Time Resolved Single Molecule Spectroscopy of Semiconductor Quantum Dot/conjugated Organic Hybrid Nanostructures

Michael Yemoh Odoi

University of Massachusetts Amherst, myodoi@gmail.com

Follow this and additional works at: https://scholarworks.umass.edu/open_access_dissertations

Part of the Chemistry Commons

Recommended Citation

https://scholarworks.umass.edu/open_access_dissertations/297

This Open Access Dissertation is brought to you for free and open access by ScholarWorks@UMass Amherst. It has been accepted for inclusion in Open Access Dissertations by an authorized administrator of ScholarWorks@UMass Amherst. For more information, please contact scholarworks@library.umass.edu.
TIME RESOLVED SINGLE MOLECULE SPECTROSCOPY OF SEMICONDUCTOR QUANTUM DOT/CONJUGATED ORGANIC HYBRID NANOSTRUCTURES

A Dissertation Presented

by

MICHAEL YEMOH ODOI

Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

September 2010

Department of Chemistry
TIME RESOLVED SINGLE MOLECULE SPECTROSCOPY OF SEMICONDUCTOR QUANTUM DOT/CONJUGATED ORGANIC HYBRID NANOSTRUCTURES

A Dissertation Presented

by

MICHAEL YEMOH ODOI

Approved as to style and content by:

__________________________
Michael D. Barnes, Chair

__________________________
Paul M. Lahti, Member

__________________________
Todd Emrick, Member

__________________________
Scott M Auerbach, Member

__________________________
Craig T. Martin, Department Head
Department of Chemistry
DEDICATION

This work is dedicated to my mother for all her continuous support and love over the years, without which I will not be here. Mama you are the best and I love.
ACKNOWLEDGMENTS

To my advisor, Prof. Michael D. Barnes,

You gave me the chance to work in your lab, guided and mentored me through graduate school and equipping me with the skills to be a good scientist.

To my committee,

Your time, guidance and direction is very much appreciated.

To my friends, classmates and labmates

The time with you will always be remembered, it was great to know you, worked and hangout with you. It was nice to also talk about things not related to science.
ABSTRACT

TIME RESOLVED SINGLE MOLECULE SPECTROSCOPY OF SEMICONDUCTOR QUANTUM DOT/CONJUGATED ORGANIC HYBRID NANOSTRUCTURES

SEPTEMBER 2010

MICHAEL YEMOH ODOI, BS, KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY

Ph.D., UNIVERSITY OF MASSACHUSETTS AMHERST

Directed by: Professor Michael D. Barnes

Single molecule studies on CdSe quantum dots functionalized with oligo-phenylene vinylene ligands (CdSe-OPV) provide evidence of strong electronic communication that facilitate charge and energy transport between the OPV ligands and the CdSe quantum dot core. This electronic interaction greatly modify, the photoluminescence properties of both bulk and single CdSe-OPV nanostructure thin film samples. Size-correlated wide-field fluorescence imaging show that blinking suppression in single CdSe-OPV is linked to the degree of OPV coverage (inferred from AFM height scans) on the quantum dot surface. The effect of the complex electronic environment presented by photoexcited OPV ligands on the excited state property of CdSe-OPV is measured with single photon counting and photon-pair correlation spectroscopy techniques.

Time-tagged-time-resolved (TTTR) single photon counting measurements from individual CdSe-OPV nanostructures, show excited state lifetimes an order of magnitude shorter relative to conventional ZnS/CdSe quantum dots. Second-order intensity correlation measurements $g^{(2)}(\tau)$ from individual CdSe-OPV nanostructures point to a weak multi-excitonic character with a strong wavelength dependent modulation depth. By tuning in and out of the absorption of the OPV ligands we observe changes in modulation depth from $g^{(2)}(0) \approx 0.2$ to 0.05 under 405 and 514 nm excitation respectively. Defocused images and polarization anisotropy measurements also reveal a well-defined linear dipole emission pattern in single CdSe-OPV nanostructures.
These results provide new insights into the mechanism behind the electronic interactions in composite quantum dot/conjugated organic composite systems at the single molecule level. The observed intensity flickering, blinking suppression and associated lifetime/count rate and antibunching behaviour is well explained by a Stark interaction model. Charge transfer from photo-excitation of the OPV ligands to the surface of the CdSe quantum dot core, mixes electron/holes states and lifts the degeneracy in the band edge bright exciton state, which induces a well define linear dipole behaviour in single CdSe-OPV nanostructures. The shift in the electron energies also affects Auger assisted hole trapping rates, suppress access to dark states and reduce the excited state lifetime.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGEMENT</td>
<td>v</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>x</td>
</tr>
<tr>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>1. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Aims and Objectives</td>
<td>2</td>
</tr>
<tr>
<td>1.2 Charge and Energy Transport in Bulk Thin Film Conjugated Organic/Quantum Dot Composite Systems</td>
<td>4</td>
</tr>
<tr>
<td>1.3 Influence of Local Environment on Single Molecule Fluorescence Lifetimes</td>
<td>7</td>
</tr>
<tr>
<td>1.4 Blinking suppression and changes in Excited State Decay Rates</td>
<td>10</td>
</tr>
<tr>
<td>2. ENERGY TRANSFER IN SINGLE CdSe CONJUGATED OLIGO-(PHENYLENEVINYLENE) HYBRID NANOSTRUCTURES</td>
<td>14</td>
</tr>
<tr>
<td>3. BLINKING SUPPRESSION AND LINEAR DIPOLE BEHAVIOR IN SINGLE CdSe-OPV NANOSTRUCTURE</td>
<td>21</td>
</tr>
<tr>
<td>3.1 Linear Anisotropy in CdSe-OPV Nanostructures Fluorescence Emission</td>
<td>31</td>
</tr>
<tr>
<td>4. TIME RESOLVED SPECTROSCOPY OF CdSe-OPV</td>
<td>36</td>
</tr>
<tr>
<td>4.1 Fluorescence Lifetime and Correlated Photon Statistics</td>
<td></td>
</tr>
</tbody>
</table>
from CdSe-OPV

4.2 Photon Pair Correlation Measurements on Single CdSe-OPV

5. SUMMARY AND FUTURE WORK

6. SINGLE MOLECULE SPECTROSCOPY OF A MODEL FLUORENONE: STUDYING THE ORIGIN OF THE GREEN BAND IN POLYFLUORENE OLEDS

APPENDICES

A. TIME RESOLVED SINGLE PHOTON COUNTING (TCSPC)
   OPTICAL SETUP AND DATA ANALYSIS FOR TIME RESOLVED SPECTROSCOPY

B. PHOTON-PAIR CORRELATION MEASUREMENT (ANTIBUNCHING) OPTICAL SETUP AND DATA ANALYSIS

C. TIME RESOLVED POLARIZATION ANISOTROPY OPTICAL SETUP AND DATA ANALYSIS

BIBLIOGRAPHY
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Structure of a single CdSe-OPV nanostructure</td>
<td>2</td>
</tr>
<tr>
<td>2.1</td>
<td>Bulk of spectra of CdSe-OPV and thin film blend of CdSe and OPV</td>
<td>15</td>
</tr>
<tr>
<td>2.2</td>
<td>Single molecule spectra of CdSe-OPV and CdSe-DOPO-Br</td>
<td>17</td>
</tr>
<tr>
<td>2.3</td>
<td>2D spectra of single CdSe-OPV, CdSe-DOPO-Br and ZnS/CdSe</td>
<td>18</td>
</tr>
<tr>
<td>3.1</td>
<td>Spectra and intensity time trace of a single CdSe-OPV</td>
<td>23</td>
</tr>
<tr>
<td>3.2</td>
<td>Comparison of peak emission wavelengths of CdSe-OPV over time</td>
<td>24</td>
</tr>
<tr>
<td>3.3</td>
<td>Fluorescence correlated AFM image of CdSe-OPV</td>
<td>25</td>
</tr>
<tr>
<td>3.4</td>
<td>Comparison of CdSe-OPV and ZnS/CdSe intensity traces</td>
<td>26</td>
</tr>
<tr>
<td>3.5</td>
<td>AFM height distribution of CdSe-OPV</td>
<td>27</td>
</tr>
<tr>
<td>3.6</td>
<td>Fluorescence duty factor of CdSe-OPV and ZnS/CdSe</td>
<td>30</td>
</tr>
<tr>
<td>3.7</td>
<td>Relative probability distribution of CdSe-OPV intensity</td>
<td>31</td>
</tr>
<tr>
<td>3.8</td>
<td>Defocused imaging of CdSe-OPV and ZnS/CdSe</td>
<td>34</td>
</tr>
<tr>
<td>3.9</td>
<td>Polarization induced intensity fluctuation of CdSe-OPV fluorescence</td>
<td>35</td>
</tr>
<tr>
<td>3.10</td>
<td>Polarization induced spectral shift from CdSe-OPV</td>
<td>36</td>
</tr>
<tr>
<td>4.1</td>
<td>Florescence correlated AFM, spectra and height distribution of CdSe-OPV</td>
<td>40</td>
</tr>
<tr>
<td>4.2</td>
<td>Count distribution from ZnS/CdSe and CdSe-OPV</td>
<td>41</td>
</tr>
<tr>
<td>4.3</td>
<td>Dark state dwell time distribution from CdSe-OPV</td>
<td>42</td>
</tr>
<tr>
<td>4.4</td>
<td>Fluorescence decay curves of ZnS/CdSe and CdSe-OPV</td>
<td>43</td>
</tr>
<tr>
<td>4.5</td>
<td>Correlated lifetime intensity trajectories of ZnS/CdSe and CdSe-OPV</td>
<td>44</td>
</tr>
</tbody>
</table>
4.6 CdSe quantum dot state diagram and excited state decay paths………………..45
4.7 Antibunching curves for CdSe-OPV and ZnS/CdSe…………………………..52
4.8 Wavelength dependent antibunching of CdSe-OPV…………………………54
4.9 Comparison of excited state decay rate from CdSe-OPV…………………..55
5.1 Excited state lifetime of CdSe-OPV under two polarization excitation…..61
6.1 Molecular structures of OFPV and OFOPV………………………………….65
6.2 Thin film spectra of OFPV and OFOPV…………………………………….67
6.3 The effect of concentration on thin film OFOPV spectra…………………..68
6.4 Wide-field fluorescence image of single OFOPV………………………….69
6.5 Single molecule OFOPV spectra……………………………………………70
6.6 Distribution of center wavelengths from single OFOPV………………….71
6.7 Intensity time trace from single OFOPV…………………………………..73
6.8 Defocused images from OFOPV…………………………………………….74
A.1 TCSPC setup scheme of photon arrival/detection incidents……………….89
A.2 Optical setup for time correlated single photon counting measurements…90
A.3 Decay curve and simulated IRF for curve fitting…………………………..99
B.1 HBT detection scheme for photon-pair correlation measurement………..103
B.2 HBT optical setup for photon-pair correlation measurement………………106
C.1 Detection scheme for time-resolved polarization anisotropy………………110
Quantum dots/conjugated organic blends have been the focus of intense research for the past two decades. These efforts have been towards the development of new materials for thin film optoelectronic devices and energy harvesting applications. These blends are formulated to take advantage of the electronic communication between the quantum dots and the conjugated organic, and also to facilitate charge and energy transfer and improve quantum efficiency. However the problem of phase segregation leads to the formation of phase-separated domains of the quantum dots and the conjugated organic component and result in a weak electronic interaction that adversely affect performance in thin film devices. Our fundamental understanding of the interaction between the two components and how it affects the photophysical properties of these blends is thus limited to the ensemble average response of the bulk blend. Recently, Emrick and co-workers have successfully developed a synthetic strategy that allows the direct coordination of conjugated organic ligands to the surface of the quantum dots to form a well-defined three-dimensional nanostructure that allows intimate contact between the quantum dot and the conjugated organic ligands. Cadmium selenide quantum dots (CdSe) with oligo-phenylene vinylene ligands (OPV) coordinated to the surface (figure 1.1(A)) hereinafter referred to as CdSe-OPV have been synthesized with this method. Figure 1.1(B) represents a 3D cartoon of a CdSe-OPV nanostructure with fully covered OPV ligands.
Aims and Objectives

The prominent work of Ginger, Greenham and Alivisatos on charge and energy transfer between CdSe quantum dots and poly-phenylene vinylene in a bulk thin film configuration, showed measurable electronic interaction between the organic and the quantum dot in spectral and photoinduced transient absorption studies. This approach required large quantum to PPV mass ratio and lacked the control of ligand proximity and orientation, which are key to studying the electronic interaction between the two systems. This project in general is focused on understanding the effect of complex environment presented by photoactive organic ligands such as OPV on the photophysical properties of CdSe quantum dots at the single molecule level with a high degree of control of the ligand proximity and chemistry. We hope to answer to the following questions;

Figure 1.1. Structure of a single CdSe-OPV nanostructure

(A) CdSe quantum dot core with OPV ligand grown through the phosphine oxide linkage (B) 3D cartoon of a CdSe-OPV nanostructure fully covered with OPV ligands.
1. How does the presence of a large number of OPV ligands (as shown in figure 1) affect the photoluminescence spectral properties of CdSe-OPV nanostructure at the bulk and single molecule level?

2. Does the well-known blinking behavior observed in single ZnS/CdSe quantum dots persist in the CdSe-OPV composite nanostructure? How does the number and length distribution of OPV ligands on the quantum dot surface affect the photophysics of CdSe-OPV nanostructures? Does the 2D degenerate dipole transition observed in “symmetric” quantum dots change in the presence of photoactive ligands? What are the polarization properties of CdSe-OPV?

3. Excited state fluorescence properties single molecules have been shown to be very sensitive to their environment.
   a. How does the presence of the OPV ligands affect the excited decay processes of the CdSe core?
   b. Does any electronic interaction between the OPV ligands and the quantum dot core render a single CdSe-OPV nanostructure to act as a single quantum system?

In this thesis, I present experiments, results and discussion on single CdSe-OPV nanostructures studied with different spectroscopic techniques to help understand the effect OPV ligands on the photophysical properties of CdSe quantum dots. This introductory chapter is a quick review of some of published work on the photophysics of quantum dot/organic polymer or dye blends. The second chapter focuses on the use of single molecule spectral measurements to study charge and energy flow between the
CdSe quantum dot and the OPV ligands. Chapter three focuses on size correlated blinking statistics. We employed atomic force microscopy (AFM) combined with wide-field imaging to correlate fluorescence properties of individual CdSe-OPV nanostructure with size (length/number of OPV ligands). We investigated the excited state photophysics of CdSe-OPV with pico-second time resolved single and photon-pair correlation measurements. A direct comparison of the CdSe-OPV excited state properties under different excitation wavelengths is presented in chapter four. The photophysical properties of single molecule 2,7-bis(3,4,5-trimethoxyphenylethenyl)fluorenone (OFOPV) and investigation into the origin of “green band” contamination in fluorene based OLEDs, are presented in chapter six. Time-resolved experimental setup for time correlated single photon counting, photon-pair correlation (antibunching) and time resolved polarization experiments including optical setups and data analysis are all presented as appendixes.

