Investigation of Dispersive Kinetics in the Time-dependent Photoluminescence of Dye-sensitized Nanoparticle Films

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ABSTRACT

(Under the direction of Christopher Fecko)

Mesoporous titanium dioxide nanoparticle films sensitized with ruthenium polypyridal chromophores provide the main architectural framework of dye-sensitized solar cells. The design of these systems is based on the interfacial photoinduced charge separation that occurs when an excited chromophore transfers an electron to acceptor states within the semiconductor material. This process is also called electron injection. If electron injection cannot occur, the excited chromophore can relax through the emission of a photon. Therefore, observing the time-dependent photoluminescence decay of these systems can provide insight on the efficiency of the electron transfer process.

This dissertation investigates the dependence of the time-dependent photoluminescence decay on various factors using time-correlated single photon counting techniques with a home-built two-photon laser scanning setup. Interestingly, the time-dependent photoluminescence follows power-law kinetics when electron injection is most efficient. Power-law kinetics are a specific type of dispersive kinetics and several other dispersive kinetic models are also examined in this work.

By adjusting the electrolyte composition of these systems as well as applying an electrical bias, the kinetic drive for electron injection can be adjusted. As the kinetic drive for injection decreases, the observed kinetics become less dispersive. At no point,
however, is there an observed unquenched, purely emissive population. It is suggested that cross-surface energy transfer provides an alternative route for excited state relaxation.

The current model for electron transfer is based upon electron injection into a continuum of acceptor states in the conduction band of the semiconductor. However, there exists an exponential distribution in energy of sub-bandgap acceptor states due to defects on the nanoparticle surface. The work presented in this dissertation provides evidence for a modification of the current model where chromophores are strongly coupled to only a small number of these localized trap states which lead to the dispersive kinetics we observe.
To all those who have supported me along the way
ACKNOWLEDGEMENTS

There have been many people who have encouraged and assisted me throughout my life and I am grateful for such a large support network. Specifically my friends and family from the 4-H program have been there for me whenever I needed encouragement, advice, or someone to share my accomplishments. So many hardships were overcome by the heartening words of a 4-H friend.

While most people remember high school educators as the ones who ignited the spark of learning, I was blessed to have an exceptional elementary school education. All of my teachers at Glade Creek Elementary- from kindergarten to 6th grade- saw my potential and provided me with a strong foundation for future learning. They continue to be invested in my success even to this day. However, my specific science interests were developed at Bridgewater College under the guidance of Dr. Kenneth Overway. His organized teaching skills and passion for science along with his earnest concern for his students fostered an environment where discovering scientific research was an enriching process.

For my graduate studies, I was lucky to work with one of the most intelligent, caring, and motivating advisors, Dr. Christopher Fecko. He introduced me to spectroscopy and was very patient in allowing me to learn my way around the lab. I respect his approach to the scientific process and he has taught me how to read and write
scientific literature. But most of all, I appreciate his concern for me as a human being. Throughout my graduate studies, he pushed me to be a greater scientist but never at the sake of my well-being and happiness.

I owe much gratitude to the other members of the Fecko group. Lori Dorward and Asima Chakraborty took me under their wings my first few years and made my transition to graduate school an easy one. Working with Matthew Daddysman and Michael Tycon has been an honor and I have learned much- both about science and life in general- through daily interactions with them.

I must also thank the many gifted scientists who were my fellow teammates in the various teams I’ve been involved with within the Energy Frontier Research Center. The project presented in this dissertation was born out of an initial collaboration with Dr. Rene Lopez and his graduate student, Rudresh Ghosh. I am also hugely grateful for the assistance and guidance of Dr. Kenneth Hanson who was never too busy to answer a question and introduced me to electrochemistry. The conversations during (and especially after) team meetings were often highly productive, and I must thank Dr. John Papanikolas and Dr. Kyle Brennamen for their insights and suggestions. And lastly, this work could not have been accomplished without my fellow collaborators who synthesized the materials used in my studies. Dr. Leila Alibabaei and Hanlin Lou synthesized the nanoparticle films and Dennis Ashford synthesized the phosphonated ruthenium chromophores.
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ADC</td>
<td>analog to digital converter</td>
</tr>
<tr>
<td>BBO</td>
<td>$\beta$-barium borate</td>
</tr>
<tr>
<td>BET</td>
<td>back electron transfer</td>
</tr>
<tr>
<td>CFD</td>
<td>constant-fraction discriminator</td>
</tr>
<tr>
<td>DSPEC</td>
<td>dye-sensitized photoelectrosynthetic cell</td>
</tr>
<tr>
<td>DSSC</td>
<td>dye-sensitized solar cell</td>
</tr>
<tr>
<td>FTO</td>
<td>fluorine doped tin oxide</td>
</tr>
<tr>
<td>frac. res.</td>
<td>fractional residual</td>
</tr>
<tr>
<td>FWHM</td>
<td>full-width at half max</td>
</tr>
<tr>
<td>GaAsP</td>
<td>Gallium Arsenite Phosphate</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>KDP</td>
<td>potassium dihydrogen phosphate</td>
</tr>
<tr>
<td>KWW</td>
<td>Kohlrausch William Watts</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest occupied molecular orbital</td>
</tr>
<tr>
<td>NA</td>
<td>numerical apperature</td>
</tr>
<tr>
<td>PMT</td>
<td>photomultipling tube</td>
</tr>
<tr>
<td>RuP</td>
<td>$[(\text{Ru}(\text{bpy})_2(4,4'-(\text{PO}_3\text{H}_2)_2\text{bpy}))^{2+}$</td>
</tr>
<tr>
<td>TA</td>
<td>transient absorption</td>
</tr>
<tr>
<td>TAC</td>
<td>time to amplitude converter</td>
</tr>
<tr>
<td>TBA</td>
<td>tetrabutylammonium</td>
</tr>
<tr>
<td>tBp</td>
<td>4-tert-butylpyridine</td>
</tr>
<tr>
<td>TCSPC</td>
<td>time-correlated single photon counting</td>
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LIST OF SYMBOLS

A  absorptivity
A  amplitude
α  disorder parameter
β  stretching parameter
c(t)  time-dependent concentration of excited state
c_A(t)  time-dependent concentration for Albery Model
c_{kww}(t)  time dependent concentration for KWW model
c_{PL}(t)  time-dependent concentration for power-law model
D*  dye excited state
D+  oxidized dye
E  Energy
E^{*}_{dye}  excited state energy level of the chromophore
f(E,E_F)  Fermi occupation at Energy E
ΔG^†  activation barrier
ΔG^†_{o}  minimum activation barrier
Γ  gamma distribution

\text{g}(E)  density of TiO_2 states
\text{g}_A(k)  log-normal rate constant distribution
\text{g}_{kww}(k)  Levy stable distribution function
\text{g}_{PL}(k)  distribution of rate constants for power-law model
γ  magnitude of the energetic dispersion
k  emission rate constant
\( k' \) observed rate of excited state decay

\( k_B \) Boltzmann constant

\( k_{em} \) rate of photon emission

\( k_{inj} \) rate of electron injection

\( k_{injection} \) rate of electron injection

\( k_{nr} \) nonradiative rate constant

\( k_o \) barrierless rate constant

\( k_r \) radiative rate constant

\( k_{wwt} \) rate constant from KWW model

\( I \) intensity

\( J_{SC} \) short circuit current

\( L_{aa} \) excitation wavelength count in sample-free solvent

\( \lambda \) reorganizational energy for electron injection

\( p_A(x) \) normalized distribution

\( P_b \) indirect emission intensity

\( P_c \) direct emission intensity

\( p_{PL}(x) \) exponential distribution

\( \Phi \) quantum yield

\( R \) gas constant

\( r \) Pearson product moment correlation coefficient

\( t \) time

\( \tau \) characteristic lifetime

\( T \) temperature
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$\Delta \tau$</td>
<td>range of characteristic times</td>
</tr>
<tr>
<td>$\langle \tau \rangle$</td>
<td>average characteristic time</td>
</tr>
<tr>
<td>$t_{\text{min}}$</td>
<td>cross over time</td>
</tr>
<tr>
<td>$V$</td>
<td>electronic coupling</td>
</tr>
<tr>
<td>$V_{\text{OC}}$</td>
<td>open circuit voltage</td>
</tr>
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CHAPTER 1. Introduction

1.1. Motivation for developing solar energy technologies

Due to the increased global demand of energy coupled with the concern of increased carbon dioxide concentrations in our atmosphere from the burning of fossil fuels, solar energy is a desirable resource that has yet to be efficiently utilized. It was estimated that earth consumed 15 TW of energy in 2008, and it has been projected that earth’s energy consumption will double by 2050.\(^1,2\) This energy gap can be overcome by tapping into the immense energy (89,300 TW) that reaches the earth from the sun.\(^2\) However, currently solar technologies only make up a small percentage of the sources of energy that we consume.\(^3\)

Some current solar technologies utilize the photoelectric effect to convert sunlight into electricity. The energy from a photon from the sun is used to excite an electron in a semiconductor material that can be extracted and used for electricity. The most familiar solar cell technology is the crystalline silicon solar cell. The ultrapure crystalline silicon in these solar cells absorbs photons from the sun and conducts the excited electrons for use as electricity. The problem with this technology is that the ultrapure crystalline silicon is expensive to produce and the lifetime of these delicate cells is not long enough to compensate for the cost.\(^4\)

Much work has been done to develop other cheaper technologies that can harvest the energy from the sun and convert it into energy we can use. These include thin-film...
technologies, organic photovoltaics, as well as dye-sensitized solar cells.\textsuperscript{5-7} While these technologies have lower efficiencies than the crystalline solar cell devises, their low costs will hopefully be able to compensate. While this achievement has yet to occur, they have become increasingly more efficient over the past few decades.\textsuperscript{8} Further research to improve the efficiencies of these devices may finally allow for solar technologies to economically compete with other energy sources.

This work focuses on one of these alternative approaches, the dye-sensitized solar cell, and aims at characterizing the different kinetic process that occur in transforming light into electricity. These different kinetic processes must occur in timescales in conjunction with one other. The process of directing an electron towards an electrode must be quicker than the detrimental processes that lead to the decay of the excited state. Therefore, it is beneficial to understand what kinetically drives these processes and how environmental factors influence the timescales of these events.

One of the kinetic processes this work investigates is the interfacial charge transfer that occurs between the dye molecule and the semiconductor in dye-sensitized solar cells. In this study, the kinetics of this process have been measured using time-dependent photoluminescence spectroscopy to observe how the excited state lifetime decay changes with different environmental factors. The excited state decay of various sensitized nanoparticle film systems has been studied before,\textsuperscript{9-13} but the work presented in this dissertation expands on these works and investigates not only the lifetime of the excited state decay, but the distribution of lifetimes as well. Understanding the origins of this distribution can help explain the current limitations of these devices and possibly lead to the more efficient designs.
1.2. Dye-Sensitized Solar Cells

The semiconductor most often used in current solar harvesting devices is ultrapure crystalline silicon which is very expensive to produce. There is an interest to incorporate other, cheaper semiconductors. One of these semiconductors is titanium dioxide (TiO$_2$), which is a cheap and abundant material often used as a white pigment in many every day materials. However, TiO$_2$ has a wider bandgap than crystalline silicon and therefore only absorbs in the UV of the solar spectrum. To solve this problem, a sensitizer dye can be attached to the surface of the semiconductor where the responsibilities of light absorption and charge transport are separately delegated to the dye and semiconductor respectively. In the simplistic model, an excited chromophore will transfer or “inject” an electron into the conduction band of the semiconductor. However, since strong coupling is required between the dye molecule and the semiconductor, only a monolayer of dye can be bound. This limits the amount of light that can be absorbed.

The solution that O’Reagan and Graetzel proposed to increase the amount of light absorbed was to increase the surface area by sintering nanoparticles into a film. This creates a mesoporous network with an increased surface area where more of the dye molecules can bind, increasing the amount of light that can be absorbed. The sintered nanoparticle network also allow for electron conduction to take place where an electron injected into TiO$_2$ from a photoexcited chromophore on the surface can diffuse from the interface of the film to an electrode to be used for work. This idea is the basis for dye-sensitized solar cells (DSSC). In complete DSSCs, the sensitized nanoparticle film is placed in an electrolyte solution including an iodide/triiodide redox couple that reduces the
oxidized chromophore back to its ground state after it has been oxidized by electron transfer. The oxidized triiodide diffuses to the counter electrode where it is reduced back to iodide, which completes the circuit of the device. Therefore a DSSC is a completely regenerative device that, in theory, could be used indefinitely to transform solar energy into electricity.

1.3. The importance and relationship of the semiconductor and the dye

One of the main components of a DSSC is the semiconductor nanoparticle film. The semiconductor most often used in DSSC is TiO$_2$ but others have been used including ZnO, SnO$_2$, and Nb$_2$O$_5$. Semiconductors are used for solar harvesting devices due to the bandgap that exists between the valence band and conduction band. The electrons of a single atom possess a highest occupied molecular orbital (HOMO) and a lowest unoccupied molecular orbital (LUMO). If multiple atoms are in close proximity and interact with each other, the orbitals for each electron will split slightly so that with many atoms there exists a band of HOMOs called the valence band where electrons are tightly held to a specific atom, and a band of LUMOs called the conduction band where electrons are free to diffuse around the entire material. If these two bands overlap in energy, such as the case in a metal, in normal conditions many electrons exist in the conduction band and can conduct electrons easily. If there is a large energy gap between the valence band and the conduction band, also called a bandgap, then it takes very large amounts of energy to excite an electron from the valence band to the conduction band. These materials do not conduct electricity well and are therefore called insulators. In a semiconductor, there exists a small bandgap so that reasonable amounts of energy can excite an electron into the conduction band. The size of the gap establishes how much
energy is required to excite an electron into the conduction band and therefore determines the amount of energy an electron in the conduction band possesses that can be used for work. This is why TiO\textsubscript{2} is an ideal candidate for use in solar harvesting devices because not only is it cheap and abundant, but it also has a wide bandgap of about 3.2 eV.

This wide bandgap however, poses a problem when you consider the solar spectrum. An ideal solar device should be able to absorb a majority of the solar spectrum. The amount of the solar spectrum a material can absorb is dependent on the bandgap. As mentioned earlier, the bandgap is the amount of energy needed to excite an electron from the valence band into the conduction band. If the light does not have enough energy to overcome this barrier, then that light is not absorbed. Therefore the bandgap determines the minimum energy, or maximum wavelength, that can be absorbed by the material. With TiO\textsubscript{2}’s 3.2 eV bandgap, it can absorb light with a wavelength of 387 nm or lower. This is a small portion of the solar spectrum. Most of the solar spectrum spans across the visible and even extends into the infrared.

In order to absorb out into the visible spectrum, semiconductors have been sensitized with dye molecules that can absorb longer wavelengths of light and be able to transfer that energy through electron transfer to the semiconductor. Dye molecules, also called chromophores, absorb a photon which evokes an electronic transition from the ground state to the excited state. If this excited state of the chromophore lies above the conduction band edge, then the chromophore can then transfer the energy through electron transfer, also called electron injection, into the conduction band of the material. This creates a charge separation where the electron can than diffuse through the material and be collected at the electrode while the hole remains on the chromophore.
The qualities of a good dye include efficient absorption over the solar spectrum, possessing an excited state above the conduction band of the metal oxide, long lived excited states, and photostability on the semiconductor surface. Much work has been done to improve the ability of the chromophore to absorb the solar spectrum. This has led to the development of the so-called “black” dye which is a polypyridal ruthenium chromophore that has a wide spectral response and is able to absorb far into the red visible spectrum.\textsuperscript{15} The series of polypyridal ruthenium chromophores have excited states above the conduction band edge of TiO\textsubscript{2}, making them viable for electron injection, but they also possess long lived excited states due to quick intersystem crossing from an initial singlet to long-lived triplet excited states. This increases the efficiency of devices because the longer the dye stays excited, the more probable the electron transfer will occur before the chromophore relaxes back to the ground state. Lastly the chromophore must be stably bound to the semiconductor. The initial dye in Graetzel’s DSSC used a carboxylate anchoring group. However it was shown that photodecomposition through loss of the carboxylated bipy-ligand occurred within only a few minutes of light exposure.\textsuperscript{16} It has recently been shown that use of a phosphonated linker increases the chromophores photostability, especially in aqueous conditions.\textsuperscript{17} With all of these considerations in mind, the chromophore used in the experiments presented in this dissertation is a polypyridal ruthenium chromophore with a phosphonated bpy ligand (hereafter referred to as RuP).

1.4. Excited state decay kinetics and dispersive kinetics

As mentioned in the previous section, electron injection needs to happen before the chromophore relaxes to the ground state. In free solution, where electron injection
does not occur, the time-dependent excited state chromophore population, \( c(t) \), relaxes through the emission of a photon following first order decay kinetics.

\[
c(t) = -k_{em}t
\]  

(1.1)

where \( k_{em} \) is the rate of photon emission. This process occurs with a well defined lifetime, \( \tau \), given by

\[
\tau = \frac{1}{k_{em}}
\]  

(1.2)

However when bound to the semiconductor with a conduction band edge lower than the excited state, the chromophore can also relax through electron injection. This nonradiative process competes with the emissive relaxation pathway and quenches the emission. Assuming injection also follows first-order kinetics with a well-defined rate \( (k_{inj}) \), as it would if injection occurred directly from the excited chromophore into the conduction band, the excited state population would decay with an observed rate, \( k' \), following eq. 1.3.

\[
c(t) = -k_{em}t - k_{inj}t = -(k_{em} + k_{inj})t = -k't
\]  

(1.3)

This current model for electron injection into semiconductors is based on theories proposed by Marcus and Gerischer.\textsuperscript{18,19} This model typically assumes that the chromophores are strongly coupled to an energetic continuum of acceptor states in the conduction band of the semiconductor. Marcus theory assumes a parabolic function with respect to the reaction coordinate that is associated with the reorganization energy of the solvent surrounding the excited chromophore. If the donor is strongly coupled to a sufficiently broad energetic continuum of delocalized semiconductor acceptor states, a subset of these states will intersect with the minimum of the donor parabola. In other words, there would be no barrier to electron transfer from the chromophore to a subset of delocalized acceptor states in the continuum and the rate of injection would only be dependent on the density of acceptor states. Since all chromophores
would inject with the same rate, the excited state would decay with monoexponential decay kinetics.

