Modification of Exciton Energies and Dynamics for Thin Film Optoelectronics

by

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Submitted to the Department of Electrical Engineering and Computer Science in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Electrical Engineering and Computer Science

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

February 2017

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Abstract

Organic and nano-crystal thin film semiconductors have proven to be effective materials for a range of optoelectronic applications including light emitting diodes, visible wavelength lasers, photovoltaics, and sensors. Mediating photons and charges, excitons are responsible for electrical and optical properties in these energetically disordered media. To improve current technology and develop novel applications, a thorough understanding of exciton dynamics is crucial.

This thesis focuses on modifying exciton dynamics in organic and nanocrystal thin films with spectroscopic monitoring for optoelectronic applications. First, we study local dielectric effects in doped organic thin films, which depends on material deposition and molecular density. An external pressure technique is used to modify molecular density, tuning exciton energies and dynamics as explained by solvation theory and exciton energy transfer. We extend this molecular density tuning method, coupled with other measurements, including optical imaging, magnetic field effect, and electric field effect to modify and monitor charge transfer (CT) exciton energy and dynamics. As intermediaries between excitons and free charges in organic photovoltaic donor-acceptor material systems, CT exciton state dynamics is still a subject of much debate. The effect of CT spin states on photocurrent generation is explored, revealing guidelines for material selection and molecule engineering with potential benefits in optimizing molecular density. Further investigation of low-energy CT exciton transport leads to evidence of spatial motion between interfacial states, driven by local energy disorder. These techniques and results directly apply to optimizing OPV devices, but may also be extended to other applications.

This thesis also includes an investigate of ultrafast electric field effect on organic and colloidal quantum dot thin films, largely unexplored in previous works. We observe exciton luminescence and non-perturbative energy tuning of exciton states under
terahertz electromagnetic radiation, developing a potential platform for detectors and cameras for coherent terahertz sensing.

Lastly, we discuss a new fabrication technique to integrate organic thin films into micro-electro-mechanical system microcavity device designs. The demonstrated electrically tunable microcavity structures not only applicable as wavelength-tunable lasers and pressure sensors, but also presents a good example of fabrication flexibility and challenges of employing organic and nano-crystal thin films.

Thesis Supervisor: Vladimir Bulović
Title: Professor of Electrical Engineering
Acknowledgments

"Education is that which remains, if one has forgotten everything he learned in school."

- Albert Einstein

There are many people I need to thank, who have enriched my PhD career and made the last 5 years an enjoyable experience. First, I would like to express my sincere gratitude to my advisor Prof. Vladimir Bulović for his indispensable expertise, guidance, and patience. In truth, he was much more than a research mentor, and I have learned so much from his cheerful and open personality. I would also like to thank Prof. Marc Baldo for his insights and guidance, which were invaluable to research projects and career development. Many thanks to Prof. Dirk Englund as a thesis committee member, providing feedback and comments on this thesis work.

A very special thanks to my colleagues Dan, Parag, Brandt, Eric, Apoorva, and Annie, who contributed time and effort on various collaborative projects. I could not have asked for better partners in crime. We spent much of the time wrapping our minds around tangled concepts and data, trying to make sense of it all.

To work among the many brilliant people of our Organic Nanostructured Electronics Laboratory (ONElab) was a wonderful opportunity. We had an unforgettable time. Many thanks goes to our Optics team, which provided a research support group for those confusing times when experiments inevitably did not proceed as planned. I would like to especially thank Farnaz for being a great friend. The many conversations and humorous stories we shared helped to keep me sane.

I have to thank my family, who has been behind me in every decision I made. Their love, encouragements, and support have been a crucial and undeniable part of my life. Last, but definitely not least, I would like to thank my fiancé Patrick for all his love and support for the past eight and half years (3130 days and counting); I hope we will cherish every day together.
Contents

1 Introduction 17

2 Excitons in Organic and Nanostructured Semiconductors 21
   2.1 Introduction .................................................. 21
   2.2 Exciton States ................................................. 21
   2.3 Radiative and Non-radiative Recombination .................. 23
      2.3.1 Frank-Condon Principle .................................. 25
      2.3.2 Solvation Effect and Stark Perturbation ................. 27
      2.3.3 Exciton Lifetime and Quantum Yield .................... 30
      2.3.4 Intersystem Crossing .................................... 32
   2.4 Exciton Transport ............................................. 34
      2.4.1 Förster resonance Energy Transfer ..................... 35
      2.4.2 Dexter Transfer ........................................... 36
   2.5 Charge Transfer Exciton ...................................... 36

3 Pressure Induced Solid State Solvation Effect 37
   3.1 Overview ..................................................... 37
   3.2 Introduction .................................................. 38
   3.3 Methods ....................................................... 40
      3.3.1 Sample Fabrication ...................................... 40
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3.2 Mechanical Setup</td>
<td>40</td>
</tr>
<tr>
<td>3.3.3 Optical Characterization</td>
<td>41</td>
</tr>
<tr>
<td>3.4 Results and Discussion</td>
<td>42</td>
</tr>
<tr>
<td>3.4.1 Steady State Photoluminescence</td>
<td>42</td>
</tr>
<tr>
<td>3.4.2 Solvation Theory Fitting</td>
<td>45</td>
</tr>
<tr>
<td>3.4.3 Transient Photoluminescence</td>
<td>48</td>
</tr>
<tr>
<td>3.4.4 Spectral Diffusion</td>
<td>50</td>
</tr>
<tr>
<td>3.5 Conclusion</td>
<td>55</td>
</tr>
<tr>
<td>4 Charge Transfer Exciton</td>
<td></td>
</tr>
<tr>
<td>Spin State Dynamics</td>
<td>57</td>
</tr>
<tr>
<td>4.1 Overview</td>
<td>57</td>
</tr>
<tr>
<td>4.2 Introduction</td>
<td>58</td>
</tr>
<tr>
<td>4.3 Charge Transfer Exciton Energy</td>
<td>60</td>
</tr>
<tr>
<td>4.4 Methods</td>
<td>64</td>
</tr>
<tr>
<td>4.4.1 Sample Fabrication</td>
<td>64</td>
</tr>
<tr>
<td>4.4.2 Mechanical and Optical Measurement Setup</td>
<td>64</td>
</tr>
<tr>
<td>4.4.3 Magnetic Field Measurement Setup</td>
<td>65</td>
</tr>
<tr>
<td>4.5 Results and Discussion</td>
<td>66</td>
</tr>
<tr>
<td>4.5.1 Pressure/Density Effect</td>
<td>66</td>
</tr>
<tr>
<td>4.5.2 Magnetic Field Effect</td>
<td>71</td>
</tr>
<tr>
<td>4.5.3 Device Characterization</td>
<td>76</td>
</tr>
<tr>
<td>4.6 Conclusion</td>
<td>77</td>
</tr>
<tr>
<td>5 Charge Transfer State Transport</td>
<td></td>
</tr>
<tr>
<td>5.1 Overview</td>
<td>79</td>
</tr>
<tr>
<td>5.2 Introduction</td>
<td>79</td>
</tr>
<tr>
<td>5.3 Methods</td>
<td>81</td>
</tr>
<tr>
<td>5.3.1 Sample Fabrication</td>
<td>81</td>
</tr>
</tbody>
</table>
5.3.2 Optical Setup for Diffusion Measurement .................................. 82
5.3.3 Magnetic Field Measurement Setup ........................................... 83
5.4 Results and Discussions ............................................................... 83
  5.4.1 Charge Transfer Exciton Diffusion ........................................... 84
  5.4.2 Charge Transfer State Characteristics .................................... 90
  5.4.3 Electric Field Dependence ...................................................... 93
  5.4.4 Monte Carlo Simulation ......................................................... 95
  5.4.5 Magnetic Field Effects .......................................................... 99
5.5 Conclusion ....................................................................................... 103

6 Ultrafast Electric Field Effects on Exciton Dynamics 105
  6.1 Overview ....................................................................................... 105
  6.2 Introduction .................................................................................. 106
  6.3 Methods ....................................................................................... 109
    6.3.1 Optical Setup for Terahertz Generation and Imaging ............... 109
    6.3.2 Sample Fabrication ................................................................. 111
  6.4 Results and Discussion ............................................................... 112
    6.4.1 Terahertz-Driven Luminescence ........................................... 113
    6.4.2 Time-Resolved Luminescence .............................................. 114
    6.4.3 Terahertz-Driven Exciton Generation Mechanisms .................. 116
    6.4.4 Quantum Confined Stark Effect ............................................ 120
    6.4.5 Application to THz Imaging .................................................. 122
  6.5 Conclusion ....................................................................................... 125

7 Electrically Tunable Organic
  Micro-Electro-Mechanical System Microcavities 127
  7.1 Overview ....................................................................................... 127
  7.2 Introduction .................................................................................. 128
7.3 Methods ................................................................. 130
  7.3.1 Device Fabrication .............................................. 130
  7.3.2 Optical Interferometry and Emission Spectrum Setup .... 133
7.4 Results and Discussion ............................................. 134
  7.4.1 Interferometry Measurement of Membrane Motion ........ 134
  7.4.2 Shift in Microcavity Emission ............................... 136
  7.4.3 Lasing Operation .............................................. 137
  7.4.4 Application to Pressure Sensing ............................ 140
7.5 Conclusion ............................................................. 142

8 Conclusion and Outlook .............................................. 143
  8.1 Conclusion .......................................................... 143
  8.2 Outlook ............................................................. 143

9 Appendices ............................................................. 147
  9.1 Appendix A: Photolithography Procedures .................... 147
    9.1.1 Negative Resist ............................................. 147
    9.1.2 Positive Resist ............................................. 147
  9.2 Appendix B: A Study of Förster Resonance
    Energy Transfer for Ion Nanosensors .......................... 149
List of Figures

1-1  PL of QDs and organics, exhibiting flexible synthesis and deposition for exciton energy tuning. ........................................... 18

2-1  Energy schematic of Frenkel and CT state excitons. ....................... 22
2-2  Spin states of Frenkel excitons. ............................................. 23
2-3  Spectra comparing fluorescence and phosphorescence of organic molecules. 24
2-4  Schematic of energy diagram illustrating Frank Condon shift. ............. 25
2-5  Mirror relationship in absorption and emission of organic molecules. . 26
2-6  Localized field effect due to molecular dipole-dipole interactions. ....... 27
2-7  Stark perturbation on ground and excited state showing solvation effect on exciton energy. ............................................. 28
2-8  Change in peak PL wavelength for DCM molecules dissolved in select solvents. ....................................................... 29
2-9  Schematic of simple exciton recombination rates. .......................... 30
2-10 Schematic of exciton spin states. ............................................. 32
2-11 Schematic of exciton transport. ............................................. 34

3-1  Organic host and dopant molecular structures and schematic of solvation effect on exciton energy. ............................................. 39
3-2  Schematic of experimental setup for in situ optical measurement of organic thin film samples under mechanical pressure. ............. 41
3-3 Schematic of experimental setup with simplified illustration of optical components. .......................................................... 42
3-4 Steady state PL of organic thin films showing SSSE. ......................... 43
3-5 Intensity plot of PL wavelength shift under pressure. ......................... 44
3-6 Theoretical modeling of SSSE. ................................................................. 46
3-7 SSSE theory fit to PL shift in organic thin film samples. ..................... 48
3-8 Streak camera data of PS:DCM2 PL under external pressure................. 49
3-9 PS:DCM2 TRPL under external pressure. ................................................. 50
3-10 PS:DCM2 spectral diffusion under external pressure. ....................... 51
3-11 PS:DCM2 spectral diffusion for various doping concentrations. ......... 51
3-12 FRET transfer models for organic doped thin films. ......................... 52
3-13 Comparison of spectral shift rate dependence on dopant molecular spacing. 54

4-1 Chemical structures of m-MTDATA, t-Bu-PBD, and 3TPYMB. ........ 60
4-2 Crucial energy levels and rates of CT states in donor-acceptor systems. 61
4-3 Fluorescence spectra of neat films of t-Bu-PBD, m-MTDATA, and 1:1 molar m-MTDATA:t-Bu-PBD. ................................. 62
4-4 Quenching of FIrpic dopant emission by t-Bu-PBD host molecules. .... 63
4-5 Diagram of magnetic field effect setup. ................................................. 65
4-6 CT exciplex PL redshifts under pressure. ........................................... 66
4-7 CT exciplex TRPL showing prompt and delayed components. ........... 67
4-8 TRPL of m-MTDATA:t-Bu-PBD under external pressure ................... 68
4-9 Comparison of CT exciplex prompt emission under external pressure. 69
4-10 Comparison of CT exciplex delayed emission under external pressure. 70
4-11 Schematic summary of density effects on CT exciton spin states and dominating changes in rates for both singlet and triplet CT states. 71
4-12 Energy schematic of singlet-triplet energy splitting as a function of electron-hole spacing. ........................................... 72
4-13 Magnetic field effect on CT exciplex PL and photocurrent. ............ 73
4-14 Magnetic field effect on TRPL for m-MTDATA:3TPYMB. .......... 74
4-15 Magnetic field effect on TRPL for m-MTDATA:t-Bu-PBD. .......... 76
4-16 Effect of lower energy LE triplet drain on overall OPV performance. . 77

5-1 Diagram of relevant CT dynamics and energies. ......................... 81
5-2 Diagram of optical diffusion imaging setup. .......................... 83
5-3 Comparison between photo-excitation and photocurrent excitation spectrum. ................................................................. 84
5-4 Fourier transform analysis of diffusion imaging. ...................... 87
5-5 Example of Gaussian fitting of broadening function in the frequency domain. ................................................................. 88
5-6 Change in standard deviation of the spatial broadening Gaussian function showing CT diffusion. ................................. 89
5-7 CT diffusion comparison with 1% doped CBP:Ir(ppy)₃. .............. 90
5-8 Normalized CT state TRPL for select excitation powers. .......... 91
5-9 Spectrally resolved streak camera measurement of CT state emission. . 92
5-10 CT steady state PL under electric field. .............................. 93
5-11 CT TRPL under electric field and Poole-Frenkel fitting to PL quenching. 94
5-12 Kinetic Monte Carlo simulation of CT state transport. ............... 97
5-13 Simulation of CT diffusion. ............................................. 98
5-14 Temperature dependence of the magnetic field modulation of CT state
PL. ............................................................................... 100
5-15 Magnetic field effects on CT state PL at open and closed circuit. ... 101
5-16 Magnetic field effects on CT exciplex PL at closed circuit on select doping ratios. ............................................................. 102
5-17 Maximum percent change in PL under magnetic field for various molar ratio of donor-acceptor blended thin film devices. .............. 102

6-1 AC electric field-driven luminescence of QDs. ......................... 107
6-2 THz spectral imaging of illicit drugs and compounds. ................ 108
6-3 Optical setup for THz generation and THz pump - optical probe measurements.
6-4 Typical characteristics of generated THz pulse.
6-5 FESs used in THz excitation of excitonic semiconductors.
6-6 Transmission electron microscope images of CdSe/CdS QDs for THz luminescence.
6-7 Energy band and typical absorption and emission of CdSe/CdS.
6-8 Images of THz-L in CdSe:CdS QD thin film.
6-10 Comparison of time-resolved THz-L and PL for QD samples.
6-11 Comparison of time-resolved THz-L at different THz pump peak field strength.
6-12 Schematic of standard samples: bare and oxide-coated microslit samples.
6-13 Field strength dependence of THz-L in CdSe:CdS QD thin films.
6-14 Schematic of charge injection from Au electrode into QDs under an ultrafast field.
6-15 Schematic of electric field-driven tunneling in QDs.
6-16 Schematic of THz driven QCSE.
6-17 THz-driven QCSE observed through exciton generation using sub-bandgap photon excitations.
6-18 Schematic of electrically assisted detection design using interdigitates microslit FES.
6-19 SEM images of electromigration of Au in microlit samples.
6-20 Schematic of optically assisted detection system with optical filtering and visible detector.

7-1 Inorganic MEMS microcavity device.
7-2 Image of free standing parylene membrane.
7-3 Schematic of MEMS microcavity fabrication process.
7-4 Schematic of organic MEMS VCSEL. ........................................... 132
7-5 Optical setup and comparison of Alq3:DCM thin film PL spectra demonstrating cavity modes. ......................................................... 133
7-6 Interferometry imaging of composite membrane deflection under electrostatic biasing. .............................................................. 135
7-7 Schematic illustrating a microcavity mode and measured interferometry deflection profile. ............................................................... 135
7-8 Cavity mode emission wavelength shift under electrostatic biasing. ... 136
7-9 Microcavity lasing operation threshold. ........................................... 138
7-10 Lasing mode emission wavelength shift under electrostatic biasing. ... 139
7-11 Longitudinal mode competition under bias demonstrating lasing mode hopping. ................................................................. 139
7-12 Effective electrostatic pressure across membrane compared to change in cavity emission peak wavelength. ................................. 141
9-1 Absorption of pH indicator compared to QD emission spectra. ......... 149
9-2 FRET-based optical sensing of potassium ions. ................................ 150
9-3 Simple streak camera setup and schematic of exciton dynamics in nanosensor. ................................................................................. 151
9-4 TRPL of QD-only system. ................................................................. 152
9-5 TRPL of various nanosensor components. ....................................... 153
9-6 FRET efficiency as a function of donor-acceptor spacing for each QD. 155
1 | Introduction

Well over a decade since the development of the quantum theory of radiation and the photoelectric effect by the likes of Planck and Einstein, the resulting field of optoelectronics has transformed our everyday lives. Ubiquitous application of optoelectronic devices is deeply integrated into the modern world: light-emitting diodes for lighting and displays, detectors for imaging and sensing, and solar cells as renewable solutions for the increasing energy demand, just to name a few. In general terms, optoelectronics are based on semiconductor materials, mediating interactions between electronics and optical radiation. However, traditional semiconductors based on inorganic crystalline structures often depends on expensive and difficult growth techniques, such as molecular beam epitaxy or Czochralski crystal growth.

A promising class of semiconductors based on energetically disordered materials has been developed and implemented over the last 30 years, expanding optically active semiconductors to a large library of organic molecules, polymers, and nano-crystals. Remarkable electrical and optical properties of these materials, including charge localization, luminescence efficiency, color saturation, and wavelength tunability, can be exploited for a wide range of applications. In addition, chemistry based synthesis methods enables simple, large area deposition techniques, such as thermal evaporation and solution processing, applicable on virtually any substrate (ex: non-flat, functionalized, flexible, transparent, light weight, etc.). Advancement in optoelectronics based on the emerging class of semiconductors include light emitting diodes [1–4], thin film photovoltaics [5,6], lasers [7,8], photodetectors [9,10], sensors [11–13], and many more.
Beyond research and development, initial market infiltration has met with much success; for example, market share projections for organic-light emitting diodes (OLEDs) alone approach $2 billion in 2016 with significant growth potentials within the next decade [14].

Supporting these technological development is a clear understanding of the fundamental properties of organic molecules and nano-crystals, such as colloidal quantum dots (QDs).

Figure 1-1: Photoluminescence of QD solutions and organic thin films exhibiting flexible synthesis and deposition technique for exciton energy tuning. (left) Solutions of colloidal QDs of varying size and composition under ultraviolet excitation, demonstrating QD size-dependence capable of spanning the visible spectrum [15]. (right) Chromaticity coordinates of host:dopant OLED emission based on 3 organic molecules in solid state thin films, demonstrating doping-dependence [16].

Due to their disordered energetic nature, these semiconductors have intriguing properties, including charge localization, leading to exciton formation. As a quasi-particle formed by a bound pair of electron and hole (electon vacancy), an exciton can be generated by high energy photons or free charges [17]. Unlike excitons in inorganic crystals, which quickly dissociates into free charges due to high dielectric screening and periodic energy landscape, in energetically disordered materials, they are localized on molecular or QD sites with much longer lifetime. Thus, excitons in organic and
nano-crystal semiconductors are exceptional mediators between electricity and light. To improve the current technology, techniques in modifying exciton state energy and dynamics are crucial for better understanding of exciton interactions. Because solid state molecular and QD thin films are dominated by van der Waals interactions, the dielectric environment can play a large role in modulating exciton energy and dynamics. Developed methods of exciton energy tuning include exciton confinement tuning using molecular or QD dimensions and changing the local dielectric through material selection and/or doping.

Under optical and electric monitoring, much can be learned by using external perturbations on exciton states, such as change in pressure, temperature, magnetic field, and electric field. In organic photovoltaics, charge transfer excitons across molecular interfaces are crucial in determining overall device properties. Thus, changes in exciton characteristics such as lifetime, spin states, charge dissociation, and transport under perturbative forces can provide key insights into device optimization. Beyond improving current technologies, we can exploit exciton properties for developing novel applications. For example, fundamental understanding of electric field modulation of excitons can enable applications in sensing and imaging of terahertz frequency electromagnetic radiation.

This thesis will present recent works and insights on exciton physics as applicable to optoelectronic devices. By no means a comprehensive study of excitonics, the thesis is divided into eight main chapters. Chapter two will provide a general theoretical background on exciton states and dynamics in energetically disordered materials, applicable to both organic and QD semiconductors. Chapter three will present detailed experiments in understanding density-dependent local dielectric effects in organic thin films. External pressure is used to modulate exciton state energy and energy transfer, as a general materials study. Chapter four considers application of external probing techniques, such as pressure and magnetic field, on charge transfer (CT) excitons in blended heterojunction donor-acceptor organic thin films. Spin-dependence of photoluminescence and photocurrent generation are presented, specifically from an organic...
photovoltaic perspective. Chapter five will employ an optical imaging technique and magnetic field effects to reveal a previously unexplored CT excitons transport mechanism.

Chapter six will focus on the effect of electric field on exciton dynamics, reflected in both exciton generation and Stark perturbation. The experimental and theoretical findings can be extended to new applications of organic and QD for THz radiation detection. Chapter seven will present an example of a fabrication challenge inherent in organic and nanocrystal based devices. A composite membrane transfer printing technique is developed to circumvent device patterning difficulties and demonstrate an organic vertical-cavity surface-emitting laser. Chapter eight includes a summary and concluding remarks.
2 | Excitons in Organic and Nanostructured Semiconductors

2.1 Introduction

To lay the theoretical groundworks for this thesis, this chapter presents basic general physics of excitons, including energetics, generation, lifetime, and transport. Although not a comprehensive study, the discussion will focus on the fundamental concepts and experimental measurement techniques relevant to the organic and quantum dot (QD) semiconductor topics presented in the following chapters. Additional theory work and detailed measurement setups will be presented in the corresponding chapter as needed.

2.2 Exciton States

Formed by pairs of bound electron and hole, excitons are quasi-particles with corresponding sets of quantum energy levels. In organic semiconductors with low dielectric and van der Waals binding between molecules in solid state, charge screening is much lower than in traditional inorganic crystalline semiconductors. This allows stronger Coulomb interactions between charge carriers (~200 meV), forming stable excitons at room temperature. Therefore, optical and electronic properties of these materials are strongly dependent on exciton interactions and dynamics. Much like inorganic semiconductors with conduction and valence bands, organic molecules have electronic
transition between the highest occupied molecular orbital (HOMO) and lowest unoc-
cupied molecular orbital (LUMO), as shown in Fig. 2-1.

Figure 2-1: Energy schematic of (a) Frenkel, or localized exciton and (b) charge transfer
state excitons.