1.2 Charge and Energy Transport in Bulk Thin Film Conjugated Organic/Quantum Dot Composite Systems

The quest for highly efficient photovoltaic materials for thin film device application has been the driving force behind extensive studies of the electronic interaction between quantum dots and conjugated organic polymers/dyes composite systems. These composite systems provide a unique medium for studying the electronic communication that allow charge and energy transport between the quantum dot and the organic component. This is facilitated by the independent control of the emission energy
of the quantum dot through its size and that of the organic through modification of side
the groups and chain length.\textsuperscript{9,13} It also allows control of the film morphology by varying
the size, concentration and surface ligands. Quantum efficiencies of up to about 12%
have been reported at high quantum dot concentration in such thin film blends.\textsuperscript{8,16}

Photoinduced absorption spectroscopy and photoluminescence quenching of the
organic emission have been used by Greenham and coworkers to detect and characterize
charge separation and transport at the conjugated organic polymers/CdSe quantum dots
interface in thin film blends.\textsuperscript{8,9,13-16} These measurements have also shown that the
polymer alky side-chains play a crucial role in the charge transfer process in these blends,
as indicated by the strong charge transfer from MEH-CN-PPV to CdSe nanocrystals.\textsuperscript{9,16}
Charge transfer from quantum dots to organic dye molecules tethered to the quantum dot
surface have also been reported. Abey \textit{et al.} have reported electron transfer from a single
ZnS/CdSe quantum dot to Fluorescein27 (F27) adsorbed on the surface of the dot. The
electron transfer from the quantum dot to the F27 is reported to be associated with
changes in fluorescence lifetimes from 25 ns in the absence of F27 to 5 ns for a single
quantum dot-F27 composite system.\textsuperscript{17}

Quantum dots have also been used extensively in Förster resonance energy
transfer (FRET) donor-acceptor based applications, such as assays for antibody-antigen,
enzyme substrate interaction and conformational dynamics.\textsuperscript{18-27} Willard \textit{et al.} have used
FRET to study the specific binding of boitinilated bovine serum albumin conjugated to
CdSe/ZnS and tetramethylrhodamine-labeled streptavidin.\textsuperscript{20} Improvement in FRET
efficiency at low acceptor-to-donor ratios can also be achieved by coupling the dye-
labeled DNA acceptor, to reduce the donor acceptor distance.\textsuperscript{22} In the studies of DNA
Holliday junction dynamics, quantum dots/Cy5 FRET pair have shown identical results compared to the conventional Cy3/Cy5 pair.\textsuperscript{25} Long range resonant energy transfer from oligo-p-(phenylene-ethynylene)-dibenzylthiols to CdSe quantum dots in a cross-linked assembly has brought evidence that point to additional energy transfer paths involving inter-chain interactions between the organic ligands.\textsuperscript{28} Dimers and aggregates in these systems act as intermediates states for the migrating excitons or emissive excitation traps and are selectively quenched by the quantum dot transition in a dipole-dipole interaction. Anni and coworkers have also observed strong FRET from blue emitting poly-\{(9,9-dihexylfluorenyl-2,7-diyl)-alt-co-(9,ethyl-3,6 carbazole)] to ZnS/CdSe using solution-phase time resolved photoluminescence measurements.\textsuperscript{29} A Förster radius of about 8nm extracted from solving the relaxation dynamics rate equations for the donor, compares favorably to 9nm reported by Weller \textit{et al}\textsuperscript{27} for FRET from a single CdSe/ZnS to a Cy5 derivative in a polystyrene matrix, with subsequent reduction in the quantum dot fluorescence lifetime. CdTe nanowires with poly(p-phenyleneethynylene) (PPE) tethered to the surface have shown FRET with a strong dependence on the orientation of the PPE ligand to the surface of the CdTe nanowire. PPE ligands oriented parallel to the surface of the nanowire show strong FRET in contrast to those tethered perpendicular to the surface.\textsuperscript{21} Dayal \textit{et al} have shown nonlinear relation between energy transfer and spectral overlap in CdSe quantum dots/phthalocyanine donor-acceptor pairs.\textsuperscript{26} However quantum dots with size between 3.4 and 4.5 nm follow a linear relation with spectral overlap as predicted by Förster. Uncapped dots have been found to show higher energy transfer efficiency compared to ZnS-capped dots. This difference in FRET efficiency between capped an uncapped dots shows that surface states play an important role in the energy
transfer process in donor-acceptor systems. Energy transfer between dots of different sizes in a close pack thin film has also been reported to show long-range electronic energy transfer from smaller to bigger dots.\textsuperscript{10,11,19,30} Studied with time resolved photoluminescence spectroscopy, show that such long range energy transfer is characterized by luminescence and lifetime quenching of the small dots followed by an increase in the lifetime of the larger dots.\textsuperscript{30}

1.3 Influence of Local Environment on Single Molecule Fluorescence Lifetime

One of the fundamental properties of a fluorescence molecule is its excited lifetime or decay rate. This is the amount of time on average (usually in nano-seconds) that the molecule spends in the excited state after excitation with a short pulse. In general the observed lifetime of decay rate is a sum of the rates of all decay paths (radiative and non-radiative) accessible to the molecule in the excited state.

Time resolved measurement is particularly useful because it contains a lot more information about the system under study than conventional steady state measurements such spectral measurements. Lifetime measurements have been widely used to study protein folding and protein-protein interaction. It has also been used to distinguish between static and dynamic quenching. In protein folding or protein-protein interaction similar residue located at different sites of the protein can easily be resolved through changes in lifetimes of those residues. For example a tryptophan residue close to the binging site of a protein will have a different lifetime compare to another tryptophan far from the binding site. Fluorescence lifetime and intensity changes of a donor or an acceptor in a single protein or between two proteins can also be used to calculate the
donor/acceptor ratio as well as the separation between them. Cellular imaging has also benefited from advance in lifetime measurements. This technique with the aid of a fluorescent probe can be use to monitor various changes inside the cell based on changes in lifetime of the molecule. This is due to the different environment encountered by the probe molecule within the cell. A new technique refered to as fluorescence lifetime imaging microscopy (FLIM) can be used to construct an image to show the different lifetimes of the probe molecule within the cell and the activities within the cell.

The spontaneous emission of a fluorescence photon from a single molecule in a homogenous environment is a random process, which is well described by a single exponential function. The presence of distinct heterogeneous environment, gives rise to a distinct distribution of decay rates that can be described by the sum of a few exponential functions. Fluorescence lifetime fluctuations and changes in quantum yields are generally due to relaxation processes that arise from fluctuations in the local nano-environment and modify the non-radiative decay rates. For single molecules immobilized in thin films the fluorescence lifetime is not only determined by changes in the non-radiative decay rates due to their local environment but also changes in the spontaneous decay rates. The radiative decay rate is strongly influenced by the geometry of the surrounding dielectric media especially the relative orientation and distance of the emitting dipole from the air-film interface. The transition rate for a two-level system in free space can be calculated from Fermi’s golden rule.

\[
\Gamma = \frac{2\pi}{\hbar} |M_{21}|^2 g(\hbar\omega) \quad (1)
\]
$M_{12}$ is the transition dipole matrix element that couples states 1 and 2 together, $g(h\bar{\omega})$ is the density of states. The transition rate of the emitting dipole differs from the free-space value in the presence of an interface. This is due to what is called the electromagnetic field effect, which is an alteration of the free-space boundary conditions imposed on the electromagnetic field of the emitter due to the presence of the interface. Fermi’s golden rule can be modified to calculated the transition rate of a an excited dipole in a dielectric medium with the expression;

$$\Gamma = \frac{\mu_{12}^2 \omega^3}{3\pi h c^3 \varepsilon_0} \quad (2)$$

$\mu_{12}$ is the electric dipole moment of the transition, $\omega$ is the emission angular frequency, $\varepsilon_0$ is the permittivity of free space, $c$ is the speed of light and $h\bar{\omega}$ is Planks constant.$^{32-34}$ The above expression can be modified further to include the refractive index of the medium and factors that include macroscopic and dielectric fields.$^{35,36}$ Shifts in spectral peak wavelengths of in single DiC$_{12}$ embedded in PMMA film have been shown to be well correlated with changes in excited state lifetimes. This is due to the dependence of the decay rate on the emission frequency $\omega$ in equation 2. It has been shown that single DiC$_{12}$ molecules with the same spectral peak but different orientation of the emission dipole show different lifetimes. This dependence of the decay rate on the orientation of the dipole emitter is a result of the electromagnetic boundary condition created by the emitting dipole at the polymer-air interface.$^{37}$ One way to change the free-space boundary condition and the decay rate is by introducing a reflecting surface in the near-field (sub-wavelength distance) of the emitting dipole. DiD, rhodamine 700 and nile blue dye embedded in a polystyrene film 20 – 200 nm away from a thin silver film show strong
dependence of the fluorescence lifetime on the separation (polystyrene film thickness) between the dye molecules and the reflecting silver surface.\textsuperscript{38}

Single CdSe-OPV embedded in thin polymer films or deposited in bare glass has the potential of modifying the electromagnetic boundary condition and changing the fluorescence decay rates compared to ZnS/CdSe quantum dots without any photo-active ligands on the surface. Control of the decay rates of quantum dot organic composite systems like CdSe-OPV will lead to the realization of new materials for optoelectronic application.\textsuperscript{31}

### 1.4 Blinking Suppression and Changes in Excited State Decay Rates

Fluorescence intermittency also known as blinking is one of the fundamental properties of quantum dots and in general single fluorescent molecules. This is the tendency of single nanocrystal to shut off its fluorescence emission even under continues excitation and turn on after sometime.\textsuperscript{39-49} This property is independent of the composition of the quantum dot and has limited its use in some applications like particle tracking.\textsuperscript{50-55}

Many models have been proposed to explain the mechanism of blinking and the observed power law statistics of “on-off” times in quantum dots fluorescence. These models in general are based on the formation of a long-lived state that result from a charge separated state, formed when one carrier is trapped in the surrounding matrix via Auger recombination. The carrier-tunneling rate from the excited quantum dots to traps is susceptible to fluctuations in tunnel-barrier heights and widths and lead to modifications in Auger recombination rates.\textsuperscript{40,41,46,47,56-61} One of the models that recovers the
experimentally observed power law distribution of “on” and “off” times has been proposed by Tang and Marcus.\textsuperscript{62-65} This model is based on modifications in Auger assisted hole trapping rates that result from a light induced slow diffusion of the energy difference between the first two excited states.\textsuperscript{66}

Since the early observation of fluorescence intermittency in single quantum dots,\textsuperscript{39} a lot of effort has been directed towards finding ways of reducing or completely eliminating it. Different methods and approaches towards blinking suppression or elimination have reported. These include, passivation of the quantum dot surface with thiol-containing ligands, or using thiol-containing polymer films as host for the quantum dots. Ha and coworkers have used β-mercaptoethanol (BME) to achieve near blinking suppression in streptavidin-coated ZnS/CdSe quantum dots in solution.\textsuperscript{67} They showed that blinking suppression depends on the ligand chain length but not on the number of thiol groups per ligand. Dithiothreitol doped in different polymers like, polyvinal alcohol, Zeonex, polymethyl methacrylate (PMMA) and polystyrene (PS) have also been shown to reduce blinking in quantum dots.\textsuperscript{68} Lakowicz and coworkers have also observed both blinking suppression and enhanced fluorescence in CdTe quantum dots deposited near silver island films.\textsuperscript{69,70}

Other methods employed in blinking suppression have focused on the chemistry of quantum dots shell thickness and its composition. Quantum dot with shell thickness ranging from 10-20 monolayers so-called “giant” quantum dots have been shown to exhibit strong blinking suppression. Hollingsworth and coworkers have observed strong blinking suppression in CdSe quantum dots with several monolayers of either CdS or CdS/CdZnS-ZnS shells.\textsuperscript{71,72} Theoretical work by Efros and Cragg has linked Auger
processes in the dot to the steepness of the interfacial potential created between the capping layer and the core. The graded composition of the thick alloy shells provides a soft/smooth confining interfacial potential, which suppresses Auger recombination, and thus reduce blinking in these giant quantum dots. Alloyed core shell dots such as CdZnSe quantum dots capped with ZnSe shell also exhibit near-complete blinking suppression.\cite{73}

In contrast to blinking suppression achieved with thiol containing ligands, giant quantum dots with alloy core or shell exhibit a strong red-shift with multiple peaks in their fluorescence spectra and an increase in fluorescence lifetime with shell thickness.\cite{51,73,74}

Carrier trapping, photoionization and subsequent Auger processes have been shown to modify the excited state decay rates in both blinking and “nonblinking” quantum dots. Nirmal et al.\cite{39,75} reported the reduction in quantum yield and fluorescence lifetimes in photoionized quantum dots compared to the neutral dots. Studies on the excited state lifetime changes of quantum dots under varying experimental conditions have shed more light on the decay processes within the dot and has led to the introduction of new models to explain the different excited state decay rates.\cite{71,76-79}

Temperature dependent radiative lifetime measurements by Klimov and coworkers show a limiting lifetime of 1.13$\mu$s when CdSe nanocrystals are cooled to about 2 K with a weak dependence on nanocrystal size.\cite{71,80} This long lifetimes quickly decrease with temperature to a few nanoseconds suggesting a thermally activated high-lying bright exciton state from dark ground state.\cite{71} Brokmann et al. have demonstrated controlled modification of the spontaneous excited state decay rate, achieved via trapping of the nanocrystal at the interface of two materials with varying refractive index.\cite{81-83} Several researchers have also observed strong correlations of fluorescence intensity with excited
state lifetime in single ZnS/CdSe quantum dots.\textsuperscript{84-87} Schlegel \textit{et al.} and Bawendi and coworkers have measured a distribution of lifetimes and assigned them different fluorescence intensity level, with high intensity corresponding to long lifetimes.\textsuperscript{77,87,88} This observation is consistent with the results of Yang and coworkers\textsuperscript{61} and point to the model of Verberk \textit{et al.} that, for a single quantum dot there exists a distribution of emissive states that correspond to different intensity levels and lifetimes. This distribution is proposed to arise from a modification of the electronic structure of the quantum dot due to the presence of trapped carrier, and thus lead distinct changes in the excited decay rates and hence the fluorescence intensity trajectory.\textsuperscript{56,58,89}
CHAPTER 2

ENERGY TRANSFER IN SINGLE CdSe CONJUGATED OLIGO-(PHENYLENE VINYLENE) HYBRID NANOSTRUCTURES

Thin film blends of quantum dots and conjugated polymers have attracted a great deal of interest in the context of light harvesting photovoltaic and optoelectronic devices. One of the interesting features of thin film blends of quantum dots and conjugated organic polymers is the electronic communication between the conjugated organic and quantum dot or quantum rod components which results in enhanced fluorescence quantum yields, energy transfer, and charge transport. Recently Emrick and coworkers have synthesized a new class of quantum dot-organic composite nanostructures with conjugated organic ligands oligo-(phenylene vinylene) directly connected to the surface of the quantum dot, to form a three dimensional CdSe-OPV nanostructures, shown in figure 1. This approach results in a significant suppression of the problem of phase-aggregation observed by several authors in bulk thin film blends. This new nanostructure also show significant differences in bulk/single molecules photoluminescence properties relative to blended samples. The CdSe-OPV composite material studied was prepared by growing the OPV ligands of three to six phenylene vinylene repeat units directly from phenylbromide functionalized ~4.3 nm diameter CdSe quantum dots, where the OPV coordination to the CdSe surface is through chain-end phosphine oxides. This procedure was used to generate the desired composite materials without the need for ligand exchange on tri-\(\text{H}\)-octylphosphine oxide (TOPO)-covered CdSe nanoparticles, which can compromise the photophysical properties of the quantum dots.
The absence of inorganic protective layers of ZnS commonly used to prevent surface oxidation and enhance the photoluminescence quantum yield of the CdSe core, also decreases the distance between the CdSe core and the surrounding environment, which can increase the electronic communication between the CdSe core and the OPV ligands. In addition, synthetic constraints imposed by such ZnS capping layer is eliminated and thus provide unlimited access to tuning the OPV ligand chemistry relative to the CdSe core itself for optimum electronic communication.

In this chapter, single-molecule fluorescence studies from single quantum dot-conjugated organic nanostructures will be presented. The experimental protocols used were as follows.

Figure 2.1. Bulk of spectra of CdSe-OPV and thin film blend of CdSe and OPV

Comparison of bulk thin film spectra of a blend of CdSe and oligo-phenylene vinylene (OPV) shown in black, and a bulk thin film of CdSe-OPV nanostructures shown in gray.
A concentrated sample of CdSe-OPV was diluted in tetrahydofuran (THF) to obtain an ultra dilute (~10^{-10} M) CdSe-OPV sample. Individual CdSe-OPV nanostructures were isolated from the dilute solution by drop casting onto clean glass coverslips. All measurements were performed under ambient conditions using a Nikon TE300 inverted microscope with 1.4NA oil objective. Spectrum from an individual CdSe-OPV nanostructure was acquired by focusing the CdSe-OPV emission from the side-port of the microscope onto an Acton SP2150i dual-grating spectrograph and detected with a Roper Scientific Pixis 400B back-illuminated CCD, with an exposure time of 2 seconds. This CdSe-OPV composite nanostructure show a significant modification in the fluorescence spectral as well as enhanced temporal stability relative to thin film blends of the inorganic and organic components. These effects are attributed to enhanced energy transfer between the conjugated ligand and the quantum dot facilitated by the molecular architecture.

Figure 2.1 shows typical emission spectra from a blended bulk thin film of OPV and dioctyl-para-bromobenzylphosphine oxide (DOPO-Br) covered CdSe quantum dots compared with the bulk emission spectrum from a film CdSe-OPV nanostructures – both excited with the 457 nm line of an Ar⁺ laser. Consistent with other reports, the spectrum from the blend film was obtained with a CdSe mass fraction of about 50%. It is obvious that even at high fractions of CdSe quantum dots in the blend, the spectrum is dominated by OPV emission\(^{12,29}\). In contrast to the blend, the fluorescence emission spectrum of a bulk film of the CdSe-OPV composite, made by growth of the OPV from the CdSe surface, is dominated by quantum dot emission. This data suggests that at the bulk level
measurement of CdSe-OPV the OPV emission is significantly quenched, even with a higher number of OPV ligands per each CdSe quantum dot.

**Figure 2.2. Single molecule spectra of CdSe-OPV and CdSe-DOPO-Br**

Fluorescence spectra from a single CdSe-DOPO-Br quantum dot (gray) and single CdSe-OPV nanostructure (black). The insert shows the absorption spectrum of the CdSe-DOPO-Br (black) overlaid with the OPV emission spectrum.

Figure 2.2 shows a comparison of the emission spectrum of a single CdSe-OPV nanostructure with that of a single DOPO-Br covered CdSe quantum dot. We observe nearly complete extinction of the OPV luminescence in the emission from the single CdSe-OPV nanostructure in the spectral region associated with bulk OPV (≈500-540 nm). We observed that, most of the CdSe-OPV single-molecule spectral features are indistinguishable from that of the DOPO-Br covered CdSe. However, for a small fraction of single CdSe-OPV spectral measurements a weak shoulder is present immediately to the blue of the quantum dot peak. This additional feature varies considerably in intensity with time. Due to the intermittency of this feature it is not
surprising it is not observed in the bulk CdSe-POV thin film spectral measurement shown in figure 1.1. This unique (double-peaked) spectral profile of single CdSe-OPV nanostructures is illustrated by time-resolved fluorescence spectral imaging. Figure 2.3 compares the time evolution emission spectra for a single DOPO-Br covered CdSe quantum dot (A), a ZnS/CdSe quantum dot (B), and a single CdSe-OPV nanostructure (C), all for similar sized quantum dot core.

![Figure 2.3. 2D spectra of single CdSe-OPV, CdSe-DOPO-Br and ZnS/CdSe](image)

Time-resolved fluorescence spectra from single (A) CdSe quantum dot covered with DOPO-Br; (B) ZnS/CdSe quantum dot; (C) CdSe-OPV nanostructure. Each spectrum was measured with a 2 s exposure time.

