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Pauline Lynch

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Exploring the Blinking Dynamics of Eosin Y Photosensitizers for Dye-Sensitized Photocatalysis Using Single-Molecule Spectroscopy

A thesis submitted in partial fulfillment of the requirement for the degree of Bachelor of Science in Chemistry from The College of William and Mary

by

Pauline Gilmer Lynch

Accepted for (Honors)

Dr. Kristin Wantanz, Director

Dr. Nathan Kidwell

Dr. James Kaste

Williamsburg, VA
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Abstract

Dye-sensitized photocatalysis (DSP) is a promising way to harvest solar energy for carbon-neutral fuel production, but a better understanding of how and why it is currently inefficient is necessary. This thesis will delve into the complex excited-state dynamics of Eosin Y (EY), a sensitizer for DSP, on glass substrates. By using single-molecule spectroscopy (SMS) to understand the underlying photophysics at play, we can gain a more complete understanding of the various photophysical events that contribute to inefficient DSP. In particular, SM blinking dynamics give insight into kinetic models.

SM blinking measurements of EY molecules in air and in N₂ were separated into on- and off-time distributions and fit to heavy-tailed functions using the robust combined Maximum Likelihood Estimation (MLE) and Kolmogorov Statistic (KS) method. Both on-time distributions in air and N₂ are power law distributed after an onset time. The off time distribution in air is best fit to a lognormal function, consistent with the Albery model for dispersive electron transfer. The off time distribution for N₂, however, contained contributions from both an exponential and lognormal function with an onset time, consistent with a model where both intersystem crossing and dispersive electron transfer occur. The off-time distribution of an individual molecule was lognormally distributed, consistent with dispersive ET kinetics.

Additionally, blinking dynamics were investigated as a function of laser excitation power, revealing a power-dependence in the on times of individual EY molecules. Furthermore, preliminary studies of EY on TiO₂ exhibit significant visual differences from blinking dynamics on glass. In future studies, the blinking dynamics and kinetics of EY on TiO₂ will be explored in order to gain a more complete understanding of ET in technologically relevant conditions for the design and development of next-generation DSP solar cells.
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Chapter 1: Introduction

1.1 Motivation

By 2050, the global energy demand is predicted to grow to at least 27.6 terawatts (TW), with some estimates as high as 106 TW.\textsuperscript{1,2} The world increasingly relies on fossil fuels, usage of which has increased in recent years and continues to rise, leading to worsening and irreversible impacts on the environment and communities across the globe.\textsuperscript{3} As the contribution of burning fossil fuels to climate change is better understood, there is an urgent need for renewable, affordable, efficient, and carbon-neutral energy sources.\textsuperscript{1,4} Solar energy is an abundant, renewable resource, and is particularly attractive because enough sunlight hits the surface of the earth each year to exceed current and future energy needs.\textsuperscript{5} Unfortunately, current technology for harnessing solar energy is inefficient and too expensive to implement widely. Research is needed to fill this void and develop renewable energy technologies that can provide an alternative to fossil fuels.

Dye-sensitized photocatalysis (DSP) (Fig. 1.1) shows promise as a renewable energy source; it utilizes a chromophore, semiconductor, and catalyst to produce fuel from sunlight.\textsuperscript{2,6,7} DSP systems are heavily inspired by dye-sensitized solar cells (DSSCs).\textsuperscript{6} Both utilize an organic dye adsorbed onto a semiconductor in order to capture the Sun’s energy. DSP systems are more favorable than DSSCs because they addresses issues of energy storage and transportation by producing carbon-neutral fuel.\textsuperscript{2} DSSCs and DSP systems utilize the same principles at the dye-semiconductor interface, but utilize the excited electrons differently. In DSSC, photoexcited electrons are converted directly into electricity. DSP, however, co-adsors an organic dye molecule and a catalyst onto a semiconductor. The photoexcited electrons are first injected into the conduction band (CB) of a semiconductor, and then their energy is used to catalyze fuel
production reactions.\textsuperscript{6} Hydrogen fuel (H\textsubscript{2}) is produced via water splitting reactions, in which two water molecules are broken into oxygen and hydrogen (2H\textsubscript{2}O \rightarrow O\textsubscript{2} + 2H\textsubscript{2}). To produce O\textsubscript{2} and release four protons and four electrons, the hydroxyl bonds of two water molecules must be broken. The protons and electrons subsequently combine to produce H\textsubscript{2} or can combine with CO\textsubscript{2} to produce hydrocarbon fuels in synthetic photosynthesis reactions.\textsuperscript{2} Fujishima and Honda were the first to develop a photo-electrochemical cell that decomposed water to oxygen and hydrogen using visible light without utilizing an external voltage.\textsuperscript{8} Since then, many advances have been made to electrochemical systems.

Unfortunately, DSP systems are currently inefficient due to several reasons. First, they must operate in aqueous environments in order to undergo water splitting for fuel production, which complicates the electron-transfer (ET) dynamics at the dye-semiconductor interface. Aqueous environments are inherently heterogeneous in nature. As a result, the ET kinetics can differ widely from molecule to molecule. Additionally, the thermodynamics and kinetics of the associated chemical reactions must be accounted for as well when considering the ET dynamics and solar cell efficiency. DSP kinetics are further complicated due to the coupling of the short timescales of photoexcitation (i.e., ps-ns) and long timescales of fuel production in the electrocatalyst (i.e., ms-s). Because the chemical reactions associated with water splitting and fuel production occur at a much slower rate than electron generation, a long-lived photo-excited state is necessary for the electron to be injected into the electrocatalyst. Low yields for solar fuel
production in DSP can be attributed in part to charge recombination, where an excited electron falls back down to the dye’s ground state and is unable to inject into the catalyst. As a result of these complications and others, current DSPs exhibit low efficiencies and the underlying photophysics contributing to DSP performance are not well understood.

In order to efficiently produce solar fuel, DSP systems must be able to prolong the lifetime of charge carriers. Ideally, ET from the dye-loaded semiconductor to the catalyst, with no recombination, would enhance the long-lived excited state and allow time for catalysis to occur. One way to extend the lifetime of the dye’s excited state is by employing chromophores containing heavy atoms, which can undergo intersystem crossing (ISC) to a long-lived triplet state. ISC is a radiationless transition between electronic states of different multiplicities and the presence of heavy atoms is known to enhance ISC. The organic dye eosin y (EY) (Fig. 1.2) shows promise as a sensitizer for DSP since it can undergo ISC to a long-lived triplet state. Indeed, in 1984, Moser and Grätzel studied aqueous EY and colloidal TiO₂ systems and found that photoinduced charge separation could achieve a lifetime of several microseconds in the semiconductor, allowing time for the electrons to be injected into the catalyst. It has been used widely in catalytic water splitting, as well as photoredox synthesis. However, little is known about ET processes in DSP, and a recent review has expressed the necessity for thorough investigation into ET in DSP systems. While it is well understood that triplet state population and depopulation via ISC follows first order kinetics, the impacts of substrate, dye structure, and the heavy atom effect on ET kinetics in DSP systems are not well understood. The goal of this research is to

![Figure 1.2: Eosin Y (EY)](image)
elucidate the ET kinetics of EY under technologically relevant conditions using single-molecule spectroscopy (SMS).