As is predicted by the Marcus-Gerischer model and illustrated in equation 1.3, the excited state decay that occurs from the quenched emission due to electron injection should follow first order decay kinetics; however it will be shown later that the decay of these quenched systems is nonexponential. This discrepancy is likely due to the fact that there exist, within the bandgap, energetic trap sites caused by defects on the nanoparticle surface. The results presented in this dissertation support a model where injection occurs into these sub-bandgap sites, rather than the conduction band itself.

Instead of a single well-defined lifetime, the excited state population of our samples decays with a distribution of lifetimes. Kinetics that occur with a distribution of lifetimes are known as dispersive kinetics. It is desirable to know the shape of this distribution. While the real distribution may take an arbitrary form, it may be approximated by a well-defined functional form. The parameters that describe this functional form include the characteristic lifetime and the width of the distribution. The characteristic lifetime is the value where it is equally likely that a value within the distribution is greater than or less than the characteristic value. The width is a parameter that defines the extent of the dispersion in the measurement values. Understanding the shape of the distribution provides physical information on why the distribution exists. Several models that define these parameters have been developed to describe dispersive kinetics and will be discussed in detail in Chapter 3.

1.5. Interfacial charge transfer kinetics

The kinetics of charge transfer are strongly influenced by the relative energetics of excited state of the chromophore and the acceptor states associated with the
conduction band. Electron transfer can only happen if the conduction band edge falls below (away from vacuum) the excited state of the chromophore, and is faster the larger this difference. Various chemical additives have been used to adjust this difference by taking advantage of the Nernstian dependence of the TiO$_2$ conduction band edge on effective pH.$^{9,10,21-27}$ It has been shown that protons in acidic aqueous solutions shift the conduction band edge away from vacuum and lithium ions in acetonitrile solutions have similar effects. This is assumed to be due to electron accumulation caused by the presence of these small cations.$^{28}$ While this increases the short circuit current ($J_{SC}$), the lower conduction band edge also reduces the open circuit potential ($V_{OC}$) which limits the overall device efficiency.$^{29}$ Conversely, the molecule 4-tert-butylpyridine (tBp) binds to the surface of the semiconductor and has the opposite effect on this electron accumulation and raises the conduction band edge. This raises the $V_{OC}$ but lowers $J_{SC}$.\(^{23,24,30}\) A careful compromise must be made to position the conduction band edge low enough to kinetically drive electron injection, but high enough to maximize the $V_{OC}$ allowing for optimal device performance. A demonstration of how the kinetics of interfacial charge transfer are influenced by the presence of these chemical additives will be discussed in Chapter 4 of this dissertation.

1.6. Layout of Dissertation

To help guide the reader through the material discussed in this dissertation, a brief overview will now be presented. The introductory chapter has provided the background and context for the work that is presented in the later chapters. In Chapter 2 I present detailed descriptions of the methods I used in the experiments performed and a background on the techniques and instrumentation.
The next three chapters will present the results of the studies on the time-dependent photoluminescence of the dye-sensitized nanoparticle film systems. Chapter 3 will present a study where the time-dependent photoluminescence decay possesses power law decay kinetics when electron injection is highly favored. Power-law decay kinetics are a type of dispersive kinetic model and this chapter will compare this kinetic model to other dispersive kinetic models. Chapter 4 will extend this study and investigate how the addition of various chemical additives and applied electric potential affect the distribution of lifetimes. In this study a relationship between the characteristic lifetime and the amount of dispersion was found and the origin of this relationship is explored. Chapter 5 will investigate how cross-surface energy transfer plays a role in the time-dependent photoluminescence decay curves.
REFERENCES


CHAPTER 2. Materials and Methods

2.1. Time-correlated single photon counting (TCSPC) laser scanning setup

To study interfacial charge transfer kinetics we used time-correlated single photon counting (TCSPC) to measure the excited state lifetime of photoexcited chromophores bound to nanoparticle films. Since electron injection quenches the emission of excited chromophores, by studying the time-dependent photoluminescent decay of the sensitized films, we can learn how different parameters influence the interfacial kinetics. TCSPC works by creating a histogram of the time it takes for a sample to emit a photon after it has been excited. It utilizes a pulsed excitation source that is split into two channels: one that is directed to a photodiode that sends a signal to the TCSPC electronics as a timing reference, and a second channel that is directed to excite the sample. The emission from the sample is detected by a photomultiplier tube (PMT) which sends a second timing signal to the TCSPC electronics. Since this whole process occurs on the microsecond timescale, this process can be repeated millions of times to develop a histogram that can be fit by different kinetic models.

One of the unique benefits of our system is the ability to excite our sample using two-photon excitation. Two-photon excitation occurs when two photons, each half the energy usually required to excite a sample, are absorbed simultaneously to achieve an excited state similar to the absorption of a single high-energy photon. This is a nonlinear process and the extent of two-photon excitation is proportional to the intensity squared. This means that two photon excitation only occurs in areas of high photon flux which can
be achieved at the focus of an objective lens. The small diffraction limited excitation volume provides spatial resolution on the order of hundreds of nanometers. The specific benefits of this spatial resolution will be discussed in Chapter 3.

A diagram of the two-photon TCSPC set up is shown in Figure 2.1. The excitation source used in our experiments is a Coherent Chameleon Ultra II Ti:sapphire laser. The output of this laser can be tuned between 680 nm to 1080 nm and produces ultrashort pulses (200 fs pulse duration). Since RuP has an absorption maximum at around 450 nm, the laser can be tuned to 900 nm to achieve maximum two-photon excitation. The initial output of our laser is approximately four Watts—a gross excess of the power needed in our experiments. Therefore we use an electro-optic modulator to reduce the power to approximately 10 mW measured at the sample position. This leads to pulse energies of ~0.12 nJ, and with our measured excitation beam radius of 206 nm (measured at the focus of the objective lens as described below), this gives a maximum energy density of 4.5 kW/cm². Only a fraction of the chromophores will be excited by two-photon absorption. The calculations used to determine the number of excited chromophores per nanoparticle per pulse can be found in Appendix 1. Achieving less than one excited chromophore per nanoparticle per pulse prevents any unwanted second order decay processes, such as triplet-triplet annihilation, which would also influence our photoluminescence decay.³ Furthermore, the light that is not absorbed simply passes through the sample which decreases photodegradation of our sample.

The initial repetition rate of the laser is 80 MHz, but this is much too fast given the long excited state of the RuP chromophore which has an excited state lifetime in free
Figure 2.1: Two-photon laser scanning TCSPC setup
solution of about 5 μs. To ensure that we allow for complete relaxation of all chromophores between subsequent excitation pulses, we used a second high-bandwidth electro-optic modulator (Con Optics 350-160) to reduce the repetition rate to 50 kHz. This electro-optic modulator works by allowing only one pulse to pass through every 20 μs while suppressing all other pulses.

After reducing both the power and the repetition rate, the excitation pulse is then passed through an angled coverslip that has been positioned within the excitation beam path. A majority of the light passes through the coverslip and is directed to the sample, but a small fraction is reflected and directed toward a fast photodiode for use as a timing reference. The emission of a single photon from the excited sample is detected by a GaAsP PMT (Hamamatsu H7422P-40mod) which sends a second timing signal to the TCSPC electronics (Bekcer & Hickl SPC-130). Since there are large pulse-to-pulse fluctuations in the PMT gain, these single-photon signals could vary greatly with respect to amplitude. In order to identify the timing of this event, a trigger must be used. However, a leading-edge discriminator would lead to a timing jitter since a defined threshold would be achieved at different times depending on the amplitude of the signal. Therefore a Constant Fraction Discriminator (CFD) is used as a trigger at a constant fraction of the pulse amplitude and subsequently removes this timing jitter. The signal from the fast photodiode that detected the small fraction of light reflected off the coverslip is used to obtain another timing signal through a second CFD. These two outputs, one from the PMT and one from the fast photodiode, are used as the start and stop pulses of a time-to-amplitude converter (TAC). The start pulse begins the charging of a capacitor and the stop pulse ends it. Therefore the voltage at the capacitor is
dependent upon the timing between the two pulses. The output of the TAC is then sent to an Analog-to-Digital Converter (ADC) which assigns a digital readout to the photon detection time. As the excitation process is repeated, the ADC allows for a histogram of photon detection times to be constructed.

Since such low powers are used, many pulse cycles do not result in an excited chromophore and do not emit a photon. To prevent starting a barren TAC through a complete cycle, the reversed start-stop method is used. Here the TAC is started only by the detection of a photon from the PMT and stopped by the subsequent timing pulse from the fast photodiode. A higher amplitude results from a shorter photon arrival time.

In order for the timing pulse from the fast photodiode to arrive at the TCSPC electronics after the detection of the photon by the PMT, the signal from the photodiode must either be delayed physically by passing the signal through increasing lengths of cable or electronically through the use of a digital delay. Since 1 ns corresponds to 20 cm of cable length and the lifetime of the chromophore is on the order of 5 μs, this would require 100 meters of cable. Rather than incorporating 100 meters of cable into our setup, the signal was delayed using a digital delay generator (Standord Reseach Systems DG535). The instrument response of the entire TCSPC system was limited by the response of this digital delay generator, which led to a full width at half max (FWHM) of about 3.6 ns.

The portion of the excitation beam that passed through the angled coverslip passes through a home-built laser scanning microscope setup before excitation of the sample. This set up allows for quick imaging of the surface and the ability to position the laser on a specific area of the sample. This was achieved by sending the excitation beam through
mirror galvanometers that provide x,y positioning of the laser. The beam is then directed into an inverted microscope and focused onto the sample by a 60x, 1.2NA water immersion objective lens (Olympus UPLSAPO 60XW). The back aperture of the lens is slightly overfilled to create a diffraction-limited focal spot. The epifluorescence is then collected through the same objective lens and directed towards the PMT for detection.

2.2. Electrochemical measurements

A working solar cell device in sunlight will have a slightly higher electric potential due to the injected electrons into the conduction band of the semiconductor. Therefore it is also imperative to study the effects of applied potential on the interfacial charge transfer kinetics. To do this, the sintered nanoparticle film is synthesized on a conductive glass surface. After sensitization with the RuP dye, this film can be incorporated as the working electrode into a three-electrode electrochemical cell. In this setup a Wavenow potentiostat (Pine Research Instrumentation AKCABLE3) maintains a constant potential on the working electrode relative to a reference electrode. There are many different types of reference electrodes that are appropriate for different solvents. Since our experiments were mainly performed in acetonitrile, we used a Ag/AgNO₃ reference electrode. Finally, the third electrode used in this setup is a platinum wire for the counter electrode.

A potentiostat uses all three electrodes to maintain a constant potential between the working electrode and the reference electrode. At the reference electrode there is a reaction that is occurring with a known potential and in our case it is the redox reaction between a silver wire and silver nitrate in solution. If we just used a working electrode and a reference electrode, the reaction at the working electrode would cause current to
flow across the reference electrode resulting a shift in that reaction’s potential. Therefore our reference would no longer be constant. To correct for this, a third electrode is incorporated called a counter electrode. This electrode is an inert electrode, in our case a platinum wire, and current passes through this electrode rather than the reference electrode. In summary, the potentiostat applies a potential between the working and reference electrode and measures the current between the working and counter electrodes.

2.3. Sample Preparations

This dissertation presents studies performed on sensitized metal oxide nanoparticle films. Most studies utilized TiO$_2$ nanoparticle films in order to study interfacial charge transfer kinetics. As a control, ZrO$_2$ films were used since the high conduction band edge of this semiconductor prevents electron injection. These films are deposited on an FTO substrate by the sol-gel process$^{4,5}$ and consist of nanoparticles that are 20 nm in diameter. The thickness of these films are 7 $\mu$m for the TiO$_2$ film and 3 $\mu$m for the ZrO$_2$ film. The benefit of these films is that they are optically transparent.

For the sensitization process, the films are immersed in 150 $\mu$m [(Ru(bpy)$_2$(4,4’-(PO$_3$H$_2$)$_2$ bpy))$^{2+6}$ (RuP) in 0.1 M perchloric acid solution (pH 1) for at least three hours. This is the time it takes for a complete monolayer of dye to adsorb to the surface which was determined by tracking the absorbance at 450 nm. After three hours, no further time in the sensitizing solution resulted in increased absorption. For convenience, films were most often left to sensitize overnight. To remove any dye aggregates from the surface, the sensitized films were then immersed in methanol for at least three hours.

To study films immersed in various electrolyte solutions, a temporary chamber is created between a glass coverslip and the sensitized nanoparticle film using Teflon
spacers. This chamber is filled with the electrolyte solution containing various concentrations of the specified chemical additive. All chemical additive experiments were performed under ambient conditions. Electrochemical studies were performed with the nanoparticule film incorporated as the working electrode in a three-electrode cell. To remove any electrochemical influence from dissolved oxygen in our solutions, the samples were sealed and deoxygenated by bubbling argon gas through the system for 40 minutes.

2.4. Data Fitting procedure

The data that we collect from our TCSPC measurements are histograms of the time it takes for a photon to be emitted after the reference photodiode identifies the arrival of the excitation pulse. For most experiments, the entire collection window is five thousand nanoseconds and with 4096 channels, each data point is a binned number of events that occur in a 1.22 ns window. In one experiment a shorter collection window of 500 nanoseconds is used to increase the time resolution so that each data point is binned into a 0.12 ns window. The time axis is corrected to identify time zero as the time the sample was excited rather than the time the photodiode observes the excitation pulse. Since the peak of the histogram would shift depending on the amplitude of the histogram, time zero is identified from a threshold in the leading edge of the peak determined from a constant fraction of the peak amplitude. All data is corrected to the same constant fraction threshold of thirty percent of the peak amplitude; this threshold was determined from the instrument response function.

These time-corrected histograms are then normalized and fit with various kinetic models. This fitting was done using in-house MATLAB (MathWorks) scripts employing the lsqnonlin fitting function. Each fitting function was convolved with the experimentally
measured instrument response function before fitting. Due to the long lived excited state of the RuP chromophore, we observed emission from a wide range of timescales, from the nanoseconds to microseconds. Initial fits that reduced the sum of the unweighted residuals did not adequately fit the long-time tails of emission decays due to the low value of the data at these times. To adequately reproduce data that spans a wide range of amplitudes, we applied a fitting function that minimized the sum of the fractional residual (frac. res.) weighted by Poisson signal-to-noise ratio (shot noise due to counting a discrete number of photons) at each time point:

\[
\text{frac. res.} = \sum \left( \frac{\text{fit}_i - \text{data}_i}{\text{data}_i} \right) \times \sqrt{|\text{data}_i|} = \sum \frac{(\text{fit}_i - \text{data}_i)}{\sqrt{|\text{data}_i|}}
\]  

(2.1)

A small constant approximately equal to the pre-pulse noise floor (typically \(\sim 10^{-3}\)) was added to the denominator to prevent division by zero. Also since baseline noise varies symmetrically about zero, absolute values of the data are used to eliminate division by negative values.
REFERENCES


3.1. Introduction

The need to develop clean, renewable energy sources has become even more pressing with increasing energy consumption in developing countries and mounting environmental concerns. The dye-sensitized solar cell (DSSC) introduced by O’Regan and Graetzel has the potential to address these concerns by inexpensively harvesting solar energy.\(^1\) Their design is based on photoinduced charge separation at the interface of a mesoporous nanocrystalline TiO\(_2\) film sensitized with a ruthenium-based chromophore. While DSSCs are relatively inexpensive to produce, further efficiency improvements are needed in order to be commercially competitive with current energy sources. Similar improvements may also enable the development of dye-sensitized photoelectrosynthesis cells (DSPECs) that use light to directly split water into hydrogen and oxygen.\(^2\)

The emission lifetime of isolated ruthenium polypyridyl-based chromophores is typically tens to hundreds of nanoseconds, but excited state electron injection of
chromophores bound to TiO$_2$ is a nonradiative process that considerably reduces emission. Spectroscopic techniques with subpicosecond time resolution, such as transient absorption with visible to near-IR light and time-resolved terahertz spectroscopy, have indicated that electron injection occurs on timescales from 10 fs to 10 ps. Based on the more than four orders of magnitude difference in rate constants, conventional kinetic arguments would predict complete chromophore emission quenching. Indeed, chromophores on metal oxide semiconductors with a conduction band energy that allows for electron injection are strongly quenched, but previous studies have repeatedly measured residual chromophore emission. The origin of this residual emission is not well understood. Although the energy lost via this radiative mechanism is very small, uncovering its origin may provide important information about the underlying physics that limits DSSC and DSPEC efficiencies.

Our study investigates the time-dependent photoluminescence decay of a phosphonate-derivatized Ru(II) polypyridyl complex bound to nanocrystalline TiO$_2$ and ZrO$_2$ films using time-correlated single photon counting (TCSPC). Most of our experiments were performed using two-photon microscopy to selectively excite chromophores bound to the film surface. This method was necessary to study films in aqueous electrolytes since the chromophore exhibits a small amount of photoinduced desorption under these conditions. Two-photon excitation involves the simultaneous absorption of two incident photons that each have approximately half the energy normally required to excite the molecule. Because this phenomenon requires a high photon flux, only chromophores that lie within the objective lens focal volume are excited.
As compared with previous dye-sensitized TiO₂ quenching studies, we have observed that the time-dependent chromophore photoluminescence exhibits a power-law decay in time. This behavior occurs in both aqueous and acetonitrile electrolytes, and it persists over three orders of magnitude in time (sub-nanosecond to microseconds). Power-law distributions may be a consequence of various physical origins,¹⁴ and in this case may provide useful information for solar cell devices, so we have investigated the kinetics further. By measuring the time-dependent residual emission of the same films immersed in varying electrolyte concentrations, we show that the power-law decay results only under conditions that favor electron injection and seems to be a limiting behavior of the dispersive kinetics observed at lower cation concentrations. To explain these observations, we propose a model in which excited state electrons are injected into localized trap states within the semiconductor. We consider the implications of this model on the performance of nanocrystalline solar cell devices.

