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Publication Date
2012

Peer reviewed|Thesis/dissertation
The Spectroscopic-Assisted Investigation into Energy Migration through Disordered Systems

A Dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy in Chemistry

by

Kathryn Anne Colby

September 2012

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Acknowledgements

First, I would like to acknowledge and thank Professor Christopher J. Bardeen for all of the help he has provided in making this dissertation a reality. I knew when I was accepted to grad school that I wanted to work under the guidance of a professor that holds potential for understanding and addressing the challenges behind harvesting solar energy on a national scale through a spectroscopic approach. Immediately after meeting and talking with Professor Bardeen, I knew that it was through him that I wanted to take part in the state-of-the-art research performed in this arena of interest. Upon questioning, he was able to lay out effectively the problems and proposed solutions faced by researchers today, demonstrating his knowledge, experience, and capability to address such topics. Five years later, I am proud to have produced this dissertation as a result of my work within his research group. I would also like to acknowledge and thank Dr. Ralph Isovitsch for first suggesting graduate school as something to think about in light of our many conversations on various topics in chemistry, including the ones pertaining to my specific interests in spectroscopy and solar energy. Without such guidance, I would never have made it to grad school. Finally, I would like to thank my mother, Vicki Colby for instilling within me at a very young age a joy for reading, my grandfather, Eli Chezar, for a desire to excel in math, and my grandmother, Loretta Amley, for the desire to address social issues, such as the global need for a sustainable source of energy.
ABSTRACT OF THE DISSERTATION

The Spectroscopic-Assisted Investigation into Energy Migration through Disordered Systems

by

Kathryn Anne Colby

Doctor of Philosophy, Graduate Program in Chemistry
University of California, Riverside, September 2012
Dr. Christopher J. Bardeen, Chairperson

Harvesting solar energy is hindered by the financial difficulties in the creation of perfect crystal silicon-based photovoltaics. The study of energy flow through disordered systems is therefore in interest as a potential way to manufacture low-cost amorphous systems. It is shown through a series of time-resolved photon-counting fluorescence sensitization experiments that in a static system with disorder, anomalous diffusion results in that measured values for the exaction diffusion constants fall short of what is predicted for crystals based on traditional steady-state measurements for Forster parameters such as $R_0$. Various strategies are discussed to successfully tune the degree of energy migration through disordered systems. The extent to which steady-state theory can be used as a simple tool in guiding the organic synthesis of potential active materials is brought to light.
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$D$ = 

1

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\]

equation 2.2

\[
\frac{(0.001 \text{ L R700}) \left( 2 \times 10^{-3} \frac{\text{mol}}{L} \text{R700} \right)}{(1.19 \text{ g PMMA}) \left( \frac{\text{mL} \text{ PMMA}}{1.19 \text{ g PMMA}} \right) \left( \frac{L}{10^3 \text{ mL}} \right)} = 2 \times 10^{-6} \frac{\text{mol R700}}{0.001 \text{ L PMMA}} = 2 \text{ mM R700in PMMA}
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**equation 2.11** \[ A = 4\pi D\sigma_{f}C_{A} \tag{2.11} \]

**Chapter 3**

**equation 3.1**

\[ r(t) = \frac{I(t)_{par} - I(t)_{per}}{I(t)_{par} + 2I(t)_{per}} = \frac{\text{excess light polarized parallel to the incident light}}{\text{total fluorescence emitted}} \tag{3.1} \]

**equation 3.2**

\[ G_{s}(t) = r(t) = r_{0}\exp\left[ -\frac{4}{3}\frac{\pi}{\sqrt{A}}\lambda^{3}\frac{1}{2}R_{0}^{3}C_{LR}\sqrt{\frac{t}{\tau_{fl}}} \right] \tag{3.2} \]

**equation 3.3** \[ r(t) = r_{0}\exp\left[ -\frac{t}{\sqrt{\tau_{pol}}} \right] + y_{0} \tag{3.3} \]

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**equation 3.6** \[ I_{D}(t) = I_{D}(0)\exp\left[ -\frac{t}{\tau_{fl}} - At - B\sqrt{t} \right] \tag{3.6} \]

**equation 3.7**

\[ A = 4\pi D\sigma_{f}C_{A} \tag{3.7} \]

\[ \]
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B = \frac{4}{3} \pi R_{DA}^3 C_A \sqrt[6]{\frac{\pi}{\tau_\beta}}
\]

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D = \frac{4 \pi C_D}{3} \left( \frac{R_0^6}{\tau_\beta} \right)
\]

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\frac{I(t)[C_{LR}]}{I(t)[10^{-4} M C_{LR}]} = \frac{\exp[-k_\beta t - At - B\sqrt{t}]}{\exp[-k_\beta t - B\sqrt{t}]} = \exp[-At]
\]

equation 3.11 \[
\sigma_F = R_{DA} \frac{\Gamma(0.75)}{2\Gamma(1.75)} \left( \frac{R_{DA}^2}{\tau_\beta D} \right)^{\frac{1}{4}} = 0.676 \left( \frac{R_{DA}^6}{\tau_\beta D} \right)^{\frac{1}{4}}
\]

equation 3.12 \[
D = \frac{1}{6} \frac{I_{hop}^2}{\tau_{hop}}
\]

equation 3.13 \[
l_{hop} = \frac{1}{\sqrt{3C_{LR}}}
\]

equation 3.14 \[
l_{hop} = \Gamma(4/3) \sqrt[3]{\frac{3}{4\pi C_{LR}}} = \frac{0.554}{\sqrt[3]{3C_{LR}}}
\]

equation 3.15 \[
k_{\text{FRET}} = \frac{1}{\tau_{\text{FRET}}} = \frac{1}{\tau_{hop}} \left( \frac{R_0}{R} \right)^{6}
\]

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\]

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\frac{A}{R_{DA}^{\frac{3}{2}}} = \frac{23.04 R_{DA}^{\frac{3}{2}}}{D^{\frac{3}{2}}} \frac{\beta^{\frac{4}{3}}}{\tau_\beta} \frac{C_A}{C_D}
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equation 4.10 \[ A = 4 \pi k C^\alpha D R^6 R_{DA} C_A \] 

equation 4.11 \[ \sigma_F = R_{DA} \frac{\Gamma(0.75)}{2\Gamma(1.75)} \left( \frac{R_{DA}^2}{\tau_{\beta} D} \right)^{\frac{\sigma}{4}} = 0.676 \left( \frac{R_{DA}^6}{\tau_{\beta} D} \right)^{\frac{1}{4}} \] 

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equation 4.13 \[ D_{trans} = \frac{k_B T}{6 \pi h r} \] 

equation 4.14 \[ \tau_r = \frac{h V}{k_B T} f W \] 

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equation 5.1 \[ D = \eta \left( \frac{4 \pi C}{3} \right)^\frac{4}{3} R_0^6 \] 

equation 5.2 \[ R_0^6 = \frac{9000 \ln(10)\phi_\beta K^2}{128 \pi^5 N_A n^4} \int_0^\infty e(v) f(v) \frac{dv}{v^4} \] 

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Chapter 1: Amorphous Organic Photovoltaics and Energy Migration through Disordered Systems

1.1 Introduction

Solar cells may be either organic or inorganic in nature. In light of the 10% minimal efficiency requirement for marketability [1], traditional inorganic Silicon-based cells dominate the market due to their relatively higher efficiencies. Today’s Si-cells possess efficiencies up to 20% in comparison with the 8% limit reached by their organic counterparts [2]. However, in order to reach efficiencies that approach the Shockley-Queisser limit of 30% [3], the silicon must be highly pure and crystalline, thus requiring the use of expensive clean rooms for manufacturing [4]. This makes a national reliance on solar energy economically infeasible. Cheap roll-to-roll printing of amorphous solar cells, however, can be produced in not so stringent of conditions. This encourages research into how energy migrates within organic photovoltaics (OPVs) so that it can be manipulated in such a way as to increase efficiencies.

Because organic materials possess low dielectric constants, a molecularly-bound electron hole pair termed an exciton is generated upon photoexcitation. The exciton must diffuse toward an interface shared with a material that possesses a higher electron affinity where it can dissociate into free electron/hole carriers. These charge carriers are then picked up by their respective electrodes, thereby generating an electronic current from which electronic work can be done [5, 6]. Ideally, the photogenerated excitons would
possess diffusion lengths on the order of 100 nm, or more precisely, the absorption length of the material \((b)\) as dictated by Beer’s Law \([7]\) (see equation 1.1).

\[ Abs = \varepsilon b c \]  

\textit{equation 1.1}

in which \(\varepsilon\) is the extinction coefficient, \(c\) is the chromophore concentration, and \(Abs\) is a measure of how much light the material absorbs given the power of the incident light, \(P_0\), and the power of light transmitted through the material, \(P\) (see equation 1.2)

\[ Abs = \log\left(\frac{P_0}{P}\right) \]  

\textit{equation 1.2}

Unfortunately, such long diffusion lengths are currently unattainable, with observed diffusion lengths maxing out around 10-20 nm \([8-17]\). This dilemma is often referred to as the exciton bottleneck \([8-12]\) and is often held responsible for the low efficiencies of OPVs \([18, 19]\). It would therefore be nice to have a theory to work with that is able to give accurate predictions for exciton diffusion lengths. Such a theory could be used to help model and design OPVs with respectable diffusion lengths. The current theories that deal with this matter follow the basic premises set forth by Theodor Forster in his initial work on Forster Resonance Energy Transfer (FRET). Forster’s theory provides a straightforward way to predict the diffusion of excited-state electronic energy through materials based on easily measured observables such as the absorption-fluorescence spectral overlap, the absorption extinction coefficient, and the fluorescent quantum yield.

Basic FRET theory describes the rate of transfer of the an exciton \((k_{FRET})\) between two molecules separated by a distance, \(R\) \([20, 21]\) (see equation 1.3)
where \( \tau_{fl} \) is the fluorescence lifetime and \( R_0 \) is the Forster radius, or the distance at which the rate of energy transfer out-competes all other deactivation pathways from the excited singlet state by 50% (see equation 1.4)

\[
R_0^6 = \frac{9000 \ln(10) \Phi_{fl} \kappa^2}{128 \pi^5 n^4 N_A} \int_{0}^{\infty} \frac{\epsilon(\nu) f(\nu) d\nu}{\nu^4}
\]

in which \( n \) is the index of refraction, \( \Phi_{fl} \) is the fluorescence quantum yield of the donor, \( \kappa^2 \) is the orientation factor that describes the relative orientations of the donor and acceptor dipoles, \( N_A \) is Avogadro’s number, \( \epsilon(\nu) \) is the absorption spectrum of the acceptor modulated by its extinction coefficient, and \( f(\nu) \) is the donor’s fluorescence spectrum whose integral has been normalized to 1.

When multiple energy transfer events occur between molecules of the same type, the phenomenon is termed energy migration or exciton diffusion, and is parametrized by an exciton diffusion length, \( L_D \), and an exciton diffusion constant, \( D \) (see equation 1.5 and 1.6)

\[
D = \eta \left( \frac{4\pi C}{3} \right)^{\frac{4}{3}} \frac{R_0}{\tau_{fl}}
\]

\[
L_D = \sqrt{6D \tau_{fl}}
\]

where \( C \) is the chromophore concentration and \( \eta \) is a theoretical proportionality constant expected to lie between 0.32 and 0.56, depending on the theory from which it was derived. From these equations, it can be demonstrated that an organic dye with a small
Stokes shift and a high fluorescence quantum yield can easily possess a Forster radius on the order of 5 nm. What this means is that theoretically, if the concentration of such a dye could be raised to 1 molecule/nm$^3$ (1 M), diffusion lengths on the order of 100 nm should become attainable. In order to understand why they are not, a closer look at the theory is warranted in order to identify and correct for any contributing factors towards this bottleneck. The basic thought underlying such work is that once the bottleneck is understood, it can be dealt with and eradicated, thus promoting OPV efficiencies.

Forster’s original derivation of a FRET-based theory for energy migration [22] was originally designed for the specific case of an ordered system that has a known crystal lattice through which $\eta$ depends upon. Subsequent theorists have rederived this expression for $D$ for application towards disordered systems [23-25]. The theory of Haan & Zwanzig, which predicts a value of $\eta = 0.32$ [23], encompasses the regime of non-diffusive behavior that takes place in the short-time limit of the exciton’s lifetime and at low donor concentrations. Non-diffusive behavior is characterized by a high degree of correlated motion in which excitons spend a non-negligible amount of time returning to previously visited sites. In contrast, diffusive behavior is thought to occur at longer time limits and higher donor concentrations. The regime of diffusive behavior is covered by the theory of Gochanour, Anderson & Fayer, who predict $\eta$ to be 0.428 [24]. The theories of Haan & Zwanzig and Gouchanour, Anderson & Fayer both assume that energy migration is occurring through a single component system in which diffusion is undisturbed by the presence of an acceptor. However, many experiments dealing with the measurement of $D$ require the use of an acceptor. The theory of Jang [25] addresses
diffusion through a two component system and takes into consideration the effect an acceptor plays on a donor’s measured diffusion constant, specifically for the case of time-resolved fluorescence sensitization experiments. Within a simplified version of this theory, $\eta$ is assigned a value of 0.56. This larger value defined in Jang’s theory overcompensates for the fact that the acceptor quenching rate is non-infinite, and that faster moving excitons are not “captured”/quenched as effectively as slower moving ones. As a result, previously measured values for $D$ based on an acceptor quenching radius that is independent of $D$ can be considered underestimates of the true values.

In reality, the kinetics Forster’s expression (see equation 1.5) seeks to describe is much more complicated. For instance, it does not consider coherent states [26], non-nearest neighbor interactions [27], or higher-order transitions [28, 29]. It also does not consider the effect that the acceptor has on the inherent energy migration within the donor as reflected by its absence within the expression for $D$. In addition, diffusion constants are assumed to be time-independent when there is ample theoretical evidence that suggests that this is not the case for disordered systems. These theories are based upon a Euclidean understanding of geometry. As pointed out by Penrose [30], geometry choice is often taken for granted, unfortunately for the sake of simplicity and at the expense of capturing complete physical accuracy. Therefore a Euclidean-based geometry may work fine for describing exciton migration within an ordered crystal lattice, but not so for a disordered system which is more accurately described by a Fractal-based approach to geometry [31]. When a Fractal approach is taken, a time-dependent diffusion process is the result. Finally, the three theories of Haan & Zwanzig,
Gouchanour, Anderson & Fayer, and Jang define a disordered system as one in which there is a random distribution of sites. The random distributions of molecular orientations are neglected in the defining of $\eta$.

The thesis upon which this dissertation is based demands another look at these theories to see whether or not they can truly describe energy migration through disordered systems given these deficiencies. Through the completion of such an evaluation, it can be deduced whether or not Forster theory yields accurate parameters governing exciton diffusion through disordered systems, as well as what direction future research should take in order to increase OPV efficiencies. The thesis is that simple Forster theory fails to quantitatively describe exciton motion due to its neglect of anomalous (time-dependent) diffusion. Through manipulation of $R$, $\kappa^2$, and the $J_{\text{overlap}}$, the effects of anomalous diffusion can be mitigated in qualitative agreement with theory.

1.2 Lumogen Red as a Test Model for Forster-Based Energy Migration Theory

Perylene diimides are very stable molecules whose photo-physical properties can be tuned by synthetic methods [32-39]. These compounds have been shown to be considered good candidates for use within organic photovoltaics [40-44]. Their n-type conduction properties [45] are seldom seen in organic materials, thus making them an attractive alternative to fullerene-derived acceptors within OPVs [40-43, 45]. The low LUMO levels [46] responsible for such conductive properties also make them highly resistant toward photooxidation [47], with absorptions decreasing only slightly after a few years of outside weathering for the particular case of the test molecule adopted here.
Lumogen Red [48-50]. Lumogen Red (see Figure 1.1) is a highly substituted perylene diimide that is resistant towards aggregation [38, 51-53]. Its the most stable structure as determined by density functional theory [54] is non-planar with all substituents oriented perpendicular to the perylene core. Such positioning of the substituents constrains the molecules from taking on the usual $\pi-\pi$ stacking that characterizes the packing of the majority of aromatics in the solid state and solution-based aggregates. Such aggregates can lead to low-energy electronic states that act as trapping sites for excitons, thus interfering with exciton migration and leading to measured values for D that fall short of those predicted by steady-state data [55].

Figure 1.1. Molecular structure of Lumogen Red.
Lumogen Red was originally designed for use within luminescent solar cell concentrators [48]. Since then, it has been investigated for potential applications in solid-state organic lasers [56-62] and light-emitting diodes [63, 64] in addition to its intended use in solar cell concentrators [49, 50, 65, 66]. Its success in such applications lies not only in its favorable photostability and solubility properties, but also in its high quantum yield (0.96 in solvent solutions [48] and 0.88 in PMMA [67]) and respectable fluorescence lifetime (6.0 ns in solvent solutions [48] and 5.7 ns in PMMA [68, 69]. Such properties favor Forster energy transfer. Thus, in many respects, Lumogen Red is an ideal molecule to use for testing out the predictions of Forster-based energy migration theory.

It is well-known that the spectroscopic properties of a molecule can change as its concentration is increased and this is also the case for Lumogen Red. As the concentration of Lumogen Red in PMMA is increased from $10^{-4} \text{ M}$ to 50 mM, the absorption broadens slightly and experiences a blue shift ~4 nm while the emission undergoes a slight red shift as can be seen in the concentration-dependent spectra displayed in Figure 1.2. Within the solvents CHCl$_3$ and DMF, it is the fluorescence that undergoes a significant red-shift with concentration while the absorption remains relatively constant. These shifts can be ascribed to solvatochromic effects due to an increase in the density of polarizable electrons in the environment with the increase in chromophore concentration [73]. As a result, the overall environment becomes more polar and is able to stabilize the more highly polarized photo-excited state of the
Figure 1.2. Concentration-dependent spectral shifts for $10^{-4}$ M - 50 mM Lumogen Red in a) PMMA b) CHCl$_3$, and c) DMF. Shown are the $10^{-4}$ M (solid line) and 50 mM spectra (dashed line).
chromophore. Red shifts occur in the fluorescence with the increase in chromophore concentration as emission comes from a more stabilized, and thus, lower energy state.