1.2 Single-Molecule Spectroscopy

SMS is an incredibly useful tool for understanding the full distribution of behaviors in heterogeneous environments, like those occurring in DSP. By probing individual molecules instead of ensemble averages, SMS provides the ability to reveal the various contributions of ET kinetics to the overall behavior of DSP systems. Photophysics at the dye-semiconductor interface can differ greatly between molecules as the result of changes in molecular orientation relative to other molecules, the semiconductor surface or catalyst. Molecules will behave differently based on their surroundings, and SMS provides the capability to examine how local environment impacts ET kinetics. Each molecule has a distinct free energy, electronic coupling, and distance from the semiconductor, all of which contribute to a molecules’ ET behavior in a solar cell.22 These details, otherwise buried within ensemble average techniques, are critical to understanding photophysics within solar cells.

Single-molecule emitters have been studied using a method called blinking, a phenomenon in which a molecule undergoes stochastic changes in emissive and non-emissive intensity under continuous laser excitation. Blinking essentially measures changes in fluorescent intensity as a function of time. Once an electron is promoted to an excited state via photoexcitation (Pathway a in Fig. 1.3A), a molecule can undergo fluorescence and fall back to the ground state (Pathway b in Fig. 1.3A) or transfer (Pathway c in Fig. 1.3A) into a ‘dark,’ or non-emissive, state (3 in Fig. 1.3A). From the dark state, the excited electron can undergo back electron transfer (BET) (Pathway d in Fig. 1.3A) back to the ground state. Once back in the
ground state, the ground state dye can be excited again. Successive cycles of excitation, fluorescence, charge transfer, and BET produce a series of emissive and non-emissive events, which together form a blinking trace (Fig. 1.3B). A single molecule can be photobleached, where some photochemistry will occur and the molecule will no longer be able to fluoresce and it will remain in a non-emissive state and will not recover emission intensity. Emissive events are called “on” times or events and non-emissive events are called “off” times or events. Durations of on times and off times are associated with rate constants of dark state population and BET, respectively. Robust statistical analysis of the probability distributions of the durations of on and off times can reveal a distribution of rate constants.

Electrons can cycle through these three states (Fig. 1.3A), but this cycling is not favorable for efficient DSP. Kinetic redundancy resulting from cycling through fluorescent pathways prevents electrons from injecting into the semiconductor from the dark state (3 in Fig. 1.3A) and contributes to inefficient DSP. When an EY single-molecule emitter undergoes ISC to a long-lived triplet state, however, the electron can wait in this dark state until the appropriate reactions have proceeded in the catalyst. This research aims to measure the blinking dynamics of

![Figure 1.3: A) Three level schematic of blinking and B) blinking trace of EY with emissive intensity (black line). Red line indicates statistical analysis of emission intensity.](image)
EY in order to understand the kinetics contributing to favorable ISC, which will in turn improve DSP efficiency.

Previous studies have demonstrated that heterogeneous excited-state dynamics can be untangled using single-molecule spectroscopy.\textsuperscript{23,24,33,25–32} Single-molecule blinking dynamics have been used to probe the inhomogeneities of ET occurring in dye-sensitized TiO\textsubscript{2} systems.\textsuperscript{27–33} The Wustholz lab has demonstrated the validity of using SMS to measure the blinking dynamics of rhodamine\textsuperscript{33} and anthraquinone dyes\textsuperscript{34} in order to gain a comprehensive understanding of ET energetics. Prior results from the group have also shown that factors such as dye structure and photodegradation contribute to the heterogeneous electron-transfer dynamics observed at the dye-semiconductor interface in DSSC systems.\textsuperscript{32,35} Studying the kinetics on glass first is an important control in understanding how the presence of a semiconductor impacts the photophysics. Using the SMS and statistical analysis methods previously used by the Wustholz group to understand chromophore blinking dynamics, this research aims to understand the kinetics responsible for blinking in EY for the development and design of efficient DSP solar cells.

1.3 Methods

1.3.1 Sample Preparation

Eosin Y (~99\%) was used as received from Sigma-Aldrich and diluted with ethanol (absolute anhydrous, 200 proof) obtained from Pharmco-Aaper. Base on known pKa values of EY,\textsuperscript{36} the predominant species of EY in ethanol is the dianionic form (EY\textsuperscript{2–}). Glass coverslips (Fisher Scientific, 12-545-102) were cleaned in a base bath for 12-24 h, rinsed in deionized water (ThermoScientific, EasyPure II, 18.2 MΩ cm), and dried with clean air (Wilkerson, X06-02-
000). All dye solutions were prepared in ethanol using base-bathed glassware. For single-molecule measurements, samples were prepared by spin-coating 35 µL of a $5 \times 10^{-10}$ M EY in ethanol solution onto a clean glass coverslip using a spin coater (Laurell Technologies, WS-400-6NPP-LITE) operating at 3000 rpm. The resulting samples were mounted in a custom designed flow cell and left open to ambient air (i.e., $\rho_{O_2} \approx 160$ torr) for oxic conditions or continuously flushed with $N_2$ (Airgas, 100%) at a rate of 0.2-0.5 scfh (Key Instruments, MR3A01AVVT) during anoxic experiments.

1.3.2 Confocal Microscopy

Samples for single-molecule studies were placed on a nanopositioning stage (Physik Instrumente, LP E-545) on top of a confocal microscope (Nikon, TiU). Laser excitation at 532 nm (Spectra Physics, Excelsior) was focused to a diffraction-limited spot using a high numerical aperture (NA) 100× oil-immersion objective (Nikon Plan Fluor, NA=1.3). An excitation power of 0.37 µW at the sample was used for single-molecule measurements. Emission from the sample was collected through the objective, spectrally filtered using an edge filter (Semrock, LP03-532RS-2S), and focused to an avalanche photodiode detector (APD) with a 50-µm aperture (MPD, PDM050CTB) to provide for confocal resolution. A z-axis microscope lock (Applied Science Instruments, MFC-

Figure 1.4: Schematic of confocal microscope for SMS studies.
2000) was used to maintain the focal plane of the objective during raster scans. A custom LabView program was used to control the nanopositioning stage and collect corresponding emission intensity using a 30-ms dwell time. Single-molecule emission was established based on the observation of diffraction-limited spots, blinking dynamics, irreversible single-step photobleaching, and concentration dependence of the spot density. The spot density was approximately 5 molecules per 36 \( \mu \text{m}^2 \) for \( 5 \times 10^{10} \) M EY in \( \text{N}_2 \) and air. For dye scans in air where the exact number of molecules was difficult to quantify (see Fig. 2.2), control experiments in which \( \text{N}_2 \) flow was turned on after ambient air scans to confirm a single-molecule film were performed. Blinking was measured on the spots with the highest number of counts (i.e. intensity), unless they were within ~1 \( \mu \text{m} \) of each other, to ensure blinking was not performed on one molecule more than once.

