PHOTOPHYSICAL CHARACTERIZATION AND ENERGY TRANSFER STUDIES OF PERYLENE DIIMIDE BASED DENDRIMER DERIVATIVES

By

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To my family, for your example, encouragement and sacrifice have been invaluable constants to me throughout my life

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LIST OF ABBREVIATIONS

MCCL	Materials Chemistry Characterization Laboratory
PDI	Perylene diimide
TCSPC	Time-Correlated Single Photon Counting
UV	Ultraviolet
UV-Vis	Ultraviolet – Visible

Abstract of Thesis Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
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By

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This thesis presents the photophysical characterization of perylene diimide based dendrimers in solution and studies the energy transfer processes occurring in these molecules. Perylene diimide derivatives have received much attention in recent years for use in donor-acceptor dendrimer systems. In this thesis, the perylene diimide derivative serves as the acceptor, and triphenylene based chromophores are the donors. Two families of dendrimers, both substituted in the "bay" position, are investigated. The arms and core of the first dendrimer family are connected by an ether linkage, while the second has acetylene bridges. The dendrimers in this thesis have been characterized using steady state and time-resolved spectroscopic methods.

CHAPTER 1
INTRODUCTION

Outline of Thesis

The purpose of this thesis is to present the photophysical characterization of perylene diimide based dendrimers in solution and study the energy transfer processes occurring in these molecules. Chapter 1 presents a brief synopsis of dendrimers, including their properties and impact on chemical research. It also identifies the type of molecules studied in this thesis, perylene diimide dendrimer derivatives, introduces energy transfer and presents a brief description of Time-Resolved and Steady State spectroscopic experimentation.

Chapter 2 describes the instrumentation used to perform the Steady State and Time-Resolved experiments, providing explanations of the involved techniques and principles governing each method. The results of the experiments are discussed in Chapter 3. The closing remarks are found in Chapter 4, summarizing the conclusions drawn from the experimental data collected during the course of this research project. The chapter concludes with a description of the experiments proposed to provide additional information, beneficial to the understanding of the characterization of the energy transfer capabilities of this perylene diimide dendrimer derivative family.

Dendrimers

Dendrimers are highly structured macromolecules consisting of a central “core”, or reaction center, a periphery composed of branching repeat units, and terminal groups.[1] Originally called cascade molecules, the term “dendrimer” was later adopted and comes from the Greek for tree, “dendron", and part, “meros”.[2] Chosen for these Greek roots, the term dendrimer reflects the similarities found within the branching, “tree-like” dendritic structure and their leafy counterparts.

Historical Perspective

In the beginning of dendrimer research, one of the main attractions revolved around the ease with which such large macromolecules could be constructed and synthesized.[3] The focus of dendrimer research has since shifted from a race to form larger molecules,[4,5] to the tremendous potential for applications exhibited by these molecules. Over the years, dendrimers have been the subject of several reviews[2,6-8] and implemented or proposed for use in many applications, including medicine[9-11] and optoelectronic devices, such as solar cells[12] and LED's.[12,13]

Due to the need for alternative, renewable energy sources, light-harvesting and the development of photosynthetic mimics[14] has been a popular area of research. Dendrimers have been at the center of attention in this field,[15-18] as the very structure of dendrimers presents them as ideal candidates for light-harvesters.[19,20]

The multitude of chromophores available for use in dendritic structure make the different types of possible dendrimers appear infinite. Nevertheless, certain families of dendrimers have remained the focus of multiple studies throughout the years and deserve note. These include PAMAM (poly(amidoamines)), polyamine, perylene diimide and poly(ether) dendrimers.[9,21] Specifically, this thesis will focus on perylene diimide dendrimer derivatives. This family of dendrimers will be discussed in more detail in Chapter 3.

Synthesis and Generation

Presently, there are two methods commonly employed in dendrimer synthesis: convergent synthesis and divergent synthesis.[22] In the convergent method (Figure 1-1A), one begins by synthesizing the end groups to form multiple dendrons, then joining them to the selected core. Conversely, in the divergent method (Figure 1-1B), synthesis begins with the central core and branches outward with the terminal end groups to form a dendrimer of the desired generation.

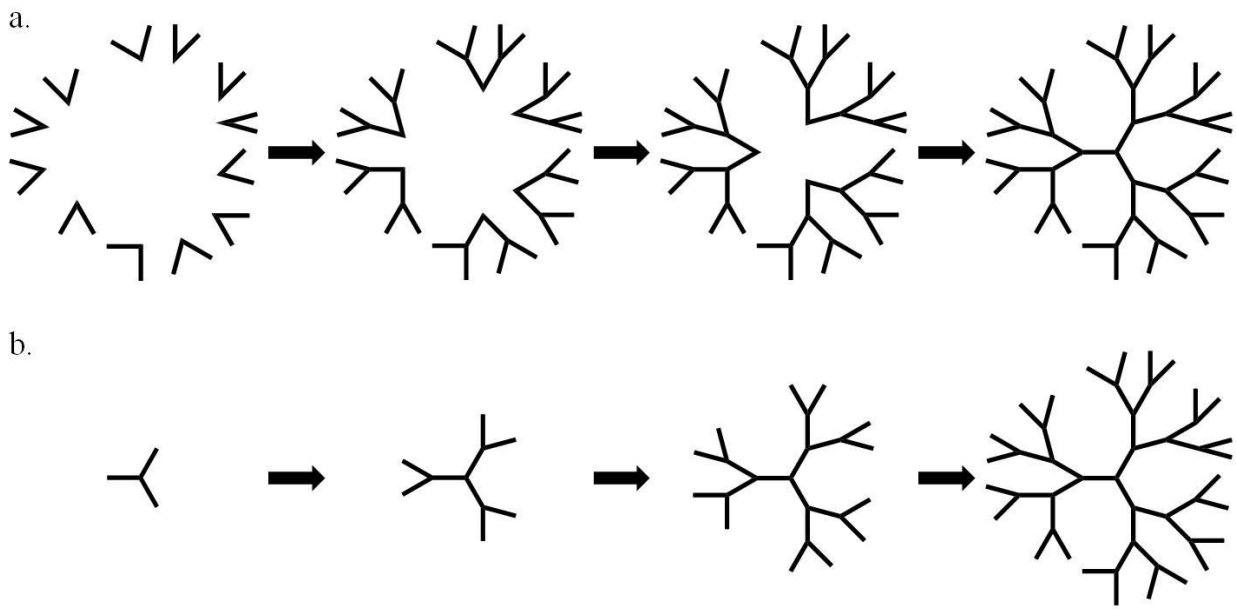


Figure 1-1. Depiction of methods for dendrimer synthesis. (a) Convergent synthesis (b) Divergent synthesis[22]

The branching patterns of the periphery, which lead to subsequent levels of dendritic growth, are termed "generations". For symmetric dendrimers, these generations extend in concentric circles around the dendrimer core and provide a practical naming convention to distinguish between dendrimers of different size within the same dendrimer family. For example, in the divergent synthesis route shown in Figure 1-1B, the first structure might be considered zeroth generation, and the structure on the right would be called a third generation dendrimer.

Structural Features and Properties

The specific properties exhibited by an individual dendrimer can be attributed to the different components composing the macromolecule. Therefore, through careful selection of the dendritic core and terminal end groups, for example, one is able to tailor the molecule for specific application enhancement.

The framework of the dendritic structure makes these macromolecules ideal candidates for energy transfer studies[23-25], particularly intramolecular energy transfer[26,27] studies. For example, consider a situation in which the periphery of the dendrimer is composed of multiple absorbing

chromophores and the core contains an energy trap. The dendrimer may simply serve as a scaffold[28], providing physical connections between the peripheral absorbing chromophores and the energy trap at the core. The branching arms in the dendrimer periphery can be used to maintain defined distances between donor and acceptor. With changes in the extent of dendritic generation, the number of absorbing chromophores can also be regulated, optimizing energy transfer efficiency.[15] By contrast, it is also possible that the backbone of the dendrimer can be constructed of absorbing chromophores to serve as the energy donor[28], and be actively involved in the energy transfer process.

The branching architecture of dendritic molecules results in exponential growth of the terminal end groups. It has been shown that the absorbance of the dendritic molecules increases with each new generation when these termini are functionalized with absorbing chromophores.[27] However, there is a limit at which the size of the molecule begins to compete with the efficacy of the absorbing chromophores. The increasing size of the molecule is an indicator of the increasing distance between the donor on the periphery and the acceptor at the dendrimer core, which in some cases may have adverse effects upon the efficiency of energy transfer.[27]

Energy Transfer

Energy transfer can be accomplished through many pathways and mechanisms, but all return to the same fundamental principle. An acceptor chromophore, A, which does not absorb the incident light of wavelength λ, can be excited to an excited state, A*, through the transfer of excitation energy from a neighboring excited donor chromophore, D*.

$$D^*—A \rightarrow D—A^*$$

Energy transfer can be classified into two categories, radiative and non-radiative energy transfer. Adequate spectral overlap of donor and acceptor molecules is a prerequisite for both processes. Radiative energy transfer occurs according to the following mechanism.

$$D + h\nu \rightarrow D^*$$

$$D^* \rightarrow D + h\nu'$$

$$A + h\nu' \rightarrow A^*$$

A donor molecule, D, is excited by incident light of energy hν to an excited state, D*. During the decay of the excited molecule, D*, a photon of energy hν' is emitted and can be absorbed by the acceptor molecule, A, resulting in the promotion of the acceptor molecule to an excited state, A*.

Conversely, non-radiative energy transfer does not require the emission of a photon. Instead, through interaction of the excited donor molecule, D*, with the acceptor molecule, A, the excitation energy can be effectively transferred. This process can occur when the overlap of the donor emission spectrum and the acceptor absorption spectrum is such that the involved vibronic transitions are said to be in resonance.