To understand transitions between these energy levels, we focus on the outer most
valence electrons in molecular orbitals, using the helium atom as an analogy. By the
Pauli exclusion principle, the wave function description of the two valence electrons \( \Psi \)
must be antisymmetric under particle exchange. The wave function of the two particles
can be separated it into space-dependent \( \psi \) and spin-dependent \( \chi \) components:

\[
\Psi_n(\vec{r}_1, \vec{r}_2, S, m_s) = \psi(\vec{r}_1, \vec{r}_2)\chi(S, m_s)
\]  

(2.1)

with position vectors \( r_1 \) and \( r_2 \) and projected spin \( m_s \). This excitonic system can be
characterized by total spin \( S \) indicating antisymmetric or symmetric spin eigenstates,
known respectively as singlet \( \chi(S = 0, m_s = 0) \) and triplet \( \chi(S = 1, m_s = 0, \pm 1) \) states.

\[
\chi(0,0) = \frac{1}{\sqrt{2}}[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle]
\]  

(2.2)

\[
\chi(1,0) = \frac{1}{\sqrt{2}}[|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle]
\]  

(2.3)

\[
\chi(1,1) = |\uparrow\uparrow\rangle
\]  

(2.4)

\[
\chi(1,-1) = |\downarrow\downarrow\rangle
\]  

(2.5)
A typical molecule has full valence electrons, thus the exciton ground state $S_0$ is usually a singlet state. Similar to a helium atom, the lowest energy excited states includes both singlet $S_1$ and triplet $T_1$ states (Fig. 2-2). Since the space-dependent wave function of triplet exciton is antisymmetric under exchange, it will have less Coulomb repulsion force between the electrons. Thus, the excited triplet is typically lower in energy compared to the excited singlet state, resulting in characteristic energy splitting found in molecular semiconductors with highly bound exciton states. In comparison, excitons in QD semiconductors are much less confined, with diameters over 10 - 100 times that of small molecules. Based on higher dielectric materials, QDs fall in the regime between the atomic and bulk semiconductor models, with spatially confined excitons of mixed spin producing states of singlet-like and triplet-like characteristics. Exciton energy in QDs is often calculated based on confinement perturbations of the valence and conduction band models.

![Figure 2-2: Spin eigenstates of a Frenkel exciton with $S = 0$ singlet and $S = 1$ triplet states.](image)

**2.3 Radiative and Non-radiative Recombination**

To a first order approximation, the spatial electronic distribution of an exciton on a molecule can be modeled as an electromagnetic dipole. Optical processes, such as absorption and emission, depend on the electric transition dipole moment between the
initial and final states:

\[ \mu = \langle \Psi_{gs} | \vec{r} \rangle \langle \Psi_{ex} \rangle = \langle \Psi_{gs} | \vec{r} \rangle \langle \Psi_{ex} \rangle \psi_{gs} \chi_{ex} \]  

(2.6)

Since singlet and triplet spin states (Eq. 2.2-2.5) are orthonormal functions, the total spin must remain the same \( S_{gs} = S_{ex} \) for non-zero transition dipole moment between ground and excited state. In other words, optical transition between singlet and triplet states are spin forbidden without perturbations in the molecule. Thus, exciton emission is dominated by fluorescence from singlet excited state \( \Psi_{ex} = S_1 \) to ground state \( \Psi_{gs} = S_0 \), with relatively low probability of lower energy emission from the triplet state \( T_1 \) as phosphorescence (Fig. 2-3). Singlet and triplet exciton energies of molecules can be estimated by measuring the emission wavelength of fluorescence and phosphorescence. Excitons can also recombine to ground state via non-radiative recombination, dominated by phonon coupling and converted into thermal energy. Without charge injection or extraction from the system, the total charge is conserved; additional processes of exciton dissociation into and recombination from free charges are balanced.

Figure 2-3: (a) Fluorescence and (b) phosphorescence of N,N'-di(naphtha-1-yl)-N,N'-diphenyl-benzidine (NPB) in poly(methyl methacrylate) (PMMA). (c) Spectra comparing fluorescence \( S_1 \) and phosphorescence \( T_1 \) in select organic molecules listed from top to bottom: tris(4-carbazoyl-9-ylphenyl)amine; 4,4'-bis(carbazol-9-yl)biphenyl; N,N'-bis(4-benzoyl-phenyl)-N,N'-diphenyl- benzidine; and NPB. [18]
While excitons can be generated by optical excitation of above-bandgap-energy photons to produce photoluminescence (PL), they can also be generated by injected charge carriers to produce electroluminescence (EL). In the latter case, charge injection rates and exciton generation rates may also need to be considered in the dynamics model. Note that while optical absorption is restricted to creating singlet excited states, free charges in the system will randomly form exciton states with near equal probability to be in any of the 4 spin states; in other words, 25% singlets and 75% triplets [19].

2.3.1 Frank-Condon Principle

Figure 2-4: Energy schematic of electronic ground state $S_0$ and excited states $S_1$ with corresponding vibrational energy levels (dashed lines). Upon photon absorption (blue arrow), an excited exciton is formed (shown here as a transition between $S_0, n_v = 0$ and $S_1, n_v = 4$). This exciton quickly relaxes in vibrational energy before emission (red arrow), causing a Stokes shift in energy between absorption and emission.

Although we have established that absorption and emission of molecules is dominated by electronic transition between the singlet ground and excited states, we still need to
consider the effects of nuclear vibration and rotation on exciton energy. In typical semiconductors, the electronic transition energy is $\sim 1 \text{ eV}$, and vibrational transition energy is $\sim 0.1 \text{ eV}$. We can model the vibrational states for the molecule as an anharmonic oscillator, with distinct energy levels $n_v$ (Fig. 2-4). Transition between these vibrational states within the same electronic state does not change orbital angular momentum, thus they are non-radiating and are much slower than radiative electronic transitions. The offset in the two electronic states in nuclear coordinates reflect perturbation of the excited electron on the molecule’s nuclear geometry.

Upon photon absorption, a molecule is instantaneously excited from the low energy $S_0$ state to a $S_1$ state with high vibrational energy. The exciton then quickly relaxes non-radiatively to a lower vibration energy level in $S_1$. After a characteristic exciton lifetime, the molecule emits a red-shifted photon by relaxing down to an $S_0$ state, which can have non-zero vibrational energy.

![Figure 2-5: Absorption and emission spectral of anthracene in cyclohexane showing vibrational energy features with mirror-image relations. [20]](image)

This is known as the Frank-Condon principle, which produces a characteristic Stoke shift between absorption and emission. For typical organic molecules and QDs, this shift is comparable to the emission linewidth. These vibrational states can be observed
in some molecular dyes in solvents as distinct absorption and emission features with a mirror-image relationship (Fig. 2-5).

### 2.3.2 Solvation Effect and Stark Perturbation

In addition to nuclear reorganization upon absorption and emission, the local environment surrounding a molecule can have a large effect on its energy levels, known as the solvation effect. Consider an exciton on guest solute molecule in a host solvent material (may be the same as the guest molecule), we can approximate each molecule as a dipole. The dipole-dipole interactions between neighboring molecules can cause nuclear and electronic reorientation and reorganization in response to a local reaction field depending on the dielectric environment (Fig. 2-6).

![Local field effect due to molecular dipole-dipole interactions between guest molecule and host molecules.](image)

Figure 2-6: Localized field effect due to molecular dipole-dipole interactions between guest molecule and host molecules.

The Onsager dielectric continuum model considers this system as interactions between solute dipoles with a continuum of surrounding solvent dielectric media [21]. In the simplest form, it assumes that the solute electronic densities are reduced to dipoles and are only affected by neighboring molecules within a certain constant radius $a$ as described by a spherical cavity. This is an implicit approximation of the solvent environment. There are many alternative models in capturing a more accurate system using explicit methods or variations on cavities and solute modeling, making model
selection nontrivial [22].

Figure 2-7: Stark perturbation on ground and excited state illustrating bathochromic and hypsochromic shifts in transition energy due to increase in dielectric response.

In this case, a spherical cavity model will simplify much of the computation while still providing a reasonable representation of the energy shifts. To calculate the change in transition energy, we consider the dipole moments of the solute and the reaction field created by the Frank-Condon effect upon absorption. This reaction field $E_{reaction}$ is dependent on the polarizability of the solvent and the corresponding solute static dipole moment for the ground and excited states. A Stark perturbation on the energy levels, both ground and excited states, can be approximated by $\Delta E = -\mu \cdot \vec{E}_{reaction}$. Since the strength of the local field is dependent on the polarizability and of the host materials, increase in the solvent polarizability would magnify the change in transition energy. Because this effect is dependent on the dipole moment of the guest solute molecule in the ground and excited states, the change in transition energy may be a bathochromic (red) shift or a hypsochromic (blue) shift.

For typical dyes such as 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM), the transition dipole is aligned such that as solvent dielectric increases, a bathochromic shift in transition energy is observed, termed positive solvatochromism. There are molecules such as the merocyanine dyes, which would exhibit
the negative solvatochromism effect where a hypsochromic shift is observed for increasing solvent dielectric [23]. Considering all the factors, the change in the transition energy as measured by emission according to Ooshika-Lippert-Mataga (OLM) solvation theory is expressed as [24-27]:

$$\Delta E_{PL} = -\frac{\Delta \vec{\mu}}{a^3} \cdot \left( \Lambda(\epsilon) \vec{\mu}_e + \Lambda(n^2) \vec{\mu}_g \right)$$

(2.7)

$$\Lambda(\epsilon) = \frac{2(\epsilon - 1)}{2\epsilon + 1}$$

(2.8)

for a molecule with respective excited and ground state dipoles of $\vec{\mu}_e$ and $\vec{\mu}_g$ in a spherical cavity of radius $a$ with transition dipole of $\Delta \vec{\mu}$. The solvent polarizability manifests in two different capacities: the nuclear reorientation $\Lambda(\epsilon)$ and the electron reorientation $\Lambda(n^2)$. Note that this transition energy was calculated for molecular emission, and the Franck-Condon shift in energy due to molecular orientation is taken into account. A similar expression could be derived for the absorption. An example of liquid state solvation effect is shown in Fig. 2-8, where emission of DCM molecules dissolved in select solvents are measured using a simple spectrometer setup. Table 2.1 lists the DCM emission peak emission wavelengths, which increases for increasing solvent dielectric, exhibiting the expected bathochromic shift in energy.

![Figure 2-8: Shift in PL for DCM molecules dissolved in select solvents. The peak emission changes due to different solvent dielectric constants](image-url)
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric Constant</th>
<th>DCM Peak Emission (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>2.38</td>
<td>560</td>
</tr>
<tr>
<td>Chloroform</td>
<td>4.81</td>
<td>576</td>
</tr>
<tr>
<td>Methanol</td>
<td>32.70</td>
<td>623</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>46.68</td>
<td>646</td>
</tr>
</tbody>
</table>

Table 2.1: Peak emission wavelengths of DCM solutions with corresponding solvent dielectric constant

Note that Stark perturbation is due to electric field in general and not limited to local reaction fields. Often, Stark shifts are observed with externally applied electric field. For an example, device EL is usually redshifted in energy compared to PL due to the external field needed for exciton generation.

2.3.3 Exciton Lifetime and Quantum Yield

In addition to absorption and emission energies, a fundamental exciton characteristic is its excited states lifetime. After initial exciton generation, there are many potential recombination pathways, radiative and non-radiative. Each has an associated probability, which we can represent as a rate of occurrence, $k$.

![Figure 2-9: Schematic of simple exciton recombination rates.](image)

Applications based on exciton emission such as LEDs often necessitate a certain fluorescence efficiency, or fraction of excitons undergoing radiative recombination. This
efficiency is characterized by the exciton fluorescence quantum yield (QY), which can be measured using an integration sphere system as discussed in detail by de Mello [28].

\[
QY = \frac{\# \text{ photon emitted}}{\# \text{ photon absorbed}} = \frac{k_r}{k_r + \sum k_{nr}} \tag{2.9}
\]

In the case of zero net charge flow out of the system, we can express excited state population \( I(t) \) as a simple rate equation to solve, where \( I_0 \) is the photo-generated exciton population at \( t = 0 \):

\[
\frac{dI(t)}{dt} = k_r I(t) - \sum k_{nr} I(t) \tag{2.10}
\]

\[
I(t) = I_0 e^{-\left(k_r + \sum k_{nr}\right)t} = I_0 e^{-\frac{t}{\tau_{ex}}} \tag{2.11}
\]

The exciton lifetime can be represented as an inverse of the sum of all the recombination rates \( \tau_{ex} = \frac{1}{k_r + \sum k_{nr}} \). This can be observed in an ensemble measurement using a variety of time-resolved optical detection including streak camera and time correlated single-photon counting avalanche photodiode (APD). The fluorescence intensity can be plotted as a function of time and fitted to an exponential decay. This simple solution assumes the same energy levels and recombination rates for all excitons, which needs further modification depending on the states involved and energy disorder in the system. For example, due to the spin state mixing, exciton emission of a single QD is well modeled by a mono-exponential function. However, differences in non-radiative rates among an ensemble of QDs (ex: neutral vs. charged QDs, variation in ligand passivation) can produce a multi-exponential decay characteristic in exciton emission [29]. In other words, in ensemble measurements, homogenous broadening of exciton lifetime can cause deviations from the mono-exponential model.
2.3.4 Intersystem Crossing

Time-resolved measurements of exciton emission in organic molecules are often dominated by a bi-exponential function, which reflects the interactions between spin states. As discussed, excited state exciton can be categorized by its spin characteristic, with high probability of radiative transition from the singlet. Transition from singlet to triplet states and vice versa is known respectively as intersystem crossing (ISC) and reverse intersystem crossing (RISC).

This adds a layer of complexity to our system diagram, and the dynamics can be modelled by coupled first order differential equations:

\[
\frac{dS_1(t)}{dt} = -(k_r(t) + k_{snr} + k_{ISC})S_1(t) + k_{RISC}T_1 \tag{2.12}
\]

\[
\frac{dT_1(t)}{dt} = -(k_{ph}(t) + k_{tnr} + k_{RISC})T_1(t) + k_{ISC}S_1 \tag{2.13}
\]

We know the general analytical solutions take the form of

\[
S_1(t) = A_1e^{-k_1t} + A_2e^{-k_2t} \tag{2.14}
\]

\[
T_1(t) = B_1e^{-k_1t} + B_2e^{-k_2t} \tag{2.15}
\]

Notice that singlet population is now modeled by a bi-exponential function, as experimentally observed. We define the two components as prompt and delayed fluorescence with respective rates \(k_1\) and \(k_2\). In most cases, non-radiative, intersystem crossing,
and phosphorescence rates are much slower compared to the radiative fluorescence rate from the singlet state. Making these assumptions, we can approximate complicated rate factors to much simpler forms: \( k_1 \approx k_v + k_{snr} \) and \( k_2 \approx \frac{1}{2}(k_{ISC} + k_{RISC} + k_{ph} + k_{tnr}) \). We can still see that the prompt component can be approximated by the singlet exciton lifetime from the simpler model, and will be applied in systems without significant intersystem crossing.\(^1\)

The mechanism behind spin mixing is strongly dependent on the local magnetic field perturbations, with two major contributors: spin orbit coupling (SOC) and hyperfine interactions.

**Spin Orbit Coupling**

From the perspective of electrons in orbit, the nucleus produces an induced local magnetic field, which depends on the electron orbital angular momentum, \( L \). This induced magnetic field perturbs the spin magnetic dipole of the electron, resulting in fine structures in the molecular energy levels on the order of 50 meV. The total spin of the electron \( S \) is coupled to its angular momentum \( L \). This allows spin mixing in the exciton state; triplet excitons gain slight singlet characteristic, allowing direct emission from the triplet state known as phosphorescence. In general, the rate of fluorescence \( k_v \) occurs on the order of \(~ 1 \text{ ns}^{-1}\), while phosphorescence \( k_{ph} \) is much slower, on the order of \(~ 1 \text{ us}^{-1} - 1 \text{ s}^{-1}\). This triplet emission is often observed in heavy metal SOC. Phosphorescence has been employed in a variety of applications. To increase overall device efficiency, phosphorescent OLEDs (PhOLEDs) exploit the \(~ 75\% \) dark triplet states formed upon charge injection [19,30].

**Hyperfine Interactions**

External magnetic fields can also perturb the energy levels of exciton spin states. Unlike SOC, the applied magnetic field defines a projection axis for the spin states. Thus,\(^1\)

---

\(^1\)As expected, if we take the general solutions and set \( k_{ISC}, k_{RISC} = 0 \), with the right initial conditions, we get our previous mono-exponential expression for \( S_1 \) from the simpler model.
the perturbation depends on $m_s$ instead of total spin $S$. This produces hyperfine splitting between the $T_1$ triplet states, on the order of 50 $\mu$eV. Although this is much smaller compared to SOC, it provides an experimental parameter to tune the ISC and RISC rates in material systems with small energy splitting between singlet and triplet states [31, 32].

### 2.4 Exciton Transport

Thus far, we have considered the energy levels and time response of an isolated exciton state. However, in an ensemble of molecules or nanocrystals, excitons can spatially diffuse to lower energy molecular sites (may be the same or different molecular species). The transport of an exciton between an excited state donor and ground state acceptor molecule can be described by two main mechanisms: dipole-dipole near field interaction known as Förster resonance energy transfer (FRET) [33] and charge exchange process known as Dexter transfer [34].

Figure 2-11: Schematic of exciton transport: (a) singlet exciton transport dominated by Förster resonance energy transfer and (b) triplet exciton transport dominated by Dexter transfer.
In FRET the donor exciton relaxes to ground state and the energy is transferred to the acceptor by a virtual photon; no charge transfer occurs. Since triplet states have weak transition dipole and are non-emissive, FRET is dominated by singlet excitons. In comparison, Dexter transfer is the direct and simultaneous exchange of electrons in the LUMO and HOMO between the donor and acceptor. Thus, triplet exciton transfer is Dexter dominated (Fig. 2-11).

2.4.1 Förster resonance Energy Transfer

Derived from Fermi’s Gold Rule with a dipole-dipole perturbation, the FRET rate between donor and acceptor molecules can be expressed in the form of [33]

\[ k_F = \frac{1}{\tau_D} \left( \frac{R_F}{r_{DA}} \right)^6 \] (2.16)

which depends on isolated donor exciton lifetime \( \tau_D \), center-of-mass separation between the donor and acceptor \( r_{DA} \), and FRET radius \( R_F \), defined as

\[ R_F^6 = \frac{9\kappa^2 \Phi_D}{128\pi^5 n^4} J \] (2.17)

where \( \kappa \) is the relative molecular orientation factor between the donor and acceptor dipoles, \( \Phi_D \) is the donor QY, \( n \) is the index of refraction of surrounding medium, and \( J \) is the overlap integral between normalized donor emission \( f_D \) and acceptor absorptivity \( \epsilon_A \).²

\[ J = \int f_D(\lambda)\epsilon_A(\lambda)\lambda^4 d\lambda \] (2.18)

\[ \epsilon_A(\lambda) = \frac{1}{N_A} \frac{-\ln(1 - \text{Absorption}(\lambda))}{(\text{optical pathlength})(\text{concentration})} \] (2.19)

Because FRET is based on dipole-dipole interactions, the rate scales with donor-acceptor distance as \( r_{DA}^{-6} \). Efficient FRET occurs when \( r_{DA} \) is comparable to the FRET

²Note that for experimental calculations, molar absorptivity obtained from Beer-Lambert law should be scaled by Avogadro’s number \( N_A \).
radius $R_F$, which in typical organic and QD thin films is on the scale of $\sim 2 - 10$ nm. (For examples of FRET analysis, see Appendix B.)

### 2.4.2 Dexter Transfer

In the case of Dexter transfer, the coupling is dependent on the donor and acceptor spatial wave function overlap. The Dexter rate scales with donor-acceptor distance as $\exp(-\zeta r_{DA})$, and is not dependent on transition dipole moments or exciton lifetime [34]. The typical interaction distance is less than 1 nm. Consequently, exciton transport rate is often dominated by FRET between singlet excitons due to high dipole oscillator strength. However, it is possible for the slower, but longer-lived triplet states to diffuse farther.

### 2.5 Charge Transfer Exciton

The discussion in this chapter has focused mainly on Frenkel excitons, which are localized to a single molecular site. However, excitons can be in various states of delocalization. A notable case is the charge transfer (CT) exciton, which is an exciton at an acceptor-donor interface with the electron and hole wave functions localized on different molecules (Fig. 2-1). CT exciton is an important intermediary step between excitons and free charges in optoelectronic applications with interfaces of different molecules or materials. The same considerations for Frenkel, or localized excitons (LE), applies to CT states. However, the absorption and emission cross section of CT excitons are much lower in comparison to LE due to reduced charge density overlap; this is also reflected in low FRET rates. With decreased interactions between electron and hole, CT excitons have lower binding energies and smaller energy splitting between the spin states, making them more susceptible to molecular density, morphology, and magnetic field effects. However, typical CT binding energy is still larger than thermal fluctuations, allowing CT excitons to be stable in heterostructured organic and QD thin films.
3 | Pressure Induced
Solid State Solvation Effect

3.1 Overview

The solvent dielectric effect in solid state thin films is a demonstrated method for exciton energy modification. It provides a fabrication parameter for tuning exciton energy of a guest dopant by changing the host material(s) or varying doping concentration. In this chapter, we will conduct an in-depth study in the solid state solvation effect (SSSE) by considering, instead, the molecular density perturbation on the local dielectric environment. We will use solvation theory previously developed to model liquid state solvation effects and doping variation SSSE to find good agreement with our observed density dependent SSSE. A comparison between density variation and doping variation techniques finds external pressure to be a reliable and reversible method of dynamically tuning exciton energy in solid state thin films, without complications such as molecular aggregation. These findings not only give insights into molecular interactions in organic thin films, but also provides a technique to study mechanical properties, exciton disorder, and dynamics in amorphous molecular and colloidal quantum dot (QD) thin films.
3.2 Introduction

Interactions between molecules or QDs at the nanoscale ultimately governs the characteristics of organic and QD-based optoelectronic devices. Modulating these molecular interactions can give crucial insights into exciton dynamics. The ability to probe and manipulate exciton energy through molecular interactions can enable improvements in device performance and operation. Due to desirable properties such as high quantum yield efficiency, fabrication flexibility, and energy tunability, host:dopant molecular thin films are often employed in many applications. Since solid state molecular thin films are dominated by van der Waals forces, dipole-dipole interactions can strongly affect the energy structure of constituent molecules [16,35-37]. This solvation effect can be particularly pronounced in doped or blended molecular thin films.

A typical method of energy tuning of luminescent dopant molecules is by changing host material or varying dopant concentration in a non-emissive host matrix. By varying concentrations of dopant laser dye 4-(dicyanomethylene)-2-methyl-6-(julolidin-4-ylvinyl)-4Hpyran (DCM2) in tris(8-hydroxyquinoline) aluminum (Alq3) (Fig. 3-1) or N,N-diphenyl-N,N-bis(3-methylphenyl)-1,1-biphenyl-4,4-diamine (TPD) host films, previous work reported up to 75 nm tuning of the DCM peak emission wavelength [16]. Based on SSSE theory, such doping variation is a simple method which can be used for a range of applications, but it is restrictive as a molecular probe due to complicating factors. This includes aggregation of the dopant molecules in host films, which often manifest similarly as a red shift in exciton energy. As would be expected of aggregated dopant luminophores, efficiency of thin film photoluminescence (PL) typically decreases at higher dopant concentrations [38]. Attempting to isolate SSSE effect from dopant aggregation, Madigan et al. focused on varying the concentration of a polar non-emissive co-dopant in a non-polar host matrix, changing the effective dielectric response of the host matrix while keeping the dopant molecule concentration constant; a 40 nm wavelength shift in peak PL was reported for a series of samples with
0.005% doping of DCM2 molecules in a polystyrene (PS) matrix by varying the doping levels of polar camphoric anhydride (CA) co-dopant molecules [37]. In addition, this work applied the liquid state Onsager model [21] and Ooshika-Lippert-Mataga (OLM) solvation theory [24–27] to show good agreement for co-doping experiments [37].