3.2. Material and Methods

3.2. A. Optical setup for TCSPC measurements

TCSPC measurements were performed using a home-built, two-photon optical microscope. This instrument uses ultrashort pulses generated by a Coherent Chameleon Ultra II Ti:sapphire laser (200 fs pulse duration, 80 MHz repetition rate), which was tuned to 900 nm for optimal excitation of the chromophore. The laser output was attenuated by a low-bandwidth electro-optic modulator (ConOptics 350-80LA-BK) and was then directed through a second, higher-bandwidth electro-optic modulator that permits individual pulse selection (ConOptics 350-160). Residual visible light was removed by a long-wave pass filter (Chroma HQ690LP) before the laser beam enters an
Olympus IX-81 inverted microscope through a dedicated laser port. The beam was focused onto the sample by a 60X, 1.2NA water immersion objective (Olympus UPLSAPO 60XW); the back aperture of this lens was slightly overfilled to create a diffraction-limited focal spot. Epifluorescence collected by the objective was separated from the excitation beam by a long-pass dichroic filter (Chroma 670DCXXRU). Full suppression of the IR light was accomplished with a short-pass dichroic (Semrock FF01-680/SP) and a bandpass filter (Chroma HQ630/100m-2P). The optically filtered fluorescence is detected by a GaAsP photomultiplier tube (Hamamatsu H7422P-40mod) whose output was sent to a custom designed preamplifier that has a high-bandwidth amplified output channel.

The pulse repetition rate of the laser output was reduced to 50 kHz by the high-bandwidth electro-optic modulator, which allows for complete relaxation of all the dye molecules to prevent excitation of an already excited chromophore, and samples were excited with infrared pulse energies of ~0.12 nJ unless specified otherwise. With our measured excitation beam radius of 206 nm, this gives a maximum energy density of 4.5 kW/cm², although it is important to note that with two-photon excitation only a small fraction of the incident light is absorbed. A cover slip placed in the laser beam path was used to direct a small fraction of the excitation light to a fast photodiode for use as a timing-reference. For most experiments this timing signal was sent to a digital delay generator (Stanford Research Systems DG535) delaying the signal by 4.8 µsec. This allowed for extended collection times (~ 5 µs) using the reverse-start-stop method. To record TCSPC curves, the digital delay output and the high-bandwidth output of the PMT preamplifier were sent to a single-photon counting module (Becker & Hickl SPC-130).
The instrument response function (full width at half maximum, FWHM ~3.6 ns) was measured by collecting the second-harmonic signal generated by potassium dihydrogen phosphate (KDP) crystals placed at the sample position. This time-resolution was limited by the digital delay generator.

### 3.2. B. Modification of optical setup for TCSPC with one-photon excitation

For experiments that use one-photon excitation, the Ti:sapphire laser output tuned to 900nm was focused into a 1 mm length BBO crystal cut for type I phase matching, and by frequency doubling creates 450 nm pulses for optimal linear excitation of the chromophore. The residual fundamental was rejected with dichroic mirrors, before directing the beam into the same microscope for sample excitation and detection. One-photon excitation experiments used visible pulse energies of ~0.012 pJ at a 50 kHz repetition rate providing an energy density of 1.0 W/cm². Under these conditions, an average of 0.5 dye molecules are excited per nanoparticle as a result of each laser pulse (see Appendix 1).

### 3.2. C. Modification of optical setup for TCSPC with sub-nanosecond time resolution

In order to collect decay lifetimes with a higher time resolution, we replaced the digital delay generator by a long coaxial cable to delay the TCSPC timing-reference signal. This method again employed reverse-start-stop data collection, but the timing-reference signal from the photodiode was delayed by a coaxial cable approximately 30 ns after the time-zero signal from the PMT. The instrument response, measured the same way as with the digital delay, was ~260 ps FWHM. The instrument response contains a secondary peak at positive times (~0.5% amplitude at a delay of 2.5 ns relative to the
main peak) due to an imperfection in the PMT. To remove this instrument imperfection, the instrument response was deconvolved from the raw data and then a Gaussian fit of the main peak of the instrument response was reconvolved with the data.

3.2. D. Modification of optical setup for TCSPC with laser-scanning excitation

Most of the experiments were performed by exciting the same diffraction limited spot for the entire data averaging time (1-4 minutes). To examine the influence of long-term charge accumulation, laser-scanning experiments were performed in which the diffraction-limited focal spot (FWHM ~300 nm) is raster scanned across the field of view at a rate of 55 nm/μsec by galvanometer-mounted mirrors placed in a plane conjugate to the objective back aperture. This method provides 1 μm or about 3 beam diameters between subsequent excitation pulses (at the 50 kHz repetition rate). The entire two-dimensional field is scanned at 4 Hz, so that a given region of the film is repeatedly excited every 250 ms.

3.2. E. TCSPC data analysis

The normalized TCSPC emission decay curves were fit using 4 different kinetic models: a three-component exponential model, the Kohlrausch-William-Watts (KWW) model\textsuperscript{15}, the Albery model\textsuperscript{16}, and a power-law decay model. More information about the models is provided in the Results and Appendix sections. The data was fit using in-house MATLAB (MathWorks) scripts employing the \textit{lsqnonlin} fitting function. Each fitting function was convolved with the experimentally measured instrument response function before fitting. Initial fits that reduced the sum of the unweighted residuals did not adequately fit the long-time tails of emission decays due to the low value of the data at these times. To adequately reproduce data that spans a wide range of amplitudes, we
applied a fitting function that minimized the sum of the fractional residual (frac. res.) weighted by Poisson signal-to-noise ratio (shot noise due to counting a discrete number of photons) at each time point:

$$\text{frac. res.} = \sum \frac{(\text{fit}_i - \text{data}_i)}{\sqrt{\text{data}_i}} \times \sqrt{\text{data}_i} = \sum \frac{(\text{fit}_i - \text{data}_i)}{\text{data}_i}$$

(3.1)

A small constant approximately equal to the pre-pulse noise floor (typically $\sim 10^{-3}$) was added to the denominator to prevent division by zero. Also since baseline noise varies symmetrically about zero, absolute values of the data are used to eliminate negative values.

3.2. F. Sample preparation

The TiO$_2$ and ZrO$_2$ nanoparticle films of about 7 micron and 3 micron thickness respectively, consist of nanoparticles that are 20 nm in diameter deposited on an FTO substrate by the sol-gel process. They are sensitized by immersion in 150 µM [(Ru(bpy)$_2$(4,4'-,(PO$_3$H$_2$)$_2$bpy)$_2$]$^{2+}$ (hereafter referred to as RuP) in 0.1 M perchloric acid solution (pH 1) overnight then soaked in methanol overnight to remove any possible aggregates. To study films immersed in various electrolyte solutions, a temporary chamber is created between a glass coverslip and the sensitized nanoparticle film using Teflon spacers. This chamber is filled with either an aqueous perchloric acid or acetonitrile solution. The pH is adjusted by the addition of perchloric acid, while the lithium ion concentration is adjusted by the addition of lithium perchlorate. All experiments were performed under ambient conditions, without degassing or otherwise removing oxygen.
3.2. G. Photoluminescence quantum yield measurements

Photoluminescence quantum yield measurements were obtained using an integrating sphere incorporated into a spectrofluorometer (FLSP 920, Edinburgh Instruments). The sensitized film was placed at a 45° angle inside a 1cm quartz cuvette which was filled with an acetonitrile solution. To calculate the absolute quantum yield, both direct and indirect measurements were obtained to account for emission from scattered light. For direct measurements, the excitation beam is directed into the integrating sphere and aimed directly onto the sample. The indirect measurement directs the beam to the side of the sample in order to quantify the amount of emission occurring from scattered light within the integrating sphere. The direct and indirect methods are used to measure both the absorbance and the emission. The absorbance is measured by observing the loss of signal at the excitation wavelength, from 435-455 nm, compared to that of the sample-free solvent ($L_a$). The absorptivity ($A$) is calculated to be 1 minus the ratio of the direct and indirect absorbance measurements. The emission intensity for both the direct ($P_c$) and indirect ($P_b$) method was detected from 550-850 nm. These measurements are used to calculate the absolute photoluminescence quantum yield ($\Phi$) by equation 3.2.

$$\Phi = \frac{P_c - (1 - A)P_b}{L_a A} \quad (3.2)$$

This equation requires that all the measurements be collected under the same instrument parameters. Since the absorbance is measured by detecting the transmitted light source, a narrow excitation bandwidth is required to protect the detector. The excitation wavelength was set to 445 nm and the excitation bandwidth was set to 1.7nm.
Due to the reduced emission of the sensitized TiO$_2$ film immersed in the electrolyte solution, the signal-to-noise of some emission measurements using a narrow excitation bandwidth was poor. To enable an accurate determination of the quantum yield, we recorded relative emission measurements for each sample by expanding the excitation bandwidth to 15 nm for only the emission measurements. These relative emission measurements were renormalized by a scaling factor determined by the ratio of the integrated relative to direct emission measurements for the sensitized ZrO$_2$ sample.

3.3. Results

3.3.A. Time-dependent photoluminescence of RuP bound to nanocrystalline TiO$_2$

exhibits a power-law decay

We used a two-photon microscopy setup with TCSPC capabilities to investigate the time-dependent residual luminescence of surface-bound chromophores on metal oxide films immersed in a pH 1 aqueous solution (Figure 3.1). The advantage of using a microscope set up with a high numerical aperture objective lens is that it yields a high dynamic range in our signal. Nanocrystalline metal oxide films were deposited using a sol-gel procedure, and then sensitized by immersion in pH 1 perchloric acid solution with a phosphonate-derivatized Ru(II) polypyridyl complex, RuP. Two-photon absorption of ultrashort 900 nm pulses was employed to obtain selective excitation of surface bound chromophores.

The chromophore bound to ZrO$_2$ exhibits a nearly exponential luminescence decay with a lifetime of ~340 ns in pH 1 HClO$_4$, while chromophores bound to TiO$_2$ under the same conditions are strongly quenched. The lifetime of RuP bound to ZrO$_2$ is slightly longer than that of the dye in free solution at pH 1 (~250 ns), perhaps due to a
rigid media effect caused by constraints imposed by the surface.\textsuperscript{21} The difference between the emission from ZrO\textsubscript{2}-RuP compared to TiO\textsubscript{2}-RuP results from the conduction band edge of ZrO\textsubscript{2} being higher in energy than the chromophore excited state, while the conduction band of TiO\textsubscript{2} is sufficiently low enough to permit electron injection, thus quenching the emission.

The time-dependent chromophore emission on TiO\textsubscript{2} films is typically fit to multi-exponential or modified exponential functions. Motivated by the nearly universal emission intermittency (blinking) behavior of single-molecules and quantum dots that exhibit a power-law distribution of on- and off-times, we decided to examine the time-dependent emission decay of the chromophore on a double logarithmic plot before fitting the data.\textsuperscript{22} Indeed, the time-dependent emission of TiO\textsubscript{2}-RuP appears as a straight line on a double logarithmic plot (Figure 3.1 C), indicating the emission obeys a power-law decay in time. This behavior is qualitatively distinct from the nearly exponential decay of the chromophore on ZrO\textsubscript{2}. Subsequent control experiments established that no emission is detected from unsensitized films under identical conditions, thus supporting the conclusion that the detected luminescence arises purely from RuP.

3.3.B. Power-law decay occurs at high H\textsuperscript{+} or Li\textsuperscript{+} concentrations in water or acetonitrile.

One of the main factors affecting the rate of injection is the relative conduction band energy level of the semiconductor compared to the excited state of the dye. Previous studies have indicated that the conduction band energy of TiO\textsubscript{2} exhibits a downward shift (away from the vacuum level) that is proportional to the logarithm of the
Figure 3.1: Time-dependent photoluminescence decay curves for RuP sensitized TiO$_2$ and ZrO$_2$ plotted on a linear scale (A), a semilogarithmic scale (B), and a double logarithmic scale (C). The semilog plot demonstrates that emission of the sensitized ZrO$_2$ film decays with an exponential time dependence. The emission from sensitized TiO$_2$ film is quenched due to electron injection. The double logarithmic plot demonstrates that emission of the sensitized TiO$_2$ film decays with a power-law time dependence.
hydrogen ion concentration (i.e. a Nernstian dependence on pH).\textsuperscript{23} Therefore, we compared the emission of the same film immersed in aqueous solutions of various pH values (Figure 3.2 A and B). In the pH 1 solution, in which the TiO\textsubscript{2} acceptor states are shifted to the lowest energy, the emission follows a power-law decay. As the pH is increased, the emission decay timescale becomes slower. In addition, since the time-dependent photoluminescence decay plots do not follow a straight line on either a double or single logarithmic plot, these curves do not exhibit either a power-law decay or an exponential decay. Rather they require another dispersive kinetic model. The range of pH values that could be examined was limited by the stability of the chromophore-TiO\textsubscript{2} phosphonate linkage, which becomes hydrolytically unstable in neutral and basic conditions.\textsuperscript{12} Since the chromophore-TiO\textsubscript{2} bonding is considerably more stable in aprotic solvents and the semiconductor still exhibits a Nernstian electrolyte dependence, we examined the chromophore emission over a larger range of conduction band energies by varying the Li\textsuperscript{+} concentration in acetonitrile (Figure 3.2 C and D). The time-dependent emission decay profiles in acetonitrile show a similar trend to those in the aqueous solution. At 1.0 M, the data exhibits a power-law behavior, but as the Li\textsuperscript{+} concentration decreases, the emission timescale increases. Again, the data obtained for TiO\textsubscript{2}-RuP in solutions with ionic concentration lower than 1.0 M require a dispersive kinetic model. It is also interesting to note that there is still significant quenching and dispersive kinetics at the 0 M Li\textsuperscript{+} concentration as compared to ZrO\textsubscript{2}. Comparing the data from the 1.0 M Li\textsuperscript{+} acetonitrile solution and the pH 1 aqueous solution (Figure 3.2 E) show that the power law occurs in both environments with a slightly reduced emission in the acetonitrile.
Figure 3.2: Lowering the conduction band energy of TiO$_2$ leads to a power-law decay. The pH dependence of the emission decay in water is plotted on a semilogarithmic (A) and double logarithmic scale (B). The emission’s lithium ion concentration dependence in acetonitrile is plotted similarly (C,D). The plots of 0 M, 0.1 mM, and 1mM Li$^+$ are nearly indistinguishable. Both scenarios demonstrate that as the conduction band energy level is lowered, the emission smoothly transitions to a dispersive exponential decay to a power-law decay. Comparing the decay of the sensitized TiO$_2$ film in both the pH 1 in acetonitrile to 1.0 M Li$^+$ in acetonitrile (E) show that this behavior is independent of solution. The combined effect of added lithium ions in an acidic pH 1 aqueous solution shows no further influence on the decay profile (F).
solution. We also examined the combined effect of Li\textsuperscript{+} on a low pH aqueous solution (Figure 3.2 F), and found that the emission still follows a power-law decay.

The time resolution of TCSPC measurements, usually limited by the PMT transient-time spread, is typically much shorter than a nanosecond. However, the time resolution of data presented to this point is limited by the timing jitter of the digital delay generator that is required to achieve long observation times at low repetition rates. By performing experiments using a long coaxial cable rather than the digital delay to delay our timing signal, we reduced the FWHM of our instrument response from ~3.6 ns to ~260 ps, though this modification limits the maximum observation time to 30 ns. Using this modified setup, we measured the time-dependent emission of a dye-sensitized TiO\textsubscript{2} film in pH1 aqueous solution (Figure 3.3) to determine if the emission exhibits a power-law decay on sub-nanosecond timescales. The raw data was corrected for a secondary peak in the instrument response function, which is a common issue in TCSPC systems, by deconvolving the instrument response from our data and reconvolving a Gaussian fit of the main peak of the instrument response into the data. This reconvolved data confirms that the emission at this shorter time scale is consistent with a power-law decay.

3.3.C. Chromophore photoluminescence also exhibits power-law decay after one-photon excitation.

The normal function of solar cells requires one-photon chromophore excitation and most previous experiments have probed emission following one-photon excitation, so it is important to determine if the decay profile is influenced by the excitation mechanism. While the initial excited states resulting from one- and two-photon absorption may be different due to selection rules, both excitation mechanisms typically
**Figure 3.3:** Time-dependent emission of TiO$_2$-RuP in pH1 aqueous solution with increased time resolution from replacing the digital delay with a cable delay showing that the emission from earlier times still follows power-law kinetics.
result in the same distribution of thermally equilibrated excited states so subsequent
dynamics are expected to be the same. To test this hypothesis, we compared the time
dependent emission collected using both excitation schemes for the same sample. To
perform the one-photon absorption experiments, we frequency doubled the output of the
Ti:sapphire laser in a BBO crystal to obtain pulses with a wavelength of 450 nm. We
found that the decay curves collected using both one-photon and two-photon excitation of
a dye-sensitized film immersed in acetonitrile agreed quantitatively (Figure 3.4 A).
However, in the aqueous solution (Figure 3.4 B and C), the one-photon and two-photon
data did not agree: the one-photon excited decay curves possess a long lived component
not present in the two-photon data. After collecting our measurements on the film in the
aqueous environment, the film was removed and the electrolyte solution itself was
excited. There was a residual signal with a long-lived component, despite the fact that
the film had been removed. The timescale for the long-lived component matches free
dye solution, and no signal is detected with fresh electrolyte solution. We attribute this
signal, as well as the long time component of the film in water measurement with one-
photon excitation, to freely diffusing dye molecules whose phosphonate bond dissociates
in the aqueous environment. In acetonitrile, this phosphonate bond is more stable and
therefore we do not see the freely diffusing dye. Thus, when accounting for the
discrepancy of the unbound dye molecules in the aqueous solution, our measurements
from the one-photon excitation and two-photon excitation schemes agree and both show a
power-law dependence.
Figure 3.4: Emission decay is not dependent on excitation scheme. One-photon and two-photon excitation of the same sensitized TiO$_2$ film showed similar decays in acetonitrile (A). However in water, the two excitation schemes show different lifetimes plotted on a semilogarithmic plot (B) and double logarithmic plot (C). The long time component from the one-photon excited film in water was determined to be due to freely diffusing dye molecules that dissociated from the surface.
3.3.D. Time-dependent emission is independent of power, not due to local charge accumulation, and is unaffected by dye loading

Common concerns in photoexcitation of these bound chromophores include photodamage of the dye, charge accumulation on the nanoparticle due to high excitation rate, or repeated excitation. The repetition rate used in all of our experiments was 50 kHz, corresponding to a pulse-to-pulse delay time of 20 μsec. This allows for complete relaxation of the chromophores ensuring we do not further excite chromophores that have been excited by a previous pulse. We were careful to ensure that the samples did not degrade during the course of the data averaging (typically 1-4 minutes for each decay curve) by comparing the luminescence decay at various time points during the data collection period. The multi-photon excitation employed in our experiments requires both a small excitation area and high average powers to provide the concentrated photon flux necessary for simultaneous absorption of multiple photons. A calculation based on the similarity between the signal amplitude of our one-photon and two-photon excitation experiments determines that our typical two-photon excitation pulse produces on average 0.5 excited dye molecules per nanoparticle per pulse (see Appendix 1). We also performed a power dependence series of measurements (Figure 3.5 A) to ensure that the high intensities do not influence the experimental outcome. The profiles of the normalized luminescence decay curves showed no dependence on power signifying that the decay is not influenced within the range of excitation powers measured. This result is consistent with previous time-resolved emission experiments that used one-photon excitation, which also noted that the signal is independent of excitation power within a similar range.⁷
Figure 3.5: Power-law decay is characteristic of the dye-TiO$_2$ interaction. The emission of a sensitized TiO$_2$ film in pH 1 aqueous solution is independent of power (A). A 6-fold range of excitation rates ($2.4^2$) explored due to two-photon excitation. Comparing the emission profile from excitation of the same area (spot) versus scanning the excitation beam (scan) shows that power-law behavior is not due to long term charge accumulation (B). Varying the surface loading of the dye on TiO$_2$ (C) and ZrO$_2$ (D) shows that the power-law is not due to energy transfer of surface bound chromophores. Percent loadings calculated from absorbance measurements and relative to data obtained from overnight soaking.
Although the time between excitation pulses (20 μsec) is sufficiently long to prevent reexcitation of excited state chromophores, it is still considerably shorter than the lifetime of charge carriers, which can persist for milliseconds or longer. Fortunately, our experiments are conducted on a laser-scanning microscope, in which the focused beam can be translated by adjusting high-speed galvanometer-mounted mirrors in the beam path. This capability allows us to conduct experiments in which subsequent pulses excite spatially distinct regions of the sample. Scanning at a rate of 55 nm/μsec with a point spread function of about 300 nm provides about a 1 μm distance or approximately 3 beam diameters between subsequent excitation pulses. The same area is re-excited only four times per second since the 2-D field is repeatedly raster scanned. As demonstrated in Figure 3.5 B, the chromophore emission exhibits the same time-dependent decay whether the beam is stationary (spot) or scanned (scan), ruling out the role of charge accumulated due to the interaction of multiple excitation pulses with the same region of the film. It is also important to note that we consistently measure the same normalized time-dependent emission profile at various positions within each film. This observation, along with the agreement between the spot and scan data collection methods, indicates that there is no heterogeneity in the emission profile on the ~300 nm length scale resolvable by our optical microscope.