These fluorescent red shifts are not as prominent in PMMA as they are in the solvents due to the static nature of the PMMA matrix which restricts the reorganization of the excited state necessary for its stabilization to occur. When comparing the spectral changes in PMMA’s absorption with increasing chromophore concentration versus those in CHCl₃ and DMF, it appears that the with such increases, the excited state within the liquids is stabilized whereas the ground state is destabilized in PMMA as seen by the prominent blue shifts in the absorption. Perhaps the static nature of the PMMA environment forces the molecules into higher energy conformations without the increase in the degrees of freedom that is offered by the solvents that is necessary to relieve any steric-based tension within the ground state. With the increase in the chromophore concentration, an increase in such steric-based tensions is to be expected, thus causing the ground state to become more destabilized and to undergo even more shifts toward the blue wing of the absorption spectrum. The net effect that these shifts have on energy transfer is to reduce the spectral overlap and thus $R_0$ (see Figure 1.2 and 1.3). The overall spectral shape remains unchanged, as does the fluorescence lifetime as shown in Figure 1.2 and 1.4. The resulting reduction in $R_0$ with concentration is taken into account in all theoretical analysis performed on the experimental data.
Figure 1.3. Concentration-dependent $R_0^6$ for $10^{-4}$ M - 50 mM Lumogen Red in PMMA (triangles), CHCl₃ (circles), and DMF (squares).

Figure 1.4. Concentration-dependent $\tau_f$ for $10^{-4}$ M - 50 mM Lumogen Red in PMMA.
1.3 The Spectroscopic Approach in Testing Predictions for Forster-Based Theories on Energy Migration

The time-resolved fluorescence for a $10^{-4}$ M – 50 mM Lumogen Red distributed homogeneously within either a PMMA matrix or liquid solvent was measured in order to monitor one of two quantities directly related to the rate of exciton diffusion. The anisotropy decay probes the first transfer step away from the initially excited molecule, whereas the fluorescence quenching experiments are sensitive to the total distance covered by the exciton within its lifetime [31, 74-85]. The two experiments both seek to measure the exciton diffusion constant, yet do so on different timescales.

Within the context of the time-resolved fluorescence quenching sensitization experiments, the donor’s decay in the presence of an acceptor is expressed by three terms corresponding to (1) the natural fluorescent lifetime of the donor ($\tau_{fl}$), (2) energy migration amongst the donors ($A$), and (3) exciton transfer between the donor and the doped acceptor ($B$) (see equation 1.7)

$$I_D(t) = I_D(0)\exp\left[-\frac{t}{\tau_{fl}} - At - B\sqrt{t}\right]$$

Forster’s original treatment of fluorescence quenching was formulated for the case in which energy is transferred between immobile donors and acceptors when the concentration of the acceptor greatly outweighs that of the donor. Under these conditions, energy migration is unable to occur and the $A$ term corresponding to energy migration drops out [86-90] (see equation 1.8)
A series of sensitization theorists followed after and improved upon the work of Forster. By taking into account the effect of energy migration on the observed quenching rates, the works of Yokota & Tanimoto [91] and Burshtein were the first to develop a sensitization theory which accounts for energy migration. Whereas Yokota & Tanimoto’s work covers the regime in which the quenching rate is diffusion-limited ($k_{DD}<k_{DA}$), Burshtein’s work covers the regime in which the quenching is trap limited ($k_{DD}>k_{DA}$) [86, 87, 89]. The former predicts a stretched exponential for the donor’s decay while the latter predicts an exponential one as reflected in the time-dependencies of the corresponding terms in equation 1.7. Joshi et al were able to confirm the correspondence between the exponentially of the measured decay and the dominating kinetic regimes [87]. However, neither theory was able to describe the dynamics corresponding to that of the other’s regime. Thus, a need arose for a more unified theory. Gosele’s [92] theory sought to do this by defining separate expressions for the two regimes accompanied by a set of conditions under which each expression should be used [88, 93]. Huber [94, 95] was able to successfully describe the intermediate regime, in which $k_{DD}=k_{DA}$ [86, 89, 96]. However, it was unable to describe the dynamics for the more extreme regimes covered by the previous theorists [96]. Finally, Loring [97] was successfully able to devise a theory that was able to cover all three regimes [86]. In reality, the coupling between the energy transfer and energy migration rates are too complex to be completely separated from each other as they are in equation 1.7 as

$$I_D(t) = I_D(0) \exp \left[ -\frac{t}{\tau_f} - B\sqrt{t} \right]$$  \hspace{1cm} \text{equation 1.8}
discussed by Seogjoo Jang [25]. However, assuming they are allows for the separation of the two processes into two distinct terms, with the two terms corresponding to the two extremities of energy transfer-dominated and energy migration-dominated kinetics.

In the context of the analysis performed here, Forster’s original expression for energy transfer is used as the $B$-term due to its precedent success in describing the kinetics of systems falling within the regime of energy-transfer dominated kinetics [69, 86-89, 96, 98-100].

\[ B = \frac{4}{3} \pi R_{DA}^3 C_A \frac{\pi}{\tau_F} \]  

*equation 1.9*

For the $A$-term corresponding to energy migration, Goesele’s original expression for the donor’s decay for the case of energy-migration dominated kinetics is used [69, 88, 98],

\[ A = 4\pi D \sigma_F C_A \]  

*equation 1.10*

where $\sigma_F$ is the acceptor’s quenching radius and is defined as being $D$-dependent as discussed by Jang (see *equation 1.11*)

\[ \sigma_F = 0.676 \left( \frac{R_{DA}^6}{D \tau_F} \right)^{1/4} \]  

*equation 1.11*

Experimental comparisons between time-resolved data taken on different time-scales through the anisotropy and fluorescence quenching sensitization experiments are compared with steady-state based predictions for $D$ to assess how appropriate FRET based energy migration theory is in describing sensitization data.
1.4 Conclusions

By using a test molecule that is resistant toward aggregation and whose photophysical properties favor large exciton diffusion constants, a detailed look at how well Forster theory can describe energy migration through an organic disordered system over a range of chromophore densities is presented within the following dissertation. Chapter 2 provides an overview of the technicalities involved in the experimental techniques used to carry out this assessment. In Chapter 3, an evaluation of Forster theory within a solid PMMA matrix is presented, with results discussed in terms of anomalous diffusion. Chapter 4 extends the evaluation of Forster theory to dynamic systems with disorder, in which a liquid solvent replaces the static PMMA matrix. The rapid sample averaging that occurs within a liquid solvent increases the probability for energy transfer within the excitons’ excited state lifetime, and thus an increase in the diffusion constant. In Chapter 5, temperature-dependent measurements of $D$ in PMMA are made to bring out the roles that rotational, translational, and energetic forms of disorder has on the expression of anomalous diffusion. Chapter 6 closes with suggestions for future work based on the manipulation of molecular translational and rotational coordinates within disordered systems to optimize energy migration within small molecule OPVs.

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Chapter 2: Experimental Methods

2.1 Introduction

Experiments performed to measure energy migration through Lumogen Red embedded within either a solid PMMA matrix or a liquid CHCl₃ or DMF solvent requires the use of a steady-state spectrometer, steady-state fluorimeter, and a time-resolved-based Ti-Sapphire laser set-up. A special mount was constructed for measurements taken on the concentrated liquid samples to provide an ultra-thin pathlength to prevent optical densities from rising above 0.2. Lumogen Red was purified to ensure high quality samples with photophysics reflecting the effects of energy migration instead of impurity-induced artifacts such as fluorescence quenching which can yield measurements that fall short of actual values for the diffusion constants. Although no quantum yield measurements were made in regards to Lumogen Red due to previous measurements reported in the literature, such measurements are described and included for the sake of completeness in regards to the general steady-state based determination of $R_0$, $D$, and $L_D$ for a given compound.

2.2 Purification of Lumogen Red

Lumogen Red (donated by BASF) was run through a silica-gel column to remove any impurities (including the previously reported impurities; carboxylic bisimide [1] and N-methyl-2-pyrrolidone [2]). 99% pure LR was obtained using a 90%/10% by volume mixture of dichloromethane and hexanes as the eluting solvent. Within the column, a
total of three bands are formed during the purification process. The bottom band is a very fluorescent red, the top band a very dark maroon, and the middle band a hot pink magenta. The bottom red band corresponding to the first band being eluted from the column is the purified Lumogen Red and can be collected from the solution eluted after the first show of pink. When running the column, it is important to keep the volume of the initial sample that is to be manually “injected” into the column at a minimum in order to achieve greater separation resolution, especially in delineating the boundary between the bottom red and middle magenta bands as this distinction can become quite difficult otherwise. In addition, the upper layer of sand was found to be quite instrumental in keeping the maroon band secluded to the top of the column. Purity was determined by NMR and LC-MS. NMR spectra were obtained on a Varian Inova 500 in deuterated-chloroform (see Figures 2.1 and 2.2). A LC-MS spectrum was obtained from the Mass Spectroscopy Facility located within the Chemical Sciences Building on UCR’s main campus. Rhodamine 700 (Exciton), Malachite Green (Exciton), PMMA [poly (methyl methacrylate)] (MW \(\approx 80,000-120,000\)g/mol, Aldrich), and all solvents (Fischer Scientific) were used as received without further purification.
Figure 2.1. NMR spectra for purified Lumogen Red in D-chloroform.
<table>
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<th>Multiplicity</th>
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<th>Peak Assignment</th>
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<td>doublet</td>
<td>24</td>
<td>a</td>
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<tr>
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<td>multiplet</td>
<td>4</td>
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<td>6.9</td>
<td>multiplet</td>
<td>8</td>
<td>c</td>
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<td>multiplet</td>
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<tr>
<td>8.2</td>
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**Figure 2.2.** NMR spectral peak assignments for Lumogen Red in D-chloroform
2.3 Sample Preparation: PMMA Films

Thin films were spin-coated at 300-3000 rpm from chloroform solutions with the appropriate PMMA : Lumogen Red : acceptor ratios to produce $10^{-4}$ M – 50 mM Lumogen Red thin films. An example calculation for a 10 mM film given a density of 1.19 g/mL for PMMA [3] is shown in equation 2.1:

$$\frac{(0.0100 \text{ g LR})(\frac{\text{mol LR}}{1079.4 \text{ g LR}})}{(1.19 \text{ g PMMA})(\frac{\text{mL PMMA}}{1.19 \text{ g PMMA}})(\frac{L}{10^3 \text{ mL}})} = \frac{1 \times 10^{-5} \text{ mol LR}}{0.001 \text{ L PMMA}} = 10 \text{ mM LR in PMMA}$$

equation 2.1

When doping the films with an acceptor, it was found that making a stock solution for the acceptor from which to add an equivalent volume to each of the PMMA-based stocks helped to ensure that the same acceptor concentration was embedded into each of the films. As an example, below is shown the calculations/measurements needed to dope the above 10 mM Lumogen Red film with 2 mM Rhodamine 700 (see equation 2.2).

$$\frac{(0.001 \text{ L R700})(2 \times 10^{-3} \frac{\text{mol L R700}}{L})}{(1.19 \text{ g PMMA})(\frac{\text{mL PMMA}}{1.19 \text{ g PMMA}})(\frac{L}{10^3 \text{ mL}})} = \frac{2 \times 10^{-6} \text{ mol R700}}{0.001 \text{ L PMMA}} = 2 \text{ mM R700 in PMMA}$$

equation 2.2

Notice that the volume of solvent used to make the PMMA solutions does not contribute to the final concentration of the films as it evaporates during the spin-coating process. To make the thinner, more highly concentrated films, ~5 mL solvent per mL PMMA was used with spin speeds ~1000-3000 rpm. For the thicker, less concentrated films, ~3 mL solvent per mL PMMA was used with spin speeds ~300-600 rpm. CHCl₃
was used as the processing solvent due to its excellent solubility properties and moderate vapor pressure.

All films were confirmed to possess peak optical densities $\leq 0.20$. Film thicknesses for the series of undoped samples used in the anisotropy experiments were measured on a Veeco DekTak 8 surface profilometer and found to be within the range of 260-4000 nm. These measurements, along with their measured absorptions and the measured extinction coefficient ($\varepsilon$) of 49900 +/- 400 M$^{-1}$cm$^{-1}$ for Lumogen Red in CHCl$_3$, were used to confirm the concentrations of the films using Beer’s Law (see equation 2.3):

$$Abs = \varepsilon \cdot b \cdot c$$  \hspace{1cm} \text{equation 2.3}

in which $Abs$ is the measured absorption of the sample, $b$ is the pathlength, or in this case, the thickness of the film (in cm), and $c$ is the concentration of the chromophore within the sample (in mol/L).

2.4 Sample Preparation: Solvent Solutions

Liquid solutions were made by combining the appropriate amount of dye into the appropriate volumes of either chloroform (CHCl$_3$) or dimethylformamide (DMF). Spectroscopic mounts with pathlengths on the order of 1 micron were custom-made in order to ensure peak optical densities below 0.2. Reverse-phase photolithography [4] was used to deposit a gold barrier onto a glass microscope slide to serve as a mount whose pathlength is dictated by the thickness of the deposited metal. To do this, photoresist was spin-coated onto the glass slide and then exposed to UV radiation with the aid of a mask.
via a Karl Suss Microtec MA6 mask aligner so as to outline within the resist the shape that would eventually become the metallic barrier of the mount. Resist 5214 was exposed to 15 seconds of radiation for the creation of the 0.4 µm mount while the thicker resist 9245 was exposed to 30 seconds of radiation for the 1.4 µm mount.

The exposed spaces within the resist were dissolved so that the gold side walls of the mount could be deposited via physical vapor deposition. A thin layer of titanium (~200 Angstroms) followed by a thicker layer of gold (1 µm) was deposited onto the developed areas of the slide with a Temescal BJD-1800 E-beam evaporator. The titanium layer was needed to “wet” the surface of the glass slide so that the gold layer could attach to a surface. Finally, the remaining photoresist was dissolved away, leaving an open area for the sample storage space surrounded by a 1 µm thick wall of evaporated gold (see Figure 2.3).

A Veeco DekTak 8 surface profilometer was used to confirm the height of the deposited metal barrier. All photolithography work was performed at UCR’s Center for Nanoscale Science and Engineering under the guidance of Dexter Humphrey. Spring-loaded binder clips were used to seal a second glass slide on top of the gold-coated mount to prevent evaporation of the solvent during measurements. Mounts were tested to be safe from evaporation effects throughout the time required to make the time-resolved measurements by measuring the change in absorption with time (see Figure 2.4).
Figure 2.3. Diagram of photolithographic-constructed mount used to contain the liquid samples during steady-state and time-resolved measurements. Note that an open storage ring was constructed around the main storage box to allow for solvent overflow from the box in the event that it is filled beyond capacity.

Figure 2.4. Absorption of 150 mM Lumogen Red doped with 2 mM Rhodamine 700 in CHCl₃ taken every 5 minutes for 40 minutes to ensure resistance towards evaporation within the homemade sample mount.
2.5 Steady-State Spectroscopy

Steady-state absorption spectra were taken on a Cary-Bio50 spectrometer except for the temperature-dependent measurements, in which case an Ocean Optics SD2000 absorption spectrometer was used so that room could be made within the sample holding area for the cryostat needed to encase the samples throughout the course of the experiment. Steady-state fluorescence spectra were obtained on a Horiba Jobin Yvon-Spex Fluorolog-3 fluorimeter set to front face detection. With an increment scale set to 0.5 nm and an integration scale set to 0.5 sec, the fluorimeter was found to yield spectra with high quality resolution. Fluorescence spectra were found to be independent of excitation wavelength for the case of 400 nm and 550 nm excitation in accordance with Kasha’s Law [5].

2.6 Steady-State Determination of $R_0$

To determine steady-state values for $R_0$, a simplified version of the Forster expression was used:

$$R_0 = 0.211 \left( \kappa^{-2} \eta^{-4} \phi_n J \right)^{1/6}$$  \hspace{1cm} \text{equation 2.4}

in which

$$J = \int F_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda$$  \hspace{1cm} \text{equation 2.5}

where $J$ (M$^{-1}$ cm$^{-1}$ nm$^4$) is determined with the aid of a computer spreadsheet and graphing program such as Origin. $F_D(\lambda)$ is the fluorescence spectrum of the donor, normalized so that the total integration of the spectra is equal to one. $\epsilon_A(\lambda)$ is the
absorption of the acceptor, modulated so that the peak absorption is equivalent to its extinction coefficient. The data corresponding to these two spectra are placed in neighboring columns so that their wavelengths correlate with each other. In order to make this process as simple as possible, it is imperative that the absorption and fluorescence spectra be collected with identical increment parameters. A third column is set to \( \lambda^4 \) and corresponds to the entire wavelength region from which the absorption and fluorescence was collected. Finally, the product of all three columns, \( F_D(\lambda) \), \( \varepsilon_A(\lambda) \), and \( \lambda^4 \), are set into a fourth column corresponding to \( J \). This final column is plotted versus \( \lambda \) and integrated to determine \( J \). The values extracted for \( R_0 \) using this methodology are done so in terms of Angstroms, thus mandating the conversion to nm for experimental analysis.

### 2.7 Fluorescence Quantum Yields

Fluorescence quantum yields [6] can be measured via relatively simple steady-state absorption and fluorescence techniques with the utilization of two standards in conjunction with the following relation [7] (see equation 2.6):

\[
\phi_x = \phi_{ST} \left( \frac{\text{grad}_x}{\text{grad}_{ST}} \right) \left( \frac{n^2_x}{n^2_{ST}} \right)
\]

\[\text{equation 2.6}\]

where \( \phi_x \) is the quantum yield of the unknown and \( \phi_{ST} \) is the quantum yield of the standard. \( \text{grad} \) is the slope/gradient extracted from a plot of the absorption versus the integrated fluorescence for a series of solutions corresponding to either the standard
(grad\textsubscript{ST}) or the unknown (grad\textsubscript{x}), while \( n \) is the refractive index of the media in which the gradient is measured.