Both the DOPO-Br covered and ZnS/CdSe quantum dots exhibit on-off blinking\[^{39,42,45,48,96,97}\] (evidenced by the vertical gaps in emission intensity), with the DOPO-Br covered sample showing a progressive blue-shift with time, associated with
photodegradation of the dot. The single-molecule CdSe-OPV fluorescence shows similar intensity fluctuations, but interestingly the wavelength channel associated with CdSe in the CdSe-OPV emission does not show evidence of a fully off dark-state.

The absence of a ZnS capping layer ensures close proximity of the OPV ligands to the surface of the CdSe quantum dot surface for optimum electronic interaction. The nearly complete extinction of OPV luminescence from individual CdSe-OPV nanostructure can be attributed to (i) highly efficient dipole-dipole energy transfer from the OPV moieties to the quantum dot core facilitated by the large overlap of the OPV emission and the broad absorption spectrum of CdSe quantum dot shown in the insert of figure 2.1 and (ii) exciton dissociation in the OPV followed by electron transfer to the quantum dot surface. A Förster radius on the order of 3 nm is within range for high energy transfer rates significantly larger than those of bulk blends of a blue-emitting polyfluorene and ZnS/CdSe quantum dots reported previously. The modification of the OPV spectral signature in the CdSe-POV nanostructure can be interpreted qualitatively as a ‘filtering’ of the OPV emission by absorption into the quantum dot. This occurs in the wavelength region (~575 nm) with a characteristic dip in the absorption spectrum of CdSe quantum dot, making energy transfer in that particular spectral range less efficient.

The suppression of blinking in the CdSe-OPV system may be attributed to fast electron transfer from photo-excited OPV ligands (followed by slow non-radiative recombination) to the surface of the quantum dot, thus modifying the rate of carrier-trapping within the CdSe core leading to a reduction in dark state formation. Similar blinking suppression has been observed by Ha and coworkers for CdSe/ZnS quantum dots in solution containing electron donating beta-mercaptoethanol (BME). They
proposed that blinking suppression was a result of electron donation from the thiol moiety of the BME to vacant trap sites on the quantum dot. In the case of the CdSe-OPV system, charge transfer from excited OPV to the quantum dot surface could facilitate such a process.

The blue shoulder in the single molecule spectrum, the observed spectral stability and the blinking suppression in individual CdSe-OPV nanostructures vary from nanostructure to nanostructure. However, the effect of the OPV ligands is clear and consistent from sample-to-sample, and the DOPO-Br covered quantum dots never exhibit this behavior.

In the following chapter (3) a detailed investigation on blinking statistics of individual CdSe-OPV nanostructures correlated with OPV ligand length and coverage using atomic force microscope (AFM) will be presented, in addition quick overview on polarization measurements is also presented.
CHAPTER 3

BLINKING SUPPRESSION AND LINEAR DIPOLE BEHAVIOR IN SINGLE CdSe-OPV NANOSTRUCTURE

One of the fundamental properties of quantum dots is fluorescent intermittency of blinking. This is especially important for photovoltaic, optoelectronic and biological applications, where device performance or continuous tracking of labeled biomolecules are adversely affected by the on-off blinking of the quantum dot fluorescence.\(^{39,40,42}\) In the previous chapter we showed that the direct surface functionalization of CdSe quantum dots with oligo-(phenylene vinylene) result in a high degree of blinking suppression and spectral stability. This observation was attributed to strong energy and charge transfer from OPV ligands to CdSe quantum dot in the CdSe-OPV nanostructure. The appearance of the residual OPV emission in single CdSe-OPV spectra was not evident in other CdSe-OPV nanostructures studied, which indicates some degree of heterogeneity in the CdSe-OPV photophysical properties. In this chapter we present results on correlated AFM and wide-field fluorescence imaging on hundreds of individual CdSe-OPV nanostructures. We also observed that charge transfer from the OPV ligands to the CdSe quantum dot surface induces a strong linear dipole behavior in individual CdSe-OPV nanostructure. This is linear dipole behavior is characterized by polarization anisotropy measurements and defocused imaging.

Among the interesting photophysical properties of CdSe-OPV nanostructures, is the degree of heterogeneity in the photophysical responds of each CdSe-OPV nanostructure studied. Here, we show a connection between intensity fluctuations in
single CdSe-OPV nanostructures with OPV ligand coverage inferred from atomic force microscopy measurements that are correlated with wild-field fluorescence imaging. By combining fluorescence with surface height measurements we gain insight into the coverage-dependent photophysics of CdSe-OPV nanostructures that are not accessible to either optical or scanning technique alone.

CdSe-OPV composite nanomaterials used in this study were prepared by growing the OPV ligands from phenylbromide functionalized ~4.3 nm diameter CdSe quantum dots, where OPV coordinates to the CdSe surface through chain-end phosphine oxides. Matrix-assisted laser desorption/ionization time-of flight (MALDI-TOF) mass spectrometry measurements were performed to determine the distribution of OPV ligand lengths. Individual CdSe-OPV nanostructures were isolated from dilute tetrahydrofuran solution (~10⁻¹⁰ M) on clean glass coverslips. The 457-nm line from a CW Ar⁺ laser (≈ 200 µW power; 15 µm diameter spot size) was used as the excitation source. All fluorescence imaging and spectroscopic measurements were obtained under ambient conditions using a Nikon TE300 inverted microscope with a 1.4 NA oil-emersion objective in a total internal reflectance (TIR) configuration. AFM measurements were performed in Tapping Mode using a Digital Instruments Bioscope model BS3-N mounted directly to the microscope. Fluorescence images were acquired with a Princeton Instruments PhotonMax CCD camera, with exposure times of 100 ms – 2 s and a typical total observation time of 1000 s. Spectra were acquired by focusing the CdSe-OPV emission from the side-port of the microscope onto an Acton SP2150i dual-grating spectrograph and detected with a Roper Scientific Pixis 400B back-illuminated CCD.
Initial correlation between fluorescence images and AFM surface height scans was performed using 20-nm FluoSpheres (Invitrogen Corporation).

We showed in chapter 2, that the spectra of both bulk and individual CdSe-OPV nanostructures is dominated by emission associated with the CdSe quantum dot channel and attributed it to efficient energy and charge transfer facilitated by the molecular architecture and the absence of a ZnS capping layer. In addition apparent blinking suppression in the quantum dot emission channel was also observed.

![Figure 3.1. Spectra and intensity time trace of a single CdSe-OPV](image)

(a) Time-resolved spectra from a single CdSe-OPV nanostructure at 300ms integration time (b) Spectrally resolved intensity trajectory showing the CdSe quantum dot (black) and OPV (gray) emission components. The dotted line represents a +2σ threshold about the mean background.

Figure 3.1 (a) shows that the time evolution spectrum of a single CdSe-OPV, at 300 ms integration time is still dominated by the quantum dot emission. It is only when the integration time increases to 2 s that the apparent blue shoulder discussed in chapter 2 become evident. Intensity time traces extracted separately for the OPV and CdSe
emission channels shown in Figure 3.1 (b) reveal approximately 20% maximum OPV emission contribution to the total CdSe-OPV fluorescence. At these exposure times a true dark (“of”) state was not observed for the CdSe-OPV nanostructures, in sharp contrast to an “of” time of approximately 9 s for ZnS/CdSe quantum dots. Figure 3.2 shows peak-to-peak wavelength fluctuations in single CdSe-OPV nanostructure spectrum compared to CdSe-DOPO-Br and ZnS/CdSe.

Figure 3.2. Comparison of peak emission wavelengths of CdSe-OPV over time

Comparison of the fluctuations in the wavelength emission maxima of a single CdSe-OPV nanostructure with CdSe-DOPO-Br covered quantum dot and ZnS/CdSe. The dotted line represents ±fwhm of the quantum dot emission peak.

We observe minimal spectral diffusion in the spectral evolution of single CdSe-OPV, with maximum peak-to-peak shifts (approximately 10 nm, \( \approx kT \)) contained within \( \frac{1}{2} \) the fwhm of the CdSe-OPV dot channel emission. This spectral stability is comparable to ZnS/CdSe quantum dots without (on this time scale) the problem blinking. The surface
oxidation of unprotected CdSe-DOPO-Br quantum dots (the precursor for CdSe-OPV) result in large a blue-shift in the emission peak over time.

A side-by-side correlation between of an AFM scan and the corresponding wide field fluorescence image of CdSe-OPV nanostructures is shown in Figure 3.3. The insert shows a representative surface height scan of an individual CdSe-OPV nanostructure indicated by the white circle. The indicated height of 13 nm is representative of a fully covered CdSe-OPV nanostructure.

![Figure 3.3](image)

**Figure 3.3. Fluorescence correlated AFM image of CdSe-OPV**

Correlation of five single particle fluorescence image with AFM height signatures (A) is the wide-field fluorescence image and (B) is the AFM image of the same CdSe-OPV nanostructures. The insert is the height trace of the circled CdSe-OPV nanostructure.

Figure 3.4 shows spectrally resolved fluorescence intensity trajectory of a single CdSe-OPV nanostructure circled in figure 3.3 compared with a typical ZnS/CdSe quantum dot of comparable size (4.3 nm) against a +2σ threshold above the mean background. The ZnS/CdSe quantum dot intensity trajectory exhibit typical “off” periods.
lasting 10’s of seconds in sharp contrast to the CdSe-OPV trajectory which is well above the 2σ noise floor and does not show an “off” period at this integration time. The absence of dark periods in the CdSe-OPV trajectory cannot be attributed to uncorrelated emission from both the OPV ligands and the CdSe core, because the fluorescence is spectrally filtered for the detector to collect only emission from the quantum dot channel.

![Figure 3.4. Comparison of CdSe-OPV and ZnS/CdSe intensity traces](image)

Fluorescence intensity trajectory of a single (A) CdSe-OPV and (B) a single ZnS/CdSe quantum dots. The dotted lines in both represent a 2σ threshold above the mean background.

A histogram of height signatures from 180 CdSe-OPV nanostructures is shown in Figure 3.5. Our estimate of OPV ligand coverage was based on the distribution of ligand lengths from MALDI-TOF measurements. An average OPV ligand length of four monomer units is obtained from an approximate Poisson distribution of ligand lengths from MALDI-TOF. We estimate the length of OPV ligand with four monomer units to be ≈4.5 nm. For a CdSe-OPV nanostructure with a CdSe core size of 4.3 nm and fully covered with OPV ligands, the end-to-end size to a good approximation will be ≈ 13-14 nm (sum of 2 OPV ligand lengths and the core). Based on a reported ≈ 10 nm persistence length for oligo-phenylene vinylene derivatives, our estimation of the CdSe-OPV
nanostructure size with a ball and stick model should be fairly accurate since a four monomer unit OPV ligand length is well below the persistence length.

Figure 3.5. AFM height distribution of CdSe-OPV

Surface height distribution of 180 individual CdSe-OPV nanostructures. The insert is a schematic of possible ligand arrangements for, (I) sparse coverage (II) intermediate coverage and (III) full coverage

The insert is a cartoon representing possible OPV ligand arrangement consistent with the CdSe-OPV height distribution. A small fraction (≈10%) of the CdSe-OPV size distribution labeled I, show very little or no coverage at all of OPV ligands perpendicular to the surface of the quantum dot. This distribution representing spares coverage overlaps well with the size distribution of CdSe quantum dot precursor shown as the black curve in the histogram. A number of different ligand arrangements are possible for slightly larger height signature regimes (labeled II in red). These would indicate nanostructures that have an intermediate degree of OPV ligand coverage and will yield heights less than
the maximum possible value. The regime labeled III (in blue) represents nanostructures that we interpret as exhibiting essentially complete coverage, a small fraction of the distribution with height signatures greater than 20 nm (colored brown) are considered to be possible aggregates and are therefore not included for further analysis.

The blinking behavior of CdSe-OPV nanostructures was characterized by the fluorescence duty factor (percent of time “on”): fraction of the time the fluorescence from a single CdSe-OPV nanostructure stays “on” (above a pre-determined threshold value) versus the total observation time for that particular nanostructure. This is related to the popular power-law kinetics used to describe blinking in ZnS/CdSe quantum dots.\textsuperscript{45,48,49,89,101-103} The pixels around a diffraction-limited CdSe-OPV fluorescence image was integrated and used to calculate the average background signal. A 2σ threshold above a mean background was used to distinguish between “on” and “off” states.

A comparison of fluorescence duty factor between ZnS/CdSe and CdSe-OPV acquired at two different exposure times under the same experimental conditions is presented in figure 3.6. The distribution of ZnS/CdSe fluorescence duty factor show very large fluctuations with an average percent time “on” of about 40%. This is significantly different from that measured for CdSe-OPV single nanostructures. Figure 5(b) shows a size correlated fluorescence duty factor representing different OPV coverage. To avoid contributions from clusters, CdSe-OPV sizes equal or less that 15 nm was used to construct the distribution of percent time “on”. At 1 s exposure time, CdSe-OPV nanostructures in the size range of 4 – 7 nm show blinking statistics indistinguishable from “bare” CdSe quantum dots. For the size range of 7 – 10 nm, the average
fluorescence duty factor is $\approx 70\%$, while particles in the size range of $11 - 13$ nm (nanostructures with a high degree of ligand coverage) show a fluorescence duty factor approaching $100\%$.

![Histogram of fluorescence duty factors from (a) 4.3 nm ZnS/CdSe quantum dots; (b) and (c) CdSe-OPV nanostructures sorted into various classes corresponding to different degrees of ligand coverage. The exposure times are 1sec for (a) and (b) and 100 ms for (c).](image)

**Figure 3.6. Fluorescence duty factor of CdSe-OPV and ZnS/CdSe**

Histogram of fluorescence duty factors from (a) 4.3 nm ZnS/CdSe quantum dots; (b) and (c) CdSe-OPV nanostructures sorted into various classes corresponding to different degrees of ligand coverage. The exposure times are 1sec for (a) and (b) and 100 ms for (c).

These show a direct correlation between size (ligand coverage) and blinking suppression in CdSe-OPV nanostructures. Even at an exposure time of 100 ms, Figure 3.6 (c), there is still strong correlation between blinking suppression and CdSe-OPV nanostructure coverage. This data also shows however, that blinking is only apparent at much shorter exposure times than with underivatized quantum dots. At this exposure time (100 ms),
we observed $\approx 500$ ms time-off for nanostructures within the $11 - 12.9$ size range. We observed for the CdSe-OPV system with higher ligand coverage (under 1 s exposure time) a clear absence of the well known binary “on-off” behavior seen in single ZnS/CdSe.

![Figure 3.7](image)

**Figure 3.7. Relative probability distribution of CdSe-OPV intensity**

Histogram showing the relative probability of emission intensity from individual CdSe-OPV nanostructures for the different size classes taken from figure 3.5.

Figure 3.7 shows the relative probability distribution of intensities for the different CdSe-OPV size classes representing varying degrees of ligand coverage presented in figure 5. CdSe-OPV within 4-6.9 nm size range corresponding to sparse OPV coverage display average peak intensities $\approx 2.1 \times 10^4$ counts, symmetric around the average $2\sigma$ reference threshold. As the OPV ligand coverage increases for 7-8.9 nm and 9-10.9 nm size nanostructures, the corresponding average intensities also increase to an average of $7.3 \times 10^4$ and $8.2 \times 10^4$ counts respectively. For those CdSe-OPV nanostructures considered to be fully covered (11-12.9 nm) we observe an average
intensity of $1.7 \times 10^5$ counts. This size correlated intensity distribution of the CdSe-OPV nanostructures suggests a complicated excited state dynamic process that involve photoexcited OPV ligands, may be involved in the mechanism leading to the observed suppression of blinking in single CdSe-OPV nanostructure.

Based on the relative electron affinities between the OPV ligands and the CdSe quantum dot core, we propose that the observed blinking suppression in single CdSe-OPV nanostructures involves an electron transfer from photoexcited OPV ligands to the surface of the CdSe quantum dot. The presence of such a charge significantly modifies the non-radiative recombination dynamics thus affecting carrier trapping and hence access to long dark periods. Our proposed mechanism of blinking suppression based on electron donating OPV ligands to the CdSe quantum dot is consistent with other published work on blinking suppression. Ha and coworkers made similar observation in solution, using the electron donating thiol groups in β-mercaptoethanol moieties to suppress blinking in quantum dots.\textsuperscript{104} Other workers have used similar electron donating species like mercaptoethyl-amide to achieve blinking suppression and have proposed similar mechanism.\textsuperscript{85}

### 3.1 Linear Anisotropy in CdSe-OPV Nanostructures Fluorescence Emission

Polarization anisotropy measurement is a contrast ratio techniques used to extract orientation information from molecular systems in condense phase. Various researchers have used it extensively in the study of conformational changes in conjugated organic systems to gain insights into intra/inter molecular charge and energy migration in such systems.\textsuperscript{27,105-113} Single molecule polarization anisotropy studies on conjugated organic
polymers and oligomers have been used to establish the orientation of the electric dipole transition along the conjugated axis. This has been facilitated with the advent of high NA objectives that allow the efficient collection of emitted photons at high angles. Unlike the well-defined linearly polarized transition in conjugated organics, quantum dots have been shown to have more complex electronic transitions. The nature of the band edge $1S_e-1S_{3/2}$ transition has been described theoretically and experimentally to arise from crystal field and exchange splitting as well as shape distortions in the crystal structure. The optically active (bright exciton state) transition is the lowest energy state with angular momentum ±1, characterized by two transitions dipole moment in the same plane and orthogonal to the crystal c-axis. These two transitions for “spherical” quantum dot nanocrystals appear degenerate, mostly referred to as 2D degenerate dipole. The small energy splitting between the two orthogonal transitions has restricted detailed studies to asymmetric shaped quantum dots/rods at cryogenic temperatures.