Figure 3-1: (left) Chemical structures of DCM2 dopant molecule with Alq3 and PS host molecules. (right) Schematic of SSSE on exciton energy levels, illustrating bathochromic (red) shift in the PL peak for typical dye molecules due to increasing dielectric matrix polarity; increase in the matrix polarizability causes a larger reaction field in response to the optical-excitation of dopant molecules and subsequent emission, creating a larger perturbation on the energy levels to red shift the transition energy.

In general, while these doping methods provide flexible parameters in energy tuning organic thin films for applications such as OLEDs and down converters [16,39], the exciton energy is predetermined during fabrication. Thus, it is desirable to develop an alternative, dynamic, reversible method for examining and probing exciton energy dynamics at the molecular level. Thus, we focus on external pressure SSSE probing of organic thin films, leading to shifts in Frenkel exciton energy and enhancement of the time-resolved spectral red shift associated with energy-transfer-mediated exciton diffusion.
3.3 Methods

Previous studies utilized pressure techniques on organic thin films to observe PL shifts [40], and at high pressures, even a deformation of polymers and large dye molecules [41, 42]. In this chapter, we employ similar mechanical pressure probing technique to demonstrate PL spectral tuning through pressure-dependent SSSE in optically-excited molecular thin film samples. This external mechanical pressure dynamically modulates molecular density, modifying the local dielectric, which manifests as observable SSSE (see Fig. 3-1).

3.3.1 Sample Fabrication

Two sets of material systems with the same dopant molecules but different host materials were prepared for this study. Films of 200 nm thick Alq3:DCM2 at 1% DCM2 doping were deposited on quartz substrates at a rate of 3.0 Å/s by using thermal co-evaporation at a chamber pressure below 10⁻⁶ Torr. Films of 200 nm PS:DCM2 were spin-cast from a 30 mg/ml chloroform solution at 2000 RPM; doping concentrations were controlled by relative mass dissolved in initial solution.

3.3.2 Mechanical Setup

The mechanical pressure setup was clamped onto a Nikon microscope stage, shown in Fig. 3-2. It allows optical accessibility for PL measurements with force and sample position scanning capabilities. A mechanical spring of spring constant 4.5 N/mm is inserted between the probe and a motorized micrometer for a linear force-displacement relationship, and pressure is estimated from force and contact area. Force is applied through a steel probe on an organic film sandwiched between a thick quartz substrate and a flexible cover glass, which is calibrated by using a load cell. The 200 μm contact diameter was estimated by imaging Newton interference rings between top and bottom glass. The measured diameter has a systematic error up to 20%, which contributes
to uncertainty in the reported applied pressure. Instead of a motorized micrometer, a manual micrometer can also be installed to apply a greater range of pressure, but is ultimately limited by sample durability, non-linear response in the spring or thin film, and possible unaccounted distribution of compression in the mechanical components.

Figure 3-2: Schematic of experimental setup for in situ optical measurement of organic thin film samples under mechanical pressure.

3.3.3 Optical Characterization

Samples were excited using a laser of $\lambda = 475$ nm and 1 kHz repetition rate focused to a spot diameter of 10 $\mu$m using a 5X Nikon objective. PL was collected by the same objective and re-imaged into a spectrograph (Princeton Instruments Acton SP2300) with a Si charge-coupled detector array (Princeton Instruments Pixis) to obtain emission spectra or streak camera (Hamamatsu) for time-resolved spectral data. For each spectrum, the peak wavelength was found by using a peak Gaussian fit, and the centroid was computed as a weighted average for all photon counts above half-maximum intensity point.
3.4 Results and Discussion

The externally applied uniaxial mechanical pressure causes deformation in the organic thin films. Within the linear regime, thin film volumetric compression can modeled by Young’s modulus and Poisson’s ratio of the host material. The resulting decrease in intermolecular distance effectively modifies the local dielectric matrix environment.

3.4.1 Steady State Photoluminescence

Since increasing the molecular density increases the matrix polarizability, we expect a bathochromic (red) shift in the PL for DCM2 dopant molecules, similar to previously reported results for films of increased doping concentration [16]. Figs. 3-4 show measured PL spectra of the corresponding sample under select pressures, with dashed lines indicating fitted peak wavelengths.
Figure 3-4: Spectral shift in PL of the (a) film of 0.5% doped DCM2 in PS, (b) film of 1% doped DCM2 in Alq3, in response to the externally applied pressure (with estimated pressure, indicated in the legend). The peak wavelength, as determined from numerically fitting the PL, is indicated for each spectrum with a vertical dashed line. (c) Plot of PL spectra of PS:DCM2 and Alq3:DCM2 films under zero pressure and the corresponding peak (solid line) and centroid (dashed line) wavelength of each spectrum. (d) Spectral shift of the PL peak wavelength and centroid as a function of applied pressure for 0.5% doping of DCM2 in PS (top) and 1% doping of DCM2 in Alq3 (bottom).

As expected, a reversible bathochromic shift in the peak PL wavelength is observed as the estimated pressure increases from 0 to 0.4 GPa: over $\Delta \lambda = 10$ nm for samples of PS:DCM2 and over $\Delta \lambda = 15$ nm for Alq3:DCM2 samples. Fig. 3-4 (d) compares fitted peaks and computed centroids for the two measured material systems. For both systems, the PL spectrum under pressure shows negligible changes in emission linewidth.
Furthermore, changes in PL centroid wavelengths are well correlated with the shifts in peak PL wavelengths, confirming the homogeneity of the spectral shift among the optically excited molecules. These observed effects on PL emission are consistent with the expected increase in the local dielectric constant due to increase in density of dopant and host molecules.

![Normalized intensity scan](image)

Figure 3-5: Typical pressure scan for PS:DCM2 at 0.5% doping, with peak PL plotted in white. Micrometer z stage position (x-axis) indicates changes in applied pressure. PL spectrum for each micrometer position is normalized to peak intensity and plotted as color intensity vs. wavelength (y-axis).

The motorized pressure probe allows full pressure scanning measurements, resulting in typical 3-D plots showing PL spectrum as a function of z position of the micrometer (Fig. 3-5). Similar spatial mapping of exciton energy under external pressure can also be performed using the setup.
3.4.2 Solvation Theory Fitting

To compare experimental measurements to expected change due to SSSE, we use the OLM model as expressed in Eqn. 2.7 and Eqn. 2.8. The high frequency solvent electron reorientation term, $A(n^2)$, with index of refraction $n$, is approximated to be on the same time scale with solute absorption and emission. Its contribution is assumed to be relatively invariant as a function of solvent (host matrix) polarizability compared to the low frequency solvent nuclear reorientation term $A(\epsilon)$, with solvent dielectric constant of $\epsilon$. We assume that the dipole moments of the excited state $\mu_e$, the ground state $\mu_g$, and the transition dipole $\Delta\mu = \mu_g - \mu_e$ are only dependent on the solute molecule and are also constant with pressure. These assumptions result in a simple relationship between the change in transition energy and the local dielectric constant:

$$
\Delta E_{PL} \approx -A\Lambda(\epsilon) + C = -A \left( \frac{2(\epsilon - 1)}{2\epsilon + 1} \right) + C
$$ (3.1)

Theoretical exciton PL of DCM2 as a function of host dielectric constant is plotted in Figure 3-6. As an example, polystyrene (PS) with 0.5% doped DCM2 has matrix dielectric constant of $\epsilon_m = 2.44$ [37]. The constants $A$ and $C$ were found for a specific dye molecules by simply fitting the peak PL emission energy of the dye dissolved in various liquid solvents as a function of the change in dielectric constants. Values of $A = 0.55$ eV, $C = 2.4$ eV for DCM2 in liquid state are taken from literature [37].

To consider the density dependent perturbation on the energy, we substitute dielectric susceptibility $\chi = \epsilon - 1$ into the model, and account for the change susceptibility under pressure $\chi = \chi_m + \Delta\chi$, where $\epsilon_m = \chi_m + 1$ is simply the bulk dielectric constant of the host-guest system under zero pressure.

$$
\Delta E_{PL} \approx -A \left( \frac{2\chi}{2\chi + 3} \right) + C \approx -A \left( \frac{2\chi_m(1 + \frac{\Delta\chi}{\chi_m})}{2\chi_m(1 + \frac{\Delta\chi}{\chi_m} + 3)} \right) + C
$$ (3.2)

Fig. 3-6 plots this theoretical expectations of the transition energy of DCM2 as a
function of dielectric constant and change in susceptibility.

Figure 3-6: DCM2 emission transition energy shift as predicted by OLM theory: (top) the theoretical prediction of the emission transition energy (on the left axis in blue) and the solvent nuclear polarizability (on the right axis in green) as a function of host dielectric constant for DCM2 dopants; (bottom) The same transition energy is plotted as a function of the percent change in dielectric susceptibility, based on initial state parameters of PS host matrix.

First order approximation of the relationship between the density of molecules and dielectric susceptibility results in a direct proportionality, such that a percent change in density would be directly reflected as a percent change in susceptibility. We can then relate this to the uniaxial pressure $P$ by the host material Young's modulus $Y$. 
and Poisson's ratio $\nu$.

$$\frac{\Delta \chi}{\chi_m \approx \frac{\Delta N}{N} = \frac{\Delta V}{V} = \left(1 + \frac{P}{Y}\right)^{1-2\nu} - 1$$

(3.3)

To further simplify our fit, we can approximate the relationship using the first term of the Taylor expansion about zero pressure. This results in a linear relationship between experimentally applied pressure and volumetric change. We define a proportionality constant of $\alpha$, depending only on host matrix mechanical properties.

$$\frac{\Delta \chi}{\chi_m} \approx \frac{1 - 2\nu}{P} = \alpha P$$

(3.4)

Substituting Eqn. 3.4 into Eqn 3.2, we obtain a model estimating the expected change of the PL energy under uniaxial pressure, using $\alpha$ as a single fitting parameter.

$$\Delta E_{PL} \approx -A \left( \frac{2(\epsilon_m - 1)(1 + \frac{\Delta \chi}{\chi_m})}{2(\epsilon_m - 1)(1 + \frac{\Delta \chi}{\chi_m}) + 3} \right) + C \approx -A \left( \frac{2(\epsilon_m - 1)(1 + \alpha P)}{2(\epsilon_m - 1)(1 + \alpha P) + 3} \right) + C$$

(3.5)

In Fig. 3-7, the PS:DCM2 peak PL wavelength shift is compared to this simplified model. We can fit the experimental results with good agreement to get a parameter of $\alpha_{PS} = 0.8 \pm 0.4 \text{ GPa}^{-1}$. We can also estimated $\alpha_{PS}$ based on literature values of PS Poisson ratio, $\nu = 0.35$ [43] and Young’s modulus, $Y = 1.3 \text{ GPa}$ [44] to find an expected value of $\alpha_{PS} = 0.23 \text{ GPa}^{-1}$. Accounting for the error in the fit, the calculated and fit-to-experiment values of $\alpha_{PS}$ are within a factor of 2. Such discrepancy could be due to the simplifying assumptions made in the above theory development, or due to the differences in $\nu$ and $Y$ of our doped PS films, as compared to the neat films measured in the literature.

The same theory fit can be performed for Alq3:DCM2 films, shown in Figure 3b, resulting in $\alpha_{Alq3} = 1.1 \pm 0.5 \text{ GPa}^{-1}$. Literature estimates for the elastic modulus of Alq3 vary widely, with a range of 1 GPa up to 100 GPa obtained by different methods such as wrinkle-based metrology measurements [44,45] and nano-indentation [46].
With more precise pressure tuning systems coupled with modeling, the demonstrated pressure-dependent SSSE technique may provide another experimental method for estimating material properties of organic thin films.

Figure 3-7: Fitting experimental results of peak PL energy shift of (a) PS:DCM2 (0.5% doping by wt.) and (b) Alq₃:DCM2 (1% doping by wt.) thin films as function of change in the molecular packing density, or equivalent change in dielectric susceptibility. The red dashed lines indicate predicted OLM theory and circles indicate the experimentally observed peak PL wavelength shift converted to change in density using fitting parameter α.

These simple steady state PL measurements under dynamic pressure tuning demonstrate consistent solvation effect by observing the same luminescent molecules in a single thin film sample. This is in stark contrast to previous studies that necessitated multiple samples with different doping concentrations or material properties to obtain similar results.

3.4.3 Transient Photoluminescence

To compare between density-dependent and doping-dependent SSSE, we use a streak camera to monitor exciton lifetime and emission energy over time. We focused time-
Figure 3-8: Streak camera data of PS:DCM2 at 0.5% doping under select pressures (labeled below each figure); with time as vertical axis, wavelength as horizontal axis, and intensity indicated in color scale. The time-integrated PL spectra are plotted in white on the bottom of each figure. The wavelength-integrated time response data are plotted in white on the left of each figure.
resolved PL (TRPL) of PS:DCM2 samples under different externally pressures, as well as samples with varying doping concentrations. Fig. 3-8 shows typical streak camera measurements of PS:DCM2 at 0.5% doping under the measured range of external pressures. This data can be integrated in time to confirm the steady-state red-shift in PL spectrum. It can also be integrated over wavelength to find exciton lifetime. Fig. 3-9 plots the wavelength-integrated time response of the PS:DCM2 under pressure.

![Wavelength-integrated TRPL of PS:DCM2 at 0.5% doping under select pressures. Intensity normalized to unity for lifetime comparison.](image)

The corresponding fitted luminescence lifetimes are within 0.2 ns for the measured range of pressures. This is in contrast to previous TRPL of DCM doping studies [38,47], where the lifetime significantly decreased with increased dopant concentration, due to the exciton quenching by aggregated dye molecules. This comparison highlights that the solvatochromic shift due to change in density does not exhibit the pronounced aggregation quenching effect on exciton lifetime.

### 3.4.4 Spectral Diffusion

Additionally, streak camera measurements from Fig. 3-8 can be parsed into 0.01 ns time bins. For each temporal slice, the peak PL wavelength is computed. Evolution of the peak PL within the exciton lifetime (~ 1 ns) after initial excitation of 0.5% doped
PS:DCM2 thin film samples under select pressures is plotted in Fig. 3-10.

Figure 3-10: Streak camera: spectral diffusion as measured by peak PL emission for PS:DCM2 (wt. 0.5%) under select pressures.

The time-resolved spectral data shows a monotonic red-shift in PL with time, consistent with the previously observed exciton thermalization through Förster resonant
energy transfer (FRET) assisted exciton spatial diffusion [33,48,49]. This thermalization allows the exciton to FRET from dopant molecules to lower energy neighboring dopant sites, which manifests in the observed spectral red shift over time. We can compare the effects of molecular density to the spectral thermalization of PS:DCM2 samples with select percentages of DCM2 doping concentration shown in Fig. 3-11. Each set of spectral shift data in Figs 3-10 and 3-11 is linearly fitted within the exciton lifetime, and the spectral shift rate corresponding to the slope of the fit is plotted in Fig. 3-13.

We expect the rate of FRET-driven energy shift to increase due to increase in molecular density or dopant concentration, both which can increase the number of acceptor sites within a sphere of interaction around a donor molecule. To model the change in exciton energy we assume a direct relationship between the spectral shift rate and the FRET rate [50]. Furthermore, we assume the Förster radius to be approximately constant. Based on Eqn. 2.16, the FRET rate between donor and $N_A$ acceptor sites can be calculated by

$$k_F = \frac{n_A}{\tau} \left( \frac{R_F}{r} \right)^6$$

for a given donor lifetime $\tau$, Förster radius $R_F$, and average DCM2-DCM2 molecular spacing $r$. We can model this effect in two limiting geometric cases: (1) dipole to single dipole interaction and (2) dipole to dipole continuum.

**Figure 3-12:** FRET transfer models for organic doped thin films showing limiting cases of single dipole-dipole interaction and dipole-dipole continuum interaction.
Single Dipole-Dipole Interactions

For the case of single dipole-dipole interaction, we consider only the effect of change in $r$ between nearest neighbor DCM2 molecules ($n_A = 1$). The ensemble-averaged change in $r$ under external pressure can be derived from the volumetric change, and can be obtained from the steady state PL measurement and solvation theory fits. We can use the fitting parameter $\alpha$ from PS:DCM2 films to estimate the change in spectral shift rate $k$, as a function of applied pressure $P$:

$$
\frac{k}{k_0} \approx \frac{r_0^6}{r^6} = \frac{1}{(1 - \frac{\Delta V}{V})^2} = \frac{1}{(1 - \alpha P)^2}
$$ (3.7)

Dipole-Dipole Continuum Interactions

For the case of dipole to dipole continuum interaction, the transfer rate is the integration, over all space, of each spherical shell of acceptor sites at radius $r$. Thus, the change in transfer rate under pressure does not follow the $r^{-6}$ relationship, but depends instead on the change in overall acceptor dipole density:

$$
\frac{k}{k_0} \approx \frac{n_A}{n_{A,0}} = \frac{r_0^3}{r^3} = \frac{1}{1 - \alpha P}
$$ (3.8)

Using the theory fit parameter of $\alpha = 0.8$ GPa, Fig. 3-13 (a) fits the two models to the change in the spectral red-shift rate as a function of estimated pressure. The experimental data shows an increase in the spectral shift rate with increasing pressure, which falls within the expected values based on FRET-mediated exciton transfer as represented by the two limiting cases. Therefore, the pressure probing technique not only perturbs the exciton transition energy, but also dynamically modulates molecular dipole interactions, leading to enhanced exciton diffusion in organic thin films.

The same simplified spectral shift rate models can be applied to the results of doping concentration variation, where the change in DCM2-DCM2 average molecular distance is estimated based only on doping density considerations. A previous study found that
even for low doping concentrations, the FRET rate dependence on doping concentration follows more closely to a $r^{-3}$ dependence rather than conventional dipole-dipole FRET $r^{-6}$ dependence [38]. Thus, we consider the limiting case of dipole to dipole continuum model (Eqn. 3.8), assuming that the spectral shift rate variation is only due to increased DCM2 acceptor molecules sites for higher concentration samples (Fig. 3-13 (b)). Comparing to the higher density continuum predictions, the spectral shift rate still deviates significantly at higher doping concentrations. Other factors such as dopant aggregation and change in dopant dipole moments, which changes the transition overlap integral, become significant variables. Clearly, more complex modeling is necessary to accurately describe measured rates when varying dopant concentration [49, 50].

Figure 3-13: Spectral shift rates of PS:DCM2 (wt. 0.5%) plotted in red for films (a) under select pressures and (b) select doping concentration. The solid lines correspond to the numerically determined spectral shift rate scale factor $\frac{k}{k_0}$, using both FRET models: dipole-to-single dipole interactions and dipole-to-dipole continuum interactions. For various doping concentrations in (b), the large discrepancy between experimental results and dipole-to-dipole continuum model at high dopant densities highlights the need to consider additional factors beyond simple density of dopant molecules.
For such traditional doping technique, molecular interactions can no longer be explained through a simple model of increased number of neighboring dye molecules in the host solvent environment. In comparison, the density variation through external pressure presents a much simpler method with fewer unaccounted factors. This external pressure technique can be applied more generally to probing spectral thermalization and exciton diffusion in thin film semiconductors.

3.5 Conclusion

In this chapter, we demonstrated that SSSE observed in molecular thin films under external pressure could be consistently predicted using a simplified model depending only on the change in the intermolecular distance. Based on solvation modeling and fit, the Förster-mediated spectral red-shift is consistent with the observed temporal and spectral-resolved PL measurements under pressure. This increase in spectral shift rate under pressure indicates enhanced exciton diffusion in organic thin films. Furthermore, comparison between density-induced and doping concentration-induced SSSE in this spectral shift rate shows an advantage in using pressure to reduce the effects of additional variables such as aggregation. Such pressure probing techniques could enable fundamental studies of electronic and excitonic energy disorder in molecular and QD thin films. Pressure setups to directly measure probe displacement could improve upon the technique for tuning exciton energy shifts and may provide additional benefits as an opto-mechanical method to estimate the material properties of molecular/polymeric host matrix films. In general, the presented work allows for fine tuning of the exciton energy and could be implemented to study the effect of change of mechanical or electrostatic pressure on exciton-based semiconductors for optoelectronic devices and will be employed in the following chapter.
4 | Charge Transfer Exciton
Spin State Dynamics

4.1 Overview

Excitonic states discussed thus far are the fundamental constituents that determined overall device characteristics, especially for optoelectronic applications. One such example is charge transfer (CT) exciton states, which play a crucial role in organic photovoltaics (OPVs) and light emitting devices, mediating both photocurrent generation and recombination losses. In this chapter, we focus on organic blended donor-acceptor systems with fluorescent CT states. By using time-resolved spectroscopy, we monitor both singlet and triplet CT state dynamics as a function of the electron-hole spacing. Using external pressure to modulate molecular spacing, experimental results indicate that large donor-acceptor separations reduce back transfer from the CT state to a lower energy localized exciton (LE) triplet or the ground state, matching theoretical expectations based on simple rate models. A lower energy LE triplet state can drain and quench CT triplets that would otherwise be spin-protected against radiative recombination, switching the most efficient origin of photocurrent from triplet to singlet CT state. This work provides design guidelines to select material systems with higher energy triplet excitons and/or to optimize donor-acceptor spacing in order to minimize recombination losses, exploiting triplet CT mediated photocurrent generation for OPV applications.
4.2 Introduction

As bound combinations of an electron and a hole located on separate molecules, CT states are formed at donor-acceptor interfaces [51–53], from LE transfer or recombination of free charges [54–56]. Modern OPV donor-acceptor material systems demonstrate ultrafast formation of CT states from LE, and efficient dissociation of CT states into charges under short circuit conditions [57], with internal quantum efficiencies (IQE) of many OPVs now commonly approaching 90-100% [58]. However, recombination losses in CT states increase dramatically at weaker internal electric fields and reduce the open circuit voltage and the power efficiency, proving to be a significant limiting factor in improving overall device performance. [59–63]

Three decades of research since the initial publication of heterojunction organic light emitting diodes (OLEDs) and OPVs have provided much insight in understanding donor and acceptor material systems for various applications. Control over molecular synthesis and processing now enables the engineering of exciton energy levels and physical overlap between the electron and hole charge densities [64–66]. Given the vast library of available molecules, a fundamental understanding of CT dynamics is essential to provide general guidelines in material selection for applications such as OPVs.

We will particularly focus on the effects of donor-acceptor overlap and CT spin state energy alignment. Modulation of molecular density at the donor-acceptor interface effectively modulates electron and hole charge spatial overlap in CT excitons, with many consequences for its dynamics. Separated or larger CT states have smaller Coulomb binding energies, which should improve dissociation into charge and overall photocurrent yield. However, large separations can also cause weaker coupling with the initial LE, reducing the exciton transfer rate into CT states at donor-acceptor interfaces [67]. Increased charge separation also can significantly reduce exchange splitting between singlet and triplet CT states.

With nearly degenerate CT spin states, intersystem crossing becomes more efficient,
potentially facilitating spin engineering to improve OPV efficiency. As discussed in chapter 2, triplet excitons are spin forbidden from radiatively recombining to the singlet ground state. This means the longer-lived triplet state could provide spin protection against a major recombination loss pathway. However, the triplet CT state also has a major non-radiative loss process by back transferring to a lower energy LE triplet state, a problem for many OPV systems. Traditional OPV designs often optimize for larger open circuit voltage, requiring high CT state energy [68]. This typically pushes the energies of the CT states above that of the LE triplet state on the donor or acceptor, which becomes the lowest energy excited state in the system. This means that exciton population in the triplet CT states can efficiently transfer into the lower energy LE triplet, or triplet "drain", where it eventually non-radiatively recombines to the ground state, creating a crucial loss pathway in photocurrent generation [59,63,69].