1.3.3 Blinking Analysis

Blinking dynamics were measured using a 10-ms integration time, defined as emission intensity per 10-ms (also referred to as bin time or dwell time) for durations \( \geq 200 \) s. Blinking traces were analyzed using the change point detection (CPD) method. CPD can resolve up to 20 distinct intensity levels and corresponding durations. It reports statistically significant changes in intensity, and it allows for multiple on and off intensity levels.\(^\text{37}\) An alternative method known as thresholding has been implemented widely, where visual analysis gives an intensity level above which are all emissive events and below which are all non-emissive events. However, studies have shown that thresholding yields false short on-time events and that CPD gives a more accurate description of emissive and non-emissive events, seen in the red line in Fig. 1.3B.\(^\text{38–41}\)
CPD also resolves two types of events called segments and intervals. A segment refers to a given intensity level and an interval corresponds to successive segments that occur prior to a switch between an emissive and non-emissive event. An on interval can be made up of several successive on segments, which occur at different on intensities, whereas an off interval is comprised of successive off segments. A single molecule has equal numbers of on and off intervals. Segments are also called “times” and “events” in this study, consistent with previous reports.\textsuperscript{32,33} In CPD, the first and last segments are disregarded since they are arbitrarily set by the experimental observation time. The lowest deconvolved intensity is designated as a non-emissive or photobleaching event, depending on if emission is recovered. Intensities greater than one standard deviation above the rms noise (for 10-ms integration time, \(~4\) counts) are designated as emissive, or on, events. In this study blinking statistics are used as a method of quantifying and comparing dynamics in air and in N\textsubscript{2}. An event rate is defined as the total number of events per time of trace.

On and off times are compiled into a probability distribution and fit by test functions. On-time distributions reveal information about electron injection and off-time distributions do the same for charge recombination events. Much like first order kinetics are fit by an exponential function, more complicated kinetic models are fit by a given function. For example, dispersive ET kinetics have been shown to follow heavy-tailed distributions, such as power law, lognormal and Weibull functions.\textsuperscript{32,33,42} While the least squares (LS) fitting method has been used widely to model power-law and other heavy-tailed functions, it has been proven to be problematic with power laws.\textsuperscript{43,44} Studies demonstrate that maximum likelihood estimation (MLE) gives a more accurate estimation of the fitting parameters.\textsuperscript{32–34,42,43}

Using this method, the power law, \(P(t) = At^{-\alpha}\), is normalized with an onset time for
power-law behavior \((t_{\min})\), giving:

\[
P(t) = \frac{\alpha-1}{t_{\min}} \left( \frac{t}{t_{\min}} \right)^{-\alpha}, \, \alpha > 1
\] (1)

MLE finds the most likely \(\alpha\) and \(t_{\min}\), where \(\alpha\) is another fitting parameter of power law. However, MLE assumes that a power-law function will fit the dataset and does not indicate whether the fit is accurate.\(^{43}\) Clauset and coworkers determined that MLE only gives accurate fitting parameters when \(t_{\min}\) is found using the Kolmogorov-Smirnov (KS) statistic. Using the statistically robust method developed by Clauset and coworkers, the probability distribution functions (PDFs) were analyzed using a combination of the MLE and KS statistic methods.

The KS test involves transforming the dataset into a cumulative distribution function (CDF) that gives the probability of an event occurring in a time less than or equal to \(t\):

\[
S(t) = \int_{t_{\min}}^{t} P(t') \, dt' = \frac{1}{N} \sum t_i \leq t
\] (2)
in which \(S(t)\) is the CDF and \(P(t')\) is the PDF. In eq. 2, the CDF is determined from the blinking data. An artificial CDF is created which fits the fitting parameters \(\alpha\) and \(t_{\min}\) exactly. The KS statistic is the maximum distance between the real \((S(t)_{data})\) and artificial \((S(t)_{fit})\) datasets, given by:

\[
D = \max_{t \geq t_{\min}} \left| S(t)_{\text{data}} - S(t)_{\text{fit}} \right|
\] (3)

where a perfect fit yields \(D = 0\). The best fit, therefore, is described by the \(\alpha\) and \(t_{\min}\) that minimize \(D\).

In order to find out the plausibility of the fit to the data, the data was analyzed using a goodness-of-fit test developed by Clauset and coworkers.\(^{43}\) The best-fit parameters \(\alpha\) and \(t_{\min}\) are used to simulate synthetic data sets, which are fit in the same way as the empirical data, and the KS statistic for the synthetic data \((D_{\text{synth}})\) is determined. The goodness-of-fit is quantified
using the $p$ value, which represents the fraction of synthetic data sets with KS statistics larger than that of the experimental data:

$$p = \frac{\sum D \leq D_{\text{synth}}}{N_s}$$

(4)

where $N_s$ is the number of synthetic data sets (typically set to $10^4$). $D_{\text{synth}}$ here represents deviations from statistical fluctuations, allowing us to determine if the fitting parameters actually fit the experimental data, and are not artificial. Even if a power-law fit yields a high $p$ value, it does not guarantee that the data are fit by a power-law function. Therefore, the MLE/KS method developed by Riley et al. was used to fit blinking dynamics to other heavy-tailed functions (Weibull and lognormal) in addition to power-law. Previous single-molecule studies have used the MLE/KS analysis to determine lognormal distributions for rhodamine dyes on TiO$_2$, consistent with the Albery model for dispersive ET, in which activation barriers are normally distributed.\textsuperscript{33,34,42,43}

In this research, on- and off-time distributions were also fit to a lognormal function with an onset time. Since analytical expressions for these fit parameters cannot be determined using MLE, a numerical method was used to refine these values. Here, an initial guess for the mean of the distribution is used to seed the numerical method and the best fit is determined by the set of parameters that minimizes the KS statistic. Standard errors in the fit parameters are determined from the second derivative of the log-likelihood with respect to the parameters. All data analyses and fitting procedures were completed in Matlab (version R2018a).

1.4 Outline

In this thesis, SMS studies of EY photosensitizers under varying environmental conditions are presented. An important first step in understanding the complex photophysics is
studying blinking on glass as a control, before proceeding to more technologically relevant substrates, such as TiO$_2$. Therefore, in Chapter 2, the blinking dynamics of EY on glass substrate are explored. First, the blinking dynamics in the absence of oxygen are examined, followed by the more complex dynamics in the presence of oxygen. Using robust KS/MLE analysis, it is shown that the complex excited-state dynamics can be modeled by multiple functions to reflect competing photophysical pathways. As a result, the relative contributions of ISC and dispersive electron transfer in EY blinking dynamics were unraveled. By understanding how competing events contribute to the overall distribution of on- and off-times, a more complete understanding of the underlying processes contributing to DSP inefficiencies is gained.