In the first section of this chapter we proposed that blinking suppression in single CdSe-OPV nanostructures was due to charge transfer from photoexcited OPV ligands to the surface of the CdSe quantum dot surface. We show here in this section that in addition to blinking suppression, charge transfer from the OPV to the CdSe quantum dot surface induce a strong linearly polarized emission characterized by linear dichroism parameters under a rotating linear polarized excitation source. This linearly polarized emission can be suppressed by tuning the excitation to the band edge absorption of the quantum dot and away from the OPV absorption.

Emission patterns from defocused images is widely used to predict the molecular orientation of single molecules in condense phase. This is achieved by translating the
high NA objective to introduce a small spherical aberration in the image that result in a constructive and destructive interference of high angle photons in the detector plane. For organic molecules like conjugated polymers and DilC\textsubscript{18} the resulting defocused image show a bright linear center with “wings” on the side.

![Defocused imaging of CdSe-OPV and ZnS/CdSe](image)

**Figure 3.8. Defocused imaging of CdSe-OPV and ZnS/CdSe**

Defocused single molecule fluorescence images of (A) a ZnS/CdSe quantum dot and (B) a CdSe-OPV nanostructure.

The bright linear center defines the orientation of the emission dipole and has been show to be nearly collinear to the absorption moment orientation. Figure 3.8 (A) shows a defocused image from a single ZnS/CdSe quantum dot, the image is representative of a 2D degenerate disk obtained by summing two orthogonal dipoles of equal magnitude.\textsuperscript{82,124,125} In sharp contrast to ZnS/CdSe, single CdSe-OPV nanostructure defocused images shown in figure 3.8 (B) under a fix excitation polarization, display a well defined linear transition dipole orientation, similar to those observed for conjugated polymers with well-defined transitions dipoles. We exclude any possible contribution from OPV emission to this linear dipole behavior by collecting fluorescence emission from only the CdSe channel and spectrally gating out all OPV fluorescence. This linear dipole behavior was only observed when the excitation source was 405 nm, where both...
the CdSe core and OPV ligands are both excited. By tuning the excitation to 514 nm where the OPV absorption is very minimal, such linear dipole behavior was strongly suppressed. Intensity time traces figure 3.9 from single CdSe-OPV nanostructures as a function of the 405 nm pump polarization orientation as a function of time, show a strong correlation between the orientations of the excitation electric field and that of the emission moment from.

![Intensity time traces figure 3.9 from single CdSe-OPV nanostructures as a function of the 405 nm pump polarization orientation as a function of time, show a strong correlation between the orientations of the excitation electric field and that of the emission moment from.](image)

**Figure 3.9. Polarization induced intensity fluctuation of CdSe-OPV fluorescence**

Single CdSe-OPV nanostructure intensity time trace (red) as a function of laser polarization (black dash line).

Spectral measurements on single CdSe-OPV nanostructure under a rotating laser polarization show shifts in emission energy as high as 70 meV and a peak-to-peak shift of \( \approx 57\text{meV} \) for two orthogonal laser polarization orientations. These shifts, shown in figure 3.10 are only observed under rotating 405 nm laser polarization and are significantly greater than the spectral diffusion shift of \( \approx 10\text{meV} \) observed in ZnS/CdSe spectral measurements.
Figure 3.10. Polarization induced spectral shift from CdSe-OPV

Single CdSe-OPV emission spectra from two orthogonal laser polarization orientations.

Figure 3.10 is a Lorentzian fit to two spectra of a single CdSe-OPV nanostructure at two orthogonal laser polarization orientations. These observations strongly support the exciton dissociation mechanism, where the electron near the surface of the CdSe quantum dot drives a Stark interaction that alters the electron and hole energies and break the degeneracy in the $\pm 1$ angular momentum states of the $1S_e - 1S_{3/2}$ optically active transitions.

Details of the polarization anisotropy measurements and Stark shift calculations on CdSe-OPV nanostructures are presented in the published papers and dissertation of Early et al. 126,127
CHAPTER 4

TIME RESOLVED SPECTROSCOPY OF CdSe-OPV

4.1 Fluorescence Lifetime and Correlated Photon Statistics from CdSe-OPV

The mechanism of blinking\textsuperscript{7,39,42,45,87,102,128-130} and blinking suppression\textsuperscript{64,102,131,132} has attracted lot of experimental and theoretical interests. Experimental reports have pointed to the use of electron donating species or conducting surfaces that modify the excited state photophysical properties of the quantum dot and ultimately suppress blinking.\textsuperscript{67,69} These electron donating species are thought to induce modifications that result in a competition between radiative and nonradiative recombination pathways. In the previous chapters, we showed that CdSe-OPV nanostructures displayed a high degree of blinking suppression that was attributed, in part, to electron transfer from photo-excited OPV ligands to the CdSe quantum dot surface.

In this chapter, we describe time-tagged time-resolved (TTTR or T3R) measurements on CdSe-OPV nanostructures that exhibit suppressed blinking in the solid state. We present measurements of fluorescence intensity trajectories and associated excited state decay times from individual CdSe-OPV nanostructures. The functionalization of the CdSe with OPV or some other complex ligands does not only create a 3D hybrid nanostructure that enhance energy and charge transport, but also help elucidate the role that the quantum dot environment plays and its affect on surface states involved in radiative and nonradiative transitions. The effect of surface environment has been used to explain many phenomena in quantum dot photophysics such as spectral diffusion\textsuperscript{133} and photodarkening recovery.\textsuperscript{134}
Recently, Frantsuzov and Marcus\textsuperscript{130} proposed a diffusive coordinate (DC) model that described the blinking behavior of quantum dots to be a result of surface hole trapping that depended on the instantaneous quantum dot electron energy difference “\(\varepsilon\)” between the (1S\(_e\), 1P\(_e\)) quantum dot energy levels.\textsuperscript{102} This model considers \(\varepsilon\) to be a function of the quantum dot nuclear coordinates. It assumes that photoexcitation drives small changes in the nuclear coordinates of the quantum dot, which generates a slow diffusion of \(\varepsilon\) in energy space. Such slow diffusion of \(\varepsilon\) dictates the rate of hole trapping and hence blinking in quantum dots. We propose that electron transfer from photexcited OPV ligands in CdSe-OPV nanostructures drive similar fluctuations in \(\varepsilon\) but with profoundly different results.

We present experimental results on the excited-state decay dynamics and associated photon statistics of individual CdSe-OPV composite nanostructures using time-tagged, time-resolved (TTTR or T3R) single photon counting techniques. The T3R technique gives access to both the arrival time of emitted photons relative to the excitation pulse and the time stamp of the detected photon relative to the start of data acquisition. From this photon-by-photon detection,\textsuperscript{135} both intensity and lifetime trajectories can be constructed to show correlation (if any) between excited state lifetimes and intensity. Recently, Yang and co-workers have used this technique to measure fluorescence intensity trajectories from isolated ZnS/CdSe quantum dots and observed a distribution of “gray” intensity levels that were correlated with different fluorescence lifetimes.\textsuperscript{77,88}

Samples of CdSe-OPV and ZnS/CdSe quantum dots with core diameters of 4.3
nm were prepared by reported methods.\textsuperscript{12} Individual CdSe/ZnS quantum dots or CdSe-OPV nanostructures were isolated from ultra dilute (10\textsuperscript{-10} M) solutions in tetrahydrofuran (Fisher Scientific Optima grade) on plasma-cleaned glass cover slips. Fluorescence measurements were performed on a Nikon Eclipse-TE2000U inverted microscope with 1.4 NA 100 oil objective in a total internal reflection (TIR) configuration. A Digital Instrument Bioscope (BS3-N, tapping mode) mounted on the TE300 microscope was used for atomic force microscope (AFM) imaging.\textsuperscript{98,136} TTTR data were acquired using a 440 nm pulsed diode laser (PDL-800-LDH-C440, Picoquant, GmBH) as an excitation source, with a repetition rate of 10 MHz and pulse width of 50 ps full width at half-maximum. The total average power at the sample was 200 \textmu W in a defocused spot of about 15 \textmu m diameter and was the same for both ZnS/CdSe and CdSe-OPV samples. The fluorescence was filtered through a 605/50 nm band-pass filter, centered approximately at the peak emission wavelength of the quantum dots used in these experiments. A Perkin-Elmer Optoelectronics, SPCM-AQR-14 avalanche photodiode (APD) was used for photon counting, and a TimeHarp 200 (Picoquant GmHB) time-to-digital converter PCI board was used for generating the TTTR data record. All TTTR data on individual nanostructures were acquired for 300 s. Comparisons of count rates under similar excitation and detection with ref 46 indicate that we are well within a linear excitation regime. Fluorescence lifetimes corresponding to different time segments of the intensity trajectory were, obtained by the process of least squares fitting or a maximum likelihood estimate (MLE) algorithm.\textsuperscript{58,89,137-139}
Figure 4.1. Florescence correlated AFM, spectra and height distribution of CdSe-OPV

Spectrally registered fluorescence (A) and AFM (B) images of the same scene of individual CdSe-OPV nanostructures. Shown in (C) is a representative spectrum from an individual CdSe-OPV. The dotted lines indicate the spectral window of the filter used for the photoncounting experiments. Panel (D) shows a histogram of height measurements for 92 individual CdSe-OPV nanostructures.

Figure 4.1 (A) and (B) shows typical correlated wide-field fluorescence image of several individual CdSe-OPV nanostructures from a CCD camera, with AFM surface height scans. The height distribution in figure 4.1(D) was constructed from 92 individual CdSe-OPV nanostructures. The histogram is peaked at 13 nm, consistent with our estimate of a 4.3 nm CdSe core with fully coordinated OPV ligands with an average ligand length of ≈ 4.5 nm. Figure 4.1(C) shows a typical emission spectrum from a single CdSe-OPV nanostructure indicating that essentially all the fluorescence collected
is dominated by the CdSe luminescence.\textsuperscript{98} Also indicated on Figure 4.1(C) are the blue- and red transmission edges of the band-pass filter (vertical dashed lines) used in the T3R experiments, which further ensure that OPV emission does not contribute to the measured APD signals.

**Figure 4.2. Count distribution from ZnS/CdSe and CdSe-OPV**

Representative intensity trace from a single, ZnS/CdSe quantum dot (A) and CdSe-OPV (B) with a 10 ms time bin. On the right are count distribution for each time trace, superimpose with each background count distribution. A Poisson fit to the background with a mean of 6.5 counts is show as the curve with open circles.

Figure 4.2 shows a comparison of intensity trajectories of an individual ZnS/CdSe quantum dots and a CdSe-OPV nanostructure from T3R measurements using a 10 ms time bin. In the case of ZnS/CdSe quantum dots shown in figure 4.2 (A), the fluorescence emission displays varying levels of intensity in qualitative agreement with the results.
reported by Yang and other researchers.\textsuperscript{42,43,57,60,64,88,89,141} The photocount distribution (probability of measuring $N$ photons as a function of $N$) is displayed to the right of each intensity trajectory; for ZnS/CdSe, this distribution is dominated by background indicating that the particle spends a significant fraction of the total trajectory in the dark state. Figure 4.2 (B) shows an intensity trajectory and a corresponding photocount histogram from a typical single CdSe-OPV nanostructure. Superimposed on the fluorescence photocount distribution is a histogram of background (source noise and APD dark counts) distribution characterized by a Poisson distribution with mean value 6.5. Fitting our measured photocount distribution from a single CdSe-OPV particle as a sum of background plus signal (Poisson) distributions indicates a background contribution to the data of about 18%. Even at 10 ms time resolution, we find little evidence of extended dark-state dwell times.

![Probability vs Off-Times graph](image)

**Figure 4.3. Dark state dwell time distribution from CdSe-OPV**

Distribution of dark-state dwell time of a single CdSe-OPV nanostructure with a 1/e value $\approx$ 170 ms.
Using a 3σ threshold to discriminate between “bright” and “dark” states, we find an exponential distribution (figure 4.3) of dark-state dwell times with a 1/e dwell-time value of 170 ms. This value is in reasonable agreement with the \(<\tau_{\text{off}}\) estimate of 500 ms obtained previously from CCD measurements.\(^{140}\)

![Figure 4.4](image_url)

**Figure 4.4. Fluorescence decay curves of ZnS/CdSe and CdSe-OPV**

(A) Comparison of the fluorescence decay curve of a single CdSe-OPV nanostructure (open gray circles) with a ZnS/CdSe quantum dot (diamond black). (B) Expanded version of the CdSe-OPV decay curve in (A), superimposed with the instrument responds function in dash black. The black solid lines in both figures are single exponential fits to the decay curves.

Analysis of the fluorescence decay curve from individual CdSe-OPV nanostructure, shown in Figure 4.4 (A) (gray open circles curve), reveals significantly shorter decay times (0.850 ± 0.040 ns) which is an order of magnitude smaller compared to ZnS/CdSe quantum dot lifetime of about 25 ns (black, diamond curve). Correlations between the fluorescence decay rate and count rate, accessed directly from the TTTR data record, provide important insights into the exciton recombination dynamics of the particles. Measurements on ZnS/CdSe nanoparticles shown in figure 4.5 (A) exhibit fluorescence decay times between 20 and 28 ns, with a positive correlation between
intensity and decay time consistent with results reported Yang and others\textsuperscript{45,77,88} and the model of Verberk \textit{et al.}\textsuperscript{89,102}. The fluorescence intensity trajectories with associated lifetime trajectories for CdSe-OPV shown in Figure 4.5 (B) suggest a very weak positive correlation between intensity and fluorescence lifetimes (ranging from 500 ps to 2.5 ns); this may be due to the relatively long binning times imposed by signal-to-noise constraints and may have obscured larger-scale fluctuations.

![Image](image.png)

**Figure 4.5. Correlated lifetime intensity trajectories of ZnS/CdSe and CdSe-OPV**

Intensity trajectories (lower panels) and associated lifetime trajectories (upper panels) from single (A) ZnS/CdSe quantum dot and (B) a single CdSe-OPV.

For the time period 25-40 s, the integrated signal was 860 counts with an average lifetime of 0.8 ns, whereas during the intensity burst (40-55 s) the integrated signal was 932 counts with an average lifetime of 1.1 ns.

43
In the diffusive coordinate model proposed by Frantzusov and Marcus, quantum dot blinking derives from a light-induced diffusional “motion” of the energy separation between the first two quantum dot electron states ($\varepsilon = E_{1Se} - E_{1Pe}$). The effect of these fluctuations on hole trapping modify the nonradiative recombination rate.\textsuperscript{130} Correlation between excited-state lifetime and fluorescence intensity (count rate) of ZnS/CdSe quantum dots as well as CdSe-OPV nanostructures provides compelling evidence suggesting a common mechanistic origin that involve modification in the excited state nonradiative decay rates.

![Figure 4.6. CdSe quantum dot state diagram and excited state decay paths](image)

Simplified state diagram of a quantum dot system with associated nonradiative decay path ($k_{\text{trap}}$, $k_{\text{relax}}$ and $k_{\text{neutral}}$)

Figure 4.6 shows a simplified state diagram based on the DC model, which describe radiative versus nonradiative recombination of excitons in CdSe-based quantum dot system, where $k_{\text{nr}}$ (determined by the rates for individual steps $k_{\text{trap}}$, $k_{\text{relax}}$, and $k_{\text{neutral}}$) represents the primary nonradiative recombination pathway. The results of two slightly
different models are presented: in the first, a narrow (Gaussian) form for the surface trap state lineshapes results in a “binary” on/off, or blinking behavior, due to a hard boundary between regions (in $\varepsilon$ space) of dominant/suppressed nonradiative transitions. In regions of $\varepsilon$ space where nonradiative decay dominates over radiative decay, no fluorescence is observed. This behavior resembles the intensity trajectories observed in single ZnS/CdSe quantum dots. In the second model, it is proposed that blinking suppression and intensity fluctuations result, when a broader (Lorentzian) line shape is assumed for the surface trap states, precisely the type of behavior observed in our CdSe-OPV composite system.\textsuperscript{142} These numerical results suggest that our modified DC model characterizes a line broadening of the surface traps due to the presence of OPV ligands resulting in modified nonradiative recombination dynamics of the CdSe-OPV system. A recent experiment\textsuperscript{58} probing the effect of substrate on blinking statistics shows fluorescence time traces of ZnS/CdSe dots on indium tin oxide that bear a striking resemblance to the time traces of CdSe-OPV nanostructures, featuring both blinking suppression and intensity fluctuations described for our CdSe-OPV nanostructures. The similarities in these results point to the importance of the electronic environment surrounding the dot and lead us to speculate that these nearby electronic degrees of freedom are the environment which has the most direct effect on the surface hole-trapping physics responsible for modulating the photoluminescence.

This chapter of experiments shows that the fluorescence properties of individual CdSe-OPV nanostructures are strikingly different from conventional ZnS/CdSe quantum dots. Fluorescence-correlated AFM measurements show that the size distribution of these nanostructures is consistent with earlier results, with the most probable size 13 nm. Time
tagged, time-resolved single photon counting measurements reveal a very short fluorescence lifetime for the CdSe-OPV composite systems compared to the ZnS/CdSe. The fluorescence decay times of the CdSe-OPV are weakly correlated with intensity and are surprisingly contained within a very narrow time distribution. We suggest that the OPV ligands form a strongly coupled electronic bath that forms the environment controlling energetic fluctuations, and hence nonradiative trapping kinetics in the CdSe quantum dot.