Finally, we examined the dye-loading dependence of luminescence, to ensure the observed kinetic decays were not influenced by surface energy transfer. The same TiO₂ and ZrO₂ films were immersed in the sensitizing solution for various times. Absorbance measurements were taken after each sensitization step to track the increase of surface loading. After sensitizing overnight, the films were immersed in methanol for 3 hours to
remove aggregates. This procedure has been shown to result in complete monolayer coverage of the metal oxide films.\textsuperscript{10} The emission of these films at each step was then observed (Figure 3.5 C and D) with no loading dependence on either the ZrO\textsubscript{2} film nor the TiO\textsubscript{2} film with respect to the profile of the normalized photoluminescence decay curves.

3.3.E. Distribution of photoluminescence decay time constants broadens in addition to decreasing with increasing electrolyte concentration

To fit the time-resolved photoluminescence data, we considered three kinetic models that have previously been applied to fit the time-resolved emission of dye-sensitized metal oxide films: a three-component exponential fit, the Albery model\textsuperscript{16}, and the KWW model.\textsuperscript{15} Additionally we introduce a fourth model based on power-law kinetics. Appendix 2 presents the mathematical form of these models and outlines some of the assumptions that underlie their application. In brief, the simple exponential model assumes a well defined barrier height while the other three models assume a distribution of barrier heights (Figure 3.6). The Albery and KWW models assume a Gaussian and asymmetric distribution of barriers, respectively. The power-law model possesses a most probable value for which the distribution of barriers falls off exponentially.

For each photoluminescence decay curve, we fit the experimental data with each model by convolving the fitting function with the instrument response function and adjusting the free parameters to minimize the fractional residual, as defined by Eq. 3.1. Figure 3.7 presents a plot of these fits for the 0 M and 1.0 M Li\textsuperscript{+} concentration samples along with the best fit parameters. The best fit parameters for all of the datasets are available in Table 3.1 and Table 3.2. The 0 M Li\textsuperscript{+} data was well fit by the
**Figure 3.6:** Basis of kinetic models used to fit time-dependent photoluminescence decay data. The simple exponential model has a well defined barrier height $\Delta G^\dagger$ (A). The Albery Model assumes a Gaussian distribution of barrier heights (B). The KWW model is comparable to the Albery model, but with an asymmetric distribution (C). The power-law model has a most probable value that falls off exponentially (D).
Figure 3.7: Fits for data of TiO$_2$ film in acetonitrile for 0 M (left column) and 1.0 M (right column) Li$^+$ with the four models: tri-exponential, KWW, Albery, and a power law. The first three models fit the data well, while the power-law model only fits the data from the highest ionic concentration. Fractional residuals (frac. res.) determine goodness of fit according to Eq. 3.1; the fitting functions and parameters are defined in the Appendix 2.
Table 3.1: Best fit dispersive kinetic model parameters for aqueous measurements

<table>
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<tr>
<th>pH :</th>
<th>ZrO&lt;sub&gt;2&lt;/sub&gt; pH 1</th>
<th>5</th>
<th>3</th>
<th>1</th>
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<td></td>
<td></td>
<td></td>
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<td>0.85</td>
<td>0.97</td>
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<td>$\tau_1$ (ns)</td>
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<td>2</td>
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<td>0.14</td>
<td>0.14</td>
<td>0.03</td>
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<td>$\tau_2$ (ns)</td>
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<td>17</td>
<td>13</td>
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<td>0.01</td>
<td>0.01</td>
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<td>$\tau_3$ (ns)</td>
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<td>256</td>
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<td>120</td>
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<td>0.12</td>
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<td><strong>Albery Model</strong></td>
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<tr>
<td>$\tau$ (ns)</td>
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<td>1.2</td>
<td>2.9</td>
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<tr>
<td>$\gamma$</td>
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<td>2.7</td>
<td>2.2</td>
<td>1.8</td>
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<td>$\beta$</td>
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<tr>
<td>$\alpha$</td>
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<td>1.59</td>
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Table 3.2: Best fit dispersive kinetic model parameters for measurements in acetonitrile

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<tr>
<th>[Li⁺]</th>
<th>ZrO₂ 0 M</th>
<th>0 M</th>
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<th>0.001 M</th>
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<td></td>
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<td></td>
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<tr>
<td>A₁</td>
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<td>0.84</td>
<td>0.93</td>
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<td>2</td>
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<tr>
<td>A₂</td>
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<td>0.41</td>
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<td>0.32</td>
<td>0.18</td>
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<td>0.07</td>
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<td>57</td>
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<td>175</td>
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<td>75</td>
<td>65</td>
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<td>0.18</td>
<td>0.14</td>
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</table>

| **Albery Model** |         |     |          |         |        |       |       |
| τ (ns) | 431     | 52  | 33       | 33      | 3.4    | 1.2   | 0.2   |
| γ     | 0.4     | 1.1 | 1.3      | 1.3     | 2.0    | 2.1   | 2.3   |
| frac. res. | 3.26 | 2.64| 1.95     | 1.25    | 0.42   | 0.14  | 0.14  |

| **KWW** |         |     |          |         |        |       |       |
| τ (ns) | 388     | 51  | 30       | 16      | 1.4    | 0.6   | 0.2   |
| β     | 0.88    | 0.65| 0.56     | 0.47    | 0.35   | 0.36  | 0.32  |
| frac. res. | 2.76 | 1.39| 0.94     | 0.77    | 0.22   | 0.15  | 0.15  |

| **Power Law** |         |     |          |         |        |       |       |
| α     | 0.79    | 1.19| 1.20     | 1.20    | 1.35   | 1.60  | 1.60  |
| frac. res. | 161.19 | 34.08| 21.44    | 16.05   | 2.14   | 0.32  | 0.10  |
The multiexponential, Albery and KWW models but was not fit by the power-law model. The 1.0 M Li\(^+\) data was well fit by all four models. In general, the multiexponential, Albery and KWW models fit all of the data well; the latter two models are appealing because they require fewer fitting parameters, and of these two the KWW model often had a lower residual. The power-law model only adequately fit the photoluminescence of films immersed in acetonitrile containing 1.0 M Li\(^+\) or pH 1 aqueous electrolyte.

To compare the dispersive kinetic models, Figure 3.8 presents the distribution of time constants for each Li\(^+\) concentration using the parameters obtained by our fits. The shaded area represents times that fall within the instrument response, and therefore only accessible to our analysis through the shape of the distribution at longer times. The majority of the log-normal and stretched exponential distributions fall into longer times for 0 M Li\(^+\), but the distribution shifts to shorter times and the broadens as the lithium concentration increases. This trend is quantified by plotting the KWW time constant and stretching parameter as a function of lithium concentrations (Figure 3.8 B and C). At 1.0 M Li\(^+\) concentration, the distribution maximum for both the log-normal and stretched exponential falls completely within the instrument response. For the timescale region accessible to our instrumentation, these distributions are all qualitatively similar which explains why all three models can be used to fit the data even though the Albery and KWW models do not truly exhibit power-law kinetics.

3.3. F. Absolute photoluminescence quantum yield measurements on TiO\(_2\)

Although it is possible to determine the relative emission quantum yield from our TCSPC data in principle, we complemented this data with absolute photoluminescence quantum yield measurements on both the sensitized ZrO\(_2\) and TiO\(_2\) films in acetonitrile
Figure 3.8: Shifting the conduction band energy increases the electron injection rate but also causes a change in the distribution of rates. Using the parameters of the best fits, the distribution of tau values for each Li$^+$ concentration in acetonitrile are plotted (A). The shaded area represents times that are within the instrument response. As the Li$^+$ concentration increases the maximum of the KWW distribution shifts to lower times (B) and the width of the distribution increases, as evident by the decrease in the stretching parameter (C).
solutions by incorporating an integrating sphere into the commercially available spectrofluorimeter. The integrating sphere allows for every photon that enters the sphere and emitted from the film to be detected by the detector. To account for excitation caused from initially scattered light that is reflected back onto the sample, both direct and indirect measurements were collected. The films, immersed in an acetonitrile solution, were excited with 445 nm light from a xenon arc lamp, and the excitation bandwidth was 1.7 nm for all measurements. As we expected, the emission from TiO$_2$ was quenched and the signal from the emission measurements was relatively weak. To adjust for this, relative emission measurements were taken by expanding the excitation bandwidth to 15 nm and these curves were normalized with a scaling factor determined by the ratio of the sum under the curve of the relative to absolute emission measurements for ZrO$_2$.

The photoluminescence quantum yield values for the sensitized ZrO$_2$ and TiO$_2$ films in acetonitrile, as well as the sensitized TiO$_2$ film in solutions of various lithium ion concentrations are plotted in Figure 3.9. The relative and absolute measurements for the TiO$_2$ film agree well with each other and the relative TiO$_2$ measurement show the decrease in the error from the absolute measurement. It is notable that there is a five-fold decrease in the quantum yield of the dye bound to TiO$_2$ compared to ZrO$_2$ in 0 M Li$^+$. This quenching is also apparent in the time-dependent photoluminescence data in Figure 3.2 for the same samples. Based on the amount of emission quenching, one might expect that the electron injection yield of sensitized TiO$_2$ films in the absence of potential determining ions should be 80%. One study that employed ultrafast transient absorption (TA) spectroscopy to monitor injection yield directly reported very little injection under these conditions,$^6,25$ while a second study found that the yield of injected electrons was
Figure 3.9: Absolute and relative photoluminescence emission quantum yield measurements of TiO$_2$-RuP and ZrO$_2$-RuP films in acetonitrile. The relative measurements, taken due to the quenched emission on TiO$_2$, compare well with the absolute value and possess less error. The emission is quenched 5-fold on TiO$_2$ compared to ZrO$_2$ and is further quenched 10-fold in a 1.0 M Li$^+$ solution.
similar to the yield in the presence of Li$^+$. Depending on which result accurately reflects the Li$^+$-dependent injection yield, the emission quenching we observe in the absence of Li$^+$ indicates either that there is significant injection or that additional nonradiative pathways could contribute to the photoluminescence quenching of the chromophore bound to TiO$_2$. However, the addition of 1.0 M Li$^+$ further quenches the photoluminescence quantum yield of the chromophore on TiO$_2$ by approximately ten-fold. Again, the origin of this quenching may be an increase in electron injection or nonradiative decay. Yet since we observe significant quenching both when changing the semiconductor material and when adding Li$^+$, there must be emission quenching in the absence of injection regardless of which of the aforementioned TA studies is correct. Further experiments are underway to resolve this discrepancy. Regardless, we note that the total chromophore emission quenching due to electron injection is at most 50-fold.

3.4. Discussion

3.4.A. Necessity of two-photon excitation scheme.

In Graetzel’s original DSSC, the ruthenium dye molecules are linked to the semiconductor using carboxylated ligands. There has been an increased interest in using the model of the DSSC to design a dye sensitized photoelectrosynthesis cell (DSPEC) to create solar fuels through the splitting of water. This design requires an aqueous environment which is incompatible with retention of the carboxylate-metal oxide linkage. The phosphonate surface binding group has been used since it has been found to be more hydrolytically stable than the carboxylate group. However, a recent study has shown that RuP, even in acidic conditions, desorbs from ZrO$_2$ and TiO$_2$ under irradiation. Two-photon microscopy allows for us to observe only bound dye molecules since the
concentration and signal is high enough to be detected only at the surface. This is in contrast to one-photon excitation that excites all of the freely diffusing dye molecules within the entire volume within the laser beam path. This feature has allowed us to observe the power-law emission of surface bound chromophores, even in the aqueous environment when freely diffusing chromophores are present in the solution.

3.4.B. Origin of highly dispersive kinetics

Numerous studies have concluded that the time-dependent photoluminescence of molecular dyes on TiO$_2$ does not follow first-order kinetics, but the origin of the dispersive kinetics is not well-understood. It is often assumed that the photoluminescence decay reflects heterogeneities in the kinetics of excited state electron injection, which quenches emission.$^{8,9,11}$ Electron injection kinetics are typically modeled using a theory for interfacial electron transfer developed by Marcus and Gerischer, in which electrons that occupy well-defined excited states of adsorbed dye molecules are injected into a continuum of states within the semiconductor. According to this formalism, the rate of electron injection is

$$k_{\text{injection}} \propto V^2 \left(1 - f(E, E_f)\right) g(E) \exp \left(-\frac{(E_{dye}^* - E - \lambda)^2}{4\lambda k_B T}\right) dE$$  \hspace{1cm} (3.3)

where $g(E)$ and $f(E, E_f)$ are the density of TiO$_2$ states that their Fermi occupation at energy $E$, $E_{dye}^*$ and $V$ are the dye excited state energy and its electronic coupling to the TiO$_2$ states, and $\lambda$ is the reorganizational energy for electron injection.$^{27-29}$

Nanocrystalline TiO$_2$ films exhibit a non-ideal density of states that includes an exponential tail below their conduction band. These sub-bandgap states are often attributed to localized charge defects, such as the reduction of some Ti$^{4+}$ to Ti$^{3+}$.$^{30-33}$ It is important to note that even with an exponential distribution of acceptor states, the
Marcus-Gerischer theory results in a single rate constant for electron injection by summing over all acceptor states. This approach inherently assumes that the entire density of acceptor states is accessible to each excited chromophore, which may be somewhat questionable given the interpretation that the sub-bandgap states are localized, as discussed below. Regardless, the predicted injection rates are less than 100 fs for most Ru-based chromophores, which is generally supported by transient absorption experiments but is inconsistent with the observation that surface-bound chromophores exhibit residual emission on the nanosecond timescale.

Several models have previously been proposed to account for incomplete chromophore quenching (at most 50-fold) under conditions that favor fast electron injection, given that the rate constants for emission and injection differ by at least four orders of magnitude. Kelly et al proposed two possible explanations for this kinetic discrepancy\(^6\): 1) excited state electrons are injected into TiO\(_2\) states that are not spatially accessible to all chromophores or 2) injection only occurs from vibrationally “hot” excited states and emission occurs from the thermally equilibrated state. Both mechanisms predict that the residual emission arises from a subpopulation of chromophores whose time-dependent decay profile is the same as a non-injecting sample, similar to emission of the sensitized ZrO\(_2\) film. This would most clearly be seen in the semilogarithmic plots of the sensitized TiO\(_2\) emission as a straight line that is parallel to the ZrO\(_2\) emission. None of our data exhibits this behavior, indicating that there is no population of completely unquenched chromophores in TiO\(_2\) at any ionic strength. The same group later introduced a model that includes cross-surface energy migration in addition to injection.\(^{34}\) Our data is not fit by the rate equation derived using this model,
which decays as an exponential at long times, nor is our data consistent with the model’s prediction that the emission profile should depend on dye-loading and excitation rate.

To account for the dispersive photoluminescence kinetics, Durrant and co-workers have employed an empirically-derived model that assumes a heterogeneous distribution of electron injection dynamics due to local variations in the density of acceptor states.\(^8,33\) They assumed that the injection rate constant is modified by the exponential of a parameter that is normally distributed; we note that this treatment is mathematically equivalent to the Albery model. Koops and Durrant find that Monte Carlo simulations based on this model can be well-fit by a stretched exponential\(^35\), which is not surprising given the similarity in the Albery and KWW pseudo first-order rate constant distributions outlined Appendix 2. They determined the mean injection rate and width of the distribution for several strongly injecting samples. Variations in the electrolyte-dependent injection rate extracted from the emission measurements compared favorably with trends in their transient absorption measurements. However, the width of the injection rate distribution they reported was similar for all samples.