There are some general considerations that must be made to avoid certain instrumental errors in measurement that can lead to erroneous results. When performing the experiments, the slits on the spectrometer and fluorimeter must be equivalent. The two standards must be cross-calibrated prior to the calculation of the unknown quantum yields to confirm the accuracy of the method. In choosing appropriate standards, it is important to find ones whose fluorescence is in the same wavelength range as that of the unknown. All fluorescence data must be collected within the same wavelength range, along with the same integration and increment settings. Cresyl violet (\( \Phi = 0.54 \) in methanol [8]), Lumogen Red (\( \Phi = 0.96 \) in chloroform [9]), thiophene (\( \Phi = 0.06 \) in methylene chloride [10]), and anthracene (\( \Phi = 0.27 \) in ethanol [8]) have all been successfully used as standards using these aforementioned guidelines. When working with anthracene, it is important to ensure that all solutions have been sonicated and filtered prior to the undertaking of any spectroscopic measurements due to solubility issues. All samples must be made fresh on the day of measurement due to possible photo-instability and oxidative degradation effects, as well as daily variations associated with the light source within the spectroscopic instruments.

2.8 Time-Resolved Fluorescence Experiments

Time-resolved experiments were performed on a regeneratively amplified Ti-Sapphire laser generating 120 fs pulses and operating at a 40 kHz repetition rate with its
fundamental wavelength centered at 800 nm (see Figure 2.5). The Ti-Sapphire oscillator is pumped by a Millennia Diode Laser. The beam is fed into a Spitfire Regenerative Amplifier pumped by a Merlin laser to increase the power of the 800 nm pulses. The 800 nm beam was focused onto an Al₂O₃ sapphire crystal plate from which a continuum was generated. A 10 nm bandwidth interference filter centered at 550 nm was used to isolate 550 nm from the continuum for excitation. Laser excitation powers were tuned to the range of 0.5 to 1.5 µW using neutral density filters to prevent the streak camera from becoming saturated at early collection times. Samples were encased within an evacuated cryostat. For the solvent-based experiments, a homemade sample mount replaced the cryostat’s position on the laser table and decays were collected under atmospheric conditions. Measurements on films taken with and without vacuum showed no change within the observed decays, thus ensuring both solvent and film data to be free from any photo-oxidative effects [11].

The diameter of the laser spot incident on the sample was ~130 µm. The sample was positioned 10 cm from the streak camera collection lens and then positioned so as to maximize the collected signal and to reduce the degree of scattered incident light from entering the detector. Polarizers were used to isolate the fluorescence signal polarized either at 0°, 90°, or 54.7° relative to the P-polarized incident beam (“P-polarization” corresponding to a polarization that is parallel to the laser table). Parallel (0°) and perpendicular (90°) polarizations were collected in the anisotropy experiments to monitor the behavior of the polarization of light initially absorbed by the system. 54.7° polarized light was detected for the sensitization experiments to extract decays free from molecular
Figure 2.5. Laser set-up for time-resolved anisotropy and sensitization experiments.
rotational effects [5]. To set the correct polarization, the polarizer is first set to the point at which there is maximum extinction of the incident light. This is assumed to be the perpendicular setting. Subtracting 90° from this value yields the setting for light polarized parallel to the incident beam, while subtracting 35° yields the setting for 54.7° magic angle detection. A Schott glass OG570 cutoff filter was placed before the streak camera’s entrance lens to minimize the detected scatter from the 550 nm incident beam. Fluorescence was detected and displayed onto a PC using a Hamamatsu C4337 streak camera with 2 nm spectral resolution and 15 ps time resolution.

2.9 Time-Resolved Fluorescence Anisotropy Experiments

Fluorescence decays polarized parallel $I_{\parallel}(t)$ and perpendicular $I_{\perp}(t)$ to the excitation beam were collected by the rotation of the thin film polarizer placed before the entrance slit of the streak camera monochromator. Raw $I_{\parallel}(t)$ and $I_{\perp}(t)$ decays collected between the wavelengths of 575-700 nm were smoothed with 5-point adjacent averaging. The background noise, defined as the average signal detected prior to the laser pulse, was subtracted from the data. Since the excitation pulse could be considered a delta function with respect to the scale of the decay, deconvolution of the retrieved decays from the instrument response function was deemed unnecessary [12]. The time axis were adjusted by setting time zero, $r_0$, to the point in the decay at which $r(t) = 0.40$ prior to extracting and fitting the anisotropy decays through the method of front-edge matching [13] via the function (see equation 2.7):
\[ r(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)} = r_0 \exp\left[-\sqrt{\frac{t}{\tau_{pol}}}\right] + y_0 \]  

\textbf{equation 2.7}

2.10 \ Time-Resolved Fluorescence Sensitization Experiments

Retrieved signals were integrated in MatLab between wavelengths so as to prevent the contribution of the acceptor’s fluorescence from contaminating the signal coming from Lumogen Red. In the case of the acceptor Rhodamine 700, this range was determined to be between 570 and 620 nm. For the acceptor Malachite Green, the range was 570 – 605 nm. All decays were collected at the magic angle of 54.7°. In the absence of an acceptor, the donor fluorescence decays by a single exponential (see \textbf{equation 2.8})

\[ I_D(t) = I_D(0) \exp\left(-\frac{t}{\tau_{fl}}\right) \]  

\textbf{equation 2.8}

where \( \tau_{fl} \) is the donor’s fluorescence lifetime. Once an acceptor is introduced into the system, the donor decay becomes multi-exponential, taking on the following general form [14] (see \textbf{equation 2.9}):

\[ I_D(t) = I_D(0)\exp\left[-\frac{t}{\tau_{fl}} - At - B\sqrt{t}\right] \]  

\textbf{equation 2.9}

in which \( A \) represents the term for exciton migration amongst donors and \( B \) represents the term for energy transfer between two different molecules. Raw data was smoothed with 5-point adjacent averaging, the background noise subtracted, and peaks normalized to 1.0 prior to dividing the two decay curves to isolate the portion of the decay corresponding to the \( A \) term for exciton diffusion [15] (see \textbf{equation 2.10})
\[
\frac{I(t)[C_{LR}]}{I(t)[10^{-4} M C_{LR}]} = \frac{\exp[-k_r t - At - B\sqrt{t}]}{\exp[-k_r t - B\sqrt{t}]} = \exp[-At]
\]

equation 2.10

where \( A \) is related to the diffusion constant \( D \) through the following relation [16] (see equation 2.11)

\[
A = 4\pi D \sigma \sigma_F C_A
\]

equation 2.11

The acceptor’s quenching radius, \( \sigma_F \), is a special parameter of interest due to the various theoretical treatments available that are associated with it. In the most basic approach, \( \sigma_F \) is taken to be a constant that is equivalent to \( R_{DA} \). This assumes that once an exciton approaches a distance from the acceptor that is on the order of \( R_{DA} \), the rate of energy transfer is so much greater than that for energy diffusion (\( k_{DA} >> k_{DD} \)), that the exciton becomes effectively captured and the fluorescence quenched. A more complex approach recognizes that the magnitude of \( \sigma_F \) actually depends on the magnitude of the diffusion constant, with slower excitons being more likely to become quenched by an acceptor than their faster moving counterparts [16]. In the latter situation, there is not enough time for such an energy transfer event to occur in the vicinity of \( R_{DA} \) due to the rapid movement of the donor’s exciton. Both approaches are dealt with here.

2.11 Temperature-Dependent Studies

Temperature-dependent studies were carried out with the use of a Janis St-100 cryostat set-up to a liquid nitrogen dewar reserve. The temperature was monitored and raised by a Lakeshore 321 Temperature Controller connected to the cryostat’s thermocouple. The temperature was lowered by flowing liquid \( N_2 \) through a cold finger
upon which the sample is attached with the aid of a standard hood’s vacuum and air outlets (see Figure 2.6).

![Diagram of cryostat set-up]

**Figure 2.6.** Cryostat set-up for temperature-dependency experiments.

**REFERENCES**


Chapter 3: On the Concentration Dependence of the Time-Resolved Anisotropy and Fluorescence Quenching of Luomgen Red in PMMA

3.1 Introduction

Electronic energy transfer plays an important role in many types of organic electronic devices, including light-emitting diodes [1], photovoltaics [2, 3], and chemical sensors [4]. Forster-type theories on exciton diffusion provide a way to calculate diffusion constants and lengths, but their applicability to amorphous polymer systems has still yet to be evaluated. In this chapter, the perylene diimide dye Lumogen Red encased within a poly(methyl methacrylate) host matrix is used to test such theories on exciton migration for Lumogen Red concentrations ranging from $10^{-4}$ M to 50 mM. Two experimental quantities are measured. The time-resolved anisotropy experiments provides estimates for the diffusion constant based on the transfer of energy from the initially photoexcited molecule to one of its nearby neighbors. The time-resolved quenching experiments provides estimates based on the entire lifetime of the exciton via the use of an acceptor. In regards to the anisotropy measurements, it is found that theory accurately predicts both the $C_{LR}^{-2}$ concentration dependence of the polarization decay time $\tau_{pol}$, as well as its magnitude to within 30%. In regards to the sensitization experiments, it is found that theory accurately predicts the correct $C_{LR}^{\alpha}$ concentration dependence on quenching, where $\alpha$ ranges between 1.00 and 1.33. On the basis of the theory that correctly describes the anisotropy data, the exciton diffusion constant is projected to be on the order of 4-9 nm$^2$/ns for the case of 10 mM Lumogen Red in
PMMA. However, based on the quenching data, the measured diffusion constant is found to be on the order of 0.32-1.20 nm$^2$/ns. Thus, theory quantitatively describes the early time anisotropy data but fails to quantitatively describe the quenching experiments that are sensitive to motion on longer time scales. Therefore, the data are consistent with the idea that translational, orientational and energetic disorder leads to a time-dependent diffusion constant, suggesting that simple diffusion models based on a time-independent diffusion constant cannot accurately describe exciton motion within disordered systems.

3.2 Time-Resolved Anisotropy in Lumogen Red - Doped PMMA Films

After a linearly polarized laser pulse excites a subset of Lumogen Red molecules embedded within a PMMA host, they will undergo electronic energy transfer toward neighboring molecular sites. In general, molecules absorb light that is polarized parallel to their absorption dipole moment, emit light polarized parallel to their fluorescence dipole moment, and exchange excited-state energy most effectively with each other when the fluorescence dipole moment of the donor is both parallel and in-line with that of the acceptor’s absorption dipole moment. The degree to which the emitted light retains the polarization of the light that was absorbed is termed the fluorescence anisotropy. The loss of polarization memory in the sample due to the initial transfer of energy between two molecules is reflected in the anisotropy decay [5].

A molecule’s initial fluorescence anisotropy can decay due to one or more of three possible depolarization mechanisms that takes place during the molecule’s excited state lifetime [6]: (1) a difference in the absorbing and emitting dipoles within the
molecule itself, (2) rotational diffusion of the molecule while in its excited state, and (3) Forster resonance energy transfer (FRET) between two molecules that differ in their relative rotational orientations. For the test molecule, Lumogen Red, the dipoles corresponding to the absorption and emission are oriented parallel to each other [7]. In addition, Lumogen Red is embedded within a static PMMA matrix in which rotational movements are prohibited. Therefore, depolarization due to energy transfer is the only mechanism whose effects are expected to exert any influence on the measured anisotropy decays.

The anisotropy is measured by collecting Lumogen Red’s fluorescence that is polarized parallel ($I(t)_{\text{par}}$) and perpendicular ($I(t)_{\text{per}}$) to the incident light. The following relation between the two polarizations is then used to determine the anisotropy decay, $r(t)$ (see equation 3.1)

$$r(t) = \frac{I(t)_{\text{par}} - I(t)_{\text{per}}}{I(t)_{\text{par}} + 2 I(t)_{\text{per}}} = \frac{\text{excess light polarized parallel to the incident light}}{\text{total fluorescence emitted}}$$

**equation 3.1**

According to the work of Gouchanour, Anderson & Fayer [5, 8], the anisotropy decay, $r(t)$, is directly proportional to $G_S(t)$, the Green’s function describing the probability that an exciton will remain at its point of origin with time (see equation 3.2),

$$G_s(t) = r(t) = r_0 \exp \left[ -\frac{4}{3} \frac{\pi}{\sqrt[3]{\lambda}} I(\frac{1}{2}) R_0^3 C_{LR} \sqrt{\frac{t}{\tau_{fl}}} \right]$$

**equation 3.2**

in which $I(x)$ is the gamma function (and $I(1/2) = 1.7725$), $\gamma = 0.8452$, and $\lambda$ is a constant which is assigned the value of 2 for the case of electronic energy transfer.
between two like molecules and $\lambda=1$ for transfer between two dissimilar molecules [9].

The interchromophore transfer time, $\tau_{\text{hop}}$, can be estimated by measuring the fluorescence anisotropy decay, $\tau_{\text{pol}}$, which takes the form of a stretched exponential due to the random distribution of acceptor molecules surrounding the initially excited Lumogen Red molecule (see equation 3.3)

$$r(t) = r_0 \exp\left[-\sqrt{\frac{t}{\tau_{\text{pol}}}}\right] + y_0$$

**equation 3.3**

The technique of front-edge matching [10] is applied to extract the measured values for $\tau_{\text{pol}}$ from the experimental decays. This technique first requires setting the time zero ($t = 0 \text{ ns}$) point in the decay at which $r(t) = 0.40$, which is the theoretically predicted value for fluorescence that emanates from a collection of randomly oriented molecules possessing a single electronic state with a dipole-allowed transition [6]. This is also the value found in the literature for perylene diimides similar in structure to Lumogen Red [7].

The decays are fitted by setting $r_0 = 0.40$ in equation 3.3 while allowing for the existence of a small residual offset for $y_0$. Experimentally, this offset is found to vary between 0.01 and 0.03. The offset takes into account the fact that at large times, $r(t)$ may not decay exactly to 0 due to slight variations in alignment and/or laser power between the parallel and perpendicular measurements. Either that or it may be because the anisotropy may not decay to 0 within an inhomogenously broadened system due to the trapping of the excitons within low energy sites. The data was also fitted by setting $y_0$ to 0 while allowing for variations in $r_0$. Doing so results in experimental values ranging
between 0.36 and 0.43 for $r_0$. Decays for various Lumogen Red concentrations are shown in Figure 3.1 along with fits obtained using equation 3.3 with $y_0$ set to 0. As the chromophore concentration is increased, the decay becomes more rapid, and in all cases both fitting strategies do a reasonably good job of describing the dynamics.

**Figure 3.1.** Concentration-dependent anisotropy decays for $10^{-4}$ M - 50 mM Lumogen Red in PMMA: $10^{-4}$ M LR (control), 1.24 mM LR, $\tau_{pol} = 26.41$ ns (dashed line), and 4.45 mM LR, $\tau_{pol} = 2.38$ ns (dotted line) for fits based on the function, $r(t) = r_0 \exp(-t/\tau_{pol})^{1/2}$.

In order to connect the experimentally measured $r(t)$ decays to $R_0$, equations 3.2 and 3.3 are combined through their relation to $r(t)$ [11] (see equation 3.4)

$$\tau_{pol} = 0.0508 \frac{\tau_d}{R_0^6 C_{LR}^2}$$

**equation 3.4**

Equation 3.4 indicates that the anisotropy decay time, $\tau_{pol}$, is theoretically proportional to $C_{LR}^{-2}$. Since $R_0^6$ also depends on $C_{LR}$, it is necessary to plot the product $\tau_{pol} R_0^6$ versus
$C_{LR}$ in order to see $\tau_{\text{pol}}$’s true experimental concentration dependence. When the decays are fitted by keeping $r_0$ set to 0.40, a log-log plot of these two quantities yield a slope of -1.54 $\pm$ 0.12 whereas a slope of -1.90 $\pm$ 0.11 is obtained when setting $y_0$ to 0 during fitting (see Figure 3.2). It turns out that this discrepancy in the slope is an artifact arising from the fact that equation 3.3 does not do a good job of fitting the 50 mM anisotropy decay when $r_0$ is set to 0.40. The decay is very fast at this concentration and comes close to coinciding with the instrument response function. Thus, the identification of the time zero point and therefore the proper point at which $r(t) = 0.40$ is hard to determine with exact certainty. Anisotropy measurements on films above 50 mM thus require the use of a femtosecond transient anisotropy set-up [12]. When the 50 mM point is excluded from the fits, the data yields a slope of -2.11 $\pm$ 0.16 when $y_0 = 0$ and -1.91 $\pm$ 0.17 when $r_0 = 0.40$. (see Figure 3.3), thus indicating that the theoretical slope of -2 can be successfully obtained irrespective of the fitting strategy adopted in agreement with previous reports pertaining to organic dyes embedded in polymer and glass systems [13, 14].

The next question of concern is whether equation 3.4 quantitatively predicts the correct value for $\tau_{\text{pol}}$ for a given concentration of dye. By assuming a $C_{LR}^{-2}$ concentration dependence, a plot of the quantity $\tau_{\text{pol}} R_0^6$ versus $C_{LR}^{-2}$ can be made to see how well the experimental data matches with what is expected by theoretical predictions (see equation 3.4). Theoretically, a slope of 0.29 should be obtained given a fluorescence lifetime of 5.7 ns. A slope of 0.18 $\pm$ 0.01 is found when using the anisotropy decays obtained by $y_0$ to 0 during fitting whereas a slope of 0.26 $\pm$ 0.02 is found when using the decay setting $r_0$ to 0.4 (see Figure 3.4). If anything, it appears that theory slightly
underestimates the decrease in $\tau_{pol}$ as $C_{LR}$ is increased, thus suggesting the presence of diffusion constants that are slightly faster than those predicted by equation 3.4. To summarize, the Lumogen Red anisotropy data show that not only does the simple theory put forth by Gouchanour, Anderson & Fayer provides a good qualitative description of initial electronic energy transfer dynamics, but that it does so quantitatively as well, with theoretical predictions for $\tau_{pol}$ differing from those measured by only 10-30%.

The experiments were carried out twice with the use of two different acceptors to ensure the results to be free from any sort of specific donor-acceptor effects. In addition, two different concentrations were used, (2 mM for Rhodamine 700 and 4 mM for Malachite Green) to ensure that the presence of the acceptor itself does not interfere with the inherent diffusion of the donor’s excited state energy. The large overlap means that both acceptor molecules are able to quench Lumogen Red’s fluorescence. Given a constant acceptor concentration as the concentration of Lumogen Red is increased, the fluorescence decay becomes more rapid due to the quenching of the fluorescence facilitated by exciton diffusion toward the acceptors (see Figure 3.5). Also consistent with expectations [17, 18], the quenching of the donor was found to be accompanied by a rapid growing in of the acceptor’s fluorescence.
Figure 3.2a. Concentration-dependent logarithmic anisotropy results for $10^{-4}$ M - 50 mM Lumogen Red in PMMA. The experimental slope is found to be -1.54 +/- 0.12 for fits based on the function, $r(t) = 0.40 \exp\left(-\left(t/\tau_{pol}\right)^{1/2}\right) + y_0$.

