

Multi-scale Dynamics of Organic Light-Emitting Devices

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Minnesota

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Russell J. Holmes, Advisor

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I would like to thank my research advisor Russell J. Holmes for all of his guidance and advice.

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Mary Beth

Dow Chemical for funding and collaboration. Dow scientists for research guidance, samples, etc.

Dedication

To some people that I value

Abstract

Over the last decade, organic light-emitting devices (OLEDs) have grown to receive tremendous attention for application in commercial displays and in lighting. While mostly successful for small format displays, challenges still exist that limit their performance for broader applications. Many of these limitations stem from a lack of understanding of charge and exciton dynamics and their impact on efficiency and stability. In this presentation, we describe novel device characterization and modelling efforts aimed at elucidating key dynamic processes in multiple regimes, including the microsecond transient behavior, steady-state, and long term degradation.

A model is presented which unifies both the transient and steady-state electroluminescence behavior of an OLED as a function of current density. The excellent agreement between the model and experiment enables a deeper understanding of efficiency reduction at high brightness. Additionally, the relatively ambiguous device efficiency parameter of charge balance is recast as an exciton formation efficiency. This framework permits a novel characterization paradigm for decoupling degradation pathways during OLED life-testing. In addition to the luminance loss, the degradation in emitter photoluminescence and exciton formation efficiency are also extracted. This technique is applied to an archetypical phosphorescent OLEDs, enabling more comprehensive design rules for device engineering to realize enhanced lifetime. Data science is a rising topic in industrial research. A system for enabling data science techniques within laboratory research is presented. Select useful applications are demonstrated.

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Chapter 1

Overview of Organic Semiconductors

1.1 Organic Semiconductors

1.2 Excitons

1.2.1 Singlets and Triplets

1.2.2 Electronic Transitions

1.2.3 Quenching Processes

1.2.4 PL efficiency

1.3 Charge Transport

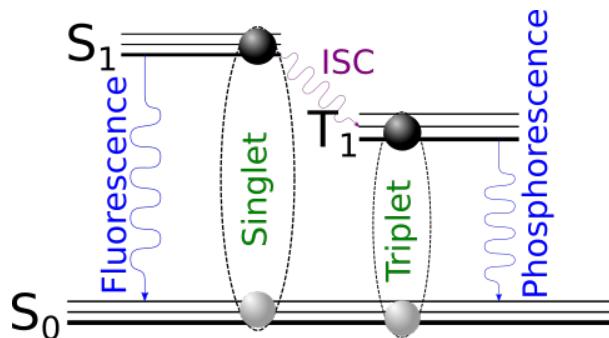


Figure 1.1: Simplified Jablonski diagram.

Chapter 2

Organic Light-Emitting Devices

2.1 Architecture and Basic Operation

Organic Light Emitting Devices (OLEDs) consist of an organic layer stack sandwiched between two electrodes. For light to escape, one of the electrodes is transparent, and in most lab scale devices, this is the bottom contact. This is often accomplished by using glass coated with Indium Tin Oxide (ITO) as a transparent conducting material. The opposing contact is typically a metal, and in most cases Aluminum. An example of this type of structure is shown in Figure 2.1.

The organic stack of devices is typically 80 nm or more and consists of multiple layers. Detailed device operation will be expanded upon in Chapter 3, but the goal of the layer stack is to efficiently form and recombine excitons. When voltage is applied, electrons are injected from the metal contact into the electron transport layer (ETL) and holes are injected from the ITO into the hole transport layer (HTL). Carriers transport through these layers to a region where exciton formation is designed to occur. This can be done in a variety of ways and is discussed in detail in Section 2.4, but most modern devices use a structure with a dedicated emissive layer (EML), as shown in Figure 2.2. In this type of device, the emitter molecule or guest, is doped at low concentration within a host matrix.¹ This composite film structure is used because most emissive molecules show a reduction in η_{PL} with increasing concentration.² The host molecule is used to help transport charge to the emissive molecule and separate the guest molecules. The host molecule is designed to have a wider energy gap, making it energetically favorable for excitons to form on the guest

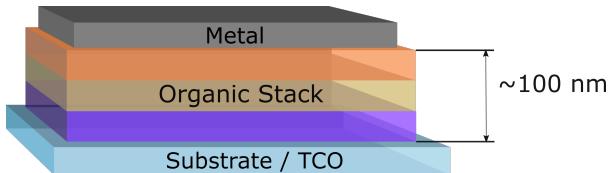


Figure 2.1: Basic layer diagram for OLED devices.

molecule.

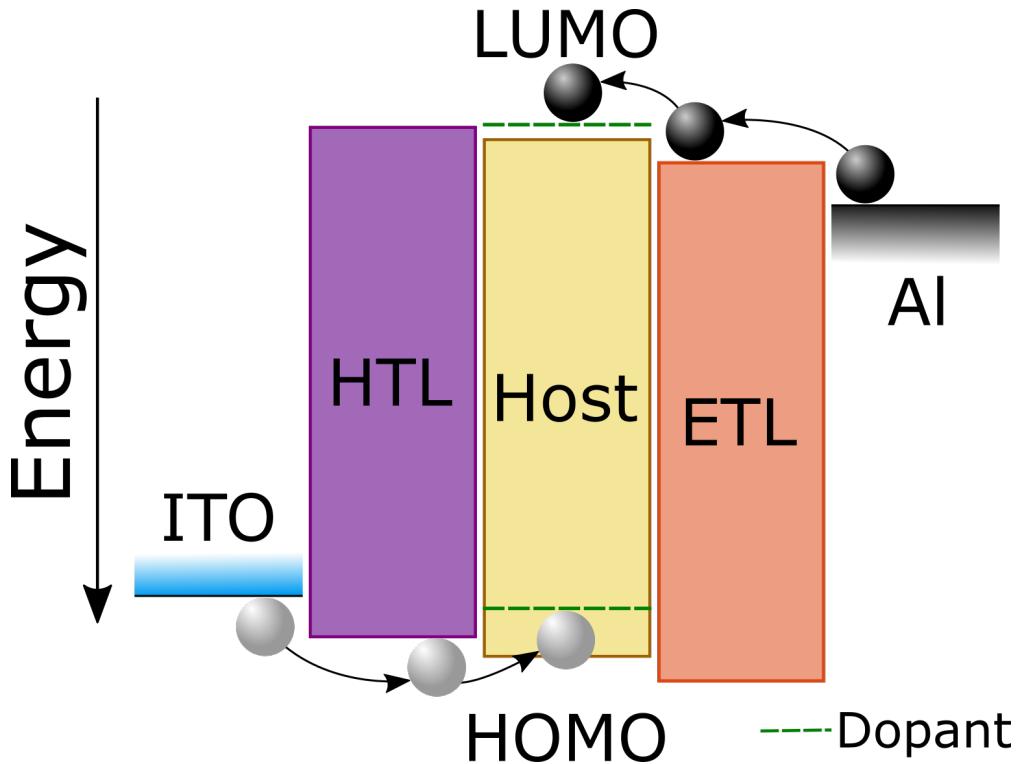


Figure 2.2: Energy level diagram of an OLED. Energy is shown in reference to the vacuum level. Electrons are shown in black spheres, holes shown in white.

The structure shown in Figure 2.2 is greatly simplified from most devices. Injection layers (HIL/EIL) are often used to aid in charge injection into the device between the electrode and transport materials. These materials will sit energetically between the electrode and the transport layer. To confine charges within the EML, blocking layers (HBL/EBL) are often used between the EML and the opposing transport layer. For example, a hole blocking layer would sit between the EML and the ETL and would have an energy level similar to the ETL, so electron transport would not be disrupted, but would have a high HOMO energy or a low hole mobility. These types of layers are often added as needed based on the energetic levels of the other materials in use.

2.1.1 Efficiency

Device efficiency is often thought of as a four component process as:³

$$\eta_{\text{EQE}} = \chi \eta_{\text{PL}} \eta_{\text{EF}} \eta_{\text{OC}} \quad (2.1)$$

The efficiency with which injected charges form excitons is the exciton formation efficiency, η_{EF} (traditionally called charge balance, γ). This is competitive with charge loss through the device and is shown in red in

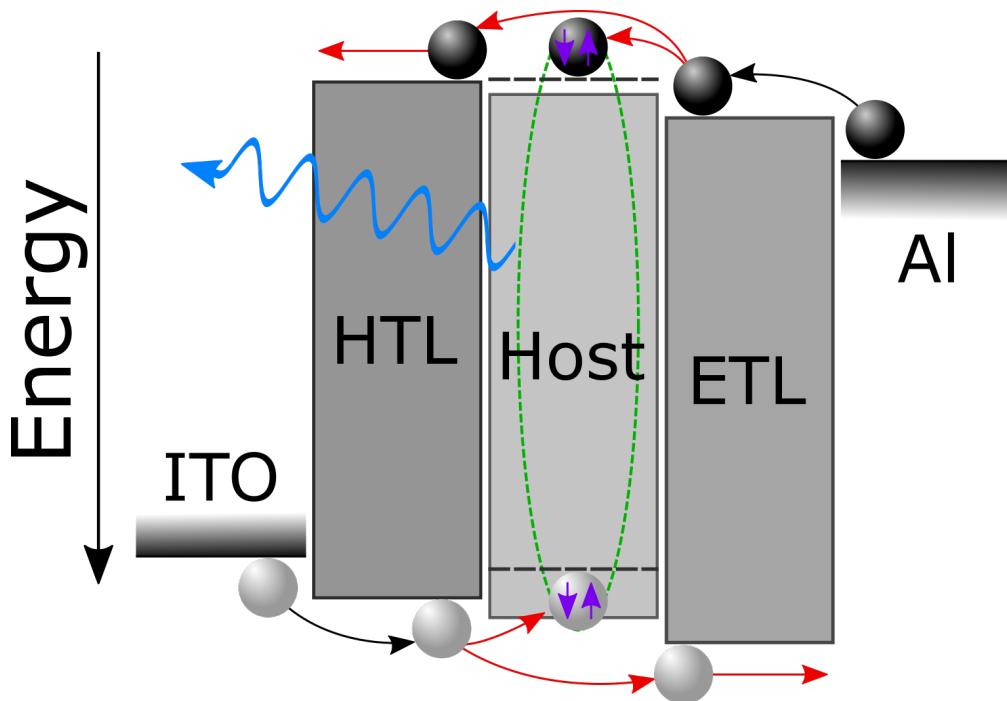


Figure 2.3: External Quantum Efficiency on energy level diagram. η_{OC} represented in blue, η_{PL} in green, χ in purple, and η_{EF} in red.

Figure 2.3. In modern devices, η_{EF} can approach 100% at the maximum efficiency point. Electrically, excitons are formed in a 3:1 Triplet:Singlet ratio, as discussed in Chapter 1.2. The radiative spin fraction, χ , captures the fraction of these formed excitons that are able to emit. For fluorescent materials, $\chi = 1/4$ and for phosphorescent materials, $\chi = 1$. The photoluminescence efficiency, η_{PL} is the efficiency of photon generation from the radiatively allowed excitons and can reach 100%. The out-coupling efficiency, η_{OC} , is the fraction of photons that escape the device in the forward viewing direction, and is competitive with wave-guided modes and surface plasmons.^{4,5} For most devices η_{OC} is the limiting process for efficiency, and typically is limited to 20-30%, but can be aided by enhancing films or layers.

2.2 Fabrication Processes

Substrates consist of glass precoated with indium-tin oxide (ITO). Prior to deposition, substrates are cleaned using 5 minutes each of sonicated Tergitol, water, and two cycles of acetone, followed by two cycles of boiling isopropynal. This is followed by a UV-ozone treatment for 10 minutes. Large area devices on patterned ITO are spin coated with a solution processed hole conducting planarizing layer. In my time in the group, this started with Pedot-PSS and has transitioned to the more commercially used Plexcore AQ-1200. Pedot-PSS is water based and seemed more susceptible to treatment conditions prior to deposition, such as freezing.

AQ-1200 has been a more reliable material. AQ-1200 has been replaced with AQ-1250, which appears to be the same formula, but with tighter control over consistency. For all solution processed layers, spin coating is done for 30 seconds at 3000 rpm, followed by a 30 minute bake at 150 °C.

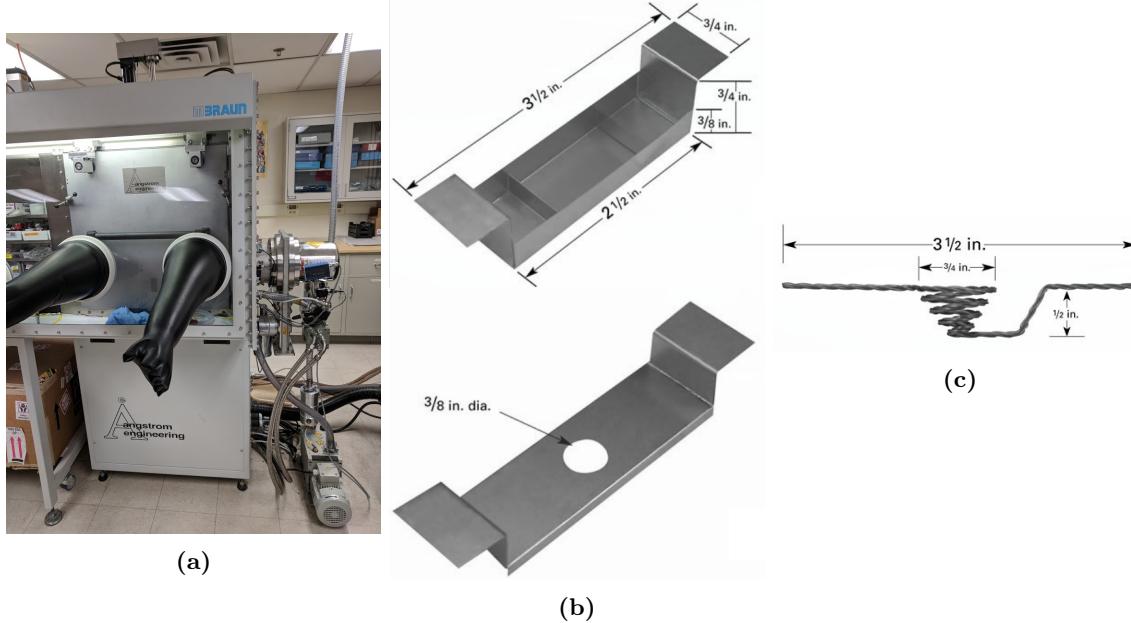


Figure 2.4: a. Angstrom vacuum chamber b. Organic deposition boat c. Aluminum deposition boat

Within our lab, the standard fabrication process for OLEDs is thermal evaporation at base pressures $<10^{-7}$ Torr. This is done in an Angstrom Engineering vacuum deposition chamber from tungsten boat sources for organic materials, shown in Figures 2.4a and 2.4b, respectively. Material deposition rates can be measured using quartz crystal monitors (QCMs) during deposition. The absolute rate of material deposition can be calibrated by conducting ellipsometry on grown films to determine thickness. This chamber allows simultaneous deposition of up to 4 materials at a time. Codeposition of materials allows for the creation of doped layers, which can even be varied with time to create graded composition profiles. For most devices, cathodes consist of 1 nm of lithium fluoride, from a dimple boat, followed by 100 nm of Aluminum, from the boat shown in Figure 2.4c.

For unpatterned devices, the whole substrate is coated in ITO, and device pixels are formed using a metal mask that defines the device area. In this case, to contact devices, contact must be made with the ITO for the anode and the Al cathode. A hard metal probe is used to contact the ITO by poking through the organic stack. However, the metal must be contacted without damaging the metal or underlying organic stack, as any damage would disrupt the device behavior, and at worst, short the contact to the ITO anode. In order to contact the metal, a 100μ gold wire is used to gently contact the metal surface.

