone/oxazine= 6/100 in acetonitrile.
Figure B-7. A1-A4) Spectral, and B1-B4) temporal components of 0.05 M benzophenone and oxazine with the ratio of oxazine/benzophenone= 2.6/1000, result of SVD analysis.
Figure B-8. A1-A4) Spectral, and B1-B4) temporal components of 0.05 M benzophenone and oxazine with the ratio of oxazine/benzophenone= 4/1000, result of SVD analysis.
Figure B-9. A1-A4) Spectral, and B1-B4) temporal components of 0.05 M benzophenone and oxazine with the ratio of oxazine/benzophenone= 5.2/1000, result of SVD analysis.
APPENDIX C

This section presents the tried kinetic models and the fitting trials according these models.

Figure C-1. Energy level scheme of the photoisomerization of oxazine.

Figure C-2. Interpolated forms of temporal components belong to the charge separated state (o) and open form of the oxazine (o) and prediction of kinetic model for charge separated state ( ), and the open form ( ).
Figure C-3. Energy level scheme of the photoisomerization of oxazine.

Figure C-4. Interpolated forms of temporal components belong to the charge separated state (o) and open form of the oxazine (o) and prediction of kinetic model for charge separated state ( ), and the open form ( ).
Figure C-5. Energy level scheme of the photoisomerization of oxazine.

Figure C-6. Interpolated forms of temporal components belong to the charge separated state (o) and open form of the oxazine (o) and prediction of kinetic model for charge separated state ( ), and the open form ( ).
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BIOGRAPHICAL SKETCH

Aysun Altan was born in 1981 in Kesap, Turkey. She lived there with her family until she finished elementary school. Afterwards, she moved to Edirne to attend Edirne Anatolian Teacher High School, which is a boarding school, for four years. Following those years, she began her studies at Bogazici University in Istanbul for six years which included the undergraduate and M.Sc. studies in teaching chemistry. After graduating from Bogazici University in 2004, she came to University of Florida and began her doctoral studies under the supervision of Dr. Valeria D. Kleiman in the area of ultrafast laser spectroscopy of photochromic oxazine.