Figure 3.2b. Concentration-dependent logarithmic anisotropy results for $10^{-4}$ M - 50 mM Lumogen Red in PMMA. The experimental slope is found to be -1.90 +/- 0.11 for fits based on the function, $r(t) = r_0 \exp\left(-\left(t/\tau_{pol}\right)^{1/2}\right)$. 
Figure 3.3a. Concentration-dependent logarithmic anisotropy results for $10^{-4}$ M - 50 mM Lumogen Red in PMMA with the 50 mM point excluded from the fit. The experimental slope is found to be $-1.91 \pm 0.17$ for fits based on the function, $r(t) = 0.40 \exp\left(-t/\tau_{pol}\right)^{1/2} + y_0$.

Figure 3.3b. Concentration-dependent logarithmic anisotropy results for $10^{-4}$ M - 50 mM Lumogen Red in PMMA with the 50 mM point excluded from the fit. The experimental slope is found to be $-2.11 \pm 0.16$ for fits based on the function, $r(t) = r_0 \exp\left(-t/\tau_{pol}\right)^{1/2}$.
Figure 3.4a. Concentration-dependent linear anisotropy results for $10^{-4}$ M - 50 mM Lumogen Red in PMMA. The experimental slope is found to be $0.18 \pm 0.01$ for fits based on the function, $r(t) = 0.40 \exp(-(t/\tau_{pol})^{1/2} + y_0$.

![Graph](image1)

Figure 3.4b. Concentration-dependent linear anisotropy results for $10^{-4}$ M - 50 mM Lumogen Red in PMMA. The experimental slope is found to be $0.26 \pm 0.02$ for fits based on the function, $r(t) = r_0 \exp(-(t/\tau_{pol})^{1/2}$.

![Graph](image2)
3.3 Time-Resolved Fluorescence Quenching in Lumogen Red Mixed with Rhodamine 700 and Malachite Green

At this point, it should be emphasized that the anisotropy decay is only able to measure $k_{\text{FRET}}$ based on the initial energy transfer step away from the initially excited molecule [5]. In concentrated systems, many subsequent steps may occur during the molecule’s excited state lifetime. To measure the dynamics for energy migration on longer time-scales, fluorescence sensitization experiments are used instead [15, 16]. The organic dyes Rhodamine 700 and Malachite Green were used as acceptors since both possess absorptions that overlap well with that of Lumogen Red’s fluorescence (see Figure 3.6).

**Figure 3.5.** Concentration - dependent fluorescence quenching for $10^{-4}$ M - 50 mM Lumogen Red in PMMA by 2 mM Rhodamine 700: $10^{-4}$ M; 2.39 ns (solid line), 10 mM; 1.74 ns (dashed line), and 50 mM; 1.01 ns (dotted line). Similar trends are seen when 4 mM Malachite Green is used as the acceptor.
Although a good overlap between the absorption of the acceptor and the fluorescence of the donor is necessary for FRET to occur, it is not the only requirement for choosing an appropriate acceptor. What follows is a summary of acceptors considered based on their suitable absorption spectral overlaps with Lumogen Red’s fluorescence, along with reasons as to why they were not able to be used in order to serve as examples as to the sorts of road blocks one may encounter when adopting one. The acceptors Cresyl Violet and DTTCI were found to possess low solubilities within the processing solvent, CHCl₃. Other solvents were considered for processing, but showed solubility issues with either the Lumogen Red, Rhodamine 700, or PMMA. The fluorescence from Methylene Blue and Styrl 6 overlapped too much with that of
Lumogen Red, thus making the isolation of Lumogen Red’s fluorescence signal from that of the acceptor too difficult. HTTCI and Cryptocyanine were found to be too unstable under laser exposure for the length of time required to make the measurements. Such degradation of HITCI acting as an acceptor for Lumogen Red in PMMA has been noted previously in the work of Clendinen et al [19]. Absorption spectra taken before and after the experiments were found to have significant decreases in their optical densities, a diagnostic sign that the compounds were photobleached by the laser.

Other acceptors were considered that are able to quench the fluorescence of the donor by an electron-transfer mechanism instead of the energy-transfer mechanism upon which the previously discussed acceptors are based. For these acceptors, it is the appropriate overlap of the HOMO and LUMO frontier orbitals that must be considered versus the overlap of the absorption and fluorescence electromagnetic spectrum for the latter. Upon photoexcitation of a donor, an electron is moved from the donor’s HOMO to its LUMO, thus leaving a hole in the HOMO that can (1) be filled by an acceptor’s HOMO provided this HOMO lies between the HOMO and LUMO of the donor, or (2) a ground state electron in the HOMO of the acceptor is transferred to the hole formed in the donor’s HOMO upon photoexcitation (see Figure 3.7). The mechanism requires the use of an electron acceptor in the former case and an electron donor in the latter. PCBM (HOMO = -6.1 eV [20], LUMO = -3.7 eV [20, 21]) was tested as an electron acceptor while 1,8-diaminonaphthalene and 9-methylcarbazole (HOMO = -5.3 eV, LUMO = -0.5 eV [22]) were tested as electron donors. However, due to Lumogen Red’s relatively low HOMO (-6.1 eV) [23] and LUMO (-4 eV based on its band gap and HOMO), none of
these charge-transfer alternatives were found to be successful in quenching Lumogen Red’s fluorescence.

![Diagram of charge transfer mechanisms]

**Figure 3.7.** Possible charge-transfer mechanisms behind fluorescence quenching.

In order to simplify the data analysis in regards to the sensitization experiments, a relatively simple analytical expression was chosen that divides the quenching into two different terms and minimizes the number of free parameters. In the absence of a quencher, the fluorescence decay of the donor is expressed as a single exponential, with the decay time corresponding to the fluorescence lifetime, $\tau_f$ (see equation 3.5):

$$I_D(t) = I_D(0) \exp\left(-\frac{t}{\tau_f}\right)$$

**equation 3.5**
When an acceptor is introduced into the system, the donor decay becomes multi-exponential [24] (see equations 3.6-8):

\[ I_D(t) = I_D(0) \exp \left[ -\frac{t}{\tau_{fl}} - At - B \sqrt{t} \right] \]  
\text{equation 3.6}

\[ A = 4\pi D \sigma_F C_A \]  
\text{equation 3.7}

\[ B = \frac{4}{3} \pi R_{DA}^3 C_A \sqrt{\frac{\pi}{\tau_{fl}}} \]  
\text{equation 3.8}

in which the \( A \) term represents the contribution due to energy migration amongst the donors while the \( B \) term represents the single step transfer of energy from donor to acceptor. \( D \) is the exciton’s diffusion constant, \( \sigma_F \) is the quenching radius of the acceptor, \( C_A \) is the concentration of the acceptor (in molecules/nm\(^3\)), \( R_{DA} \) is the donor to acceptor Forster radius, and \( \tau_{fl} \) is the fluorescence lifetime of the donor. The \( A \) term depends on \( D \) and through it, the donor concentration \( C_D \) (see equation 3.9)

\[ D = \eta \left( \frac{4\pi C_D}{3} \right)^2 \frac{R_0^6}{\tau_{fl}} \]  
\text{equation 3.9}

The \( B \) term is independent of the donor concentration and at low donor concentrations (i.e. \( C_D = 10^{-4} \) M), should dominate the behavior of \( I_D(t) \). By fixing \( C_A \) and then dividing the variable \( C_D \) decays by the \( 10^{-4} \) M decay, the isolation of \( A \) can be achieved [25] (see equation 3.10)

\[ \frac{I(t)[C_{LR}]}{I(t)[10^{-4} \text{ M } C_{LR}]} = \frac{\exp[-k_{fl}t - At - B\sqrt{t}]}{\exp[-k_{fl}t - B\sqrt{t}]} = \exp[-At] \]  
\text{equation 3.10}
In other words, by ratioing the variable $C_D$ decays by the intrinsic decay at which $D$ is negligible, the $A$ term that reflects exciton diffusion can be isolated [25]. Figure 3.8 shows the ratioed decays for different Lumogen Red concentrations given a fixed acceptor concentration. All resulting decays can be fit reasonably well using a single exponential. In this way, $A$ is obtained as a function of $C_{LR}$.

### 3.4 Dependence of $A$ Term on Lumogen Red Concentration

In order to compare the experimental dependence of $A$ on $C_{LR}$ to theoretical predictions, the two ways in which $\sigma_F$ depends on $C_{LR}$ must be considered. By assuming $\sigma_F$ to be constant, $D$ depends on $C_{LR}$ with the $4/3$ power law given by Forster’s expression for the diffusion constant (see equation 3.9). More sophisticated theories take into account the fact that $\sigma_F$ depends on $D$ and thus $C_{LR}$. Following the treatment of Jang et al [26, 27] (see equation 3.11),

$$\sigma_F = R_{pA} \frac{\Gamma(0.75)}{2\Gamma(1.75)} \left( \frac{R_{DA}^2}{\tau_\beta D} \right)^{1/4} = 0.676 \left( \frac{R_{DA}^6}{\tau_\beta D} \right)^{1/4} \quad \text{equation 3.11}$$

Using this expression for $\sigma_F$ in equation 3.7, a $A \propto C_D^{1.00}$ dependency is predicted rather than the $A \propto C_D^{1.33}$ dependency obtained when $\sigma_F = R_{DA}$. Figures 3.9 and 3.10 shows a log-log plot of the $A$ term, scaled by the concentration-dependent $R_0^6$, versus $C_{LR}$ to
Figure 3.8a. Concentration-dependent increase in $A$, the energy migration term in the donor’s fluorescence for $10^{-4}$ M - 50 mM Lumogen Red in PMMA quenched by 2 mM Rhodamine 700: 1 mM; $A^{-1} = 262.23$ ns (solid line), 5 mM; $A^{-1} = 18.18$ ns (dashed line), and 20 mM; $A^{-1} = 4.45$ ns (dotted).

Figure 3.8b. Concentration-dependent increase in $A$, the energy migration term in the donor’s fluorescence for $10^{-4}$ M - 50 mM Lumogen Red in PMMA quenched by 4 mM Malachite Green: 1 mM; $A^{-1} = 109.73$ ns (solid line), 5 mM; $A^{-1} = 9.69$ ns (dashed line), and 20 mM; $A^{-1} = 3.62$ ns (dotted).
determine the experimental $\alpha$. The plot yields a power law dependence of $1.2 \pm 0.2$ for Rhodamine 700 and $1.1 \pm 0.2$ for Malachite Green. It is reassuring that the values for both acceptors are similar, despite the fact that these molecules have different chemical structures. The data is more consistent with the $A \propto C_D^{1.33}$ dependence as determined by previous studies performed over a limited donor concentration range in both liquid solutions [28] and doped polymers [29]. The error in the slope is sufficiently large enough to make it difficult to conclude which dependence is actually occurring. Nevertheless, it can be said that the simple theory behind equations 3.7 and 3.9 does predict the correct qualitative behavior of the fluorescence quenching as a function of $C_D$.

3.5 Values for $D$ Calculated Using Various Theories

Equations 3.2 and 3.4 do a good job at describing not only the qualitative trends for $\tau_{pol}$ with regards to chromophore concentration, but that they do so in a quantitative one as well. In a similar vein, we can ask whether or not the theoretical approach embodied in equations 3.6 – 3.8 quantitatively predicts the decay rate of the quenched donor, $I_D(t)$ in addition to its ability to qualitatively predict the decay’s concentration dependency. In the following discussion, only the theoretical case for which 10 mM Lumogen Red is quenched by 2 mM Rhodamine 700 is considered.

Based on steady-state data, $D$ ranges between 4.89 nm$^2$/ns (when $\eta = 0.32$) to 8.56 nm$^2$/ns (when $\eta = 0.56$) given a $R_0$ of 4.77 nm. Theoretical estimates for $D$ based on the time-resolved anisotropy data assumes that there exists an average hopping time, $\tau_{hop}$,
Figure 3.9a. Concentration-dependent logarithmic sensitization results for $10^{-4}$ M - 50 mM Lumogen Red in PMMA quenched by 2 mM Rhodamine 700 assuming $\sigma_F = R_{DA}$. The experimental slope is found to be $1.24 \pm 0.17$ with an intercept at $-2.37 \pm 0.38$. Theoretically, a slope of 1.33 with an intercept between -1.48 and -1.23 is expected.

Figure 3.9b. Concentration-dependent logarithmic sensitization results for $10^{-4}$ M - 50 mM Lumogen Red in PMMA quenched by 4 mM Malachite Green assuming $\sigma_F = R_{DA}$. The experimental slope is found to be $1.09 \pm 0.15$ with an intercept at $-2.45 \pm 0.35$. Theoretically, a slope of 1.33 with an intercept between -1.18 and -0.93 is expected.
Figure 3.10a. Concentration-dependent logarithmic sensitization results for 10^{-4} M - 50 mM Lumogen Red in PMMA quenched by 2 mM Rhodamine 700 assuming $\sigma_F$ depends on the diffusion constant. The experimental slope is found to be 1.21 +/- 0.13 with an intercept at -1.42 +/- 0.30. Theoretically, a slope of 1.00 with an intercept between -1.35 and -1.16 is expected.

Figure 3.10b. Concentration-dependent logarithmic sensitization results for 10^{-4} M - 50 mM Lumogen Red in PMMA quenched by 4 mM Malachite Green assuming $\sigma_F$ depends on the diffusion constant. The experimental slope is found to be 1.06 +/- 0.12 with an intercept at -1.51 +/- 0.28. Theoretically, a slope of 1.00 with an intercept between -1.04 and -0.86 is expected.
along with a specific intermolecular distance through which the exciton must travel, \( l_{\text{hop}} \)
(see equation 3.12)

\[
D = \frac{l_{\text{hop}}^2}{6 \tau_{\text{hop}}}
\]

For the case of a cubic lattice, the average distance between chromophores is expressed as the cube root of the density \([24]\) (see equation 3.13)

\[
l_{\text{hop}} = \frac{1}{\sqrt[3]{C_{LR}}}
\]

whereas the case of an isotropically disordered system is a little more complicated and is expressed as follows \([30, 31]\) (see equation 3.14)

\[
l_{\text{hop}} = \frac{4}{\sqrt{\pi C_{LR}}} = 0.554
\]

Equation 3.14 pertaining to an isotropic system is the more appropriate way to estimate \( l_{\text{hop}} \), although equation 3.13 has also been applied to amorphous solids \([32]\).

\( \tau_{\text{hop}} \) can be either equated with the anisotropy decay time, \( \tau_{\text{pol}} \), or the steady-state determination of \( k_{\text{FRET}} \) based on \( R_0 \) (in which \( R = l_{\text{hop}} \)) (see equation 3.15).

\[
k_{\text{FRET}} = \frac{1}{\tau_{\text{FRET}}} = \frac{1}{\tau_{\text{hop}}} = \frac{1}{\tau_{\beta}} \left( \frac{R_0}{R} \right)^6
\]

For the case of 10 mM Lumogen Red, \( l_{\text{hop}} = 3.1 \) nm using equation 3.14 and \( D = 4.0 \) nm\(^2\)/ns when \( \tau_{\text{hop}} = \tau_{\text{pol}} = 0.4 \) ns from the anisotropy data and 0.4 nm\(^2\)/ns when \( \tau_{\text{hop}} = \tau_{\text{FRET}} = 13.4 \) ns from the steady-state data. If equation 3.13 is used to describe \( l_{\text{hop}} \)
instead, $l_{\text{hop}} = 5.5$ nm, and $D = 12.6$ nm²/ns using $\tau_{\text{hop}} = \tau_{\text{pol}}$ and $0.4$ nm²/ns using $\tau_{\text{hop}} = \tau_{\text{FRET}}$.

### 3.6 Estimating $D$ from Experimental Data

The next question is whether the theoretical values for $D$ predicted in the previous section are consistent with those obtained from the analysis of the fluorescence quenching data. Analysis of the fluorescence quenching experiments becomes problematic due to the presence of two unknowns in the $A$ term for energy migration: $D$ and $\sigma_F$ (see equation 3.7). The most straightforward approach is to assume that the quenching radius, $\sigma_F$, is equivalent to $R_{DA}$, the Forster radius between 10 mM Lumogen Red and 2 mM Rhodamine 700 in PMMA. Experimentally, it is found that $A = 44.6C_{LR}^{1.24}$ (see Figure 3.11). From this relation, $A = 0.079$ ns⁻¹ for 10 mM Lumogen Red. Given the relation between $D$ and $A$ (equation 3.7), $D = 0.89$ nm²/ns given $R_{DA} = 5.85$ nm.

A more sophisticated approach is to use Jang’s estimate for $\sigma_F$ in equation 3.11, assuming a linear dependence of $A$ on $C_{LR}$. Even though this assumption contradicts the power law dependence found in the data (see Figure 3.9), it can be assumed that uncertainties in the power law are large enough that the $A \propto C_D^{1.00}$ case is worth examining. Using the $D$-dependent $\sigma_F$ (see equation 3.11) with $\eta = 0.56$ as defined by Jang, a scaling factor, $\beta$, is added to the expression for $D$ to take into account the possibility that the actual value of $D$ is different from that predicted by equation 3.9.
\[ D = 0.56 \left( \frac{4\pi C}{3} \right)^{\frac{4}{3}} \frac{\beta R_0^6}{\tau_{\beta}} \]  
\text{equation 3.16}

An analytical expression for \( A \) in terms of \( \beta, C_D, \) and \( R_0 \) can be derived using equations 3.7, 3.11, and 3.16

\[ \frac{A}{R_{DD}^{9/2}} = \frac{23.04 R_{DA}^{3/2} \beta^{3/4} C_A}{\tau_{\beta}} C_D \]  
\text{equation 3.17}

A plot of \( A/R_{DD}^{9/2} \) versus \( C_{LR} \) as shown in Figure 3.12 yields a slope of 0.016. In order to obtain this slope experimentally given \( C_A = 2 \text{ mM}, C_D = 10 \text{ mM}, \) and \( R_{DA} = 5.85 \text{ nm}, \) \( \beta \) must be 0.14. When this value for \( \beta \) is plugged into Forster’s altered expression for diffusion (equation 3.16), a value of \( D = 1.23 \text{ nm}^2/\text{ns} \) is obtained.