Patterned devices consist of a patterned ITO substrate with a corresponding patterned metal mask,

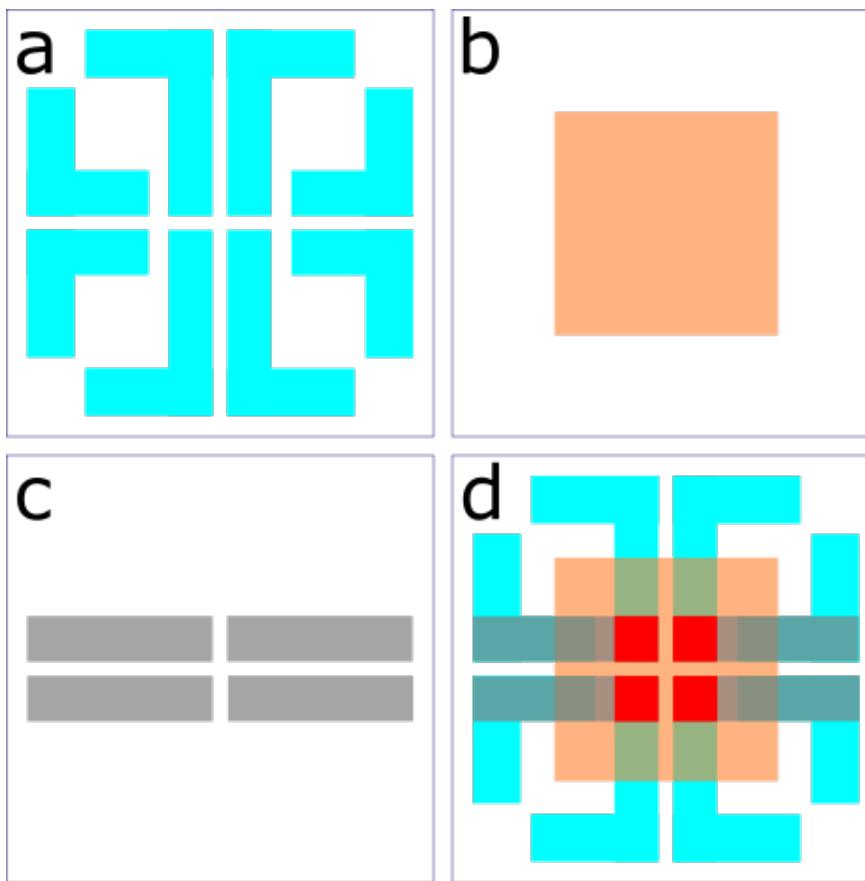


Figure 2.5: a. ITO Pattern b. Organic Mask c. Metal Mask d. Mask Overlays. Device area shown in red.

where the intersection forms the device area. To ease contacting, an ITO pad is typically placed below the metal at the contact point outside of the organic deposition region as demonstrated in Figure 2.5. This method allows for contacting the device off of the device active area, and does not suffer from the difficulty of contacting and is essential for devices to be encapsulated. In this case, it is important to consider lateral transport within the HIL. A sharp edge on the ITO pattern can result in a discontinuity of the organic stack at the device edges and can frequently short the device with metal directly in contact with the ITO. To prevent this, a planarizing layer is used which minimizes the effects of ITO roughness and the discontinuity of the step edge. While this is effective, planarizing layers are designed to have high mobility and lateral conduction could become important as it may lead to shorting between the anode and cathode ITO pads. To prevent this in our devices, the planarizing layer is disturbed between the two pads in order to disrupt lateral transport.

For device lifetimes, to minimize oxygen exposure, devices are packaged. This is done before devices are exposed to oxygen levels outside of a glovebox. A UV cured epoxy seal is formed around the device active area and is capped with a glass microscope slide cover slip. The epoxy is then cured with 3 minutes of

exposure to a UV lamp. For extreme long lived devices or higher shelf life, a dessicant can be used, but this is not common in our lab due to the relatively short lifetimes that we are studying.

2.3 Characterization

Though numerous characterizations exist to analyze devices, the standard metrics of performance consist of current-voltage, luminance, and efficiency. Luminance is typically calculated in candellas per meter squared (cd/m^2). There are three common efficiency metrics for devices, including the external quantum efficiency (%), the power efficiency (W/W) and the luminance efficiency (lm/W). Though dependent on field of study, for academic OLED interests, the most commonly explored metric is the external quantum efficiency (η_{EQE}).

2.3.1 Current Voltage and Luminance

The current-voltage behavior of most OLEDs follows a diode-like current-voltage dependence. This is characterized by a weak dependence of current on voltage below some threshold, followed by a strong dependence at high voltage, as shown in Figure 2.6. In terms of device operation, at low voltage below turn-on (Region I), carriers do not have enough energy to make the transitions between molecular orbital energy levels and cannot be injected into the device. Soon after turn on, carriers are overcoming the injection barriers of the material stack and in an ideal device, forming a strong recombination current for light emission (Region II). In this region, the current is limited by carrier injection and follows an exponential dependence as carriers overcome the injection barrier potential.⁶ At high voltage, injection barriers have been overcome and there is a charge buildup in the device which limits the current. This region is known as the space-charge limit and the current-voltage characteristic shows a power law dependence.⁶⁻⁸ In a well formed device, luminance should closely follow current, as most current should be going to recombination and exciton formation.

For device brightness characterization, either optical power or luminance can be used. Optical power is simply a characterization of the total photon power exiting a device. This is typically calculated by measuring the total device light output using a large area photodiode. For optical power or optical power density measurements, it is important to know the measured light producing region being measured. This

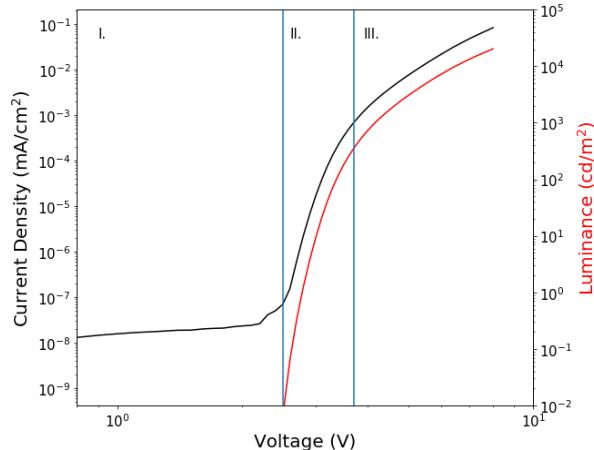


Figure 2.6: a. Device current voltage and luminance voltage behavior

can either be done by ensuring the total device area and all light output is measured, in which case the area of interest is the device area, or by measuring a known subsection of the device. The current output by the detector can be related to the incident optical power by the responsivity function of the detector, reported as a function of wavelength as W/A . A typical responsivity for a silicon detector is shown in Figure 2.7a.

Luminance is reported in candelas per meter squared (cd/m^2), sometimes called a 'nit'. The candela is a measure of perceived light intensity per solid angle and is equivalent to 1 candle power. To measure luminance, the light output must be normalized to the wavelength dependent response of the human eye, known as the photopic response, shown in Figure 2.7b. This is typically done in one of two ways. The first method (employed by our group) is to use a spectrometer to measure the output light spectrum in Watts per nanometer. Then the spectrally averaged photopic response can be found for the light source of interest. Then, the output optical power can be measured by a simple photodiode and calibrated using the average photopic response. Alternatively, a photodiode can be filtered and modified so that the responsivity function matches the photopic response. In this case, the photodiode would directly output the luminance. Both methods are standardly used in research groups.^{9–11}

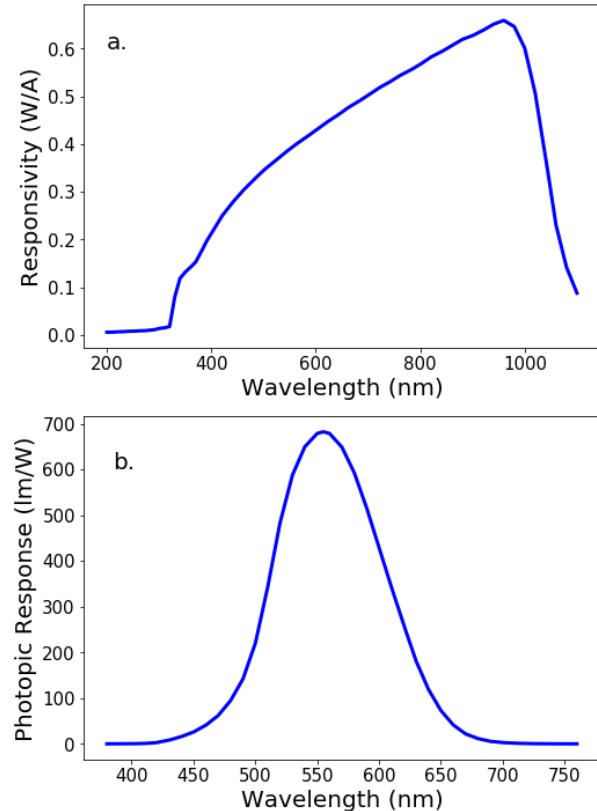


Figure 2.7: a. Silicon detector responsivity b. Photopic response

2.3.2 Efficiency Analysis

As mentioned previously, there are three common measures of device efficiency. The first is power efficiency, measured in W/W . This is straight forward to calculate given the previous discussion of measuring optical power. The luminance efficiency lm/w is related to the luminace output. The lumen is a measure of total light output and is related to the candela by $1 \text{ lm} = 2\pi \text{ candelas}$. A keen eye would note that the candela is normalized per solid angle and a factor of 4π may be expected, but OLEDs are only able to emit in the forward direction.

The external quantum efficiecy (η_{EQE}) is a measure of photons exiting the device per electron injected.

The photon flux out of the device can be calculated from the optical power by dividing by the average photon power, hf_{avg} , where f_{avg} can be calculated from the measured spectrum. The injected electron flux is simply I/q where I is the device current. The mathematical details of this model are discussed in detail by Forrest et al. [11].

2.4 Historical Developement

2.4.1 The First OLEDs

Early interest in organic materials was generated based on use for organic laser dyes and the high fluorescence efficiency demonstrated.^{13–15}

Early attempts at producing electroluminescent devices tried contacting organic crystals, but required extremely high voltages to produce any light. **Williams1970, Helfrich1965** The first successful OLED was demonstrated by Tang and VanSlyke [12] in 1987, one of the first to utilize vacuum deposition for thin films. This was a bilayer device, with the

structure shown in Figure 2.8, using TAPC at 75 nm thick and Alq₃ 60 nm, responsible for the emission of the device, centered around 550 nm. These devices achieved $\eta_{EQE} \approx 1\%$ and showed rapid degradaton.

In fluorescent cells, $\chi = 0.25$ and without out-coupling enhancement $\eta_{OC} \approx 0.20$, leaving a maximum η_{EQE} of just 5%. Doped films were investigated soon after these initial findings in order to capitalize on the improved η_{PL} at low concentration.¹⁶ This host with emissive guest system is utilized by almost all devices.

2.4.2 Phosphorescence

OLEDs saw a massive improvement in possible efficiency in 1998 with the introduction of phosphorescent dyes.³ These dyes use a heavy metal atom to create a metal-ligand charge transfer state, which allows mixing of the singlet and triplet states, and thus emission from the triplet exciton. With all excitons able to emit, including the triplet state, the internal quantum efficiency (η_{IQE}) raises to 100%. These devices utilized the red phosphor PtOEP in conjunction with the laser dye DCM2. This work comments on quenching at high current of the phosphor, a continuing problem which

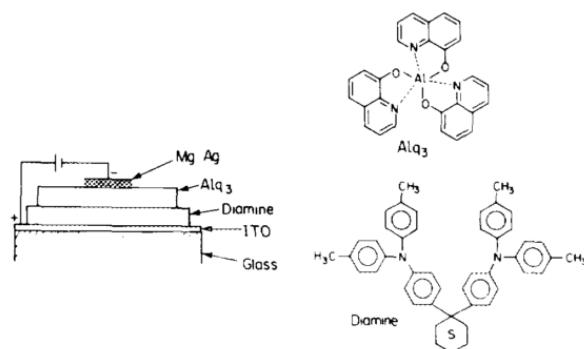
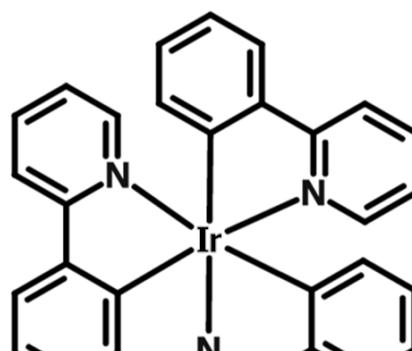


Figure 2.8: Structure of the first oled cell from Tang and VanSlyke [12]. Diamine is commonly referred to now as TAPC.



will be discussed further in Section 2.5.^{9,17} Pure red and green emission devices utilizing only a phosphorescent dopant were developed soon after, along with the development of the ubiquitous green emitter, Tris[2-phenylpyridinato-C²,N]iridium(III) ($\text{Ir}(\text{ppy})_3$), shown in Figure 2.9.^{18,19}

Since the realization of the phosphorescent OLED, internal quantum efficiencies nearing 100% for green, red, blue, and white devices have been demonstrated.^{20,21} With high efficiency achieved, attention has shifted to maximizing lifetimes.²² Despite the high efficiency of blue phosphorescent devices, lifetimes still remain limiting and blue fluorescent materials are still used in commercial technologies.

2.4.3 Thermally Activated Delayed Fluorescence

While phosphorescent devices have been able to demonstrate high efficiency necessary for commercialization, this has come at a cost. Namely, in the use of expensive and rare heavy metal atoms, such as Ir(III), Pt(III), and Os(II).²⁴ In order to utilize the triplet excitons, reverse intersystem crossing is utilized. Chapter 1.2 and Figure 1.1 discuss intersystem crossing as an energetically favorable process as the triplet is lower energy than the singlet. However, if molecules are designed where the singlet and triplet energies difference (ΔE_{ST}) is small ($< 1\text{ eV}$), thermal energy can make the reverse intersystem crossing competitive with intersystem crossing ($k_{RISC} \approx k_{ISC}$). This allows for Thermally Activated Delayed Fluorescence (TADF), shown in Figure 2.10.^{23,25,26} TADF materials are a rapidly developing technology that has shown many benefits for efficiency, and rules are being established for molecular design.^{10,23,25–40} These materials are also being investigated for benefits to device lifetime.^{41,42}

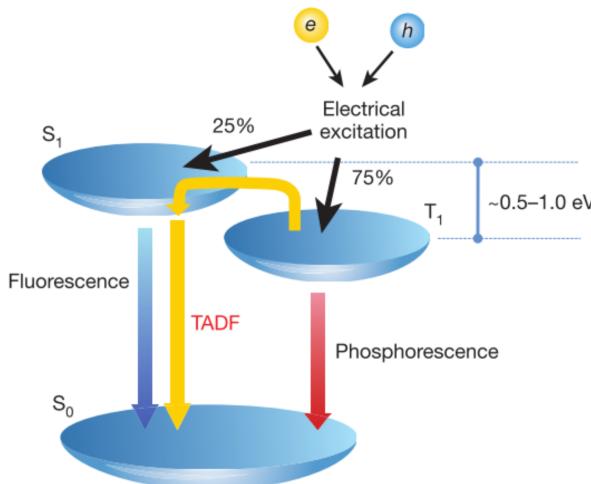


Figure 2.10: Reverse intersystem crossing for TADF materials. Figure taken from Uoyama et al. [23].

2.5 Efficiency Roll-Off

In operational OLEDs, it is almost universally observed that efficiency reduces at high brightness and current density, an affect known as the efficiency roll-off, demonstrated in Figure 2.11.^{9,17,43-56} This has been extensively studied and largely attributed to the bimolecular quenching processes discussed in Chapter 1.2, though exciton formation efficiency (η_{EF}) is also known to contribute at a lesser degree. This is detrimental to commercialization as high brightness is a necessity for display and lighting applications. The bimolecular quenching at high brightness is also detrimental to device lifetime because quenching processes produce hot excited states that release excess energy into the device, which is thought to be a key factor in molecular degradation.⁵⁷⁻⁵⁹ Developement of electrically pumped organic lasers has proved unsuccesful because the exciton densities required to achieve population inversion lead to excessive quenching and the inability to create stimulated emission.^{3,60-64}

Devices are often investigated to try to reduce the roll-off, often through the broadening of the exciton recombination zone.^{10,20,29,65-70} These devices have not been successful in removing the roll-off, but rather in reducing it. Section 2.1 discussed the characterization of quantum efficiency using a four component efficiency model. This model fails to reproduce the roll-off behavior as it does not account for quenching. Modeling the efficiency roll-off has been the study of numerous works and is the motivation for Chapter 3.^{9,17,43,47} These models center around a differntial equations model for exciton dynamics, such as:

$$\frac{dn_{ex}}{dt} = -\frac{n_{ex}}{\tau} - \frac{1}{2}k_{TT}n_{ex}^2 - k_{TP}n_{pol}n_{ex} + G_{ex} \quad (2.2)$$

where n_{ex} is the exciton population density, τ is the exciton lifetime, k_{TT} is the triplet-triplet annihilation rate, k_{TP} is the triplet-polaron quenching rate, n_{pol} is the charge density, and G_{ex} is the exciton genertion rate. Here we can see that the natural lifetime is competitive with the bimolecular quenching rates, and at high exciton and charge density, the second order dependence of the quenching terms allows them to dominate. This reduces the relative number of excitons that are decaying via the radiative rate, thus decreasing the efficiency. These models have been successfull in characterizing the rate constants and describing the roll-off behavior. For further details, see Chapter 3.

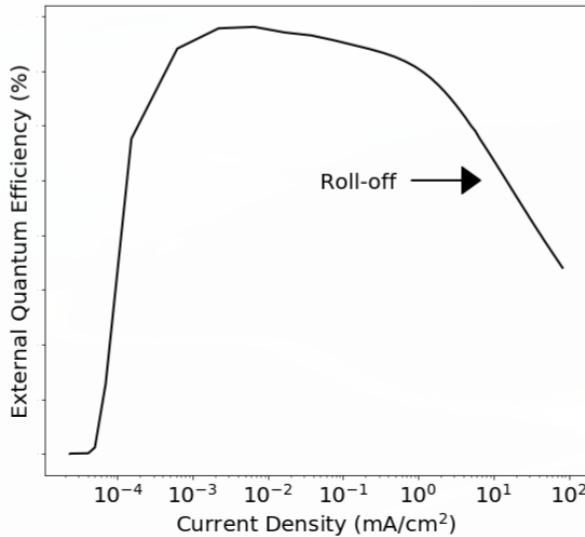


Figure 2.11: Efficiency roll-off as a function of current density

2.6 Recombination Zone Characterization

Both degradation and bimolecular quenching can be highly dependent on the exciton density and location, known as the exciton recombination zone (RZ).^{Bangsund2018, 9,17,48,57,71–73} Therefore, it is important to be able to characterize the spatial profile of excitons. This has been done by a variety of researchers using thin doping layers of a sensitizer molecule.^{Bangsund2018, 56,58,68,73,74}

In these experiments, the dopant is used to efficiently siphon excitons off of the emitter molecule and onto the sensitizer. In order to do this, Förster transfer to the sensitizer must be efficient, requiring significant overlap of the emitter emission and the sensitizer absorption. Erickson and Holmes [56] looked at the spatial extent of Förster transfer and found that transfer was efficient within a < 4 nm radius. To characterize the recombination zone, sensitized layers are used and the effect of the local perturbation of the exciton density can be measured. Translating the sensitized strip across the device as shown in Figure 2.12 allows for comparison of the relative effects and thus determination of the relative magnitude of the recombination zone. The Förster radius gives the maximum spatial resolution that can be obtained using this strip translation.