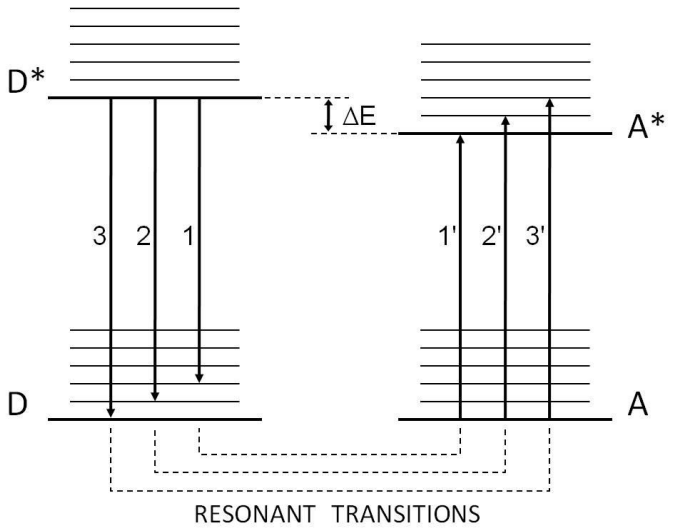


Figure 1-2. Resonant transitions of donor and acceptor molecules[29]

The efficiency of energy transfer between donor and acceptor molecules can be expressed by the equation,

$$\Phi_T = 1 - \frac{\Phi_D}{\Phi_D^0}$$

Φ_T is the transfer efficiency and Φ_D and Φ_D^0 are the quantum yields of the donor in the presence and absence of the acceptor molecule, respectively. However, to characterize the energy transfer efficiency of the molecular system under investigation, it is not necessary to obtain the absolute quantum yields. Instead, the efficiency can be related to the change in intensity observed in the fluorescence spectra of the donor and acceptor molecules. Under efficient energy transfer conditions, the fluorescence spectrum intensity of the donor (in the presence of acceptor molecules) should be expected to decrease as the intensity of the fluorescence spectrum of the acceptor (in the presence of donor molecules) increases.[29,30]

Time-Resolved and Steady State Spectroscopy

Both time-resolved and steady state[31] methods are employed in this thesis to characterize the dendrimers of interest. This section will introduce the underlying principles governing steady state and time-resolved spectroscopy. Details concerning the specific experimental methods will be addressed in Chapter 2.

In time-resolved measurements the sample is exposed to a short pulse of light, and the response is recorded as a function of time. On the other hand, steady state measurements are collected under constant illumination and observation conditions. Essentially, steady state experiments are "an average of the time-resolved phenomena over the intensity decay of the sample".[32] While steady state experiments are typically more affordable and much easier to perform, the intensity decays of time-resolved experiments provide information unable to be determined from steady state methods. Both time-resolved and steady state spectroscopy each have merit, but the limitations of each method must be considered when designing an experiment. Consider the following example provided by Lakowicz.

> The intensity decays … contain information that is lost during the averaging process. Frequently, macromolecules can exist in more than a single conformation,

and the decay time of a bound probe may depend on conformation. The intensity decay could reveal two decay times, … [but] [t]he steady-state intensity will reveal an average intensity dependent on a weighted average of the two decay times.[32]

CHAPTER 2
EXPERIMENTAL METHODS

This chapter describes the instrumentation utilized to complete the experiments for this thesis, and the basis for the operating principles behind those instruments. This is followed by a description of the experimental methods required to perform the experiments. Each sample has been characterized using steady state and time-resolved spectroscopic methods. The chapter concludes with a section describing the methods used in sample preparation.

Instrumentation

The Steady State and Anisotropy experiments were conducted in the Materials Chemistry Characterization Laboratory (MCCL). Absorption data was collected using a PerkinElmer® Lambda 25 UV/Vis Spectrometer. All emission, excitation and anisotropy data were collected on a Jobin-Yvon Horiba FluoroLog®-3 Spectrofluorometer. The fluorescence lifetime data was collected using a PicoQuant Fluorescence Lifetime system.

FluoroLog®-3 Spectrofluorometer

The FluoroLog®-3 is an L-shaped, modular spectrofluorometer, presenting the researcher with the opportunity to tailor the spectrofluorometer to fit the experiment. Spectrofluorometers can exist in either T-shaped or L-shaped configurations. The T-shaped format uses two separate detection channels, while the L-shaped configuration has a single detection channel. The FluoroLog®-3 is capable of both right angle and front-face detection[33,34]. In right angle detection, only the fluorescence emitted from the center of the excited sample is collected. Front-face detection is commonly used for samples of high concentration.

PicoQuant Fluorescence Lifetime System

The PicoQuant Fluorescence Lifetime System is a modular system, operating on the principles of time-correlated single photon counting (TCSPC).[35,36] The underlying principles

behind the theory of TCSPC are quite simple. Time-correlated single photon counting is based on the premise that the probability of detecting a photon at a time, *t*, is proportional to the intensity of the sample fluorescence at that time. Photon detection is recorded during each period in conjunction with the time of detection. "At low levels of excitation power, each sample … absorbs one photon at the most, on a time scale which is effectively instantaneous."[35] For that reason, detection of multiple photons during a single period is not an anticipated difficulty.

For the experiments described in this thesis, the PicoQuant Fluorescence Lifetime System consists of the following components: FluoTime 100, PicoHarp 300, and PDL 800-B. FluoTime 100 is a compact time-resolved spectrometer, used to measure the decay of fluorescence. PicoHarp 300 is the TCSPC module used for data acquisition. PDL 800-B is the pulsed laser diode driver used to control such parameters as the repetition frequency and laser pulse energy. The intrinsic frequency for the system is 40 MHz, and the average pulse energy at this frequency is 0.3 mW. The experiments described here were conducted at 10 MHz. FluoFit is the fluorescence decay data analysis[37] software used to analyze, fit and save the data collected using the PicoQuant Fluorescence Lifetime system.

Steady State Methods

Absorbance

Absorbance, as determined by the Beer-Lambert Law, is defined as

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

I_λ^0 is the intensity of the beam entering the absorbing species and I_λ is the intensity of the beam exiting the absorbing species. $\varepsilon(\lambda)$ is the decadic molar absorption (or extinction) coefficient, c is the concentration of the solution, and l is the thickness of the cell, determined by the path length

the light traverses through the absorbing medium.[32] The absorbance characterizes the ability of a species to absorb light of wavelength, λ.

The absorbance is directly proportional to sample concentration. Some deviations from the Beer-Lambert Law may occur and can be attributed to a number of issues, including instrumental effects, a competing absorbing species, aggregation or other complications amplified by unfavorable concentration levels.[32]

All reported absorbance data was collected on a PerkinElmer® Lambda 25 UV/Vis Spectrometer, using both detection channels. In an effort to decrease the background noise of the spectrum, a reference cell, filled with pure solvent, was also inserted into the sample compartment of the spectrometer. The true absorbance of the sample,

$$A(\lambda) = A_S - A_R = \log\left(\frac{I_R}{I_S}\right)$$

was then recorded. A_S and A_R are the absorbances determined from the sample and reference paths, respectively, and I_R and I_S are the intensities measured after passing through the reference and sample-containing cuvettes, respectively. This served to account further for the effects due from the solvent and the cuvette walls.

Emission and Excitation Spectra

The emission spectrum shows the wavelength distribution of the fluorescence intensity, measured at a defined excitation wavelength. In contrast to emission spectra, an excitation spectrum displays the changes of the fluorescence intensity detected at a single wavelength, while scanning through the range of excitation wavelengths.[32]

Typically, the excitation spectrum should be identical to the absorbance. However, certain factors may affect the ability to superimpose the absorbance and excitation spectra. For example, the presence of multiple fluorophores or aggregate formation can alter the shape of excitation

spectra. These deviations from the symmetry of the absorbance and excitation spectra can later be exploited to gain information about a given sample under study.

Fluorescence Anisotropy

Anisotropy is a property of molecules used to gauge the degree of polarization of a sample due to photoselection. The steady state anisotropy[38], *r*, is defined as

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

where $I_{\parallel}$ and $I_{\perp}$ are the intensities of the fluorescence with the emission polarizer oriented parallel (∥) or perpendicular (⊥) to the polarized excitation. The anisotropy is the difference in the polarized signal, normalized to the total intensity, $I_T = I_{\parallel} + 2I_{\perp}$,

In order to perform the fluorescence anisotropy[39] experiments, two polarizers are mounted within the sample chamber, before and after the sample. A total of four intensity measurements, I_{VV}, I_{VH}, I_{HV}, and I_{HH}, are required to calculate to observed anisotropy (Figure 2-1). This is because the transmission efficiency of the monochromator is polarization-dependent.[29]

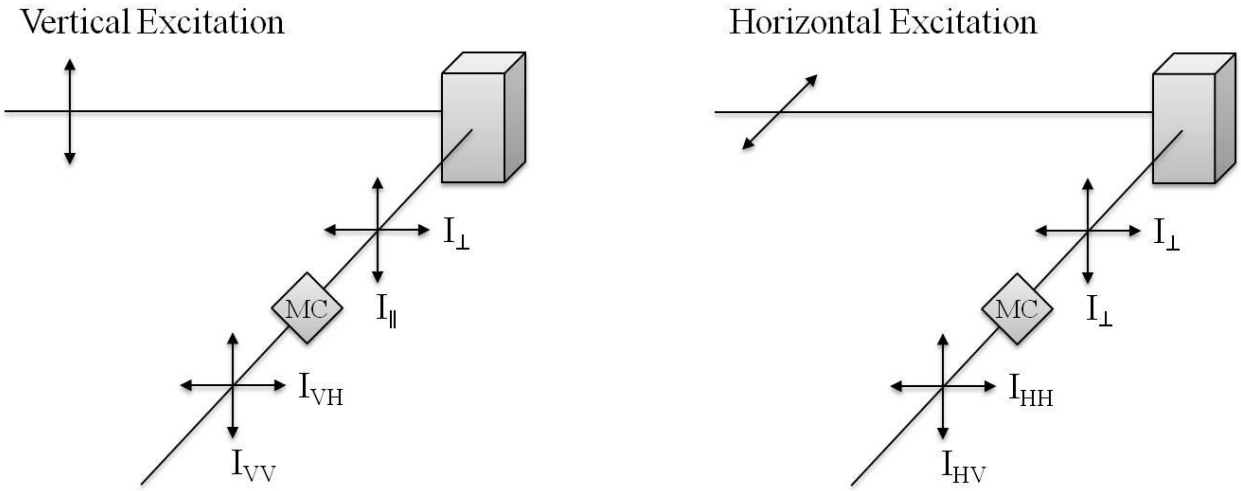


Figure 2-1. Schematic diagram for measurements of fluorescence anisotropy. MC, Monochromator[32]

The subscript denotes the orientation (vertical or horizontal) of the excitation and emission polarizers, respectively.

$$I_{VV} = kS_V I_{\parallel}$$

$$I_{VH} = kS_H I_{\perp}$$

$$I_{HV} = kS_V I_{\perp}$$

$$I_{HH} = kS_H I_{\perp}$$

S_V and S_H are the sensitivities of the detector channel for vertically and horizontally polarized emission, respectively, and k is proportionality factor used to compensate for instrumental factors.