A final approach as suggested by Powell & Soos [24] avoids the problems encountered in adopting an assumption in regards to \( \sigma_F \). Given the linear relationships for both the \( A \) and \( B \) terms on the acceptor’s concentration (see equations 3.7 and 3.8), it becomes possible to derive an expression for \( D \) purely in terms of the two slopes, \( a \) and \( b \) (see equations 3.18-20)

\[ D = 0.2196 \left( \frac{a^2}{b} \right)^{2/3} \]  
\text{equation 3.18}

where

\[ A = a \ C_A \]  
\text{equation 3.19}

\[ B = b \ C_A \]  
\text{equation 3.20}
A similar relation has been derived by other theories pertaining to sensitization experiments performed on systems possessing a complex understanding of $\sigma_F$, including the simple Chandreshankar diffusion model [33, 34] (see equation 3.21)

$$D = 0.1263 \left( \frac{a^2}{b} \right)^{2/3}$$  \hspace{1cm} \text{equation 3.21}$$
as well as the related model put forth by Ali et al.[35] (see equation 3.22)

$$D = 0.2005 \left( \frac{a^2}{b} \right)^{2/3}$$  \hspace{1cm} \text{equation 3.22}$$
and other relations that have been developed to describe energy migration through molecular crystals [33]. Rather than relying on knowledge of the steady-state parameters such as $R_0$, and $R_{DA}$ diffusion constants are found purely in terms of time-resolved observables. Given the experimentally determined relation $A = 44.6 C_{LR}^{1/2}$, (see equation 3.11) $a = 66 \, \text{nm}^3/\text{ns}$ for when $C_{LR} = 10 \, \text{mM}$ and $C_{R700} = 2 \, \text{mM}$. To find $b$, the complimentary experiment is performed in which the donor concentration is held constant while the acceptor concentration is varied. Given a known $A$ and $\tau_{fl}$ for a given sample, the donor’s quenched fluorescence decay can be refitted using equation 3.6 with $B$ as the only adjustable parameter. Figure 3.13 shows the decays for when $C_{LR} = 10 \, \text{mM}$ and $C_{R700}$ is varied. These decays are fitted to extract $B$ values which can then be plotted versus $C_{R700}$ as shown in Figure 3.14. A linear fit to the data yields $b = 1060 \, +/- 50 \, \text{ns/nm}^3$. Using these values for $a$ and $b$ with equations 3.18-3.20, $D = 0.32\text{-}0.56 \, \text{nm}^2/\text{ns}$ is found for the particular case of 10 mM Lumogen Red and 2 mM Rhodamine 700.
Figure 3.11. Determination of $D$ from the sensitization of Lumogen Red by 2 mM Rhodamine 700 in PMMA assuming $\sigma_F = R_{DA}$. Shown is the experimental relation between $A$ and $C_{LR}$. In combination with the expression for $A$ (equation 3.7), the diffusion constant for 10 mM Lumogen Red in PMMA is determined to be 0.89 nm$^2$/ns. (Extracted slope = 44.6 +/- 1.9).
Figure 3.12. Determination of $D$ from the sensitization of Lumogen Red by 2 mM Rhodamine 700 in PMMA assuming $\sigma_F$ is dependent on $D$. Shown is the experimental relation between $A$ and $C_{LR}$ used to extract $\beta$. The combination of the expression for how $A$ relates to $D$ (see equation 3.17) and the expression for how $D$ relates to $R_0$ (see equation 3.16) results in a diffusion constant of 1.23 nm$^2$/ns for 10 mM Lumogen Red in PMMA. The slope extracted here is 0.016, thus yielding 0.14 for $\beta$. 
Figure 3.13. Concentration-dependent fluorescence quenching of 10 mM Lumogen Red in PMMA by 0.1 - 10 mM Rhodamine 700: 0.1 mM Rhodamine 700, $B^f = 0.16$ ns (solid line), 2 mM Rhodamine 700, $B^f = 0.97$ ns (dashed line), and 10 mM Rhodamine 700. $B^f = 6.63$ ns (dotted line).

Figure 3.14. Determination of $D$ from the sensitization of Lumogen Red by 2 mM Rhodamine 700 in PMMA based on the experimental parameters $a$ and $b$. Shown is the experimental relation between $B$ and $C_{R700}$ used to extract $b = 1060$ (the slope),
Theoretical and experimental values for $D$ and $L_D$, the exciton diffusion length, are summarized in Table 3.1. All three analytical approaches to recover $D$ from the fluorescence quenching data lead to the same results - the experimentally measured values for $D$ (which range between 0.31 and 1.20 nm$^2$/ns) are less than those predicted theoretically based on the steady-state and the time-resolved anisotropy data (in which $D$ ranges between 3.7 and 8.6 nm$^2$/ns). Discrepancies can be attributed to a nonrandom distribution of donor and/or acceptor molecules, a breakdown of the point-dipole approximation, acceptor perturbation of the exciton’s diffusion, and/or anomalous diffusion, each of which merits its own discussion.

3.7 Nonrandom Distributions of Donor and/or Acceptor Molecules

One possible explanation for the observed discrepancy between the diffusion constants extracted from the steady-state and time-resolved anisotropy data versus those obtained from the time-resolved sensitization experiments is that the donor and acceptor molecules are not uniformly distributed within the PMMA host. Previously, deviations from Forster theory at low concentrations have been observed and ascribed to clustering of ionic donor and acceptor dyes within a polymer matrix [36]. Using Monte Carlo simulations, it has been shown that nonrandom chromophore distributions can both accelerate and retard energy migration, depending on the type of clustering [37, 38]. If donor and acceptors cluster together, this would result in enhanced energy transfer, the opposite of what is observed here. In order to explain the data, the clustering would have to be between dyes of the same molecular structure. For example, if the Rhodamine
<table>
<thead>
<tr>
<th>Method for Estimating D</th>
<th>(D (\text{nm}^2/\text{ns}))</th>
<th>(L_D ) (nm)</th>
</tr>
</thead>
</table>
| Steady State Measurement, \(\eta=0.56\)  
(equation 3.10) | 8.56 | 17.1 |
| Steady State Measurement, \(\eta=0.43\)  
(equation 3.10) | 6.57 | 15.0 |
| Steady State Measurement, \(\eta=0.32\)  
(equation 3.10) | 4.89 | 12.9 |
| Time-Resolved Anisotropy Measurement,  
\(\tau_{\text{hop}} = \tau_{\text{pol}}\)  
(equations 3.12 and 3.14) | 4.0 | 11.7 |
| Time-Resolved Anisotropy Measurement,  
\(\tau_{\text{hop}} = \tau_{\text{FRET}}\)  
(equations 3.12, 3.14, and 3.15) | 3.7 | 11.2 |
| Time-Resolved Sensitization Measurement,  
\(\sigma_F = R_{DA}\)  
(equation 3.7) | 0.89 | 5.5 |
| Time-Resolved Sensitization Measurement,  
\(\sigma_F\) depends on \(D\)  
(equations 3.16 and 3.17) | 1.20 | 6.4 |
| Time-Resolved Sensitization Measurement,  
\(D = c \left(\frac{a^2}{b}\right)^{2/3}\)  
\(c = 0.2196\)  
(equation 3.18) | 0.56 | 4.4 |
| Time-Resolved Sensitization Measurement,  
\(D = c \left(\frac{a^2}{b}\right)^{2/3}\)  
\(c = 0.1263\)  
(equation 3.19) | 0.32 | 3.3 |
| Time-Resolved Sensitization Measurement,  
\(D = c \left(\frac{a^2}{b}\right)^{2/3}\)  
\(c = 0.2005\)  
(equation 3.20) | 0.51 | 4.2 |

**Table 3.1** - \(D\) and \(L_D\) for 10 mM Lumogen Red in PMMA based on various steady-state theories and experimental analysis of fluorescence anisotropy and quenching data. \(L_D\) is calculated using the relation \(L_D = (6D \theta)^{1/2}\) and assuming a fluorescence lifetime of 5.7 ns.
700 molecules were to cluster together, their effective concentrations around individual Lumogen Red donors would decrease so that the average distance that the excitation would have to travel would increase. A similar problem would occur if the Lumogen Red donors were clustered together. Such Lumogen Red clustering might also help to explain the solvatochromic shifts seen in Lumogen Red as well as the fact that the $\tau_{pol}$ measurement are faster than those predicted by steady-state theory. However, if any clustering were present, it would be fairly weak, since the molecules are not close enough for either their spectral shape [39] or their fluorescence lifetime [40] to be affected. In addition, work performed by Wasey et al [41] using spin-coated Lumogen Red-doped polycarbonate thin films as a control in a study on birefringence was carried out under the assumption that the molecular dipoles are truly homogeneously distributed throughout the polymer (versus the parallel alignments that occurs within birefringent species). Experimental evidence to prove this assumption otherwise was not evident/reported.

The dielectric constant can be considered a measurement of how well a compound responds physically to a photoexcited state, with higher values indicating a greater degree of motion that occurs upon photo-excitation in order to stabilize the photoexcited state. Dielectric measurements made on Lumogen Red in PMMA as a function of temperature indicate that Lumogen Red is considered an antiplasticizer of PMMA [42, 43]. As such, the presence of Lumogen Red hinders movement amongst PMMA substituents/subunits, thus suggesting the existence of strong guest-host interactions. Such results would be expected to work against clustering.
Finally, at higher Lumogen Red concentrations, one might expect clustering to lead to deviations from the theoretical $\tau_{\text{pol}} \propto C_{LR}^{-2}$ and $A \propto C_{LR}^{-\nu/2}$ dependences. Although the data in Figures 3.2, 3.3, 3.9 and 3.10 are too noisy to conclusively rule out small deviations, such deviations are certainly not a dominant effect.

### 3.8 Breakdown of the Point-Dipole Approximation

All reported estimates of $D$ rely on point dipole-dipole assumptions to describe energy transfer kinetics. This approximation is known to break down for small chromophore separations. Improved expressions have been derived by a variety of workers [44-50]. Within this study, the average separation between molecules is much greater than a molecular diameter, even at the highest concentrations used, thus ruling out the possibility for volume exclusion effects. Good agreement between GAF theory, which assumes point-dipole interactions, and the anisotropy data suggests that any nonidealities in the intermolecular interaction term should be relatively small, if at all present within the sensitization data. If simple FRET theory describes the early time dynamics correctly, there is no reason to suspect the need for more complicated expressions for energy transfer later on in points within the exciton’s lifetime.

### 3.9 Acceptor Perturbation of Exciton Diffusion

A major assumption made within the analysis of the data is that the diffusion constants theorized for Lumogen Red–only films can be applied to films containing both Lumogen Red and Rhodamine 700. It is assumed that the presence of the acceptor does
not perturb the inherent rate of energy diffusion through the donor system. As discussed earlier in the context of equations 3.7 and 3.11, there is always some experimental uncertainty in regards to \( \sigma_F \), the donor-acceptor quenching radius, which is dealt with analytically. It should be noted that this parameter governs the effect an acceptor has on the measured rate of exciton diffusion, not the actual one. In addition to being a less than ideal quencher, it is also possible that the presence of the acceptor changes the diffusion rates between the donor molecules themselves (i.e. through changing the local refractive index or through excluded volume effects). Excluded volume effects has recently been explored with the use of Monte Carlo simulations [51]. It was found that volumes excluded from donors by acceptor occupancy could lead to a small but noticeable slowdown in the Green’s Function describing the decay of the donors. Such excluded volume effects can be taken into account analytically, but at the cost of introducing additional parameters [26]. The effect of a nonspherical molecular shape would introduce even more complexity. An attempt at addressing this concern was made experimentally rather than analytically through the use of two acceptors. Unfortunately, since both are salts with roughly the similar size and dimensions, it is possible that their perturbative effects on the exciton diffusion would also be similar. One way to determine the importance of acceptor-perturbed exciton diffusion would be to compare the experimental data to higher-level simulations of energy transfer that takes the molecular-level structure into account [52-56]. If such effects are found to be important, than \( D \) is dependent on the molecular structure and concentration of the acceptor and Forster’s
expression for diffusion as encompassed by equation 3.9 becomes invalid in describing the exciton diffusion that takes place in the presence of an acceptor.

3.10 Disorder-Induced Anomalous Diffusion

Many experimental studies on fluorescence quenching designed to measure exciton diffusion [24, 27, 29, 57] rely on analytical expressions [6, 24, 35, 58-62] that assume that the diffusion constant $D$ is truly constant and that it does not change over the course of the excitons’ entire lifetime. A fundamental question is whether any theoretical approach that relies on a time-independent diffusion constant can adequately describe exciton diffusion at all times. In fact, it has long been recognized that approximated analytical expressions like equations 3.6-3.8 and 3.12 fail to capture the complexity of energy transfer in the presence of diffusion through a random environment. There are many experimental studies [63-69] and numerical simulations [70-76] that have shown anomalous (time-dependent) diffusion to play an important role in determining exciton kinetics within organic solids.

Several types of more sophisticated analytical theories have been developed to take this nonideal situation into account [8, 18, 26, 77-87]. These approaches have had some success in describing experimental results in both liquid solutions [27, 88, 89] and disordered solids [90-94]. The discrepancy between the exciton diffusion constant measured by the anisotropy experiments sensitive to early time dynamics as opposed to the sensitization experiments that are sensitive to motion over the exciton's entire lifetime within disordered systems may be ascribed to the breakdown of the time-independent
diffusion model. Following the initial hop, which determines the anisotropy decay, there may be a slowdown in the energy transfer rate over subsequent transfer events due to an energetic, translational and/or orientational disorder. Photon echo measurements on dyes embedded in PMMA have indicated values up to several hundred wavenumbers for the width of the static energy distribution [95-100]. Such values are within the range expected to significantly affect exciton motion [71]. The development of new models to reproduce the experimental results is beyond the scope of this dissertation. Recently a relatively simple model for exciton diffusion in energetically disordered materials has been developed [101] and may show to be applicable to the current system. For now, the empirical fact stands that the data is consistent with the idea that static disorder in an amorphous system can lead to a significant slowing down of the exciton motion over the course of its excited-state lifetime.

3.11 Conclusions

The work in this chapter shows that the sterically congested perylene diimide dye Lumogen Red is a suitable chromophore for testing the predictions of simple Forster-type exciton diffusion theory. Many earlier experiments were performed on neat solids where there was no way to vary the donor concentration to confirm true Forster type behavior without complications due to trapping states. The Lumogen Red/PMMA system provides a very clean model with which to test the limitations of simple FRET diffusion theory. This theory is found to do a good job at describing the concentration dependence of both the anisotropy decays and the fluorescence quenching for chromophore densities up to 50
mM in a PMMA. However, whereas standard GAF theory leads to estimates for the anisotropy decay times that are in near quantitative agreement with experiment, it predicts values for $D$ that are overestimates of the experimentally measured values. Several possible reasons for this discrepancy have been discussed. It seems likely that this problem can be resolved through the use of high-level Monte Carlo simulations of energy migration through a realistic molecular environment - a challenging task. While the values of $L_D = 3.3$-6.4 nm extrapolated from experiment are smaller than those predicted by theory, it is encouraging that they are relatively large and follow a consistent trend with chromophore concentration. In principle, if the quasi-linear scaling observed in Figure 3.9 and 10 holds at even higher concentration than those investigated here, and if concentration-induced quenching of Lumogen Red’s excited state lifetime can somehow be circumvented, then increasing $C_{LR}$ by a factor of 100 from 10 mM to 1 M should result in $L_D$ values up to 50 nm, on the order of what is attainable using incoherent hopping transport in highly ordered systems [102].

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spectroscopy data on low-temperature dynamics of organic amorphous solids.


4.1 Introduction

In Chapter 3, time-resolved fluorescence anisotropy and sensitization experiments were used to investigate whether or not exciton diffusion amongst Lumogen Red molecules distributed randomly within a PMMA matrix could be described by Forster Resonance Energy Transfer (FRET) theory in which the diffusion constant, \( D \), is related to the Forster parameter, \( R_0 \) [1-3] (see equation 4.1)

\[
D = \eta \left( \frac{4 \pi C}{3} \right)^{\frac{4}{3}} \frac{R_0^6}{\tau_{fl}}
\]

equation 4.1

\( C \) is the chromophore concentration, \( \tau_{fl} \) is the fluorescence lifetime of the chromophores, \( \eta \) is a constant that theoretically ranges between 0.32 and 0.56, and \( R_0 \) is the Forster radius, or the distance at which energy transfer occurs with 50% probability over other excited state energy deactivation mechanisms (see equation 4.2)

\[
R_0^6 = \frac{9000 \ln(10) \phi_{fl} \kappa^2}{128 \pi^5 N_A n^4} \int_0^\infty \varepsilon(\nu) f(\nu) \frac{d\nu}{\nu^4}
\]

equation 4.2

\( N_A \) is Avogadro’s number, \( \kappa^2 \) is an orientational factor, \( n \) is the refractive index, \( \phi_{fl} \) is the fluorescence quantum yield, and \( \varepsilon(\nu) \) and \( f(\nu) \) correspond to the absorption and fluorescence spectra. The time-resolved anisotropy decays reflect the dynamics involved in the first energy transfer event that occurs from the initially excited Lumogen Red
molecule to one of its neighbors, and as such, is a direct measurement of $k_{FRET}$, the rate of energy transfer between two molecules [1-3] (see equation 4.3)

$$k_{FRET} = \frac{1}{\tau_\beta} \left( \frac{R_{0}}{R} \right)^6$$  \hspace{1cm} \text{equation 4.3}$$

When compared with the theory presented by Gochancour, Anderson & Fayer that relates the rate of energy migration to the depolarization of light [4], quantitative agreement was found with experimental data. Therefore, the anisotropy experiment was able to confirm the validity of this well-established Forster expression for $k_{FRET}$. However, such measurements do not consider the motion of the exciton beyond the first energy transfer step, and so are unable to give a direct/accurate measurement of the multiple-step transfer process involved in energy migration [2, 5-9]. Fluorescence sensitization experiments were used to assess exciton diffusion on longer timescales. Results indicate that theory overestimates the measured diffusion constants. Thus, through the use of two different time-resolved fluorescence techniques, the slow-down of the exciton’s diffusion constant with time was successfully captured.