4.2 Photon Pair Correlation Measurements on Single CdSe-OPV

We have observed from chapters 2 and 3 that, fluorescence intensity fluctuations from individual CdSe-OPV nanostructures are qualitatively different from conventional ZnS/CdSe quantum dots. In particular, the high degree of blinking suppression observed in these systems was suggestive of multi-chromophoric emission either from, multi-exciton formation within the CdSe core or contribution from OPV emission independent of the quantum dot. In this section we describe results of wavelength-dependent second-order fluorescence intensity correlation function $g^{(2)}(\tau)$, measurements on individual CdSe-OPV nanostructures to definitively assess any multiexcitonic character in the fluorescence emission from these nanostructures. Our results point to a weak multiexcitonic character ($g^{(2)}(0) \approx 0.2$) under 405 nm excitation where both the organic ligand and quantum dot absorb. Using 514.5 nm excitation, where the ligand absorption is negligible, the quantum dot emission is completely antibunched ($g^{(2)}(0) \approx 0.05$), similar to that of ZnS/CdSe quantum dot control samples. These results provide insights into to
the mechanism of intensity fluctuations and electronic interactions in composite CdSe-OPV nanostructures.

Electronic interaction between the CdSe quantum dot and the conjugated organic component has been shown to facilitate charge transport, enhance energy transfer and improve fluorescence quantum yield. In the precious chapters we showed a number of interesting photophysical behavior including suppressed blinking, spectral stability, ‘gray level’ intensity flickering and polarization dependent emission, features which are closely linked to OPV ligand coverage on the quantum dot surface. We propose that observed blinking suppression and reduced fluorescence lifetime with a weak correlation to intensity (count rate) from time-tagged time-resolved measurements, could be explained in the context of the diffusive coordinate model proposed by Frantsuzov and Marcus, that connect blinking in quantum dots to Auger assisted hole trapping rates due to fluctuations in $1S_e-1P_e$ electron energy difference in the quantum dot. A common feature in reports of quantum dot blinking suppression makes use of electron donating species, that can influence the electron $1S_e-1P_e$ energy separation via Stark interaction. This, in turn, suppresses Auger-assisted hole trapping and hence the non-radiative decay rates. In the diffusive coordinate model applied to our system, such slow fluctuations of the quantum dot electron energy separation are confined to regions of energy space where non-radiative and radiative decay rates are in competition, resulting in a ‘gray level’ (non-binary) intensity flickering and a significantly reduced fluorescence lifetime consistent with experimental observation. Polarization anisotropy studies also showed that excitations formed within the OPV ligands result in a linear-polarized transition dipole moment both in absorption and emission.
Here, we investigate the multi-excitonic character of isolated CdSe-OPV nanostructures using photon-pair correlation spectroscopy to address the question of charge and energy transfer between the OPV ligands and the quantum dots. To do this we used a standard Hanbury Brown-Twiss,144-147 2-detector configuration with two different excitation wavelengths (405nm and 514 nm) corresponding to OPV + CdSe absorption and CdSe absorption respectively. This measurement provides us with key information about exciton recombination rates (the radiative lifetime) and number of independent emitters that is not directly accessible in conventional time correlated single photon counting measurements.

Fluorescence intensity correlation techniques have been a major tool for characterizing the quantum nature of single fluorescent molecules or nanostructures such as, quantum dots,81,148-154 single polymer chain,106,110,115,116,128,155-158 sodium atoms159 and color centers in diamond.160 In particular, it has proven useful in the investigation of multi-chromophoric systems such as conjugated polymers.106,110,115,116,128,155-158 For a 2-level quantum emitter the second order intensity correlation function \( g^{(2)}(\tau) \) vanishes for \( \tau = 0 \), where \( \tau \) is the time difference between two consecutive photon detection events. In the limit of saturated absorption, the spontaneous radiation is rate limiting in the absorption/emission cycle. For a molecular system with \( N \)-independent emitters, \( g^{(2)}(\tau) \) can be modeled approximately as;

\[
g^{(2)}(\tau) \approx 1 - \frac{1}{N} \exp[-\tau(W_p + \Gamma)]
\]  

(1)

Where \( W_p \) is the pump rate and \( \Gamma \) is the electron-hole pair recombination rate (1/\( \Gamma \) is the pure radiative lifetime). The second order intensity correlation function was obtained
by constructing histograms of time intervals ($\tau$) between successively emitted photons from a single CdSe-OPV at two different excitation wavelengths where either, both the quantum dot and the OPV absorb (405 nm), or quantum dot only (514 nm). Since two photons from radiative recombination are required to generate the correlation function, the rise-time in $g^{(2)}(\tau)$ provides a direct measure of the radiative decay rate (in the saturation limit). Another piece of important information we get from the correlation measurement is the number of independent emitters extracted from $g^{(2)}(0)$, a well known technique used to report excitonic energy transfer within a single polymer chain to localized emissive sites.\textsuperscript{110,115,116,155,157,158}

Single CdSe-OPV nanostructures, synthesized in the Emrick group according to previously reported procedures,\textsuperscript{12,127} were obtained by drop casting from an ultra dilute ($\approx 10^{-11}$ M) sample of CdSe-OPV in THF onto a plasma-cleaned cover slip and allowed to air dry under ambient conditions. The excitation sources were a cw 405 nm of a diode laser (Crystalaser) and the 514 nm line of an air-cooled Ar$^+$ ion laser (Spectra Physics), focused through a 1.4 NA oil immersion objective in a total-internal-reflection geometry onto the sample plane on a Nikon Eclipse TE 2000-U inverted microscope. The average CdSe-OPV nanostructure size was inferred from fluorescence correlated atomic force microscopy measurement\textsuperscript{136,143} to be $\approx$13nm with a CdSe quantum dot core diameter of about 4.5 nm. The fluorescence from single CdSe-OPV nanostructures was collected through the same objective and sent through appropriate filters to ensure that we collect fluorescence from both the OPV and the CdSe quantum dot channel, and to remove scattered excitation light.
Time intervals for photon-pair coincidences were obtained from individual CdSe-OPV nanostructures by collimating the fluorescence through the side-port of the microscope and focused onto the photocathode of two orthogonally aligned single photon counting avalanche photodiode (APD) detectors (Perkin Elmer SCPM AQR-14), using a 50/50 non-polarizing beam splitter. The two APDs were registered with a confocal image point to detect photons from only one and the same molecule at anytime.

![Antibunching curves for CdSe-OPV and ZnS/CdSe](image)

**Figure 4.7. Antibunching curves for CdSe-OPV and ZnS/CdSe**

Normalized intensity correlation function from a single ZnS/CdSe quantum dot from Evident Technologies (black) and a single CdSe-OPV nanostructure (gray) under a 405 nm excitation source. Total integration time was 20 min with 340 ps bin. The smooth solids curves are single exponential fits to the data that gave $g^{(2)}(0)$ of 0.05 and 0.25 for ZnS/CdSe and CdSe-OPV respectively.

Relative arrival times between consecutive photon were recorded in a start-stop fashion with a PC based time-to-digital converter (TimeHarp 200, Picoquant GmbH) with a timing resolution of 34 ps. Contribution from background counts (source and dark noise) to the coincidence histogram was kept to a minimum by employing low excitation power.
(150 $\mu$W) to reduce source noise. We used a 50-ns time delay in the stop channel to access both positive and negative times and thus the full correlation function symmetric about zero time delay.

Figure 4.7 shows a representative photon pair correlation measurement of a single CdSe-OPV (gray) and a single ZnS/CdSe dots (Evident Technologies) (black) under 405 nm cw excitation. The data was acquired within 20 minutes and binned into 340 ps time intervals. To ensure that we collect fluorescence from both the OPV and the quantum dot channels of CdSe-OPV, the fluorescence was sent through a long pass filter with a cut-on at 460 nm. We observe significant change in modulation depth of $\approx 95\%$ ($g^{(2)}(0) = 0.05$) for ZnS/CdSe dots consistent with published work,\textsuperscript{81,151,161} and $\approx 75\%$ ($g^{(2)}(0) = 0.25$) for CdSe-OPV. Two important features of the data are illustrated in figure 1: (i) Though there are about 15-20 OPV ligands on the CdSe quantum dot surface, single CdSe-OPV nanostructure acts to a very good approximation as a single quantum system. Fits obtained using equation (1) suggests a weak multi-excitonic character with $\approx 1.3$ emissive sites (ii) the rise time of 18 ns is consistent with coincidence measurement on ZnS/CdSe dots reported in literature thus inferring a similar radiative decay rate.\textsuperscript{81,151} We investigated the effect of tuning the excitation wavelength from 405 nm to 514 nm, on the rise time and modulation depth. Figure 4.8 (a) and (b) show coincidence histograms and $g^{(2)}(0)$ distribution for single CdSe-OPV respectively, under 405 nm (black curves) and 514 nm (gray curves).

The $g^{(2)}(0)$ obtained with 405 nm excitation (open black circles with a solid black fit) in figure 2(a) shows a modulation depth of about $70\%$ ($g^{(2)}(0) = 0.3$) compared to about $95\%$ ($g^{(2)}(0) = 0.05$) with 514 nm excitation (gray with a smooth gray fit). This
difference in modulation depth is observed in several of the CdSe-OPV nanostructures studied in this measurement.

Figure 4.8 (b) shows a distribution of the number of independent emitters with two different excitation wavelengths. We extracted a higher number of independent emitters, 1.3 ±0.1 with 405nm (black curve) compared to 1.1±0.1 under 514 nm (gray curve).

![Figure 4.8. Wavelength dependent antibunching of CdSe-OPV](image)

(a) Coincidence histogram from single CdSe-OPV cw excitations. Open black circles with black fit show a $g^{(2)}(0) = 0.3$ with 405 nm excitation and 0.05 with 514 nm. (b) Distribution of $g^{(2)}(0)$ black (405 nm) and gray (514 nm) with average values of 0.22 and 0.05 respectively.

This indicates a significant probability of multi-exciton radiative recombination in single CdSe-OPV nanostructures. This multi-excitonic behavior (> 1 number of emissive sites or $g^{(2)}(0) > 0.1$) was evident in the nanostructures studied with 405 nm excitation, where the OPV ligands have a strong absorption. We identify two possibilities that could lead to incomplete photon antibunching; (i) Multi-exciton formation in the quantum dot core (ii) simultaneous emission from both the quantum dot and the ligands. We rule out the first option based on our experimental conditions, the excitation flux was kept in the
regime with low probability of multiple excitation formation in the dot. The results from 405nm excitation present compelling evidence that emission from the ligands also contribute to the coincidence histogram that leads to incomplete antibunching in the correlation function. However the number of independent emitters estimated at $g^{(2)}(0)$ from a fit to equation (1) showed an average of 1.3 emitters per nanostructure, it is therefore reasonable to conclude that most of the excited state generated in the ligands decay non-radiatively through charge/energy transfer to the dot with a small fraction radiatively relaxing and hence contributing to the coincidence histogram.

![Image](image_url)

**Figure 4.9. Comparison of excited state decay rate from CdSe-OPV**

(a) Representative decay curve (gray open circles) of a single CdSe-OPV with a lifetime of 1.5 ns. The solid black curve is a single exponential fit to the data with an instrument response function shown in dotted black. (b) Distribution of rise times using 405 nm (black) and 514 nm (gray) excitations constructed from 20 and 17 nanostructures respectively. The average rise times are 19 ns for 405 nm and 34 ns for 514 nm.

Time-correlated single photon counting measurement on a single CdSe-OPV shows a relatively short fluorescence lifetime of about 1.5 ns shown in Figure 4.9 (a), an order of magnitude shorter than ZnS/CdSe dots (25 ns). Figure 4.9 (b) compares the distribution of the radiative lifetimes of single CdSe-OPV under the two excitation
wavelengths. These histograms were constructed from 20 and 17 different individual CdSe-OPV nanostructures under 405 nm and 514 nm excitation respectively. The rise time distributions obtained from 514 nm (34 ± 12 ns) and 405 nm excitation (19±6 ns) are consistent with other published work on ZnS/CdSe quantum dots.\textsuperscript{88,151,152,161} We find strong evidence in the data from figure 4.9 (b) that the radiative decay rate in CdSe-OPV is not affected by the presence of the ligands and support the explanation that the observed changes in the photophysics (blinking suppression and reduced lifetime) of CdSe-OPV is a result of changes in the non-radiative decay rates in the quantum dot component of the nanostructure. This is consistent with our explanation based on the diffusive coordinate model\textsuperscript{130} that exciton dissociation in the ligands followed by charge transport to the quantum dot surface induces low amplitude fluctuations in the electron 1S\textsubscript{c}-1P\textsubscript{e} energy separation and hence Auger-assisted hole trapping rates, giving rise to a competition between radiative and non-radiative decay rates in the dot. This competition ensures that neither dark nor bright periods dominate and result in “gray level” intensity fluctuations and a drastic reduction in excited state lifetime in CdSe-OPV nanostructures.

In this chapter, we have used photon-pair correlation measurement to show that single CdSe-OPV nanostructures exhibit non-classical photon emission, with wavelength dependent modulation depth as evidence that fluorescence from photo-excited ligands also contribute to the coincidence histogram. We find the average radiative lifetime of \(\approx 19\) ns to be consistent with ZnS/CdSe quantum dots and shows that the radiative decay rate of the dot in CdSe-OPV remains unchanged. We deduce that the previously observed fluorescence lifetime (1.5 ns) in CdSe-OPV is attributed to non-radiative decay rates.
influenced by surface charges provided by exciton dissociation in photo excited OPV ligands. This results provide additional support to the mechanistic picture of electron donating species near the dot surface induce fluctuations in non-radiative decay rates that underline the ‘gray level’ intensity flickering, spectral stability, reduced lifetime and polarized emission in the fluorescence intensity trajectories of CdSe-OPV nanostructures.
CHAPTER 5

SUMMARY AND FUTURE WORK

We have investigated the photophysical properties of CdSe-OPV nanostructures at the bulk and single molecule level to study the electronic interaction between the OPV ligands and the CdSe quantum dot core. This interaction is enhanced by the 3D architecture formed by coordinating the OPV ligands directly to the surface of the quantum dot, which has also be shown to present phase segregation of the organic and the quantum dot components. We used various spectroscopic techniques, including spectral measurements to study energy and charge transport from the OPV to the CdSe, scanning probe microscopy combined with wide-field imaging to study the structure property relation of the CdSe-OPV nanostructure, picosecond time resolved single molecule spectroscopy and polarization anisotropy to access the excited state properties and the effect of the OPV ligands on the photoluminescence properties of CdSe-OPV nanostructures.

Single molecule and bulk spectral measurements on CdSe-OPV nanostructures provided evidence of enhanced energy transfer between the CdSe core and the OPV ligands. This strong energy transfer results in very different fluorescence properties of CdSe-OPV compared to bulk blends; this is manifested as strong quenching of the OPV emission in both the bulk and single molecule CdSe-OPV spectra. We also observed strong spectral stability and blinking suppression in single molecule CdSe-OPV spectra compared to ZnS/CdSe quantum dots. Blinking suppression was attributed to charge transfer from photo-excited OPV to the surface of the quantum dot, consistent with other
published work that use thiol-containing ligands. However not all CdSe-OPV nanostructures observed showed this desired blinking suppression character. To investigate why each CdSe-OPV photophysical property was different, we used fluorescence correlated AFM measurements. We showed that fluorescence blinking in quantum dot systems is completely suppressed in particles with a high OPV ligand coverage on the surface of the quantum dot. Combined single molecule fluorescence and scanning probe microscopy studies on individual CdSe-OPV composite nanostructures reveal a clear connection between blinking suppression and the degree of ligand coverage. For nanostructures in the size range of 10 – 14 nm (a surface height in agreement with a quantum dot fully coordinated with 4 – 5 nm OPV ligands), we observe an average fluorescence duty factor of greater than 90% with 1 s integration time. In contrast, nanostructures in the size range of 4 – 7 nm, suggesting a low coverage of the ligands, show fluorescence duty factors similar to conventional alkane-covered quantum dots (< 50%).

We used time tagged time resolved single photon counting and photo-pair correlation measurements to investigate the role of the OPV ligands on the excited state property of CdSe-OPV nanostructures. Time tagged time resolved single photon counting measurements reveal a very short fluorescence lifetime for the CdSe-OPV, an order of magnitude shorter compared to the ZnS/CdSe quantum dots. The decay times of the CdSe-OPV show a weak correlation with intensity within a very narrow distribution. We suggest that the presence of the OPV ligands through charge and energy transfer, results in increase in the non-radiative rates. Photon-pair correlation measurement showed that single CdSe-OPV nanostructures exhibit non-classical photon emission, with wavelength
dependent modulation depth as evidence that fluorescence from photo-excited ligands also contribute to the coincidence histogram. An average of 1.3 independent emitters for a single CdSe-OPV nanostructure was extracted from fits with the second-order intensity correlation function. This supports the argument that for a CdSe quantum dot covered with OPV ligands a significant fraction of those ligands are involved in electronic interaction such as charge and energy transfer with the quantum dot, which lead to quenching of the ligand emission. We find the average radiative lifetime of \( \approx 19 \text{ ns} \) to be consistent with ZnS/CdSe quantum dots and shows that the radiative decay rate of the dot in CdSe-OPV remains unchanged. We deduce that the previously observed fluorescence lifetime (1.5 ns) in CdSe-OPV is attributed to non-radiative decay rates influenced by surface charges provided by exciton dissociation in photo excited OPV ligands. Polarization anisotropy results and defocused images from single CdSe-OPV nanostructures show that the presence of carriers on the surface of the CdSe quantum dot induces a wavelength dependent linear dipole behavior.