An equivalent expression for the steady state fluorescence anisotropy can be written as

$$R = \frac{I_{VV} - GI_{VH}}{I_{VV} + 2GI_{VH}}$$

where G is the so called G-factor, defined as the ratio of the emission channel sensitivities for vertically and horizontally polarized emission. The G-factor can be determined from the ratio of I_{HV} and I_{HH}.

$$G = \frac{S_V}{S_H}$$

The fundamental anisotropy is the anisotropy observed after excitation but prior to the depolarization of fluorescence, and is defined as

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

where β is defined as the angle between the absorption and emission transition dipoles. Therefore, the fundamental anisotropy observes a maximum value of 0.4 when the transition dipole moments are parallel and a minimum value of -0.2 when the transition dipole moments are in a perpendicular orientation.[32]

The transition dipole moments are expected to be parallel when observing corresponding transitions from the same states. For example, consider the excitation of the $S_0 \rightarrow S_1$ transition and emission of the $S_1 \rightarrow S_0$ transition. Such a situation, however ideal, is unlikely to achieve the maximum value of 0.4 for the fundamental anisotropy. Potentially, this discrepancy could be attributed to effects due to rotational diffusion.

Materials and Sample Preparation

This thesis will focus on two families of dendrimers. The fundamental structure consists of a perylene diimide and triphenylene arms, with two triphenylene rings and six triphenylene rings for generation 0 and 1, respectively. The two families differ only in the bridge bond between the peripheral arms and dendrimer core. In both cases, the core is substituted in the "bay"[40] position; while the first family has an ether connecting arms and core, the second one has acetylene bridges. The dendrimer samples studied in this thesis were provided by Dr. Zhonghua Peng from the University of Missouri – Kansas City. The names and structures of the molecules are listed in Chapter 3, Table 3-1.

All experiments were performed in solution using one centimeter quartz cuvettes. Sample solutions were prepared by dissolution in dichloromethane, tetrahydrofuran or chloroform, each solvent obtained from Fisher Scientific. Further purification of prepared solutions was not deemed necessary. Optical densities were kept between 0.1 and 0.3 to avoid aggregation and self-absorption. The optical density for PBI-OB, PBI-TB, POG0 and PTG0 was determined from the absorbance of the perylene diimide core between 500-600 nm.

CHAPTER 3
ENERGY TRANSFER IN PERYLENE DIIMIDE DENDRIMER DERIVATIVES

As mentioned previously, dendrimer research has shifted from an initial interest in the synthesis of large molecules to a focus on the potential for applications, which these molecules possess. One such molecule, perylene diimide (PDI), has been widely studied and incorporated into different areas of dendritic structure and will be the dendritic core under investigation for this thesis.

Perylene diimide dendrimer derivatives have been a popular area of study for some time. Dendrimers based on perylene diimide characteristically exhibit strong absorption and fluorescence spectra. Research has shown that although some of these molecules tend to exhibit poor solubility, this can often be minimized by building a network of peripheral molecules around the core. Furthermore, the emissive band for the molecule can be tuned[41] by careful selection of those peripheral molecules, as interactions with different molecules will impose a shift in the characteristic spectra. In contrast to tuning the emission bands by selective functionalization of the periphery, Müllen et al. have displayed tuning of the emissive band due to increasing the size of the aromatic core[42] (terrylene and quaterrylene diimides[43]).

The synthesis and characterization of perylene diimide film samples[44,45] has also been investigated, for further applications such as solar cells and LED's. The donor-acceptor properties of perylene diimide dendrimer derivatives make them attractive candidates for use in optoelectronic devices[46] and photosynthetic mimic systems. Consequently, many research groups have focused on these molecules,[47] particularly on their light-harvesting[48] and energy transfer[40,49-51] abilities.

The advantages expected to be provided by using perylene diimide for the core of the dendrimer have been discussed above and were a prime motivational factor in the choice of the

dendrimers for this study. Furthermore, it has been said that a given dendrimer can be tailored to exhibit different photophysical properties based on the components which comprise said dendrimer. Previous studies of triphenylene-based dendrons[52] have indicated that the additional π-conjugation provided by triphenylene systems may prolong the excited state lifetime, as compared to less conjugated systems. Also, the triphenylene units have several sites suitable for further functionalization. It is believed that these properties will enhance the efficiency of energy transfer in the perylene diimide dendrimer derivatives, and for these reasons, the triphenylene chromophore was specifically chosen for the peripheral molecules in this study.

In order to improve the efficacy of the perylene diimide dendrimer derivatives for the applications identified previously, a study of energy transfer properties of these compounds will be most helpful. This chapter will discuss the results obtained from the steady state and time-resolved experiments performed upon the perylene diimide dendrimers and their fundamental components (Table 3-1) and draw conclusions about the energy transfer capabilities for this group of dendrimers.

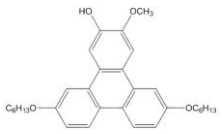
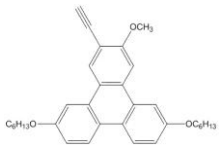
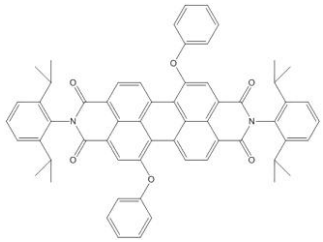
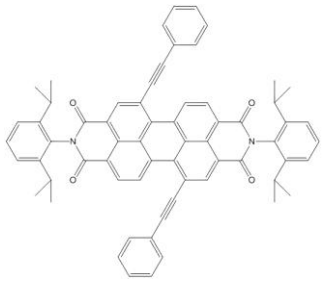
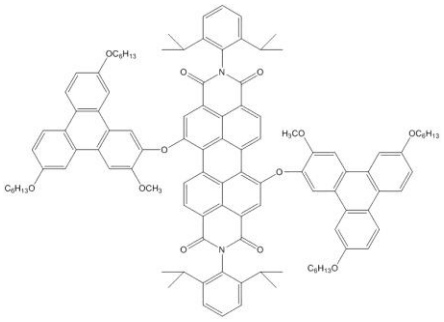
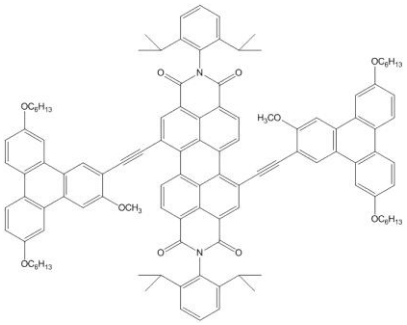
Experimental Results

The results expected from the steady state and time-resolved experiments can be understood by considering the contribution made by the model compounds forming the complete dendrimer. For example, in the POG0 dendrimer, G0-OH forms the periphery or dendritic arms, and PBI-OB is a close approximation to the POG0 dendrimer core.

Solvent Effects

The solvent used in an experiment can have an affect on the shape, position and intensity of spectral bands of a molecule.[53] These dendrimers are no exception, and the effects of solvent environment are seen in the absorption and emission spectra. Figure 3-1 shows how the emission spectrum can change as a result of changing the solvent. The samples were studied in

Table 3-1. Peng Dendrimers

Name	Structure
G0-OH	
G0-T	
PBI-OB	
PBI-TB	
POG0	
PTG0	

tetrahydrofuran, dichloromethane, and chloroform. The absorption spectrum of PBI-TB in the more polar solvent (THF) is blue-shifted with respect to that of the other spectra, while the absorption spectrum of PBI-TB in the least polar solvent (chloroform) is seen slightly to the red. These solvatochromic shifts in the spectral data can be attributed to the stabilization of the

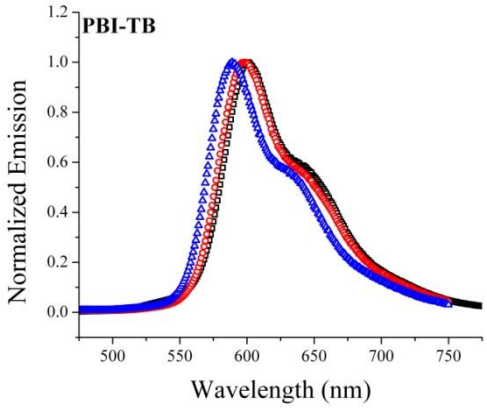


Figure 3-1. Solvent effect on PBI-TB in Chloroform (black squares), DCM (red circles) and THF (blue triangles).

ground state or excited state, caused by interactions of the molecule with the solvent environment.[54] Similar results were observed for all the samples in this study except PTG0, which was only partially soluble in DCM and THF. Due to the low solubility of PTG0 in DCM and THF, further experiments were only performed in chloroform solutions.