Our results build on these earlier studies in several ways. We have systematically investigated the time-resolved emission of dye-sensitized TiO\(_2\) and ZrO\(_2\) films over a wide range of electrolyte concentrations. The sensitized ZrO\(_2\) emission is largely exponential but the sensitized TiO\(_2\) emission is dispersive under all conditions. The rate constant and degree of dispersion qualitatively increases with cation concentration in both water and acetonitrile, which we quantified by fitting the emission decay curves by the Albery and KWW models. Although the data are fit well by both models, the KWW fits have a smaller residual for most conditions. Figure 3.8 demonstrates that the
logarithm of the KWW pseudo first-order rate distribution decreases linearly with the logarithm of the cation concentration, which is consistent with the Nernst equation. However, rather than a simple shift in the conduction band energy with ionic strength, our data indicate that there is a change in the width of the rate constant distribution. The KWW stretching parameter decreases roughly in proportion to the logarithm of the cation concentration before exhibiting saturation-like behavior above ~10 mM, which may be caused by the time limitations of our instrument.

At the highest cation concentrations, the time-dependent emission of sensitized TiO$_2$ films is linear when plotted on double logarithmic axes, which is characteristic of a power-law decay in time. The data are also well fit by the power-law model. We note that within the limitations imposed by the time resolution and signal-to-noise of our experimental data, we cannot unambiguously differentiate a power law decay from the decay that would result from either the KWW or Alberty model with a highly broadened rate distribution, since either of these models can yield a kinetic decay that approaches power law behavior over a limited range of time and amplitude. Nonetheless, a linear decay on a double logarithmic plot reflects a high degree of dispersion in the emission kinetics, which has not been previously noted and may provide insight into the physical origin of the residual emission.

It is well known that electron transport dynamics in nanocrystalline TiO$_2$ and other amorphous semiconductors depend on the density of charge carriers and exhibit dispersive behavior.$^{36-38}$ These observations have been explained using a multiple-trapping model, in which charges are transported by thermally activated hopping between an exponential distribution of localized sub-bandgap trap states. When the detrapping
time is much longer than the intertrap diffusion time, this model predicts that the trap release times exhibit a power law distribution.\textsuperscript{39,40} It also predicts that various experimental observables, such as the transient photoconductivity and charge recombination, exhibit power-law kinetics of the form

$$I(t) \propto t^{-(1+\alpha)}$$

where the disorder parameter $0 < \alpha < 1$ and typically $\alpha \approx 0.5$.\textsuperscript{41}

The similarity between power-law dye emission kinetics and transport kinetics suggests that the phenomena may be related. We first considered a model in which a charge injection event impedes subsequent injection events until the injected charge is removed via diffusive transport. However, this model is unlikely because injected charges are efficiently screened in nanocrystalline TiO\textsubscript{2}.\textsuperscript{42} A more plausible link between injection and transport may be based on the distribution of trap site energies. As outlined in Appendix 2, dispersive injection kinetics result from a distribution of activation barriers, and power-law kinetics are predicted for an exponential distribution of activation energies. It is tempting to account for the distribution of activation energies in terms of the distribution of trap states. However, Marcus-Gerischer theory predicts barrierless injection into a TiO\textsubscript{2} state whose energy lies $\lambda$ below the dye excited state energy, provided that there are unoccupied TiO\textsubscript{2} states at this energy that are strongly coupled to the dye. This model assumes that the dye is electronically coupled to the entire TiO\textsubscript{2} density of states, which is questionable since transport kinetics indicate that the sub-bandgap trap states are localized. Rather, we believe our data could be explained by a model in which each dye molecule is strongly coupled to, and therefore can inject into, only a small number of trap states.\textsuperscript{43} This scenario would result in an injection rate
constant for each dye that is determined by summing the integrand of Eq. 3.3 only over those relevant acceptor states; the bulk sample would exhibit a distribution of injection rate constants that depends on the energetic distribution of trap states, though the two distributions would not necessarily be directly correlated.

As mentioned above, a broad distribution of trap sites in the semiconductor can result from the interaction of a spatially random distribution of localized charge defects. The TiO₂ nanoparticles are likely to contain intrinsic Ti³⁺ charge defects, but in the presence of an electrolyte, the interaction of small charged cations like Li⁺ or H⁺ would undoubtedly create additional localized charge sites. We suggest that the intrinsic charge defects yield the moderate amount of kinetic dispersion observed at the lowest cation concentrations, and that the photoluminescence rate constant distribution broadens further as the number of charge defects is increased by Li⁺ (or H⁺) adsorption or intercalation. Indeed, several previous studies have noted that high Li⁺ concentrations may significantly widen the exponential conduction band tail of nanoporous TiO₂ films. At the highest cation concentrations, the exponential tail of trap sites is sufficiently broadened to yield power-law emission kinetics. Finally, we note that this model offers only a qualitative explanation of the kinetic dispersion observed in our experiments, but a more quantitative treatment will be the subject of future investigations.

3.4. C. Implications for DSPECs

This model based on injection into localized surface states is relevant for DSSCs and DSPECs, though it has more important implications for the later. Here, a cycle of four electron injections occur to produce a strongly oxidizing catalyst that then has the capability of splitting water. The catalyst must remain in its oxidized state during each
cycle long enough to inject an additional electron. However if electrons are trapped in deep localized surface states, these catalysts have a higher probability of being reunited with a previously injected electron due to back electron transfer (BET). The localized surface state injection model can help to explain some previously reported BET measurements. Brennamen et. al. used transient absorption to measure the timescale of BET at different pH values\(^{10}\). They found that at pH 1, although injection occurred most rapidly, the quickest BET was also experienced.\(^{10}\) This can be understood in our model where at lower pH, injection into deep surface trap states allows for charge carriers to persist near the surface increasing the chance for BET. Finally, the involvement of diffusive charge transport involving local trap states is further supported by the recent observation that recombination kinetics of photoinjected electrons exhibit power-law kinetics.\(^{24}\) For the most efficient DSPEC, the nanoparticle film needs to be in an environment that encourages the transportation of charge carriers away from the surface.

### 3.5. Conclusion

We have quantitatively demonstrated that the photoluminescence of dye-sensitized TiO\(_2\) films, which is quenched by electron injection, exhibits kinetics in both acetonitrile and water that decay on a shorter timescale and become more dispersive as the electrolyte cation concentration is increased. In conditions that most favor efficient electron injection, the time-dependent emission follows a power-law decay profile. We believe that this behavior may be related to the kinetics of charge transport, which also exhibit power-law behavior, through the involvement of localized trap states. We have proposed that each dye molecule injects electrons only into a small number of localized states that have well-defined energies, rather than injection into the full density of states.
Dispersion in the dye emission kinetics reflects the distribution of energies of these localized states within the ensemble. The moderately dispersive kinetics observed at low cationic strength result from intrinsic charge defects in the semiconductor lattice, but the degree of dispersion is increased by the addition of randomly positioned adsorption or intercalation of Li\(^+\) or H\(^+\). The involvement of localized acceptor states is likely to increase the amount of charge recombination, which is an important consideration for devices intended to photocatalytically split water.
REFERENCES


Nanocrystalline Solar Cells: The Minimization of Kinetic Redundancy.


CHAPTER 4. Investigation of factors that affect the distribution of excited state lifetimes of dye-sensitized nanoparticle films

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4.1. Introduction

Dye-sensitized solar cells (DSSC) have been extensively studied due to their potential of providing a means to cheaply harvest solar energy. Their design is based on the photoinduced charge separation that occurs at the interface of a nanoporous TiO₂ nanoparticle film sensitized with a ruthenium-based chromophore.¹ The interfacial photoinduced charge separation includes multiple events such as electron injection, charge transport, and back electron transfer. Device efficiency is significantly influenced by the kinetics of these events²-³ which are affected by the concentration of various chemical additives as well as the application of electrical bias.⁴⁻⁹ There is wide-spread interest in these devices, but further efficiency improvements are needed before they can become commercially competitive with current energy sources.

The driving force for the electron injection process is the relative relationship between the energies of the excited state of the chromophore and the accepter states associated with the conduction band of the semiconductor. It has been shown that the
TiO$_2$ conduction band energy has a Nernstian dependence on effective pH; various chemical additives can adjust the efficiency of electron injection by either raising or lowering the conduction band energy level of the semiconductor.$^{4,5,7}$ It has been shown that lithium ions intercalate into the semiconductor lattice structure and shift the conduction band energy level lower (away from vacuum).$^3$ This drives electron injection and increases the short-circuit current density ($J_{SC}$).$^{10}$ However, this improvement occurs at the cost of lowering the open-circuit voltage ($V_{OC}$). The chemical additive 4-tert-butylpyridine (tBp) has been shown to bind to TiO$_2$ and raise the conduction band edge, raising the $V_{OC}$, but with a reduction in $J_{SC}$.$^{2,7,11}$ A careful compromise must occur to position the conduction band optimally for device performance. Although the effects of these two additives are counteractive, they are both commonly found in complete devices due to the good overall performance which is still not fully understood.$^{12,13}$ Another chemical additive that is commonly added to devices are tetrabutylammonium solts (TBA). This bulky cation cannot interact strongly with the nanoparticles due to steric hinderence. It is often the counter ion of the ruthenium dye.

In a previous study, we discovered that the time-dependent emission decay of photoexcited chromophores bound to TiO$_2$ exhibit power-law kinetics at high lithium ion concentrations.$^{14}$ The power-law model is one of many dispersive kinetic models that take into account distributions of characteristic lifetimes. We compared several dispersive kinetic models to better understand how the presence of lithium ions lead to power-law kinetics. As the lithium ion concentration is increased, the emission decay kinetics smoothly transition from a stretched exponential decay in neat acetonitrile to this highly dispersive power-law behavior in a 1.0 M lithium acetonitrile solution. However,
when the chromophores are bound to zirconium oxide where injection is prohibited due
to the high conduction band edge energy, the lifetime increases over 7-fold compared to
neat acetonitrile and the decay follows nearly monodisperse exponential kinetics. We
desired to investigate the regime between the stretched exponential kinetics in clean
acetonitrile and the nearly monodisperse kinetics on zirconium oxide.

This study furthers our investigation of kinetic dispersion in the
photoluminescence of dye-sensitized TiO$_2$ by examining the effect of other chemical
additives (tBp and TBA) and of applying an external electrical bias on the time-resolved
chromophore emission. We observe a systematic shift of characteristic lifetimes as the
presence or absence of the chemical additives vary the kinetic drive for electron injection.
Along with the shifting characteristic lifetimes, we also observe a concentration
dependence on the amount of dispersion in the distribution of these lifetime values.
Furthermore, since it has previously been shown that an applied negative electrical bias
enhances the excited state lifetime of photoexcited chromophores bound to TiO$_2$,$^4$ we
also investigated kinetic dispersion with the application of an electric bias. We observed
longer characteristic lifetimes with applied negative potential with an increasingly narrow
lifetime distribution.

4.2. Materials and Methods:

4.2.A. Optical Setup for Chemical Additive Experiments

Experiments exploring the effects of chemical additives were performed using a
home-built, two-photon optical microscope.$^{15}$ An ultrashort pulse generated by a
Coherent Chameleon Ulta II Ti:sapphire laser (200 fs pulse duration, 80 MHz repetition
rate) tuned to 900 nm for optimal excitation of the chromophore was focused onto the
sample by a 60x, 1.2NA water immersion objective lens (Olympus UPLSAPO 60XW); the back aperture of this lens was slightly overfilled to create a diffraction-limited focal spot. The epifluorescence collected by the objective was optically filtered to suppress IR light from the excitation beam and then detected by a GaAsP photomultiplier tube (Hamamatsu H7422P-40mod) whose output was sent to a custom-design preamplifier that has a high-bandwidth-amplified output channel.

The pulse repetition rate of the laser output was reduced to 50 kHz by a high-bandwidth electro-optic modulator (ConOptics 350-160). This allows for complete relaxation of all dye molecules to prevent excitation of an already excited chromophore. Samples were excited with infrared pulse energies of ~0.12 nJ. With our measured excitation beam radius of 206 nm, this gives a maximum energy density of 4.5 kW/cm$^2$, although it is important to note that with two photon excitation only a small fraction of the incident light is absorbed. Under these conditions, we estimate an average of 0.5 chromophores per nanoparticle were excited with each pulse.$^{16}$ We aimed to achieve such a low concentration of excited chromophores per pulse to prevent any influence of second order kinetics, such as triplet-triplet annihilation, upon the time dependent photoluminescence decay.$^{17}$ A small fraction of the excitation light was reflected from a coverslip placed within the excitation beam path and detected by a fast photodiode for use as a timing reference. This timing signal was sent to a digital delay generator (Standord Research Systems DG535) to allow for extended collection window (~5 µs) using the reverse-start-stop method. To record TCSPC curves, the digital delay output and the high-bandwidth output of the PMT preamplifier were sent to a single-photon counting module (Bekcer & Hickl SPC-130). The instrument response function defined
by the full width at half-maximum (FWHM) was ≈ 3.6 ns (which was primarily limited by the digital delay that was necessary to temporally separate pulses to allow for complete relaxation of the long-lived excited state), which was measured by collecting the second-harmonic signal generated by potassium dihydrogen phosphate (KDP) crystals placed at the sample position.

4.2.B. Optical Setup for Spectroelectrochemical Measurements

Experiments measuring the effects of an applied bias on emission lifetimes were performed using the same optical set up as described above, but instead of directing the excitation beam into the microscope, the beam was directed to a 10x, 0.3 NA objective lens which focused the excitation beam onto a three-electrode photoelectrochemical cell held in free-space. The three-electrode photoelectrochemical cell incorporated a TiO₂ film as the working electrode, a platinum wire counter electrode, and a Ag/AgNO₃ reference electrode. The acetonitrile solution was purged with argon for 45 minutes prior to the experiment. The applied bias was implemented and monitored using a Wavenow potentiostat (Pine Research Instrumentation AKCABLE3). To calibrate the Ag/AgNO₃ reference electrode the cyclic voltamgram of ferrocene in a 100mM TBA acetonitrile solution was collected and used as an internal standard (Figure 4.1).

4.2.C. TCSPC Data Analysis

The normalized TCSPC emission decay curves were fit using the Kohlrausch-William-Watts model also referred commonly as a stretched exponential with the form

\[ I = A_0 e^{-(t/\tau)^\beta} \]  

(4.1)

where \( \tau \) is the characteristic lifetime and \( \beta \) is the stretching parameter that quantifies the degree of dispersion (0<\( \beta \)≤1, where \( \beta =1 \) corresponds to a monoexponential decay and
smaller values indicate more dispersion). In other words, if all chromophores emit with
the same kinetics, the decay would be monoexponential and the beta value will be one.
However, if emission of a population of excited chromophores occurs with varying
Figure 4.1: Cyclic voltammogram of an unsensitized TiO$_2$ film in 100mM TBA with a ferrocene internal standard. The redox potential of ferrocene with respect to our Ag/AgNO$_3$ reference electrode is 82 mV.
kinetic timescales then the kinetics are dispersive and the beta value will be less than one. A smaller beta parameter value indicates that the range of kinetic timescales is larger. Details of our data fitting procedures have been described in detail elsewhere\textsuperscript{14} but in brief, data were fit using in-house MATLAB (MathWorks) scripts employing the \textit{lsqnonlin} fitting function. The stretched exponential fitting function (Eq. 4.1) was convolved with the experimentally measured instrument response function before fitting. For the 100mM TBA applied potential experiments, an increase in the emission at time zero occurred. This emission increased in intensity as more negative potentials were applied. This was confirmed to be due to nearly instrument response limited emission of the TiO\textsubscript{2} by observing the emission of an unsensitized TiO\textsubscript{2} slide under an applied bias. To account for this artifact, the photoluminescence decay curves for TBA samples at negative potentials were fit with a (preconvolved) function consisting of the sum of the stretched exponential term and a monoexponential term whose time constant is constrained to 0.1 ns. This had little effect on the values of the extracted stretched exponential fit parameters.

\textbf{4.2.D. Sample Preparation}

The TiO\textsubscript{2}\textsuperscript{18} and ZrO\textsubscript{2}\textsuperscript{19} nanoparticle films of about 7 and 3 \textmu m thickness, respectively, consist of nanoparticles that are 20 nm in diameter deposited on an FTO substrate by the sol-gel process. They are sensitized by immersion in 150 \textmu M [(Ru(bpy)\textsubscript{2}(4,4'-\text{PO}_{3}\text{H}_{2})\text{bpy})]^{2+}\textsuperscript{20} (hereafter referred to as RuP) in 0.1 M perchloric acid solution (pH 1) overnight and then soaked in methanol overnight to remove any possible aggregates. To study films immersed in various electrolyte solutions, a temporary chamber is created between a glass coverslip and the sensitized nanoparticle film using
Teflon spacers. This chamber is filled with an acetonitrile solution containing various concentrations of the specified chemical additive. All chemical additive experiments were performed under ambient conditions.

4.3. Results

4.3.A. Chemical additives influence the distribution of excited state lifetimes

In this study, we indirectly probe electron injection efficiency by monitoring the time-dependent emission decay of photoexcited ruthenium-based chromophores bound to a TiO$_2$ nanoparticle film. A photoexcited chromophore bound to TiO$_2$ has access to multiple relaxation pathways including the emission of a photon or the nonradiative injection of an electron into the TiO$_2$ conduction band. The quenching of emission, due to electron injection, can be monitored with TCSPC measurements as a decrease in the emission lifetime.

Complete DSSCs employ a combination of chemical additives to maximize photovoltaic performance.$^{12,13}$ This enhanced efficiency arises from improved interfacial kinetics due to the effect these chemical additives have on the relative position of the TiO$_2$ conduction band edge compared to the dye excited state.$^{11,21,22}$ The concentration dependence of lithium, tBp, and TBA upon the time-dependent photoluminescence decay of excited ruthenium chromophores bound to a TiO$_2$ nanoparticle film is shown in Figure 4.2. The double logarithmic plots (Figures 4.2 B, D, and F) are presented to note the power-law behavior of the 1.0 M lithium solution discussed elsewhere$^{14}$ and to emphasize the smooth transitions that occur with the addition of various chemical additives. The effects of lithium on the photoluminescence can be seen in Figure 4.2 A and B. Lithium ions are small cations that bind to the surface as well as insert into the
anatase lattice. This is coupled to electron accumulation and shifts the conduction band edge to lower energies.\textsuperscript{23} This lower energy level drives the electron injection process and quenches the chromophore emission. The photoluminescence decay curves qualitatively show that as the lithium concentration increases, the emission timescale is shortened and the kinetics become more dispersive.