These results provide support to the mechanistic picture of electron donating species near the dot surface induce a Stark interaction which mixes electron/hole states and breaks the symmetry in the 2D degenerate transition dipole. The Stark effect also induces fluctuation in the electron 1\( S_e \)-1\( P_e \) energy, which affect Auger assisted hole trapping and hence non-radiative decay rates. These changes underline the ‘gray level’ intensity flickering spectral stability, reduced lifetime and polarized emission in the fluorescence intensity trajectories of CdSe-OPV nanostructures. This behavior is expected to track with the size of the quantum dot, and should allow for the tailored
synthesis of nanostructures with tunable properties. These new materials could be used in nanoscale optoelectronic contexts, such as high-sensitivity sensor and focal plane array applications.

In this work we have shown clear evidence that the presence of the OPV ligand on the surface of the quantum dot provides a complex electronic environment that affects the photophysical properties of the CdSe-OPV hybrid nanostructure. Future work will be focus on a systematic variation of (1) the type of ligand (the chemical composition) (2) the number and type of substituents on the ligands and (3) the length of the ligands and their distance from the quantum dot core. These modifications will allow detailed study of our the variations in the electronic nature of the ligands affect the photophysics of the whole QD-Ligand system and will provide key insights on how such hybrid systems can be developed in to next generation material for optoelectronic and light harvesting applications.

In the time resolved studies of single CdSe-OPV nanostructures, we observed a significantly shorter excited state lifetime with a weak correlation to intensity, this was in sharp contrast to the ZnS/CdSe case where the excited state lifetimes are well correlated with the fluorescence intensity. In the T3R experiment a fix polarization was used without knowledge of the electric field orientation of the laser with respect to the emission dipole orientation. The may be part of the reason why relatively low count rates were generally observed in CdSe-OPV compared to the ZnS/CdSe quantum dots.
We propose experiment to investigate correlations between excited state lifetimes and fluorescence intensity as a function of $\theta$ (and time) shown in figure 5.1. Polarization anisotropy studies on single CdSe-OPV nanostructures by Early et al. showed contrast ratios that were consistent with linear dipole behavior. However these measurements were taken on a coarse time scale (milliseconds to seconds) and are therefore blind to any fast time scale dynamics that may occur in the quantum dot due to the presence of a charge from photo-excited OPV ligands. We propose that pico-second polarization contrast ratio measurements on single CdSe-OPV will shed more light on the nature of the states involved in the observed linear dipole behavior in CdSe-OPV.

Figure 5.1. Excited state lifetime of CdSe-OPV under two polarization excitation

Comparison of the excited state lifetime for a single CdSe-OPV at two well defined polarization orientation, $E_H$ along the emission dipole axis and $E_V$ orthogonal to the emission dipole axis with corresponding lifetimes $\tau_H$ and $\tau_V$ respectively.
CHAPTER 6

SINGLE MOLECULE SPECTROSCOPY OF A MODEL FLUORENONE: STUDYING THE ORIGIN OF GREEN BAND IN POLYFLUORENE OLEDS

Fluorene-based polymers have become quite popular over the past few years as materials in organic light emitting diodes (OLEDs).\textsuperscript{162-166} These blue-emitting conjugated organic chromophores show much promise as OLED components because of their remarkable color purity and high photoluminescence quantum yields. These desirable features are especially apparent in 9,9-disubstituted polyfluorenes, which have garnered a great deal of attention due to the tunability of their electronic, photonic, and morphological properties by structural modification of the fluorene 9-position.\textsuperscript{164,167} Bulk blends involving polyfluorenes also allow for a range of emission colors created by energy transfer to longer wavelength emitters, such as other conjugated polymers or phosphorescent dyes.\textsuperscript{168-170} Additionally, covalently adding energy transfer traps to the ends of polyfluorene chain prevents the slow phase separation that takes place over time within the blends.\textsuperscript{171-173}

Despite the promise and popularity of these chromophores, numerous fluorene and polyfluorene-based devices have unexpectedly exhibited undesired long wavelength bands in the green region of the visible spectrum, especially after prolonged device operation in the presence of air.\textsuperscript{174,175} These are often collectively referred to as g-bands.\textsuperscript{176} Since the green emission contribution is associated with a reduction in electroluminescence efficiency and color purity,\textsuperscript{164} eliminating them is important for the development of polyfluorene-based fluorescence-based applications. Surprisingly, there is still much debate as to origin of these spectral impurities. Here we show that the
emission of isolated fluorenone molecules strongly resembles these g-bands, and we suggest that the color impurity, often-observed in fluorine and polyfluorene-based devices are likely the result of fluorenone impurities in low concentrations.

The polyfluorene absorption profile is dominated by a strong $\pi-\pi^*$ transition that peaks at about 380 nm; in solution, only a single blue emission band around 400–450 nm is observed. The additional green emission band is only observed in the solid state. One proposal for the origin of green or even yellow emission involves formation of polyfluorene aggregates and resulting excimer emission.\textsuperscript{177-181} The aggregates possess lower excited-state energies and therefore function as effective energy sinks that exhibit excimer emission at longer wavelengths than expected. Aggregates, and therefore excimers, could potentially form in polyfluorenes through interchain interactions due to their often rigid planar chain geometries and through interactions between polar end groups. As a consequence, there have been a number of reports suggesting ways of reducing potential excimer-producing interactions by a variety of methods.\textsuperscript{178,182}

Another proposed mechanism for the origin of g-bands suggests emission from either isolated fluorenone oxidative defects\textsuperscript{183} or from fluorenone excimers.\textsuperscript{176,184,185} It has been shown that such ketone defects can be readily formed during synthesis or as a result of photo- or electro-oxidative degradation processes.\textsuperscript{186} The electronic and optical properties of fluorenone-containing polymers are very different from those of pure fluorenes. Although the lowest energy transition in fluorenones possesses $n-\pi^*$ character, there is a charge-transfer $\pi-\pi^*$ transition of similar energy.\textsuperscript{187-190} Relaxation from this charge-transfer state has been proposed to be the origin of the green emission. Since the fluorenone defects possess lower transition energies than fluorenes, energy transfer from
the dominant fluorene components can be highly favored and occur rapidly prior to fluorene radiative decay. As a result, the observed color is green rather than blue, and device performance is significantly degraded. Since the fluorenone defects act as electron traps, the fact that the addition of hole-trapping molecules can suppress the green emission lends support to the postulation that fluorenones are g-band emitter sites. Rathnayake et al. recently reported that when bulk solid films of 2,7-bis(3,4,5-trimethoxyphenylethenyl)-9,9-diethylfluorene (OFPV) are heated in the presence of air prior to incorporation into an OLED emissive layer, photoluminescence and electroluminescence g-band peaks centered at about 540 nm occur in addition to the desired OFPV blue emission. These peaks were not evident upon heating in a vacuum and at that time were attributed to a very low concentration of a newly formed ketone impurity. This assignment was not verified, however, since a confirming carbonyl infrared transition was not detected. Chen and co-workers recently concluded in a similar study that the lack of an infrared transition indicated the presence of fluorene aggregation and that the green emission they observed was not the result of oxidative defects.

Herein, in an effort to clarify the origins of the g-band emission in OFPV, we report bulk film and single-molecule photoluminescence studies of OFPV and its corresponding oxidation product 2,7-bis(3,4,5-trimethoxyphenylethenyl)fluorenone (OFOPV; Figure 6.1). Particularly, we were interested in whether emission from very low concentrations or even single molecules of the fluorenone impurity can result in the spectral observation of green bands analogous to those observed in other studies of fluorene-based luminophores.
Single-molecule spectroscopy has proven very successful in elucidating the contributions from individual components of complex heterogeneous systems.\textsuperscript{191,192} In particular, Lupton and co-workers recently reported emission from single polyfluorene molecules that incorporate fluorenone defects and concluded that such impurities could, in fact, lead to the observed g-bands without the need to invoke fluorenone excimer formation.\textsuperscript{183} The authors clearly demonstrated a linear dependence between g-band emission and fluorenone incorporation into fluorene copolymers. In that work, a single polyfluorene chain contained, on average, 2–4 fluorenone units. Herein, we concentrate on the properties of single-molecule fluorene and fluorenone chromophores to see if the emissive properties of the fluorenone moiety are preserved in the absence of a polymeric fluorene backbone. Notably, we discovered that the green emission from the fluorenone molecules is only preserved at low concentrations, and that at higher solidstate concentrations intermolecular interactions and possibly aggregation of the fluorenone molecules lead to red emission only (ca. 630 nm).

OFPV was synthesized as described by Rathnayake \textit{et al.}\textsuperscript{1} Single OFPV and OFOPV molecules were deposited from dilute dichloromethane solution (ca. 0.1 nm) and bulk

\begin{figure}
\centering
\includegraphics[width=\textwidth]{structures.png}
\caption{Molecular structures of OFPV and OFOPV}
\end{figure}

Molecular structures of 2,7-bis(3,4,5-trimethoxyphenylethenyl)-9,9-diethylfluorene (OFPV) and 2,7-bis(3,4,5-trimethoxyphenylethenyl)fluorenone (OFOPV).
thin films were deposited onto clean glass coverslips. Excitation of the samples was
carried out using radiation of 457 nm from a continuous-wave Ar\textsuperscript{+} laser, 405 nm from a
diode laser, and 355 nm from the third harmonic of a diode-pumped Nd\textsuperscript{3+} laser, with a
typical power of approximately 100 mW and laser spot size of 15 mm diameter.
Fluorescence imaging and spectroscopic measurements were obtained using a Nikon
TE300 inverted microscope with a 1.4 NA oil objective in a total internal reflection (TIR)
configuration.\textsuperscript{98,193,194} Fluorescence images were acquired using a Princeton Instruments
PhotonMax CCD camera with a typical exposure time of 1 s. Spectra were acquired by
focusing the single-molecule emission from the side port of the microscope onto an
Acton SP2150i dual-grating spectrograph and detected with a Roper Scientific Pixis
400B back-illuminated CCD. Dipole emission patterns were obtained through slight
defocusing of the microscope objective. Bandpass filters were employed to obtain
emission patterns from the green and red-emitting OFOPV molecules (or aggregates).

Figure 6.2 compares the bulk photoluminescence emission spectra from OFPV
and OFOPV thin films deposited on clean glass coverslips. For OFPV, 355-nm laser light
from a 76-MHz diode-pumped mode-locked Nd\textsuperscript{3+} laser (pulse width 12 ps) was
employed, and for OFOPV, the 457-nm line from a continuous wave Ar\textsuperscript{+} laser was used.
From Figure 2 it is evident that the presence of the ketone dramatically affects the
fluorescence emission. The OFPV thin films emit a band centered at 480 nm, the position
of which is independent of the excitation wavelength employed (355, 405, or 457 nm).
On the other hand, emission centered at about 630 nm is exhibited in the bulk thin film
OFOPV spectra.
This strong red emission is not consistent with reported spectra, which exhibit green emission from fluorenone defects on polyfluorene polymer chains. To investigate the origins of the red emission from OFOPV, thin films were created using varying concentrations and by dispersing OFOPV in a polymer matrix of Zeonex (Zeon Corporation). Figure 6.3 summarizes the effects of reducing molecular interactions by dilution and clearly demonstrates that concentration plays a dominant role in the band position of OFOPV photoluminescence spectra. The green band is present only at conditions where the individual molecules are widely dispersed and not strongly interacting. Such conditions are present both in low concentrations on top of glass as well as at higher concentrations when dispersed in the Zeonex matrix. This observation suggests that the red band at 630 nm could originate from dimer or higher aggregate emission due to π–π interactions. Alternately, this red emission could stem from energy transfer from high-energy single fluorenone molecules to those few of low energy.

Figure 6.2. Thin film spectra of OFPV and OFOPV

Bulk thin film emission spectra of OFOPV (black, 457 nm laser excitation) compared to that of OFPV (gray, 355 nm laser excitation)
A variety of molecular environments and different interactions of the polar chromophores with the glass coverslip could well lead to this spread in energies. At lower concentrations, energy transfer is not favored, and thus only higher energy emission is observed. Both mechanisms imply that the “true” emission maximum of monomeric OFOPV is at 540 nm, in agreement with proposals by earlier studies that oxidative fluorenone defects on polyfluorene backbones are the source of g-band emission. This assertion also agrees well with the recent conclusion made by Rathnayake et al., who argued that any green-emitting ketone impurity must be present in low concentrations.
because of the absence of expected bands in the infrared spectra.

![Image](image_url)

**Figure 6.4. Wide-field fluorescence image of single OFOPV**

Representative intensity scene (approximately 8 x 8 mm) showing single diffraction limited emission sites from OFOPV molecules.

Single-molecule fluorescence studies were performed to confirm that the OFOPV monomer is the likely origin of the g-bands observed in OFPV-based OLEDs. A representative fluorescence image obtained with a high-resolution electron-multiplying (EM) CCD camera (Princeton Instruments Photonmax) for an area measuring 818 mm is shown in Figure 6.4. The emission from single sites was dispersed using an imaging spectrograph to obtain single-molecule spectra. Figure 6.5 shows representative fluorescence emission spectra from the OFOPV single-molecule measurements. For these measurements, 457-nm laser light from an Ar+ laser was employed for excitation. The OFOPV emitter sites yielded variable spectra, where the position of the peak maximum varied significantly from molecule to molecule. The single-molecule spectral positions spanned the range of the bulk OFOPV emission, but the peak widths were much narrower than those obtained from the bulk.
While the spectrum peaking at 550 nm (green site) in Figure 6.5 is in the same region as the diluted-concentration bulk-film spectra from Figure 6.3, the spectrum that peaks at 620 nm is in the same region as the band found at higher bulk concentrations (red site).

Figure 6.6 shows a histogram of the center wavelengths from 118 OFOPV single-molecule measurements. Whereas there are a few instances of long-wavelength emission, which are possibly due to dimers or higher aggregates deposited on the glass (“red” emitters), most spectra are centered around 540 nm, in agreement with the bulk measurements for diluted OFOPV described above (dark gray curve) and similar to reports in other studies of fluorenone defects on polyfluorene chains.

**Figure 6.5. Single molecule OFOPV spectra**

Representative single site emission spectra from high dilution deposition. The spectrum peaked at 610 nm is assigned to emission from a dimer or larger aggregate site.
Overlaid in light gray is the luminescence curve of OFPV after heating in air, taken from the results of Rathnayake et al.\(^1\) That work attributed g-band formation to a fluorenone impurity formed in very low concentrations, given the lack of infrared signatures of the fluorenone component. The similarity between the earlier bulk luminescence emission result and the histogram from single-molecule fluorescence measurements strongly supports the conclusion that a low concentration of fluorenone impurities rather than fluorenone excimer formation\(^{176,184,185}\) is the origin of the g-bands in OFPV-based OLEDs. Single-molecule measurements of OFPV, on the other hand, revealed a distribution of emission wavelength maxima centered at around 475 nm, consistent with

![Histogram of center wavelengths from single OFOPV](image)

**Figure 6.6. Distribution of center wavelengths from single OFOPV**

Histogram of center wavelengths from 118 individual OFOPV single molecule fluorescence spectra. The overlaid curve is data taken from the publication by Rathnayake, et al.\(^1\)
the results from bulk films.

The wide variation in single-molecule peak position for OFOPV is likely due to varying molecular environments and different interactions of the polar chromophores with the glass coverslip. The histogram of 118 single-molecule measurements agrees well with the bulk emission curve in which the OFOPV molecules are dispersed in Zeonex and also with the earlier OLED measurement. However, very few of the single-molecule spectra are in the region of the red band observed in the high-concentration films. The high-concentration results suggest that the intimate intermolecular effects are important for red emission to be favored strongly. In an effort to differentiate the red emitter sites from the green, intensity time traces of individual red- and green-emitting sites were obtained using red (602–657 nm) or green (510–560 nm) bandpass filters. Representative fluorescence time traces of red and green emitters shown in Figure 6.7 reveal different behavior. Whereas the green-emitting traces exhibited blinking from on to off states, multiple red traces showed more complex behavior. This difference suggests that some of the red-emitting sites could stem from energy transfer within multiple molecules, possibly giving excimer emission. Notably, solution OFOPV fluorescence measurements show a fine-structured peak at 440 nm that decreases at higher concentrations, while a featureless, broad band at 570 nm increases; this is characteristic behavior for solution excimer formation. If the single-molecule red emitter sites arise from excimers, their red shift relative to the solution excimer band at 570 nm is attributable to changes in the local environment.
In order to gain further insight into the differences between the green- and red-emitting OFOPV single-molecule emitters, dipole-emission patterns of the two groups were obtained. Single molecules exhibit characteristic features upon irradiation, such as blinking and distinctive dipole emission patterns. These features help corroborate the assignment of fluorescence emission and spectra to single molecules. In addition, dipole patterns reveal the orientation of the transition dipole moment of the molecular framework relative to the surface. Such patterns are obtained by a slight defocusing of the microscope objective and have allowed for the assignment of 3D molecular orientations.191,197,198

Figure 6.7. Intensity time trace from single OFOPV

Representative single emission time traces from (a) red-emitting and (b) green-emitting OFOPV sites.
Figure 6.8 shows dipole emission patterns from the linear control system DiIC$_{18}$ (left) and from OFOPV green-emitting (middle) and red-emitting (right) sites. The characteristic emission pattern from the well-studied DiIC$_{18}$ single molecule indicates that it is lying in the x-y plane (parallel to the glass surface)\textsuperscript{191} Interestingly, although the green-emitting OFOPV single-molecule image has a remarkably similar pattern, the red-emitting site is somewhat different, suggesting that the emission may not originate from a single molecular dipole.