Steady State Spectra

The absorption and emission spectra of the peripheral chromophores, G0-OH and G0-T (Figure 3-2), show very little spectral overlap; the Stokes shift for G0-OH and G0-T is approximately 110 nm and 135 nm, respectively. The fluorescence of G0-T is seen slightly to the red of the fluorescence from G0-OH. The loss of the mirror-image symmetry in the emission spectra, and the subsequent loss of fine structure in the emission of G0-T, could be attributed to aggregation and vibronic coupling.[55] Furthermore, for solutions of comparable concentrations,

the relative intensity of the fluorescence of G0-T is much greater than that of G0-OH (Figure 3-3). This has been attributed to the extension of the conjugated π-system in G0-T.[52]

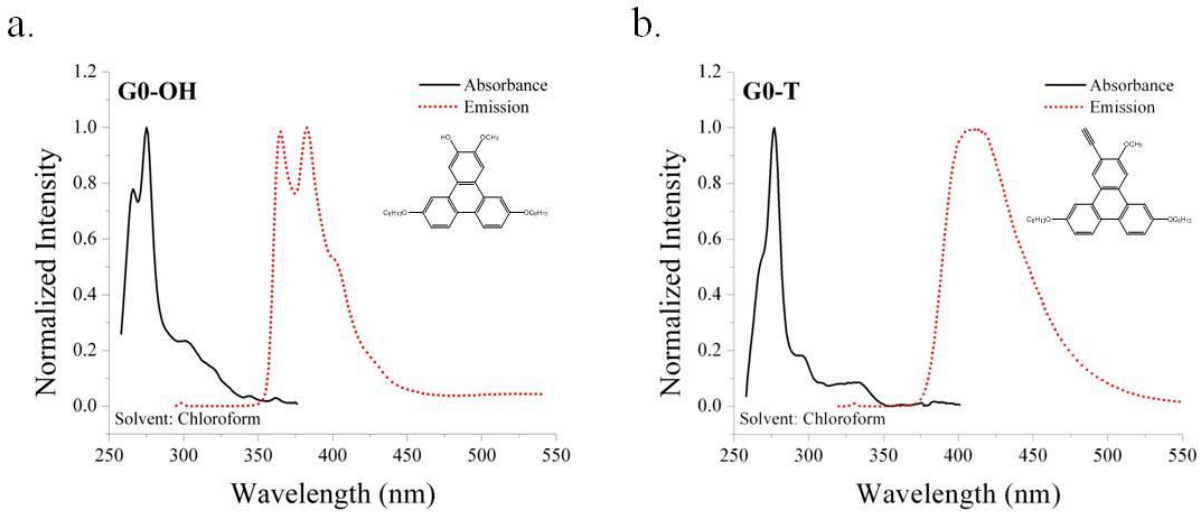


Figure 3-2. Absorbance and Emission spectra of (a) G0-OH and (b) G0-T.

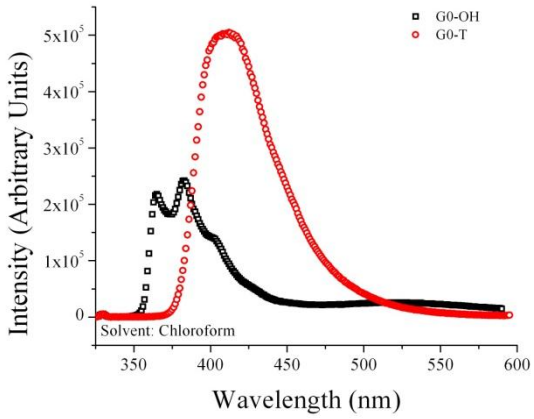


Figure 3-3. Emission spectra of G0-OH and G0-T in chloroform.

Figure 3-4 displays the absorbance and emission spectra of the core molecules, PBI-OB and PBI-TB. The absorbance and emission maxima of PBI-TB are red-shifted with respect to PBI-OB. Additionally, PBI-OB and PBI-TB partially absorb in the same region where the peripheral chromophores emit (Figure 3-5).

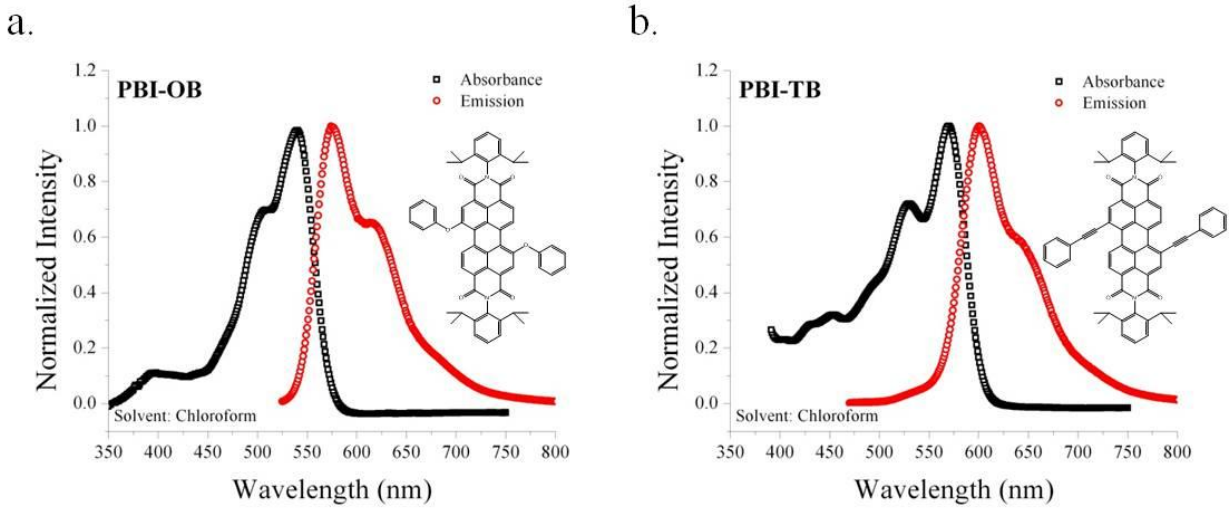


Figure 3-4. Absorbance and Emission Spectra of (a) PBI-OB and (b) PBI-TB.

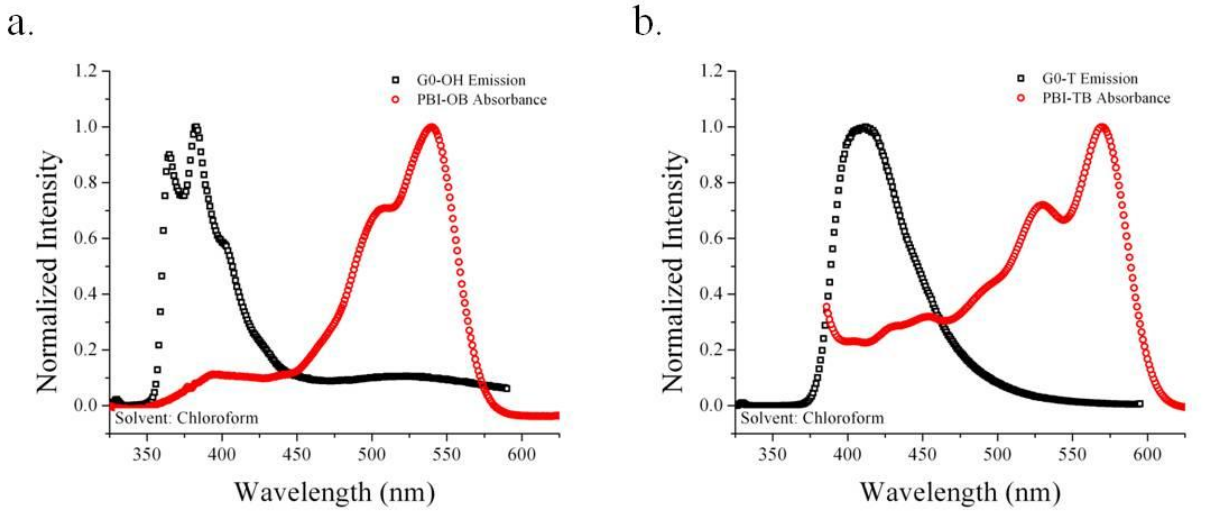


Figure 3-5. Donor-Acceptor overlap. (a) Model compounds, G0-OH and PBI-OB, of the POG0 dendrimer (b) Model compounds, G0-T and PBI-TB, of the PTG0 dendrimer.

Now that these model compounds have been discussed, consider the properties observed in the associated dendrimers. Figure 3-6 displays the normalized absorbance and emission spectra of G0-OH, PBI-OB and POG0. When using PBI-OB to estimate the expected absorbance from the POG0 core, it is important to recognize that the full absorption spectrum also exhibits absorption below 300 nm (not shown) in the UV region and is attributed to the dendritic arms, and the absorption detected at longer wavelengths in the visible region is due to the perylene diimide core.