In this chapter, the evaluation of Forster-type theories on exciton diffusion in disordered environments continues as the test model, Lumogen Red is transferred from PMMA’s static environment into the dynamic ones offered by the two liquid solvents, chloroform (CHCl$_3$) and dimethylformamide (DMF). Time-resolved fluorescence decays of in 10$^{-4}$ M to 50 mM solutions of Lumogen Red quenched by 0.5 mm Rhodamine 700 are measured to study exciton motion, with results compared to previous experiments carried out in PMMA.
Energy migration in the liquids is found to be a factor of 2-3 faster than in the solid polymer, even after taking molecular translation into account. For the case of 10 mM Lumogen Red, measurements ranged from 2.2 to 3.1 nm$^2$/ns in the liquid solvents versus 1.1-1.2 nm$^2$/ns in PMMA. This discrepancy is discussed in the context of the rapid sampling of various intermolecular distances, relative molecular orientations, and spectral energies that occur in the liquid environments but that are absent in the PMMA. In the polymer, unfavorable configurations and low energy trapping sites are frozen in by the static disorder.

### 4.2 Theoretical Basis for the Extraction of Energy Diffusion Observables

In this section, the method used to determine $D$ from the sensitization experiments is reviewed. A general form for the fluorescence decay in the presence of quenchers can be posited as [9-13] (see equations 4.4-4.7)

$$I_D(t) = I_D(0) \exp\left[ -\frac{t}{\tau_B} - A t - A'_t - B \sqrt{t} \right]$$

**equation 4.4**

in which

$$A = 4\pi D \sigma \pi C_A$$

**equation 4.5**

$$A'_t = 4\pi D_{trans} \sigma \pi C_A$$

**equation 4.6**

$$B = \frac{4}{3} \pi R_{D,1}^3 C_A \sqrt{\frac{\pi}{\tau_B}}$$

**equation 4.7**

where $A$ is the decay term due to energy migration, $A'$ results from enhanced quenching due to molecular translation, and $B$ represents the single-step energy transfer of energy
between the donor and acceptor. \( \tau_{fl} \) is the fluorescent lifetime of the donor, \( D \) is the exciton diffusion constant, \( D_{\text{trans}} \) is the sum of the translational diffusion coefficients of the donor and acceptor, \( \sigma_F \) is the quenching radius, \( C_A \) is the acceptor concentration and \( R_{DA} \) is the donor-acceptor Forster radius. Since the parameter of interest is the energy migration rate of the donor, the \( A \) term within the donor’s fluorescence signal must be isolated. This is accomplished by dividing the fluorescence signal for large values of \( C_D \) in which energy migration is active, by the signal for a low \( C_D \), in which energy migration is negligible [14]. In agreement with what has been found by others [15], the \( 10^{-4} \text{ M} \) samples were used as the denominating factor corresponding to the case in which energy migration is unable to occur. When the fluorescence decay of the higher \( C_{LR} \) is divided by that of the lower \( C_{LR} \), all the concentration-independent terms cancel out, leaving only the decay component corresponding to the \( A \) term for energy migration [14] (see equation 4.8)

\[
\frac{I(t)[C_{LR}]}{I(t)[10^{-4} \text{ M } C_{LR}]} = \frac{\exp[-k_{fl}t - A t - A't - B\sqrt{t}]}{\exp[-k_{fl}t - A't - B\sqrt{t}]} = \exp[-At] \quad \text{equation 4.8}
\]

From equations 4.5 and 4.8, it would appear that extracting \( D \) from \( A \) should be a simple matter of dividing by the quantity \( 4\pi\sigma_F C_A \). In general, however, \( \sigma_F \) is not a constant but depends on \( D \). This dependence arises from the fact that as the donor’s intermolecular distance becomes smaller, excitons travel faster so that the donor-donor transfer rate becomes competitive with the donor-acceptor quenching rate and exciton quenching by the doped acceptor becomes less effective. In this chapter, both of these two limits for \( \sigma_F \) are considered for obtaining \( D \) from \( A \).
For the simple case for when $\sigma_F$ is independent of $D$ (see equation 4.9)

$$D = k C_D^{\alpha} R_{DD}^6$$

in which $\alpha = 4/3$ and $k = \eta (4/3 \pi)^{4/3} \tau^{-1}_{fl}$ according to theory (see equation 4.1). In this approach, $\alpha$, the power-law dependence of $D$ on $C_D$, is an experimentally determined variable. By substituting equation 4.9 into equation 4.5, the following expression for $A$ is obtained (see equation 4.10)

$$A = 4 \pi k C_D^{\alpha} R_{DD}^6 R_{DA} C_A$$

An alternate approach involves using a diffusion-dependent expression to describe $\sigma_F$ as put forth by Jang [9] (see equation 4.11)

$$\sigma_F = R_{DA} \left[ \frac{\Gamma(0.75)}{2\Gamma(1.75)} \right]^{1/4} \left( \frac{R_{DA}^2}{\tau_{fl} D} \right)^{1/4} = 0.676 \left( \frac{R_{DA}^6}{\tau_{fl} D} \right)^{1/4}$$

Assuming that equation 4.1 provides an accurate qualitative description of $D$, equations 4.1, 4.5, and 4.11 can be used to derive an analytical expression for $A$ which explicitly depends on the scaling factor, $\eta$ (see equation 4.12)

$$A = \eta^{3/4} \frac{35.58 R_{DA}^{3/2} R_{DD}^{3/2} A C_D}{\Gamma_{fl}}$$

where $\eta$ is the same constant found in equation 4.1 pertaining to Forster’s basic expression for exciton diffusion. All parameters in equation 4.12 are known except $\eta$, so that a plot of $A$ versus $C_{LR}$ yields $\eta$. The experimentally determined $\eta$ is then used in conjunction with equation 4.1 to determine the experimentally-measured diffusion constant.
Recall from Chapter 3 that there exist different methods for extracting the diffusion constant from the fluorescence quenching data. Applying these different theories to the experimental data collected in PMMA resulted in experimental values for $D$ varying by roughly a factor of 4. Thus, the values extracted for $D$ should be viewed as most useful for making relative comparisons between environments rather than as absolute determinations of the actual values.

4.3 Energy Migration in Liquids

The goal behind the liquid-based experiments presented here is to examine whether or not there is a difference between hosts offering a static environment with time (and thus characterized by a “static” disorder) as offered by PMMA, and those characterized by a “dynamic” disorder, such as in the liquid solvents, in which the environment is dynamically changing with respect to time. Liquid solvent experiments were performed in two different solvents for similar reasons as to why the PMMA experiments were performed using two different acceptors - to ensure the universality of the results.

Ideally, a liquid/solid matrix pair should be compared in which there is a high degree of molecular similarity. Therefore, the environments would possess similar molecular volumes, shapes, and specific donor-acceptor interactions. However, solubility incompatibility between the donor and acceptor made such a task not possible. The fact that Lumogen Red is nonpolar (possessing a dipole moment = 0.002 Debye [16]) while Rhodamine 700 is a polar salt eliminated several classes of solvents from
consideration. For instance, comparisons between PMMA and ethyl acetate as a solid/liquid matrix pair has been made previously to investigate the stability of Lumogen Red for its use as a solid-state dye laser [17]. However, Rhodamine 700 possesses a low solubility in ethyl acetate. The PMMA molecular mimics methyl isobutyrate and methyl propionate [18] were considered as well, along with the solid/liquid pair, polystyrene and toluene. Once again, Rhodamine 700 showed poor solubility compatibility. The PVA/ethanol matrix pair was considered as an alternative since Rhodamine 700 dissolves readily in alcohol. However, Lumogen Red displays poor solubility in both alcohol and the water needed to dissolve the PVA. Acetone was considered as an alternative liquid matrix to compare with PMMA, but Lumogen Red was found to be insoluble at the higher concentrations needed to conduct the experiment. After much searching, Lumogen Red and Rhodamine 700 were both found to be soluble in the two solvents, DMF and CHCl₃.

Some of the crucial photophysical constants needed to calculate $R_0$ for Lumogen Red change upon going from the PMMA matrix to the liquid solvents. Whereas the quantum yield of Lumogen Red is 0.88 in PMMA [19], it is 0.96 in the solvents, with the fluorescence lifetime being 5.7 ns in PMMA and 6.2 ns in the liquids [19, 20]. The $\kappa^2$ term that describes the relative rotational coordinates of the molecular pair involved in the energy transfer event is set to the theoretical value of 0.667 in the solvents and 0.476 in PMMA [21]. Refractive indices for PMMA, CHCl₃, and DMF were taken to be 1.49, 1.45, and 1.43. Given these parameters, $R_0$ for the case of 10 mM Lumogen Red was
found to be 4.36 nm, 4.46 nm, and 4.77 nm in CHCl₃, DMF, and PMMA, respectfully. $R_{DA}$ was taken to be 5.85 nm for all cases.

As observed for the case of Lumogen Red in PMMA, the quenching of Lumogen Red’s fluorescence by Rhodamine 700 increased with the increase in the concentration of Lumogen Red (see Figure 4.1). The experimental analysis outlined in section 4.2 and performed previously for PMMA was repeated in CHCl₃ and DMF. The Lumogen Red concentration was varied between 0.01 and 50 mM, while the Rhodamine 700 concentration was fixed at 0.5 mM. Note that a lower quencher was used in the liquids than in PMMA (in which $C_{R700} = 2.0$ mM) since the fluorescence quenching was found to be significantly stronger in the case of the liquids (see Figure 4.2). This stronger quenching gave rise to decays for higher Lumogen Red concentrations that were unable to be fully resolved by the streak camera. In the analysis of the experimental data used to extract and compare $D$ amongst the three matrices, consideration for this variation in the acceptor’s concentration is accounted for in the same way that the concentration-dependence of $R_0$ is dealt with – through the scaling of the y-axis.

To address the extent to which the time-resolved sensitization data qualitatively describes predictions for $D$ based on steady-state data and equation 4.1, log/log plots of $A/R_{DD} \sigma_F$ versus $C_{LR}$ were made to determine $\alpha$, $A$’s power-law dependency on concentration. A slope of 1.33 would be expected for the case of a $\sigma_F$ independent of concentration and 1.0 for the case of a concentration-dependent one [20]. Figure 4.3 shows some of the ratioed decays used to determine $A$ as a function of $C_{LR}$ in CHCl₃ and DMF. Experimentally, $\alpha$ was found to be 1.0 +/- 0.2 for the case of CHCl₃, 1.1 +/- 0.2
Figure 4.1a. Concentration – dependent quenching of Lumogen Red by 0.5 mM Rhodamine 700 in CHCl₃: 10 mM (solid line), 25 mM (dashed line), and 50 mM (dotted line).

Figure 4.1b. Concentration – dependent quenching of Lumogen Red by 0.5 mM Rhodamine 700 in DMF: 10 mM (solid line), 25 mM (dashed line), and 50 mM (dotted line).
Figure 4.2  Observed quenching for 10 mM Lumogen Red in PMMA (dashed line) and CHCl$_3$ (solid line) doped with 2 mM Rhodamine 700.

for DMF, and 1.2 +/- 0.2 in PMMA (see Figure 4.4), thus confirming the correct experimental concentration –dependence of $A$ as predicted by theory.

The dependence of $R_0$ on $C_{LR}$ is taken into account by scaling the y-axis by $R_0^6$, as suggested by equation 4.10 for the case of a concentration-independent $\sigma_F$, and $R_0^{9/2}$ as suggested by equation 4.12 for the case of a concentration-dependent one. Scaling the data by $R_0^6$ or $R_{DD}^{9/2}$ had no effect on the corresponding obtained values for $\alpha$, a reflection of the experimental robustness of the parameter. The fact that both solid and liquid media exhibit an $A$ dependence on $C_{LR}$ similar to that predicted theoretically is encouraging. Likewise, the smaller $\alpha$ values observed in the liquids relative to solid
Figure 4.3a. Concentration – dependence in the ratioed decays for $10^{-3}$ M – 50 mM Lumogen Red quenched by 0.5 mM Rhodamine 700 in CHCl$_3$: 10 mM, $\lambda^\text{1} = 28$ ns (solid line), 25 mM, $\lambda^\text{1} = 9.5$ ns (dashed line), and 50 mM, $\lambda^\text{1} = 4.6$ ns (dotted line).

Figure 4.3b. Concentration – dependence in the ratioed decays for $10^{-3}$ M – 50 mM Lumogen Red quenched by 0.5 mM Rhodamine 700 in DMF: 10 mM, $\lambda^\text{1} = 37$ ns (solid line), 25 mM, $\lambda^\text{1} = 12$ ns (dashed line) and 50 mM, $\lambda^\text{1} = 5$ ns (dotted line).
PMMA is consistent with the prediction that in a solid environment, \( D \), and thus \( A \), exhibits a stronger dependence on \( C_{LR} \) than in liquids [9].

The next question of concern pertains to the quantitative extraction of \( D \) from the data. Although the data in Figure 4.4 is consistent with an \( \alpha = 1.0 \) dependence of \( A \) on \( C_{LR} \) as predicted by equation 4.12 for the case in which \( \sigma_F \) is diffusion dependent rather than the \( \alpha = 1.33 \) dependence as predicted for the case of a diffusion-independent \( \sigma_F \), both cases are dealt with in the extraction of \( D \) from the sensitization data. In reference to equation 4.10, which assumes \( \sigma_F \) to be a constant and \( \alpha \) to be experimentally determined, \( A=11.4C_{LR}^{1.0} \) in CHCl\(_3\), \( A=13.5C_{LR}^{1.1} \) in DMF, and \( A=44.6C_{LR}^{1.2} \) in PMMA.

For the case of 10 mM Lumogen Red, \( D \) was found to be 3.1 nm\(^2\)/ns in CHCl\(_3\), 2.2 nm\(^2\)/ns in DMF, and 1.1 nm\(^2\)/ns in PMMA\(^1\). For the case of a diffusion-dependent \( \sigma_F \), equation 4.12 is used and the unknown variable, \( \eta \), is extracted and used to calculate \( D \) from equation 4.1, Forster’s expression for exciton diffusion. Displayed in Figure 4.6 is a plot of \( A/(R_{DD}^{9/2}C_{R700}) \) versus \( C_{LR} \), from which slopes \( \eta \) can be obtained. Experimentally, \( \eta = 0.31 \) in CHCl\(_3\), 0.23 in DMF, 0.08 in PMMA, with \( \eta \) in CHCl\(_3\) lying close to the theoretical limit of 0.32 as put forth by Haan & Zwanzig [5]. Diffusion constants calculated using these experimentally-determined values for \( \eta \) are found to correspond to 2.6 nm\(^2\)/ns in CHCl\(_3\), 2.2 nm\(^2\)/ns in DMF, and 1.2 nm\(^2\)/ns in PMMA for the case of 10 mM Lumogen Red. Experimentally determined diffusion constants along with their corresponding steady-state based theoretical predictions are listed in Table 4.1.

\(^1\)This value for PMMA is slightly larger than the value of 0.89 nm\(^2\)/ns reported for the same approach in Chapter 3, due to the use of \( \alpha = 1.2 \) instead of \( \alpha = 1.24 \) in the earlier work. In this chapter, we have rounded the \( \alpha \) value to be consistent with the number of significant figures used in the other calculations.
Figure 4.4. Logarithmic results for the concentration-dependency of $D$ on $C_{LR}$ in CHCl$_3$, DMF, and PMMA. The slope = $\alpha = 1.0 \pm 0.2$ in CHCl$_3$ (circles and solid line), 1.1 $\pm 0.2$ in DMF (triangles and dashed line), and 1.2 $\pm 0.2$ in PMMA (squares and dotted line).
Figure 4.5. Determination of $D$ from the sensitization of Lumogen Red by 2 mM Rhodamine 700 in PMMA and 0.5 mM Rhodamine 700 in CHCl$_3$ and DMF assuming $\sigma_F^\alpha = R_{DA}$. Shown is the experimental relation between $A$ and $C_{LR}^\alpha$ used to calculate the diffusion constant for 10 mM Lumogen Red: $A = 11.4C_{LR}^{1.0}$ in CHCl$_3$ (circles and solid line), $A = 13.5C_{LR}^{1.1}$ in DMF (triangles and dashed line), and $A = 44.6 \times C_{LR}^{1.2}$ in PMMA (squares and dotted line).
Figure 4.6. Determination of $D$ from the sensitization of Lumogen Red by 2 mM Rhodamine 700 in PMMA (squares and dotted line), 0.5 mM Rhodamine 700 in CHCl$_3$ (circles and solid line), and 0.5 mM Rhodamine 700 in DMF (triangles and dashed line) assuming $\sigma_r$ is dependent on $D$. $\eta$ is extracted from each of the slopes to determine the diffusion constant for 10 mM Lumogen Red in each of the systems. Experimental slopes are 34 for CHCl$_3$, 27 for DMF, and 13 for PMMA, which translates into 0.31, 0.23, and 0.08 for the respective values of $\eta$ and 2.6 nm$^2$/ns, 2.2 nm$^2$/ns, and 1.2 nm$^2$/ns for the diffusion constants.
Table 4.1. $D$ and $L_D$ for 10 mM LR in CHCl$_3$, DMF, and PMMA Based on Various Theories and Experimental Analysis of Fluorescence Sensitization Data. $L_D$ is calculated using the relation $L_D = \sqrt[6]{6D\tau_f}$ and assuming a fluorescence lifetime ($\tau_f$) of 5.70 ns in PMMA and 6.2 ns in the solvents. $R_0$ for $C_{LR} = 10$ mM is 4.77 nm in PMMA, 4.46 nm in DMF, and 4.36 nm in CHCl$_3$.

While the case of 10 mM Lumogen Red has been the focus in the determination of $D$, it is important to note that equations 4.5, 4.10, and 4.12 permit the calculation of $D$ for any value of $C_{LR}$.

4.4 Anomalous Diffusion in Solid versus Liquid Matrices

The study of energy migration through a liquid solvent matrix presented here is a continuation of earlier work on the study of energy migration within a PMMA matrix in
order to develop a better understanding as to how excited state energy migrates through disordered systems. Previously, it was found that for the case of Lumogen Red embedded in PMMA, energy migration as measured by the time-resolved sensitization experiments falls short of steady-state based predictions for $D$. This has since been confirmed through the work of Fennel and Lochbrunner [22]. In their investigation into energy migration through 50 – 150 mM Lumogen Red PMMA films doped with 0.3 – 3 mM Oxazine 1, $\eta$ was assumed to be 0.428 in accordance with GAF theory, and energy migration was found to be half that predicted by steady-state spectral data. When measured in CHCl$_3$ and DMF, diffusion constants could be quantitatively obtained by setting $\eta$ to 0.23 in DMF and 0.31 in CHCl$_3$. Similar work done by Miller et al [8, 23] found $\eta$ to be 0.20 for their investigation into energy migration through the liquid-based systems, disodium fluorescein in ethanol [23], as well as for oxazine 1 perchlorate in methanol [8]. Therefore, it can be said with confidence that although static systems serve to decrease the diffusion constant with time, such effects are mitigated within a fluid environment.