The effects of tBp concentration on the time-dependent chromophore emission are presented in Figures 4.2 C and D. The tBp molecules bind to the titania surface and raise the TiO\textsubscript{2} conduction band edge to higher energies.\textsuperscript{24} The rate of electron injection is reduced by this lower driving force, leading to longer excited state lifetimes. Thus, it makes sense that increasing the tBp concentration lengthens the photoluminescence decay timescale. However, we note that this change is accompanied by a concomitant transition to less dispersive decay profiles.

Lastly we looked at the concentration dependence of TBA on the photoluminescence decay (Figures 4.2 E and F). TBA is often used as the counter ion to the RuP dye and is a bulky ion that, due to steric hindrance, has little influence on the TiO\textsubscript{2} semiconductor. This behavior is confirmed in our data as the increase in TBA concentration shows minimal effect on the photoluminescence decay.

To quantify these observations our photoluminescence curves were fit with the stretched exponential form (Eq. 4.1) convolved with the instrument response function. A stretched exponential form is used to take into account the heterogeneity of the emission decay kinetics.\textsuperscript{25} We have previously shown that the addition of lithium not only quenches the emission of photoexcited ruthenium chromophores bound to TiO\textsubscript{2}, but we also observed an increase in the distribution of these kinetic rates which reached a
Figure 4.2: Concentration dependence of chemical additives on the time-dependent photoluminescence of RuP-sensitized TiO₂ films. (A and B) The addition of lithium quenches emission; power law decay in time is observed for the highest lithium concentration. (C and D) The addition of tBp enhances the excited state lifetime of the photoexcited chromophore. (E and F) TBA has minimal influence on the time-dependent photoluminescence decay.
limiting power-law behavior at high lithium concentrations. The use of the stretched exponential form quantifies the degree of dispersion through the beta parameter, $\beta$, which has a value between 0 and 1 where a value of 1 indicates monodisperse kinetics. Best fit parameters for all data are given in Table 4.1

The concentration dependence of the three chemical additives on the characteristic excited state lifetime, $\tau$, and the stretching parameter, $\beta$, are shown in Figure 4.3. The systematic trends of the characteristic excited state lifetimes match the expected outcome predicted by the respective shifts of the TiO$_2$ conduction band edge: the increased concentration of lithium leads to a decreased characteristic lifetime and the presence of tBp increases the value of this parameter. Something that is not necessarily predicted is the concentration dependent shift in $\beta$ for both lithium and tBp. As we have shown before, the addition of lithium causes an increase in dispersion with a decrease in characteristic lifetime. However, here we observe a similar relationship where the addition of tBp causes a decrease in dispersion along with an increase in the characteristic lifetime. Further analysis of this correlation between the characteristic lifetime and the amount of dispersion in the distribution is presented below. The concentration of TBA has no effect on either the excited state lifetime or the stretching parameter. The 0 M concentration values of the different additives, shown to the left of the axis break in Figures 4.3 A and B, are technically the same conditions. Film-to-film variations caused slightly different kinetics for this condition, but the observed concentration-dependent trends are reproducible from film-to-film.

The dispersive kinetics described by the stretched exponential fit can be expressed as a Laplace transform of a first-order kinetic time constant distribution. A graphical

80
Table 4.1: Best fit stretched exponential model parameters for chemical additive experiments

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<th>+/-</th>
<th>$\beta$</th>
<th>+/-</th>
<th>frac. res.</th>
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**Figure 4.3:** Analysis of the concentration dependence of chemical additives on the time-dependent photoluminescence of RuP-sensitized TiO$_2$ films. (A and B) Photoluminescence decay curves in Figure 4.1 were fit with a stretched exponential providing two concentration-dependent parameters: the characteristic excited state lifetime, $\tau$, and the stretching parameter, $\beta$. (C) The distribution of excited state lifetimes determined by Laplace transform of the stretched exponential fits as described in the text.
representation of this distribution for various chemical additive conditions is shown in Figure 4.3 C. It is important to note that the stretching parameter $\beta$, while a quantifier for the amount of dispersion, is not a direct measure of the width of the distribution. We measure the width of the distributions by calculating the coefficient of variation and provide those values in the Table 4.1. High lithium concentrations lead to a short characteristic lifetime with a wide distribution with respect to the average lifetime. As the lithium concentration is reduced and the tBp concentration is increased, the characteristic lifetime shifts to longer times and the distribution becomes narrower with respect to the average lifetime. The correlation of best fit $\tau$ and $\beta$ values is explored in more detail below. It is also interesting that $\beta$ adopts a larger range of values for the addition of tBp compared to the addition of Li$^+$, which is consistent with the observation that power-law kinetics are indeed a limiting behavior.$^{14}$

4.3.B. Applied bias influences distribution of excited state lifetimes

To understand the effects of increasing electron density of devices under solar illumination, the dependence of applied bias on device efficiency is important.$^{8,9}$ To measure the effect of applied bias on the photoluminescence decay, the sensitized TiO$_2$ film was incorporated as the working electrode in a three-electrode electrochemical cell which was placed into the TCSPC set up (Ag/AgNO$_3$ reference electrode and Pt counter). We first performed cyclic voltammetry on a sensitized TiO$_2$ film in 100 mM TBA to identify the range of potentials we could access without electrochemically reducing the ruthenium chromophore (Figure 4.4 A). We chose a range from 0-800 mV (vs. Ag/AgNO$_3$) as an appropriate series of positive biases. It is important to note that the oxidation of sensitizer on TiO$_2$ with applied bias greater than 800mV is via charge
percolation through the dye monolayer since TiO$_2$ is not conducting at that potential.\textsuperscript{27} However, application of a positive bias had no effect on the photoluminescence decay in either 100 mM Li$^+$ or 100 mM TBA solutions (Figure 4.4 B and C). This agrees with previous work where applied positive bias had no effect on electron recombination kinetics.\textsuperscript{28}

We next observed the effect of raising the electron density of nanoparticle films by applying a negative bias (Figure 4.5). No effect on the photoluminescence decay was observed with applied potentials less negative than -400 mV (vs Ag/AgNO$_3$). However, applied potentials more negative than -400 mV showed an increase in the excited state lifetime. The same trend occurred in both 100 mM Li$^+$ (Figures 4.5 A and B) and 100 mM TBA (Figure 4.5 C) electrolyte solutions.

To quantify these observations, we again fit the data with a stretched exponential form; the best fit parameters are given in Table 4.2. The quantitative analysis of the effects of applied bias on $\tau$ and $\beta$ are shown in Figure 4.6. The $\tau$ and $\beta$ values remain constant from applied bias of +800 mV to -400 mV. Application of a bias more negative than -400 mV shows increased characteristic times as well as an increase in the stretching parameter. There seems to be a strong correlation between $\tau$ and $\beta$, which is reminiscent of the relationship observed between these two parameters in the chemical additive experiments.

**4.3.C. The characteristic excited state lifetime and the amount of dispersion in the distribution are correlated**

For both the chemical additive experiments and the electrochemical experiments a trend is observed where longer characteristic times are accompanied by less dispersive
Figure 4.4: Photoelectrochemical measurements on RuP-sensitized TiO$_2$ nanoparticle film. (A) Cyclic voltamogram of the sensitized TiO$_2$ nanoparticle film in 100 mM TBA (sensitized TiO$_2$ working electrode, Ag/AgNO$_3$ reference, and Pt counter) showing the redox couple of the ruthenium chromophore at high positive potentials and the reduction of TiO$_2$ at highly negative potentials. (B and C) The time-resolved photoluminescence is unaffected by a positive bias up to 800 mV in either a 100 mM Li$^+$ solution (B) or a 100 mM TBA solution (C).
Figure 4.5: Time-resolved photoluminescence of RuP-sensitized TiO$_2$ films under negative bias in 100 mM Li$^+$ (A and B) and 100 mM TBA (C) acetonitrile solutions (Ag/AgNO$_3$ reference and Pt counter).
Table 4.2: Best fit stretched exponential model parameters for electrochemical experiments

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Figure 4.6: Analysis of the effects of applied electric bias on the time-dependent photoluminescence of RuP-sensitized TiO$_2$ films. (A and B) Photoluminescence decay curves in Figures 4.2 and 4.3 were fit with a stretched exponential to determine the characteristic excited state lifetime, $\tau$, and the stretching parameter, $\beta$. (C) The distribution of excited state lifetimes determined by Laplace transform of the stretched exponential fits.
kinetics. To investigate this, correlation scatter plots of $\tau$ and $\beta$ for both types of experiments are shown in Figure 4.7 A and B. Both plots show two regimes with an inflection point at about 10 ns. The first regime shows that the beta value remains fairly constant ($\beta \propto \tau^{0.05}$) at about 0.3 before this time. After this turnover point, beta increases more dramatically with an increase in the lifetime ($\beta \propto \tau^{0.35}$). The Pearson product-moment correlation coefficients were calculated using equation 4.2:

$$r = \frac{n \sum_i \tau_i \beta_i - \sum_i \tau_i \sum_i \beta_i}{\sqrt{n \sum_i \tau_i^2 - (\sum_i \tau_i)^2} \sqrt{n \sum_i \beta_i^2 - (\sum_i \beta_i)^2}}$$  \hspace{1cm} (4.2)$$

where $i$ is an index summed over all $n$ number of data points. In both cases the values are strongly correlated with a value of 0.93 for the chemical additive experiments and 0.92 for the electrochemical experiments.

The shape of the plots in Figure 4.7 A and B look to be very similar so we directly compared these two plots by overlaying them in Figure 4.7 C where the chemical additive results are plotted with triangles and the electrochemical results are shown as squares. The shapes of the two plots are nearly identical with the chemical additive values systematically having a slightly higher $\beta$ value than those of the electrochemical experiments with the same excited state lifetime. This may be due to the differences in the way the two measurements were collected. The chemical additive measurements were collected on the microscope which created a diffraction limited excitation spot. The electrochemical experiments used a larger excitation spot and any heterogeneity within the film would become magnified and manifest itself as a lower $\beta$ value.
Figure 4.7: Scatter plots of best-fit $\tau$ and $\beta$ values demonstrate that the values of these parameters are correlated for both the addition of chemical additives (A) and application of electric potentials (B). The correlation coefficients are 0.93 and 0.92 respectively. A direct comparison of scatter plots obtained for chemical additive experiments and electrochemical measurements, which exhibit a nearly identical relationship (C).
4.4. Discussion

4.4.A. Expanding parameter space to explore the entire realm of injection kinetics

This study aims at investigating excited state lifetime decay kinetics in the presence of chemical additives and applied electric potential, including how these parameters affect the relationship between the characteristic lifetime and amount of dispersion in the distribution. Others have performed similar measurements to assess the concentration dependence of potential determining ions on the characteristic excited state lifetime and have even noted that the kinetics are highly dispersive.\textsuperscript{4,8,30} Our results agree with these previous studies, but we have systematically expanded the parameter space used in these experiments allowing us to quantify the concentration dependence of the width of the distributions as well. Our data spans the whole realm of injecting kinetics from the highly efficient injection in the 1.0 M lithium case leading to power law kinetics, to semi-efficient injection in the neat acetonitrile case leading to stretched exponential kinetics, and finally the non-injection regime in the 6.8 M tBp electrolyte solution leading to a nearly monodisperse exponential decay similar to the emission kinetics of sensitized ZrO\textsubscript{2} films. This study investigates the kinetics of these three regimes and the intermediate cases, as well as the related effects of applied electric bias.

4.4.B. Exploring dispersive kinetics through the addition of potential determining ions

The chemical additive experiments provide information on the nature of the dispersive kinetics. As the driving force for electron injection increases (by increasing [Li\textsuperscript{+}] or decreasing [tBp]), the photoluminescence decays more quickly but the kinetics also become more dispersive. This result is not consistent with the conventional model.
for excited state electron injection into semiconductors, which is based on theories proposed by Marcus and Gerischer.\textsuperscript{31,32} This model typically assumes that the chromophores are strongly coupled to an energetic continuum of acceptor states in the conduction band of the semiconductor. Marcus theory assumes a parabolic function with respect to the reaction coordinate that is associated with the reorganization energy of the solvent surrounding the excited chromophore. If the donor is strongly coupled to a sufficiently broad energetic continuum of delocalized semiconductor acceptor states, a subset of these states will intersect with the minimum of the donor parabola. In other words, there would be no barrier to electron transfer from the chromophore to a subset of delocalized acceptor states in the continuum. This would lead to a monoexponential decay of the excited state population dependent only on the density of acceptor states. However, the observed time-resolved photoluminescence decays are non-exponential, as evidenced by their curvature on semilogarithmic plots. Most decays are also not well fit by a biexponential form (to account for two distinct populations), but rather require many components or a function composed of a broad distribution of lifetimes, like the stretched exponential.

The observed time-resolved photoluminescence decays are dispersive and exhibit a lifetime distribution whose width varies with solvent conditions. The dispersive kinetics indicate that there is a distribution of excited state lifetimes, and since the excited state is quenched by electron injection, this also indicates that there is a distribution of injection rate constants within the sample. Such a distribution would occur if each chromophore were only strongly coupled to a small number of acceptor states and if these states are distributed in energy.\textsuperscript{14} As the conduction band edge shifts in the presence of
potential determining ions, the density of available acceptor states also changes. The acceptor states must be somewhat localized, since they couple to a subset of chromophores, and distributed in energy. These are characteristics of the sub-bandgap trap states, which are common in TiO₂ and other semiconductors.²⁸ Thus, we believe it is likely that the acceptor states are primarily composed of the sub-bandgap states. It is well established that the density of sub-bandgap states varies exponentially with energy below the conduction band, and that these states shift in energy with the conduction band edge (Figure 4.8).³³ Injection is possible only for states whose energy is similar to or below the chromophore excited state energy, so additive-induced energetic shifts can change the distribution of available acceptor states in the semiconductor.

We note that an alternate explanation for the origin of dispersive kinetics is that the chromophore-acceptor state coupling strength varies within the sample.⁸ We believe this is less likely because the degree of dispersion can be modulated by either chemical additives or by applying an external bias. While chemical changes may modify chromophore-acceptor state coupling, it is not clear how application of a bias would directly affect coupling strength. Thus, our data are consistent with electron injection into a distribution of localized sub-bandgap acceptor states.

4.4.C. Influencing the dispersive kinetics by raising the Fermi level with applied bias

To further investigate these dispersive emission decay kinetics, we studied the relationship between the characteristic excited state lifetime and the amount of dispersion in the distribution with applied electric potential. Previously we showed that emission decay followed power law kinetics in conditions where electron injection was highly favored.¹⁴ We initially suspected that the injection kinetics could be limited by charge
mobility, which can also exhibit power-law scaling behavior\textsuperscript{34}, and hypothesized that the application of a positive bias would draw injected electrons out of the film allowing for the photoluminescence kinetics to be quenched beyond the power-law behavior. This was not the case and in fact a positive bias has no effect on the time-dependent emission decay kinetics. Furthermore application of a negative bias between 0 V and -400 mV (vs. Ag/AgNO\textsubscript{3}) had no affect either. The applied negative potential fills lower energy acceptor states in the semiconductor, i.e. raises the Fermi level (Figure 4.8). Since we see no significant change in the time-dependent photoluminescence decay curves between +800 mV and -400 mV (vs. Ag/AgNO\textsubscript{3}), we can assume that the position of the Fermi level does not reside within an energy level that is densely populated by acceptor states within this potential range. Only after shifting the Fermi level with a -400 mV bias does the density of occupied acceptor states start to influence the signal. Interestingly, we observe a trend similar to the chemical additive experiments, in which application of a negative bias led to a concomitant increase in the characteristic excited state lifetime and decrease in the width of the distribution, as discussed below.

Previous studies have suggested that the enhancement of the emission observed with applied negative bias is due to emission of unbound chromophores.\textsuperscript{8} This supposition is based on the observation that negative applied potentials destabilize the binding of the chromophore to the surface. However, the two-photon setup used in this study is only sensitive to bound chromophores. Since two-photon excitation only occurs in areas of high photon flux, if chromophores become unbound and diffuse into the solution, the spatially localized excitation spot would not excite them. Therefore the enhancement of the emission in our experiments with applied negative potential is not
Figure 4.8: Effect of chemical additives and applied bias on the TiO₂ conduction band edge and sub-bandgap states, which are assumed to follow an exponential distribution in energy. Chemical additives shift the TiO₂ conduction band edge relative to the excited state energy of the chromophore (indicated as D*/D⁺); the sub-bandgap states likely shift with this band edge. Application of an applied bias modulates the TiO₂ Fermi level. Blue areas indicate acceptor states available for injection, while gray areas denote those that are unavailable for injection from the chromophore excited state.
due to unbound chromophores, but rather must be due to the changes in ability of the
chromophores to inject electrons, depending on the density of available acceptor states.

4.4.D. Significance of the correlated characteristic excited state lifetime and amount
of dispersion in the distribution

One novel aspect of this research is the discovery of a correlation between the
characteristic excited state timescale and the amount of dispersion in the
photoluminescence lifetime distribution. This correlation seems to be universal for the
conditions tested. The scatter plots in Figure 4.7 A and B directly illustrate the
relationship between the characteristic lifetime and the distribution, but its effect is also
apparent in the distributions plotted in panel C of both Figures 4.3 and 4.6. As injection
becomes more favorable, the characteristic lifetime shifts towards shorter times and the
distribution broadens. No matter how high the driving force for injection, there is still a
population of chromophores that continue to emit on the hundreds of nanoseconds
timescale. This population is not the result of a purely emitting unquenched population,
which would appear as a peak in the distribution, since the smooth distribution fits the
data very well. We can also rule out any contribution from unbound chromophores
because the two-photon absorption scheme selectively excites only surface-bound
chromophores. On the other hand, as the density of acceptor states is reduced (either by
decreasing \([\text{Li}^+]\), increasing \([\text{tBp}]\) or by the application of a negative bias), the
characteristic excited state lifetime shifts towards longer times and becomes less
dispersive. Again, decreased quenching is not surprising but the continuously decreasing
dispersion is notable. The nature of this transition may be due to cross surface energy
transfer and it will be investigated elsewhere.
It is interesting that the correlation values for the three different chemical additives fall on the same curve. These three additives interact with the TiO$_2$ in very different ways with Li$^+$ intercalating, tBp binding to the surface, and TBA having little interaction with the semiconductor. Despite these differences and regardless of film to film variations, the values of the characteristic excited state lifetime and the stretching parameter seem to be coupled similarly. The overlaying correlation plots from the various chemical additives suggest that although the additives interact with the semiconductor through different mechanisms, they all influence the relationship between the lifetime and the dispersion similarly. Therefore the removal of tBp from the electrolyte solution may have a similar effect of electron accumulation that is coupled with increased lithium concentrations. Furthermore, the ability of lithium ions to intercalate into the lattice network does not affect the semiconductor much differently than tBp only binding to the surface.