This chapter provides a detailed study of spin dynamics in CT states, focusing on consequences from the OPV perspective, but the general findings may provide insights to other applications. By applying external pressure, as discussed in the previous chapter, and monitoring CT photoluminescence (PL) [40], we observe density effects on the principal spin-dependent loss pathways for CT excitons. Singlet CT state recombination directly to the ground state is exacerbated for CT states under compression. Increased molecular density also enhances back transfer from triplet CT states to low-lying triplet LE drain present on either the donor or acceptor molecule.

Intersystem crossing between singlet and triplet CT excitons via hyperfine interactions can be modulated by an external magnetic field. Thus, applying a magnetic field to decrease the conversion of singlet CT states to triplet CT states allows us to identify the spin states responsible for efficient photocurrent generation.¹ We find that when a triplet drain is present, singlet CT states are more efficient in photocurrent generation. However, in the absence of a triplet drain, photocurrent is more efficiently generated from the longer-lived triplet CT states.

¹In collaboration with Dan Congreve.
4.3 Charge Transfer Exciton Energy

The emissive exciplex material systems used in this study were originally designed for OLEDs with unique thermally activated delayed fluorescence (TADF) properties due to the small splitting energy between the singlet and triplet CT states [70, 71]. Two specific TADF thin film blends were selected: 4,4',4''-tris[3-methylphenyl(phenyl) amino]triphenylamine (m-MTDATA) as the donor and either tris-[3-(3-pyridyl)mesityl] borane (3TPYMB) or 2-(biphenyl-4-yl)-5-(4-tert-butylphenyl)-1,3,4-oxadia-zole (t-Bu-PBD) as the acceptor (Fig. 4-1). Temperature-dependent dynamics, characteristic of TADF emitters, can be observed in both systems [71].

![Chemical structures of m-MTDATA, t-Bu-PBD, and 3TPYMB.](image)

Figure 4-1: Chemical structures of m-MTDATA, t-Bu-PBD, and 3TPYMB.

Fig. 4-2 shows schematics of CT state energy and dominating dynamics of both material systems. Upon absorption of the incident optical excitation, singlet excitons are initially generated on the donor molecules, which dissociates on ultrafast time scales into singlet CT excitons across a donor-acceptor interface. With quantum yield (QY) of approximately 20% [71], CT state emission is dominated by the singlet exciplex CT state between nearest neighbor donor-acceptor molecules, which efficiently quenches luminescence from LE singlet on the donor and acceptor molecules.
Figure 4-2: Crucial energy levels and rates for (a) m-MTDATA:t-Bu-PBD and (b) m-MTDATA:3TPYMB heterojunction systems. The LE singlet state S1 of m-MTDATA is initially populated by optical excitation, which quickly dissociates into a singlet CT exciton across the donor-acceptor interface. The diagrams illustrates material systems (a) with and (b) without triplet back transfer loss.

In both systems, the singlet CT state \( ^1(D^+A^-) \) energy is approximately 2.6 eV as
determined by exciplex CT state fluorescence. The triplet CT state $^3(D^+A^-)$ is nearly iso-energetic with the singlet CT state; the CT exciton splitting energy for t-Bu-PBD acceptor system is estimated to be between 5 meV and 50 meV [71, 72].

![Fluorescence spectra of neat films of t-Bu-PBD, m-MTDATA, and 1:1 molar m-MTDATA:t-Bu-PBD. Phosphorescent spectrum of m-MTDATA is taken at 10 K. The donor-acceptor blend thin film emission demonstrates quenching of LE on both donor and acceptor by CT states, which luminesces through the singlet exciplex CT state. [71]](image)

Figure 4-3: Fluorescence spectra of neat films of t-Bu-PBD, m-MTDATA, and 1:1 molar m-MTDATA:t-Bu-PBD. Phosphorescent spectrum of m-MTDATA is taken at 10 K. The donor-acceptor blend thin film emission demonstrates quenching of LE on both donor and acceptor by CT states, which luminesces through the singlet exciplex CT state. [71]

Typically, temperature dependent intersystem crossing (ISC) and reverse intersystem crossing (RISC) dominate interactions between singlet and triplet CT states. However, donor-acceptor systems with such small splitting energy may also exhibit hyperfine interactions. Temporary delocalization of a CT state forms a polaron pair (PP), which results in degeneracy (or near degeneracy) of the CT spin states. Hyperfine coupling between the triplet CT states due to local magnetic nuclei could contribute to ISC and RISC, which can be affected by an external magnetic field [31, 32, 73, 74].

The main differentiation between the two systems is the LE triplet energies. The
m-MTDATA triplet energy is approximately 2.7 eV [71], which higher than the triplet CT state energy. The 3TPYMB triplet energy is approximately 3.1 eV, energetically inaccessible from the triplet CT state, effectively preventing back transfer to a triplet drain on 3TPYMB [71]. On the other hand, previous measurements of the low temperature phosphorescence of t-Bu-PBD derivatives estimated a t-Bu-PBD triplet energy of 2.54 eV [75], a significant triplet drain in the system.

Figure 4-4: Quenching of Flrpic emission by t-Bu-PBD host molecules. t-Bu-PBD significantly quenches the triplet from Flrpic, indicating t-Bu-PBD triplet energy is lower than 2.65 eV.

Unable to obtain clean phosphorescent spectra for t-Bu-PBD at low temperature, we confirm this estimation by comparing the triplet energy of t-Bu-PBD to that of Flrpic, a phosphor with triplet energy of 2.65 eV [76]. Using t-Bu-PBD as host molecules, Flrpic was doped at 5% by weight. Flrpic (5% wt.) doped in N,N'-dicarbazolyl-3,5-benzene (MCP) was made as reference samples. We observed Flrpic emission from the t-Bu-PBD film (purple line) less than 2% as bright as that of the MCP film (green line), demonstrating that Dexter transfer of triplets from Flrpic dopant and t-Bu-PBD host is energetically favorable [77, 78]. This measurement supports that t-Bu-PBD triplet energy is less than that of Flrpic.
Thus, the t-Bu-PBD triplet exciton is lower than or approximately isoenergetic with the m-MTDATA:t-Bu-PBD CT triplet states, enabling significant triplet back transfer, whereas triplet back transfer is blocked in the m-MTDATA:3TPYMB system due to the high energies of the triplet excitons. Since typical OPVs push for higher open circuit voltage leading CT triplet with higher energy than LE triplet state, the t-Bu-PBD system may be a closer analog for traditional, high efficiency OPV material systems.

4.4 Methods

4.4.1 Sample Fabrication

The thin films for pressure testing consisted of 60 nm of 1:1 molar of the specified donor-acceptor blend, thermally evaporated on thick glass substrates, with 100 nm of aluminum (Al) deposited on top of the organic for consistency in reflection. For measurements of magnetic field effect (MFE) on photocurrent and PL, simple bulk heterojunction OPV devices were fabricated with 60 nm of 1:1 molar donor-acceptor blended thin film sandwiched between 15 ohms/square ITO (bottom electrode) and 100 nm of Al (top electrode). All organic materials were purchased from Luminescence Technology Corp (Lumtec) and used as received. All samples and devices were encapsulated with thin flexible glass covers and epoxy to avoid photo-oxidation effects.

4.4.2 Mechanical and Optical Measurement Setup

The mechanical and optical setup described in the previous chapter is employed for pressure dependent measurements. Optical characterization was performed through the glass substrate using a microscope setup with a \( \lambda = 405 \) nm pulsed 31.25 kHz repetition rate excitation laser (PicoQuant LDH) focused to \( \sim 10 \) \( \mu \)m spot size. A 405 nm dichroic and a 450 nm long-pass was used to filter for CT exciplex emission. Spectrometer with Si CCD camera (Princeton Instrument Acton and Pixis) was employed for steady state
PL measurements. Time-resolved PL (TRPL) under external pressure and magnetic field were measured using an single-photon avalanche photodiode (PicoQuant PDM).

### 4.4.3 Magnetic Field Measurement Setup

![Diagram of magnetic field effect setup.](image)

Figure 4-5: Diagram of magnetic field effect setup.

Measurements of steady state MFE in photocurrent or fluorescence were performed using a monochromatic 365 nm optical pump, generated by a LED with a mechanical chopper (Fig. 4-5). An electromagnet applied the magnetic field at a frequency of 13 mHz with a duty cycle of 50%, with the dominating field component parallel to the plane of the substrate. The thin film fluorescence is focused onto a silicon photodetector and measured by a lock-in amplifier. A second lock-in amplifier measured the device photocurrent simultaneously. Magnetic field strength was measured by an FWBell 5100 gaussmeter, queried at a frequency of 1 Hz. TRPL MFE was measured using the microscope setup previously described with magnetic field applied by a pair of permanent rare-earth magnets; the applied magnetic field at the sample position is approximately 0.35 T.
4.5 Results and Discussion

We first confirm that in a blended thin film, exciplex CT state emission quenches both fluorescence and phosphorescence from LE on donor and acceptor molecules [71]. To eliminate contributions from potential interactions with m-MTDATA excimers [72], we focus on the relative changes between samples with different acceptors (3TPYMB or t-Bu-PBD) while maintaining a constant fraction of the m-MTDATA donor molecules.

4.5.1 Pressure/Density Effect

Steady State Photoluminescence

Fig. 4-6 demonstrates the effects of pressure on steady-state PL of the CT state emission in both material systems. Increasing external pressure leads to a red shift in emission energy. The red shift is due to both the solvation effect from increased molecular density and the increased Coulomb interaction between the donor and acceptor in
the compressed geometry [37, 40]. As expected for increased Coulomb binding energy, a significant increase in fluorescence intensity was also observed.

**Time-Resolved Photoluminescence**

In order to better understand and compare the exciton dynamics, we measured TRPL of each donor-acceptor sample under pressure. Fig. 4-7 plots the typical TRPL measurements under zero external pressure for each material system.

![TRPL graphs](image)

Figure 4-7: CT exciplex TRPL under zero pressure for (a) m-MTDATA:3TPYMB and (b) m-MTDATA:t-Bu-PBD thin film samples with simple lifetime fits of prompt (cyan) and delayed (purple) fluorescence components.

As expected for excitons with two spin states coupled by ISC and RISC, there are distinct prompt and delayed components in the TRPL. Based on the rate models
discussed in chapter 2 and the literature, the prompt emission is dominated by direct PL from the singlet CT state, and mainly depends on singlet CT fluorescence rate and ISC rate. Since the fluorescence rate is faster than RISC rate, the delayed emission is dominated by triplet CT states dynamics. We define the prompt emission to be within the first 0.3 - 0.7 μs and delayed emission to be between 4 - 9 μs for m-MTDATA:t-Bu-PBD and 8 - 12 μs for m-MTDATA:3TPYMB. Fitting a single exponential to each of these time windows, we compare the pressure dependent transient dynamics of m-MTDATA:t-Bu-PBD and m-MTDATA:3TPYMB. This reveals the effect of the low-lying t-Bu-PBD triplet exciton drain on the dynamics of singlet and triplet CT states.

![Figure 4-8](image)

Figure 4-8: Typical measurement of m-MTDATA:t-Bu-PBD TRPL under external pressure, showing changes in exciton dynamics in both prompt and delayed emission.

Under external pressure, the molecules are pushed closer together. Red shift in the PL spectrum suggests that the overlap between the donor HOMO and acceptor LUMO increases, which is also reflected in the transient dynamics (Fig. 4-8). Recombination rates back to LE states increase, most notably fluorescence from the singlet CT state due to an increase in the transition dipole moment. We also expect both the forward and reverse ISC rates to decrease for CT states localized on neighboring molecules; the
exchange energy splitting is proportional to the overlap of the donor HOMO and the acceptor LUMO and therefore will increase under pressure. Thus, under the Marcus theory of electron transfer $k_{ISC} \propto \exp(-\Delta E/k_BT)$ [79], mixing between triplet and singlet states should decrease for increased molecular density.

Multiple measurements were performed for estimated pressures of 0 - 0.3 GPa for both material systems; the average fitted values of exciton lifetimes and PL intensities are plotted with corresponding standard deviation errors. The trends in prompt dynamics under pressure are shown in Fig. 4-9, with changes in lifetime and intensity plotted in (a) and (b), respectively.

![Figure 4-9: Comparison of m-MTDATA:3TPYMB and m-MTDATA:t-Bu-PBD prompt emission under external pressure, where prompt emission is defined as 0.3 $\mu$s - 0.7 $\mu$s after excitation. (a) Prompt lifetime and (b) integrated intensity changes with applied pressure for the two exciplex systems. Blue represents m-MTDATA:3TPYMB and red presents m-MTDATA:t-Bu-PBD material systems.]

As expected, a large increase in prompt intensity under pressure is observed in both material systems due to increase fluorescence rate. The accompanying prompt lifetime change is determined by competition between a decrease in the ISC rate and an increase in the fluorescence. Indeed, for the m-MTDATA:t-Bu-PBD system, we see little change
in the overall lifetime, indicating that the increase in recombination rate is offset by the decrease in ISC rate. On the other hand, a similar prompt lifetime measurement of the m-MTDATA:3TPYMB system shows that the increase in the recombination rate dominates the decrease in the ISC rate.

![Figure 4-10: Comparison of m-MTDATA:3TPYMB and m-MTDATA:t-Bu-PBD delayed emission under external pressure. (a) Delayed lifetime and (b) integrated intensity changes with applied pressure for the two exciplex systems. Blue represents m-MTDATA:3TPYMB and red presents m-MTDATA:t-Bu-PBD material systems. The delayed fluorescence quenching with increasing pressure in m-MTDATA:t-Bu-PBD clearly indicates increased triplet back transfer loss.](image)

Fig. 4-10 shows the trend in delayed dynamics under pressure. Significant deviation between the two material systems can be observed, which reflects differences in triplet CT states dynamics. In the m-MTDATA:3TPYMB system, the probability of back transfer to a molecular LE triplet is minimal, thus, an increase in delayed lifetime is observed due to the reduced rate of RISC. The exciton population is essentially trapped in the CT triplet until RISC allows fluorescence loss from singlet CT. The intensity of integrated delayed emission thus tracks the change in prompt intensity and radiative rate from the singlet CT state. In contrast, for m-MTDATA: t-Bu-
PBD system, increasing the pressure significantly decreases the delayed lifetime and intensity. We can attribute this to an increase in triplet back transfer loss: the CT population is drained through this loss channel due to better coupling with the t-Bu-PBD LE triplet (reflected in the decreased lifetime). Thus, triplet back transfer is a significant loss mechanism in the m-MTDATA:t-Bu-PBD system that only worsens as the spacing between electron and hole decreases. The effect of donor-acceptor spacing on the exciton dynamics including recombination and ISC rates should be a significant design consideration in material selection for optoelectronic applications.

![Figure 4-11: Schematic summary of density dependent effects on CT exciton dynamics for both singlet and triplet CT states. Decreased donor-acceptor spacing for singlet CT state increases radiative recombination loss and decreases ISC; RISC similarly decreases for triplet CT state, but given a lower energy LE triplet, back transfer loss also increases.](image)

4.5.2 Magnetic Field Effect

To gain a better understanding of CT spin-dependent effects on OPV devices, instead of thin film samples, we fabricate simple bulk heterojunction device samples to allow charge dissociation of CT excitons to be extracted as photocurrent. Since complicating factors such as recombination and conductivity also change under external pressure, we employ external magnetic fields to modulate ISC rates. As discussed in chapter 2, magnetic fields can be use to modulate ISC rates via hyperfine splitting between
CT triplets. To observe the direct consequences of triplet back transfer loss on OPVs, we monitor both changes in PL and photocurrent. As a double check, no measurable MFE on the dark conductivity was observed in the devices, indicating the absence of magnetoresistance phenomena.

**Steady State Photoluminescence and Photocurrent**

We monitored simultaneous PL and photocurrent in device samples made from the two organic blends. The external magnetic field splits the triplet levels by up to $E_{\text{Zeeman}} = g\mu_B B_{\text{ext}}/\hbar \sim 50 \mu\text{eV}$ to create hyperfine structures, which modulates ISC rates.

![Energy schematic of singlet-triplet energy splitting as a function of electron-hole spacing. (inset) Schematic of Zeeman splitting due to external magnetic field in relation to hyperfine coupling $V_{hf}$.](image)

As studied extensively in literature [31,32,73,74], an initial population of singlet CT states temporarily separates beyond their exchange radius and forms Coulombically-bound PP states with zero effective exchange splitting. Such an extended singlet state may undergo ISC to a triplet mediated by hyperfine interactions.

This Zeeman splitting is inconsequential for ISC in tightly bound CT states, because the exchange splitting between the singlet and triplet states is much larger than the hyperfine splitting. Instead, the magnetic field only modulates ISC between singlet
and triplet states of larger CT states (PPs) whose exchange splitting is comparable to or less than the hyperfine energy. If the state remains as a singlet, it may collapse back and radiatively recombine within the spin-relaxation time [31, 32, 73, 74]. Therefore, we expect an increase in the probability of germinate recombination in the singlet CT under magnetic field, leading to an increase in the fluorescence quantum yield.

Figure 4-13: Magnetic field effect on CT exciplex (a) PL and (b) photocurrent for m-MTDATA:t-Bu-PBD (red) and m-MTDATA:3TPYMB (blue). Increases in PL from both systems demonstrate that the applied magnetic field increases the population of singlet CT states. Positive MFE on photocurrent in t-Bu-PBD acceptor samples indicates that charge dissociation is more efficient in the singlet CT state. On the other hand, negative MFE on photocurrent in 3TPYMB samples indicates that charge dissociation is more efficient in the triplet CT state.

An increase in fluorescence under magnetic field was indeed observed in both material systems (Fig. 4-13). However, there is a striking difference when we examine the MFE on photocurrent measured simultaneously with the fluorescence in Fig. 4-13 (b). In the m-MTDATA:t-Bu-PBD system, the MFE on the photocurrent is positive; the singlet CT population increases with applied field, and the photocurrent
also increases. This signifies that the photocurrent is more efficiently generated from the singlet CT state, confirming our observation of significant back transfer loss processes quenching the triplet CT states in this material system. However, this effect in m-MTDATA:3TPYMB system is negative; photocurrent decreases with applied magnetic field. As the initial emissive singlet CT population increases with an applied external magnetic field, the triplet CT population must correspondingly decrease. Because the change in photocurrent is negative with increasing applied field, we conclude that the triplet CT state must be more efficient in photocurrent generation in the m-MTDATA:3TPYMB system.

**Transient Photoluminescence**

These results from the steady state MFE measurements are further support by TRPL of the thin film samples under magnetic field, revealing the complex exciton dynamics involved in changing ISC rates.

![Figure 4-14](image)

Figure 4-14: (a) Experimental and fitted model of TRPL under MFE for a 1:1 blended film of m-MTDATA:3TPYMB at with (green) and without (blue) external magnetic field (B ~ 0.35 T). Inset: Initial rapid decay of PL signal. (b) The ΔPL/PL₀ based on the experimental TRPL (black line) and fitted model (blue dots). Courtesy of Eric Hontz [80].
Fig. 4-14 (a) shows the MFE on TRPL for a typical sample of m-MTDATA:3TPYMB, with Fig 4-14 (b) showing the percent difference in PL between the two normalized curves. We observe that the MFE on TRPL can be separated into 3 time regimes: change in PL is negligible at short times (< 100 ns), positive at intermediate times (~1 μs), and negative at long times (> 5 μs). These changes can be explained using a quantum mechanical rate model in which the distance between the electron and hole fluctuates as a function of time [80].

A photo-generated exciton on the donor molecule quickly dissociates into emissive singlet CT exciplex across an interface. This initial CT state has a large exchange splitting, and the ISC rates are unperturbed by MFE at the short time scale (< 100 ns). After a period of time, a fraction of charges in the singlet CT state separate to a distance beyond the exchange radius, forming PP states with singlet characteristics. In this state, the exchange energy is on the order of the Zeeman energy of the applied field (~50 μeV). Thus the magnetic field slows ISC rates, producing more CT singlets from the PP states compared to zero field. This is reflected as an increase in the PL from the singlet exciplex during the intermediate time period (~1 μs).

Meanwhile, a longer lived population is building in the triplet CT state, a fraction of which is from PP states. A larger singlet population means a smaller fraction of triplet exciton is generated. Without a LE triplet drain in m-MTDATA:3TPYMB samples, the CT triplet traps the exciton population. Due to the relatively fast fluorescence rate from the singlet state, luminescence at longer time (>5 μs) is dominated by RISC triplet CT excitons. Thus, the positive PL observed during intermediate time is compensated by the negative PL during later time.

For comparison, we performed the same TRPL MFE measurement on m-MTDATA:t-Bu-PBD samples (Fig. 4-15) to find little changed in normalized TRPL with and without field. A slight increase in PL during intermediate time is still observed. With LE triplet drain on the CT triplet population, the effect of any change in ISC rates after long period of time is dominated by back transfer loss. This results indicates

\[ ^2 \text{In collaboration with Eric Hontz.} \]
that modulations in ISC rates would have little effect in overall exciton dynamics in material systems with significant LE triplet drain.

Figure 4-15: TRPL under MFE for a 1:1 blended film of m-MTDATA:PBD showing little change between zero and high field (B ~ 0.35 T).

These direct measurements of MFE on CT state PL and photocurrent generation indicate that the triplet CT is more efficient in photocurrent generation for systems where back transfer to an LE triplet is energetically unfavorable. These results are strong confirmations for studies performed on P3HT:PCBM OPVs, where alternative methods showed evidence of spin-protected triplet CT states can lead to longer lifetimes and greater probability of dissociation to free charges [81, 82].

4.5.3 Device Characterization

Based on the density-dependent and magnetic field measurements presented thus far, we consider the effect of LE triplet drain on overall OPV performance. Shown in Fig. 4-16 (a), we observe a drastic reduction in external quantum efficiency (EQE) for m-MTDATA:t-Bu-PBD devices. In comparison, EQE for m-MTDATA:3TPYMB devices is general larger by a factor of 4, demonstrating the necessity of minimizing
triplet back transfer in photovoltaic material designs and the potential benefits of spin-protected triplet CT states. Although the two material systems have similar CT state energies, Fig. 4-16 (b) shows that the open circuit voltage of m-MTDATA:3TPYMB is significantly higher than that of m-MTDATA:t-Bu-PBD, demonstrating that decreased recombination losses resulting from spin-protection in the absence of a triplet drain is preserved at weak internal electric fields.

Figure 4-16: (a) External quantum efficiencies of m-MTDATA:3TPYMB (blue) and m-MTDATA:t-Bu-PBD blends (red). Back transfer to the triplet drain on t-Bu-PBD is associated with decreased efficiency relative to the 3TPYMB system. (b) Current-voltage curves for m-MTDATA:3TPYMB (blue) and m-MTDATA:t-Bu-PBD blends (red). Turning off the triplet drain is correlated with a higher open circuit voltage.