In fluid systems, the dynamic fluctuations that take place rapidly throughout the donor’s excited state lifetime provide a qualitatively different type of disorder from that which characterizes PMMA. The inherent ergodicity displayed by the liquid solvents that allows for the Lumogen Red molecules to freely sample various spatial, rotational, and energetic conformations within the exciton’s lifetime [24, 25] increase the probability for a favorable and successful energy transfer event to occur [26]. Such effects are expected to be greater in chloroform than in the more viscous DMF, in which the
rotational and translational diffusion rates are larger in accordance with the Stokes-Einstein relation that relates viscosity to translational diffusion, $D_{\text{trans}}$ [26] (see equation 4.12)

$$D_{\text{trans}} = \frac{k_B T}{6 \pi h r} \tag{equation 4.13}$$

and the Stokes-Einstein-Debye relation that relates viscosity to rotational diffusion, $\tau_r$ [27] (see equation 4.13)

$$\tau_r = \frac{h V}{k_B T} f W \tag{equation 4.14}$$

in which $k_B$ is Boltzmann’s constant, $T$ is the temperature, $V$ is the volume of the solvent, $r$ is the molecular radius, $f$ is a descriptor of the shape of the molecule, $W$ describes the coupling between the solvent and solute, and $h$ is the solvent’s viscosity.

It should be emphasized that within the framework of the performed analysis, the increase in $D$ due to $D_{\text{trans}}$ within the liquids cannot be attributed to simple translational motion alone. Molecules within the solvents by which fluctuations in the intermolecular separation, $R$, allowed in a liquid but not in the solid provides transient opportunities for electronic energy transfer that would not otherwise occur. The term for $D_{\text{trans}}$ is independent of $C_{LR}$ (see equation 4.13), and, like the $B$ term in equation 4.7, is divided out through the ratioing of the high and low donor decays via equation 4.8. In the case that translational motion and energy migration are not completely decoupled as assumed, then it is possible for $D$ to be enhanced beyond its theoretical values. This phenomenon has been explored theoretically [9, 28] and becomes important at very high donor
concentrations. Experiments by Joshi et al appear to suggest that this effect can enhance exciton diffusion up to 2 orders of magnitude beyond that predicted by theory [29]. There is no indication that such an enhancement is going on within these experiments.

The dynamic nature of the liquids can affect the temporal variations in parameters in addition to $R$ that determine the energy transfer rate as given by equations 4.2 and 4.4. Rotational diffusion can permit the $\kappa^2$ orientation factor between two molecules to fluctuate with time. In principle, this difference is taken into account in that the system’s theoretical value for $\kappa^2$ that differs in the amorphous solid (0.476) and within the liquid solvents (0.667). However, because $\kappa^2$ varies with each transfer step [30], the overall effect is a slow down in energy migration within the solid with respect to the solvents in which a similar temporal variation in $\kappa^2$ with respect to the exciton’s lifetime as discussed for $R$ is able to occur.

Another aspect of disordered environments that theory does not explicitly address is the fact that different local configurations can shift the energies of neighboring molecules and cause the spectral overlap turn in equation 4.2 to vary from site to site. Hole-burning and photon echo experiments have shown that spectral diffusion in liquids permits chromophores to sample the entire absorption line shape within a nanosecond or less, going from high to low energy configurations many times within their excited state lifetime [31-35]. Just as the rapid translational and rotational diffusion averages over different molecular orientations and intermolecular distances, spectral diffusion can average out different energy configurations in liquids [36, 37]. These effects would
explain why a theory that does not take energetic disorder explicitly into account can still accurately describe energy migration in a liquid. It seems likely that the spectral diffusion observed in other types of dyes would be present in Lumogen Red as well. Dyes in a solid polymer, on the other hand, are truly inhomogenously broadened with chromophores that can never fully explore the available energy landscape [38-42]. Many earlier studies have implicated static disorder as a culprit responsible for dispersive transport and lower-than-expected exciton diffusion rate in solids [43-49]. Currently, anomalous diffusion has only been taken into account using more sophisticated numerical models whose implementation is beyond the scope of this dissertation [30, 50-52]. However, recent theoretical results suggests that a knowledge of the distribution of energies may be sufficient to modify equation 4.1 so that it can still give a quantitative description of exciton diffusion in disordered solids [53]. One way to test this concept is to vary the amount of dynamic versus static energetic disorder (analogous to homogenous and inhomogeneous broadening) in a controlled manner, for example by changing the temperature [54] or the solvent viscosity, and seeing how $D$ is affected. Parallel measurements in the characterization of the degree of homogenous and inhomogeneous types of energetic disorder using four-wave mixing experiments like the photon echo [55] along with exciton diffusion measurements using fluorescence quenching or the transient grating could then be used to establish a quantitative connection between these two quantities.
4.4 Conclusions

For the case of Lumogen Red embedded in PMMA, the time-resolved diffusion constant falls short of Forster theory predictions based on equation 4.1 which relates steady-state parameters to $D$. Agreement with equation 4.1 could only be made by setting $\eta$ to the experimentally determined value of 0.08 instead of the theoretically ones that range between 0.32 and 0.56. When measuring exciton diffusion in liquid solvents, $\eta$ is determined to lie close to the theoretical value of 0.32 predicted by Haan & Zwanzig theory, being 0.23 in DMF and 0.31 in CHCl$_3$. While such theoretical agreement within the liquids may be fortuitous, our results clearly demonstrate that exciton diffusion is more rapid in fluid environments, even after the molecular center-of-mass translational diffusion that takes into account the variation in $R$. One possible explanation for this phenomenon is the ability of the liquid environments to “wash out” energetic configurations that can trap the excitation on relatively short time scales. If the exciton is pictured as traversing an inhomogeneous energy landscape, than the peaks and valleys provide opportunities for the exciton to become trapped. In a solid, these peaks and valleys are stationary, and the exciton remains trapped during its lifetime. In a liquid, these peaks and valleys are rapidly shifting like waves on the sea, allowing the exciton to escape during its lifetime. In the drive to increase solar energy conversion efficiencies, engineering disorder in organic semiconductors may provide an avenue to enhance exciton diffusion lengths and improve photocurrent yields.
REFERENCES


Chapter 5: On the Temperature Dependence of the Time-Resolved Fluorescence Quenching of 10 mM and 100 mM Lumogen Red in PMMA

5.1 Introduction

A dominating concern over the ability of FRET theory to accurately describe energy migration through disordered systems pertains to the concept of anomalous diffusion. The Forster model assumes that exciton motion is diffusive at all times, while more sophisticated approaches have shown that positional, energetic, and orientational disorder can all lead to anomalous behavior in which the diffusion constant slows down with time [1-13]. In such systems, the molecules are positioned in such a way so that the rate corresponding to each possible transfer even varies with respect to changes in the intermolecular distance, the relative molecular orientations and the molecular spectral overlap. As a consequence, successive steps serve to slow down the exciton diffusion constant with time as low energy transfer sites possessing suitable distances and orientations for energy transfer dissipates with time.

Time-resolved anisotropy and sensitization experiments for Lumogen Red in PMMA, CHCl₃, and DMF at room temperature were performed and are presented in Chapters 3 and 4. The results of the time-resolved anisotropy and sensitization experiments performed in PMMA showed that after the first initial hop, there is slowdowns in the diffusion constant with time as subsequent steps occur due to the random distribution of chromophores within the host material. In the PMMA system, static energetic, translational, and orientational disorder directs exciton motion toward
low energy sites from which there is no way out [5, 8, 10, 14-29]. As a result, the time-
resolved sensitization experiments provide measurements for $D$ that fall short of those
predicted by Forster’s theory based on the steady-state data. In the liquid solvents,
diffusion constants were able to approach the lower theoretical limits set by theory.
Results were discussed in terms of the rapid averaging of the relative orientational,
translational and spectral energies that takes place within a fluid environment that can
provide transient opportunities for energy transfer between molecules that would not
otherwise occur [30-38]. In principle such variations in the intermolecular distance ($\Delta R$),
the relative orientations ($\Delta \kappa^2$), and spectral overlap ($\Delta J$) are taken into account by using
averaged values for each ($\bar{R}, \bar{\kappa^2}, \bar{J}$) in the calculations made for the determination of $D$
[30, 39-43] (see equations 5.1 and 5.2)

$$D = \eta \left( \frac{4\pi C}{3} \right)^{\frac{4}{3}} \frac{R_0^6}{\tau_{fl}}$$  \hspace{1cm} \text{equation 5.1}

$$R_0^6 = \frac{9000 \ln(10) \Phi_{fl} \kappa^2}{128\pi^5 N_A n^4} \int_0^\infty \varepsilon(\nu) f(\nu) \frac{d\nu}{\nu^4}$$  \hspace{1cm} \text{equation 5.2}

in which $\tau_{fl}$ is the fluorescence lifetime, $N$ is Avogadro’s number, $\Phi_{fl}$ is the fluorescence
quantum yield, $\eta$ is a constant that theoretically ranges between 0.32 and 0.56, $n$ is the
refractive index, and the integral is referred to here as $J$, and corresponds to the spectral
overlap between the acceptor’s absorption modulated by its extinction coefficient ($\varepsilon(\nu)$)
and the normalized fluorescence spectra $ff(\nu)$ of the donor. $C$ is the chromophore
concentration, and as such, an indication of the intermolecular distance.
$J$ is taken to be the steady-state spectral overlap of the donor’s fluorescence and acceptor’s absorption measured from a collection of molecules. Technically, spectra are compilations of individual absorptions and emissions [44, 45]. It is therefore possible that there are points in the exciton’s lifetime in which an acceptor’s absorption is too red or the donors fluorescence is too blue for the transfer to occur with substantial efficiency. In the work of Gaab & Bardeen, comparisons between the time-resolved anisotropy decays of MEH-PPV as a function of temperature are made with changes in the steady-state spectral overlap with temperature [29]. Results showed that anisotropy decays became longer with the decrease in temperature than predicted by the steady-state change in $J$ with the decrease in temperature. Thus changes in the spectral energy overlap were not able to quantitatively describe what was measured in the anisotropy experiments. It appears here that variations in $J$ due to disorder ($\Delta J$) thus serve to hinder energy migration in the polymer system. In light of these results, can an average value for $J$ ($\bar{J}$) describe energy migration through a system of small molecules (versus polymer system) that is also more accurately described by a variation in $J$ ($\Delta J$)?

A similar argument can be made in assessing the appropriateness of using the averaged values $\bar{\kappa}^2$ and $\bar{R}$ in regards to the site-to-site variations in relative molecular orientations and intermolecular distances. In regards to the site-to-site variation in $R$ ($\Delta R$), Forster's expression for the diffusion constant (see equation 5.1) is based on the multiple energy transfer events that occur between molecules of the same type, each of which is characterized by an energy transfer rate, $k_{FRET}$ [39, 46, 47] (see equation 5.3)
\[ k_{\text{FRET}} = \frac{1}{\tau} \left( \frac{R_0}{R} \right)^6 \]  

\textbf{equation 5.3}

\( D \), as expressed by \textbf{equation 5.1}, assumes that variations in the intermolecular distance can be accounted for by using an averaged value for \( R (\bar{R}) \) based in one way or another on the chromophore number density. However, can an averaged value for \( R (\bar{R}) \) describe energy migration through a system more accurately described by a variation in \( R (\Delta R) \)? Similarly, can an “averaged” value for \( \kappa^2 \) be used in place of \( \Delta \kappa^2 \) given that \( \kappa^2 \) can range anywhere between 0 for perpendicular dipole alignments and 4 for parallel ones [48]? Such questions are probed here in the form of time-resolved and steady-state experiments performed over a temperature range from 77 K to 298 K using Lumogen Red in PMMA as the model test system.

\textbf{5.2 Temperature-Dependent Studies on Energy Migration through Disordered Systems}

Low temperature studies can be considered a standard approach in characterizing the types of disorder present within a system as well as discussing how exciton motion is affected by each [15, 17, 20, 49-53]. When it comes to optical spectra, the most common division line for the classification of disorder occurs between what are referred to as heterogeneous and homogeneous types of disorder.

Heterogeneous disorder pertains to the variation in molecular site-to-site energies giving rise to a correlating variation in the molecule’s spectral signature [44]. As such, it
is responsible for the broadening of the system’s spectral widths beyond that predicted by
the Heisenberg Uncertainty Principle in regards to $\Delta \tau$ and $\Delta E$ (see equation 5.4) [54]
\[
\Delta E \Delta \tau \geq \frac{\hbar}{2}
\]
equation 5.4
in which $\Delta E$ is the uncertainty in the energy of the state in question and $\Delta \tau$ is the
uncertainty in the lifetime of that state. Heterogeneous disorder is further classified as
diagonal or off-diagonal in reference to the matrix algebra used to describe the system’s
energetics. Diagonal disorder has as its source the specific variations in site-to-site
energies due to intramolecular properties pertaining to molecular configuration [55]. Off-
diagonal disorder, on the other hand, describes variations in the energy of a molecule due
to variations in intermolecular properties such as intermolecular distances and relative
intermolecular orientations. Homogenous disorder refers to the ability of phonons
within the system to assist in the transfer of energy between energetically dissimilar
molecules within an inhomogenously broadened landscape [7, 56]. As a result,
allowance is made for the population of more energy states in comparison to those
allowed by the heterogeneous landscape, and thus a broadening of the spectra with the
increase in temperature. At low temperatures, the degree of homogeneous disorder is
reduced, thus requiring exciton kinetics to be described in terms of a purely
heterogeneously broadened system [15, 49], with parameters such as $J$, $R$ and $\kappa^2$ exerting
larger effects on exciton kinetics.

As the temperature is lowered, the associated FRET parameters $\kappa^2$ and $R$ are not
expected to change as the molecules remain fixed within position in the PMMA matrix.
In contrast, $J$ does change with the changing temperature due to the decrease in homogenous broadening that accompanies the decrease in temperature. As the spectral overlap of the narrowing spectra decreases with temperature, $R_{\theta}$, and thus energy migration diffusion constants are reduced as well. This brings with it a decrease in quenching by the doped acceptor with the decrease in temperature as excitons are less able to reach the acceptor’s quenching radius. A series of time-resolved sensitization experiments are performed on 10 mM and 100 mM films for temperatures ranging from 298 K to 77 K and compared with the temperature-dependent change in $R_{\theta}$ based on steady-state data to see if the changes in $R_{\theta}$ give the correct corresponding changes in fluorescence quenching.

In the context of the time-resolved sensitization experiments, the degree of quenching of a donor’s fluorescence by an acceptor is related to the diffusion constant of the exciton. In the absence of an acceptor, the donor’s fluorescence decays exponentially (see equation 5.5)

$$I_D(t) = I_D(0) \exp(-\frac{t}{\tau_D})$$

**equation 5.5**

Once an acceptor is introduced into the system, the decay of the donor’s fluorescence becomes multi-exponential in form, with the simplest analytical expression possessing two additional terms corresponding to the diffusion constant ($A$) and the energy transfer rate between the donor and doped acceptor ($B$) (see equations 5.6-5.8)

$$I_D(t) = I_D(0)\exp\left[-\frac{t}{\tau_D} - At - B\sqrt{t}\right]$$

**equation 5.6**
\[ A = 4\pi D \sigma_F C_A \quad \text{equation 5.7} \]

\[ B = \frac{4}{3} \pi R_{DA}^3 C_A \sqrt{\frac{\pi}{\tau_B}} \quad \text{equation 5.8} \]

\( \sigma_F \) is the acceptor’s quenching radius, \( C_A \) is the concentration of the acceptor, and \( R_{DA} \) is the Forster radius for donor to acceptor transfer. \( A \), the term for energy migration is isolated by ratioing the quenched decay of a given film with a given concentration by that of a 10\(^{-4}\) M film, through which energy migration is negligible. Since \( B \) is independent of the donor’s concentration, it theoretically retains the same value for both the 10\(^{-4}\) M and films of higher concentration, thus allowing for the isolation of \( A \) [57] (see equation 5.9)

\[
\frac{I(t)[C_{LR}]}{I(t)[10^{-4} M \ C_{LR}]} = \frac{\exp[-k_F t - A t - B \sqrt{t}]}{\exp[-k_F t - B \sqrt{t}]} = \exp[-At] \quad \text{equation 5.9}
\]

As done previously with the PMMA-based room temperature sensitization experiments presented in Chapter 3, 2 mM Rhodamine 700 was used as the acceptor.

### 5.3 10 mM versus 100 mM Trends with Temperature: Steady-State Results

Temperature-dependent steady-state spectra for 10 mM and 100 mM Lumogen Red in PMMA are presented in Figure 5.1. As the temperature is lowered, so is the degree of homogenous disorder with the result that the spectra narrow with the decrease in temperature. The effect is greater for the more highly concentrated 100 mM film than for the 10 mM one. In addition, the fluorescence is red-shifted in the 100 mM film to a greater degree than the 10 mM film, thereby suggesting that fluorescence is occurring
Figure 5.1a. Temperature-dependent spectral shifts for 10 mM Lumogen Red in PMMA: shown are spectra taken at 293 K (solid line) and 77 K (dashed line).

Figure 5.1b. Temperature-dependent spectral shifts for 100 mM Lumogen Red in PMMA: shown are spectra taken at 293 K (solid line) and 77 K (dashed line).
from lower energy sites within the 100 mM film. Given that energy migrates toward lower energy sites within the films, perhaps the 100 mM films possess a greater degree of disorder that allows for deeper energy sinks. Shifts due to the formation of new electronic states, such as in charge-transfer crystals (in which the fluorescence is extremely red-shifted, as well as broader and weaker [58]) and J-aggregates (in which there is a dramatic increase in the 0-0 peak with the decrease in temperature [59]) are not expected to play a significant role as the spectra do not change their overall shape. The overall result of the spectral narrowing with temperature is the decrease in the spectral overlap with temperature, and therefore a decrease in $R_0$ as shown in Figures 5.1 and 5.2. Whereas the 10 mM film shows a 13% change in $R_0$ with a temperature change from 298 K to 77 K, the 100 mM exhibits a 57% change in $R_0$.