Chapter 3 explores several secondary studies that motivate future research and pose interesting questions regarding the complex blinking dynamics of EY. Changes in laser excitation power alter the on-time distribution of EY in the presence of oxygen, revealing a power dependency of the blinking dynamics. Finally, future studies of the blinking dynamics of EY on TiO$_2$ are discussed. Preliminary dye film images and blinking traces indicate that the excited-state dynamics of EY are significantly altered in the presence of a semiconductor, encouraging more study of EY under technologically relevant conditions.
Chapter 2: Unraveling the Excited-State Dynamics of EY Photosensitizers Using Single-Molecule Spectroscopy

2.1 Introduction

As mentioned in Chapter 1, EY shows great promise as a photosensitizer for DSP systems because it can undergo ISC. It was hypothesized that these heavy atoms would make the ISC pathway in EY more likely to occur, and the goal of this research was to probe the excited-state dynamics of EY in order to gain a better understanding of the ET dynamics. Initially, the aim was to analyze the blinking dynamics of EY on glass and TiO$_2$ in N$_2$, consistent with previous studies.$^{32-34}$ However, the project changed course significantly. During control experiments and the process of finalizing experimental setup parameters, raster scans and blinking traces were performed with and without N$_2$ flow. Significant visual differences were observed in the spot density and pixilation of dye-film images, as well as in the number and duration of on and off events during blinking traces. The presence of oxygen is known to play a role in the excited state dynamics of EY through quenching of the triplet state to produce singlet oxygen,$^{20,45-47}$ and preliminary observations indicated a stark modification of EY blinking dynamics in ambient air relative to N$_2$. It became clear that the observations in the blinking traces resulted from this phenomena, and thus the scope of the study was expanded to include the impact of oxygen on the photophysics of EY. In this chapter, the blinking dynamics of EY photosensitizers in the absence and presence of oxygen are quantified and analyzed using robust MLE/KS analysis in order to gain a more complete understanding of how triplet state quenching impacts the excited-state dynamics and resulting on- and off-time distributions.
2.2 Blinking Studies in Anoxic Environments

Fig. 2.1 shows a representative false-colored image of $5 \times 10^{-10}$ M EY spun coat onto a glass slide (A) and blinking trace (B) in an anoxic environment. CPD analysis (red line in Fig. 2.1B) of the blinking trace gives 14 intensity levels, 24 on events, and 2 off events, with an average event rate of 0.15 s$^{-1}$. A photobleaching event is seen at 85.9 s. Blinking dynamics of EY with multiple emissive intensities occurring before photobleaching is consistent with previous studies of xanthene and anthraquinone dyes on glass.\textsuperscript{33,34}

In order to examine the full range of photophysical behaviors of EY on glass in N$_2$, the blinking dynamics of 127 molecules were measured and analyzed. Fig. 2.2 presents the on-time distribution that contains 1872 events, with an average on time of 3.5 s and values ranging from 0.02 s to 151.66 s. The off-time distribution contains 513 events, with an average off time of 17.15 s and values ranging from 0.04 s to 195.62 s. The average off time is significantly longer than literature values for the triplet lifetime of EY (e.g. 55 $\mu$s in water,\textsuperscript{48} 3.6 ms in poly(methyl methacrylate)\textsuperscript{47}, and 1 ms on alumina\textsuperscript{49}), which suggests that triplet-state decay is not the primary mechanism responsible for blinking dynamics. The average event rate is $0.09 \pm 0.01$ s$^{-1}$ molecule$^{-1}$. Of the 127 molecules examined, 87 (69%) underwent single-step photobleaching within the observation period (200 s). To understand the nature of the non-emissive state, the on-
and off-time probability distributions were fit to several functions that allow us to glean kinetic information. For example, if blinking is the result of the population and depopulation of the triplet state, it will be consistent with first-order kinetics and the on- and off-time probability distributions will be exponentially distributed. Visual analysis of the distributions in Fig. 2.2 tell us that these are not described by exponential functions, since they are not a straight line on the log-log axes, prompting us to explore more complex photophysical kinetic models and corresponding test functions. The compiled distributions were fit to power-law, lognormal, and Weibull functions using the MLE/KS method, described in 1.3.3.

The resulting fit parameters of the on- and off-time probability distributions for EY in N\textsubscript{2} are shown in Table 2.1. According to p-values alone, the on-time distribution is best fit by a power-law function with $\alpha = 2.46 \pm 0.03$ and $p = 0.02$. Although the positive p-value supports the power-law fit, the given $t_{\text{min}} = 7.55 \text{s}$ means that the fit is only operative for 4% of the data, so it is not an accurate description of the entire distribution. Our efforts to fit the on-time data to Weibull and lognormal functions gave p-values equal to zero. Ultimately, analysis of on-time distributions with the MLE/KS method demonstrates that power-law is operative after an onset time of $\sim 10^1 \text{s}$, but does not fit the majority of the on-time data.

Figure 2.2: The (A) on- and (B) off-time probability distributions of events in air (blue) and in N\textsubscript{2} (red) and their best fit parameters.
The off-time distribution is also best fit to a power law with \( \alpha = 6.7 \pm 0.3 \), \( t_{\text{min}} = 107.43 \text{ s} \), and \( p = 0.74 \). Similar to on-time data, though, the power law does not describe the majority (98%) of the data. Instead, a lognormal distribution is most representative of the off-time data, as demonstrated by a \( p \)-value of 0.03. The lognormal distribution occurs when the logarithm of the sampled variable \( (t) \) is normally distributed according to:

\[
P(t) = \frac{1}{\sqrt{2\pi \sigma t}} e^{-\frac{[\ln(t)-\mu]^2}{2\sigma^2}}
\]

where the scale parameters \( \mu \) and \( \sigma \) correspond to the geometric mean and standard deviation of the variable’s natural logarithm, respectively. The off-time probability distribution for EY in \( \text{N}_2 \) is best fit to a lognormal function corresponding to \( \mu = 1.64 \pm 0.08 \) and \( \sigma = 1.72 \pm 0.05 \) (Fig. 2.2).