4.6 Conclusion

In summary, this chapter demonstrates how delocalization of excitons is a crucial point of consideration for improving devices performance in various applications. We specifically focused on CT excitons modulated by donor-acceptor spacing for OPVs. Results indicate that triplet CT states are more efficient in photocurrent generation in the absence of low energy LE triplet state, since they are spin-protected against radiative
recombination. Devices without triplet drains tolerate compressed CT states, even showing extended CT state lifetimes under applied pressure, which could further improve charge dissociation of CT excitons. Under the constraint of LE triplet drain in the material system, we demonstrated that CT state recombination and back transfer losses can be reduced by maximizing the electron-hole spacing at the interface. Optimal donor-acceptor spacing needs to consider both formation rate of the CT state from the molecular LE as well as excitonic recombination losses. These results also indicate that striving for higher open circuit voltage by maximizing CT state energy may not be the optimal solution. Substantial benefits in both EQE and open circuit voltage were shown to result from the spin-protection of triplet CT states when the CT energy is low enough to prevent back transfer to LE triplets. Quantum dots or TADF materials, with minimal Stokes shift and negligible splitting between singlet and triplet states [83], may be a more ideal alternative to traditional OPV materials.
5 | Charge Transfer State Transport

5.1 Overview

In this chapter, we investigate charge transfer (CT) state transport mechanisms using a direct optical imaging technique of exciton diffusion. Using the organic blended donor-acceptor molecular system discussed in the previous chapter, we demonstrate that germinate, bound CT state, can diffuse along a molecular interface to lower energy sites, driven by local energetic disorder. This observation is confirmed by both time-resolved spectroscopy and electric field quenching of photoluminescence (PL). Furthermore, magnetic field dependence studies reveal a fluctuating exchange splitting, indicative of variations in electron-hole spacing during diffusion. The results suggest that the CT states undergo an asynchronous charge hopping transport mechanism with modulations in electron-hole distance, in contrast to conventional transport of Frenkel excitons. Given the short exciton lifetimes characteristic of bulk heterojunction organic solar cells, this work points to the potential importance of CT state transport, suggesting that CT excitons in many donor-acceptor blends may diffuse farther than Frenkel excitons.

5.2 Introduction

For the applications of organic photovoltaics (OPVs), much controversy surrounds the dynamics of CT states. A CT exciton, even stretched across separate molecules at the
donor-acceptor interface, has a Coulomb binding energy on the order of 100 meV, much higher than thermal energy. This presents a puzzling dichotomy between high binding energy and efficient charge dissociation observed in many organic blends [57, 58, 67, 68]. Previous reports have described CT state dissociation into free charge including mechanisms that are independent [54, 55, 84] and dependent [57, 85] on initial energy of the localized exciton (LE) state. For the latter mechanism, transfer of optically generated LE into a lower energy interfacial CT exciton can result in residual energy, which can aid in dissociation into polaron pair (PP) at ultrafast timescales (~100 fs - 1 ps). These "hot" CT excitons may exhibit coherent charge transport mechanism which can be observed using ultrafast pump-probe techniques in some high efficiency OPV systems [82, 85].

On the other hand, based on the literature, the apparent efficient generation of photocurrent from low energy, bound CT states needs further investigation [86, 87]. Breakup of low energy CT states is critical for both geminate states (those generated from an initial photo-excitation) as well as non-geminate states generated by free charge recombination in blended molecular thin films.

As discussed in the magnetic field dependence study in chapter 4, modulation of the charge separation in the CT state can lead to a decrease in splitting energy between the spin states, allowing hyperfine interactions. This indicates a degree of CT delocalization associated with charge hopping between molecular sites. This chapter will focus on this spatial dynamics of bound CT states in the donor-acceptor blend of m-MTDATA:3TPYMB, offering new insight into CT transport mechanisms (Fig 5-1). This particular donor-acceptor material system is amorphous, with localized, highly fluorescent CT states, with a higher LE triplet energy level than that of the CT states, preventing back transfer loss through triplet drain (see chapter 4). Consequently, the CT triplet states are long-lived (on the order of ~μs), and the external quantum yield of photocurrent generation in m-MTDATA:3TPYMB is as high as 34%, with an internal quantum efficiency (IQE) of 40%. By studying transport of CT states in m-MTDATA:3TPYMB, we can observe the fundamental mechanisms driving charge
dissociation. It is worthwhile to note that traditional OPV material systems exhibit much shorter CT state lifetimes \[88,89\], thus we use theoretical modeling and numerical simulation based on the experimental observations that can be applied to other OPV material systems.

Figure 5-1: (a) Schematic of charge transfer state dynamics. (b) Energy diagram and chemical structures of the donor-acceptor material system. The energy levels of HOMO and LUMO states are in eV and are referenced to the vacuum level. The energies in eV of the lowest energy excited state singlet \( (S_1) \) and triplet \( (T_1) \) excitons of m-MTDATA and 3TPYMB are also indicated.

5.3 Methods

5.3.1 Sample Fabrication

Films of 1:1 M ratio m-MTDATA:3TPYMB were thermally evaporated at a thickness of 700 nm on #1.5 glass coverslips for diffusion imaging and streak camera measure-
ments. Simple bulk heterojunction OPV devices were fabricated for magnetic field
effect (MFE) and electric field effect studies, which consisted of glass substrates with
ITO, 60 nm thermally evaporated donor-acceptor blend film of specified molar ratio,
and 100 nm aluminum (Al). Organic materials were purchased and used as received
from Luminescence Technology Corp. (Lumtec). To avoid photooxidation degrada-
tions, all samples were encapsulated in a nitrogen environment with top cover glass
and epoxy. PL measurements were performed through the bottom glass substrate.

5.3.2 Optical Setup for Diffusion Measurement

We use an optical microscope with a scanning detector (Fig. 5-2) to characterize the
physical diffusion of CT excitons by spatially imaging time-resolved photoluminescence
(TRPL). Measurements were performed following the method described in Akselrod et
al. [90]. A λ = 405 nm pulsed 31.25 kHz excitation laser (PicoQuant LDH) is focused
down to a near diffraction-limited excitation spot (~250 μm) using a 100X, NA = 1.45,
oil immersion objective. To avoid bi-excitonic effects, we use variable laser powers be-
tween 1 - 10 nW. The thin film emission is filtered using a λ = 405 nm wavelength
dichroic and a λ = 450 nm long-pass, and finally imaged at the detection plane with
500X overall magnification. By magnifying and re-imaging the excitation spot onto a
linearly scanned avalanche photodetector (APD), we can monitor the spatial broaden-
ing associated with exciton diffusion. The APD (PicoQuant PDM) with 50 μm × 50
μm active area, was scanned across the image plane in 5 μm steps.

A time correlated single photon counting technique is used to generate lifetime decay
plots corresponding to points on the scanned trajectory. The information from these
plots is then compiled together to form a 3D PL intensity plot with position along
x, time along y and intensity along z direction. To avoid photo-degradation effects
over measurement time scales, simultaneous scanning of the excitation spot across the
sample allows for ensemble-averaged measurements of each thin film sample.
5.3.3 Magnetic Field Measurement Setup

MFE measurements of changes in PL were performed following the procedure discussed in previous chapter (Fig. 4-5).

5.4 Results and Discussions

We first compare fluorescence excitation intensity and photocurrent in a bulk heterojunction OPV device as a function of excitation wavelength to find overlapping characteristics. This demonstrates direct correlation between the population of luminescent CT states and the exciton population responsible for charge generation. Henceforth, we use the CT state PL as an optical monitor of these bound CT states responsible
for charge dissociation.

![Graph showing normalized intensity vs. excitation wavelength](image)

Figure 5-3: Comparison between photo-excitation and photocurrent excitation spectrum of CT exciton in m-MTDATA:3TPYMB thin film at 1:1 molar doping. The correlation between photo-excitation and photocurrent indicates that the fluorescent CT states are also responsible for the generation of photocurrent.

5.4.1 Charge Transfer Exciton Diffusion

Diffusion Analysis

To understand the CT exciton diffusion analysis, we first consider the basic drift-diffusion equation, which, in the general 3-dimensional form, is given by

$$\frac{\partial n(r, t)}{\partial t} = \nabla \cdot [D \nabla n(r, t)] + \nabla \cdot [vn(r, t)] - Kn(r, t) + Gn(r, t) \quad (5.1)$$

The four terms on the right-hand side correspond to diffusion, drift, exciton recombination and generation, respectively, with exciton density distribution $n(r, t)$, diffusivity $D$, drift velocity $v$, exciton recombination rates $K$, and exciton generation rate $G$. Since excitons are quasi-particles with net zero charge, drift is not associated with electric
field, but with exciton energy gradients in the material. We assume for amorphous organic thin films, the energy landscape is disordered, with spatially random variations, resulting in zero net drift \( \mathbf{v} = 0 \). Since we use a pulsed laser to produce exciton population on time scale much faster than that of the exciton lifetime, we set the generated exciton population as initial condition \( n(r, t = 0) \) and a generation rate \( G \) of zero. Assuming diffusion is independent along the 3 spatial dimensions and independent of density, which holds true for the low excitation intensities used in measurements, we can simplify Eq 5.1 to

\[
\frac{\delta n(x, t)}{\delta t} = D \frac{\delta^2 n(x, t)}{\delta t^2} - Kn(x, t) \tag{5.2}
\]

We can use the Fourier Transform method and solve this equation in spatial frequency \( k \).

\[
\tilde{n}(k, t) = \int_{-\infty}^{\infty} n(x, t)e^{-2\pi i k x} dx
\]

\[
\frac{\delta \tilde{n}(k, t)}{\delta t} = [-D(2\pi k)^2 - K] \tilde{n}(k, t) \tag{5.3}
\]

Approximating diffusively \( D \) and exciton recombination rate \( K \) as constants during the exciton diffusion, we find a general solution in the form of

\[
\tilde{n}(k, t) = e^{-Kt} \tilde{n}(k, 0)e^{-4\pi^2Dt k^2} = A(t)\tilde{n}(k, 0)\tilde{g}(k, t) \tag{5.4}
\]

The spatially independent term \( A(t) = e^{-Kt} \) is the simplified solution of exciton recombination, both non-radiative and radiative, as discussed in chapter 2. The spatially depended terms of the solutions describes the spatial distribution of an ensemble of particles dependent on an initial condition \( \tilde{n}(k, 0) \) and diffusion characteristic given by a Gaussian function broadening function

\[
\tilde{g}(k, t) = e^{-4\pi^2Dt k^2} \tag{5.5}
\]
The inverse Fourier transform of the solution results in the more familiar Gaussian solutions of the diffusion equation.

$$g(x,t) = \frac{1}{4\pi Dt} e^{-\frac{x^2}{4Dt}} = B(t)e^{-\frac{x^2}{2\sigma_x(t)}}$$

$$n(x,t) = A(t)n(x,0) * g(x,t) = \frac{A(t)}{4\pi Dt} \int n(\xi,0)e^{-\frac{(x-\xi)^2}{4Dt}} d\xi \quad (5.6)$$

In the case of a single particle system where \(n(x,0)\) is a delta function, \(n(x,t) = A(t)g(x,t)\) would give the probability distribution of the particle. In experimental measurements, \(n(0,t)\) is the spatial profile of the excitation pulse. In preceding studies using optical imaging of exciton diffusion, the initial excitation profile \(n(\xi,0)\) was assumed to be a diffraction-limited spot modeled by a Gaussian function [90,91]. This would simplify the solution such that for each discrete time binning interval \(t_j = j\Delta t\), a simple Gaussian fit of emission spatial profile \(g(x,t_j)\) would produce the spatial change in emission width \(\sigma_x(t)\). However, due to the additional spatial constraints of interfacial states between donor and acceptor molecules, CT excitons should have much smaller diffusion length compared to LE previously measured in organic and nanocrystal thin films, which were on the order of or larger than \(~100\ \text{nm}\). Thus, the residual in Gaussian approximating the initial excitation profile can have a significant impact on measured changes in emission profile width.

To reduce any errors associated with approximating the initial exciton density with an analytic function, we use the measured emission profile at \(t = 0\) instead. Additionally, we push the resolution limit of the imaging system and analyze the measured emission profile in the spatial frequency domain. The spatial profile for each time slice was normalized to remove the recombination rate dependence \(A(t)\). Fig. 5-4 illustrates the analysis steps using the Fourier transform method. Fig. 5-4 (a) plots the typical CT emission in m-MTDATA:3TPYMB 1:1 molar doping thin film, reconstructed as an intensity color plotted vs. space and time.

The 2-D mapping consists of 655 ns binned temporal slices of spatial profile, two
Figure 5-4: Fourier transform analysis of diffusion imaging. (a) Example of fluorescence intensity (color scale) plotted vs. time and sample position, normalized for each 655 ns time bin. (b) Normalized spatial profile for $t = 0$ ns and $t \sim 30$ µs. (c) Fast Fourier Transform of spatial profile at select temporal slices illustrating change in spatial frequency content in frequency domain. (d) Ratio between $\tilde{n}(k, t_j)$ and $\tilde{n}(k, 0)$ resulting in broadening function $\tilde{g}(k, t)$ plotted in spatial frequency domain.
of which are shown in Fig. 5-4 (b) for \( t = 0 \) ns and \( t = 30.8 \) \( \mu \text{s} \). We perform Fourier transform on the measured spatial profiles to get \( \tilde{n}(k, t_j) \) (Fig. 5-4 (c)). A limited range of low spatial frequencies was used to eliminate high frequency noise in the analysis. The spatial broadening function \( \tilde{g}(k, t_j) \) (Fig. 5-4 (d)) can be calculated in frequency domain using

\[
\tilde{g}(k, t_j) = \frac{\tilde{n}(k, t_j)}{\tilde{n}(k, 0)} = e^{-\frac{k^2}{2\sigma_k(t)}} \tag{5.7}
\]

To eliminate the effects of background noise offset for each time slice in real space, we ignore the zero frequency point and perform Gaussian fits of \( \tilde{g}(k, t_j) \) (see Fig. 5-5), resulting in values of \( \sigma_k(t) = \frac{1}{2\pi\sqrt{2Dt}} \).

We convert the fitted change in the broadening function into real space axis using \( \sigma_x(t) = \frac{1}{2\pi\sigma_k(t)} \) to attain a better intuition of the spatial dependence. Measurement artifacts due to the high intensity and large variations in emission lifetime were observed at \( t = 0 \). Thus, we compared the change in standard deviation at each time point to that at \( t = 400 \) ns (\( \Delta\sigma(t) = \sigma_x(t) - \sigma_x(t = 400 \text{ ns}) \)).

![Figure 5-5: Example of Gaussian fitting of \( \tilde{g}(k, t) \) in frequency domain.](image)

Four independent sets of CT diffusion intensity maps were analyzed for samples of m-MTDATA:3TPYMB thin films at 1:1 molar doping. Fig. 5-6 plots the average value and standard error of \( \Delta\sigma(t) \) between the independent measurements for each time bin.

88
As discussed in previous chapter, without radiative recombination and back transfer losses, CT triplet excitons in m-MTDATA:3TPYMB are long-lived, allowing exciton diffusion to be observed up to $\sim 30 \mu s$ after excitation.

Figure 5-6: Change in standard deviation of the spatial broadening Gaussian function, extracted from Fourier analysis technique, showing CT state diffusion. Each red circle indicates average value with error bars plotting standard error between 4 independent diffusing imaging measurements. The overlaid line indicates results of averaged CT motion from kinetic Monte Carol simulation.

To evaluate the CT state transport, we compare the results with that of CBP:Ir(ppy)$_3$ at 1% doping by weight. Fig. 5-7 compares the change in standard deviation for the two organic thin film samples, scaled by triplet exciton lifetime measured for each material. Note that for both samples, the change in standard deviation is consistently compared to that at $t = 400$ ns to avoid measurement artifacts. We expect the exciton transport in the reference samples of CBP:Ir(ppy)$_3$ to be dominated by Dexter transfer for triplet excitons, which is limited by the large spacing between Ir(ppy)$_3$ molecules in the low concentration samples. The same imaging system and analysis technique shows statistically significant differences between the measured diffusion for the 2 material systems. This validates the direct spatial and temporal visualization of CT exciton
motion, revealing that CT states can travel over 5 - 10 nm along molecular interfaces.

Figure 5-7: Diffusion comparison between m-MTDATA:3TPYMB at 1:1 molar ratio and 1% doped CBP:Ir(ppy)₃ control samples. Change in standard deviation of the spatial Gaussian broadening component plotted as a function of exciton lifetime. Each circle indicates an average value with error bars plotting standard error between independent diffusing imaging measurements for samples of m-MTDATA:3TPYMB at 1:1 molar ratio (red) and for reference samples of CBP:Ir(ppy)₃ at 1% doping by weight (black). The fitted delayed fluorescence lifetime used in comparison is noted in the legend. The solid lines show linear fits and corresponding 95% confidence interval for all data sets, indicating significant deviation from reference sample.

5.4.2 Charge Transfer State Characteristics

Most of the PL study on m-MTDATA:3TPYMB thin films can be found in the previous chapter. Here, we focus more on measurements and properties relevant to understanding transport mechanism behind the observed CT diffusion.
Excitation Power Dependence

To investigate the artificial contribution of bi-exciton interactions towards observed spatial broadening of CT exciton luminescence, we measure excitation power dependence in TRPL. Fig. 5-8 shows no notable change in the transient dynamics as a function of optical pump power over the range of powers used in diffusion measurements. This is consistent with luminescence from tightly bound, geminate CT exciplex states.

As previously discussed, m-MTDATA:3TPYMB exhibits the transient characteristic of typical thermally activated delayed fluorescence (TADF) materials [83], with prompt fluorescence from the singlet CT states followed by delayed fluorescence (~19 μs) as the triplet CT states are thermally-activated back to the fluorescent singlet CT state [71, 72].

Figure 5-8: Normalized CT state TRPL of m-MTDATA:3TPYMB (1:1 molar ratio) for select excitation powers. The overlap in CT state TRPL over the measured time interval indicates a geminate emissive CT population, whose dynamics are independent of excitation power.

Combined with delayed fluorescence and the slow radiative rate, the dynamics of CT states in m-MTDATA:3TPYMB are much slower than that of a typical OPV material.
system [88, 89]. However, as shown in Fig. 4-16 (a), the peak external quantum efficiency (EQE) of simple bulk heterojunction devices is comparable to other material systems, despite the slow dynamics. Thus, CT states in m-MTDATA:3TPYMB present a good modeling system to explore the dichotomy between Coulombic binding and charge separation. Albeit on a slower timescale, the CT dynamics in this system are representative of the key physics in OPVs that do not exhibit hot CT state dissociation.

**Charge Transfer State Energy Shift**

To confirm observed CT exciton diffusion, we use a streak camera to measure the spectrally resolved TRPL of m-MTDATA:3TPYMB 1:1 molar ratio thin films. Concurrent with CT state diffusion, a red shift in peak emission wavelength is observed (Fig. 5-9). The overall spectral shift between \( t = 0 \) to \( t = 30 \) \( \mu \)s corresponds to a decrease in energy of approximately 60 meV. This is within the order of binding energies expected for tightly bound, geminate excitations. We observe consistent trends between spectral redshift and the spatial broadening, identifying a correlation between CT state transport and change in CT energy. Confirmation with theoretical modeling will be further discussed in a later section on Monte Carlo simulation.

![Figure 5-9: Spectrally resolved streak camera measurement of CT state emission showing red shift in peak emission wavelength. The centroid of the data (dotted line) is compared to the spectral shift predicted by the kinetic Monte Carlo simulation (circles).](image)
5.4.3 Electric Field Dependence

Since this change in CT energy has ramifications for charge separation in OPVs, we explore the effect of external electric field on charge dissociation and PL quenching.

Steady State Photoluminescence

We start by measuring steady state CT emission on device samples of 1:1 molar ratio as a function of externally applied electric bias. The resulting PL spectrum shows the expected quenching effect as described by the Poole-Frenkel model of charge tunneling under electric field \([17, 92]\). Furthermore, the normalized PL spectrum shows slight blue shift under bias. This suggests CT states stretching under electric field, resulting in lower CT binding energy.

![Figure 5-10: (a) CT state PL spectrum under electric fields showing steady state quenching effects. (b) Normalized CT state PL spectra showing blue shift under applied electric field, suggesting lower binding energy due to stretched CT states.](image)

Time-resolved Photoluminescence

The TRPL of the same device samples were measured under external electric bias. We focus on the first few \(\mu s\) after excitation, the time frame with largest change in CT
emission energy from Fig. 5-9. For comparison, we integrate intensity under TRPL curves over three separate time bins: 50 - 200 ns, 1 - 1.5 μs, and 3 - 3.5 μs resulting in PL1, PL2, and PL3, respectively (Fig: 5-11 (a)).

Figure 5-11: (a) CT time-resolved photoluminescence indicating the three time bins for (b) intensity quenching plot under external bias. Poole-Frenkel model is used to fit observed PL quenching. The estimated change in CT binding energy for the time interval matches Monte Carlo simulation and streak camera results from Fig. 5-9.

Assuming the change in PL intensity is due to field-induced exciton dissociation, then we define a relative PLQY under external field $E$ compared to that of zero field

$$rQY(E) = \frac{PL_i(E)}{PL_i(0)} = \frac{QY(E)}{QY(0)}$$  \hspace{1cm} (5.8)

Using Eq. 2.9, we can express this equation in terms of field-independent radiative recombination rate $k_r$, non-radiative recombination rate $k_{nr}$, and field-dependent quenching $k_q(E)$.

$$rQY(E) = \frac{k_r}{k_r + k_{nr} + k_q(E)} = \frac{k_r + k_{nr}}{k_r + k_{nr} + k_q(E)}$$  \hspace{1cm} (5.9)

Given that $k_0 = k_r + k_{nr}$ can be found by fitting the zero-field TRPL over the corresponding time intervals, we can calculate the field-induce quenching rate for each field
The quenching rate corresponding to each time interval is plotted in Fig. 5-11 (b). Assuming a direct relationship between PL quenching and charge tunneling, tunneling current \( J \) due to exciton dissociation can be modeled using Poole-Frenkel theory for bound states at high external electric fields as [17,92]

\[
 k_q \propto J \propto \exp \left( \frac{-q}{kT} \left( \phi - \sqrt{\frac{qE}{\pi \epsilon_r \epsilon_0}} \right) \right) 
\]

(5.11)

where \( \phi \) is the charge tunneling energy barrier. We can fit the observed quenching rate using Eq. 5.11 at the applicable high external fields, using \( \epsilon_r = 3.5 \) at room temperature. By taking the difference between the zero-field intercept of the fits for the 3 time regimes, we can estimate the change in binding energy \( \Delta \phi \) of the CT exciton over time. The results show a systematically increase in CT binding energy, consistent with the red shift observed in the spectral dynamics; the change in binding energy is estimated to be 12 meV between \( t = 1 \) \( \mu s \), and \( t = 3 \) \( \mu s \), which agrees with CT energy redshift over the same time interval. Since the delayed fluorescence stems from generated triplet population, which reverse intersystem crossing back to the emissive singlet, we estimate the exchange splitting to be \( \sim 51 \) meV, consistent with prior report [71] based on the temperature dependence of TRPL. The observed effects of excitation power and electric field dependence confirm that CT excitons in this system behave as tightly bound particles with geminate characteristics.

5.4.4 Monte Carlo Simulation

In conjunction with the diffusion imaging, these experimental results suggest bound, geminate CT exciton diffuse by transport of both charges in the exciton. However, the detailed mechanism of CT state transport remains unclear. The optical absorption of the CT state is negligibly low, suggesting that Förster transfer is not likely to be
effective. Although the Dexter mechanism is possible, CT states are weakly bound compared to most intra-molecular excitonic states. More efficient transport of CT excitons may occur via asynchronous charge hopping, whereby the electron and hole navigate the material in a non-simultaneous, but correlated fashion as Coulomb-bound particles. The consequences associated with this description of CT state dynamics is explored using a numerical kinetic Monte Carlo (KMC) simulation. The resulting theoretical model, where a CT state is treated as separate charges diffusing in the field of its partner, predicts CT dynamics that coincide with experimental results (see Fig. 5-6 and 5-9).