A quenching (non-radiative) or emissive (radiative) sensitizer can be used for these experiments. With a quenching sensitizer, if the recombination zone overlaps with the sensitizer position, emission is lost and the efficiency is reduced. The reduction in EL intensity can be quantified by the EL ratio of the sensitized intensity compared to the unsensitized intensity, β . β is directly proportional to the unquenched excitons, therefore $1 - \beta$ gives the ratio of quenched excitons.

For emissive sensitizers, given the requirement of emission-absorption overlap, red sensitizers are used. For simplicity, the sensitizer should show spectral separation of the emission from the emitter. The intensity of the sensitizer emission is a direct measure of the local exciton density. However, since the out-coupling is so strongly dependent on emitter position in the EML, it is essential to correct the intensity using a calculation of η_{OC} , discussed in Chapter 8. One may note that the quenching sensitizer method should also require out-coupling correction, but since the emission is not spatially isolated, calculation of the spatially averaged out-coupling effiency would require prior knowledge of the recombination zone shape and therefore cannot be done. Emissive sensitizers often rely on the use of Pt(II) complexes, such as PtOEP or PtTPTBP.^{73,74} Compared with Ir(III) complexes, Pt(II) shows a much longer exciton lifetime, and is therefore far more sucesptible to bimolecular quenching.⁵³ If the sensitizer is in a regime of bimolecular quenching during the

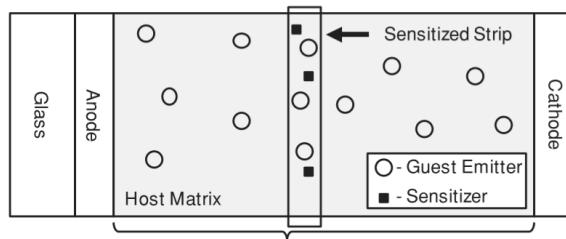


Figure 2.12: Recombination zone measurement architecture. The curly brace indicates the device stack. Figure taken from Erickson and Holmes [56]

measurement, a compressed version of the recombination zone will be measured. This can be difficult to avoid at high current densities that may be of interest for measurement.

An advantage of the emissive sensitizer is that the data generated can be analyzed either using the quenched ratio or using the emitted intensity. This can be helpful for quantifying error in the method, and is demonstrated in Figure 2.13. Here, we see the spatial dependence of the recombination zone for an architecture peaked at the ETL interface. Notice that the emissive sensitizer, PtTPTBP shows a less exaggerated RZ for all current densities. This is likely due to bimolecular quenching on the sensitizer, which is stronger at the higher exciton densities present at the ETL interface.

When constructing these sensitizer layers, there are two popular methods. First, the EML can be reproduced exactly with the addition of a light doping of the sensitizer. This creates a strip that exactly replicates EML, but increases the difficulty of the growth, requiring one more material in a codeposition. An alternative is to use an extremely thin deposition of the sensitizer molecule in isolation, known as delta doping. A deposition of 1 Å is used, which since the molecular radius of the deposited material is larger than that, in reality, a discontinuous layer is produced. When the EML is continued on top of this discontinuous layer, this is equivalent to an extremely narrow strip of a mixed layer. This is advantagous because it make the deposition much easier and creates a very narrow strip. However, it can be difficult to control the doping percentage as it is difficult to accurately measure films this thin. No quantification of error on these types of doping have been reported.

In order to accurately compare the recombination zone intensity, it is essential to ensure that no differences in the transport and injection properties occur with the introduction of the sensitizer. Since the sensitizer molecules will likely result in a trap state, it is essential to keep doping concentrations low, on the order o 1%. Evidence of minimal interference on the electrical properties by the sensitizer is provided by the current-voltage behavior. If the current-voltage characteristic is within error between all of the sensitizer devices, it is often assumed that the device is representative of the control.⁵⁶

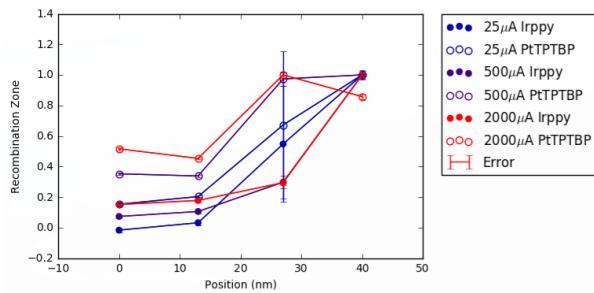


Figure 2.13: Recombination zone comparison for an emissive sensitizer analyzed using the quenched ratio and the emitted ratio as a function of current density.

2.7 Single Carrier Devices

2.8 Operational Lifetime

In typical lifetime characterization, devices are degraded while held at constant current density, recording the resulting luminance loss and voltage gain as a function of time. The lifetime is then reported as the time to reach some arbitrary fraction of the initial luminance.

$$\frac{L(t)}{L_0} = \exp(-t/\tau)^\beta \quad (2.3)$$

2.8.1 Degradation Mechanisms

As degradation studies are an ongoing an extensive aread of research, this section does not represent an all inclusive picture of degradation mechanisms. However, it does seek to outline the dominant mechanisms observed in typical devices. In the most simple case, the degradation of an OLED can be viewed wholistically as a stretched exponential curve with minimal physics.^{75,76} This approach is able to reproduce the decay behavior relatively well and the scaling with luminance, but only describes the decay by attributing behavior to emissive centers.

Dark Spots and Delamination

Exciton and Polaron

Interfaces

Oxygen

2.8.2 Luminance Scaling

For commercially relevant devices, where the time to reach 50% of the initial luminance, t_{50} can be tens of thousands of hours, it is impractical to test devices under their intended operating conditions. Instead, lifetime testing can be done at an increased luminance from the true operating condition.⁷⁵ This can dramatically reduce the testing time of devices. The lifetime at other luminances can then be found using the scaling relation

$$L_0^n t_x = C \quad (2.4)$$

where L_0 is the initial luminance, n is a scaling factor characteristic to the device, and C is a constant.

To utilize this relation, several lifetimes are obtained at luminances above the operating condition in order to experimentally obtain a value for n . Subsiquently, the lifetime of interest can then be extrapolated.

While widely used and observed, caution should be observed in the application of this relation. A variety of degradation mechanisms have been attributed to OLED behavior, as discussed in Section 2.8.1. All of these mechanisms are subject to different temporal dependences and have a variety of degrees of understanding to their fuctional dependence on time and luminance. At different luminances, different mechanisms may be dominant. For example, single excitonic processes may be dominant at low luminance, but may be overtaken by a bimoleculat process at high luminance. The fact that OLEDs are frequently subject to several degrdation mechanisms throughout the decay only further complicates the issue. The very idea of scaling law for all devices and at all current densities is unsound, and should be treated as a loose prediction. Over and underestimates of lifetimes using this relation are observed when trying to predict actual lifetimes.^{77,78}

2.8.3 Analysis Techniques

Chapter 3

Transient and Steady-State Dynamics

This section is an extension of my previous work entitled “*Unified analysis of transient and steady-state electrophosphorescence using exciton and polaron dynamics modeling*”.⁹

3.1 Motivation

As discussed in Chapter 2, modern OLEDs are typically based around Phosphorescent emitters in order to realize 100% internal efficiencies.^{1,3,18,79} However, these phosphorescent emitters, while allowing emission out of the triplet excitonic state, also suffer from the drawback of a longer exciton lifetime, typically on the order of 10^{-6} - 10^{-3} s.^{3,80} An increased lifetime leads to a larger steady-state triplet exciton density compared to a fluorescent device operating at the same luminance. This becomes problematic at the high current densities associated with high brightness due to well documented quenching events.

Efficiency roll-off is well attributed to quenching and is ubiquitous to phosphorescent OLED behavior.^{17,43,47,48} While previous works have attributed the roll-off to quenching, they have failed to provide a complete picture of the exciton and charge dynamics within the device. All of these works have utilized a differential equations model for the exciton dynamics, solved in the steady state. This becomes apparent

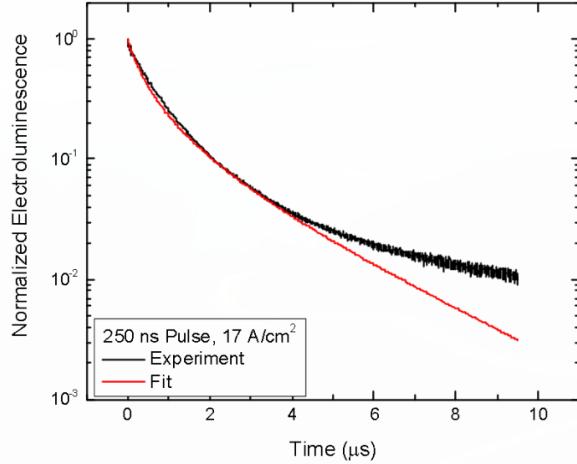


Figure 3.1: Fitting the transient electroluminescence decay without polaron dynamics.

^{17,43,49,52,53,68,81} These quenching events lead to a reduced quantum efficiency at high-current, and termed the “Efficiency roll-off”.

when investigating the transient electroluminescence (EL), where a transient voltage pulse, on the order of 500 ns is applied to the device and the resulting luminance is recorded as a function of time. Figure 3.1 is an attempt to fit the transient luminance decay using the model presented by Reineke *et al.*¹⁷ which well fits the efficiency roll-off. Indeed, this is a well known problem with existing models, and previous attempts to model the transient EL have utilized an empirical biexponential function to quantify the decay.^{43,48,54,82} In addition to failing to replicate the luminance decay, no known previous efforts have been made in trying to replicate the experimental transient EL luminance rise.

In addition to the problems with the transient electroluminescence, the interpretation of the existing model without a full dynamics picture can lead to false predictions. Figure 3.2a shows what a quenching model predicts for the roll-off as a function of increasing recombination zone width.⁴³ However, even in the most idealized case of a gradient emissive layer device, where no additional interfaces come into play, the predictive model fails to replicate the behavior, as shown in Figure 3.2b. While this device is of little interest for further investigation due to the extreme thickness, the point stands that this model has glaring assumptions for it's applications.

Both the transient EL and the recombination zone dependence issues arise due to an incomplete picture of the device physics, more specifically in the area of polaron dynamics. This work sought to address these issues by including polaron dynamics. Since the steady-state solution of existing models is able to accurately replicate steady-state performance, the transient EL is utilized as well as the steady-state solution to ensure that the underlying physics are accurately captured. A valid solution should be able to accurately fit both regimes using the same model parameter values. In order to leverage previous work, the archetypical green-emitter tris[2-phenylpyridinato-*c₂,N]Iridium(III) ($\text{Ir}(\text{ppy})_3$) is used for the extensively characterized photophysics.^{1,54,83–86}*

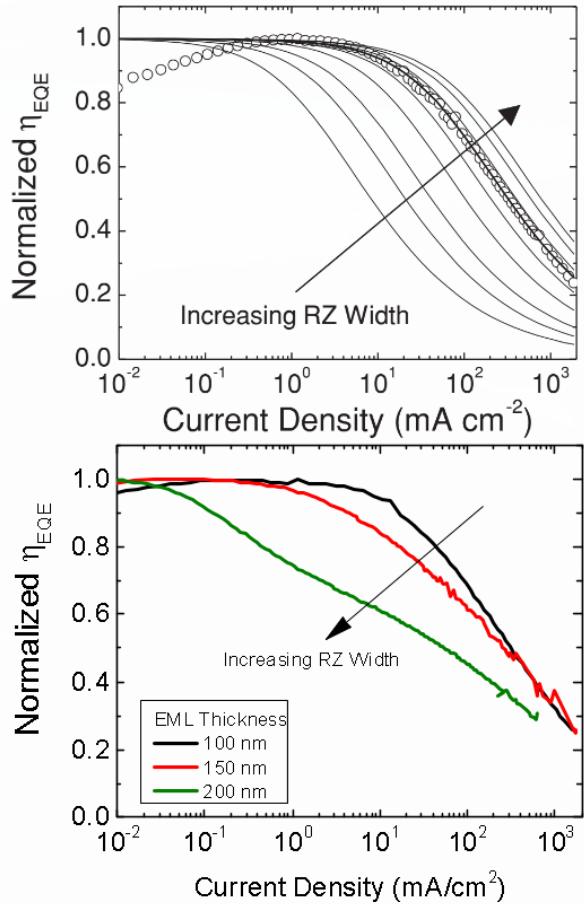


Figure 3.2: (a) Efficiency roll-off predicted by Erickson *et al.* 2014 as a function of recombination zone width.⁴³
(b) Observed efficiency roll-off for gradient EML devices.

3.2 Theory

3.2.1 Exciton Dynamics

The dominant processes that influence the exciton population, first formalized by Reineke *et al.*¹⁷, have been identified as natural exciton decay, via radiative and non-radiative processes, triplet-triplet annihilation, triplet-polaron quenching, and exciton generation.^{43,49} In triplet-triplet annihilation, two triplets are able to interact, and one exciton transfers its energy to the other, resulting in one molecule relaxing to the ground state and the other forming a hot exsuperated state. This hot state releases this additional energy to heat and typically relaxes back to the T_1 state. Triplet-polaron quenching is the interaction of a polaron with a nearby triplet exciton. Here, one of the charges of the exciton non-radiatively recombines with the polaron of the opposite charge, leaving a remaining loose charge. Excitons are also subject to field dissociation, but this mechanism is ignored in this work. Field dissociation is typically observed for fields larger than 2.5×10^6 V/cm. This is near the maximum field used for this study, and would be important to consider for higher voltage characterization.

In agreement with previous models, singlet-triplet exciton intersystem crossing and host-guest exciton energy transfer are assumed to be fast compared to exciton decay.^{2,17,54} Since these mechanisms are much faster, they will not be rate-limiting processes and can thus be omitted from the differential equations model without sacrificing accuracy. Within an operational device, electron and hole populations are indistinguishable. Therefore, the electron (n_e) and hole (n_h) densities are treated as a single generalized polaron population, $n_{pol} = n_e + n_h$. For simplicity, the model developed here treats the exciton and polaron populations as spatially uniform and confined to the exciton recombination zone. An spatial inhomogeneity in exciton and polaron density as well as their overlap is absorbed into the bimolecular rate constants. It is important to note that due to this assumption, rate constants are a property of the device stack, and not just a material property. With these assumptions, the dynamic processes determining exciton density (n_{ex}) can be summarized in the following one-dimensional rate equation:

$$\frac{dn_{ex}}{dt} = -\frac{n_{ex}}{\tau} - \frac{1}{2}k_{TT}n_{ex}^2 - k_{TP}n_{pol}n_{ex} + G_{ex} \quad (3.1)$$

where τ is the natural exciton lifetime, determined by the radiative (k_r) and non-radiative (k_{nr}) decay rates by $\tau = 1/(k_r + k_{nr})$, k_{TT} is the rate constant for triplet-triplet annihilation, k_{TP} is the rate constant for triplet-polaron quenching, and G_{ex} is the exciton generation rate. As this is a one-dimensional model, G_{ex} is a spatially uniform generation rate, a simplifying assumption. Many studies have modeled the exciton recombination zone profile, relying on material energy levels, as well as mobilities.^{87–91} While these

models are more accurate and explicit, in the way that they capture the physics, they also increase the dimensionality of our model, as well as increasing the parameterization; requiring separate electron and hole rate equations, mobilities and energy levels for every material. Even with this increased accuracy of the physical processes, identifying if the predicted exciton recombination zone is accurate requires significant additional measurements. Since the goal of this work is to provide a functional model to accurately predict the transient and steady-state device behavior, spatially uniform dynamics are assumed. Here, exciton formation is treated using a Langevin recombination formalism based on the polaron density.^{90,92,93}

$$G_{ex} = \frac{k_F}{4} n_{pol}^2 \quad (3.2)$$

where k_F is the rate constant for exciton formation. The factor of four accounts for the diversity of the polaron population and assumes that electrons and holes are in equal proportion. The accuracy of this prefactor is reduced for imbalanced charge, and is investigated in Section 3.7.2. For $n_e:n_h$ ratios 2:1 or better, less than 20% error is found in this term.

3.3 Polaron Dynamics

Previous models for efficiency roll-off have ignored polaron dynamics and assumed that all polarons readily form excitons. The steady-state polaron density is then modeled using a space charge limited model.⁶ To attribute physics to this process, a simple picture of polaron dynamics is assumed, consisting of charge injection and transport, exciton formation, and polaron loss. In order to preserve our one-dimensionality, polarons must be uniformly distributed. Without competing losses in the transport layers, all injected polarons must eventually reach the emissive layer. We further assume that polarons easily enter that emissive layer and that the majority of polaron build up occurs within the emissive layer, rather than the transport layers. Therefore, the charges injected from the current density, J , are uniformly generated in the emissive layer by $G_{pol} = 2J/ew$. Here, e is the electron charge, and the factor of two arises from an assumption of equal charge injection. In a well balanced device, the measured current forms holes on one side of the device and electrons on the other, and are both injected into the device. This is discussed extensively in Section 3.7.1. Polaron losses to exciton formation mirror the exciton formation rate presented in Equation 3.2, though at twice the rate due to two polarons forming one exciton.