Overall, MLE/KS analysis of blinking dynamics of EY on glass in \( \text{N}_2 \) shows that on times are power-law distributed after an onset time and off times are weakly lognormally distributed. These results are consistent with previous studies, which attribute power-law and lognormal behavior to dispersive electron transfer between dyes and trap states on glass.\(^{32,33,50,51}\)

In this case, however, statistically insignificant \( p \)-values indicate that dispersive electron transfer is not the only mechanism responsible for the blinking dynamics observed. Previous ensemble-

<table>
<thead>
<tr>
<th>Power Law: ( \frac{\alpha^{-1} - \frac{t}{t_{\text{min}}}}{t_{\text{min}}} ), ( \alpha ), ( p )</th>
<th>Lognormal: ( \frac{1}{t_{\text{min}}} e^{-\frac{[\ln(t)-\mu]^2}{2\sigma^2}} ), ( \mu ), ( \sigma ), ( p )</th>
<th>Weibull: ( \frac{A}{B} \left( \frac{t}{B} \right)^{A-1} e^{-\left( \frac{t}{B} \right)^A} ), ( A ), ( B ), ( p )</th>
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<tr>
<td>( \text{ON} )</td>
<td>( \text{N}_2 )</td>
<td>7.55</td>
</tr>
<tr>
<td></td>
<td>( \text{Air} )</td>
<td>0.83</td>
</tr>
<tr>
<td>( \text{OFF} )</td>
<td>( \text{N}_2 )</td>
<td>107.43</td>
</tr>
<tr>
<td></td>
<td>( \text{Air} )</td>
<td>4.73</td>
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</tbody>
</table>

\( \text{Table 2.1. Best-fit parameters and } p \)-values for power-law, Weibull, and lognormal distributions. Errors represent one standard deviation. Physically significant fitting results are highlighted in gray.
averaged research shows that upon photoexcitation, EY undergoes rapid ISC (i.e., \( k_{\text{ISC}} \sim 10^8 \text{ s}^{-1} \)) to its lowest energy triplet state, which can be long-lived on solid substrates.\(^{20,47,49,52}\) Triplet blinking could be responsible for blinking events at early times, even if the probability of a 1-s off event occurring for a 1-ms triplet lifetime is minute (\(\sim 10^{-44}\)). If this were the case, the off-time distribution would contain contributions from two competing processes: triplet-state population and dispersive electron transfer. The presence of oxygen is known to significantly impact the excited-state dynamics of EY through quenching of the triplet state to produce singlet oxygen.\(^{20,45-47}\) Therefore, comparing the blinking dynamics of EY in N\(_2\) with that in air will give insight into the hypothesis that ISC to and from the triplet state affects the photophysics of EY.

### 2.3 Impact of Oxygen on Blinking Dynamics

Fig. 2.3 shows a representative false-colored image of 5\( \times \)10\(^{-10}\) M EY spun coat onto a glass slide (A0 and blinking trace (B) in an oxic environment. Although there are a few round spots, typically indicative of a single molecule, image is pixelated in comparison to that in N\(_2\) (Fig. 2.1), demonstrating that non-emissive events longer than the 30-ms bin time are observed frequently. The blinking statistics of EY in air are also distinctive. CPD analysis of the blinking trace in Fig. 2.3B gives 11 intensity levels, 113 on events and 36 off events, with an average event rate of
While 69% of molecules in N$_2$ underwent photobleaching within 200 s, none in air demonstrated photobleaching within this time frame. On the contrary, EY exhibited persistent blinking dynamics for as long as 1000 s (Fig. 2.4). Our observations are consistent with previous studies that show increased photostability of EY in oxic environments.\textsuperscript{46}

Because of these long observation windows and high event rates, the probability distributions of 17 molecules contained 6681 on events and 1810 off events. Emissive event durations ranged from 0.02 s to 193.07 s with an average of 0.66 s. Non-emissive event durations ranged from 0.06 s to 36.2 s with an average of 2.0 s. The average on and off times are an order of magnitude shorter in air than in N$_2$, and the average blinking rate of 0.90 ± 0.07 s$^{-1}$molecule$^{-1}$ is also an order of magnitude higher than that of N$_2$. Like the distributions in N$_2$, the air on- and off-time probability distributions were fit using MLE/KS analysis, and fitting parameters are summarized in Table 2.1. The distributions and best-fit parameters are given in Fig. 2.2. The on-time distribution is fit best by a power law with a $p$-value of 0.11, corresponding to $\alpha = 2.38 \pm 0.02$ and $t_{min} = 0.83$ s, which describes 31\% of the dataset. Fits to Weibull and lognormal functions gave $p$-values of zero. The off-time distribution was best fit by power law, corresponding to $p = 0.20, \alpha = 2.83 \pm 0.04, t_{min} = 4.73$ s. However, the late onset time means that power law only fits a small subset (10\%) of the off-time data. Unlike the on times, a non-
zero $p$-value of 0.007 suggests that a lognormal distribution with $\mu = 0.10 \pm 0.03$ and $\sigma = 1.07 \pm 0.02$ is a plausible model for the off-time data.

Substantial differences in the single-molecule blinking dynamics are seen for EY in oxic and anoxic environments. The increase of an order of magnitude in the average single-molecule event rate and short event durations in air lead to significantly more events occurring in the presence of oxygen. Additionally, most of the molecules in anoxic environments photobleached within 200 s, whereas persistent blinking in EY in air was observed for durations up to 1000 s. Both on-time distributions are modeled by power law functions after an onset time, and $\alpha$ is modified in $\text{N}_2$ ($\alpha = 2.46 \pm 0.03$) versus air ($\alpha = 2.38 \pm 0.02$). The best-fit parameters of the off-time probability distributions are significantly different for $\text{N}_2$ (i.e., $\mu = 1.64 \pm 0.08$ and $\sigma = 1.72 \pm 0.05$) as compared to air (i.e., $\mu = 0.10 \pm 0.03$ and $\sigma = 1.07 \pm 0.02$). Overall, the presence of oxygen has a significant impact on the blinking dynamics of EY, which is consistent with a physical mechanism that involves the population and depopulation of the triplet state.

2.4 Discussion

2.4.1 Albery Model for Power Law and Lognormal Distributions

Previous research has shown that power-law and lognormal distributions are consistent with dispersive electron transfer between an excited dye and substrate (Fig. 2.5A).\textsuperscript{33} In this expression, $k_{\text{exc}}$, $k_{\text{fl}}$, $k_{\text{inj}}$, and $k_{\text{rec}}$ are rate constants for excitation, emission, and population (injection) and depopulation (recombination) of the dark state, respectively. Injection and recombination rate constants support the Albery model of electron transfer, which gives a Gaussian distribution of activation barriers to electron transfer.\textsuperscript{53} In this model, the duration of an
off event \( (\tau_{\text{off}}) \) is equivalent to the lifetime of the dark state (i.e., \( \tau_{\text{rec}} = 1/k_{\text{rec}} \)). The Albery model predicts a lognormal distribution of off events. The lifetime of the emissive state \( (\tau_{\text{on,A}}) \) is more convoluted, as it is dependent on the rate constant for injection \( (k_{\text{inj}}) \), which is partially responsible for depopulating the excited state, as well as the population and depopulation resulting from excitation \( (k_{\text{exc}}) \) and emission \( (k_{\text{fl}}) \). The expression for the emissive state lifetime is:

\[
\tau_{\text{on,A}} = \left[ k_{\text{inj}} \left( \frac{k_{\text{exc}}}{k_{\text{inj}} + k_{\text{fl}}} \right) \right]^{-1} \quad (6)
\]

Previous studies have shown that the on-time probability distribution can be power-law or lognormally distributed.\(^{32-34}\)

The observation of power-law and lognormal distributions for EY does support the role of dispersive electron transfer for blinking dynamics, but this explanation fails to account for the oxygen-dependent photophysics (i.e. triplet blinking) as well as the statistically insignificant \( p \)-values \(<0.05\) corresponding to the lognormal fits of the off-time distributions. This suggests that the Albery model does not give a complete picture of the blinking kinetics of EY, and that the lognormal distribution is an inadequate description of the data. As a result, alternative kinetic

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**Figure 2.5:** Energy level diagrams for blinking consisting of a singlet ground state \( (S_0) \), an excited singlet state \( (S_1) \), an excited triplet state \( (T_1) \), and a dark state \( (D) \), with corresponding rate constants. (A) dispersive electron transfer; triplet blinking and dispersive electron transfer in the (B) presence and (C) absence of oxygen. Dotted arrows indicate dispersive ET and solid arrows indicate a single rate constant.
models and expressions were explored to incorporate triplet blinking and dispersive electron transfer to describe the data.