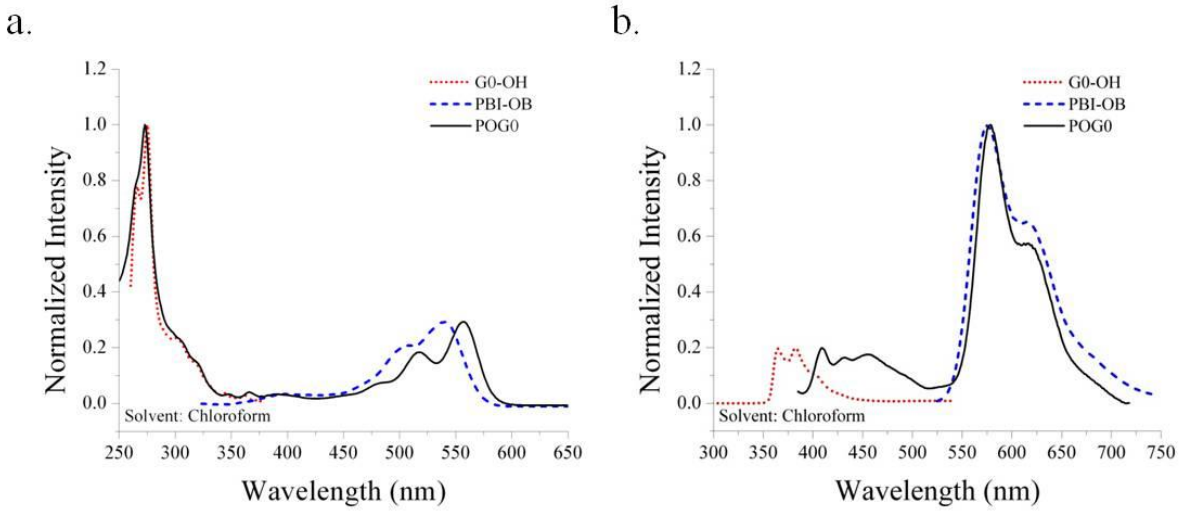


Figure 3-6. Normalized (a) Absorbance and (b) Emission Spectra of G0-OH (dotted red line), PBI-OB (dashed blue line) and POG0 (solid black line)

A shift to longer wavelengths, a bathochromic or "red" shift, from 540 nm to 557 nm is observed in the absorbance of the perylene diimide core of POG0. This lowering of transition energy is likely caused by an increase in the extent of π-conjugation of the dendrimer. The absorbance band from the perylene diimide core of POG0 seen between 500-600 nm is associated with the S_0-S_1 transition.[56] The greatest absorption is seen in the UV region of the electromagnetic spectrum, and this corresponds to the periphery of the POG0 dendrimer. As the absorbing chromophores should be capable of efficient light-harvesting, a high absorbance for this part of the dendrimer is ideal. The absorptions of the periphery and core components are well separated, indicating that the periphery could be selectively excited for the study of intramolecular energy transfer.[57] At all excitation wavelengths, the maximum emission of POG0 occurs around 575 nm. Emission at this wavelength corresponds to emission from the perylene diimide core.

The normalized absorption and emission spectra of G0-T, PBI-TB and PTG0 are shown in Figure 3-7. The absorption spectrum of PTG0 (Figure 3-7A) shows significant inhomogeneous broadening[58], which is attributed to changes in the structure of the solvation shell.[29] Similar to

POG0, the greatest absorption occurs below 300 nm, and is assigned as the absorption from the periphery. The emission of PTG0 (Figure 3-7B) at excitation wavelengths less than 300 nm, results in a spectrum dominated by emission from the peripheral molecules, which exhibits a slight red shift with respect to the emission of G0-T. Excitation of PTG0 at wavelengths greater than 400 nm (the perylene diimide core) exhibits an emission band of low intensity, centered around 650 nm.

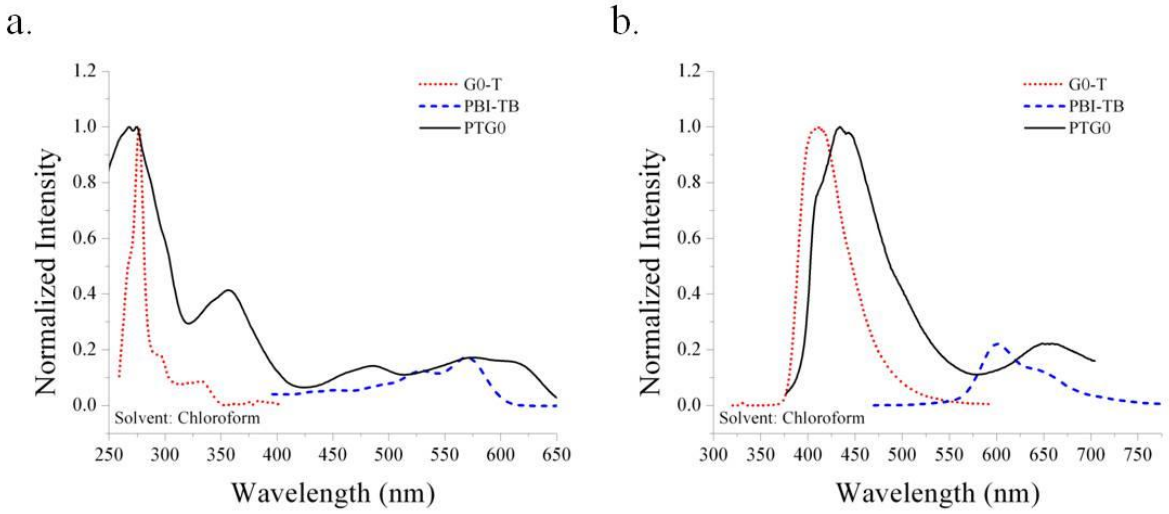


Figure 3-7. Normalized (a) Absorbance and (b) Emission Spectra of G0-T (dotted red line), PBI-TB (dashed blue line) and PTG0 (solid black line)

Irrespective of excitation wavelength, the fluorescence of POG0 (Figure 3-6B) is dominated by the fluorescence from the perylene diimide core, which is a strong indication that intramolecular energy transfer occurs in this dendrimer family. Conversely, significant energy transfer does not occur in PTG0 as excitation of PTG0 at wavelengths less than 425 nm results in an intense emission band which can be attributed to the emission of the periphery, the emission of G0-T. Excitation of PTG0 at 576 nm, the absorbance maximum of the perylene diimide core, results in a relatively weak emission band, centered around 650 nm.

Fluorescence Anisotropy

Perylene has been used and studied since the early twentieth century. The orientation of the absorption transition moment for perylene[29] (Figure 3-8) is known to be along the long axis for the S_0-S_1 transition and along the short axis for the S_0-S_2 transition. Analogous results are expected for the perylene diimide dendrimer derivatives, and steady state fluorescence anisotropy[59] methods have been employed to ascertain more information about the transition dipole moments of POG0.

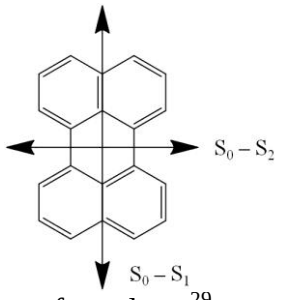


Figure 3-8. Absorption transition moments of perylene.[29]

To gain information about the angle between the absorption and emission transition dipoles of a molecule using steady state spectroscopic methods, the ideal solution would be dilute and prepared in a highly viscous solvent. The high viscosity of the solvent hinders the rotational diffusion of the molecule under investigation, making it possible to deduce information regarding the transition dipole moments.

Unfortunately, due to problems with the solubility of the samples, the use of a highly viscous solvent was not possible. Instead, the solutions were prepared in chloroform, a solvent in which perylene diimides have already been studied[50] and which posed no solubility problems. The results from the steady state emission anisotropy experiments performed on G0-OH and the full POG0 dendrimer are discussed below.

The steady state fluorescence anisotropy of G0-OH has been conducted at varying excitation wavelengths. From the absorption spectrum of G0-OH in chloroform (Figure 3-2A),

two peaks are observed at the maximum of the most intense absorbance band. These peaks are believed to be vibrational structure and are not expected to affect the results of the steady state anisotropy experiments.

When excited at 275 nm (Fig. 3-9A), and longer wavelengths, G0-OH displays no anisotropy. A zero-value for the anisotropy is an indication that the transition dipole moments of the fluorophores have assumed a random orientation. This is most likely due to the rotational diffusion of the molecules in the solution phase. Without further information about the rotational correlation time, this would be a reasonable assumption to explain the results of the anisotropy experiments for G0-OH. However, when G0-OH is excited at 265 nm (Figure 3-9B), an anisotropy value of nearly -0.2 is observed. This presents several problems.

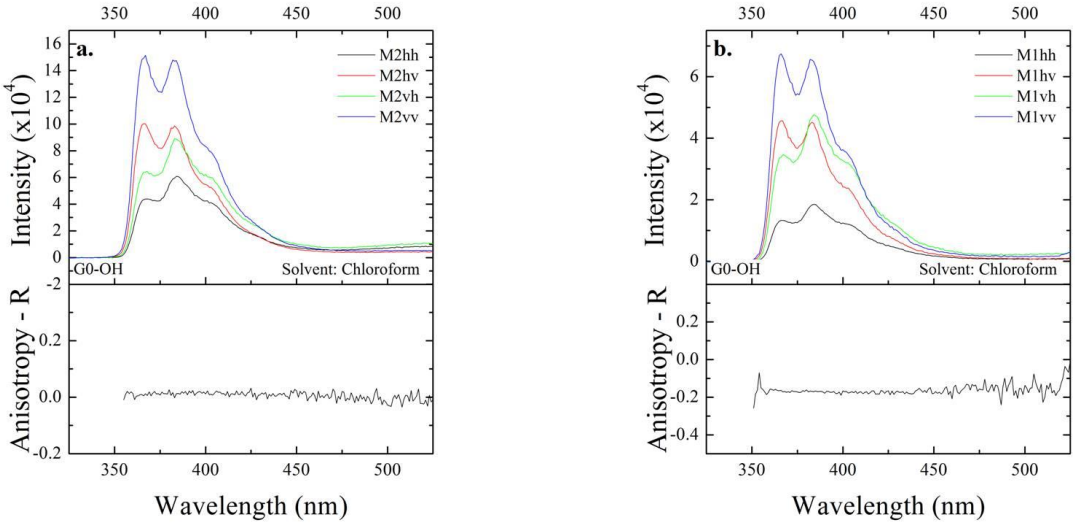


Figure 3-9. G0-OH Emission Anisotropy (a) $\lambda_{Exc.}$ = 275 nm (b) $\lambda_{Exc.}$ = 265 nm

First, an anisotropy value of approximately -0.2 occurs when the absorption and emission transition dipole moments are nearly perpendicular. If the peaks observed at the absorbance maximum of G0-OH are true vibronic structure of the same electronic transition, it is not feasible to believe that excitation of G0-OH at 265 nm and 275 nm should result in different values for the anisotropy. Furthermore, if this data is correct, then the assumption that rotational diffusion

contributed to the random orientation of the fluorophores (and a zero-value anisotropy) is no longer accurate.