The introduction of polaron loss from the emissive layer through the device without forming excitons is essential to address the limitations of previous models. Without this term, peak internal quantum efficiency of all devices is assumed to be 100% and the roll-up of efficiency at low current can not be explained. In

order to capture polaron loss, a first order approximation is made for loss in that only the majority charge carrier can be lost and leaks through the device with a characteristic time, τ_l . With these mechanisms, the full polaron dynamics can be expressed as:

$$\frac{dn_{pol}}{dt} = \frac{-k_F}{2} n_{pol}^2 - \frac{n_{pol}}{\tau_l} + G_{pol}. \quad (3.3)$$

3.3.1 Transient Electroluminescence

In this work, given a full model for polaron dynamics, the model is easiest to solve starting from the application of the current pulse, rather than at peak luminace. Under pulsed electrical excitation, Equations 3.1 and 3.3 can be solved at the beginning of the pulse with the initial conditions $n_{ex} = n_{pol} = 0$. Upon the application of a voltage pulse, there is a time delay before polarons reach the emissive layer, as evidenced by the delay in luminance turn on. This has been previously attributed to charge injection and transport in the emissive layer.⁹⁴ The injection time varies with device area due to the device capacitance and accounts for the majority of the delay time for large devices. Transport is dependent on the mobility, as well as the field, which is a function of time due to the device capacitance. These times can be well predicted using the following equations:

$$t_{inj} = \tau \log \left(1 - \frac{V_{th}}{V_0} \right) \quad (3.4)$$

$$d = \int_0^{t_{trans}} \mu_0 E_0 \exp \left(\sqrt{\gamma E_0 \left[1 - \left(1 - \frac{V_{th}}{V_0} \right) e^{-t/\tau} \right]} \right) \left[1 - \left(1 - \frac{V_{th}}{V_0} \right) e^{-t/\tau} \right] dt \quad (3.5)$$

where τ is the RC time constant of the device, V_{th} is the voltage injection threshold, t_{inj} is the injection time, t_{trans} is the transport time, d is the tranport layer thickness, μ_0 is the base mobility, γ is the field dependent mobility term, E_0 is the field and V_0 is the voltage. A prediction of the delay time as well as experimental values are shown in Figure 3.3. Interestingly, the functional dependence of the model accurately reproduces the extracted data. The mismatch in absolute value is due to the use of the geometric capacitance

in the model, and requires a scaling factor of 2.5 of the geometric capacitance for the calculated and fit delay times to agree. This factor is similar to that predicted by Liu *et al.* for similar structures.⁹⁵ This suggests that the effective charge distribution in our devices is about twice as wide as the emissive layer.

After this delay, constant current polaron generation is assumed for the remainder of the voltage pulse to calculate polaron generation. When the voltage pulse is removed, G_{pol} goes to 0 and the decay can be solved using Equations 3.1 and 3.3. This model does allow polarons to continue to form excitons after the voltage has been removed. In the transient regime, if the pulse width is shorter than τ_l , polarons are not able to traverse the emissive layer during the voltage pulse. Once the voltage is removed, there is no longer a driving force for polaron leakage via drift. Under this assumption, the leakage term in Equation 3.3 can be ignored. After the full device behavior is fit, the validity of this assumption can be assessed based on the fit values for τ_l .

3.3.2 Efficiency Analysis

The maximum external quantum efficiency of an OLED is often expressed as^{3,96}

$$\eta_{EQE} = \eta_{OC} \eta_{PL} \chi \eta_{EF} \quad (3.6)$$

where η_{EQE} is the external quantum efficiency, η_{OC} is the out-coupling efficiency, η_{PL} is the photoluminescence efficiency of the emissive molecule, χ is the fraction of excitons that are quantum mechanically allowed to emit (In the case of phosphorescent molecules, $\chi = 1$ and γ is typically referred to as the charge balance. While frequently applied, this expression suffers from two major limitations: first, there is no accounting for losses due to exciton quenching, and second, charge balance losses are not strictly defined. Since this equation is intended for the maximum efficiency, further modification would have to be done to account for quenching, as is done in Chapter 4. The charge balance factor, γ is typically used as a correction factor to account for differences between the observed η_{EQE} and the other calculated factors in Equation 3.6. It is widely hinted at that charge balance relates to the carrier balance, but no formalism is ever given, so it cannot be calculated. Given our full dynamics model, we are able to be explicit in both of these areas in a meaningful way. The internal quantum efficiency of a device is simply the ratio of the radiative exciton rate to the rate of electron injection, and we can therefore recast Equation 3.6 as

$$\eta_{EQE} = \eta_{OC} \frac{n_{ex} k_r}{G_{pol}/2}. \quad (3.7)$$

Note that in this equation, exciton quenching is accounted for in the n_{ex} term because in the steady-

state, n_{ex} is reduced according to this quenching, which is competitive with k_r . Dynamically, the charge balance factor is the fraction of injected polarons contributing in exciton formation. This can be viewed as the efficiency of Equation 3.3 to form excitons. Given this interpretation, we will recast the charge balance factor γ , as an explicitly defined exciton formation efficiency η_{EF} as

$$\eta_{EF} = \gamma = \frac{\frac{1}{2}k_F n_{pol}}{G_{pol}} = \frac{\frac{1}{2}k_F n_{pol}}{\frac{1}{2}k_F n_{pol} + \frac{1}{\tau_l}} \quad (3.8)$$

Equations 3.7 and 3.2 allow us to rigorously tie η_{EQE} and η_{EF} to dynamic processes within the device in a quantitative manner.

3.4 Experimental Details

Devices used for measurements of transient and steady-state EL had the following structure: ITO (150 nm)/poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT-PSS) (40 nm)/tris(4-carbazoyl-9-ylphenyl)amine (TCTA) (30 nm)/10% tris[2-phenylpyridinato-C2,N]Iridium(III) ($\text{Ir}(\text{ppy})_3$) doped in 4,4-Bis(N-carbazoyl)-1,10-biphenyl (CBP) (10 nm)/bathophenanthroline (Bphen) (30 nm)/LiF (1 nm)/Al (100 nm). Transient PL decays were measured using 60-nm-thick films of CBP doped with 10% $\text{Ir}(\text{ppy})_3$ deposited on quartz slides. The hole-only device structure used for steady-state PL quenching measurements had the following structure: ITO (150 nm)/PEDOT-PSS (40 nm)/10% $\text{Ir}(\text{ppy})_3$ in CBP (60 nm)/Au (50 nm). The gold cathode was used to prevent electron injection. Transient EL measurements were conducted using a voltage pulse generator (HP 8114a) with pulse amplitudes ranging from 5–40V and pulse widths ranging from 250 ns–500 ns with a period 500 ls. Luminescence was recorded using a set of collection lenses focused onto a fast photodiode (Thorlabs DET36A). Pulsed η_{EQE} measurements were conducted using the HP 8114a pulse generator until the device reached steady state current and luminance, which were recorded. Overlapping points with the steady state η_{EQE} measurement were used to calibrate the luminance-current ratio to the η_{EQE} . The photodiode signal was recorded using an oscilloscope (Tektronix TDS5104b). Transient PL measurements were collected using a pulsed nitrogen laser (Optical Building Blocks) with a pulse length of approximately 1 ns and emission wavelength of $\lambda = 337$ nm at a repetition rate of 6 Hz. Laser light was focused on the sample using a series of lenses, with collection carried out using the same techniques already described for transient EL. Incident laser power was measured using a Coherent EnergyMax 10MB-HE detector. Film thicknesses and optical constants used for modeling the out-coupling efficiency in Eq. (9) were obtained using a J. A. Woollam variable angle spectroscopic ellipsometer (VASE) using a Cauchy dispersion model.

3.5 Exciton Quenching in Photoluminescence

Photoluminescence measurements have been previously used to extract the rate constants for triplet-triplet annihilation and triplet-polaron quenching.^{17,43} This is important because it allows an independent confirmation of the extracted rate constants extracted during the electroluminescence fitting. The transient photoluminescence exposes the natural exciton lifetime, τ and at high incident flux, the triplet-triplet annihilation rate constant, k_{TT} . This measurement involves an incident laser pulse, in this case, from a 337 nm nitrogen laser, which is able to exsuperate a large exciton population. The pulse width of the nitrogen laser is 1ns and is much faster than τ or k_{TT} , allowing us to use Equation 3.1 with the initial boundary condition $n_{ex} = A(E_{pulse}/hfV)$ where A is the absorbed fraction of photons, E_{pulse} is the pulse energy, hf is the photon energy and V is the film volume. Since this is optical only excitation, the other boundary condition is $n_{pol} = 0$ and we can ignore Equation 3.3.^{17,43,54} For CBP films doped with Ir(ppy)₃, good agreement with the model is observed across a range on initial exciton densities, as shown in Figure 3.4(a). The exciton lifetime, τ was found to be mostly independent of exciton density and was globally fit to $1.5 \pm 0.2 \mu s$. The triplet-triplet annihilation rate constant appears to be a function of intensity and ranges from $k_{TT} = 2.4 \times 10^{-13} \text{ cm}^3/\text{s}$ at $n_{ex_0} = 4.1 \times 10^{18} \text{ cm}^{-3}$ to $k_{TT} = 6.9 \times 10^{-14} \text{ cm}^3/\text{s}$ at $n_{ex_0} = 1.1 \times 10^{20} \text{ cm}^{-3}$. These extracted values and trend with intensity are in good agreement with previous reports.^{17,43,97} It is important to note, that the exciton environment is very important for these values. Previous studies have shown that the presence of a metal cathode on top of the film can significantly reduce the exciton lifetime by allowing additional non-radiative recombination via surface plasmon coupling.⁴⁴ This becomes important in the comparison of these parameters with those

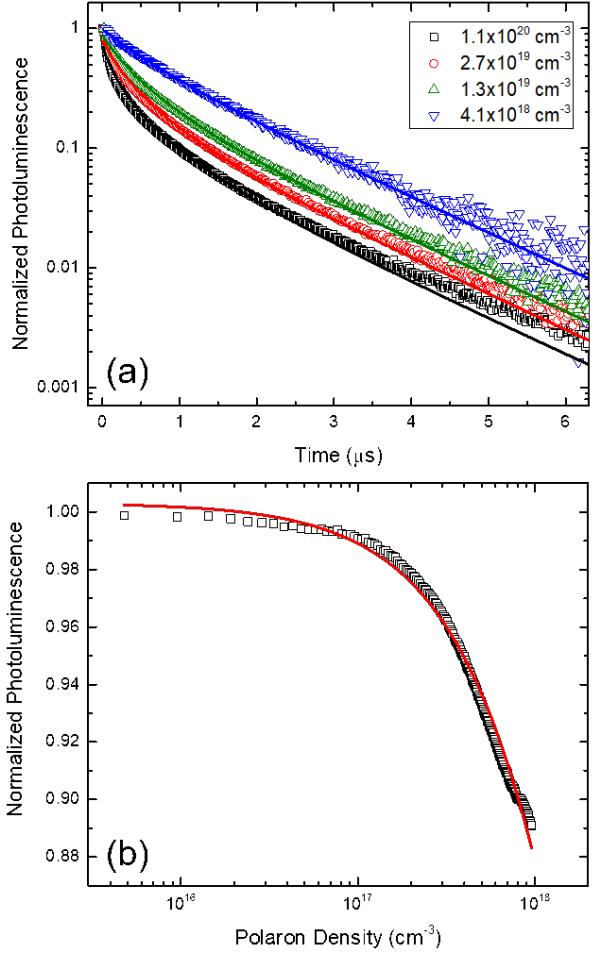


Figure 3.4: (a) Transient photoluminescence (PL) decays for several initial exciton densities with fits shown as solid lines using Eqn. 3.2. Fit parameters are discussed in SECTION. Exciton densities are calculated using measured incident power and beam size in combination with Beer's Law. (b) Steady-state PL quenching as a function of polaron density and the resulting fit from Eqn. 3.11 shown as the solid line.

mostly independent of exciton density and was globally fit to $1.5 \pm 0.2 \mu s$. The triplet-triplet annihilation rate constant appears to be a function of intensity and ranges from $k_{TT} = 2.4 \times 10^{-13} \text{ cm}^3/\text{s}$ at $n_{ex_0} = 4.1 \times 10^{18} \text{ cm}^{-3}$ to $k_{TT} = 6.9 \times 10^{-14} \text{ cm}^3/\text{s}$ at $n_{ex_0} = 1.1 \times 10^{20} \text{ cm}^{-3}$. These extracted values and trend with intensity are in good agreement with previous reports.^{17,43,97} It is important to note, that the exciton environment is very important for these values. Previous studies have shown that the presence of a metal cathode on top of the film can significantly reduce the exciton lifetime by allowing additional non-radiative recombination via surface plasmon coupling.⁴⁴ This becomes important in the comparison of these parameters with those

obtained under electroluminescence within a device. A more representative experiment would have involved a full device stack with cathode, rather than just a film. Alas, I did not have that foresight for this experiment.

Triplet-polaron quenching rate constant measurement is done in single carrier devices as a function of polaron density. It is largely uninvestigated as to the differences between electrons and holes, but in previous works, hole only currents are used, a precedent which will be followed in this work.^{17,43} A steady-state exciton population is generated optically, in this case, a 405 nm laser. In a single carrier device, a space charge limited current model featuring an exponential trap distribution is often used.^{6,8,72} This model is employed largely because it fits the obtained current-voltage behavior most closely. In reality, a single trap state would be expected, as that is what is introduced by Ir(ppy)₃ in a doped film. These models are frequently employed, despite their inaccuracies, largely for simplicity. A more accurate determination of polaron density is discussed in Chapter C. However, in a space charge limited model with an exponential trap distribution, the current density voltage relationship can be modeled using

$$V = \left[\frac{J}{e\mu N_C} d^{2l+} \left(\frac{eN_0 k_B T_t}{\epsilon} \right)^l \right]^{\frac{1}{l+1}} = CJ^{\frac{1}{l+1}}, \quad (3.9)$$

where N_C is the density of states at the transport level, ϵ is the permittivity, μ is the mobility, L is the device thickness and $l = T_t/T$ with T_t being an experimentally determined characteristic temperature of the trap distribution. The Polarond density is then given by

$$n_{pol} = eN_c \left(\frac{\epsilon V}{ed^2 N_0 k T_t} \right)^l. \quad (3.10)$$

Combining Equation 3.10 with Equation 3.1, the ratio of the steady-state PL intensity (L) to the PL intensity in the absence of polarons (L_0) can be written as¹⁷

$$\frac{L(n_{pol})}{L_0} = \frac{1}{1 + \tau k_{TP} n_{pol}} \quad (3.11)$$

After fitting the current density-voltage characteristics of the device are fit using Equation 3.9, Equations 3.10 and 3.11 can be used to extract the triplet-polaron rate constant for a given value of τ . In this case, we use τ as extracted from the transient PL measurements. The fit obtained for a CBP Ir(ppy)₃hole only device is shown in Figure 3.4b. This devices utilizes a gold cathode to prevent electron injection and shows minimal exciton formation, as expected. The organic stack is the same as the emissive layer of the inviestigated device. In fitting the current density-voltage characteristics using Equation 3.9, a value of $l = (2.4 \pm 0.2)$ was found. The extracted triplet-polaron quenching rate constant from fitting Equation 3.11 was $k_{TP} = (2.8 \pm 0.2) \times 10^{-13}$ cm³/s and is agreement with previous measurements.^{17,43}

3.6 Application to Devices

In order to fit both the steady-state and transient regimes, decisions need to be made as to a methodology for extracting parameters. The obvious choice may seem to be to try to produce a global fit by fitting both regimes simultaneously. The major draw back of this approach is the value of τ_l . Since this is a function of the applied field, this is not single valued and relies on knowing the field dependence. Additionally, the steady-state provides little insight into the actual quantities of τ , k_{TT} , k_{TP} , and k_F , and only the ratio of radiative and non-radiative processes is needed for a quality fit of the efficiency roll-off. Additionally, within this model, only n_{ex} is experimentally available to fit, and the fit parameters are not independent. The most obvious example of this is the values of k_{TT} and k_{TP} , which have similar impact on the exciton population and similar formulation. This makes it near impossible to distinguish a dominant mechanism between these two, and results for exact values of quenching constants need to be considered with caution. This methodology only gives a net effect of the two quenching mechanisms in total, rather than a true separate measurement of both quantities as is obtained in the PL quenching measurements, discussed in Section 3.5.

With these limitations addressed, the method used for this discussion to fit all of the device physics has been carefully considered to achieve the highest parameter sensitivity. The bimolecular quenching constants are most sensitive to the efficiency roll-off since small changes in the quenching constants make a large impact on the roll-off behavior. However, the lifetime and exciton formation can only be determined to within a fixed ratio. In contrast, the exact values of lifetime and exciton formation rate are critical to the behavior of the transient EL while the bimolecular quenching constants are difficult to probe in the current regime investigated. In order to use these sensitivities, a quenching only model (ignoring τ_l) to fit the normalized efficiency roll-off, such has been previously reported, is used to determine the bimolecular quenching rates, k_{TT} and k_{TP} . Quenching only models can only fit the normalized η_{EQE} roll-off because without a polaron loss term, η_{EF} is assumed to be 100% and the exact magnitude of efficiency cannot be reproduced. Initial values for all parameters, except k_F which is previously unmeasured, are determined by the photoluminescence measurement values. With these quenching rates fixed, the transient EL is fit using Equations 3.1 and 3.3 in order to determine τ and k_F . Remember that in the transient regime for short pulses, we can assume that $\tau_l = \infty$ and can be ignored.