2.4.2 Kinetic Expressions for Triplet Blinking and Dispersive Electron Transfer

Single-molecules studies in polymer\textsuperscript{50} and crystal\textsuperscript{54} environments have utilized a four electronic state system with a triplet state and a dark state to model power-law behavior. For EY, both power law and lognormal behavior is observed, although \( p \)-values are modest. In Fig. 2.5B, a four level system is proposed to take into account the impact of singlet oxygen formation on the blinking dynamics of EY in oxic conditions. Here, photoexcitation of EY to its excited singlet state (\( S_1 \)) is followed by rapid ISC to a triplet state (\( T_1 \)). The triplet is quenched in the presence of triplet oxygen (\( ^1O_2 \)) to form singlet oxygen (\( ^1O_2 \)), with rate constant \( k_q \). If depopulation of \( T_1 \) via quenching is fast relative to population of \( T_1 \) via ISC, then a small steady-state concentration of \( T_1 \) is present. Thus, the four-level system effectively reduces to a three-level system (Fig. 2.5A). In this case, population of the dark state via dispersive electron transfer will likely occur from \( S_1 \) (i.e. the oxidation potential of EY in the excited singlet state, \( E^0 (EY^*/EY) \), is -1.53 V vs. NHE\textsuperscript{15,55} to localized trap states on glass\textsuperscript{51}.

In this expression, \( \tau_{off} \) is equal to the lifetime of the dark state (\( \tau_{rec} \)) and we predict that the off-time distribution will be lognormally distributed. The on times for Fig. 2.5B (\( \tau_{on,B} \)) are dependent on the rate constant for population of the dark-state as well as the fractional populations of the excited singlet and triplet states. The on-time probability distribution is a convolution of the kinetics for emission as well as dark-state population and depopulation. On time durations follow the expression:

\[
\tau_{on,B} = \left[ k_{inj} \left( \frac{k_{exc}}{k_{inj} + k_{fl}} \right) \left( \frac{k_{lsce}}{k_{lsce} + k_{inj}} \right) \right]^{-1}
\]

(7)
The fast quenching of $T_1$ by singlet oxygen formation effectively reduces the four level system to a three-state model with dispersive electron-transfer for blinking, in which “on” corresponds to $S_0 \rightleftharpoons S_1$ and “off” is the non-emissive radical cation state of EY.$^{15}$

On the other hand, if there is no oxygen present, or $k_q$ is not significantly larger than $k_{isc}$, then a more complex kinetic picture is at play (Fig. 2.5C). In this case, both triplet blinking and dispersive electron transfer contribute to the kinetics, so the measured on times come from $\tau_{rec}$ as well as the lifetime of triplet state (i.e., $\tau_T = 1/k'_{isc}$). The off-time distribution is then predicted to be a combination of an exponential distribution (first order kinetics for triplet blinking) and a lognormal distribution (dispersive electron transfer from $S_1$ and/or $T_1$).$^{15}$ For Fig. 2.5C, the on times ($\tau_{on,c}$) depend on intersystem crossing to the triplet state ($k_{isc}$) and the fractional population of the excited state according to:

$$\tau_{on,c} = \left[k_{isc} \left(\frac{k_{exc}}{k_{inj}+k_{fl}}\right)\right]^{-1}$$

The on-time probability distributions are very complex, and are not well represented by any test function, consistent with the proposed models in Fig. 2.5B and 2.5C. The presence of a small $p$-value for a lognormal distribution of off times for EY in $N_2$ implies that the kinetics modeled by Fig. 2.5C may be present. The statistically insignificant $p$-value could indicate more complex behavior and an onset time for lognormal behavior. The current MLE/KS method does not allow us to distinguish between competing photophysical processes in one probability distribution. However, we hypothesize that the off-time distributions could be fit with an exponential distribution, to account for triplet blinking at early times, and a lognormal distribution, to account for dispersive electron transfer at later times. To test this theory, fitting methods that allow for differentiation between competing photophysical processes were explored.
2.4.3 Modeling Competitive Photophysical Processes

Recently, a “scanning” MLE/KS method was developed by Mitsui and coworkers, in which the onset time \( t_{\text{min}} \) of lognormal behavior is progressively changed to determine whether there are contributions from other functions in the data.\(^{56} \) They calculated the \( p \)-value as a function of \( t_{\text{min}} \) and showed that the off-time distribution of Atto 647N dyes on TiO\(_2\) is described by a combination of exponential, power law, and lognormal functions. Similarly, Clauset and coworkers developed a method that uses MLE/KS to determine the best \( t_{\text{min}} \) such that the data is fit by a lognormal function with an onset time. This method normalizes the lognormal distribution from \( t_{\text{min}} \) (instead of zero as is done for eq. 5) to yield:

\[
P(t) = \frac{1}{\sqrt{2\pi\sigma t}} \text{erfc} \left( \frac{\ln t - \mu}{\sqrt{2}\sigma} \right) e^{-\frac{(\ln(t) - \mu)^2}{2\sigma^2}}
\] (9)

The data were analyzed using both methods in order to determine if more than one function could be fit to the off-time probability distributions. The scanning MLE/KS method did not yield a \( t_{\text{min}} \) value that was statistically significant and physically relevant. As a result, we used the approach where the best \( t_{\text{min}} \) is determined using eq. 9. Although all of the on- and off-time distributions were analyzed using this method, only the off times in N\(_2\) gave a \( t_{\text{min}} \) greater than the first data point. The off time distribution of EY in N\(_2\) is shown in Fig. 2.6, with the best fit lognormal function corresponding to \( t_{\text{min}} = 0.14 \) s.