In summary, we have presented single-molecule and bulk thin film fluorescence measurements on a model molecular fluorine and compared them to those of its oxidative fluorenone derivative. Whereas the molecular fluorene (OFPV) exhibits an emission spectrum insensitive to concentration and centered at approximately 480 nm, the photoluminescence spectra obtained from the fluorenone derivative (OFOPV) was found to vary dramatically with changing concentration and intermolecular interactions. Whereas highly concentrated OFOPV thin films result in fluorescence emission spectra with maxima around 620 nm, thin films created from low-concentration solutions and
from the dispersion of OFOPV molecules in a polymer matrix result in a band centered at 540 nm, in agreement with earlier studies of fluorenone defects along polyfluorene backbones. These results strongly support the conclusion that aggregation leads to excimer formation or other energy transfer phenomena in OFOPV. Single-molecule fluorescence measurements reveal narrow emission bands for OFOPV with a distribution of peaks mostly centered around 540 nm. There is a good correlation of the OFOPV single-molecule emission spectral distribution with both the low-concentration spectra and with the results of Rathnayake et al., in which the fluorenone impurity was thought to have been created through heating in the presence of oxygen (oxidation). The difference in the emission bands for monomeric and bulk (likely aggregated or excimer) OFOPV represents strong additional evidence that the green emission in OLEDs made with thermally annealed fluorene derivatives can originate from monomeric fluorenone emitter sites rather than from fluorene aggregation or fluorenone excimer formation.
APPENDIX A

TIME CORRELATED SINGLE PHOTON COUNTING (TCSPC) OPTICAL SETUP AND DATA ANALYSIS

Time correlated single photon counting experiments can be performed in two ways to determine the fluorescence lifetime of a fluorophore. The first is the time domain method, this measures the relative arrival time between a fluorescence photon and the excitation laser pulse that generated the photon. The second is the frequency domain measurement, which measures the relative modulation and phase shift in rf-signal between the sample of interest and a reference sample. This appendix only focuses on the time domain measurements.

The fluorescence lifetime ($\tau$) of a molecule is the amount of time the molecule spends in the excited state before relaxing back to the ground state after a short pulse excitation. In general the molecule is excited high above the band-edge and it quickly relaxes to the lowest excited state from where it decays to the ground state by emitting a photon after the some time equal to $\tau$. The decay process from the excited state follow two paths (i) the radiative path or (ii) the non-radiative path characterized by the decay rates $k_r$ and $k_{nr}$ respectively. The observed or measured lifetime $\tau_{obs}$ is a result of both $k_r$ and $k_{nr}$. Under varying condition both $k_r$ and $k_{nr}$ can be modified directly or indirectly.

If we consider a sample solution or a thin film of millions ($n_0$) of fluorophores, after an exposure to an infinitely sharp ($\delta$-function) excitation laser pulse, a fraction of the initial population ($n_t$) gets promoted into the excited. The rate of the excited state population decay is a sum of the radiative and non-radiative decays;
\[-\frac{dn(t)}{dt} = (k_r + k_{sr})n(t)\]
\[-\int_0^t \frac{dn(t)}{n(t)} = (k_r + k_{sr})dt \quad \text{integrating from } t = 0 \text{ to } t = t\]
\[-\ln(n)|^t_0 = (k_r + k_{sr})t\]
\[-(\ln(n(t)) - \ln(n_0)) = (k_r + k_{sr})t\]
\[-\ln\left(\frac{n(t)}{n_0}\right) = (k_r + k_{sr})t\]
\[\ln\left(\frac{n(t)}{n_0}\right) = -(k_r + k_{sr})t\]

\[\frac{n(t)}{n_0} = e^{-(k_r+k_{sr})t} \quad \text{After time } t \text{ the population } n(t) \text{ is a fraction of } n_0\]

\[n(t) = n_0e^{-(k_r+k_{sr})t} \quad ; \quad (k_r + k_{sr}) = \frac{1}{\tau_{obs}}\]

\[n(t) = n_0e^{-\gamma t} \quad \text{In experiments we measure intensity } (I) \text{ not } n\]

\[I(t) = I_0e^{-\gamma t}\]

From the above expression the excited state population decays exponentially. A quick estimate of the lifetime from decay curve is the time it takes for the intensity to drop from its maximum value to 1/e of that value. Note that in real experiments an infinitely sharp pulse is not available a good approximation is a sharp laser pulse with a few 10s of picoseconds fwhm. The need for a sharp pulse is to ensure that the probability of re-excitation of the same sample with the same pulse is zero; this is required for the above rate equation to hold. If instead a very broad pulse is used (with fwhm of a few nanoseconds), it means that molecules in the excitation volume with decay time faster than the pulse width will be re-excited multiple times within the duration of the pulse.

The principle above also holds in single molecule measurements. In the bulk we collect millions of photons from millions of molecules for a short time to construct the decay
curve. In the single molecule case illustrated in the figure A.1 below, we collect millions of photons from the same molecule integrated over a long time to construct the decay curve. This is however limited by blinking and photobleaching. When working with organic dye molecules or any other fluorophore that bleaches quickly, and therefore very difficult to extract enough photon to construct a decent (good S/R ration). In such a situation, a single decay curve can be constructed from 5-10 different single molecules. The assumption here is that each molecule that is used for this decay curve construction must possess the same molecular environment and must see the same excitation flux. For a well dilute solution (single molecule concentration ~nM) of a fluorophore the probability of excitation and emission of a photon from each molecule in a thin film, should be and indeed is governed by the same Poisson statistics. If this condition is fulfilled and most of the time that is the case in single molecule detection, then several few molecules can be used to construct a single decay curve. Note however that this is not the same as the ensemble measurement (in solution or thin film case), because in the ensemble case, eventhough the absorption/emission process still follow poisson statistics, intermolecular collisions give rise to possible energy and charge transport event the significantly change the lifetime. However ever for a solution phase experiment, if the solution is dilute enough (nM concentration), then the probability of such intermolecular collisional events and hence charge and energy migration is small and the lifetime measured is approximately equal to the single molecule value (note that there may be a slight different between the solvent and the thin film single molecule values). It must be said that the single molecule solution phase lifetime measurement requires a long waiting/integration time, because the probability of excitation and emission is limited by the diffusional
motion of the molecules and low long they stay in the excitation volume, assuch such measurements generally have high background noise and a separate background measurement should be subtracted from the data to correct it.

In our experimental setup the time-to-digital converter (TDC) is an on-board PicoHarp300 photon counter (from PicoQuant). Refer to PicoHarp300 manual for connection of APDs and laser sync source. The experiment can be run in two modes. The first is the conventional TCSPC mode, which outputs a histogram (decay curve) of relative arrival times. The second is the TTTR or T3R mode (time-tagged time resolved TCSPC). In this mode the PicoHarp300 collects relative arrival time (referenced to the excitation pulse) and coarse time information (referenced to the start of the experiment or data taking for a given molecule). The coarse time allows us to construct intensity

Figure A.1. TCSPC setup scheme of photon arrival/detection incidents

A schematic of the measurement of the relative and absolute arrival times of photons from a single molecule with reference to the excitation pulse and the start of the experiment of that molecule.
trajectories from which we can obtain decay curves for any arbitrary segment of the intensity trajectory.

**Optical Setup for Single Molecule TCSPC**

This requires an inverted microscope with a high numerical aperture objective lens to hold sample for excitation and collection of fluorescence. Two CCD cameras are used for initial alignment; one of the CCDs is replace with an APD for final alignment and data collection. We also need lenses to collect and send the fluorescence photons to the APD. This setup can be constructed for either wide-field or confocal illumination configuration. The description here is for wide-filed illumination.

1. Prepare a yellow (or orange or red) bead sample that give well isolated fluorescence image on CCD1 camera on the eyepiece. Make sure the image is in focus.

2. Place a 50 mm collimating lens on the side-port of the microscope as show in figure A.2. This lens should be exactly 50 mm from the focal spot on the side-port. This is the appropriate way to do it but it can be tricky and hard hard. If you are successful, the size of the image after the collimating lens should be

![Figure A.2. Optical setup for time correlated single photon counting measurements](image)
the same over some distance. Use a business card to check this. Place another
camera (CCD2) at the end of the setup as shown and place the focusing lens
100 mm from it (use appropriate lens tubes/connectors). Include an iris
between the focusing lens and CCD2, the iris should be wide open at this
point. If this setup is done correctly there should be an image on CCD2 (with
slightly different magnification from CCD1.

3. An alternative to step 2 is a reverse configuration. Start from CCD2 instead
and place the focusing lens 100 mm from it (use appropriate lens
tubes/connectors). Include an iris between the focusing lens and the CCD2,
the iris should be wide open that this point. Mount the collimating lens on a
post and place it ≈ 50 mm from the side focus. Make sure all the optics and
CCD2 are aligned (use the tapped hole in the optical table for easy alignment).
Send the image on CCD1 to the side port, with CCD2 running, translate the
collimating lens back and forth until and image is formed on CCD2 (this
should be done in open space with room light off. Mark the spot for the
collimating lens

4. Connect everything in lens tubes with the appropriate lenses and iris to CCD2.

5. Ensure that you can correlate the images on both CCD1 and CCD2. It will be
easy (but not necessary) if the two images are oriented in the same way. If any
reorientation to match the two images need to be done it will be better to do it
on CCD2.

6. If the images on the two CCDs can be correlated, close the iris in front of
CCD2 tight and place the cursor in the middle of the aperture and then open
the iris back up with the cursor still in the middle. Use the joystick or any stage control software (for example “StageControl-V2d-mod-04-08-2010.vi”) to translate one of the fluorescence beads to the middle of the cursor (which is also the middle of the iris) on CCD2.

7. Identify same particle on CCD1 that was placed in the cursor and the middle of the iris on CCD2 in 6 above. *Note the pixel coordinate (x,y) of this particle or bead on CCD1. It is the coordinate of intereste of a particle on CCD1 that corresponds to the middle of the iris on CCD2.*

8. Close the iris in front of CCD2 down tight. Use electrical tape to ensure the iris is light tight. To recheck if the pixel coordinate marked up in step 7, randomly place fluorescent beads at this pixel coordinate of CCD1 and check if they appear in the iris on CCD2. If after this is check the result is satisfactory move on to step 9.

9. Gently uncouple CCD2 from the lens tubes and make sure the connection is well stabilized all the way to the side port. Mount APD1 on a 3D micrometer stage (you may or may not need a 1D stage or an aluminum slab as a base to give the 3D state some height). Align the mounted APD with the xyz axis of the 3D stage so that the photocathode of the APD is aligned with the center of the closed iris (you will have to eye-ball this to get it close) and its also 100 mm from the focusing lens like we did with the CCD2. If the alignment is satisfactory use electrical tape and some dark clothe to tape the APD to the lens tube so it is light tight. To give room for translation after taping ensure the clothe between the APD and the lens tube is a enough and a bit lose.
Optimization of APDs and Data Acquisition

10. After aligning and enclosing the APD, prepare a thick film of any fluorophore (quantum dots, beads, organic dyes etc what ever is available for the wavenght being use) on glass. This sample under excitation will normally saturate the CCD1 camera, use appropriate laser power and turn it up as needed to increase the fluorescence intensity. Send the fluorescence to the side port. The goal is to have a large/intense enough a scene to fill the whole iris in front of the APD.

11. Connect the APD to either the PicoHarp300 channel-1 or the “input1” of the SR400 photon counting controller from Stanford research. If you use the PicoHarp300 then the Symphotime (operation) software must be used to look at the intensity time traces. The SR400 is recommended.

12. Make sure the SR400 is connected via the GPIB/USB cable and turned on. Connect the APD signal to the input1 of the RS400. Run the “SR400 Program-V2c.vi” LabView vi. If the input levels and discriminators on the SR400 is set correctly in both the Labview vi and the controller, there vi should start recording counts from the APD. If there is no sample on the slide the APD will register just the dark counts. The Parameters for SR400 Program-V2c.vi are:

input levels: 100mV

Disc level; 100 mV for both input 1 and 2 this should be done on the controller itself.
Slope: negative or falling

CW Mode ‘T’/B Set: 10

Scan Mode Scan Step: 1x10^-6

‘T’ Select: 10MHz

Gate Mode: CW

Gate Width: 1x10^-6

Gate Delay: 1x10^-8

Trig Level: 0.05V

Trig Slope: Falling or negative

Count Mode: A,B for T

Dwell Source: int

At N: Stop

Dwell: 2x10^-2s

N Periods: 1 [at 1]

Display: Continuous

D/A Range: ****432*

D/A Out: A

13. Send the fluorescence from the thick film sample to the side port. While looking at the counts from the ADP on the “SR400 Program-V2c.vi”, translate the APD slowly in one direction using the 3-axis on the APD stage to maximize the counts. Do this for all the other axes to maximize the counts. For a thick film of fluorophore the APD should be recording counts in
excess of 50,000 counts per second. Keep in mind that this also depends on the input laser power.

14. If the counts on the APD is maximize, it means that the ADP is now looking into the iris in front of the focusing lens on the side port. Change the sample to a single molecule bead concentration using CCD1 so that you have about 8-12 isolated florescence spots on the scene.

15. Identify one of the spots on CCD1 and translate it to the pixel coordinate (x,y) that corresponds to the center of the iris. Send the fluorescence from CCD1 to the side port and look for counts from the APD on the SR400 LabView vi (hopefully it is still connected and running, if not do 12 above).

16. Maximize the counts on the APD by translating the axis as in 13 above. The counts registered here should be on the order of about a few 1000 counts per second again this depends on the input laser power. To ensure the fluorescence spot in the x,y pixel coordinate is the only one the ADP1 is registering counts do step 17.

17. Translate the molecule in the x,y coordinate out of that spot using the stage control vi (“StageControl-V2d-mod-04-08-2010.vi”) or whatever programe you have available to control the stage motion. First in the x-direction then in the y-direction. You may have to do this blindly because the signal must be sent to the APD, unless the microscope allows you to send signal to both the side port (APD) and the eyepiece (CCD1) at the same time. By translating the fluorescence spot in and out of the x,y pixel coordinate the counts on the APD should drop and increase at the same time. This establishes that the APD is
targeted towards that pixel coordinate. Any single molecule placed in that
coordinate should send its fluorescence to the APD for time resolve
measurements. Note that translating a fluorescent bead in and out of the
registered coordinate will not always restore the counts to its maximum
value due to photobleaching. The intensity takes on an exponential form.

18. The setup is ready for data taking. The sample used needs to be dilute enough
to ensure that two fluorescence spots do not end up in the iris.

**Taking Data**

19. Refer to the PicoHarp 300 manual for detailed direction on cable connection and
control panel values for taking data. One can also use the optimized control
level values from previously taken data by just opening the old file of interest
in the current PicoHarp300 window. There are a few things to note when
taking data.

20. **IRF:** The instrument response function is needed for data analysis (curve
fitting either in symphotime or in Igor). It is important that you obtain an IRF
as narrow as possible based on the time response of the APD being used. One
thing to note is that the width of the IRF is dependent on the source being
used. For a PDL with 70 ps pulse width and an id-100 APD an IRF with fwhm
of about 90 to 120 ps can be achieved using the laser scattering from a cover
slip at high laser power. Note that the APD will saturate at high power so to
achieve a narrow IRF at high power, a neutral density filter need to be
employed (ND20 or ND30). This however requires that the data have to be
taken at the same laser power because the peak position of the IRF shifts with the laser power and can affect the data fitting.

21. When taking data with the PicoHarp300 (with or without a router) it is better to use the time-tage mode (TTTR), which allows the collection of both decay curves and intensity traces. Choose the rep-rate of the laser and the resolution of the PicoHarp300 so that no data is lost. The PicoHarp300 has a maximum resolution of 4ps and 4096 channels; at such a resolution the time window accessible is (4 x 4096) ≈ 13 ns irrespective of the rep-rate of the laser. Choose the rep-rate of the laser and the resolution of the PicoHarp300 such that the lifetime of the molecule is approximately a factor of 3 less than the time between pulses and the time window the resolution chosen allows.

**Data Analysis**

22. **Symphotime:** This software allows T3R files to be imported for analysis. The coarse time resolution is 1ms and displays the count rate per millisecond. For detailed information on data analysis with symphotime refer to the SymPhoTime Technical Data Manual Version 4.7.

Note that even though symphotime displays both the average and raw lifetime trajectory for a given time trace, it only allows the export (as a text file) of the raw lifetime trajectory together with the count rate (amplitude) for any given lifetime in the trajectory. To calculate the average lifetime trajectory \( \tau_{\text{ave}} \) we sum the count rate (amplitude) for any given lifetime over \( i \) as:
\[ \tau_{\text{ave}} = \frac{\sum \text{CountRate}_i \times \tau_i}{\sum \text{CountRate}_i} \]

23. For curve fitting of lifetime data, it is straightforward if an IRF was taken (in T3R mode) in addition to the data. In this case the data fitting only requires an import of the T3R data and the IRF. However if an IRF was not taken or it was taken in TCSPC mode (which cannot be imported directly into symphotime) then an ASCII text file of the desired IRF can be imported with the following adjustments. Copy the IRF curve in TCSPC mode into an empty Igor or any spreadsheet file. This will be just a single column of data. To be able to export this into symphotime, add the following two (2) rows to the single column data at the end. The last but-one data point should be “Resolution”. The last data point should be the numeric value of the resolution for example “0.016” that is 16ps. This is the resolution of the PicoHarp300 used for taking the IRF in TCSPC mode or that of a simulated IRF and this should be the same as the resolution used in taking the data.