With these critical rate constants determined, we will revisit the efficiency as a function of current density. In the first pass, we ignored the exact value of efficiency and only fit the normalized roll-off. Now, since we know the other parameters, we can revisit η_{EQE} , now matching the exact profile for all currents, by conducting a point-by-point fit for k_F . This fit for k_F can then be used to calculate η_{EF} and can be compared to a drift model, to assess its validity.

3.6.1 Quenching Only Steady-State Fit

To measure transient and steady-state EL, devices were constructed using the architecture discussed in Section 3.4. These devices had an η_{EQE} of $(9.7 \pm 0.1)\%$. Equations 3.1 and 3.3 were used to fit the peak normalized steady-state efficiency roll-off with $\tau_l = \infty$. Again, omitting a polaron loss term, this model assumes that all roll-off behavior comes from quenching. Parameters were initialized using the values obtained from PL quenching measurements, described in Section 3.5. An experimental fit is shown in Figure 3.5 and shows good agreement, except at very high currents associated with pulsed η_{EQE} measurements. Parameters are summarized in Table 3.1 and are in good agreement with those previously reported.^{17,54}

	Transient EL	Efficiency Roll-off
τ (s)	$6.9 \pm 0.1 \times 10^{-7}$	6.1×10^{-7}
k_{TT} (cm ³ /s)	7.1×10^{-12}	7.1×10^{-12}
k_{TP} (cm ³ /s)	3.3×10^{-13}	3.3×10^{-13}
k_{F} (cm ³ /s)	$7.7 \pm 3.5 \times 10^{-12}$	1.6×10^{-11}

Table 3.1: Fit parameters extracted from transient and steady-state electroluminescence. Transient EL fit parameters averaged over all measured current densities. η_{EQE} roll-off parameters averaged over several measured devices. Triplet-triplet annihilation and triplet-polaron quenching rates are fixed to those obtained from fitting the normalized efficiency roll-off.

3.6.2 Transient Modeling

Transient EL measurements were conducted on the same devices used for the efficiency measurements described in Section 3.6.1. Pulse widths ranging between 250–500 ns with a period of 500 ls were used with current densities ranging between 0.5–50 A/cm². Fast Fourier Transform (FFT) filtering is used to remove experimental noise from the measured signal to increase fit accuracy. The bimolecular quenching rate constants are fixed to the values determined from the fitting of the steady-state efficiency roll-off (Table 3.1). The exciton lifetime and exciton formation rate constant are allowed to vary to fit the transient EL and are summarized in Table 3.1. The value of τ is shorter than that obtained under transient PL, likely due to the cathode present for EL transient studies.⁴⁴ Fits using this model are shown in Figure 3.6 and show excellent

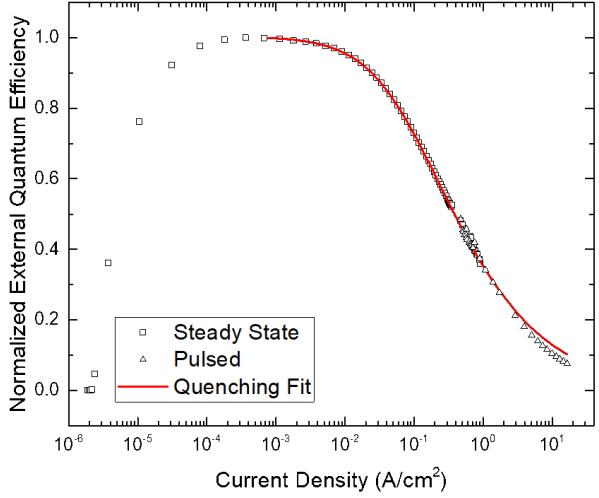


Figure 3.5: Normalized experimental η_{EQE} as a function of current density. Solid line is a fit to the data using Eqn. 3.1 and 3.3 in the absence of polaron loss. Pulsed eqe measurements are conducted using low duty cycle pulses to steady-state luminance to reduce Joule heating in device.

agreement above the detection limit. The initial turn on is well replicated by the luminance delay model discussed in Section 3.3.1

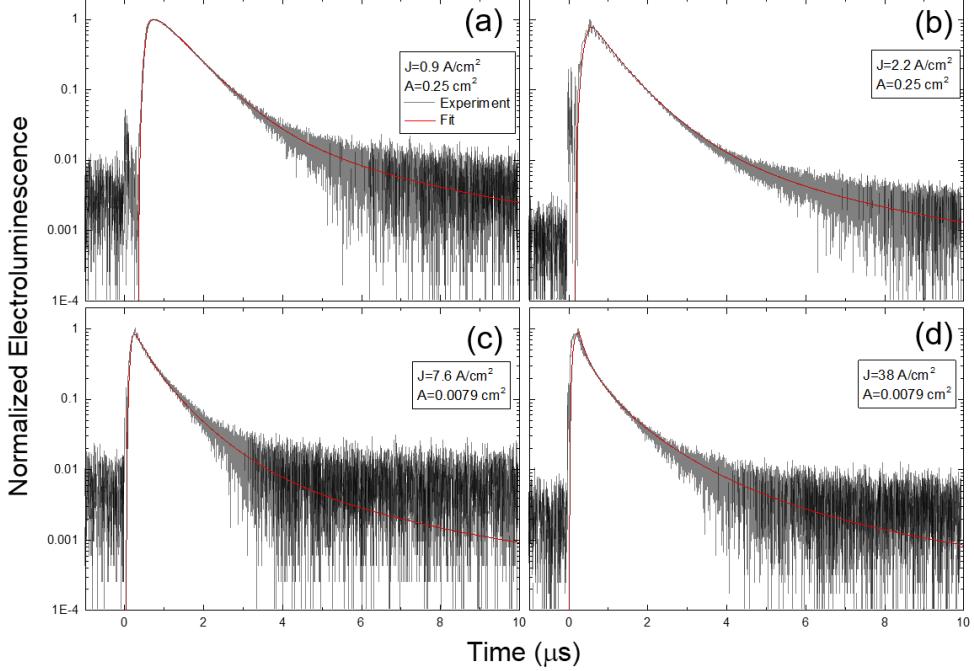


Figure 3.6: Transient electroluminescence (EL) for four different current densities (J) and device areas (A). (a) 0.25 cm^2 device at a current density during the pulse of $J = 0.9\text{ A}/\text{cm}^2$ (b) 0.25 cm^2 device at $J = 2.2\text{ A}/\text{cm}^2$ (c) 0.0079 cm^2 device at $J = 7.6\text{ A}/\text{cm}^2$ (d) 0.0079 cm^2 device at $J = 38\text{ A}/\text{cm}^2$

3.6.3 Transient Term Efficiency

Utilizing the understanding of dynamics developed here, the efficiency of each component in Equation 3.1 for the transient EL can be analyzed. This is shown for representative high and low current density behavior in Figure 3.7. At the application of the voltage pulse, exciton generation is the dominating feature, resulting in a steep rise in luminescence. As the exciton and polaron populations peak, the resulting dependence is seen on the bimolecular quenching terms, leading to the curvature seen before and after the removal of the injected current. During the decay, the exciton and polaron populations rapidly decrease due to quenching, resulting in the natural exciton lifetime becoming the dominant behavior. As the exciton population further diminishes, formation of excitons from the residual polaron population is observed, resulting in the slow decay seen at long times. Figure 3.7a shows the decoupled EL transient behavior at a low current density where exciton formation and the natural lifetime are always competitive processes, resulting in the slow rollover in the experimental behavior of Figure 3.6a. Slightly higher current densities do not show the bimolecular terms rise to prominence, resulting in the linear decay after the pulse seen in Figure 3.6b. Bimolecular quenching terms show increasing importance with current density, especially at times soon after the removal of voltage.

We see this behavior in Figures 3.6c and 3.6d with the decoupled high current density behavior of Figure 3.6d demonstrated in Figure 3.7. Here, we are able to see that bimolecular quenching events dominate when the exciton density is peaked after the removal of voltage.

3.6.4 Extracting Exciton Formation Efficiency

Thus far in the fitting, the introduced model has successfully fit the transient EL and steady-state efficiency roll-off using Equations 3.1, 3.2, and 3.3 by including polaron dynamics in the absence of charge leakage. However, only the efficiency roll-off and the normalized reduction in magnitude have been modeled. By including the polaron transit time in the analysis, the exact magnitude can be fit for both the rise and fall of efficiency. Starting with the experimental η_{EQE} as a function of current density, Equation 3.7 can be used to find the exciton density, n_{ex} , as a function of current density, which in turn allows Equations 3.1 and 3.3 to be solved in the steady-state for τ_l . The out-coupling efficiency, η_{OC} , is separately determined using optical modeling and found to be $\eta_{\text{OC}} = 17.7\%$.^{4,5} The details of this calculation are discussed in Chapter 8. The radiative rate in Equation 3.7 can be extracted from measurements of τ and η_{PL} as $\eta_{\text{PL}} = \tau k_r$. Once the exciton population is known, Equation 3.1 can be solved for the polaron population, n_{pol} using the fit values from the transient EL. With n_{pol} and G_{pol}

known, Equation 3.3 can be used to extract the τ_l needed to reproduce the experimental η_{EQE} . This technique produces an exact match of the shape and magnitude of the efficiency, including both the roll-up and roll-off. This is the first time in literature that a quantitative physical explanation has been attributed to the roll-up. Any error in this method are absorbed into τ_l . Extracted values of τ_l are shown in Figure 3.8. In order to justify these values, a simple drift model explanation can be used, quantified by

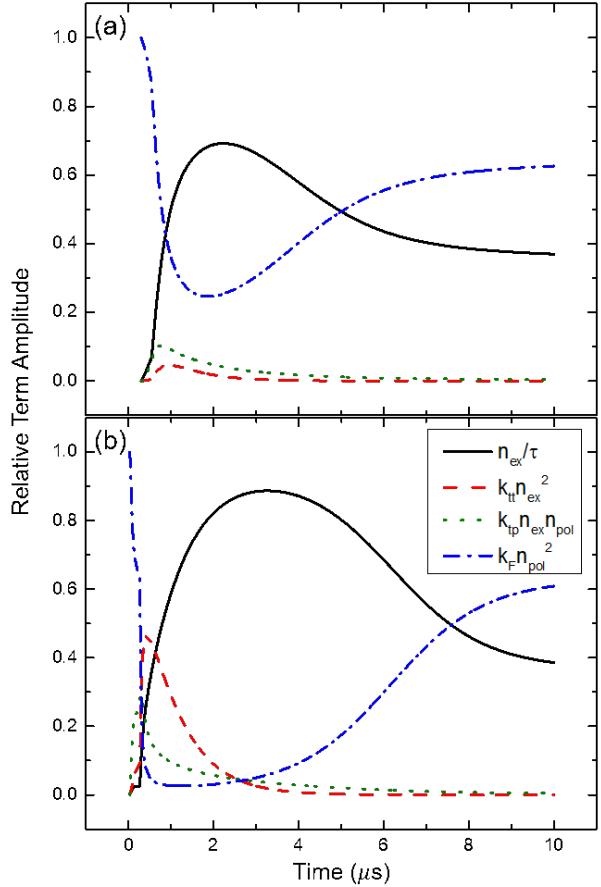


Figure 3.7: Term efficiency for each dynamical process influencing the exciton population for (a) 0.25 cm^2 device operated at 0.9 A/cm^2 for 500 ns and (b) 0.785 mm^2 device operated at a current density of 38 A/cm^2 for 250 ns. Relative term amplitude is calculated as the magnitude of each term in Eqn. 3.1 divided by the sum of absolute values of each term.

$$\tau_l = \frac{w}{E\mu(E)}. \quad (3.12)$$

Where μ is the mobility, obtained from Parshin *et al.*,⁹⁸ w is the device width, and E is the electric field. This simple explanation for τ_l holds very well at low current density, corresponding to the efficiency roll-up, as well as the peak efficiency. Deviation from this model occurs as current density increases past 10^{-1} A/cm². However, in this regime, exciton and charge densities are becoming increasingly high, and the predicted values become increasingly non-physical. It is expected that in this regime, this simple model described in Equation 3.12, would break down.

3.6.5 Drift Model

With the transit time known, Equation 3.8 can be used to find η_{EF} , shown in Figure 3.8. Charge balance remains relatively constant throughout the onset of roll-off and only falls when the efficiency approaches one quarter of its initial value. Using a different modeling approach, Giebink and Forrest⁴⁸ find that for a similar system, a larger portion of the roll-off is due to a loss of charge balance, likely due to a thicker emissive layer and differing transport layers than those used in this study. With the dependence of the charge balance factor on current density established, the validity of the assumption of uniform charge balance during the fit of the normalized efficiency roll-off in Section 3.6.1 can now

be assessed. The charge balance, seen in Figure 3.8, remains almost constant for the majority of the roll-off but deviates at high current density, suggesting that the high current density regime should not be fit with the quenching only model. However, the fit shown in Figure 3.5 is not limited by this restriction as there is excellent agreement between the model and experiment in the regime of near constant charge balance, with the only discrepancy in the fit coming at high current density where the model assumptions break down. Returning to fit the normalized efficiency in the regime of near constant charge balance, as defined by Figure 3.8, while holding τ and k_F constant, k_{TT} and k_{TP} are found to be $(4.5 \pm 0.4) \times 10^{-12}$ cm³/s and $(2 \pm 3) \times 10^{-12}$ cm³/s, respectively. This small variation of quenching parameters does not change the fit quality for the

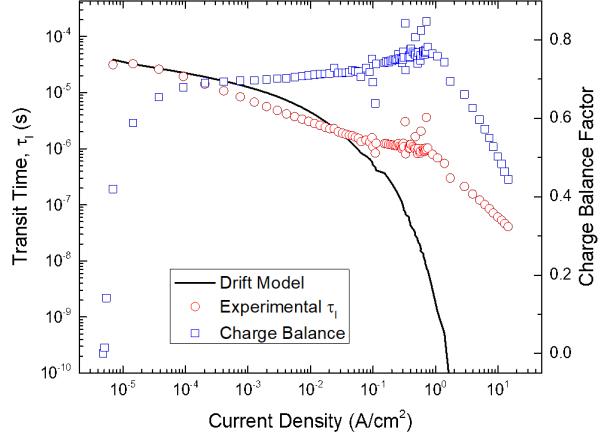


Figure 3.8: Transit time extracted from η_{EQE} measurements are shown as the red circles. Predictions using the drift model are calculated using Eqn. 3.12. The drift model assumes a uniform electric field. Good agreement between the experimental transit time and the drift model is found for a field distributed over 20 nm. The charge balance factor is shown as a function of current density in blue squares.

regime in question. Repeating the fitting process in this regime yields no significant differences in τ and k_F or the dependence of charge balance on current density.

3.7 Understanding Assumptions of Polaron Model

In the model described in this work, electrons and holes are summarized into a generalized polaron population with the dynamics described using Equation 3.3. To understand the impacts that this has on calculating the polaron injection rate and the exciton formation rate, the electrons and holes must be independently examined. The most complete dynamics picture related to the developed model would express individual electron and hole injection as well as individual transit times. This full picture can be written as:

$$\frac{dn_h}{dt} = -k_F n_e n_h - \frac{n_h}{\tau_{lh}} + \frac{J_h}{ew} \quad (3.13)$$

$$\frac{dn_e}{dt} = -k_F n_e n_h - \frac{n_e}{\tau_{le}} + \frac{J_e}{ew} \quad (3.14)$$

where n_e and n_h are the electron and hole population densities, τ_{lh} and τ_{le} are the electron and hole transit times, respectively, J_h and J_e and are the single carrier injected currents. While more accurate, Equation 3.13 and 3.14 pose several problems for replicating device behavior due to the inability to distinguish between carriers during device operation. This is further complicated by the inability to separately measure the single carrier injected currents and leak rates due to transit times. To better understand the approximations used in Eqn. (3), a detailed analysis of current injection is presented, followed by error analysis of the exciton formation term based on the composition of the polaron population.

3.7.1 Carrier Injection

Let J be the total current within our device. This must be maintained throughout our circuit assuming no charge buildup. Within the device, the total current can be written as $J = J_e + J_h$. Experimentally, J is the only measurable current as we are not able to distinguish between electron and hole or leaked currents. The current incident on either contact will be referred to as J_1 and J_2 . These currents are summarized in Figure 3.9. In the case of no leakage current, there must be complete recombination in the emissive layer. Therefore all of the externally measured current from one side of the device contributes only to electron current and all current on the other side contributes only to hole current.

$$J_1 \rightarrow J_h = J_2 \rightarrow J_e \quad (3.15)$$

This maintains constant current throughout the external circuit. No charges are allowed to leave the emissive layer without recombining with the opposite charge species and constant current maintains that $J_e = J_h$. The injected polaron density is then:

$$\frac{J_e}{ew} + \frac{J_h}{ew} = \frac{J_1 + J_2}{ew} = \frac{2J}{ew} \quad (3.16)$$

This expression becomes more complicated when charge leakage is allowed. Let us assume that holes are the only leaking species. Let J_l be the current leaking through the emissive layer. On the hole side of the device, all current is hole current. However, on the electron side of the device, the measured current is a combination of the electrons injected and the leaked holes.

$$J_1 = J_h \quad (3.17)$$

$$J_2 = J_e + J_l \quad (3.18)$$

For current continuity, the current on either side of the device must be equal.