In this 2-D coarse-grained model, the organic thin film is represented as individual molecules arranged on a square lattice that is divided by a linear donor-acceptor interface. To reflect the inhomogeneous broadening due to local energy disorder, energies of individual molecular sites are perturbed according to a Gaussian distribution with a mean and variance derived from experimentally observed spectral data. Each CT exciton is modeled as separate electron and hole, each localized on a single acceptor or donor molecule, respectively. The energy of CT state is simply the difference of the donor HOMO and acceptor LUMO energies, with a screened Coulomb potential acting between the electron and hole (effective dielectric constant of $\epsilon_r = 3.5$). A hopping rate that depends on the change in electron-hole separation and CT state energies determines the CT exciton temporal evolution via site-to-site hopping for each individual quasi-particle [93]).

IQE can also be modeled by accounting for the fraction of CT excitons that undergoes charge dissociation, and can be tuned by charge hopping rates. When the electron and hole reside on neighboring sites along the donor-acceptor interface, the exciplex CT state can undergo geminate recombination with probability based on exciton lifetimes estimated from TRPL (Fig. 5-8). The average distance and energy difference between the randomly generated initial CT exciton and the site of eventual exciplex emission is modeled and recorded. The theoretical results simultaneously account for both the

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1In collaboration with Liang Shi and Chee Kong Lee.
Figure 5-12: (a) A schematic of a representative trajectory from KMC simulations. Red and blues circles are, respectively, the donor and acceptor molecular sites in a square lattice. The color gradient represents the distributions of the HOMO energy of the donors and the LUMO energy of the acceptors, as indicated by the color scale. The labels (a-d) indicate time stamps in the trajectory. (b) The time evolution of the CT exciton energy (top, magenta line) and the electron-hole separation (bottom, dark green line). The labels (a-d) correspond to the time stamps from (a). Courtesy of Liang Shi and Chee Kong Lee.
transient red-shift of CT energy (white circles in Fig. 5-9) and spatial broadening due to CT diffusion (blue line in Fig. 5-6), supporting experimental observations. Charges preferentially diffuses to lower energy sites due to local energy disorder reflected as an energy change. Correlated diffusion of electrons and holes along the interface, bound by Coulomb attraction, results in a stretching and contraction motion (Fig. 5-12).

Figure 5-13: Simulated average root mean square displacement (RMSD) of the CT excitons as a function of time after excitation for a system with charge hopping rate of 50 $ns^{-1}$ and $k_{PL} = 0.2$ $ns^{-1}$. This model system has IQE of 68% - 75%. Courtesy of Liang Shi and Chee Kong Lee.

Ideally, we should applied the same measurement techniques on traditional OPV materials to directly observe CT state transport. However, diffusion dynamics cannot be optically imaged for short-lived CT states due to poor luminescence. Instead, we simulated OPV material systems using the developed KMC model based on energetic disorder, first order hopping, and geminate radiative recombination. Diffusion distances are unaffected when hopping and recombination rates are scaled by the same factor. Thus, for a short-lived CT exciton with reasonable IQE parameters, we find that CT state diffusion characteristics are comparable to the measured long-lived CT states (Fig. 5-13).

Note that this model includes energetic disorder, hopping or geminate recombination, and does not account for short-lived CT exciton with significant physical mecha-
nisms not observed in m-MTDATA:3TPYMB, such as transport of hot CT states.

5.4.5 Magnetic Field Effects

The stretching and contraction of charges in CT state transport is further confirmed using the magnetic field technique, which is capable of exploring relative displacement of the electron and the hole. As noted in detail in the previous chapter, MFE in excitonic states are only observed if the Zeeman splitting induced by the field is comparable to or larger than the exchange splitting. Thus, MFE should not be observed in CT states with exchange splitting of ~50 meV. The m-MTDATA:3TPYMB system, however, does exhibit magnetic field effects on both PL and photocurrent as shown in Fig 4-13 and 4-14 suggesting that the CT states can stretch while remaining bound.

The shape of the magnetic field dependence provides insight into the spatial dynamics of the electron and hole, due to spin relaxation effect in charge hopping. According to the model of Schulten and Wolynes [94–96], the saturation of the magnetic field effect is determined by the applied magnetic field, the strength of the hyperfine field at each molecule, and the rate at which a charge hops to neighboring molecules. Assuming that the effective hyperfine field at each molecule is randomly oriented with deviations in the nuclear magnetic fields, as a charge hops from molecule to molecule, it experiences fluctuating local magnetic field. This induces transitions between spin states, leading to spin relaxation of a stretched CT state [97]. Consequently, stronger magnetic fields are required to suppress intersystem crossing when the charges are more mobile and visit more sites, with a less sharp saturation curve. Thus, the curve shape of MFE on CT PL can reveal the relative degree to which these charges travel; a more sloped saturation at higher fields reflects charges visiting a larger number of molecular sites, before radiative recombination.
Temperature Dependent Magnetic Field Effect

We start by examining the temperature dependence of the MFE on CT state PL. As shown in Fig. 5-14, we find the magnitude of MFE on PL to be thermally activated, consistent with expectations that fewer CT states should stretch at lower temperatures. The shape of the magnetic field dependence as a function of temperature shows no obvious changes in saturation behavior above 100 K (Fig. 5-14(b)). In other words, within the measured range of temperatures, no measurable change in spin relaxation is observed. Instead, the more significant effect of lower temperature is the decrease in the number of CT states that stretch beyond the exchange radius, thus decreasing the overall magnitude of the observed change in PL.

![Figure 5-14](image)

Figure 5-14: Temperature dependence of the magnetic field modulation of CT state PL. (a) MFE is defined as the percent change in steady state PL with applied magnetic field. The magnitude of the change in PL decreases at lower temperature, indicating magnetic field-dependent hyperfine mediated intersystem crossing decreases with lower thermal energy. (b) MFE normalized to high field shows no change in the shape of the magnetic field dependence over this range of temperatures.

Electric Field Dependent Magnetic Field Effect

However, a significant change in spin relaxation is observed under different electric fields (Fig. 5-15). A device under open circuit condition experiences photo-generated...
voltage of $V_{OC} = 1.5$ V over the 60 nm thin film (see Fig. 4-16(b)), which is removed under closed circuit with charge extraction. Under open circuit condition, charges in CT excitons can visit more molecular sites before radiatively recombining, increasing the observed spin relaxation to produce a slower saturation of the magnetic field effect.

Figure 5-15: Magnetic field effects on CT state PL at open and closed circuit. The magnetic field effect of bulk heterojunction devices (1:1 molar ratio) under magnetic field at open-circuit and closed-circuit demonstrates that application of an electric field distorts the size of the CT state.

On the other hand, in the closed circuit condition, CT excitons experience more charge dissociation, which reduces the observable spin relaxation effect in PL. This is consistent with a net extension in the CT states seen in the PL slightly blue shifting under an electric field in Fig. 5-10.

**Dopant Ratio on Magnetic Field Effect**

We also measured the MFE on PL for blend films of select molar doping ratio of donor and acceptor molecules (Fig. 5-16). Similar to the temperature dependent MFE, a change in the MFE magnitude is observed. The effect of dopant ratio on MFE in terms of maximum change in PL is plotted in Fig. 5-17. We observe the MFE peaks around the doping ratio of 3:1 donor/acceptor, indicating holes may dominate in charge hopping in stretched CT states.
Overall, MFE studies support asynchronous electron and hole hopping CT exciton transport mechanism. We observe fluctuations in the electron-hole spacing during the lifetime of the CT states, but the relative displacement is sufficiently small that the electron-hole pair remains bound as they move between molecular sites.

Figure 5-16: (a) Magnetic field effects on CT exciplex PL at closed circuit on m-MTDATA:3TPYMB device samples of select donor-acceptor doping ratios. (b) MFE on CT exciplex PL normalized at 0.054 T to compare changes in saturation curve.

Figure 5-17: Maximum percent change in PL under magnetic field for various molar ratio of donor/acceptor blended thin film devices. Each circle indicates average of independent measurements with error bars representing standard error.
5.5 Conclusion

In this chapter, we explore transport of CT states in m-MTDATA:3TPYMB blended thin films using direct optical imaging, TRPL, and MFE studies under various electric field, temperature, and doping conditions. Combined, these results demonstrate transport of bound CT excitons by asynchronous charge hopping mechanism to lower energy CT states. We observe CT exciton motion on the order of 5 - 10 nm with significant decrease in CT energy over time, consistent with theoretical modeling. In summary, we consider the effect of this observed CT state transport for organic optoelectronic devices. Since donor-acceptor blends typically exhibit ultrafast conversion from excitons to CT states, it is possible that CT state diffusion distances in many organic bulk heterojunction-based devices may exceed that of the initial exciton, highlighting the potential importance and impact of CT state transport on device performance.

For the purpose of exciton dissociation, the probability of charge separation is significantly higher if the CT state is aligned with the electric field [17, 92, 98]. The ability of the CT state to move may help to reorient the CT states to lower energy, field-aligned sites in a donor-acceptor bulk heterostructure film. Constraining the percolation networks in phase-separated donor-acceptor blends, where CT states can only diffuse along the grain boundaries, may significantly reduce the diffusion distances and still allow the states to orient for charge separation. Alternatively, CT state transport may also enhance photocurrent yields if diffusion occurs between higher CT energy states in finely mixed regions of the blend and phase separated boundaries, where the CT state energies are lower [99] and the photocurrent yield may be higher [100]. On the other hand, mobile CT states have freedom to seek lower energy trap states where binding energy is higher, consequently reducing overall charge dissociation in OPVs. A study of various heterostructure morphologies coupled with simulations should help identify the optimum tradeoff between diffusion and trapping for various applications.
6 | Ultrafast Electric Field Effects on Exciton Dynamics

6.1 Overview

Since excitonic materials have many interesting properties for optoelectronic applications, the effects of direct current (DC) and low frequency alternating current (AC) electric field on exciton generation and dynamics have been well investigated. In this chapter, we consider the largely unexplored regime of ultrafast electromagnetic radiation on exciton dynamics and generation, using an electric field with picosecond oscillations. These terahertz (THz) frequencies fall between electrical and optical regimes on the electromagnetic radiation spectrum. By focusing intense THz radiation in organic and quantum dot (QD) thin films with metallic field enhancement structures (FESs), we observe electric field-based THz-driven exciton luminescence (THz-L). Unlike electroluminescence (EL) or photoluminescence (PL), THz-L does not require direct charge injection from electrodes nor photon energy to be higher than exciton bandgap energy. We explore the main mechanisms behind THz generation of excitons in QD thin films through THz field strength dependence. These high strength, ultrafast electric fields also enables observations of non-perturbative field effects in QD thin films, demonstrating quantum confined Stark effect (QCSE) with over 0.5 eV change in exciton bandgap energy. Observations of THz-L and changes in exciton dynamics suggest potential application of excitonic thin films for THz detection and imaging.
6.2 Introduction

Thus far, we have mainly focused on PL characterizations and photocurrent generation. We have briefly touched upon some perturbative effects of external electric fields on optical and electrical properties of excitons. For example, electric field quenching of exciton PL [17, 92] was observed for CT state excitons in chapter 5 (Fig. 5-11). Also, Stark perturbation of the exciton under electric field contributes to solvation effects in chapter 3 and can also be observed in typical redshifts in energy between EL and PL [101, 102].

For exciton generation, we often optically excite semiconductors to produce PL (ex: optical downconversion [103], lasers [104], bio-imaging [105]) or electrically drive charge injection to produce EL (ex: OLED [2] or QDLED [4]). For the latter, EL mechanism based on direct charge injection from electrodes into organic or QD semiconductors is typically assumed, but is not the only method.

Often overlooked, AC electric fields can also generate exciton luminescence, without charge injection in both organic and QD thin films in capacitive structures. For example, AC field-driven QD luminescence has been demonstrated, where an electric field perturbs the relative energy levels of exciton sites, aiding in charge tunneling between conduction band (CB) and valence band (VB) between neighboring QDs. This charge hopping effectively ionizes neutral QDs, creating excited charges in the semiconductor. Unlike DC fields, which would pull the charges apart, time-dependent AC field allows exciton formation and recombination due to oscillatory field directions [102, 106]. A similar effect can be observed for AC excitation of organic thin films in capacitor devices. [107, 108].

Exciton generation under AC electric fields has a threshold depending on the voltage difference across exciton sites, which need to be comparable or larger than the band gap energy per charge. This voltage difference scales with the applied field strength. Additionally, previous works explored the frequency dependences for AC driven lumi-
nescence, up to \( \sim 100 \) kHz [102].

On the other hand, optical excitation is often considered as quantized photons, with the exciton generation threshold requiring photon energies equal or larger than the exciton band gap. However, photons are simply pulses of electromagnetic radiation in the sub-petahertz frequency regime. Consequently, between kHz and pHz frequency range, the key to exciton generation switches from electromagnetic field intensity to photon wave-packet energy. Thus in this chapter, we explore the extent by which exciton generation and properties can be controlled by ultrafast electric fields.

![Figure 6-1: AC electric field-driven luminescence of ZnSe/ZnS:Mn/ZnS QDs in capacitor device structure to prevent direct charge injection. Comparison of AC driven EL with solution and thin film PL indicates exciton emission from multiple exciton populations including neutral and charged QDs. Increase in luminescence intensity is shown to increase with applied field strength and frequency. [102]

Different regimes of the electromagnetic spectrum have been exploited for a range of applications, from microwave electronics and radio communications to \( \gamma \)-ray detection for astrophysics. Between the radar frequencies and IR lies the THz regime. Drawing recent attention, THz radiation has many intriguing properties that would enable novel applications in detection and sensing. Due to unique THz spectral signatures of compounds, it is possible to image through material without the risks of high-energy radiation techniques such as X-ray imaging. This technology has range of compelling
potential applications, including high-resolution imaging [109–111], security screening and explosives detection [112,113], industrial quality control [114,115], biomedical testing [116], and high-performance wireless communications [117]. Despite recent developments in more intense sources, inexpensive, room-temperature, large area THz detection technology still needs improvements, limiting wide range applications. Thus, understanding material response under ultrafast electric fields may provide insight into new THz detection methods.

Figure 6-2: THz spectral imaging of illicit drugs and compounds. (left) Absorption spectra of MDMA, aspirin, and methamphetamine. (right) Imaging of MDMA (yellow), aspirin (blue), and methamphetamine (red), placed inside a shipping envelope. Yellow outline presents imaging area. Figure from Ref [112].

Many recent works focused on THz manipulation of material and charge properties including field ionization [118], impact ionization [119,120], and material phase transitions [121]. In these studies, to achieve high field strengths (over MV/cm peak fields), many have made use of field enhancement structures (FESs), including subwavelength, metallic antennas and split ring resonators (SRRs) [118,121–124]. Here, we apply THz FES techniques to study exciton properties of organic and QD thin films under ultrafast electric fields, with promising applications in THz detection and imaging.
6.3 Methods

6.3.1 Optical Setup for Terahertz Generation and Imaging

Figure 6-3: Single cycle THz pulses are generated using an ultrafast Ti:sapphire laser in an optical rectification setup with a LiNbO$_3$ crystal. A pair of wire grid polarizers with variable relative angle controls the field strength of the vertically polarized THz pump. A pair of gold parabolic mirrors focus the THz radiation on to the sample, and subsequent luminescence is filtered and imaged into visible detectors. A wavelength tunable optical probe can be generated using a NOPA setup. We can place a ZnTe crystal in the sample position and a removable mirror in the beam path to divert the optical probe beam to an electro-optic sampling setup for THz characterization.

To generate high strength single-cycle THz fields, we use a common technique known as optical rectification [125,126]. A vertically polarized 800 nm wavelength laser beam with 1 kHz repetition rate and 35 - 100 fs pulse width is directed towards a grating to create a tilted wavefront. This tilted wavefront propagates through a half-wave plate for polarization matching, then is focused into a LiNbO$_3$ crystal to generate THz.

\textsuperscript{1}In collaboration with Brandt Pein.
radiation (Fig. 6-3). A teflon filter transmits THz radiation while blocking 800 nm laser excitation. A pair of wire grid filters with variable relative angle transmits a vertically polarized THz field with controllable field strength. A pair of gold-coated parabolic mirrors focuses the generated THz radiation onto the sample holder with a beam waist of \( \sim 1 \) mm. A pair of optical lenses is used to image sample luminescence into a spectrometer or single photon avalanche photodiode detector (APD) for characterization.

For THz pump - optical probe measurements, a 90/10 beam sampler is placed in path of the 800 nm laser to divert a fraction of laser intensity into a non-collinear optical parametric amplification (NOPA) system. This generates a wavelength tunable optical probe over 500 - 900 nm. Band filters are used to select the probe wavelength at NOPA output. The optical delay between the THz pump and optical probe pulses for temporal matching is adjusted using a motorized mechanical stage. The probe is focused onto the sample through the second parabolic mirror.

Fig. 6-4 shows typical characteristics of the generated THz pulse as measured using electro-optic sampling technique, with a ZnTe crystal at sample position and 800 nm probe pulse.

![Figure 6-4: Typical characteristics of generated THz pulse, with excitation frequency centered around 0.5 THz. Courtesy of Brandt Pein.](image-url)
6.3.2 Sample Fabrication

The samples under test have two major components: FES patterned substrate and excitonic thin film. Both microslit and SRRs structures were fabricated (Fig. 6-5) with various dimensions to tune the frequency dependent enhancement factors. Non-resonant microslit FES with 98 μm gold (Au) bar with 2 μm gaps were used as standard samples, with large active area (7 mm x 7 mm), for more in-depth studies. Standard negative photolithography technique was used to pattern the FES on quartz substrates (See Appendix A).

Figure 6-5: FESs used in THz detection devices. (left) Optical microscope imaging of microslit and SRRs FES. The schematics show field enhancement within the gap, as indicated in red. (right) Front and cross sectional view of completed device with organic or QD emissive layer deposited on standard Au FES of 100 μm periodicity microslit with 2 μm gaps (not to scale).

Organic thin films of 200 nm thick neat Alq₃ or doped Alq₃:DCM (2% wt.) were thermally evaporated on FES substrates for organic THz samples. To avoid photo-oxidation effects, organic samples were packaged with quartz cover glass and epoxy.
Thin films of ~ 200 nm CdSe/CdS QD with oleic acid ligands (synthesized by Igor Coropceanu [127]) were spun coated from solutions of octane onto FES substrates to create QD THz samples. For the characterization of THz-L, CdSe cores of 4.1 ± 0.3 nm diameter were used to synthesize core-shell QDs with varying thicknesses of CdS shells. As shown in the tunneling electron microscope (TEM) image in Fig. 6-6, the synthesized QDs are labelled as QD1 (diameter = 8.5 ± 0.6 nm), QD2 (diameter = 11.9 ± 0.6 nm), and QD3 (diameter = 14.0 ± 0.9 nm), in increasing shell thickness.

![TEM images of CdSe/CdS QDs](image)

Figure 6-6: Transmission electron microscope images of CdSe/CdS QDs for THz luminescence.

### 6.4 Results and Discussion

Organic Alq3:DCM thin films have similar characteristics to those of Alq3:DCM2 previously studied (See chapter 3), where excitons generated in Alq3 can quickly Förster transfer to the lower energy dopant DCM.

As shown in Fig. 6-7 (a), absorption and photoluminescence of CdSe/CdS QD thin films exhibit typical optical characteristics with 2 eV exciton energy. The measured PL quantum yield of QD thin films were ~ 18 - 21%. Fig. 6-7 (b) shows the work function of Au and energy bands of CdSe and CdS as reference.
Figure 6-7: (left) Typical absorption (blue) and emission (red) of CdSe/CdS QD1 thin film. (right) Work function of Au and energy levels of VB and CB of bulk CdSe and CdS semiconductors.

6.4.1 Terahertz-Driven Luminescence

Figure 6-8: Camera images of THz-L. (left) CdSe/CdS QDs on 98 μm periodicity Au microslits with 2 μm gaps. The blue dotted line indicates the typical spot size (~ 1 mm) of focused THz radiation. (inset) Magnified view of microslit gap showing intense THz-L from gap edges. (right) Alq₃:DCM 2% wt. on 80 x 80 μm SRRs with 3 μm gaps. Yellow dotted lines outlines Au SRR structures.

In the absence of electrical current or optical excitation, THz-L was observed in both organic and QD devices. Using a Si CCD camera, we can capture images of sample
THz-L (Fig. 6-8). Both microslits and SRRs devices shows that THz-L is dominated by emission from the gaps of the FESs.

Fig. 6-9 plots the THz-L spectra of typical organic and QD THz devices, which are similar to the corresponding PL spectra. Consistent with standard PL, QD exciton energy is red shifted for thicker-shelled dots due to lower confinement. As expected, intensity of THz-L is non-linearly dependence on the peak field strength of the THz pump, with no emission observed below a certain incident THz peak field strength (\(\sim 100 - 150 \text{ kV/cm}\)), which we define as THz-L threshold \(F_{th}\).

![Figure 6-9: Typical THz-L spectra of fabricated CdSe/CdS QD and Alq3:DCM devices](image)

**6.4.2 Time-Resolved Luminescence**

Focusing on QD samples, we compare time resolved THz-L and PL using an avalanche photodiode (APD), as shown in Fig. 6-10. The same samples were measured in corresponding THz-L and PL measurements to avoid sample dependent variations.

In all QD samples, THz-L shows clear multi-exponential curves compared to the time-resolved PL (TRPL), with a significant drop in exciton lifetime during early time (0 - 20 ns). The contrast highlights differences in emissive exciton population between THz-L and PL. While PL shows the mono-exponential characteristics of neutral QDs, THz-L seems to be dominated by multiple populations of short-lived excitons on charged QDs, reminiscent of TRPL observed in QD blinking [29,128].
Figure 6-10: Comparison of time-resolved THz-L and PL for QD1, QD2, and QD3 microslit samples. Multi-exponential characteristic of THz-L indicates emission dominated by charged QD populations compared to mono-exponential PL.

Figure 6-11: Comparison of time-resolved THz-L at different THz pump peak field strength for QD1 microslit sample. Each curve is fitted to a bi-exponential modeling neutral and charged QD populations as indicated by dashed lines.

For more in-depth study, we focus on standard samples of QD1 on microslit with 98 μm Au bars and 2 μm gaps. Charging of QDs is further confirmed by THz peak field strength dependent measurements (Fig. 6-11). Comparing the time-resolved THz-L just above the THz-L threshold (130 kV/cm) and maximum THz pump intensity (320
kV/cm), we can see an increase in the non-radiative recombination rates for the higher pump field strength. However, even around the threshold, THz-L exciton lifetimes are drastically different than that of TRPL. This indicates exciton formation under THz is likely due to recombination of free charges, producing luminescence modulated by high non-radiative recombination rates.

6.4.3 Terahertz-Driven Exciton Generation Mechanisms

Spatially dependent field enhancement factors in standard bare microslit FES were simulated using CST Microwave Studio \(^2\) and shown in (Fig. 6-12). Enhancement factors are highest at the gap edge near the substrate, matching our observed spatial THz-L intensity.

![Diagram](image)

Figure 6-12: (left) Schematic of standard samples: bare and oxide-coated microslit samples. (right) Simulated THz field enhancement of a bare microslit sample showing enhancement factors over 100 at gap edges near the substrate.

\(^2\) In collaboration with Harold Hwang.
To understand the mechanisms behind THz generation of excitons, two different types of QD1 microslit samples were fabricated: bare microslits and microslits with plasma-enhanced chemical vapor deposited (PECVD) SiO₂ (Fig. 6-12). The 50 - 80 nm oxide acts as a charge blocking layer to prevent the direct charge injection from the Au FES into the QD layer, isolating field-only mechanism between QDs under THz radiation. We measured THz-L intensity as a function of incident THz peak field strength for both samples to not only find a lower THz-L threshold for bare samples, but also differences in the nonlinear field dependence (Fig. 6-13).