24. **Igor Analysis:** Curve fitting in Igor can also be used to extract lifetime from TCSPC data. This generally requires the use of a simulated IRF that is the sum of 3-gaussian functions with different amplitudes and peak position. An IRF can also be imported from a TCSPC file.

25. To simulate an IRF, make waves in Igor and call it “IRF-SIM” this should be equal to something similar to,

\[
\text{IRF - SIM} = 0.9 \times \exp\left(\frac{p - 19.97}{11.50}\right) + 0.095 \times \exp\left(\frac{p - 29.5}{130.6}\right) + 0.005 \times \exp\left(\frac{p - 55.5}{89}\right)
\]
$p$ in Igor represents a general variable. The number of points in this new wave should be the same as the raw decay data. Changing the numerator values of the argument in the exponent can shift around the IRF-SIM function. This is important because to ensure a good fit, the falling edge of the IRF-SIM should intersect the raw decay curve at about 3/4ths of its maximum intensity value as shown in the figure bellow.

![Decay Curve and IRF-SIM](image)

**Figure A.3. Decay curve and simulated IRF for curve fitting**

26. Create an exponential function called “Expo” with the same number of points as the IRF-SIM and the raw data. The exponential function is of the form,

$$
Expo = A \cdot \exp\left(-\frac{p}{\tau}\right)
$$

where $\tau$ is the lifetime and $p$ is a general variable in Igor that is also represented by $t$ or $x$ in other cases. $A$ is the amplitude and can be adjusted after each re-convolution iteration to match the amplitude of the raw decay curve. To enter the “Expo” function in Igor an initial guess of $\tau$ is required.

27. Change the wave scalling in Igor for both IRF-SIM and Expo to what the raw decay data contains. This is the PicoHarp300 resolution at which the data was
taken. To do this in Igor, on the menu bar go to “Data>>Change Wave Scalling>>” and change “Delta” to the resolution of the data for example 0.016 ns. Remember to select all the waves for which the scalling need to be changed.

28. To fit the data, choose an arbitrary $\tau$ value for the Expo function. Perform a convolution between the “IRF-SIM” and the “Expo” functions this in theory should reproduce the decay curve of the raw data. To do this in Igor go to the menu bar and select “Analysis>>Convolve>>, then choose “Expo” and “IRF-SIM” as your sources and choose “make a new wave” for your output.

29. Plot the new output wave (if the name was not changed it should be W_Convolution or which ever name that was use) as y-values against x-time (ns). On the same graph plot the raw decay curve data and compare the two curves. It maybe helpful to normalize both the fit and the raw data to one (1) though sometimes this may not be necessary. On way to compare them is to calculate the residual (the difference between the two curves ie Residual= W_Convolution - Data), if the fit is good, a plot of the residual versus time (ns) should be symmetric (or oscilate) about zero. Points of poor fit normally show up as large spikes in the residual plot.

30. If the fit is not satisfactory, change the $\tau$-value in Expo and repeat points 28-29 above. Do this until a satisfactory fit is obtained. Similar changes to the IRF-SIM (shifting changing its peak and width) can also be done followed by point 28-29 but these changes should be done one after the other to know what change helps the fit and what doesn’t.
APPENDIX B

PHOTON-PAIR CORRELATION MEASUREMENT (ANTIBUNCHING)
OPTICAL SETUP AND DATA ANALYSIS

The nature of streams of photons (or in general fermions or bosons) emitted from a source can be characterized by the second-order intensity correlation function \( g^{(2)}(\tau) \) which determines whether the statistics of a photon stream can be described by Poisson, Sub-Poisson or Super-Poisson statistics. Light sources that are classified under Poisson or Super Poisson photon statistics also called \textit{partially coherent or bunched light} can be adequately explained by the classical theory of light and for such cases \( g^{(2)}(0) = 1 \) or \( g^{(2)}(0) > 1 \) respectively.

However light sources that show Sub-Poisson statistics cannot be described by the classical theory of light. This non-classical or quantum mechanical behavior is characterized by the second order intensity correlation function as \( g^{(2)}(0) < 1 \) and such a source is generally described as being \textit{antibunched}. This is a fundamental requirement for the generation of single-photon source required for quantum information processing and other related applications. For a source to satisfy this requirement it must emit one and only one photon in response to an optical or electrical trigger. Robust single molecules such as quantum dots or conjugated organic polymers under optical excitation show this behavior of a single-photon emitter source. This is possible because for a single molecule driven by a laser source, the probability of emitting two photons at the same time is zero. This is because after the successful emission of a photon, the molecule must necessarily be in the ground state from where it cannot emit another photon. Some time (> 0) must elapse after the emission of the first photon before the molecule can be excited.
again to emit another photon. The second-order intensity correlation function must be equal to or approach zero as the time between detection of successive photons events approach zero.

The second-order intensity correlation function can be measured experimentally by recording and histogramming the time interval between two successive photon detection events from a source (for our case a single molecule). Due to the inherent long dead time a single APD is inadequate to construct the intensity correlation function with picoresond resolution. The dead time refers to the time the detector (APD) takes to recover after detecting a photon, whiles it is recovering there is no chance for it to detect the next successive photon therefore, photons arriving shortly after the first detection cannot be distinguished or will be completely lost. To avoid the detector dead time problem the Hanbury-Brown-Twiss (HBT) setup shown in figure B.1 bellow is used.

![Figure B.1. HBT detection scheme for photon-pair correlation measurement.](image)

The fluorescence photons from a single molecule is sent through a 50/50 nonpolarizing beamsplitter and fed onto two APDs aligned perpendicular to each other (APD1 and APD2). One APD delivers the start pulse and the other, the stop pulse. A PicoHarp300 time-to-digital convertor (TDC) constructs a histogram of the time
difference between two successive photons, this histogram is represents the second-order
intensity correlation function \( g^{(2)}(\tau) \). Because two separate detectors are use the problem
of dead time does not arise. It must however be noted that this configuration requires a
large photon count rates to construct a correlation function with good signal-to-noise ratio
as shown in figure B.3. This constrain on signal may be due to the follwing reasons. One,
the set up requires two photons to generate a single data point (time interval between two
successive photons, one to start the clock and the other to stop it). Two, if successive
photons are dectected in the same detector channel for example in the start channel, the
TDC restarts the “clock” over and over again until the next photon hits the other detector.

The HBT setup can be used with both a continuous wave laser or a picosecond
pulsed laser. The continuous wave excitation gives rise to the second order-correlation
function with modulation at \( \tau = 0 \) delay, for a single molecule \( g^{(2)}(0) < 1 \) and the stream
of photons are said to be *antibunched*. The correlation function can be fit to an
exponential growth function from which we can extract the number of independent
emitters \( N \) and the excited state decay rate \( \Gamma \).

\[
g^{(2)}(\tau) \approx 1 - \frac{1}{N} \exp\left(-|\tau| (\Gamma + W)\right)
\]

\[
W = \frac{I\lambda\sigma}{hc}
\]

\( W \) is the rate of excitation, \( I \) (W/cm\(^2\)) is the laser intensity and \( \sigma \) (cm\(^2\)) is the
absorption crossection of the molecule, \( h \) (J.s), \( c \) (cm/s) and \( \lambda \) (nm).

The second-order intensity correlation function for a single molecule under pulse
excitation give rise to a series of correlation peaks separated by the time between
pulses. In this case the *antibunching* or the coincidence peak is depicted as a
modulation of the central peak height relative to the others. The number of emitters is
the ratio of the peak height of the central peak (the modulated peak) and the adjacent peak.

**Optical Setup for Antibunching**

The optical setup for the photo-pair correlation measurements is same as that for TCSPC with an additional arm.

1. Follow the procedure explained for setting up the optics along the side-port for TCSPC. Setup the two lenses (collimating and focusing lense) and CCD2 along the side port as described earlier. In addition place a 50/50 nonpolarizing beamsplitter in the cage as shown bellow. Mount the beamsplitter on the base of the cover of the cage using crazy glue. The presence of the beamsplitter should not affect the image on CCD2.

2. Place another focusing lens (preferably with the same focal length ≈100 mm) and another iris on the “T” similar to the one on the optical axis. The lens must be at a distance equal to its focal length from the CCD3 chip.

3. Couple a third camera CCD3 to the optics along the “T”.

4. Place a fluorescence bead sample and image onto CCD1 is the image is satisfactory, send the signal to the side-port. Open the two irises wide; there should be an image on CCD2. If there is no image on CCD3 rotate the beamsplitter gently with your hand until an image appears on CCD3. This will not affect anything on CCD2. Fine-tune the focusing lens position relative to the cameras CCD1 and 3 to generate a good infocus image in parfocality with CCD1 with the right magnification.
5. Identify the pixel coordinates on CCD1 that corresponds to the center of the iris on the optical axis as shown in the TCSPC optical setup. At this point close the iris but do not tape it.

6. Now identify the counterpart of the particle located at the center of the iris on the optical axis on CCD2 and on the “T” CCD3 camera. Note the location of this particle on CCD3 with respect to the center of the iris on the “T”.

7. Use the cursor to mark the center of the iris on CCD3.

8. **This is tricky and difficult to do.** Use an align renche (or two or three at the same time) on the hexagonal 3D adjusters on top of the cube cage holding the beamsplitter, to translate the particle of interest to the cursor location on CCD3 (the center of the iris). You may rotate the top cover of...
the cube, to allow one easy translation in either the horizontal or vertical direction, depending on how CCD3 is oriented, then fine tune with the align renches.

9. If this is successful CCD2 and CCD3 should have the same particle in the center of both irises corresponding to the image spot x,y on CCD1.

10. Close both irises tight and use electrical tape to ensure they are light tight.

11. Pull the CCD2 and CCD3 and replace them with two APDs mounted on a 3D stage as described in the TCSPC setup earlier.

12. Make sure both APDs are looking into the center of the two irises by using a thick film of fluorophore and sending the fluorescence to the side-port.

**Optimizing the setup**

13. Follow the process of optimizing and fine-tuning the two APDs (one after the other) as described in the TCSPC setup.

**Taking Data**

14. To take data send the APD1 signal to the PicoHarp300 or TimeHarp200 sync or channel-0 port. Send the ADP2 signal through a time-delay then through an inverter/attenuator to the stop or channel-1 port. The attenuator/inverter may not be needed for the PicoHarp300 TDC.

15. If you are using cw laser ensure that the full correlation function symmetric about zero time day will appear in the time window. To do this connect the signal from one APD to both the sync and stop ports on the TDC and run the experiment with a low intensity scattered laser light. This should result in the single peak in the PicoHarp or TimeHarp software.
The fwhm of this peak is also the time responds of that APD. Use the
dealy to shift this peak to a satisfactory spot then reconnect the APDs and
the TDC as explained in 14 above. The peak position corresponds to zero-
time dealy.

16. Now deliver a fluorescence particle to the the pixel coordinate x,y then
send the fluorescence signal to the side port and run the PicoHarp
software. Integrate as long as desirable with the appropriate resolution.
Higher resolution requires more photons low resolution require less
photon but give an approximate modulation depth.

17. Due to blinking and photobleaching (especially for organic molecules) a
single molecule antibunching curve is generally accumulated from more
that one molecule. If the molecular environment is homogenous this
should not affect the data. For robust systems like quantum dots with high
quantum yields, a single dot may be enough to generate a good signal to
noise antibunching curve.

Data Analysis

18. It is not clear if the second-order correlation function can be imported into
symphotime. However the data can be copied straight from the PicoHarp
window into excel or Igor for analysis. This is a single column data of
counts, change the wave scalling in Igor to the resolution at which the data
was taken to reflect the timing correctly (if this is not done the x-axis will
just be a series of natural numbers ie 1,2,3,4…..to the end of the data).
19. This one-column data should be saved as a text file so it can be loaded into Igor or LabView (file: “g²-Binning and FittingProg-V3a”). Perform least-squares-fitting using the equation below by varying N and Γ.

\[ g^{(2)}(\tau) \approx 1 - \frac{1}{N} \exp - |\tau| (\Gamma + W) \]

\[ W = \frac{I \lambda \sigma}{hc} \]

The variables have their usual meaning explained earlier above. The goodness of the fit can be estimated by calculating the residual or \( \chi^2 \) values.
APPENDIX C

TIME RESOLVED POLARIZATION ANISOTROPY OPTICAL SETUP AND DATA ANALYSIS

This technique is very similar to the photon-pair correlation measurement described earlier in this section. The only difference is that the 50/50 non-polarizing beamsplitter is replaced in this case with a polarizing beamsplitter. This configuration separated photons into vertically and horizontally polarized channels or parallel and perpendicular channels depending on the nomenclature used. The time evolution polarization anisotropy on the picosecond resolution can be calculated from the experimentally measured lifetime decay curves from the two orthogonal APDs as shown in the setup below. It allows access to dynamics in the excited state that is otherwise obscure to conventional polarization anisotropy measurements on the second time scale.

![Detection scheme for time-resolved polarization anisotropy](image)

**Figure C.1. Detection scheme for time-resolved polarization anisotropy**

Time resolved polarization anisotropy setup. The red bars represent decay curve from the horizontally polarized channel and the black bars that of the vertically polarized channel.

This experiment requires a router connected to the PicoHarp TDC. For details of the connection cables and requirements refer to the PicoHarp300 manual.
Optical Setup and Optimization

20. The time resolved polarization setup and optimization follows the same procedure, as the antibunching setup the only difference is the replacement of the 50/50 nonpolarizing beamsplitter in the antibunching setup with a polarizing beamsplitter for the time resolved polarization setup.

21. The excitation source needs to be delivered from the top of the microscope without the use of a dichroic mirror. This is done to avoid any polarization artefacts in the data caused by the unequal transmission of “s” and “p” polarizations by the dichroic which introduces an average of about 15% error in the linear dichroism value when combined with the polarizing beamsplitter (refer to my lab notebook #3 pages 83-89). The absence of the dichroic mirror reduces this error to about 2-5%, which is expected from the polarizing beamsplitter that has an unequal transmission for either polarization.

Data Taking

22. Data is taken in T3R mode with the router enabled in PicoHarp300. Make sure that the two decay curves from each APD have the registration of the rising edge to the same time. Any offset (though can be corrected) may affect the quality of the data. Avoid “Ts” in the connection to the PicoHarp300, this introduces a lot of electrical noise (ringing) in the IRF. Make sure an IRF is taken for both APDs. This can be done by using a
depolarizer in the beam path or using a halfwave plate to rotate the polarization of the beam so that there is about an equal contribution to each APD. Note this experiment can be prone to a lot of artefacts that include poorly aligned APDs which will introduce a bias to the data because one APD is seeing a low count rate which may have nothing to do any dynamics in the excited state. For linear molecules like DiIC$_{18}$ with well-defined linearly polarized emission, unequal signal in both APDs is expected. This may be different for beads or colloidal quantum dots or CdSe-OPV. A good knowledge of the fluorescence properties of the sample is required in this sort of experiment.

Data Analysis

23. Extract the decay curves for each APD channel using symphotime or whatever program is appropriate. Use Igor or LabView to calculate the contrast ratio (anisotropy), $M(\tau_i)$ for each data point (or time – ns). $I(\tau_i)$ is the intensity in a particular channel after time some time $\tau_i$.

$$M(\tau_i) = \frac{I_{par}(\tau_i) - I_{per}(\tau_i)}{I_{par}(\tau_i) + I_{per}(\tau_i)}$$

24. A plot of $M(\tau_i)$ versus $\tau_i$ show the evolution of the contrast ratio on time scales on the order of the fluorescence lifetime of the molecule being studied. Note that $\tau_i$ is not the same as the overall excited state lifetime obtained from curve fitting. $M(\tau_i)$ can either be calculated from the raw decay curves or from the fits.
BIBLIOGRAPHY


155321-10.


8999.


(74) Spinicelli, P.; Buil, S.; Quelin, X.; Mahler, B.; Dubertret, B.; Hermier, J.

(75) Nirmal, M.; Norris, D. J.; Kuno, M.; Bawendi, M. G.; Efros, A. L.; Rosen,

(76) Tinnefeld, P.; Herten, D. P.; Sauer, M. J. Phys. Chem. A 2001, 105, 7989-
8003.


(83) Coolen, L.; Brokmann, X.; Spinicelli, P.; Hermier, J. P. *Phys. Rev. Lett.* **2008**, *1*, -. 


(86) Fomenko, V.; Nesbitt, D. J. *Nano Lett.* **2008**, *8*, 287-293. 


(117) Mehta, A.; Kumar, P.; Dadmun, M. D.; Zheng, J.; Dickson, R. M.;

(118) Kumar, P.; Mehta, A.; Dadmun, M. D.; Zheng, J.; Peyser, L.; Bartko, A.
P.; Dickson, R. M.; Thundat, T.; Sumpter, B. G.; Noid, D. W.; Barnes, M.


(121) Furis, M.; Htoon, H.; Petruska, M. A.; Klimov, V. I.; Barrick, T.; Crooker,

**2008**, *77*, -.

(123) Hu, J. T.; Li, L. S.; Yang, W. D.; Manna, L.; Wang, L. W.; Alivisatos, A.


(127) Sudeep, P. K.; Early, K. T.; McCarthy, K. D.; Odoi, M. Y.; Barnes, M. D.;


(144) Brannen, E.; Ferguson, H. I. S. Nature 1956, 178, 481-482.