There are several possible reasons to explain the contradictory results displayed by the G0-OH data. A likely explanation is instrumental or human error. A mistake committed by the researcher during the experiment is not beyond the realm of possibility. Fluctuations in lamp intensity and scattered light are among the possible contributing factors to instrumental errors. Finally, the less likely explanation is that the peaks observed in the absorption spectrum of G0-OH are contributions from two separate electronic transitions.

Due to the anomalous anisotropy value for G0-OH when excited at 265 nm, further experimentation will be necessary to ensure the reproducibility of the data. Time-resolved anisotropy experiments, which are discussed in Chapter 4, promise information about the rate of rotational diffusion of the chromophore in solution. If the rate of rotational diffusion is faster than the rate of fluorescence emission, the anisotropy is expected to be zero.[61] Therefore, one could conclude the anisotropy value of G0-OH when excited at 265 nm to be erroneous and most likely the result of experimental or instrumental error. However, if the rate of rotational diffusion is much slower than the rate of fluorescence emission, then the effect of rotation is negligible.[32] In that case, more information will be necessary to determine to cause for the change in anisotropy.

With investigation of POG0, one wishes to observe the changes in the behavior of the anisotropy caused by excitation of the donor and acceptor chromophores of the dendrimer. This data is shown below in Figure 3-10. When POG0 is excited in the peripheral region of the dendrimer, a loss of anisotropy is observed in the region corresponding to emission of the donor (Figure 3-10A). The loss of anisotropy could be attributed to several factors. In this case, as the

size of the full dendrimer minimizes the effect rotational diffusion could have on the depolarization process, and the data is supported by the steady state characterization studies, the loss of anisotropy is believed to be an indicator of energy transfer from the excited donor to the acceptor component of the dendrimer. Figure 3-10B displays the anisotropy resulting from excitation of the perylene diimide core.

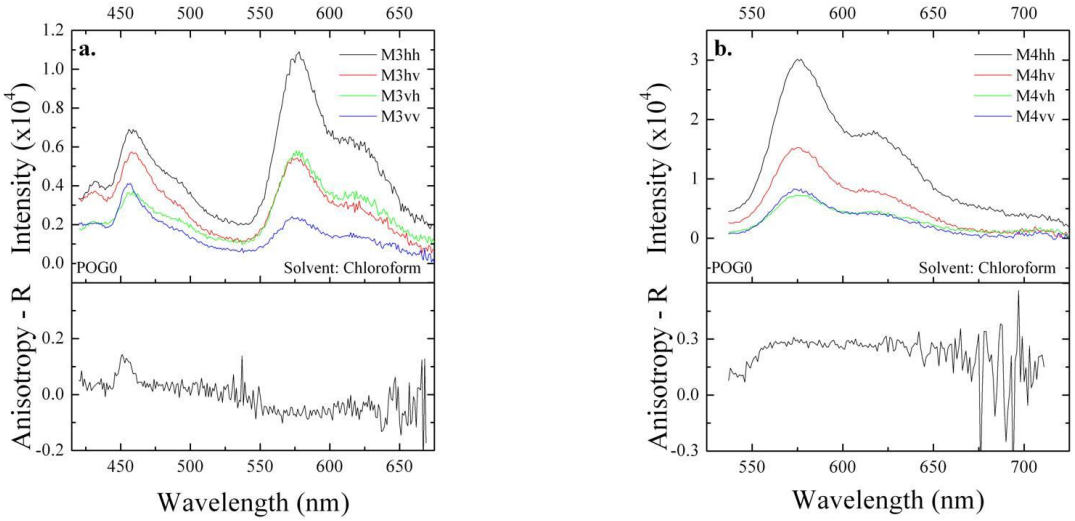


Figure 3-10. POG0 Emission Anisotropy (a) Excitation of donor (b) Excitation of acceptor

An anisotropy value of 0.37 has been reported[60] for perylene in glycerol. The anisotropy of POG0, when excited at the perylene diimide core, displays a value close to 0.30 (Figure 3-10B). Rotational diffusion is believed to be the cause of this lower anisotropy value. POG0, a much larger molecule, would be expected to rotate slower than perylene, and therefore have a higher anisotropy value. However, one must consider that the anisotropy for perylene reported in the literature was measured at temperatures ranging from 170-300 K. The lowered temperature ranges reported in the literature were used to minimize the affects of rotational diffusion in the molecules under investigation. Therefore, at room temperature, for POG0 samples capable of moving freely in solution, rotational diffusion would be a reasonable explanation for a lower anisotropy.

Fluorescence Lifetimes

The fluorescence decay lifetimes of the samples were collected using a PicoQuant Fluorescence Lifetime System, which was described in generality in Chapter 2. Specifically, the samples were excited at 370 nm; the repetition rate for the experiments was 10 MHz, and the average power was approximately 0.075 mW. The fluorescence lifetimes, amplitude weighting (fractional intensities) and χ^2 value for each molecule are summarized in Table 3-2.

Table 3-2. Fluorescence lifetime data of dendrimer samples in chloroform

Molecule	τ_1 (ns)	FI_1	τ_2 (ns)	FI_2	χ^2
G0-OH	1.84	53.30 %	8.82	46.70 %	1.699
G0-T	2.06	20.90 %	5.62	79.10 %	1.315
PBI-OB	---	---	4.65	100.00 %	1.179
PBI-TB	---	---	6.85	100.00 %	1.163
POG0	1.63	53.66 %	5.01	46.34 %	1.381
PTG0	2.84	59.59 %	5.43	40.41 %	1.246

FI_1 and FI_2 are the Fractional Intensities of the lifetimes τ_1 and τ_2, respectively. The Fractional Intensity is calculated using the equation, $FI_n = A_n\tau_n/(A_1\tau_1 + A_2\tau_2 + \ ... \ + A_n\tau_n)$, where A_n is the amplitude of the n^{th} component.

As can be inferred from Table 3-2, the triphenylene molecules, G0-OH (Figure 3-11) and G0-T (Figure 3-12), which form the periphery of the two dendrimer families, exhibit a two-exponential decay. The two core molecules, PBI-OB (Figure 3-13) and PBI-TB (Figure 3-14) show single exponential decays. And the full dendrimers, POG0 (Figure 3-15) and PTG0 (Figure 3-16) also display a two-exponential decay.

For excitation at 370 nm, it is expected that the fluorescence decays of the full dendrimers, POG0 and PTG0, should reflect contributions from both the periphery and core components. For example, in POG0 the resulting lifetimes are expected to reflect the lifetimes observed for G0-

OH and PBI-OB. The component observed at early times (τ_1) in the fluorescence decay of POG0 and PTGO is attributed to the fluorescence decay of peripheral molecules. The second lifetime (τ_2) of POG0 results from a combination of the lifetimes of G0-OH (τ_2) and PBI-OB (τ_1). Similarly, τ_2 for PTG0 reflects contributions from the lifetimes of G0-T and PBI-TB.

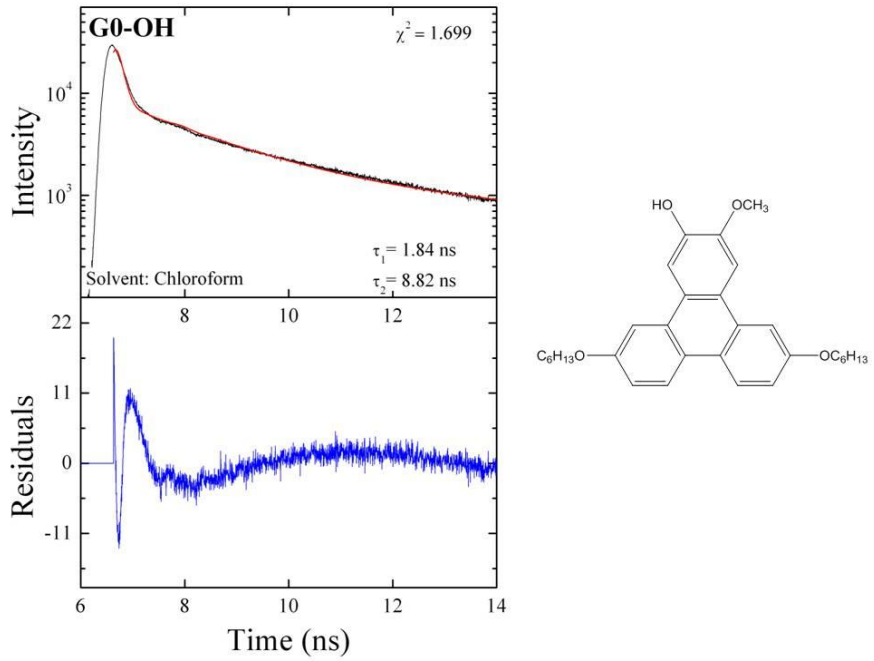


Figure 3-11. Fluorescence lifetime decay of G0-OH in chloroform.

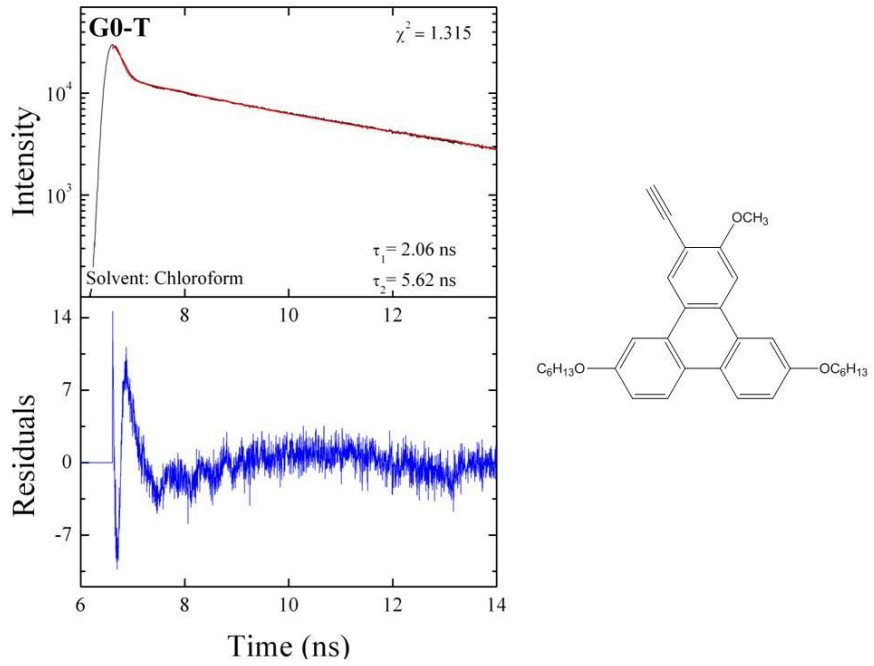


Figure 3-12. Fluorescence lifetime decay of G0-T in chloroform.