![Figure 2.6: Off-time probability distribution (solid black line) of EY in N\(_2\) with best fit to a lognormal function after an onset time of 0.14 s (red dashed line) and an exponential function at early times (blue dotted line).](image)
\( \mu = 1.63 \pm 0.06, \sigma = 1.8 \pm 0.1, \) and \( p = 0.07. \) The statistically significant \( p \)-value suggests that the lognormal distribution could be operative for the 98% of the data that occurs after the onset time, \( t_{\text{min}} = 0.14 \text{ s}. \) The observation that a lognormal distribution does not fit off times occurring before 0.14 s indicates that there is another photophysical process at play, such as triplet state blinking. The first part of the distribution was fit to an exponential fit, consistent with triplet state population and depopulation.

Because we observe that the off-time probability distribution for EY in N\(_2\) is best fit to a lognormal distribution following an onset time, it suggests that the kinetic model shown in Fig. 2.5C is operative. Both dispersive electron transfer and triplet blinking occur in anoxic environments, so the off-time durations \((\tau_{\text{off}})\) result from both processes. The off-time probability distribution contains an exponential distribution at early times, accounting for the contribution of triplet state decay, and a lognormal distribution at later times, accounting for electron transfer. It was considered that a power law could describe the tail of the distribution well, as seen by the power-law fitting parameters from Table 2.1, but the third function was not included due to two reasons. First, since a statistically significant \( p \)-value is seen for the lognormal function after \( t_{\text{min}} \), the tail of the distribution is already fit by a test function. Secondly, the physical meaning of a third function is unclear and could not be connected to the proposed kinetic models in Fig. 2.5. As a result, using three functions to fit the distribution was not justifiable.

The best fit of early times (i.e. before the onset time of the lognormal function, from 0.04 to 0.14 s) to an exponential decay \((P(t) = \frac{1}{\tau} e^{-t/\tau})\) is shown in Fig. 2.6, and corresponds to \( \tau = 93 \text{ ms}. \) Although the time constant is much longer than the reported triplet lifetime of EY on alumina (1 ms),\(^{49}\) we suggest that triplet-state decay is occurring at timescales faster than the 10-
ms bin time of our experiment. In order to test this hypothesis, blinking measurements of EY with a 1-ms integration time were performed.

A recent study by Mitsui and coworkers progressively shortened the bin time for measuring the single-molecule blinking dynamics of perylenediimide (DMP-PDI) in a matrix of poly(methyl methacrylate) (PMMA). They observed bin time dependence in the resulting probability distributions as they changed the bin time over five orders of magnitude (0.08-100 ms). By capturing shorter time events, they are able to see events that occur on different timescales, and in their analysis they attribute early times to ISC and later times to charge transfer. While the probability of seeing an event corresponding to triplet state decay is very

Figure 2.7: (A) Blinking trace of EY in air at 1-ms bin time and (B) corresponding trace binned up to 10-ms. (C) 1-ms bin time blinking trace of EY in N₂ and (D) corresponding binned up trace.
small for both 10- and 1-ms bin times, in theory the contribution of shorter time events should become more apparent as the bin time is lowered.

Blinking dynamics of EY in both N₂ and in air (Fig. 2.7) were using a 1-ms bin time. In order to determine that the data was valid, the 1-ms blinking traces were “binned up” to 10-ms. Here, counts from 10-ms windows are summed, and this value is a data point on a 10-ms bin time blinking trace. Binning up the data allows for comparison between the experimental 10-ms data and the binned up 1-ms data. They should exhibit the same blinking statistics and their probability distributions should be fit by the same test function. After performing CPD analysis on the binned up traces, it was determined that the resulting traces did not reflect the dynamics seen with an experimental 10-ms bin time. Changing the bin time is known to introduce artificial events and can alter the resulting probability distributions and fits.⁵⁸,⁵⁹ The resulting signal-to-noise was too low to prevent the introduction of binning artifacts. As a result, the 1-ms bin time experiments were not included in the analysis of the EY blinking dynamics.

Analysis of the on- and off-time probability distributions of EY blinking dynamics using the MLE/KS method unveil the contributions of the competing photophysical processes of triplet state blinking and dispersive electron transfer. In anoxic environments, both processes contribute to the blinking dynamics. However, in the presence of oxygen, the triplet state (T₁) is rapidly quenched by the formation of singlet oxygen species such that electron transfer is the primary contributor to blinking dynamics. The relationship between the lognormal fitting parameters and dispersive electron-transfer kinetics has been demonstrated in previous studies, where −μₐ₉ is proportional to the average rate constant for dark state depopulation (−μₐ₉ = ln(kₐ₉)) and σₐ₉ corresponds to the energetic dispersion around the mean activation barrier. ³² In this study, we find that −μₐ₉ of EY in air is −0.10 ± 0.03, similar to values for rhodamine dyes not
containing heavy atoms.\textsuperscript{33} This supports the hypothesis that EY triplet blinking does not occur in the presence of oxygen. The observation of persistent blinking dynamics of EY in air is consistent with previous work and suggests that the short lifetime of singlet oxygen limits the oxidative degradation of EY.\textsuperscript{46} It is also possible that fluctuations in the triplet state lifetime and fluorescence quantum yield result from spectral diffusion, like during photoinduced debromination events.\textsuperscript{46} These observations motivate more research in order to understand how spectral diffusion impacts the excited-state kinetics of EY.

Observed $\sigma$ values are very different for EY in air ($\sigma_{\text{off}} = 1.07 \pm 0.02$) versus N\textsubscript{2} ($\sigma_{\text{off}} = 1.8 \pm 0.1$), which suggests that there are different photophysical processes at play. It is likely that both static and dynamic heterogeneity of electron transfer is operative, which is consistent with our observation of dispersive kinetics in an individual molecule of EY in air. Static heterogeneity refers to individual molecules with homogeneous kinetics that contribute to a heterogeneous environment, whereas dynamic heterogeneity involves individual molecules with kinetics that evolve over time. In addition to analyzing the probability distributions of the on and off events for all molecules measured in air, the probability distribution of an individual molecule of EY in air was analyzed using the MLE/KS method. During a 500 s observation window, CPD analysis gave 338 emissive and 99 non-emissive events, which were plotted in on- and off-time probability distributions, respectively (Fig. 2.8). The on-time distribution is best fit to a power law corresponding to $\alpha = 1.94 \pm 0.06$, $t_{\text{min}} = 0.20$ s, and $p = 0.27$. The off-time distribution is best fit by a lognormal function with fitting parameters $\mu = -0.17 \pm 0.09$, $\sigma = 0.92 \pm 0.07$, and $p = 0.67$. All other test functions yielded statistically insignificant $p$-values. A lognormal fit of off times for an individual molecule is consistent with dispersive kinetics that incorporate dynamic heterogeneity; that is, the rate constants evolve over time.\textsuperscript{60–63}
Dispersive kinetics in an individual molecule have been reported for multichromophoric systems,\textsuperscript{62} molecules in crystals\textsuperscript{63} and in polymer,\textsuperscript{57,64,65} but our observation is unique, as it is one molecule on glass in the presence of oxygen. Although consistent with dispersive electron transfer, the fitting parameters calculated in this analysis are significantly modified from the multi-molecule distributions analyzed in 2.3. The ability to analyze an individual molecule’s blinking dynamics using the MLE/KS method opens the door to further untangle the single-molecule photophysics of EY as a photosensitizer, and to investigate more deeply the relationship between kinetics and environment.