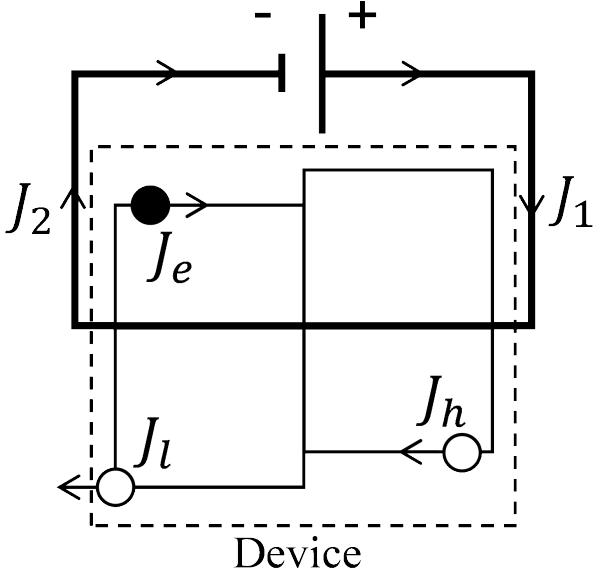


Figure 3.9: Current density formalism within the circuit. J_1 and J_2 are the currents measured on either side of the device. J_e and J_h are the electron and hole currents within the device and J_l is the unbalanced current, assumed to be only holes, that leaks out of the opposing contact.

$$J = J_h = J_e + J_l \quad (3.19)$$

From this expression and the experimentally measured current, it is not possible to know the electron and hole currents independently without making some assumption about the leaked current. If both carriers are allowed to leak, there is a leakage term on the hole current side of Equation 3.18 as well. Without additional information about the proportion or magnitude of the leaked current, there is no exact expression for polaron injection in terms of J . Therefore, the approximation is used that the polaron injection and loss due to leakage can be written as:

$$G_{pol} - \frac{J_l}{ew} = \frac{2J - J_l}{ew} \quad (3.20)$$

This is the expression used in the final model, assuming the charge leakage can be written in terms of the

total population and a transit time for leakage as $J_l/ew = n_{pol}/\tau_l$ and $G_{pol} = 2J/ew$. The approximation in Equation 3.19 is strong assuming is small relative to J_h and J_e .

3.7.2 Charge Imbalance

In the exciton formation term of Equation 3.3, the factor of two in the denominator assumes that charges are in equal proportion. More generally, Equations 3.14 and 3.13 can be used to evaluate the error in this term as the charge balance increases. Let the carrier ratio be defined as:

$$\alpha = \frac{n_h}{n_e + n_h} \quad (3.21)$$

This is different from the charge balance we have defined in the text as this is an actual ratio of carriers, rather than the exciton formation efficiency. Additionally, let $n + pol = n_e + n_h$ be the polaron population density. With these definitions, the terms for polaron loss to exciton formation of Equations 3.14 and 3.13 can be summed as:

$$\left[\frac{dn_{pol}}{dt} \right]_{formation} = -2k_F n_{pol}^2 \alpha(1 - \alpha) \quad (3.22)$$

In the case of perfect balance, the expression $\alpha(1 - \alpha) = 1/4$ and agrees with Equation 3.3. The variation in $\alpha(1 - \alpha)$ as a function of α can be seen in Figure 3.10. With charge ratios up to 1:3, there is less than a 20% error in this expression. The high efficiency devices examined in this work are expected to operate in this regime, and the value of $\alpha(1 - \alpha)$ should not change the value of k_F significantly.

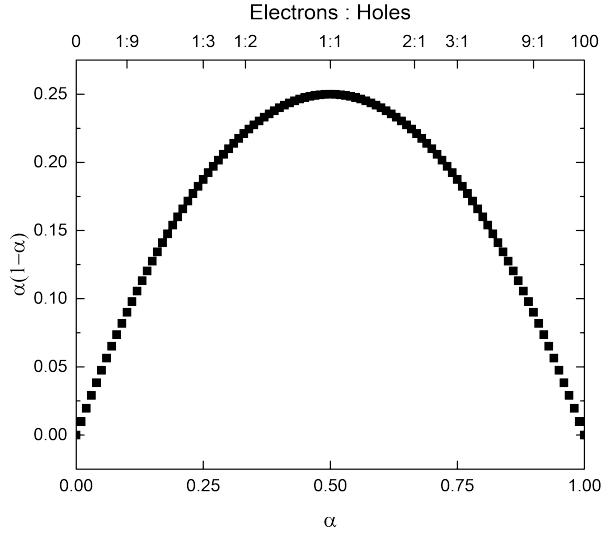


Figure 3.10: The quantity $\alpha(1 - \alpha)$ is plotted as a function of the polaron composition, α and the electron to hole ratio.

3.8 Conclusion

A universal dynamics model has been successfully implemented that allows the fitting of the transient and steady-state EL behavior of OLEDs using Ir(ppy)₃ as an emitter. This model relies upon the previously studied parameters τ , k_{TT} , and k_{TP} as well as introducing polaron dynamics in the form of an exciton formation rate, k_F and polaron leakage time τ_l . This model has been used to deconstruct all features of the transient EL over three decades of decay. The fit parameters τ , k_{TT} , and k_{TP} have all been verified

independently using PL studies in agreement with the proposed model. The steady-state efficiency has been fully characterized using quenching and charge leakage through the device. The behavior of the investigated devices suggests that charge leakage through the emissive layer dominates the roll-up in efficiency, while bimolecular quenching is responsible for the majority of the roll-off in efficiency.

This model has successfully been able to model all of the device physics present in the electroluminescence behavior. However, one of the initial goals of this project was to be able to quantify the bimolecular rate constants more effectively within a device. In this regard, the model is not useful as k_{TT} and k_{TP} are codependent and their relative values are still unknown.

Chapter 4

Integrated Photoluminescence Lifetimes

As OLEDs become fully a fully commercialized technology, several challenges still exist that need to be overcome to realize full potential. Chief among these is the operational lifetime, which has been a key focus of recent studies.^{75,99–102} Lifetime is typically characterized at constant current density, recording the luminance loss and voltage as a function of time. The lifetime is then reported as the time to reach some arbitrary fraction of the initial luminance. Unlike the steady-state efficiency, it is difficult to optimize a device lifetime by brute force. Due to the long lifetime of devices, even under accelerated aging, it takes a substantial amount of time to characterize devices and iteravly improve a design. This reality makes it essential to have a deeper insight into the processes that are limiting lifetime.

While this simple lifetime characterization is effective for device to device comparision, further insight into the mechanism is found wanting. Modeling techniques are used extensively for degradation characterization, using the mechanisms outlined in Chapter 2.8.1.^{57,58,103} While these techniques are able to reproduce the decay characteristics with a root in physical mechanisms, they suffer from over-parameterization and introduce parameters that cannot be experimentally confirmed. As discussed in Chapter 2.8.3, a variety of chemical, structural, and spectroscopic techniques are often employed to gain further insight into the physical processes.^{75,100,101,104,105} These techniques can be insightful, but are difficult to apply on a large scale due to the additional processing time. Post degradation analysis does not provide a temporal characterization of degradation without processing individual devices at several decay points, which can be extremely time consuming. Additionally, it may be helpful to catagorize luminance loss into different luminance loss pathways, which few of these techniques are able to do. It would be benificial to have a technique that is able to provide more information during the degradation, without increasing experimental time, as well as provide a way to decouple loss pathways. This is done by introducing an optical pump to independently measure

η_{PL} as a function of time. Similar techniques have been utilized before, but have lacked completeness in their care to treat assumptions, as well as their resolution.^{106–108}

This chapter demonstrates a method for decoupling the device photoluminescence loss from the exciton formation losses during operational lifetime testing. This is a summary and extension of my work entitled *Decoupling degradation in exciton formation and recombination during lifetime testing of organic light-emitting devices*.⁷³

4.1 Luminance as Efficiency Loss

When OLEDs are degraded at constant current density, luminance loss is observed. As discussed in Chapter 2.3.2, quantum efficiency is the ratio of photons leaving the device per electron input. Therefore, at constant current density (or constant electron flux), luminance loss is actually an efficiency loss. Chapter 3 extensively discussed a revised formalism for understanding OLED efficiency. In particular, we will take advantage of the formalism of exciton formation efficiency. For decoupling luminance loss pathways, a categorical expression for η_{EQE} is desired, rather than the dynamics approach taken in Equation 3.7, therefore Equation 3.6 is modified to include a quenching term, yielding

$$\eta_{EQE} = \eta_{PL} \eta_{OC} \chi \eta_{EF} \eta_\tau \quad (4.1)$$

where η_τ is the fraction of excitons that relax via the natural exciton lifetime, τ . this term is current-density dependent and captures the quenching events discussed in Chapter 3. It is also important to note that during degradation, η_{EF} captures not only the previously discussed polaron loss due to leakage events, but also the formation of non-radiative recombination centers (NRRCs). NRRCs are states that form excitons off of the emissive molecule and allow charge recombination without forming light, which have been shown to be present in degrading devices.^{107,109} The interpretation of η_{EF} as the exciton formation efficiency needs to be clarified to be the efficiency of exciton formation on the emissive molecule, but remains otherwise unchanged.

During degradation, to categorize efficiency loss, each term in Equation 4.1 could be considered to be time dependent. However, it is reasonable to assume that some of these terms are unchanged, or have minimal impact. The exciton's radiative spin fraction, χ is a quantum mechanical property of the emissive molecule. Therefore, without changes in the emissive molecule, this term should remain constant. If emission from another state was observed spectrally, this would indicate a need to adapt Equation 4.1 for multiple emissive states, greatly complicating this process. Thankfully, that is of yet unobserved in our research.

The out-coupling efficiency, η_{OC} , is a property dependent on the layer optical constants and thicknesses. Without significant changes in molecular composition and morphology, it is unlikely that η_{OC} should change. The most likely was to create these changes would be through crystallization. This can be investigated by looking at the devices under crossed polarized optical microscopy.¹¹⁰ Figure 4.1 shows that in our devices, no crystallization is observed. The reference photo, taken from Fielitz *et al.*¹¹⁰ demonstrates how apparent crystallization would be if present. It is also important to note that η_{OC} depends on the emitter distribution within the device, and thus the recombination zone. If there is a shift in RZ, out-coupling is likely to change. It is difficult to assess recombination zone and unprecedented to measure as a function of degradation.

However, this problem is minimized in thin emissive layers, so studies should attempt to focus on thinner EML devices to reduce error.

Lastly, η_τ is assumed to be constant for this work since it cannot be measured quantitatively. An approximation of the impacts of this term are discussed in Section 4.2.4

With these terms assumed to be constant, the only time dependent terms are η_{PL} and η_{EF} , and the time dependent version of Equation 4.1 can be written as

$$\frac{\eta_{EQE}(t)}{\eta_{EQE}^0} = \frac{\eta_{PL}(t)}{\eta_{PL}^0} \frac{\eta_{EF}(t)}{\eta_{EF}^0} \quad (4.2)$$

where X^0 is the initial value of the parameter before degradation. Since $\eta_{EQE}(t)$ is the luminance loss as a function of time, an independent measurement of η_{PL} would allow a full decoupling of η_{EQE} into η_{PL} and η_{EF} .

4.2 Photoluminescence Characterization

In order to independently measure η_{PL} during degradation, intermittent optical excitation is done using a laser, as shown in Figure fig:schematic. The laser forms a 1mm diameter circular spot on the active device

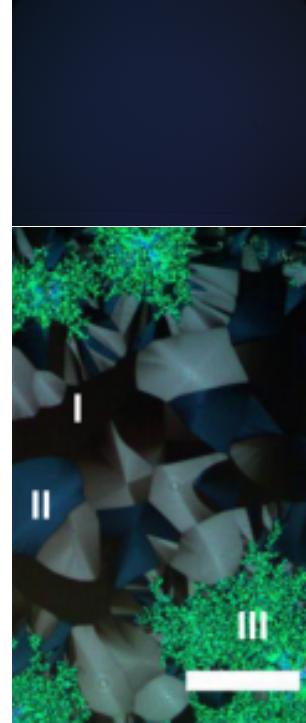


Figure 4.1: Cross polarized optical micrographs of (a) active device area (b) crystalized film from Fielitz *et al.*¹¹⁰ (I) Orthorhombic phase, (II) Triclinic Phase, (III) 200 μm scale bar

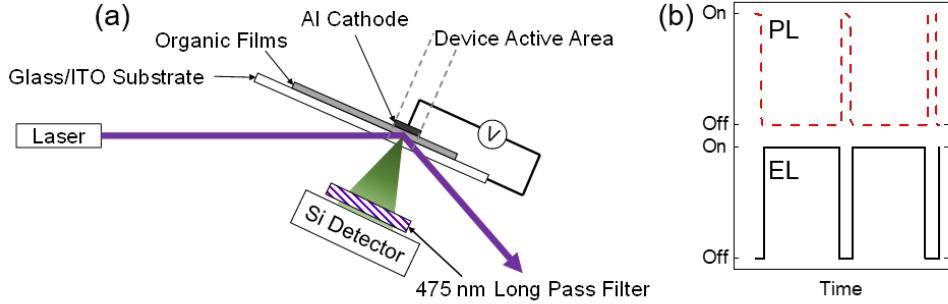


Figure 4.2: (a) Experimental configuration for the measurement of electro- (EL) and photoluminescence (PL) during OLED degradation. Laser excitation is incident on a subsection of the device area. The laser is aligned so that neither the incident nor reflected beam strikes the detector. Stray laser light is removed by a $\lambda=475$ nm dielectric long pass filter. (b) Excitation scheme. EL and PL signals are probed independently with no temporal overlap. (c) External quantum efficiency versus current density and luminance for devices having emissive layer thickness of 10 nm, 20 nm and 30 nm.

area. The photoluminescence loss observed from this measurement can be related to the photoluminescence efficiency loss by

$$\frac{\eta_{PL}(t)}{\eta_{PL}^0} = \frac{L_{PL}(t)}{L_{PL}^0} \frac{I^0}{I(t)} \frac{\alpha^0}{\alpha(t)} \quad (4.3)$$

where L_{PL} is the experimentally measured luminance, I is the pump intensity, and α is the film absorption. The pump intensity, I , can be measured and is observed to remain constant within error during the degradation. The absorption, α , has also been measured before and after degradation, and is found to be constant within error. However, the sensitivity of the absorption measurement may not reflect the sensitivity of the η_{PL} measurement. An alternative method to verifying the η_{PL} measurement is presented in Section 4.2.5.

In traditional lifetime measurements, constant current density excitation is used. In order to measure η_{PL} as well, the current is paused every 10 minutes long enough to stabilize the laser and take a measurement, before the current is resumed. This takes on the order of 20 seconds, and is shown in Figure 4.2b. To make these measurements comparable with traditional lifetimes, time is reported as the elapsed time under

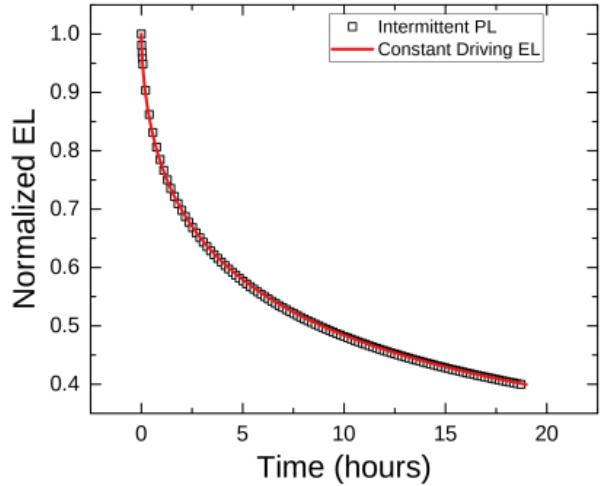


Figure 4.3: Lifetime obtained under a constant driving current is shown in red solid line. Lifetime under the same conditions but with PL measurement breaks is shown in open squares. Strong agreement is observed.

electrical current, with the laser breaks subtracted. This method has been shown to accurately match the traditional lifetime measurements, without additional degradation due to the PL measurement or relaxation from the breaks in current, as shown in Figure 4.3.

The accuracy of this measurement technique relies heavily on several testing considerations and assumptions. Important considerations of testing conditions and sources of error are discussed in the following sections.

4.2.1 Light Selection

Light sources for optical pumping are required to be powerful enough to pump the emitter sufficiently for measurement, stable enough to maintain output power for lifetimes over 100 hours, and long lived. Ideal candidates are lasers and high power lamps, though lamps often have a long warmup time, which is not ideal for the short on time needed for this experiment. Lamps do have the advantage that they can pump all of the device active area, getting a better sample of the behavior, though lasers can be expanded for the same effect.

During the optical pumping, it is important to only pump the emissive layer, and for the most direct measurement of η_{PL} , only the emitter molecule. To accomplish this, careful selection of wavelength must occur. Figure 4.4 shows the optical extinction coefficient for several materials. Ideally, the pump wavelength should be selected so that the emitter molecule has significant absorption, but the host does not. This is relatively easy for the green emitter, $\text{Ir}(\text{ppy})_3$ where a wide range of pumps would work between 375 and 500 nm. However, this becomes extremely difficult for blue emitters such as $\text{Fir}(\text{pic})$, where hosts are more resonant with the emitter. In this case, the host may have to be pumped and exciton transfer from the host to the guest will be included in the measurement. Even with this, the transport layers would have to have higher triplet energies than the emitter.