![Figure 5.2](image.png)

**Figure 5.2.** Changes in $R_0^6$ with temperature for 10 mM (squares) and 100 mM (triangles) Lumogen Red in PMMA.
5.4 10 mM versus 100 mM Trends with Temperature: Time-Resolved Results

The decrease in the quenching of the fluorescence decays by the acceptor that occurs with the decrease in temperature is displayed in Figure 5.3 for the case of 100 mM Lumogen Red in PMMA doped with 2 mM Rhodamine 700 at 293 K and 77 K. Collections of the ratioed decays used to extract A are shown in Figure 5.4. As quenching decreases from 293 K to 77 K, so does A and D. The question remains, does it do so in quantitative agreement with that predicted by Forster’s steady-state based determinations for D. Figure 5.6 shows A for the two films scaled by the corresponding steady-state change in \( R_0 \) with temperature. The relation between A and \( R_0 \) are shown here to remain constant with temperature. In other words, the temperature dependent trends in \( R_0 \) accurately describe the temperature-dependent trends in A. Experimentally, the change in A is 16% for 10 mM Lumogen Red and 61% for 100 mM. When compared to the steady-

![Figure 5.3](image-url)  

**Figure 5.3.** Temperature – dependent quenching of 100 mM Lumogen Red by 2 mM Rhodamine 700 in PMMA. Shown are decays corresponding to 77 K (—) and 298 K (—).
Figure 5.4a. Temperature – dependence in the isolation of A for 10 mM Lumogen Red by 2 mM Rhodamine 700 in PMMA. Shown are ratios corresponding to 77 K (—) and 298 K (—).

Figure 5.4b. Temperature – dependence in the isolation of A for 100 mM Lumogen Red by 2 mM Rhodamine 700 in PMMA. Shown are ratios corresponding to 77 K (—) and 298 K (—).
**Figure 5.5.** Change in $A$ with temperature for 10 mM (squares) and 100 mM (triangles) Lumogen Red in PMMA quenched by 2 mM Rhodamine 700.

**Figure 5.6.** Change in $A/R_0^6$ with temperature for 10 mM (squares) and 100 mM (triangles) Lumogen Red in PMMA quenched by 2 mM Rhodamine 700.
state change in $R_0$ of 13% for 10 mM and 57% for 100 mM, it can therefore be said that
the change in the diffusion constant that occurs with the decrease in temperature as
predicted by Forster is accounted for in the time-resolved determination of $D$ based on
the sensitized decays. It is therefore the variation in $R$ and/or $\kappa^2$ that are the dominating
contributors toward anomalous diffusion as observed for the case of Lumogen Red in
PMMA. This may not be the case for all disordered systems. Lumogen Red is a fairly
rigid molecule with a corresponding narrow distribution of configurational states, and
thus absorption and fluorescence spectra. Such results may not be the same for more
flexible materials, such as conjugated polymers, in which there is a wider distribution of
molecular site energies to play a greater effect on energy migration. For example, in the
work of Gaab & Bardeen [29], temperature-dependent time-resolved anisotropy
experiments performed on MEH-PPV were compared to temperature-dependent steady-
state spectra to see if time-resolved one-step energy transfer rates occur as predicted by
steady-state spectral overlaps. It was found that the time-resolved rates were slower than
predicted by Forster theory based on the steady-state measurements of the spectral
overlap. Therefore, the variations in $J (\Delta J)$ within this more flexible chromophore system
serves a more critical role in slowing down the diffusion constant with time than it does
for the case of the more rigid molecule, Lumogen Red.

5.5 Conclusions

A series of time-resolved fluorescence quenching experiments were conducted at
temperatures ranging from 77 K to 273 K to determine whether or not the temperature-
dependent changes in $J$ as observed in the steady-state data can explain the temperature-dependent changes in energy migration as observed in the time-resolved sensitization data. Results are discussed in terms of how the site to site variations in the parameters $R$, $\kappa^2$, and the $J$ contribute towards the slowing down of the diffusion constant with time within a solid-state matrix. The homogeneous bandwidth of a Lumogen Red/PMMA-based system is reduced through a series of low-temperature steady-state and time-resolved experiments to see how the heterogeneous landscape effects energy migration through the system. It was found that the resulting decrease in $R_0$ obtained from the steady-state data is equivalent to the observed decrease in $A$ as determined from the time-resolved experiments for both the case of 10 mM and 100 mM films. Since the parameter $R_0$ is temperature-dependent whereas the parameters $R$ and $\kappa^2$ are not, it was concluded that while current Forster-based theories covering energy migration are accurate in regards to the $\Delta J$ term given the ability for $\overline{J}$ to explain changes in $A$ with temperature, they are not in regards to the variability in $R$ and $\kappa^2$. Therefore, for the case of rigid small organic molecules such as Lumogen Red, in order to optimize OPV efficiencies, future work should be directed toward controlling $\kappa^2$ and $R$ within the system in order to optimize energy migration.

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Chapter 6: Conclusions and Future Work

6.1 Introduction

The investigation into exciton diffusion through amorphous organic materials has brought to light that within disordered systems in which translational and rotational coordinates as well as spectral site energies remain constant throughout the exciton’s lifetime, there exists a discrepancy between what the diffusion constant should be in terms of the steady-state-based predictions as laid out by FRET theory versus what is measured in the time-resolved fluorescence sensitization of Lumogen Red by 2 mM Rhodamine 700 in PMMA. Results are interpreted in terms of anomalous diffusion, whereby an exciton slows down with time due to a progressive trapping process that takes place within a static heterogeneously-broadened landscape. When the sensitization experiments were repeated within CHCl₃ and DMF, where dynamic fluctuations provide a qualitatively different type of disorder in which there is significant spectral, translational, and rotational degrees of freedom of the molecule that takes place throughout the exciton’s lifetime, it was concluded that the ill-effects of disorder could be effectively diminished as measured diffusion constants become more in sync with the theoretical predictions based on the steady-state data. Thus, engineering the system into one characterized by a dynamic state of disorder in which there exists a rapid averaging over different configurations that prevents the exciton from becoming trapped amongst stationary low energy sites provides a promising path toward optimizing OPV efficiencies. Unfortunately, in terms of OPV-based applications, liquid systems are
impractical due to concerns regarding the evaporation of the active layer. However, the fact that disordered systems can be engineered to enhance exciton diffusion is reassuring in that there may be other ways to work with disordered systems in order to obtain respectable diffusion constants. The aim of future work should therefore be directed towards engineering disordered systems to enhance exciton diffusion. A look at how this is accomplished by naturally occurring photosynthetic light harvesting antenna can help to motivate such endeavors. Such systems contain ordered domains within a disordered environment to direct and transport excitons to the reaction center [1-5]. Perhaps similar systems can be created artificially in the lab given the correct synthetic strategy. In tandem to the development and testing of such strategies, it would be helpful to develop an experimental method that can provide direct measurements of exciton diffusion without the inherent uncertainty that comes with indirect measurements that require the use of an acceptor. In what follows, a closer look is taken at such spectroscopic-assisted strategies involved in future OPV research.

6.2 On the Direct Measurement of the Exciton Diffusion Length through the use of Transient Gratings

The use of sensitization experiments for the determination of exciton diffusion lengths brings with it criticisms requiring the use of an acceptor [6-16]. An inadequate picture of exciton capture by an acceptor can lead to good qualitative agreement with theory, whereby $D$ displays the correct concentration-dependency as predicted by theory, but with actual measurements falling short of those put forth by the same theory [8].
These trends are exactly what has been observed in the experiments discussed within this dissertation. Therefore, there is a need within the field for an optically-based method of measurement that is free of such acceptor-related constraints to achieve more accurate measurements. Alternative methods that either monitor the exciton throughout its lifetime without the aid of an acceptor involves the spatial imaging [17-20] of the excitons or the use of transient gratings [21-24].

Transient gratings are the temporary interference patterns that form when two coherent laser beams intersect each other within a given material. The grating formed within the material is based on the resulting change in the complex index of refraction of the material that occurs upon photoexcitation and corresponds to the constructive and destructive interference patterns of the two incident laser beams. The lifetime of the grating is measured by a third off-resonant probe beam which is diffracted by the grating. The diffracted beam is monitored through time to obtain an exponential decay from which the grating’s lifetime can be extracted through simple fitting techniques. At the higher concentration needed in order for exciton diffusion to occur within the system, the grating becomes distorted as excitons diffuse away from the grating peaks marked by a high concentration of excitons, to grating nulls marked by low concentrations of excitons. As a result, $\tau_{TG}$ decreases as a function of the diffusion constant, $D$, and therefore concentration, with the intensity of the diffracted beam probing the grating decaying at a faster rate [21, 25-29]. Traditionally, methods for measuring $D$ based on transient gratings are used to measure diffusion constants for materials possessing relatively large diffusion lengths [26, 30-36]. A grating with a large interfringe spacing requires the
exciton to travel greater distances to achieve the same degree of destruction of the grating that is obtained by a situation in which the interfringe spacing is small. The interfringe spacing, in turn, is proportional to the angle of the intersection of the two incident beams, \( \theta \), as well as their exciting wavelength, \( \lambda_{ex} \) [22] (see equation 6.1)

\[
\Lambda = \frac{1}{2 \sin \left( \frac{\theta}{2} \right)}
\]

The challenge remains in how to minimize the interfringe spacing to allow for the detection of the small 5-20 nm lengths that characterizes organic materials [10, 12-15, 37-41], a feat that has not yet been accomplished. Currently, the minimization of the interfringe spacing, \( \Lambda \), is accomplished by adopting a suitable pulse-beam geometry set-up. The expression that relates the interfringe spacing, \( \Lambda \), to the angle of the incident beam’s crossing, \( \theta \), leads one to the conclusion that the use of counter-propagating beams is best able to minimize \( \Lambda \) through the optimization of \( \theta \). Prism compression of the incident beams [42] aids in the formation of the highly time-resolved grating needed to detect small diffusion lengths through the ability to detect small changes in the grating with time. Finally, the use of heterodyne detection, in which a control beam is mixed with the signal beam, has been shown to improve signal-to-noise levels of the diffracted signal beam by raising the signal level above that of the instrument response function [43, 44]. Although these tips help to prime the development of an appropriate experimental set-up, further research and experimental work must go into determining what else can be done to make the experimental design adaptable for the measurement of the small diffusion lengths within organic systems.
6.3 On the Use of a Non-volatile Fluid Matrix

Studies on energy migration through a PMMA matrix have shown that anomalous diffusion serves to dampen the measured exciton diffusion with respect to that predicted by steady-state FRET theory. Similar studies performed in liquids showed that such hindrance of exciton motion is due to the restrictions on rotational, translational, and energetic degrees of freedom while embedded in PMMA [45]. The fluidity of the DMF and CHCl₃ liquid matrices allows for a dynamic sampling of rotational, translational and spectral energies during the exciton’s lifetime that promotes exciton diffusion [46]. However, such solvent-based devices are not realistic for OPV-designated applications due to their inherent volatility which raises the concern of the evaporation of the active layer. The use of a nonvolatile solvent such as an ionic liquid, on the other hand, could maintain the fluidity advantage observed within the volatile solvents without the concern over evaporation. Then again, such a matrix does introduce the possibility of Coulombic-based disruptions in exciton motion. Alternatively, a more fluid polymer such as a rubbery polymer [47] may provide a way to enhance exciton diffusion through the mechanism of enhanced configurational degrees of freedom as observed in the fluid solvents. Malachite Green is often used as a probe to determine the relative degrees of freedom allowed within a polymer matrix since its fluorescent properties depends on the level of restriction of its rotational degrees of freedom within a given matrix, with increases in the fluorescence quantum yields occurring with the increase in conformational restriction [48-50]. The characterization of potential polymer candidates
can be accomplished by experimentally monitoring Malachite Green’s fluorescence as a function of $D$ as measured by sensitization experiments similar in fashion to the ones presented in *Chapters 3 and 4*. As Malachite Green’s fluorescence quantum yield increases, energy migration can be expected to decrease due to the increase in staticity of the system.

### 6.4 On the Use of PDIs that form Self-Assembled Nanostructures

Generally speaking, aggregation formation has negative consequences for energy diffusion due to the formation of low energy sites which serve to trap and/or slow down excitons. This is why Lumogen Red’s resistance toward aggregated states makes it an ideal model with which to test out FRET theory. Nonetheless, in light of the fact that photosynthesis utilizes cylindrical-type aggregates to aid in directing excitons to the reaction center, it is not out of the realm of curiosity to wonder whether or not aggregate design is a viable option for enhancing energy migration. In *Chapter 5*, a series of sensitization experiments performed at temperatures ranging from 293 K to 77 K indicated that it is the orientational and translational (versus spectral) disorder that hinders exciton motion through small molecular disordered systems. Heterogeneous disorder is composed of diagonal disorder in which there is a variation in the site energies related to molecular configurations, and off-diagonal disorder, in which there is a variation in the degree of coupling with other molecules [51]. The correlation between the diagonal and off-diagonal elements within a disordered system has been suggested as a means by which to enhance energy migration through the system [51, 52]. Such
correlation can be said to be responsible for the desirable exciton migration rates that are believed to occur naturally within the photosynthetic systems in which the molecular dipoles are aligned with each other in such a way so as to optimize energy transfer rates amongst chromophores despite being embedded within a heterogeneously broadened background [1, 2, 4, 5, 53-57]. There are many perylene diimides that have been shown to display self-assembled ordered aggregates related in structure to these cylindrical photosynthetic aggregates; the so-called J-aggregates [51, 58-62] and chiral helices [60, 61, 63-68]. It would therefore be interesting to see how energy migrates through an amorphous solid, such as PMMA, filled with such aggregated molecules. Evaluation of the presence/strength of such aggregates can be explored via Circular Dichroism (CD) spectroscopy [64, 69-71]. Only chiral helical species give rise to a CD signal. Sensitization experiments can be ran in parallel to determine how $D$ scales with CD strength. A look into the occurrence of exciton fission [72] within such systems might also be of interest, as well as the possibility of energy transfer from states higher than the first excited singlet [73]. Finally, certain PDIs have also been shown to form highly ordered domains within originally amorphous films [17, 74-84], either spontaneously after being spin-coated or with the aid of thermal or solvent annealing. The placement of self-assembled PDI liquid crystals [81, 85, 86] onto solid substrates to form ordered films represents yet another way in toward obtaining semi-ordered systems via self-assembly [64, 87-90].
6.5 On Directing Energy Flow Through the Use of Gradient Cells

Section 6.3 focused on engineering disorder via the temporal variation in $\kappa^2$ and $R$ through the use of nonvolatile liquids to enhance energy migration. Section 6.4 focused on ways to manipulate the variation in $\kappa^2$ via the formation of cylindrical/helical/J-type aggregates within an otherwise disordered systems. This section focuses on how to engineer systems based on variations in the intermolecular distances as a way to funnel/direct excitons through disordered systems. Energy migration has been shown to be limited in static solid-state system by anomalous diffusion due to site-to-site changes in the relative intermolecular distances, molecular orientations, and spectral-site energies. By manipulating the relative site-to-site changes in these parameters, energy flow can be directed as desired [91-94]. In photosynthesis, light is harvested from the photosynthetic antennas and directed toward a reaction center where charge separation takes place. The funneling of energy toward the reaction center is similar in principle to the desired funneling of excitons toward an interface for charge separation to occur within an OPV. There have been attempts made by researchers to find such ways to direct energy flow [95-98]. For instance, the creation of cells with in-built gradient systems can aid in directing energy flow toward an interface placed at the bottom of the gradient. The gradient may be a concentration gradient, by which the decrease in the intermolecular distances between the chromophores serves as a means by which to direct exactions to an interface. Alternatively, the gradient can be formed by changes in the refractive index of
the matrix, given the relation between \( n \) and \( R_0 \) in Forster theory [99, 100] (see equation 6.2)

\[
R_0^6 = \frac{9000 \ln(10) \phi \kappa^2}{128 \pi^5 N_A n^4} \int_0^\infty \varepsilon(v) f(v) \frac{d\nu}{\nu^4}
\]

with changes in the refractive index controlled by the mixing of one or more polymer systems [101]. Actual formation of the gradients, whether concentration-based or matrix-based, can be formed as reported previously for Lumogen Red within a polymer matrix via the use of a microextruder [102]. The challenge here would be to change the scale of the extruder form that of a microextruder to a “nanoextruder”. The evaluation of such gradients could be accomplished using evanescent waves as the fluorescence intensity changes with the depth of the evanescent wave [103]. Alternatively, energy networks can be formed through means of self-assembly. Many PDIs possess the capability to form self-assembled nanofibers [61, 104] and organogels [105-109] which could be dried and used to create OPVs with built in percolation networks. In such an OPV, the nanofiberous network aids in directing excitons and/or charge carriers through a given material that acts as either donor or acceptor, whichever role compliments that of the nanofiberous network [110].

6.6 Conclusions

In this thesis, it was found that for the case of Lumogen Red embedded in PMMA, energy migration falls short of steady-state based predictions for \( D \). This has since been confirmed through the work of Fennel and Lochbrunner in their investigation into energy migration through 50 – 150 mM Lumogen Red PMMA films doped with 0.3
– 3 mM Oxazine 1 [111]. Theoretically, $\eta$ in the expression for $D$ should range between 0.32 and 0.56. When diffusion constants were measured in CHCl$_3$ and DMF, quantitative agreement with theory was obtained in that the scaling constant, $\eta$, was determined to lie between 0.23 for the latter and 0.31 for the former versus 0.08 in PMMA. Miller et al. similarly found $\eta$ to be on the order of 0.20 in their investigation of energy migration through the two liquid-based systems, disodium fluorescein in ethanol [112] and oxazine 1 perchlorate in methanol [113]. It can therefore be said with confidence that although static systems serve to decrease the diffusion constant with time, such effects are mitigated within a fluid environment as the liquid environment serves to essentially “wash out” unfavorable conditions that can serve to trap excitons. Strategies have been discussed regarding the engineering of disorder in OPVs as a way to enhance exciton diffusion lengths and improve cell efficiencies along these lines.

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