This coupled relationship is also observed with the application of applied bias, regardless of the electrolyte solution. As indicated in Figure 4.8, chemical additives effect the acceptor state distribution in a different way than applied bias. Chemical additives shift the relative energies of sub-bandgap states, and thereby change the availability of the higher energy acceptor states. Applying a negative bias raises the Fermi level and thus changes the availability of the lower energy acceptor states. However, both changes lead to a nearly identical correlation between the characteristic lifetime and the amount of dispersion in the distribution. We are unsure why such a relationship exists, but it is likely due to the exponential form of the sub-bandgap density of states.
Understanding the origins of the dispersive kinetics could provide information on improving working device efficiency. While complete DSSC device performance is not typically limited by the number of injected electrons, DSSCs and many related devices are limited by other interfacial kinetic processes including back electron transfer (BET).\cite{35,36} BET occurs when an injected electron reunites with either an oxidized chromophore or the redox couple in the electrolyte solution. Since the injected electron is no longer available for work, this is detrimental to device performance. Previous studies have shown that BET is a kinetically dispersive process that is influenced by both the concentration of potential determining ions and applied electric potential.\cite{3,28} There may well be a relationship between the dispersion in the injection kinetics and the dispersive BET kinetics; a likely origin of both is the energetic distribution of acceptor states within the semiconductor. It would be interesting to test whether there is a related correlation between the characteristic timescale of BET and the distribution of those kinetics.

4.5. Conclusion

The excited state lifetime of a chromophore bound to TiO$_2$ can be adjusted either through the addition of potential determining ions or the application of an applied bias. These two methods change the density of acceptor states that are available for injection either by raising acceptor states above the excited state of the chromophore or occupying acceptor states by raising the Fermi level, which initially resides at an energy level within the bandgap at a low density of acceptor states. Adjusting the injection kinetics with these methods not only shifts the characteristic excited state lifetime of the chromophore, but also introduces a systematic change in the width of the lifetime distribution. There is
a strong correlation between the characteristic excited state lifetime and the amount of
dispersion in the distribution for both the chemical additive experiments as well as the
applied electric potential experiments. Furthermore this correlation is similar for both
experiments despite the differences in the way these parameters influence the density of
acceptor states available for injection. Understanding these dispersive kinetics may
provide insight on other dispersive interfacial processes such as back electron transfer
which is a major limitation to device performance.
REFERENCES


CHAPTER 5. Influence of Cross-Surface energy transfer on time-dependent photoluminescence of sensitized nanocrystalline semiconductor films.

5.1. Introduction:

Mesoporous nanocrystalline TiO$_2$ films sensitized with ruthenium polypyridal chromophores have been studied for potential photovoltaic applications.$^{1,2}$ In these devices, known as dye-sensitized solar cells (DSSC), the absorption of a photon promotes an electron into a metal to ligand charge transfer excited state.$^3$ This excited state can either relax through the emission of a photon, or through the radiationless charge transfer of an electron to the conduction band of the semiconductor. We have recently characterized the dispersive emission kinetics of sensitized TiO$_2$ nanoparticle films in environments that favor varying degrees of electron injection.$^4$ Since electron injection into TiO$_2$ is efficient, especially in high lithium concentrations,$^4$ it may be tempting to assign the residual emission observed to chromophore sites that cannot inject. If chromophore sites were partitioned between two sub-populations, injecting and non-injecting, the photoluminescence observed would exhibit an unquenched sub-population. However, in no case is there evidence for a purely emissive sub-population. One explanation for the lack of evidence for an unquenched population is that cross-surface energy transfer provides an alternate pathway for relaxation.
Cross surface energy transfer is a type of self-exchange reaction where energy is transferred from one species to the other without the breaking or formation of chemical bonds as illustrated in eq 5.1.

\[ A^* + A = A + A^* \]  (5.1)

Self-exchange reactions are used in natural and artificial photosynthesis in order to direct energy towards reaction centers.\(^5\) Our previous results showed no evidence for cross surface-energy transfer but this could be due to the use of solvent conditions that cause the emission to be insensitive to this kinetic process.

Previous reports have investigated cross surface energy transfer through transient polarization spectroscopy\(^5\) and by studying the extent of photoluminescence quenching of varying fractional surface coverage of osmium chromophores.\(^6\) The former report used transient anisotropy measurements to track energy migration by using linear polarized light to photoselect a sub-population of ruthenium chromophores bound to a nanoparticle film and measured how the polarization of the emission changed over time. The later report explores energy migration on ZrO\(_2\) nanoparticle films co-sensitized with ruthenium and osmium chromophores. Although our previous studies did not show evidence for cross-surface energy transfer in a highly efficient injection regime, nor a non-injecting regime, this report does provide evidence for cross-surface energy transfer by performing a load dependence of the ruthenium chromophore on the time-dependent photoluminescence decay in a moderate injecting regime.

Considering cross-surface energy transfer could also help to explain the results of one of our other studies which investigated the influence of electrolyte composition and applied electric potential on the time-dependent photoluminescence decay.\(^7\) In this report
we observed a smooth transition between the power-law emission behavior and exponential decay kinetics by reducing the kinetic drive for electron transfer. As explained earlier, if there was no cross-surface energy transfer we would expect our data to show evidence for two distinct sub-populations: an unquenched population from emitting chromophores and a quenched population from injecting chromophores. On the other hand, if there was abundant cross-surface energy transfer, we would expect to see evidence for only a single quenched population where self-exchange reactions direct the energy to injecting chromophores. Our previous data shows evidence for a continuous population where there is a distribution of quenching times.

This study aims at investigating the influence of cross-surface energy transfer in a range of injection efficiency regimes. We use time-correlated single photon counting (TCSPC) to measure the time-dependent photoluminescence decays of TiO\textsubscript{2} and ZrO\textsubscript{2} nanoparticle films sensitized with ruthenium chromophores in either neat acetonitrile or an acetonitrile solution with 100 mM Li\textsuperscript{+}. The time-dependent Stokes shift, attributed to energy transfer, is studied by performing a Franck-Condon analysis on the spectrally-resolved excited state decay curves. We offer an explanation for the smooth transition observed between the highly efficient injecting case and the non-injecting case by employing a model where chromophores are strongly coupled to only a small number of localized acceptor sites in the semiconductor which leads to a barrier to injection. However, cross-surface energy transfer provides an alternative relaxation pathway for chromophores that are unable to inject.
5.2. Experimental section

The TiO$_2$ and ZrO$_2$ nanoparticle films are deposited on an FTO substrate by the sol-gel process. They are sensitized by immersion in 150 μM with [(Ru(bpy)$_2$(4,4’- (PO$_3$H$_2$)$_2$bpy)]$^{2+}$ (hereafter referred to as RuP) in 0.1 M perchloric acid solution (pH 1). For load dependence studies, an individual film was sensitized incrementally. Between each sensitization step, the film was immersed in an equal length of time in methanol to remove any possible aggregates, the absorbance was measured to track relative surface coverage, and the time-dependent photoluminescence was measured. To study films immersed in an electrolyte solutions, a temporary chamber is created between a glass coverslip and the sensitized nanoparticle film using Teflon spacers. This chamber is filled with the acetonitrile solution. The lithium ion concentration is adjusted by the addition of lithium perchlorate. All experiments were performed under ambient conditions, without degassing or otherwise removing oxygen.

Time dependent photoluminescence measurements were collected using a home-built, two-photon optical microscope integrated with time-correlated single photon counting (TCSPC) electronics (Bekcer & Hickl SPC-130). An ultrashort pulse generated by a Coherent Chameleon Ultra II Ti:sapphire laser (200 fs pulse duration, 80 MHz repetition rate) tuned to 900 nm for optimal excitation of the chromophore was focused onto the sample by a 60x, 1.2NA water immersion objective lens (Olypmus UPLSAPO 60XW); the back aperture of this lens was slightly overfilled to create a diffraction-limited focal spot. The epifluorescence was collected by the objective and optically filtered, as described below, to suppress IR light from the excitation beam. The selected emitted light was then detected by a GaAsP photomultiplier tube (Hamamatsu
H7422P-40mod) whose output was sent to a custom-design preamplifier that has a high-bandwidth-amplified output channel.

For load dependence measurements, a wide bandwidth filter was used to optically filter the emission (Chroma HQ630/100m-2P). For the time-dependent Stokes shift measurements, TCSPC curves were collected sequentially with narrow bandwidth filters (Thorlabs FB570-10, FB590-10, FB610-10, FB630-10, FB650-10, FB670-10, FB690-10, FB710-10) to detect emission for each wavelength. After collecting all wavelengths, the first wavelength was retested to ensure no signal degradation had occurred. For calibration of the intensity at each wavelength the integrated emission spectra was collected for each sample with a spectrofluorometer (FLSP 920, Edinburgh Instruments). The integrated counts for each TCSPC curve, which was allowed to decay completely to baseline within the collection time window, was corrected to match the emission profile. We considered the spectral response of the system and the scalings were consistent.

The pulse repetition rate of the laser output was reduced to 50 kHz by a high-bandwidth electro-optic modulator (ConOptics 350-160). This allows for complete relaxation of all dye molecules to prevent excitation of an already excited chromophore. Samples were excited with infrared pulse energies of ~0.12 nJ. With our measured excitation beam radius of 206 nm, this gives a maximum energy density of 4.5 kW/cm², although it is important to note that with two photon excitation only a small fraction of the incident light is absorbed.
5.3. Results

5.3.A. Load dependence in moderate injection regime

Since self exchange reactions are distance dependent\(^5\), performing load dependence experiments is one way to test for evidence of an influence from cross surface energy transfer. As the concentration of dye molecules increases, the distance between individual chromophores decreases and cross surface energy transfer is more likely to occur. We previously have shown that there is no load dependence on the time-dependent photoluminescence decay on a ZrO\(_2\) film sensitized RuP\(^4\). Injection is prohibited in this case due to the sufficiently high conduction band edge of ZrO\(_2\). Additionally, no load dependence was observed on a sensitized TiO\(_2\) film immersed in pH 1 aqueous solution where injection is highly favored due to the Nernstian dependence of TiO\(_2\)’s conduction band edge on pH\(^{13}\). Increased H\(^+\) concentration lowers the conduction band edge relative to the excited state of the RuP chromophore and kinetically drives electron injection. It was suspected that the lack of a load dependence on these two samples may be due to the fact that these two cases were the extreme injection efficiency regimes.

To test the influence of cross surface energy transfer on excited state decay kinetics within a moderate injection regime, a load dependence of RuP on the time-dependent photoluminescent decay was performed on a TiO\(_2\) nanoparticle film immersed in neat acetonitrile and the results are shown in Figure 5.1 A and B. A single sensitized TiO\(_2\) nanoparticle film was immersed in the sensitizing solution for various lengths of time and the percent dye coverage was tracked by measuring the absorbance at 450 nm. The absorbance at 450 nm after the overnight sensitization was assumed to be from a
Figure 5.1: (A and B) Load Dependence of RuP on a TiO$_2$ nanoparticle film in neat acetonitrile suggests evidence for cross-surface energy transfer. Relative coverage was determined by measuring the absorbance at 450 nm. An overnight sensitization procedure was assumed to be a 100% coverage. (C) The time-dependent emission of the most dilute loading is nearly identical to the exponential decay of free (unbound) RuP in acetonitrile solution.
100% coverage. The time-dependent photoluminescence was measured using TCSPC. To avoid second order kinetics, such as triplet-triplet anhilation, we used low pulse energies to achieve a low concentration of excited chromophores per pulse. Under our conditions, we estimate an average of 0.5 chromophores per nanoparticle were excited with each pulse.

In the most dilute loading, nearly exponential decay kinetics are observed. Figure 5.1 C shows that in the most dilute loading, the time-dependent photoluminescent decay nearly matches that of RuP in solution. As the coverage of RuP increases, the time-dependent emission is systematically quenched. While this could mean we are preferentially sensitizing non-injecting sites first, this also agrees with a model incorporating cross-surface energy transfer. In an initial population of excited chromophores, some chromophores cannot inject. If there are no neighbors, then they are forced to emit with exponential decay kinetics. However, if there is a neighbor to transfer the energy, cross surface energy transfer can provide an alternative pathway to injection.

5.3.B. Analysis of the time-dependent emission spectral shift

Another way to measure cross-surface energy transfer is by analyzing the time-dependent emission spectra. Since energy will preferentially move downhill, if cross surface energy occurs, we expect the emission to shift towards longer wavelengths over time since energy would travel from higher energy to lower energy sites. However, there is also a higher probability of injection from higher energy sites with an equivalent accepter state energy. This necessitates the need for a control where cross surface energy transfer could occur in the absence of injection. Therefore, a sensitized ZrO₂ film is used
as a control as a non-injecting medium compared to TiO$_2$ film where both cross-surface energy transfer and injection can occur concurrently. We assume the surface sites of the two films behave the same since they both consist of similar nanoparticles and are prepared by the same method. The ZrO$_2$ film was placed in a temporary chamber which was either filled with neat acetonitrile or a 100mM Li$^+$ acetonitrile solution and the time-dependent photoluminescence was measured using TCSPC. To map the spectral response, the emission at each designated wavelength was collected sequentially by optically filtering the emission light using narrow bandwidth (10 nm) filters, which we indentify by the central wavelength of the passband. The time-dependent photoluminescence was measured at each wavelength range for both solvent conditions. The normalized results are shown in Figures 5.2 A and C. Figures 5.2 B and D plot the unnormalized data, which have been scaled relative to one another by ensuring the integrated count rate of each measurement matches the steady-state emission profile of a RuP sensitized ZrO$_2$ film immersed in the same acetonitrile solution. These plots show that emission from shorter wavelengths is partially quenched and emission from longer wavelengths decays exponentially as evident by falling on a straight line in the semilogarithmic plots. One explanation for the partial quenching is that cross surface energy transfer is occurring, however this might also be due to high energetic sites injecting into deep surface trap states, as suggested in a previous study.$^{16}$

Spectral mapping was also performed on a TiO$_2$ sensitized film to observe the cross surface energy transfer effects in an efficiently injecting regime (100mM Li$^+$ acetonitrile solution) and a moderate injecting regime (neat acetonitrile). The difference in the injection efficiency between these two solvent conditions is due to the Nernstian
Figure 5.2: Spectral Mapping of the time-dependent emission of RuP on a ZrO₂ nanoparticle film in neat acetonitrile (A and B) and 100mM Li⁺ in acetonitrile (C and D) provides further evidence or cross-surface energy transfer or injection from high energy sites into deep trap states. (A and C) Normalized TCSPC curves show the quenching of the emission from higher wavelengths. (B and D) The integrated count of normalized TCSPC curves are corrected to match the emission profile of RuP on ZrO₂.
dependence mentioned earlier, but where Li\(^+\) in acetonitrile behaves similarly to the H\(^+\) ion in aqueous solutions. As the conduction band is lowered by the increased concentration of Li\(^+\), the kinetic drive for electron injection increases. The same procedure as the ZrO\(_2\) film experiments was performed with a single TiO\(_2\) film and the results are shown in Figure 5.3. However, analysis of these systems is more complicated because emission can be quenched not only by cross surface energy transfer but also by electron injection.

In the neat acetonitrile run, we see that the emission from shorter wavelengths is quenched and the emission from longer wavelengths trends towards more exponential. However, the emission from every wavelength in the 100 mM Li\(^+\) run exhibits power-law decay kinetics. This is consistent with previous experiments in where we observed no influence of cross-surface energy transfer on the excited state decay kinetics in efficiently injecting regimes.

5.3.C Franck-Condon analysis of time-dependent emission spectra

To quantitatively characterize the energy transfer process we applied a Frank-Condon analysis on the corrected TCSPC curves at each time point using eq 5.2.\(^{6,17}\)

\[
\frac{I(E)}{I(E_{\text{max}})} = \sum_{\nu} \left( \frac{E_\nu - \nu \hbar \omega}{E_o} \right)^3 \frac{S}{v!} \exp \left( -\frac{4 \ln 2 \left( \frac{E - E_0 + \nu \hbar \omega}{\Delta \omega_{1/2}} \right)^2}{\hbar} \right) \tag{5.2}
\]

Equation 5.2 expresses the energy dependence of the emission intensity relative to the maximum in the spectrum at \(E_{\text{max}}\) in terms of four parameters: \(E_o\), \(\hbar \omega\), \(S\), and \(\Delta \omega_{1/2}\). \(E_o\) is the difference in energy of the \(\nu^* = 0\) to \(\nu = 0\) vibrational levels which correspond to the excited and ground state of the chromophore. \(S\) and \(\hbar \omega (=\hbar \nu)\) are the associated electron-
Figure 5.3: Spectral Mapping of RuP on TiO$_2$ in neat acetonitrile (A and B) and in a 100mM Li$^+$ acetonitrile solution (C-F) also shows influence from cross-surface energy transfer. (A and C) The normalized TCSPC curves show the quenching of the higher energy emission. (B and D) The integrated count of the normalized TCSPC curves were corrected to match the emission profile of RuP on TiO$_2$. (E and F) The normalized and corrected plots for RuP on TiO$_2$, plotted on a semilogarithmic plot show power-law behavior for every emission wavelength.
vibrational coupling constant and quantum spacing for the coupled mode. The full width at half maximum $\Delta \nu_{1/2}$ includes contributions from the solvent and low-frequency modes treated classically. In the fits $\hbar \omega$ for the average mode was fixed at 1350 cm$^{-1}$. The best fit curves at select times for each measurement are shown in Figure 5.4. The energy values (cm$^{-1}$) were converted to wavelength (nm) and the nonnormalized fits are on the left while the normalized fits are on the right to better show how the spectra changes over time.