Due to these limitations, lasers are ideal light sources for green emitters, since they are easily manipulated optically to pump multiple devices. Here, the limitations of available laser wavelengths are less important due to the wide pumping window. However, for blue emitters, a lamp may be a more viable option as it would allow filtering or monocromation to be more selective of wavelength.

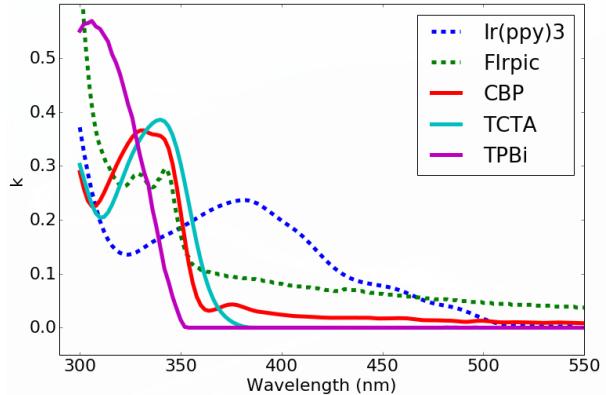


Figure 4.4: Extinction coefficients shown for the green emitter $\text{Ir}(\text{ppy})_3$ and blue emitter $\text{Fir}(\text{pic})$ as well as a few host materials.

4.2.2 Absorption - Recombination Overlap

For the measurement of η_{PL} to accurately reflect the useful degradation of the emissive layer, it is important for the optical pump absorption to agree with the recombination zone within the device. To illustrate this, Figure 4.5 shows a device where there is disagreement between the absorption and the recombination zone. Assuming an exciton driven process, defect formation and degradation will focus around the recombination zone. However, optical measurements will probe in the absorption region, which is less degraded than the electrically driven luminance is reflecting. This leads to a systematic underestimate of the actual η_{PL} degradation within the device.

To quantify this error for a particular device, a degradation and defect generation model must be employed in order to quantify the degradation profile within the device. Additionally, the absorption profile and recombination zone must be known (or estimated). The absorption profile can be calculated using a transfer matrix formalism.¹¹¹ The code used to calculate this is provided in Appendix D. The recombination zone can be measured using sensitizer molecules using the method outlined in Chapter 2.6. An excellent example of executing this analysis demonstrated by Bangsund *et al.*^{Bangsund2017}

4.2.3 Contact Degradation

Exposure to UV light has been shown to enhance photodegradation of the organic/LiF/Al interface within devices.^{104,112} This has been shown to be due to the dissociation and diffusion of positive ions from this interface, likely due to LiF. This becomes problematic in this measurement due to the η_{PL} measurement, as illustrated in Figure 4.6. Here, the optical pump has formed a dark spot on the active area of the device and accelerated degradation.

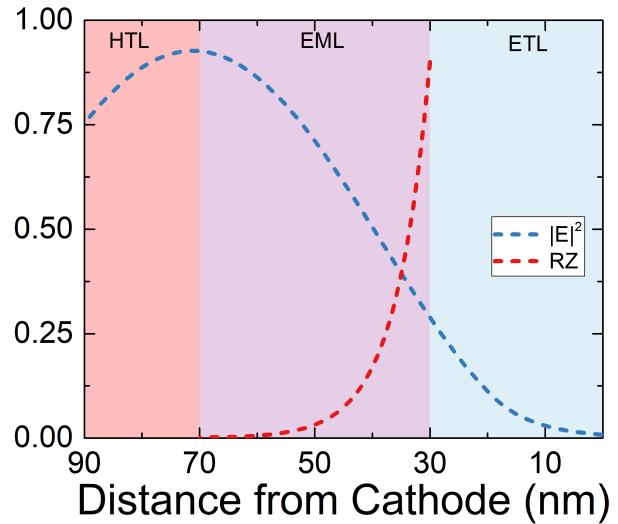


Figure 4.5: Exciton recombination zone (RZ) and pump intensity $|E|^2$ for a hypothetical thick EML device are shown.

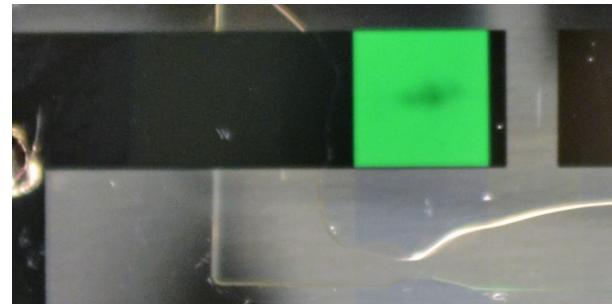


Figure 4.6: Dark spot formation on a device after exposure to a 405 nm laser.

To minimize this behavior, the laser intensity incident on the device must be kept low. We have found through trial and error that incident powers below 10 mW/cm^2 for a 405 nm laser do not exhibit this dark spot formation. Devices can be inspected after lifetime testing to ensure that no degradation occurred. We have also observed that for longer wavelengths, the damage power threshold increases and higher power can be used.

4.2.4 Quenching Changes During Degradation

Equation 4.1 introduces a quenching term, η_τ , into η_{EQE} . This term captures bimolecular quenching losses which occur at high current and exciton densities. During lifetime measurements, the exciton density decreases as the efficiency reduces, which will change η_τ . To quantify this, the model presented in Chapter 3 can be used. Using this dynamics formalism, we can define η_τ as

$$\eta_\tau = \frac{1/\tau}{1/\tau + \frac{1}{2}k_{\text{TT}}n_{ex} + k_{\text{TP}}n_{pol}}. \quad (4.4)$$

To find η_τ at the end of degradation, the change in n_{ex} , n_{pol} , and τ must be known. The exciton population, n_{ex} , is known from luminance as discussed in Chapter 3 and the temporal dependence follows the luminance loss assuming the radiative rate remains constant (which we assume). The polaron population likely increases to account for the decrease in our exciton density, but is difficult to quantify. Therefore, for this argument, we will assume it remains constant, though it will likely counteract some of the error that this method will estimate. With the temporal dependence of these quantities known, the time dependence of Equation 4.4 can be written as

$$\frac{\eta_T(t)}{\eta_T^0} = \frac{1/\tau}{1/\tau + \frac{1}{2}k_{TT}n_{ex} + k_{TP}n_{pol}} \frac{1/(R_{PL}(t)\tau) + \frac{1}{2}k_{TT}(R_{EL}n_{ex}) + k_{TP}n_{pol}}{1/(R_{PL}(t)\tau)} \quad (4.5)$$

where R_X is the degradation ratio of that term. Since degradation decoupling results are presented assuming $\eta_\tau(t) = C$, the presented out-coupling results can be corrected using $\eta_\tau^0/\eta_\tau(t)$ as a multiplicative correction factor, presented in Figure 4.7. In this figure, minimal correction is needed for low exciton and polaron populations. This only becomes important in regimes where bimolecular quenching are strong.

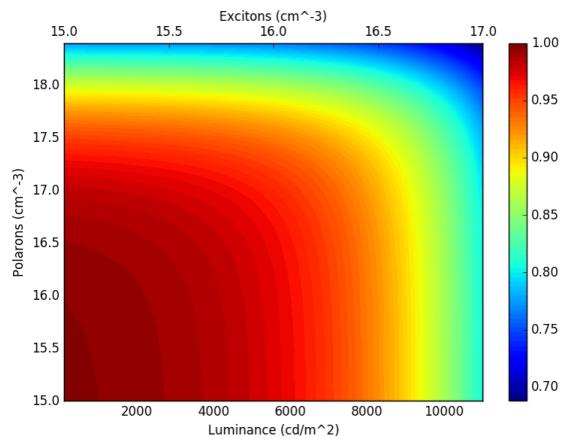


Figure 4.7: Multiplicative correction factor for exciton formation efficiency due to changes in quenching during lifetime. Shown as a function of polaron and exciton density as well as luminance, assuming a 10 nm emissive layer.

Again, it is important to note that if changes in the polaron population are accounted for, this correction factor would be further reduced.

4.2.5 Verification with Exciton Lifetime

Alternative to the method for establishing the accuracy of the η_{PL} degradation presented in Equation 4.3, the exciton lifetime can be used. From photophysics, we have

$$\eta_{PL} = \frac{k_r}{k_r + k_{nr}} \quad \tau = \frac{1}{k_r + k_{nr}} \quad (4.6)$$

where k_r and k_{nr} are the radiative and non-radiative decay rates, respectively. From these equations, it is apparent that if k_r remains constant during the degradation,

$$\frac{\tau(t)}{\tau^0} = \frac{\eta_{PL}(t)}{\eta_{PL}^0}$$

Therefore, if the exciton lifetime, τ is measured as a function of decay, it should have a 1-to-1 correlation with the observed PL loss if an accurate measure of η_{PL} is being conducted. To do this, τ is measured from the transient photoluminescence decay at low pump intensity so that minimal triplet-triplet annihilation is observed. This is done on a 337 nm pulsed nitrogen laser, recorded with a fast photodiode connected to an oscilloscope. This has been done for a variety of device architectures, an example of the results being shown in Figure 4.8 for the devices discussed in Chapter 5.1. Here we see that we are accurately measuring η_{PL} for this device since a strong correlation is observed. The large amount of scatter observed in the 10 nm EML results are believed to be due to the thin EML and small amount of material, producing low signal.

It is important to note for this confirmation of η_{PL} , that this only demonstrates that no absorption or pump intensity deviations are causing error in our measurement. Since the transient photoluminescence and photoluminescence degradation are both pumped optically, both are subject to the recombination zone and absorption mismatch problem discussed in Section 4.2.2.

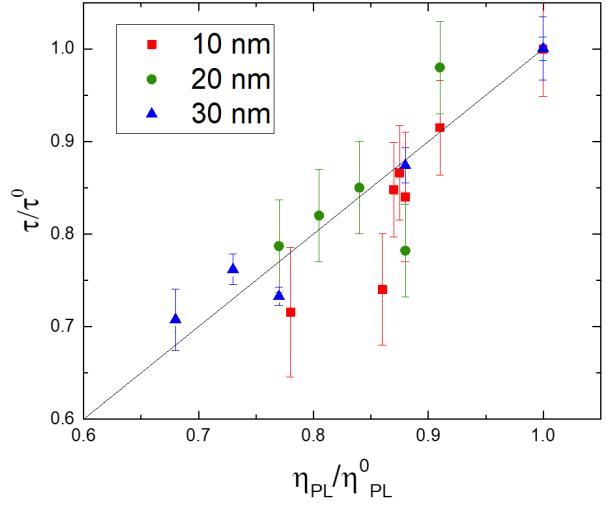


Figure 4.8: Exciton lifetime ratio extracted from transient PL measurements on degraded and undegraded devices as a function of PL degradation for several emissive layer thickness.

4.3 Experimental Implementation

4.3.1 Hardware Setup

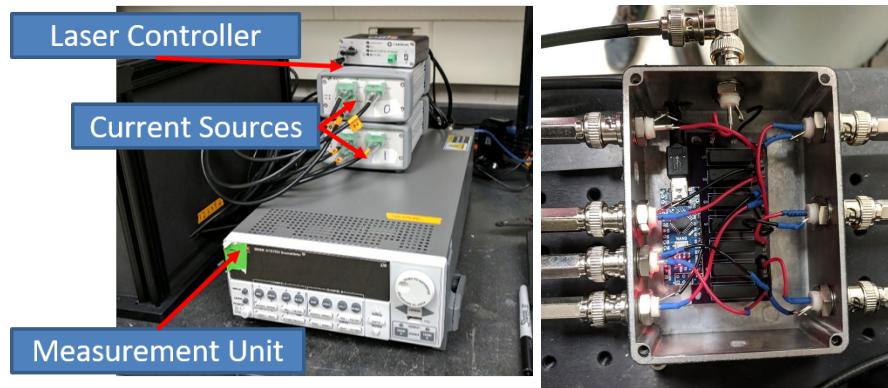


Figure 4.9: Source-Measure hardware and laser controller

Hardware for this setup requires control of current sources, voltage measurement, light source, as well as light measurements. Currently, there are four operational testing setups, termed “boxes”, with varying hardware configurations. Several boxes are multiplexed to allow multiple measurements from the multiple compartments. Source units for providing current and voltage measurements have used either the Keithley 26xx or Keysight u2722a source meters. The Keithley 26xx units are a two channel, low noise, high precision unit. The Keysight u2722a provides three channels with higher noise and lower precision at a lower price point per channel. Light sources for all boxes are conducted using Coherent OBIS lasers, with wavelengths of either 405 nm or 473 nm. Light measurements are conducted using the Keithley 26xx for all boxes, connected to a Hamamatsu S2281 photodiode. Figure 4.9a shows the electronic hardware setup for a box utilizing Keysights for source units and a Keithley for measurement. To reduce measurement units, the photodiodes in each compartment can be switched between using an Arduino relay system shown in Figure 4.9b. All of these pieces of hardware are compatible with the National Instrument VISA command library for control.

Each device is held by a custom 3D printed vertical mount. The photodiode is wired into this mount with enough space for the laser to avoid the diode. A long pass filter is provided to minimize stray laser signal. The laser is optically split into six paths us-

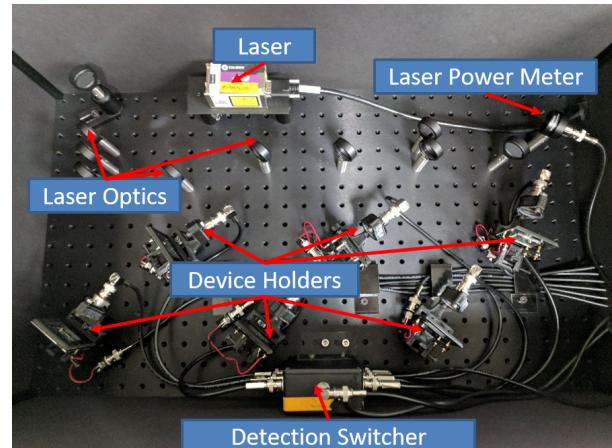


Figure 4.10: Device contacting, measurement, and optical hardware. Version 3 of the hardware is shown. Controlling hardware is shown in Fig. 4.9

ing beam splitters and neutral density filters are used where necessary to normalize laser power on each device.

4.3.2 Software Developement

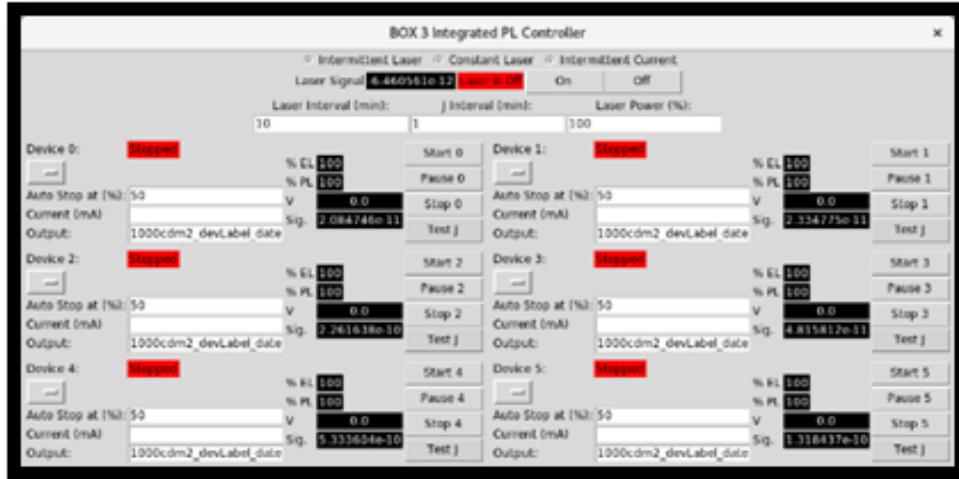


Figure 4.11: 6 channel software controller. Selection of test type, laser control for alignment, and global settings are accessible on the top of the interface. Individual channel settings are grouped on the bottom.

Software to control this measurements is implemented by myself in Python and outlined in Appendix E. The code is able to control the hardware to run constant current, intermittent laser integrated PL measurements, optical degradation, as well as optical degradation with current break degradations. The frequency of laser breaks and laser power can be controlled on a whole box level. Laser emission can be turned on for alignment. The software is able to be configured to the number of channels available depending on the hardware. Each channel can be individually controlled for current, stop, and labeling.

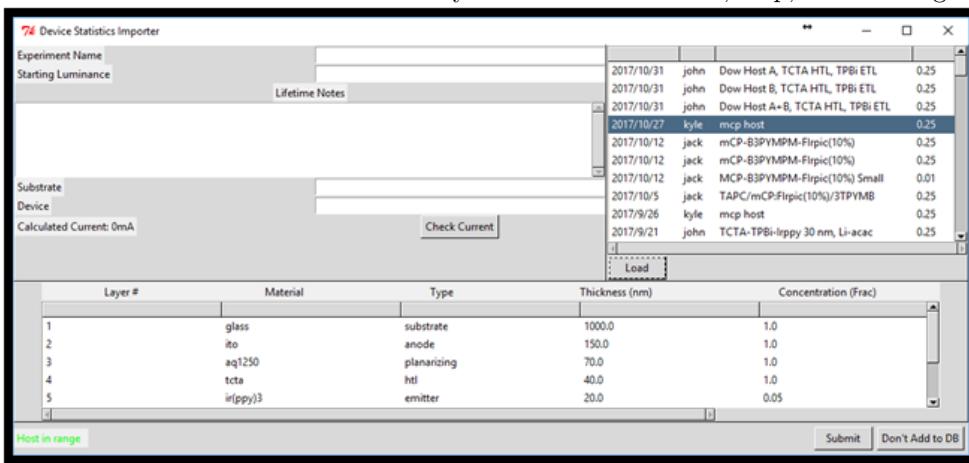


Figure 4.12: Test information for database import interface. The top left panel collects information about the specific device and lifetime. The right panel connects the device to a particular growth and architecture. The bottom panel confirms the architecture.