2.5 Conclusion

In this study, single-molecule spectroscopy was used to unveil the excited-state dynamics of EY. We utilized the statistically robust MLE/KS method to quantify the blinking dynamics in oxic and anoxic environments, and revealed the relative contributions of triplet-state decay and dispersive electron transfer. The on-time probability distributions in N\textsubscript{2} and air are power-law distributed after about 1 s, and the fitting parameters are altered significantly in the presence of oxygen.
The off-time probability distribution for EY in \( N_2 \) contains contributions from exponential and lognormal functions. Based on this, a kinetic model that accounts for competing triplet state population and dispersive electron transfer was proposed. The off-time distribution in air is best fit to a lognormal function, consistent with dispersive electron transfer. The results in this study reveal the underlying photophysical kinetics for EY sensitizers on glass substrate, which is an important first step in the development and design of more efficient DSP systems, in addition to its relevance in photodynamic therapy\textsuperscript{45,66} and cultural heritage applications.\textsuperscript{46,67,68}
Chapter 3: Secondary Experiments

3.1 Power Dependent Blinking Dynamics

Power-dependent blinking analysis was also performed, in which the power of laser excitation was varied from 3.7 µW to 21.2 µW. The excitation power was varied with the intention of photobleaching a molecule of EY in air, since none had exhibited single-step photobleaching within the observation period at 0.37 µW. However, a change in the blinking dynamics of EY in air as the laser power increased from 3.7 µW to 21.2 µW was observed. Visual inspection of the on-time distributions (Fig. 3.1) indicates that there is a power-dependency in the blinking dynamics. All blinking traces were performed on distinct individual molecules and had an observation period of 300 s, but exhibited a variation in the number of on and off events. Indeed, the event rate changed drastically with laser power. Blinking traces were taken at 3.7, 6.7, 9.9, 14.8, and 21.2 µW, with event rates of 1.93 s⁻¹, 2.35 s⁻¹, 1.23 s⁻¹, 0.85 s⁻¹, and 0.43 s⁻¹, respectively. Additionally, the observation of a significant change in fitting parameters to their on-time probability distributions (Table 3.1) indicates that the laser power significantly alters excited-state behavior. The fitting parameters also differ from that of the

<table>
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<th>Power Law: $\frac{\tau}{t_{\text{min}}}^{\alpha} \left( \frac{\tau}{t_{\text{min}}} \right)^{-\alpha}$</th>
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<th>Weibull: $\frac{A}{\beta} (\frac{\tau}{\beta})^{A-1} e^{-\left(\frac{\tau}{\beta}\right)^A}$</th>
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</tr>
<tr>
<td>21.2 µW</td>
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Table 3.1: Fitting parameters for on-time probability distributions of individual EY molecules with varying excitation power.
individual molecule in air (included in Table 3.1). Off-time probability distributions were not analyzed due to the low number of off times (for 3.7 µW, 64 off segments, 78 for 6.7 µW, 67 for 9.9 µW, 43 for 14.8 µW, 28 for 21.1 µW).

By increasing the excitation power, the rate constant \( k_{\text{exc}} \) increases as well. As a result, the lifetime of the singlet excited state \( \tau_{\text{on, A}} \) should decrease based on the kinetic expressions proposed in 2.4.1 and in eq. 6. In the distributions in Fig. 3.1, the on-time distributions at higher powers are skewed to shorter durations than the on-time distribution at 0.37 µW (black), supporting this hypothesis. For excitation powers less than 6.7 µW, power law appears to be operative for the majority of the data. Although power law yields a statistically significant p-value for 6.7 µW, it only fits 12% of the data. Other test functions yielded p-values equal to zero at for 6.7 µW. At higher powers, a lognormal fit yields non-zero p-values. Here, \( -\mu_{\text{on}} \) is proportional to the average rate constant for on-state population \( -\mu_{\text{on}} \propto \ln k_{\text{on}} \), so one would expect the distributions to shift towards shorter on events as \( -\mu_{\text{on}} \) decreases. This trend is not readily apparent, but decisive conclusions cannot be drawn, because the observations are for an individual molecule at each power. Further investigation, however, could give more clues to the roles of static and dynamic heterogeneity at play in the excited-state dynamics of EY.

**Figure 3.1:** On-time distributions of individual molecules of EY with varying excitation power: 0.37 µW (black), 3.7 µW (red), 6.7 µW (blue), 9.9 µW (green), 14.8 µW (purple), 21.2 µW (yellow).
3.4 Blinking Dynamics of EY on TiO₂

As with previous studies in the Wustholz lab, studies of dyes on both glass and TiO₂ substrate are necessary to fully comprehend the complete range of photophysical activity of a sensitizer for solar energy and DSP applications. The blinking studies of EY performed on glass in the presence and absence of oxygen are critical first steps to understanding the complex dynamics of EY operative in DSP systems. For EY, it is crucial to conduct studies in both air and N₂, as done on glass, in order to understand the role of substrate in modifying the blinking dynamics. The kinetic models proposed in Chapter 2 (Fig. 2.4) could be significantly altered when a semiconductor like TiO₂ is introduced.

Preliminary studies have been conducted (Fig. 3.2), and visual analysis of the dye scans and blinking traces indicates that TiO₂ changes the kinetic activity significantly. The observed changes in air (Fig. 3.2 C and D) are particularly intriguing, as they differ greatly from the dynamics observed on glass (Fig. 2.3). On glass, the dye film scans were very pixelated, but on TiO₂ individual molecules can be discerned (Fig. 3.2C), indicating that fewer non-

Figure 3.2: False-colored image of $1 \times 10^{-9}$ M EY on TiO₂ in (A) N₂ with (B) corresponding blinking trace and (C) in air with (D) corresponding blinking trace.
emissive events longer than the 30-ms bin time are observed as compared to glass (Fig. 2.3). In the blinking trace in air, there are long non-emissive events, which suggests that EY more readily injects into the dark state on TiO$_2$. The dynamics observed in N$_2$ (Fig. 3.2 A and B) are not visually drastically altered from that on glass, so no conclusions can be drawn from these data yet. A full dataset of molecules in air and N$_2$ need to be collected and analyzed with the MLE/KS method in order to give a comprehensive understanding of the excited-state photophysics of EY under more technologically relevant conditions.

By probing the complex excited-state dynamics, this research has provided new insights into the ET dynamics of EY photosensitizers. Through the analysis presented here, proposed kinetic models and corresponding test functions give a more complete understanding of how EY behaves. SMS and robust statistical analysis reveal contributions from both dispersive ET and ISC, as well as altered kinetics in the presence of oxygen. Moving forward, studies on TiO$_2$ will reveal more technologically relevant kinetic models. This study is a crucial first step towards the development and design of next-generation DSP solar cell technology.
References