![Figure 6-13: Field strength dependence of THz-driven luminescence in CdSe: CdS QD1.](image)

Varying the incident peak THz field from 0 to 320 kV/cm generates luminescence with a nonlinear dependence. THz-L threshold $F_{th}$ occurs at 85 ± 5 kV/cm in bare samples and 180 ± 7 kV/cm in oxide samples.

Based on these observations, we consider two main sources of free charge under THz radiation: direct charge injection at Au-QD "electrode" interfaces and field-driven tunneling between QDs.
Electrode-Based Charge Injection

Similar to traditional LED operation, an external electric field causes charge injection from the Au FES into the QDs. However, the gap between the lateral Au "electrodes" in this case is on the μm scale and too large for long-range charge transport from opposite electrodes to generate exciton luminescence on the observed time scales. Thus, instead of electron and hole injection at opposite electrodes, we focus on a single Au-QD interface (Fig. 6-14).

Figure 6-14: Schematic of charge injection from Au electrode into QDs under an ultrafast field. The THz field contains multiple temporal lobes with opposite electric field vectors. The electric field can bend the energy levels to allow injection of both hole and electrons during time periods $t_1$ and $t_2$, respectively.

The single cycle THz pulse has oscillating electric fields that could drive both electrons and holes into the QD semiconductor layer from the same metal-semiconductor interface in the bare microslit samples [129, 130]. Sufficient field intensity can cause charge injection at ultrafast time scales, where excited electrons and holes can recombine as excitons. This process depends on the metal work function, which affects the
charge tunneling barriers. However, both negative and positive charges need to be considered; lowering the work function can allow electron tunneling to occur at lower fields, but will raise the hole tunneling barrier, and vice versa. Despite lower work functions compared to Au ($W_{Ag} = 5.1 \text{ eV}$), preliminary results shows THz-L generation in organic devices using aluminum ($W_{Al} = 4.08 \text{ eV}$) or silver ($W_{Ag} = 4.26 \text{ eV}$) [131,132] as FES material.

Following similar works [118,133,134], we assume triangular energy barriers between Au FES and QD under external fields. Fowler-Nordheim equation [135] can be used to estimate the tunneling probabilities to find charge injection threshold. At incident peak THz fields, we estimate injection thresholds for electrons and holes at 125 kV/cm and 220 kV/cm, respectively. These values are higher than the observed bare microslit sample THz-L threshold of $85 \pm 5 \text{ kV/cm}$ in bare samples, which requires both electron and hole injection. Since metal interfaces not only inject charges, but can also quench both charges and excitons, this mechanism is inefficient and cannot account for the observed threshold.

Field-Driven Tunneling in Quantum Dots

At higher incident fields (200 - 300 kV/cm), charge injection mechanism likely contributes to exciton generation, however another mechanism must be involved in THz-L generation around threshold. Not only is charge injection unable to satisfactorily explain the low THz-L threshold, THz-L emission can also be readily observed in oxide samples.

As previously mentioned, external fields can cause charge tunneling from CB to VB between neighboring QDs [102,106]. Assuming an effective dielectric constant of $\varepsilon_r = 3$ for CdSe/CdS QD thin films [106,136] and center-to-center QD distance of 10 nm (QD diameter with oleic acid ligands). The field enhancement factor is integrated at $z = 0$ and multiplied by the peak field strength at THz-L threshold to find the local peak fields experienced by the QDs (Fig. 6-12). Due to the geometry of oxide samples,
the thin oxide barrier layer replaces the QD at the highest field enhancement position, nearest to the Au, so a higher threshold is expected. We find a dot-to-dot voltage drop of 2 V is achieved for the bare microslit and oxide samples around incident peak fields of 86 kV/cm and 186 kV/cm, respectively, closely matching observed THz-L threshold.

Figure 6-15: Schematic of electric field-driven tunneling in QDs. Field enhancement taken from Fig. 6-12 is magnified and overlaid on QDs to illustrate locations of high field strength.

6.4.4 Quantum Confined Stark Effect

The purely field-driven tunneling effect in THz-L generation indicates significant energy band bending between QDs. We can also consider the effect of high local fields (over 10 MV/cm) on the energy and exciton states within a single QD. QCSE has been demonstrated using high DC voltage, where the external fields perturb exciton states and cause red shifts in the absorption and emission on the order of ~ 0.05 eV [137–139].

To observe QCSE using THz, instead of applying high intensity THz to directly generate THz-L, we use THz radiation with field strengths below the THz-L threshold as an ultrafast perturbation field. A coincident sub-bandgap energy optical probe (690 nm - 850 nm) is focused on to samples of QD1 on standard bare microslit; the optical focus is spatially overlapped but smaller than the THz focus spot to ensure an ensemble measurement of QDs under THz perturbation (Fig. 6-3). Without THz fields,
QD absorption is negligible for the long wavelengths optical probes (Fig. 6-7), and no exciton emission is observed. However, in the presence of the THz field, the energy band within a QD can significantly change (Fig. 6-16). At sufficiently high fields, a lower energy photon could be absorbed, which can be observed as exciton emission. Note that since this field effect is limited to picosecond time scales, the emission energy does not change significantly.

Figure 6-16: Schematic of THz driven QCSE on absorption. Without THz pump, sub-bandgap optical probe is not absorbed. In the presence of THz pump, electric field significantly changes the band gap energy. This allows absorption of low-energy optical probe, leading to higher energy exciton emission.

We vary the THz field strength to find the threshold of exciton emission for each optical probe energy. Using the threshold absorbed optical probe energy as a proxy for the QD bandgap, we can monitor the change in QD bandgap energy as a function of THz field strength. Fig. 6-17 shows a clear relationship between QD bandgap energy and incident THz field threshold of exciton emission. This demonstrates unprecedented shifts in bandgap energy (over 0.5 eV) due to QCSE, a first step in exploring the potentials in THz techniques for control and applications of exciton dynamics in QDs and organic optoelectronics.
Figure 6-17: THz-driven QCSE observed through exciton generation using sub-bandgap photon excitations. (left) Photon energy of optical excitation compared with QD1 PL spectrum (dotted line). (right) Threshold of incident THz necessary to observe 2 eV QD luminescence for each optical pump. For higher incident THz, change in absorption energy is over 0.5 eV. Courtesy of Brandt Pein.

6.4.5 Application to THz Imaging

While THz-L and THz-driven QCSE demonstrate how THz radiation can be applied as an insightful experimental technique for excitonic semiconductors, they also have direct applications. Despite the increasing availability of high-power THz sources, current THz frequency applications are limited by their detection. State of the art THz detection often rely on thermal-based detectors such as bolometers and pyroelectrics. These detectors have millisecond responses, cryogenic cooling, with deployment difficulties as camera array detectors. THz imaging is often performed by scanning a single pixel detector, making imaging based applications a time consuming endeavor. To advance THz applications, inexpensive, room-temperature, arrayed detectors with sufficiently high speed, sensitivity, and bandwidth are necessary. A natural progression
of the observed THz-L in organic and QD thin films is developing a scintillator platform for THz detection based on up-conversion of coherent THz field into visible photons. THz-L emission from scintillators can be coupled with visible detectors or cameras, to leverage matured Si-based detection technology for THz frequencies.

**Passive Detection**

The thin film on FES samples used in these work is a prototypical demonstration of a passive detection device. Since simple solution processing of organic or QDs can be used to fabricate a device sample, detection area and resolution is determined by FES structure and geometry and limited by photolithography. The standard samples used in this chapter can be readily used as array detectors (see Fig. 6-8). Resonant and non-resonant FES selection can also lead to devices with corresponding frequency dependent or broad-band frequency response. Furthermore, work exploring solution-based, microscale or nanoscale metal particles could replace lithographic patterning of FES to provide a single step, solution processed fabrication technique.

However, to expand the range of applications, the current THz detection threshold needs further optimization. Since field enhancement depends on the FES dimensions, scaling down gap geometry could significantly improve THz-L threshold. The sensitivity of the device can be further enhanced by using an active detection system instead.

**Electrically Assisted Detection**

Fig. 6-18 illustrates a potential implementation of electrically active detection, where the FES is designed as interdigitated electrodes. By applying a DC field, we pre-bias the QDs, allowing field effect charge tunneling to occur at a lower incident THz field. While preliminary results of DC biased interdigitated samples do show increased THz-L intensity, eventual THz-induced electromigration, bridging of microslit gaps [141], is exacerbated by DC bias field.
Figure 6-18: Schematic of electrically assisted detection design using interdigitate microslit FES. The applied DC bias creates steady state electric fields with alternating field alignments within the microslit gaps (shown in red and blue arrows). In field aligned gaps, the DC field augments incident THz radiation, decreasing the THz field strength necessary to achieve THz-L.

As shown by SEM images in Fig. 6-19, degradation of microslits makes DC operation unstable over time scale of minutes. This effect may be mitigated by using AC assisted detection.

Figure 6-19: SEM images of microslit samples with Alq3:DCM showing degradation due to electromigration. From left to right: pristine sample, sample post-THz exposure (30 min), and solvent cleaned, post-exposure sample without organic thin film showing electromigration of Au bridging microslit gap.
**Optically Assisted Detection**

Based on THz-driven QCSE, we can use a sub-bandgap optical backlight to assist THz detection. By using 1.8 eV optical photons, Fig. 6-17 demonstrates a threshold reduction by a factor of 2. Fig. 6-20 illustrates the general design for optically active detection systems, where the lower energy optical pump can be spectrally filtered from the THz-L for visible detection and imaging. A potential design implementing optical enhancement structures such as a 1-D photonic crystal resonator to increase photon density of states could increase overall sub-bandgap absorption and/or exciton emission. An optical resonator designed for exciton emission enhancement could also enable better frequency filtering of optical pumps. This allows the sub-bandgap photon excitation to approach the exciton energy (i.e. using optical probe approaching 2 eV for QCSE effect in Fig. 6-17), to further decrease the THz detection threshold.

![Figure 6-20](image.png)

Figure 6-20: Schematic of optically assisted detection system with optical filtering and visible detector.

### 6.5 Conclusion

In this chapter, THz frequency pulses were used for exciton generation in organic and QD thin films. With high field enhancement from FES substrates, ultrafast electric fields can cause charge tunneling from metal FES into the thin film. An alterna-
tive field-only mechanism based on charge tunneling between exciton sites within the semiconductor, as demonstrated by bare vs. oxide-coated microslit samples, is also observed. These free charges can recombine as excitons, producing THz-L. For QD samples, we observed a modulation of the QD bandgap on the picosecond scale due to THz-driven QCSE; a redshift in absorption energy over 0.5 eV is demonstrated, a magnitude higher than previous works. These findings highlight the utility of THz techniques in examining exciton dynamics. Further optimization and device design can build upon this simple platform for THz detection and imaging, in various passive or active schemes.
7 | Electrically Tunable Organic Micro-Electro-Mechanical System Microcavities

7.1 Overview

Organic and nano-crystal materials can be exploited for a range of potential applications based on the fundamental excitonic physics. These semiconductors can be deposited using simple methods such as evaporation or solution processing. However, incompatibility with most traditional inorganic device fabrication and processing techniques can constrict device design. In this chapter, we expand upon a transfer printing technique previously developed to print large area metallic thin films [142] to transfer print composite membranes with organic thin film layers. We present an example of using this technique to enable integration of optically active exciton semiconductors into traditional micro-electro-mechanical system (MEMS) structures, obviating the need for lithography and etching on molecular thin films. By apply this fabrication technique to wavelength-tunable organic MEMS microcavities, we successfully demonstrate an electrically tunable organic vertical cavity surface emitting laser (VCSEL) array with reversible, dynamic tuning range of 10 nm in the visible wavelengths under 6 V actuation.
7.2 Introduction

While the exciton physics determines the emission wavelength of photoluminescence (PL) and electroluminescence (EL), the local photon density of state, as determined by device structure and geometry, can drastically alter exciton characteristics and overall device emission. For example, thin films PL can be enhanced or suppressed due a nearby reflector [143]. In devices such as organic LEDs, thin metallic electrodes can form lossy microcavities, with corresponding characteristics such as wavelength dependence of emission angle [144,145]. Thus, design parameters of opto-electronic devices can play an important role in enabling applications based on organic and quantum dot (QD) semiconductors. In addition to fundamental studies of exciton physics presented in previous chapters, an example of fabrication challenge in implementing organic and QD thin films in various device design is present in this chapter. Specifically, we seek to combine the benefits of broad emission spectrum over the visible wavelengths offered by organic semiconductors [7,146-148] with traditional electrically tunable MEMS microravity devices [149-151].

A wide range of applications, including spectroscopy, optical switching, and sensing, would benefit from the development of compact, visible wavelength tunable lasers. Molecular and polymeric organic solid state thin films have been validated as broad spectrum lasing gain media over the visible wavelengths, including work reporting over >100 nm lasing wavelength range using a single organic guest-host material system [148]. However, the emission spectrum of a typical wavelength-tunable organic solid-state laser is fixed during fabrication by device parameters. An array of distributed feedback lasers with varying dimension is one such example [147,152,153]. In such cases, laser wavelength tuning is performed by spatially selecting from multiple resonators fabricated on the same device for the laser with the desired emission wavelength. In other words, laser emission cannot be dynamically varied post-fabrication. In works that have demonstrated dynamically-tunable organic lasers, spectral tun-
ing was often implemented by mounting mirrors on translation stage [154] or with manually-switchable gain media modules [155]. These systems can exhibit the gain media potentials, but are not easily translated into compact, thin film device design. Compact, dynamically tunable organic laser systems have employed electroactive polymers or liquid crystals, but such scheme often require high operation voltages on the order of $\sim 1$ kV [156,157].

![Figure 7-1: An example inorganic MEMS microcavity laser showing IR emission wavelength tuning at low bias voltages. Figures from Ref [150].](image)

On the other hand, inorganic tunable MEMS VCSEL with epitaxially grown III-V gain medium have been well studied. As shown in Fig. 7-1, these compact devices are often fabricated with an air gap and a suspended top reflector, designed for low voltage, dynamic tuning of microcavity optical path length (OPL) [149–151]. Standard lithography fabrication processes enables definition of small physical dimensions in these structures, leading to large electric fields at low operating voltages. While inorganic materials can withstand solvent treatments and conditions used in conventional fabrication processes, molecular and QD semiconductors are largely incompatible with techniques such as lithographic patterning and etching. To circumvent these fabrication challenges, we develop and employ a solvent-free, composite membrane transfer technique. This technique enables integration of organic thin films into a compact MEMS
microcavity design, with sufficiently small dimensions to allow low voltage tuning of cavity emission and lasing mode.

7.3 Methods

7.3.1 Device Fabrication

We use organic thin film of tris-(8-hydroxyquinoline)aluminum (Alq3) host matrix doped with $\sim 1 - 2.5\%$ guest molecules of 4-(dicyanomethylene)-2-methyl-6-(4-dimethylamino styryl)-4H-pyran (DCM) as the gain medium. As detailed in previous chapter, this guest-host material is a well studied system used as emissive layer in OLED and solid state gain medium in organic lasers [7]. Fig. 7-3 details the fabrication procedures for the MEMS microcavity structure, which can be separated into three main components: fabrication of the composite membrane, deposition and patterning of the bottom substrate, and solvent-free composite membrane transfer printing.\(^1\)

\[\text{Parylene-C} \quad \left(\overbrace{\text{H}_2\text{C} - \text{C} - \text{CH}_2}^n\right)\]

$1 \mu m$ thick

Figure 7-2: Chemical structure and image of free standing parylene membrane.

\(^1\text{In collaboration with Apoorva Murarka and Annie Wang.}\)
1. Bottom Substrate

Sputter 6.5 layers of SiO$_2$/TiO$_2$ to form a DBR on an ITO coated glass substrate.

Spin 1-µm-thick SU-8 spacer layer. Photolithographically pattern SU-8 layer to form circular cavities.

Thermally evaporate 250 nm of Alq$_3$:DCM (2.5% doped) gain medium.

2. Top Membrane

Spin Micro90 release layer on a glass substrate. Deposit a 300-nm-thick Parylene-C film via CVD.

Thermally evaporate a 250 nm film of Alq$_3$:DCM (2.5% doped) gain medium, through a shadow mask.

Thermally evaporate a 100 nm film of silver (mirror) and a 50 nm film of gold (electrical contact) through a shadow mask.

3. Transfer Process

Adhere a flexible cutout handle frame to the parylene film, and peel off the composite membrane.

Align and transfer the composite membrane over the receiving substrate.

Cut away the handle frame from the parylene film to form the final MEMS device.

Figure 7-3: Schematic of MEMS microcavity fabrication process. (1) The bottom SiO$_2$/TiO$_2$ DBR mirror and SU-8 spacer layer are patterned on ITO-coated glass. (2) A 700 nm-thick composite membrane comprising ultra-thin parylene, Alq$_3$:DCM gain material, Ag mirror, and Au electrode layers is prepared on a glass carrier. (3) The membrane is released and directly transferred to the patterned substrate to complete the device.
For the composite membrane, a layer of Micro-90 is spun-cast on a carrier glass as a release layer. Under high vacuum, a 0.3 - 1 μm thick parylene-C is deposited on the substrate as a transparent support layer using standard chemical vapor deposition (CVD). Fig. 7-2 shows a 4 inch diameter of transparent, free standing membrane of parylene. In sequential order, layers of 500 nm Alq3:DCM (1 - 2.5% doping), 100 nm silver (Ag) mirror, and 50 nm gold (Au) top electrode are thermally deposited to form the completed composite membrane.

![Composite Membrane Diagram](image)

Figure 7-4: (a) Schematic of organic MEMS VCSEL. Voltage applied between the top Au and bottom ITO causes membrane deflection due to electrostatic force. (b) Optical imaging of patterned SU-8 circular cavities. (c) Optical imaging of Au surface of composite membrane transferred on patterned SU-8 circular cavities of the same device.

The bottom substrate is fabricated on a glass sample, with a 150 nm-thick indium tin oxide (ITO) bottom electrode layer. We sputter-deposit alternating layers of silicon dioxide (SiO2) and titanium dioxide (TiO2) to form a distributed Bragg reflector (DBR) mirror. The DBR is designed with a 100 nm stop-band centered at λ = 620 nm, matching the peak PL emission of the organic gain medium (Fig. 7-5). An SU-8
photoresist spacer layer is then deposited and patterned with circular cavities of 25 - 100 μm in diameter using standard positive resist photolithography (see Appendix A). The bottom substrate can have an additional layer of thermally evaporated Alq₃:DCM to increase the gain volume and fine-tune microcavity OPL.

Completed composite membrane is attached to a flexible cutout handle frame and mechanically delaminated from the carrier. The membrane is transferred in nitrogen atmosphere to the cavity-patterned bottom substrate, where the bottom parylene layer gently adheres the composite membrane to the substrate, and the handle is removed. This use of ultra-thin parylene enables solvent-free transfer of a large area (8 mm x 8 mm) composite membrane that encloses an array of microcavities.

7.3.2 Optical Interferometry and Emission Spectrum Setup

Optical interferometry imaging (Wyko NT9100, Bruker Nano Inc.) was used to measure membrane physical deflection under electrostatic actuation; reflection of coherent light off of the top Au surface of the composite membrane enables interferometric measurement of displacement with nanoscale precision.

![Optical setup for spectral analysis](image)

![Comparison of Alq₃:DCM thin film PL on glass, on DBR, and in completed MEMS microcavity structure with cavity modes](image)

Figure 7-5: (left) Optical setup for spectral analysis. (right) Comparison of Alq₃:DCM thin film PL on glass, on DBR, and in completed MEMS microcavity structure with cavity modes. For the latter two, excitation and emission was taken through the DBR substrate.
Microcavity emission spectra and power dependence results were obtained using the familiar microscope setup to focus a $\lambda = 400$ nm pulsed excitation laser (1 kHz repetition rate, 100 fs pulse duration) through the bottom planar DBR into the cavity. This excitation wavelength is outside the DBR photonic stopband, allowing for efficient excitation of the organic film. The same objective captures subsequent cavity mode emission, and the emission is focused into a grating spectrograph (Princeton Instruments Acton SP2300) for spectral analysis (Fig. 7-5). In order to correlate cavity mode wavelength shift and membrane deflection, cavity emission spectra were collected on the same devices, biased under same actuation voltages as that of interferometry measurements of membrane deflection. The optically pumped devices were tested in a nitrogen-rich environment at atmospheric pressure to minimize photo-oxidation damage to the organic gain medium.

7.4 Results and Discussion

7.4.1 Interferometry Measurement of Membrane Motion

In general, optical resonators such as microcavities constrict the available photon states; a cavity structure consisting of two reflectors limits perpendicular optical transmission to longitudinal modes, which depends on cavity OPL. For on axis (perpendicular) emission, the transmission mode wavelengths are $\frac{\lambda_m}{2} = \frac{OPL}{m}$, where $OPL = \sum n_i L_i$ is dependent on the index of refraction $n_i$ and thickness $L_i$ of each layer in the cavity. For the cavity design shown in Fig. 7-4, the transmission wavelength $\lambda_m$ can be calculated using

$$OPL = m \frac{\lambda_m}{2} = n_{organic} L_{organic} + n_{parylene} L_{parylene} + h_{air}$$  \hspace{1cm} (7.1)

From henceforth, we will refer to the microcavity or lasing mode using the OPL. For example, a $4\lambda$ OPL cavity refers to $m = 8$ mode.
In an parallel capacitor plates of area $A$, electrostatic force on the plate is given by

$$F_{\text{electrostatic}} = \frac{\varepsilon A}{2} \left( \frac{V}{h} \right)^2$$  \hspace{1cm} (7.2)

Figure 7-6: Interferometry imaging of composite membrane surface under 0 V and 20 V bias showing uniform membrane deflection of cavity array. Curtesy of Apoorva Murarka.

Figure 7-7: (left) Schematic illustrating a microcavity supporting 4λ mode. Mode wavelength depends on OPL and can be tuned by varying the air gap $h_{\text{air}}$. (right) Optical interferometry measurement of height difference profile of a composite membrane under electrostatic actuation compared to 0 V. Profiles show membrane deflection due to applied voltage for devices with a 1 μm-thick SU-8 layer.

A voltage bias between the top Au electrode in the composite membrane and the
bottom ITO electrode in the microcavity causes membrane deflection under electrostatic force. It decreases the vertical air gap height $h_{air}$, as shown by surface plots in Fig. 7-6 for $h_{air} = 1 \, \mu m$ deep microcavities. Fig. 7-7 plots the membrane deflection profiles for a range of applied biases from 0 - 20 V for a single cavity, showing a maximum center deflection of nearly $\Delta h = 60$ nm at 20 V. The increasing membrane deflection at higher voltages results in a decreasing optical cavity length, causing a blue-shift in optical emission.

### 7.4.2 Shift in Microcavity Emission

![Graphs showing spectral shift](image)

Figure 7-8: (a) Device emission below lasing threshold, demonstrating spectral shift in cavity modes under increasing applied voltage. A cavity mode spacing of 71 nm is observed, consistent with the $4\lambda$ cavity OPL. (b) Shift in the $\lambda = 592$ nm cavity mode peak as a function of applied voltage bias (blue) obtained from cavity emission spectrum and average membrane profile obtained via interferometry. The error bars represent the standard deviation due to membrane roughness and membrane deflection variation within the illuminated excitation spot size.

Typical cavity mode emission spectrum of MEMS VCSEL devices with 1 $\mu m$-thick SU-8 layer under a range of applied biases is plotted in Fig. 7-8 (a). Cavity mode peak wavelength blue-shifts over 10 nm as applied voltage increases from 0 V to 20
V, with demonstrated reversibility. Since membrane curvature, hence cavity length variation, increases with applied voltage, the cavity resonator experiences higher loss as evidenced by a slight decrease in peak intensity and increase in spectral width with increasing applied bias. The 30 μm excitation spot was centered to avoid the cavity edges where height difference is largest, which would cause additional mode broadening and intensity loss.