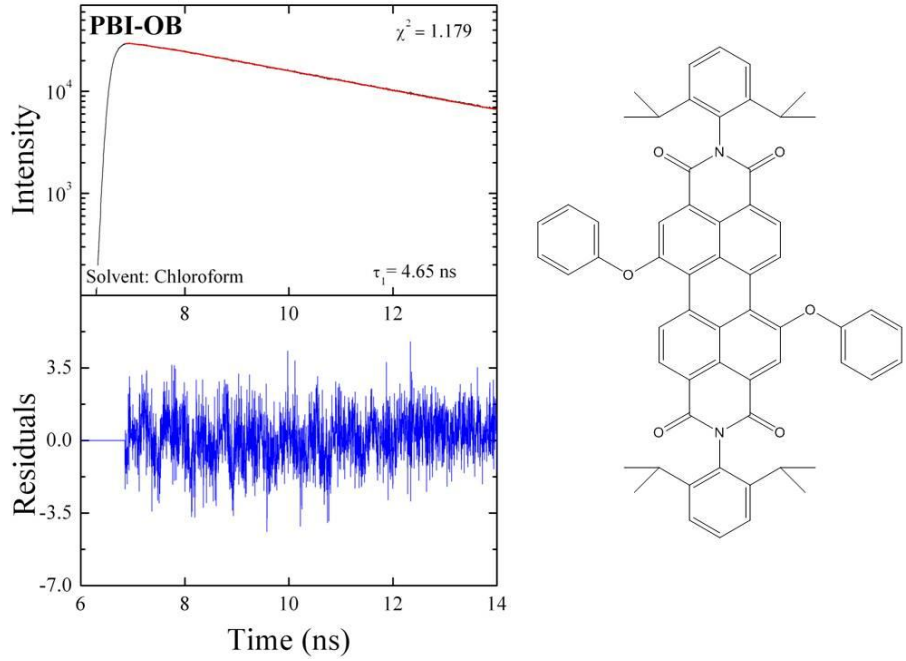


Figure 3-13. Fluorescence lifetime decay of PBI-OB in chloroform.

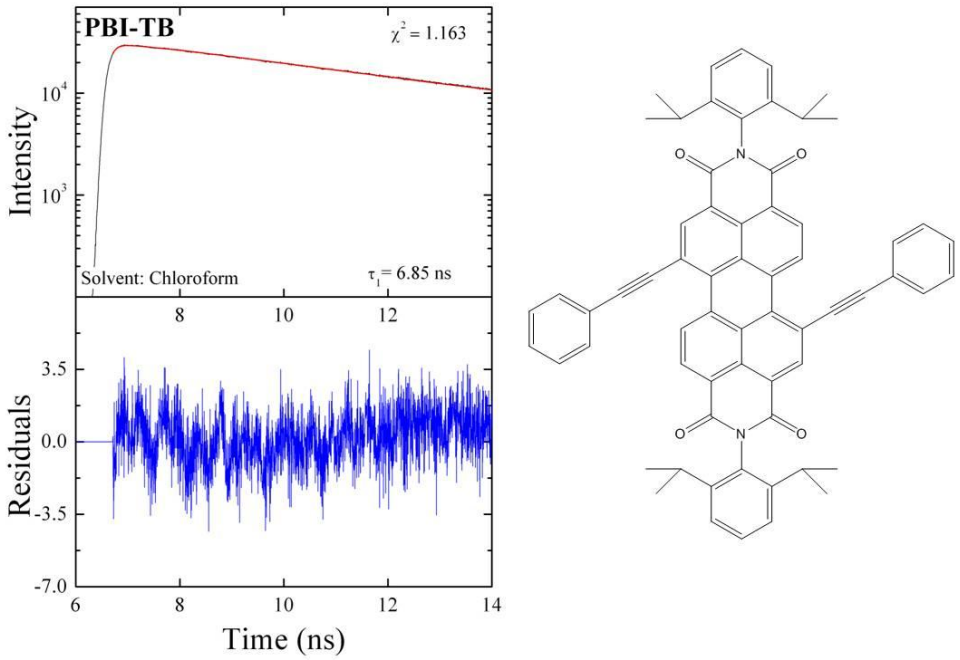


Figure 3-14. Fluorescence lifetime decay of PBI-TB in chloroform.

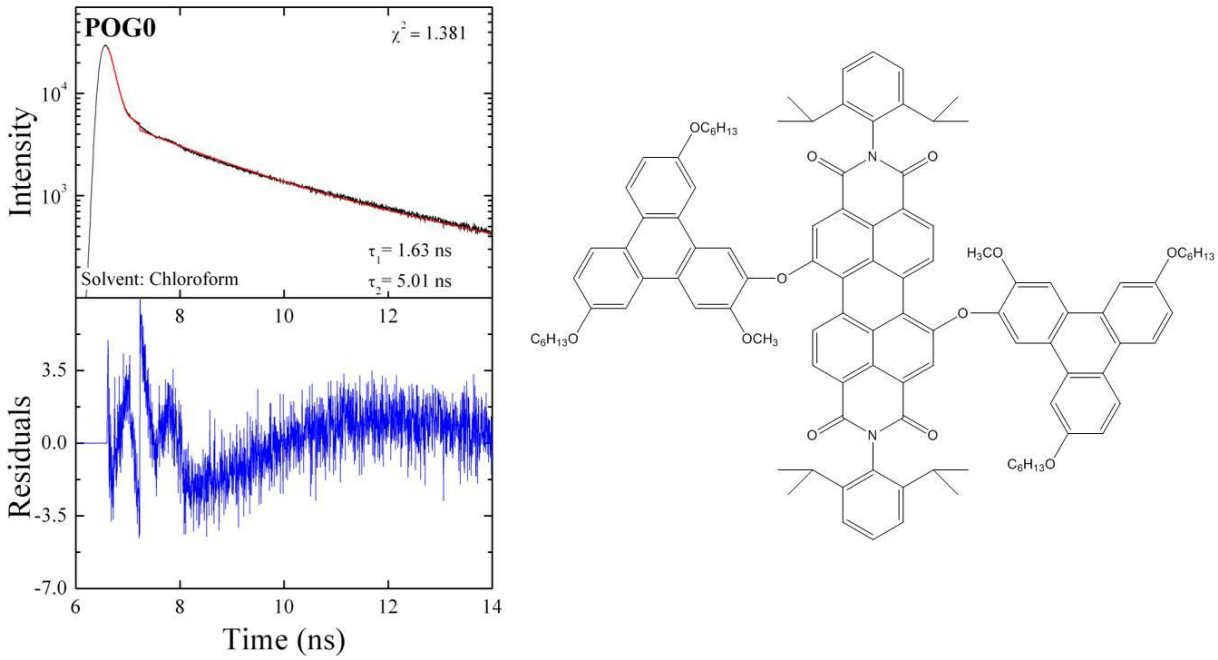


Figure 3-15. Fluorescence lifetime decay of POG0 in chloroform.

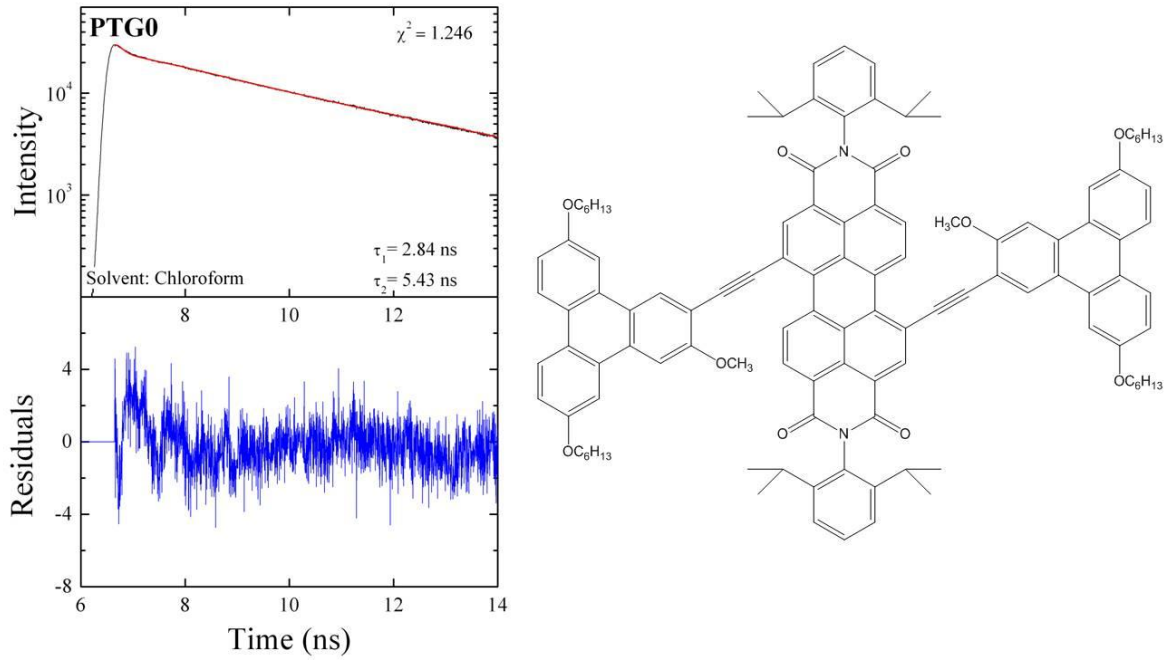


Figure 3-16. Fluorescence lifetime decay of PTG0 in chloroform.