In order to quantitatively compare the spectral shifts, for each measurement, the time-dependent shifts of $E_{\text{max}}$ were converted to wavelength and plotted in Figure 5.5. These plots were then fit with an exponential recovery fit (eq 5.3)

$$y = A_1 * (1 - \exp(-t/\tau)) + A_2$$

(5.3)

where $\tau$ is the exponential time constant, $A_1$ is a preexponential coefficient and $A_2$ is an offset value. The best fit parameter values are provided in Table 5.1.

The spectral mapping shows that in all cases, $E_{\text{max}}$ shifts to lower energies and therefore longer wavelengths over time. This shift does not occur with RuP in solution, which suggests it is due to the environment of a bound chromophore. While this implies the influence of cross surface energy transfer, this could also indicate injection from higher energy sites. However, injection into ZrO$_2$ from high energy sites occurs within 200 fs which is much faster than our instrument can detect.$^{16}$ Therefore, on ZrO$_2$, this shift in $E_{\text{max}}$ observed must be due to cross-surface energy transfer.

The ZrO$_2$ emission exhibits a smaller shift than the TiO$_2$ films, but it takes longer on ZrO$_2$ for the emission to plateau. This shows evidence for multiple cross-surface energy transfer steps occurring with one excitation pulse. On TiO$_2$ in neat acetonitrile,
Figure 5.4: Fits from Eq 5.2. of the time-dependent emission profile of RuP on ZrO$_2$ (A - D) and TiO$_2$ (E-F) in neat acetonitrile (A,B,E,F) and 100mM Li$^+$ acetonitrile (C,D,G,H) show how the emission profile changes over time. (A,C,E,G) Non-normalized curves show $E_{\text{max}}$ shifting towards lower wavelengths over time in all cases. (B,D,F,H) Normalized curves also show the shifting $E_{\text{max}}$, but also indicates a widening of the emission profile for the TiO$_2$ in neat acetonitrile case (F).
Figure 5.5: The shift in $E_{\text{max}}$ over time for RuP on ZrO$_2$ (A and B) and TiO$_2$ (C and D) are fit with a single exponential recovery with an offset. Note the time axis in panel (D) is different from the others. The recovery on ZrO$_2$ in both neat acetonitrile (A) and 100mM Li$^+$ acetonitrile (B) show slow recovery (204 ns and 308 ns respectively). The recovery on TiO$_2$ in neat acetonitrile (C) shows a shorter recovery (93 ns) while the recovery on TiO$_2$ in 100mM Li$^+$ acetonitrile (D) shows the quickest recovery (30ns).
Table 5.1: Best fit parameters for the shift of $E_{\text{max}}$ over time

<table>
<thead>
<tr>
<th>Material</th>
<th>$A_1$ (nm)</th>
<th>$\tau$ (ns)</th>
<th>$A_2$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO$_2$ 0 M Li$^+$</td>
<td>25</td>
<td>203</td>
<td>633</td>
</tr>
<tr>
<td>ZrO$_2$ 100 mM Li$^+$</td>
<td>16</td>
<td>308</td>
<td>650</td>
</tr>
<tr>
<td>TiO$_2$ 0 M Li$^+$</td>
<td>50</td>
<td>93</td>
<td>626</td>
</tr>
<tr>
<td>TiO$_2$ 100 mM Li$^+$</td>
<td>30</td>
<td>29</td>
<td>662</td>
</tr>
</tbody>
</table>
the emission has a shorter recovery time of 93 ns. This shorter recovery time is the result of electron injection competing with cross-surface energy transfer reactions. The TiO$_2$ 100 mM Li$^+$ film possess a very short recovery timescale of 29 ns. This agrees with previously published timescales for self-exchange reactions on sensitized nanoparticle systems.$^{17}$ This suggests that self-exchange reactions can occur on these systems, but that multiple self-exchange reactions with one excitation pulse are unlikely.

Of particular interest is the widening of the emission profile for the sensitized TiO$_2$ film in neat acetonitrile. Figure 5.6 shows how $\Delta \nu_{1/2}$ changes over time for each sample. For the TiO$_2$ in 100 mM Li$^+$ case there is no change in $\Delta \nu_{1/2}$. There seems to be short-lived, small scale widening for the ZrO$_2$ film in neat acetonitrile and a small widening of the ZrO$_2$ film in 100 mM Li$^+$. However on the TiO$_2$ film in neat acetonitrile, the value of $\Delta \nu_{1/2}$ systematically increases over time until the value doubles by about 250 ns. This parameter is related to the reorganization energy, from both solvent and low-frequency vibrational modes treated classically. The large reorganization energy reflects the combined occurrence of injection and cross-surface energy transfer that is absent in the other cases.

5.4. Discussion

These results further support our model presented previously for localized chromophore coupling. The current model for electron transfer is derived from models proposed by Marcus and Gerischer.$^{18,19}$ This model typically assumes that the chromophores are strongly coupled to an energetic continuum of acceptor states in the conduction band of the semiconductor. This would lead to a monoexponential decay of the excited state population dependent only on the density of acceptor states. However,
Figure 5.6: The emission profile width over time, determined by the parameter $\Delta \nu_{1/2}$, are plotted for RuP on ZrO$_2$ (A and B) and TiO$_2$ (C and D). The only sample to show significant change is the RuP on TiO$_2$ in neat acetonitrile.
the observed time-resolved photoluminescence decays or RuP on TiO₂ where injection is allowed are non-exponential. On the other hand, if a chromophore is only strongly coupled to a small number of localized acceptor states, there would exist a barrier to injection. Furthermore, since there is an exponential distribution of sub-bandgap acceptor states, there could also be an exponential distribution of barrier heights to injection. This exponential distribution of barrier heights would lead to power-law decay kinetics. This is exactly what we see on the RuP sensitized TiO₂ film in 100mM Li⁺. Furthermore, the power-law kinetics observed previously are not due to the fact that a large bandwidth filter was used. The emission at every wavelength exhibits this behavior.

To explain the difference between the two TiO₂ measurements it is important to note that on this semiconductor emission of a photon, electron injection, and cross surface energy transfer are all competing processes. In high lithium concentrations, electron injection is kinetically favored and cross surface energy transfer is less likely to occur beforehand. Yet, even though injection is kinetically favored, we still observe the emission of a photon. However, these photons are not from a purely unquenched species. The emission follows power-law kinetics and can be modeled by localized coupling and an exponential distribution of barrier heights to injection.

As the lithium concentration decreases the energy level of the acceptor states in the TiO₂ increase. This increase reduces the kinetic drive for electron injection and allows for cross surface energy transfer to occur with a higher probability. If these acceptor states continue to rise above the excited state of the dye, then these acceptor states are no longer available for injection and the chromophore must either transfer its
energy to a neighbor or emit a photon. The reason we previously have seen a smooth transition in the emission decay kinetics and never see a completely unquenched population in these systems is likely due to the fact that there are multiple pathways to relaxation: emission, injection, and cross surface energy transfer. The combination of these processes prevents a significant population of observed chromophores emitting with exponential kinetics.
REFERENCES


Appendix

Appendix 1. Calculations for number of excited dyes per nanoparticle per pulse

Due to the high energy density needed to perform two-photon microscopy, we wanted to calculate the number of excited dye molecules per nanoparticle. However, it is hard to compare directly the excitation rates of one-photon and two-photon absorption. Therefore we calculated the number of excited electrons per nanoparticle per pulse using single photon absorption with powers that resulted in similar signal to that of the two-photon experiments.

The TiO$_2$ film is approximately 7 µm thick, composed of 20 nm diameter nanoparticles. Assuming a cubic packing arrangement, the number of nanoparticles contained within a 1 cm$^2$ area is:

$$\left(\frac{1}{2 \times 10^{-6} \text{ cm/nanoparticle}}\right)^2 \left(\frac{7 \times 10^{-4} \text{ cm}}{2 \times 10^{-6} \text{ cm/nanoparticle}}\right) \approx 8.8 \times 10^{13} \text{ nanoparticles/cm}^2$$

(A.1)

The coverage of RuP dye molecules on the nanoparticles is 0.6 +/- 0.2 molecules per nm$^2$. This gives us ~450 dye molecules per nanoparticle.

The films have an absorbance of ~2, so 99% (~100%) of incident 450 nm photons are absorbed in the linear excitation scheme. The number of photons contained in a 0.012 pJ pulse is:

$$\left(\frac{0.012 \times 10^{-12} \text{ J}}{\text{pulse}}\right) \left(\frac{450 \times 10^{-9} \text{ m}}{6.626 \times 10^{-34} \text{J}s \cdot 3 \times 10^8 \text{ m/s}}\right) \approx 2.7 \times 10^4 \text{ photons/pulse}$$

(A.2)
The area irradiated in the single photon experiment is determined by the diffraction-limited beam radius, which we measured to be 139 nm. The number of nanoparticles in the focused beam area is:

\[ \pi \cdot (139 \times 10^{-7}\text{cm})^2 \cdot 8.8 \times 10^{13} \text{ nanoparticles/cm}^2 \approx 5.3 \times 10^4 \text{ nanoparticles} \quad (A.3) \]

The number of excitations per nanoparticle per pulse are therefore:

\[ \frac{2.7 \times 10^4 \text{ photons/pulse}}{5.3 \times 10^4 \text{ nanoparticles}} \approx 0.51 \frac{\text{photons}}{\text{nanoparticle-pulse}} \quad (A.4) \]

**Appendix 2. Dispersive kinetics models**

The time-dependent emission of isolated chromophores generally exhibits first-order kinetics with a radiative rate constant \( k_r \) (which may include both radiative and non-radiative contributions to the isolated chromophore relaxation). In the presence of an additional non-radiative deactivation process (such as electron injection) that is characterized by a single rate constant, \( k_{nr} \), the chromophore emission continues to exhibit first-order kinetics, but with a rate \( k = k_r + k_{nr} \). In the limit that the non-radiative process is fast, the time-dependent emission is dominated by the quenching kinetics, \( k \approx k_{nr} \). If the quenching process does not exhibit first-order kinetics but is fast compared with the isolated chromophore relaxation, the time-dependent emission still reflects the quenching kinetics. For simplicity, and because most injection kinetics are fast compared with Ru(II) emission, we assume the quenching kinetics dominate the time-dependent photoluminescence of dye-sensitized TiO\(_2\) films.

**Appendix 2.A. Homogeneous first-order injection kinetics**

The simplest model for electron injection involves standard first-order kinetics, in which excited state electrons localized on the chromophore must surmount a well-defined activation energy \( \Delta G^\ddagger \) in order to be injected into the semiconductor. Assuming the
barrier is homogeneous, in the sense that all excited state electrons encounter the same
ΔG⁺, the injection rate constant is defined by the Arrhenius equation:

\[ k \propto e^{-\frac{-\Delta G^+}{RT}} \]  \hspace{1cm} (A.5)

In this case, the time-dependant concentration of excited-state molecules after
photoexcitation is:

\[ c_1(t) \propto e^{-kt}. \]  \hspace{1cm} (A.6)

**Appendix 2.B. Albery model**

Reactions that occur on surfaces or within materials may exhibit microscopically
heterogeneous dynamics due to local variations in the activation energy. Albery and co-
workers\(^{36}\) introduced a model for dispersive kinetics by assuming that the activation
energy for a given site varies from a reference value by a quantity that is linearly
dependent on a variable, \(x\):

\[ \Delta G^+ = \Delta G_0^+ + \gamma xRT \]  \hspace{1cm} (A.7)

The parameter \(\gamma\) determines the magnitude of the energetic dispersion. Substitution of
this expression in the Arrhenius equation yields the rate constant:

\[ k \propto e^{-\frac{-\Delta G_0^+}{RT} - \gamma x} \equiv k_0 e^{-\gamma x}. \]  \hspace{1cm} (A.8)

Albery further assumed the site-to-site deviations described by \(x\) are distributed
normally:

\[ p_A(x) \propto e^{-x^2}. \]  \hspace{1cm} (A.9)

The time dependent concentration of reactants is given by integrating the first-order rate
law across the distribution:

\[ c_A(t) \propto \int_{-\infty}^{\infty} e^{-x^2} e^{-k_0te^{-\gamma x}} \, dx. \]  \hspace{1cm} (A.10)
By change of variables, Eq. A.10 can also be expressed as a Laplace transform of a rate constant distribution, $g_A(k)$:

$$c_A(t) \propto \int_0^\infty \frac{g_A(k)}{k} e^{-kt} dk \quad (A.11)$$

where:

$$g_A(k) = e^{-(ln(k) - ln(k_0))^2/(\gamma^2)} \quad (A.12)$$

In other words, the Albery model is equivalent to a superposition of first-order decay functions whose rate constants are lognormally distributed.16

**Appendix 2.C. Kohlrausch-Williams-Watts (KWW) model**

The KWW model, also known as the stretched-exponential model, has been used extensively to model dispersive kinetics, perhaps because of its relatively simple, closed-form expression in the time domain:

$$c_{KWW}(t) \propto e^{-(k_{KWW}t)\beta} \quad (A.13)$$

The stretching parameter $\beta$ can take on values between 0 and 1 (where $\beta=1$ corresponds to first-order kinetics). Lindsey and Patterson15 demonstrated that this function can be expressed as a Laplace transform:

$$c_{KWW}(t) \propto \int_0^\infty \frac{g_{KWW}(k)}{k} e^{-kt} dk \quad (A.14)$$

where $g_{KWW}$ is a Levy stable distribution function:

$$g_{KWW}(k) = -\frac{1}{\pi} \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \sin(m\pi\beta)\Gamma(m\beta+1) \left(\frac{k}{k_{KWW}}\right)^{-(m\beta)} \quad (A.15)$$

In this expression, $\Gamma$ is the gamma function. Like the Albery distribution, the KWW model also accounts for heterogeneous dynamics using a superposition of first-order decay functions. Although the form of this expression is not as transparent as Eq. A.12,
the distribution of rate constants plotted on a logarithmic scale can be qualitatively described as an asymmetric Gaussian-like function.

**Appendix 2.D. Power-Law model**

In order to account for power-law kinetics, we consider an additional model for heterogenous dynamics in which the activation energy and rate constant depend on the variable $x$ according to Eqns. A.7 and A.8, but the site-to-site deviations described by $x$ are distributed exponentially:

\[ p_{PL}(x) \propto e^{-x} \]  
(A.16)

where $x$ can adopt only non-negative values. The concentration is defined in an analogous manner to Eq. A.10:

\[ c_{PL}(t) \propto \int_{0}^{\infty} e^{-x} e^{-k_0 t e^{-\gamma x}} dx. \]  
(A.17)

Evaluation of the integral in Eq. A.17 involves the incomplete gamma function, but in the limit $k_0 t \gg 1$, Tachiya and Mozumder have shown that the time-dependent concentration follows a power-law decay in time:

\[ c_{PL}(t) \propto (k_0 t)^{-1/\gamma}. \]  
(A.18)

For completeness, we note that this expression can also be written as a Laplace transform:

\[ c_{PL}(t) \propto \int_{0}^{\infty} \frac{g_{PL}(k)}{k} e^{-kt} dk \]  
(A.19)

where the distribution of rate constants is:

\[ g_{PL}(k) \propto \left(\frac{k}{k_0}\right)^{1/\gamma}. \]  
(A.20)

Note that all of the distributions, $g(k)$, are expressed as functions of $k$, but the plots we have given in our figures are functions of $\tau$ where $\tau = 1/k$. 

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Equation A.18 cannot be applied directly to fit experimental data because it diverges at early times. This limitation is due to the mathematical assumption that $t \gg 1/k_o$, which has the physical interpretation that power-law kinetics result only after many attempted barrier crossings. (Note in Eq. A.8 that $k_o$ is included in the Arrhenius pre-exponential frequency factor.) Since the typical timescale for electron injection is much shorter than the nanosecond time resolution of TCSPC, the power-law model can be applied to our time-dependent photoluminescence data. However, the ability to fit our data at all times by convolving a fitting function with our instrument response function required a model that does not diverge at early times. We chose to use a piecewise function that exhibits a power-law decay for times longer than a cutoff, $t_{min}$, and an exponential at early times, but maintains a continuous value and first derivative at $t_{min}$:

$$c(t) \propto \begin{cases} 
\left(\frac{t}{t_{min}}\right)^{-d} \text{ for } t \geq t_{min} \\
\quad e^{-d(\frac{t}{t_{min}} - 1)} \text{ for } t < t_{min} 
\end{cases} \quad \text{(A.21)}$$

Fits that apply this function restrict the value of $t_{min}$ to be less than the FWHM of the instrument response function.

**Appendix 3. Fitting procedure for Chapter 5.** All TCSPC data was fit with a convolution of the experimentally measured instrument response function and the stretched exponential equation (Eq. A.22). Initial fits that reduced the sum of the unweighted residuals did not adequately fit the long-time tails of emission decays due to the low value of the data at these times. To adequately reproduce data that spans a wide range of amplitudes, we applied a fitting function that minimized the sum of the fractional residual (frac. res.) weighted by Poisson signal-to-noise ratio (shot noise due to counting a discrete number of photons) at each time point:
\[
\text{frac. res.} = \sum \frac{(\text{fit}_i - \text{data}_i)}{\sqrt[2]{\text{data}_i}} \times \sqrt{\text{data}_i} = \sum \frac{(\text{fit}_i - \text{data}_i)}{\sqrt[2]{\text{data}_i}}
\]  \hspace{1cm} (A.22)

A small constant approximately equal to the pre-pulse noise floor (typically ~10^{-3}) was added to the denominator to prevent division by zero. Also since baseline noise varies symmetrically about zero, absolute values of the data are used to eliminate negative values.

Since \(\beta\) is not a direct measurement of the width of the distribution we calculated the coefficient of variation, which is a normalized measure of dispersion of the distribution, which is dependent on \(\beta\) by the following equations.\(^2\) The average excited state lifetime is

\[
<\tau> = \frac{\tau}{\beta} \Gamma\left(\frac{1}{\beta}\right)
\]  \hspace{1cm} (A.23)

and the second moment is given by

\[
<\tau^2> = \frac{\tau^2}{\beta} \frac{\Gamma(2/\beta)}{\Gamma(2)}
\]  \hspace{1cm} (A.24)

The coefficient of variation is the standard deviation normalized by the average excited state lifetime and is therefore

\[
\frac{\Delta \tau}{<\tau>} = \frac{\sqrt{<\tau^2> - <\tau>^2}}{<\tau>}
\]  \hspace{1cm} (A.25)
REFERENCES