Given Eq. 7.1, we estimate OPL based on device dimensions to find $\lambda = 592$ nm emission corresponds with a $4\lambda$ cavity mode. Peak wavelength shifts ($\Delta \lambda$) should thus follow the relationship $\Delta \lambda = \frac{\Delta h}{4}$. In Fig. 7-8 (b), we scale the change in membrane deflection to find good agreement with changes in peak wavelength of the $4\lambda$ cavity mode, zeroed to initial wavelength of $\lambda_0 = 592$ nm at 0 V. The error bars accounts for membrane roughness and increased deflection curvature within the excitation spot size at each applied voltage bias; the relatively consistent magnitude in error suggests that cavity length variation within the excitation spot is dominated by membrane roughness rather than deflection curvature.

### 7.4.3 Lasing Operation

For lasing operation, we fabricated a separate set of devices with thinner, 570 nm-thick SU-8 spacer layer to reduce the number of allowed cavity modes within the gain spectrum, lowering lasing threshold. The doping percent of DCM in Alq₃ was selected at 2.5% to increase volume of emissive molecules, but still low enough to avoid major aggregation losses. Microcavity emission of these thinner devices were dominated by $3\lambda$ cavity mode, which allowed larger wavelength tuning under lower bias.

Fig. 7-9 (a) plots the emission intensity of the $3\lambda$ mode around the lasing threshold. Fig. 7-9 (b) shows a typical excitation power-dependent emission intensity and spectral mode linewidth, computed using the full-width half-maximum. At pump powers over the lasing threshold of 200 μJ/cm² incident power, the observed cavity modes reduce to a single lasing mode with significantly increased peak intensity. Concurrently, the
emission linewidth of the cavity mode reduces to that of the monochromatic lasing mode.

Figure 7-9: (a) Device emission spectra for select pump energy densities to illustrate spectral output just below and above the typical lasing threshold. (b) Peak intensity of spectral mode (left axis) and emission linewidth (right axis) as a function of estimated excitation energy density. The nonlinear increase in emission peak intensity and sudden decrease in mode linewidth are indicative of a lasing threshold around 200 $\mu$J/cm$^2$ incident power.

We will consider two different methods of laser emission wavelength tuning. Not only can we blue-shifting emission by reducing OPL, but also use lasing model competition to select between cavity emission modes.

**Continuous Single Mode Tuning**

Cognate of tunable cavity modes (Fig. 7-8), lasing modes blue-shifts under electrostatic actuation of composite membrane. For these thinner microcavities, a $\Delta \lambda = 10$ nm laser mode shift is observed under an applied voltage of 6 V, as shown in Fig. 7-10 (a). The reversibility of the laser spectral shifts is highlighted in Fig. 7-10 (b). The laser emission hysteresis error is below 1 nm.
Figure 7-10: (a) Tuning laser emission wavelength using electrostatic pressure, demonstrating reversible tunable range from $\lambda = 637$ nm to $\lambda = 628$ nm in response to 6 V actuation. (b) Peak wavelength of lasing mode as a function of applied bias, demonstrating less than 1 nm hysteresis between forward and reverse sweeps.

**Lasing Mode Hopping**

Figure 7-11: (a) Longitudinal mode competition under bias. (a) For increase in applied bias, the blue shifted $3\lambda$ mode drops out of lasing due to lower gain. (b) Normalized laser emission demonstrating reversible lasing mode hopping between $3\lambda$ and the high order $\frac{7}{2}\lambda$ mode.
Since the Alq3:DCM organic medium has such broad gain spectrum, the microcavity structure supports multiple cavity modes, only one of which can lase due to model competition in gain saturation. However, as the cavity path length changes, gain saturation and spatial hole burning effect could change the lasing mode. Based on this effect, we also demonstrate reversible lasing mode-hopping between different cavity mode under external bias (Fig. 7-11). In this case, blue shifting the 3λ lasing mode at the edge of gain spectrum significantly lowers the gain. This allow higher order cavity mode to out compete and lase as the cavity length changes under external bias, demonstrating over 60 nm laser tuning range via mode-hopping. This demonstration enables possible device designs for non-continuous wavelength tuning of the lasing mode, with increasing sensitivity to external forces on the membrane.

7.4.4 Application to Pressure Sensing

Because the flexible composite membrane can be actuated either electrically or mechanically, in addition to tunable lasing in the visible or near-infrared wavelengths, these organic MEMS VCSEL structures can also enable all-optical, contactless, large area pressure-sensing applications. The composite membrane can be mechanically/pneumatically actuated, where shifts in the device emission wavelength (microcavity or lasing mode) are calibrated to indicate changes in pressure above the membrane. For cavity devices shown in Fig. 7-6 and 7-7, effective electrostatic pressure at each voltage V can be calculated using the interferometry membrane deflection measurements. For each point \((x_i, y_j)\) on the membrane surface with discretized area \(\delta A\), we use a circuit model of series of parallel plate capacitors to calculate the capacitance for each layer \(k\).

\[
C_k = \frac{\delta A \epsilon_k \epsilon_0}{L_k(x_i, y_j)} \tag{7.3}
\]

To simplify the estimation, we assume that the air gap is the only layer with a spatially varying thickness \(h_{air}(x_i, y_j)\); all other \(L_k(x_i, y_j)\) are constants, determined during layer deposition. Using total series capacitance, \(C_{total} = \sum \frac{1}{C_k}\), we can calculate voltage
across air gap as

\[ V_{air}(x_i, y_j) = V \frac{C_{total}}{C_{air}(x_i, y_j)} \]  

(7.4)

Thus, the total effective pressure can be computed as a sum of electrostatic pressure on each discretized area over the entire membrane surface using Eq. 7.2.

\[ P = \sum P(x_i, y_j) \]

\[ P(x_i, y_j) = \frac{\varepsilon_{air}}{2} \left( \frac{V_{air}(x_i, y_j)}{h_{air}(x_i, y_j)} \right)^2 \]

(7.5)

Figure 7-12: (left) Effective pressure across membrane due to applied bias was calculated using discretized series of parallel plate capacitors. (right) Comparison between effective membrane pressure and observed change in cavity emission peak wavelength. Since both varies quadratically with applied voltage, the linear relationship between the two can be fitted to find a pressure sensitivity of 85 Pa/nm for 4\( \lambda \) cavity mode devices.

For the 4\( \lambda \) cavity mode from Fig. 7-8, Fig. 7-12 plots the effective electrostatic pressure against cavity emission peak wavelength shift. Since both the membrane deflection and electrostatic pressure scale with the square of the applied voltage, the calculated pressure is proportional to the change in measured peak cavity emission. Thus a linear fit of the relationship results in a device pressure sensitivity of 85 Pa/nm. Assuming the same membrane deflection under equivalent mechanical pressures for
both demonstrated device arrays, the estimated pressure sensitivity of the thinner 3λ lasing device from Fig. 7-10 suggests a sensitivity of 64 Pa/nm for continuous tuning of a single lasing mode.

For such pressure sensor system, response rates could potentially approach 2 MHz, as determined using a lumped-parameter force-deflection model and assuming no viscous-damping losses in the membrane. The pressure sensor sampling rate could instead be limited by the lasing sampling rate above threshold. Due to triplet loss mechanism in the organic gain medium, organic lasers often operate with repetition rates in the range of kHz [158]. This response rate limitation can be circumvented by operating in cavity emission mode or by engineering thin film gain media to support continuous wave (CW) or quasi-CW lasing operation [159].

7.5 Conclusion

In this chapter, we demonstrated an electrostatically tunable organic MEMS VCSEL, enabled by a solvent-free additive membrane transfer fabrication technique. Electrical actuation and optical characterization of a typical device show single mode spectral tuning Δλ = 10 nm under 6 V and lasing mode-hopping tuning of over Δλ = 60 nm under 10 V. By varying the device geometry (e.g. spacer layer thickness, cavity diameter, and membrane thickness), the composite membrane-cavity structure demonstrated in this work can be optimized to enable spectral tuning over a wider range at low voltages, thus utilizing the full spectral range of the organic gain medium. For the single mode tuning, tunable range is limited by the need to avoid membrane pull-in and permanent stiction of the membrane to the bottom reflector [160,161].

Device stability and lifetime also need further consideration. Oxygen-sensitivity of organic thin films, and resulting photo-bleaching degradation, limits device stability in non-inert environments, necessitating device encapsulation for stable, long-term operation. Alternatively, replacement of the Alq3:DCM material system with a more air-stable, flexible gain medium may be necessary to avoid device encapsulation.
8  |  Conclusion and Outlook

8.1 Conclusion

The ever-expanding library of molecules and nano-crystals presents a promising class of energetically disordered semiconductor materials. Despite the vast body of literatures, much still needs to be understood regarding exciton-mediated electronic and optical properties to improve organic and quantum dot-based optoelectronic devices and to develop novel applications. In this thesis, we present an array of perturbative effects, such as external pressure, magnetic field, and electric field, to modify and control exciton dynamics. Through these methods, we have gained much insight into specific exciton physics, including energy level perturbations, spin-dependence characteristics, and transport of charge transfer excitons. These findings provided avenues and guidelines for device improvement. We also studied the effect of ultrafast electric fields on exciton generation and energy states. Finally, a fabrication challenge focusing on integration of excitonic thin films into traditional device design is considered, to produce an electrically tunable micro-electro-mechanical system structure.

8.2 Outlook

Through this body of work, we hope to provide a better understanding and control of exciton physics for optoelectronic applications. Building upon the fundamental physics to eventually develop mature technologies, we face many challenges and possible
directions for future exploration. To conclude, a few research and application directions are discussed for further investigation.

**Charge Transfer State Exciton**

Although many studies have focused on CT dynamics, there is still much to be learned. Charge transfer (CT) state work in this thesis focused on two main aspects as applied to organic photovoltaics (OPVs): spin depend dynamics and transport. While spin dependence was theorized with immediate implications for photocurrent generation, direct observations of transport in previously thought immobile low energy CT states was unexpected. Focusing on local morphology and engineering energy disorder in organic thin film may exploit these properties (ex. minimizing recombination losses for OPVs). Further experimental work exploring this effect in other material systems may lead to a more general phenomenon, which can be applied to a wide array of excitonic devices.

Efforts in developing efficient CT emitters (ex: exciplex, intra-molecular CT) with efficient radiative recombination and intersystem crossing could lead to applications beyond OPVs, such as light-emitting devices [71, 162]. Structured morphology with spatially orientated CT emitters could lead to more efficient polarized emission, helping to mitigate out-coupling issues in organic LEDs [163,164]. With more efforts to reduce exciton lifetimes with high quantum yield, CT states, which can more easily access dark triplet states, may have potentials toward continuous-wave or electrically driven organic laser [158].

**Excitons under Electric Field**

The presented work on ultrafast electric field on organic and nano-crystal thin film is only the tip of the iceberg. Our demonstration of exciton emission and large energy tuning under enhanced terahertz (THz) radiation provides a platform to answer fundamental questions, regarding frequency dependent dynamics, field-dependent effects,
exciton energy tuning, etc. Devices with simple fabrication based on field enhancement structure and organic or QD thin films can be implemented and improved for passive or active THz detection and imaging. Development of and optimization of this targeted technology could prove fruitful, bringing the advantages of mature Si-based visible detection technology to the developing THz frequency regime.

Field enhancement structures (FES) were used for focusing THz radiation, a technique which could also be implemented for optical enhancement in visible wavelengths to enhance exciton absorption and emission in thin films. Device design using FES in THz as well as the optical wavelengths could prove successful for applications in THz modulated optical switching.

**Tunable Enhancement Structures**

Incorporating MEMS structures with organic and QD optoelectronic devices may inspire novel applications. Specifically, employing MEMS structures to tune optical resonance and coupling lead to applications in imaging and sensing. For example, the demonstrated electrically tunable organic microcavity structures can be optimized for and applied to lasing devices or pressure sensors. Beyond vertical cavity structures, novel fabrication methods integrating optical MEMS techniques [165,166] with organic and QD photonic crystal structures [167,168] could be used to develop on-chip, visible wavelengths, optical switches or tunable laser for integrated circuit applications.
9 Appendices

9.1 Appendix A: Photolithography Procedures

9.1.1 Negative Resist

We use AZ5214 as purchased for standard negative resist lithography. Exposure times and other procedural values can be tuned to produce desired results.

- Spin coat at 2000 rpm for 60 s
- Soft bake for 60 s at 75°C
- Exposure through a chrome mask for 5s at 10 mW/cm² (MA-4)
- Post exposure bake for 120 s at 75°C
- Flood expose the resist for 60 s
- Develop in AZ400K solution for 60 s

9.1.2 Positive Resist

We use SU-8 resist, which may be diluted with cyclopentanone for thinner resist films. Procedural values can be tuned to produce desired results.

- Spin coat at 3000 rpm for 60 s
- Soft bake on hotplate for 5 min at 95°C, then cool for 2 min
- Expose through transparency mask for 30 s
- Post-exposure bake on hotplate for 2 min at 95°C
- Develop in PGMEA for 60 s and rinse using IPA.
- Hardbake for at least 4 hours at 170°C
9.2 Appendix B: A Study of Förster Resonance Energy Transfer for Ion Nanosensors

In this section, we discuss a specific application of FRET between organic molecules and quantum dots (QDs) for solution-based optical sensing of ions. We will focus on spectroscopy of nanosensor device components to monitor exciton dynamics for device optimization. See Ref [169] for detailed description of the nanosensor and biological testing of prototypes.

The ion sensor works on the principles of a pH indicator combined with an ion-specific binding molecule, in this case, a Nile red derivative (CHII) and a potassium-binding crown ether, respectively. When a K⁺ ion binds to the crown ether, a proton diffuses out of the sensor unit to maintain charge neutrality. Exciton energy of the pH indicator molecule depends on the presence of H⁺ ion, showing different absorption energy in protonated and deprotonated states (Fig. 9-1). Two quantum dot species are selected with emission wavelengths matching the absorption features of the pH indicator.

![Figure 9-1: Absorption of protonated (acid, red dashed line) and deprotonated (base, blue dashed line) CHII pH indicator compared to emission spectra of QDs in nanosensor, QD490 (blue line) and QD640 (red line).](image-url)
The completed, solution-based nanosensor consists of the ion-sensing molecules and QDs enclosed in plasticizer matrix. We can optically generate excitons in both species of QDs, which have relatively high photoluminescence quantum yield of $QY_{QD490} = 0.42$ and $QY_{QD640} = 0.64$. However, excitons in QDs can efficiently FRET to CHII due to the spectral overlap between the donor QD emission and acceptor CHII absorption (See Eqn. 2.18).

The Nile red derivative CHII has low photoluminescence quantum yield, and observed nanosensor emission is dominated by QDs. Since the absorption feature of CHII depends on its protonation state, we can use ratio of QD emission intensity to sense ion concentration (Fig. 9-2). This novel organic/QDs nanosensor reduces the photobleaching effects of simple organic dye sensors, and radiometric readout allows more accurate recording of ion concentration.

![Diagram](image)

**Figure 9-2:** FRET-based optical sensing of potassium ions. In protonated sensors, CHII absorption overlaps with QD640 emission, which increases FRET and decreases direct exciton emission from QD640. In potassium rich environment, the opposite is observed for deprotonated sensors; CHII absorption overlapping with QD490 emission causes increased FRET and decreased exciton emission from QD490. By measuring the ratio of QD emission intensities in known concentrations of potassium ions, the nanosensors can be calibrated.
Figure 9-3: (left) Simple streak camera setup and (right) schematic of exciton dynamics between optically active components of the nanosensor. FRET rates between components are indicated as $k_{f1}$, $k_{f2}$, and $k_{QD}$. Exciton recombination rates are indicated as $k_1$, $k_2$, and $k_A$.

To experimentally measure the exciton dynamics between the various optically active components, we use a simple streak camera setup shown in Fig. 9-3. Each solution was placed in a quartz cuvette (Starna Cells, Atascadero, CA) for fluorescence imaging. Time-resolved fluorescent spectra were collected on a custom-built apparatus. Laser excitation of 400 nm at 1 kHz (Coherent Libra with OPerA) is focused down into the cuvette at a 45° angle to minimize detection of reflected laser light. A portion of the subsequent sample fluorescence is focused into the streak camera (Hamamatsu C5680) using simple optical re-image systems.

Using this setup, we measure various combinations of the sensor components (QD490, QD640, and CHII) in 0 M and 2 M potassium chloride (KCl) solutions. From the streak
image, exciton emission of each QD donor was selected based on the full-width half-maximum of the photoluminescence (PL) spectrum. The resulting spectrally integrated time-resolve PL for each QD is plotted on a semi-log scale and approximated using a single exponential. Normalized intensity time resolved photoluminescence (TRPL) of QD490 and QD640 in a QD-only system is plotted in Fig. 9-4.

![Normalized intensity TRPL of QD490 and QD640](image)

Figure 9-4: Normalized intensity TRPL of (left) QD490 and (right) QD640 in QD-only system without organic CHII acceptor molecules. No significant change in exciton dynamics is observed, confirming relatively insensitive nature of excitons in QDs to changes in external ion concentration. FRET between QD species can be estimated by comparing exciton lifetimes of two QD system with that of QD490 - only measurements of Fig. 9-5 (a).

In addition, Fig 9-5 shows TRPL of excitons in QD only ((a) and (d)), single QD specie with CHII ((b) and (e)), and completed nanosensor ((c) and (f)). A fitting is performed for each QD emission within 3 ns D 40 ns of excitation to compute exciton lifetime, $\tau_{ex}$. For donors, this exciton lifetime is determined based on rate of radiative recombination ($k_r$), non-radiative recombination ($k_{nr}$), and energy transfer to lower energy QDs and/or acceptor molecules ($k_{trans}$).

$$\tau_{ex} = k^{-1} = \frac{1}{k_r + \Sigma k_{nr} + k_{trans}}$$  \hspace{1cm} (9.1)
Figure 9-5: Normalized intensity TRPL of (a)-(c) QD490 and (d)-(f) QD640 in solutions of various nanosensor components, as indicated in the left bottom corner of each plot: (a) QD490 only, (b) CH and QD490, (d) QD640 only, (e), CH and QD640, and (c,f) complete nanosensors.
The fitted exciton lifetimes of Fig 9-5 and 9-4 are listed in Table 9.1. Relatively small solvation-based change in exciton dynamics is observed in QD-only systems compared to that with ion-sensitive organic acceptor molecules. As expected, large modulations of exciton lifetime is observed in systems with CH molecules.

<table>
<thead>
<tr>
<th>Nanosensor components</th>
<th>$\tau_{ex}$ (ns)</th>
<th>$\tau_{ex}$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 M KCl 2 M KCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>QD490 - only</td>
<td>20.2 ± 0.2</td>
<td>19.2 ± 0.2</td>
</tr>
<tr>
<td>QD490 (both QDs)</td>
<td>18.5 ± 0.3</td>
<td>17.5 ± 0.3</td>
</tr>
<tr>
<td>QD490 (CH, QD490)</td>
<td>17.5 ± 0.2</td>
<td>12.3 ± 0.3</td>
</tr>
<tr>
<td>QD490 (CH, both QDs)</td>
<td>15.9 ± 0.3</td>
<td>12.3 ± 0.3</td>
</tr>
<tr>
<td>QD640 - only</td>
<td>19.2 ± 0.2</td>
<td>20.7 ± 0.3</td>
</tr>
<tr>
<td>QD640 (both QDs)</td>
<td>26.7 ± 0.4</td>
<td>26.2 ± 0.3</td>
</tr>
<tr>
<td>QD640 (CH, QD640)</td>
<td>7.9 ± 0.4</td>
<td>17.9 ± 0.3</td>
</tr>
<tr>
<td>QD640 (CH, both QDs)</td>
<td>11.5 ± 0.3</td>
<td>23.0 ± 0.4</td>
</tr>
</tbody>
</table>

Table 9.1: Fitted exciton lifetime in deconstructed nanosensor systems. As expected, a largest changes in QD exciton dynamics due to ion presence is observed in systems with CH molecules (highlighted in bold face text).

Comparing these QD exciton lifetimes, we can estimate the FRET rates $k_{f1}$, $k_{f2}$, and $k_{QD}$ (Table 9.2).

<table>
<thead>
<tr>
<th>Exciton donor</th>
<th>Exciton acceptor</th>
<th>FRET rates</th>
<th>0 M KCl</th>
<th>2 M KCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>QD490</td>
<td>QD640</td>
<td>$k_{QD}$ ($10^6$ s$^{-1}$)</td>
<td>4.5 ± 1.5</td>
<td>4.9 ± 1.5</td>
</tr>
<tr>
<td>QD490</td>
<td>CH</td>
<td>$k_{f1}$ ($10^6$ s$^{-1}$)</td>
<td>3.2 ± 1.7</td>
<td>24.4 ± 2.6</td>
</tr>
<tr>
<td>QD640</td>
<td>CH</td>
<td>$k_{f2}$ ($10^6$ s$^{-1}$)</td>
<td>74.4 ± 6.6</td>
<td>7.7 ± 1.4</td>
</tr>
</tbody>
</table>

Table 9.2: Fitted exciton lifetime in deconstructed nanosensor systems. As expected, a largest changes in QD exciton dynamics due to ion presence is observed in systems with CHII molecules.
To optimize nanosensor design, we can apply FRET theory (see FRET section in chapter 2) to compute the overlap integral based on CHII absorption and QD PL (Fig. 9-1). We can estimate the FRET radius between each QD and CHII, in both protonated and deprotonated state (Table 9.3).

<table>
<thead>
<tr>
<th>Exciton donor</th>
<th>Exciton acceptor</th>
<th>Protonated</th>
<th>Deprotonated</th>
</tr>
</thead>
<tbody>
<tr>
<td>QD490</td>
<td>CH</td>
<td>2.77 nm</td>
<td>4.39 nm</td>
</tr>
<tr>
<td>QD640</td>
<td>CH</td>
<td>6.24 nm</td>
<td>2.82 nm</td>
</tr>
</tbody>
</table>

Table 9.3: Estimated FRET radius $R_F$ between QD and CHII based on measured absorption and PL spectra.

Figure 9-6: FRET efficiency at a function of donor-acceptor spacing $r$ for (a) QD490 and (b) QD640. Optimal spacing is the maximum change in FRET efficiency.
Based on Eqn 2.16 and 9.2, we define FRET efficiency for each donor QD as

$$E_{FRET} = 1 - \frac{\text{QD PL intensity w/ CHII}}{\text{QD PL intensity w/o CHII}} = \frac{k_F}{k_r + \Sigma k_{nr} + k_F} = \frac{1}{(\frac{r_a}{R_F})^6 + 1}$$  \hspace{1cm} (9.2)

Fig 9-6 plots the FRET efficiency at a function of donor-acceptor spacing $r$ for each QD, to find the maximum change in $E_{FRET}$ between protonated and deprotonated CHII. We estimate optimal spacing of 3.49 nm for QD490 - CHII and 4.19 nm for QD640 - CHII for maximum change in QD PL intensity and highest ion detection sensitivity. Ideal system should place the two QDs on opposite sides of acceptor molecule to reduce the effects of FRET between exciton donors.

The steps outlined can be used to calculate optimal spacing for any FRET-based devices using organic molecules and/or QDs; this procedure can aid in material selection, especially for the proposed ratiometric ion sensor. Future work focusing on spatial engineering of donor-acceptor systems may be necessary to achieve optimal performance.
Bibliography