From the emission spectrum of POG0 (Figure 3-6B), one can see that the emission from PBI-OB dominates the POG0 emission spectrum. On the other hand, most of the emission of PTG0 (Figure 3-7B) comes from G0-T. For these reasons, τ_2 for POG0 more closely resembles the lifetime of PBI-OB, while that of PTG0 is closer to the second lifetime (τ_2) of G0-T. Further experiments should be conducted using bandpass filters to detect only the fluorescence decay coming from a selected wavelength range. In this way, it will be possible to determine how changes in the fluorescence decay of the complete dendrimer, with respect to the decay of fluorescence of the core and periphery, are affected by energy transfer.

CHAPTER 4
CONCLUSIONS AND FUTURE WORK

Conclusions

Absorption and emission spectra have been collected for these dendrimers using steady state methods. The emission of POG0 has been determined to be independent of excitation wavelength. Excitation of POG0 at wavelengths corresponding to absorbance of the periphery results in emission due to the perylene diimide core, indicating the presence of intramolecular energy transfer. Similar experiments for PTG0 have revealed that excitation at wavelengths less than 425 nm produces an emission spectrum dominated by emission of the dendrimer periphery, while excitation at longer wavelengths reveals a low intensity emission attributed to emission of the perylene diimide core.

Anisotropy experiments have been conducted for samples POG0 and G0-OH. Excitation of POG0 at the core results in an anisotropy value of approximately 0.30, while excitation of POG0 at the periphery results in a loss of anisotropy in the core region. This loss of anisotropy is believed to be induced by the transfer of energy from the periphery to the core. Independent of excitation wavelength, no anisotropy is observed for G0-OH. This is attributed to the rate of rotational diffusion of the molecules in solution. The reproducibility of the data set must be confirmed by further experimentation using time-resolved anisotropy. Time-resolved anisotropy experiments can provide information about the rate of rotational diffusion, which will help determine if the signal observed from G0-OH is accurate.

The lifetime of the decay of fluorescence has been measured for each sample in chloroform solutions. The fluorescence decay lifetimes of the full dendrimers, POG0 and PTG0 have been considered with respect to the lifetimes of their individual model compounds. Further experiments should be performed to confirm the existence of energy transfer.

Steady state and time-resolved spectroscopic methods have been used to study energy transfer properties of perylene diimide dendrimer derivatives in solution. These molecules show much promise in the energy research field. While data for POG0 indicates that intramolecular energy transfer is most likely occurring in this dendrimer, more experimentation will be necessary to confirm this conclusion.

Future Work

As the experiments were conducted for these molecules, and the data was analyzed, it became apparent that further experimentation might be advantageous. The following sections address additional experimental methods which could offer more information about the questions presented in this thesis. Although not included in the original design of the experiment, these experimental methods should further the understanding of the energy transfer in these dendrimers..

Time-Resolved Fluorescence Anisotropy

With the understanding that the steady state fluorescence anisotropy is the time-averaged response over the lifetime of the fluorescence decay, the time-resolved fluorescence anisotropy[62] can thus be written as

$$R(t) = \frac{I_{VV}(t) - GI_{VH}(t)}{I_{VV}(t) + 2GI_{VH}(t)}$$

The obvious advantage between steady state and time-resolved fluorescence anisotropy is the retention of the time-resolution using the time-resolved experimental method.

The time-resolution of the acquired data provides a direct way to approximate the fundamental, or limiting, anisotropy, r_0. Typically, the anisotropy observed at time zero, r(0), is a good estimation of the fundamental anisotropy. Time-resolved anisotropy measurements also provide the decay, and therefore the lifetime of the anisotropy. This additional information may

make it possible to draw further conclusions about the steady state anisotropy experiments discussed previously.

Excimers

Preliminary data from my collaborator, the research group of Dr. Zhonghua Peng, has indicated the presence of additional emissive bands in the fluorescence spectra of G0-OH film samples. It is believed that these bands may contribute to a band appearing at similar wavelengths in the fluorescence of POG0, supporting the existence of possible of excimer formation.

The term excimer was coined by Stevens and Hutton in 1960,[63] and comes from a blending of the words, "excited dimer". An excimer is formed during the interaction of two identical molecules, one in and unexcited state and the second in an electronically excited state.

$$M^* + M \rightleftarrows (MM)^*$$

Properties of excimers As excimers exist and are formed in the excited state,[64] they can only be observed in emission experiments, and no change should be observed in the absorption spectra[64,65] of the sample under investigation. Typically, excimers exhibit several distinctive properties, enabling the identification of excimer formation from study of the sample fluorescence.

For example, excimer[65] bands exist at wavelengths longer than the characteristic monomer emission (red-shifted), and appear as broad bands without the presence of vibronic structure. The intensity of the emission band of the excimer is inversely proportional to the intensity of the monomer emission band. That is to say, with an increase in concentration, the intensity of the excimer emission should increase while the emission band due the monomer decreases.

Excimer formation Intermolecular excimers are formed from the collision the excited and unexcited states of two separate, but identical molecules. The formation of an excimer by this

method is dependent upon the translational diffusion of the molecules during the excited state lifetime of the monomer. By contrast, intramoleculer excimers are formed by interactions between the excited and unexcited states of two fluorophores, connected by a flexible chain, within the same molecule. In this case the formation of the excimer is dependent upon the ability of the fluorophores to come into close proximity to one another through rotational motion. Therefore, intramolecular excimers are not dependent upon sample concentration.[66]

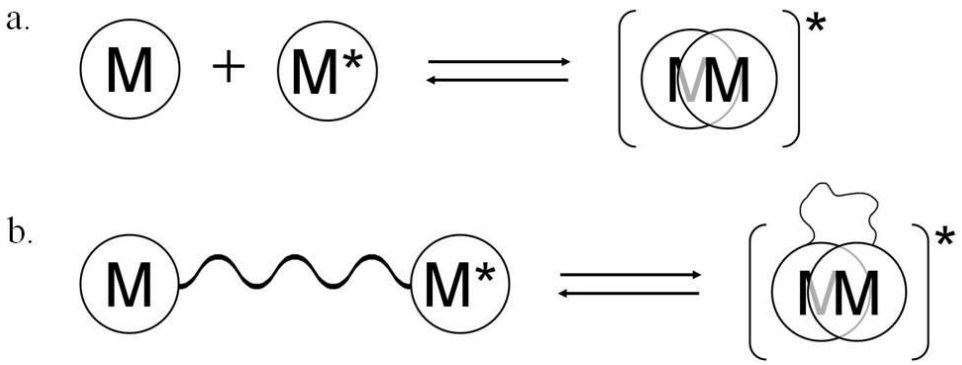


Figure 4-1. Excimer formation. (a) Intermoleculer excimer formation (b) Intramolecular excimer formation[29]

Preliminary data The data obtained from Dr. Peng's laboratory, shown in Figure 4-2, displays the comparison of fluorescence spectral data for G0-OH and POG0. The region of interest lies in the film sample of G0-OH with the appearance of additional emissive bands at wavelengths longer than those known to be attributed to the monomer emission of G0-OH. These bands appear to have excellent overlap with a low-intensity component of the POG0 emission. This component of POG0 appears as a relatively broad structureless band, and presents the possibility of excimer formation. For the purposes of future solid-state applications, the ability to determine whether or not this is true excimer formation would be invaluable to the energy transfer studies of these molecules.

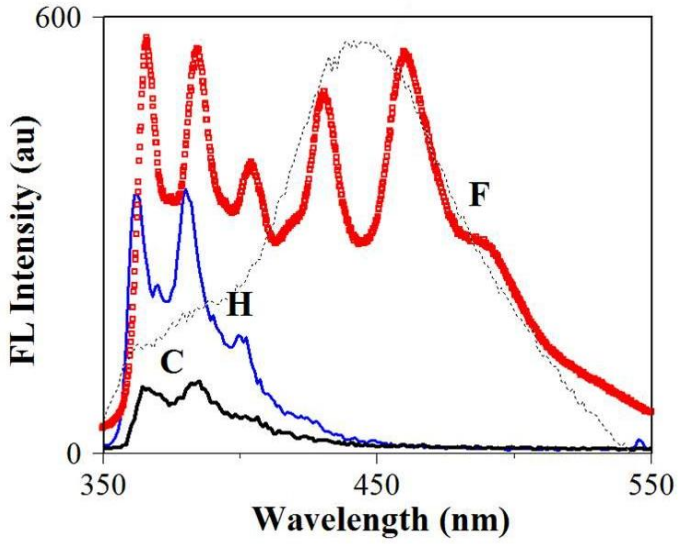


Figure 4-2. Comparison of fluorescence spectral data for G0-OH in (1) Chloroform – **C**, bold black line (2) Hexane – **H**, bold blue line and (3) Film – **F**, bold red squares, with the fluorescence curve of POG0 (dashed black line). Courtesy of Z. Peng, 2010.

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BIOGRAPHICAL SKETCH

Allison Jean LaFramboise was born in Ypsilanti, Michigan in 1986 to Donald and Deborah LaFramboise. At the age of six, her family relocated to Lynnville, Tennessee, a rural town located near the Tennessee-Alabama state line. The youngest of three daughters, Allison is the self-proclaimed nerd of the family.

After graduating from Richland High School, Allison left home to attend Lee University, a private, Liberal Arts Institution situated in Cleveland, Tennessee. While a student at Lee, Allison had the opportunity to participate in two cross-cultural trips: the first, touring with Lee University's Symphonic Band in Amman, Jordan, and the second, a study of Art History stretching through the heart of Italy. In May of 2008, Allison earned her bachelor's degree in chemistry with minors in Bible and mathematics. Upon her graduation from Lee University, Allison began her graduate studies at the University of Florida in the Fall of 2008, joining the research group of Dr. Valeria Kleiman.