To organize collected data, a database for all lab data has been developed and is discussed in Chapter 7. Lifetimes integrate with this system when lifetimes are started, using the interface shown in Figure 4.12. Here, a lifetime test is connected to a particular growth, as well as the individual substrate and device pixel. Information about the lifetime is also connected. The lifetime operating current can be determined for a desired luminance by utilizing the current-voltage-luminance curve for the exact device within this interface. Additional notes and information are also able to be stored.

4.4 Conclusion

This chapter has outlined a system for decoupling degradation during operational lifetimes. Extensive care has been taken to outline the assumptions and assess error within the extracted parameters. Many of these assumptions need to be assessed for any device system to be tested to ensure accuracy. Applying this method to lifetime decoupling in device systems is the subject of Chapter 5.

Chapter 5

Applied Integrated Lifetimes

5.1 CBP Host Thickness

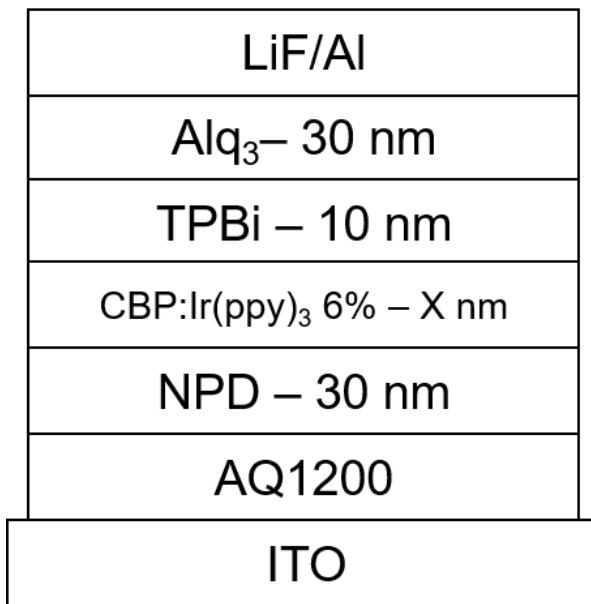


Figure 5.1: Device architecture, featuring EML thicknesses of X=10,20, and 30 nm

5.2 MEML Luminance Scaling

5.3 Dow Cohost

Long lived deep blue emitters are important for developing displays. This is still an active field of research.^{113,114}

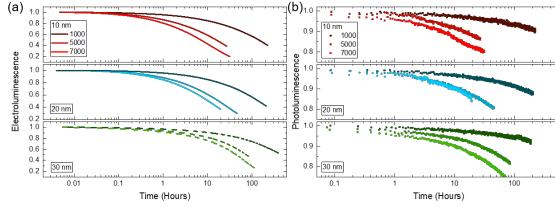


Figure 5.2: Device decay curves for multiple values of the initial luminance as a function of emissive layer thickness. Loss in (a) electroluminescence (EL) and (b) photoluminescence (PL) are shown and decrease monotonically with increasing luminance. For devices with a 10-nm-thick emissive layer, initial luminance values are $1000 \text{ cd}/\text{m}^2$, $5000 \text{ cd}/\text{m}^2$, and $7000 \text{ cd}/\text{m}^2$. For devices with a 20-nm- or 30-nm-thick emissive layer, initial luminance values are $1000 \text{ cd}/\text{m}^2$, $5000 \text{ cd}/\text{m}^2$, and $7100 \text{ cd}/\text{m}^2$.

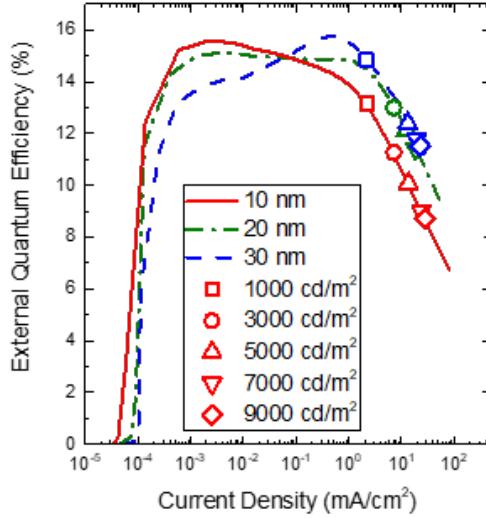


Figure 5.3: External Quantum Efficiency (η_{EQE}) for the three architectures. Operational points for lifetime are shown in symbols.

d_{EML} (nm)	L_0 (cd/m ²)	J (mA/cm ²)	V_0 (V)	t_{50} (hours)
10	1000	2.2	4.2	139.0
	3000	7.2	5.1	39.9
	5000	13.6	5.4	15.8
	7000	14.4	6.2	6.9
	9000	28.0	6.3	5.3
20	1000	2.2	5.4	141.1
	3000	7.2	6.0	33.1
	5000	12.4	7.2	17.2
	7100	19.2	7.3	10.0
	9000	24.0	7.5	8.0
30	1000	2.2	5.9	474
	5000	13.6	7.3	74.4
	7100	19.6	7.6	46
	8000	22.4	7.7	38.1

Table 5.1: Summary of device lifetimes. For each device, the starting luminance (L_0), current density (J), starting voltage (V_0) and time at which 50% of the initial luminance is reached (t_{50}) are reported.

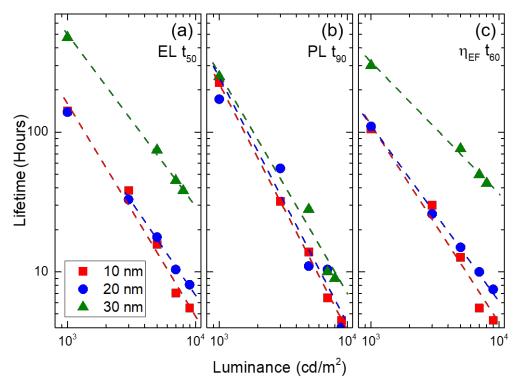


Figure 5.4: Extracted lifetimes for all 3 architectures as a function of luminance.

Chapter 6

Novel Blue Emitter Development

6.1 Molecular Systems

6.2 Performance Optimization

6.3 Solution Molecular Aggregation

Chapter 7

Data Management for Devices

Chapter 8

Modeling Out-Coupling

8.1 Theory

Code used for implementation of this theory is provided in Appendix D

8.2 Recombination Zone Overlap During Lifetime

Chapter 9

Future Research

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Appendices

Appendix A

List of Publications

- Hershey, K. W.; Cottingham, J. P. *The Journal of the Acoustical Society of America* **2011**, *129*, 2520–2520
- Hershey, K. W.; Holmes, R. J. *Journal of Applied Physics* **2016**, *120*, 195501
- Hershey, K. W. et al. *Applied Physics Letters* **2017**, *111*, 113301
- Xu, F. et al. *Journal of the American Chemical Society* **2016**, *138*, 12739–12742

Appendix B

Measuring Triplet Energies

As discussed in Chapter 1.2, singlet excitons are typically responsible for molecular emission because the triplet state is quantum mechanically forbidden in the first order approximation.² Emission from the triplet state is allowed with the addition of spin-orbit coupling.³ For applications including OLEDs, solar cells, and organic lasers, spectroscopic characterization of the triplet state is needed, often for molecules where the spin-orbit coupling is weak.^{117–120}

Most measurements of the triplet energy are conducted via optical pumping.^{2,80,118,121} However, triplet populations are not generated optically in most materials.² In order for a triplet population to be established, k_{ISC} must be greater than 0. Additionally, the radiative rate, k_r must be at least competitive with k_{nr} . Since the triplet state is quantum mechanically disallowed without spin-orbit coupling, the radiative rate is typically low compared to the singlet, on the order of $10^6 s^{-1}$. At room temperature, k_{nr} is often seen to be $10^2 - 10^6 s^{-1}$.¹²² In order to reduce k_{nr} , cryogenic temperatures are often employed, though room-temperature techniques do exist.¹²²

In our lab, I have utilized Janis liquid helium cryogenic optical system to measure triplets. This takes the temperature to 10K and severely reduces k_{nr} . Samples are prepared on Silicon to take advantage of the strong thermal conductivity compared to glass. If the total emission is collected, the singlet still is far more emissive than the triplet. However, the difference in their lifetimes can be utilized to separate them. Using a pulsed nitrogen laser, the

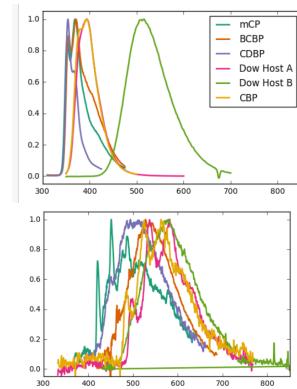


Figure B.1: Fluorescence (a) and Phosphorescence (b) spectra for several materials obtained from this system.

exciton population is exsuperated. The singlet population decays quickly, within a few nanoseconds. However, the triplet lifetime at low temperatures is much longer. A triggered spectrometer can be used to measure the delayed phosphorescence, and thus measure the triplet emission only. I have done this with a Princeton Instruments Fergie spectrometer, with a delay of 5ms from the laser pulse.

This system has been used to measure triplet spectra for a variety of materials, shown in Figure B.1. To extract triplet energies, the short wavelength turn on of the triplet spectra can be used. This is the highest energy, which seems counter intuitive, but the observed spectra is a decay from T_1 to vibrational states of the ground state, S_0 . The triplet energy is defined as the difference between the lowest vibronic of T_1 to the lowest vibronic of S_0 , which is the highest energy transition observed in the spectra. These spectra show different behavior for sharpness of the leading edge, but a 20% of the maximum intensity is chosen as the threshold for defining the triplet energy.

Appendix C

Single Carrier Device Modeling

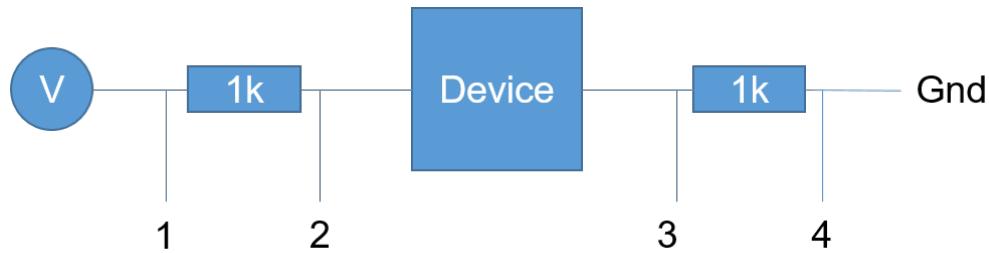


Figure C.1: Circuit used for measuring polaron density. Voltage readings are taken at 1-4 over a $1M\Omega$ termination.

When trying to understand device behavior, it is often important to investigate single carrier devices to understand one charge species at a time or isolate dynamic processes. An example of this is measurement of the triplet-polaron quenching rate constant, demonstrated in Chapter 3.5. Determination of the polaron density is often critical in order to quantify these results. This is often done by assuming the device is operating within the space charge limit, in which charges have overcome injection barrier limits and transport through the bulk of the material is the limiting process.^{17,43} In the space-charge limit, current is most simply described using the Mott-Gurney Law, and can be modified to include various trap states to adapt to different semiconductor properties.⁶ However, space-charge limited current is really only accurate for device behavior at high voltages for thick devices. Often, organic layer stacks of interest feature relatively thin layers, and voltages close to the injection limits. It can be difficult to identify when a device is operating in the space-charge limit.

In order to reduce some of the uncertainty associated with determining polaron density, a differential current measurement can be conducted. For a single carrier device, only one type of carrier is injected. As charge is being injected into the device and a steady-state polaron density is being achieved, the current on the side of the device where charges are injected should be greater than on the other side. This can be seen

in Figure C.1, where for a hole only device, the current over R_{12} should be greater than the current over R_{34} . All of these signals can be measured using an oscilloscope. Once steady-state is achieved, the currents should be equal. The polaron population injected into the device can be calculated using the following equation

$$N_{pol} = \int J_{1-2} - J_{3-4} dt \quad (C.1)$$

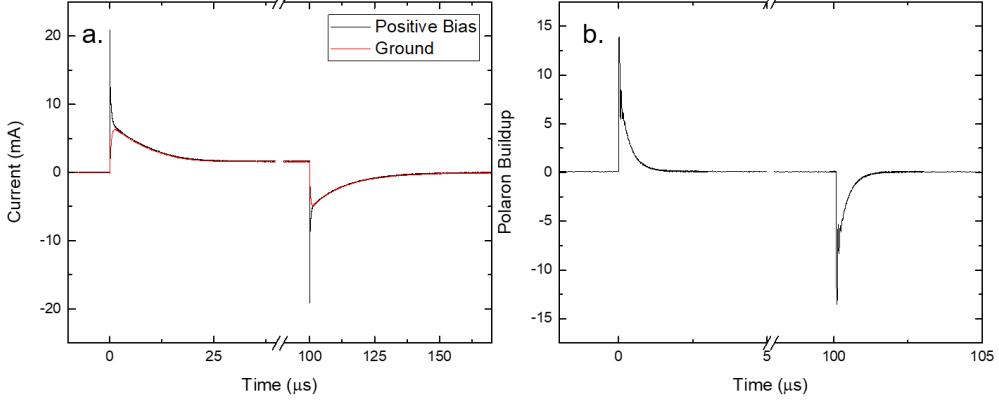


Figure C.2: Differential currents for a hole only device. Currents on either side of the device are shown in a. while the difference between them is shown in b.

where J is the current and 1-4 are labeled in Figure C.1. When voltage is removed from the device, the currents will diverge and the polaron density will be drained from the device. This is demonstrated in Figure C.2, with the currents on either side of the device and the differential current shown in C.2a and C.2b, respectively. Notice the positive differential when current is applied and polarons enter the device, and negative when they are removed.

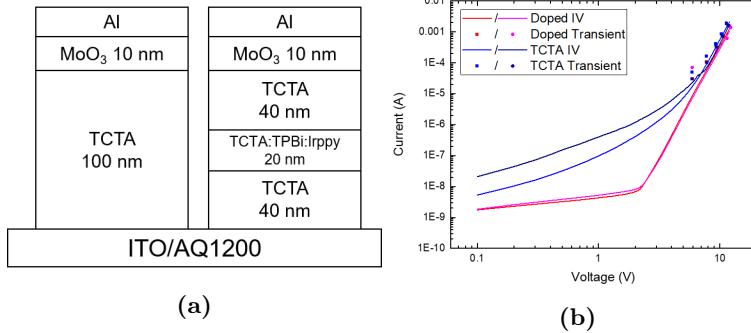


Figure C.3: a. Hole only device architectures. b. Current Voltage characteristics for the devices shown in a. Steady-state sweeps as well as current measured from the differential technique are shown.

While this technique is able to accurately tell the injected polaron population, the distribution of that population is still unknown. This technique does provide the advantage that with the total polaron population known, the current or voltage dependence of the population can be compared to different models to further validate the operational regime. Then, a model can be applied to show the spatial dependence of charge.⁶⁻⁸ This technique has the advantage that only the spatial dependence is needed, rather than hav-

ing to estimate the total charge population, and is more accurate than previous methods relying on solely modeling.

Ideally the polaron population can be restricted to a small area of the device to minimize the extent of the spatial distribution. To achieve this, the devices shown in Figure C.3a were investigated. The region of interest is the mixed doped layer in the right hand device. This doped region should show a greater ability to facilitate trapped charge and show a larger polaron population. The current-voltage profile of these devices is shown in Figure C.3b where the doped devices show a stronger diode behavior. The currents obtained from the displacement current measurements show agreement with the steady state current.

The polaron population as a function of current is shown for these devices in Figure C.4. Unfortunately, polaron populations for both devices are almost identical and the hypothesis of increased trapping in the doped region is not correct. This means that charges are not confined and there is likely a wide distribution of the polaron density. Despite these drawbacks, the polaron population is still obtained and can be compared to space-charge limited current models.

C.1 Future Work

This technique is useful for a variety of techniques where polaron population needs to be known precisely. One ready application of this technique is for triplet-polaron quenching measurements. As discussed in Chapter 3.5, measurement of k_{TP} relies on optically pumping a single carrier device under an applied current. To accurately determine the constant, the polaron density must be known precisely. The differential current technique would be useful for comparing different materials and their values of k_{TP} . Another application with similar motivations would be the optical degradation of single carrier devices.

Differential current analysis of single carrier devices provides a straight forward way of determining the polaron population within a single carrier device. While the spatial distribution of the polaron population may not be known, this can be easily modeled with the current dependence of the polaron population available for validation of the model. Though so far unused in a relevant application, this technique allows more sophisticated comparison of devices when matched polaron population is important.

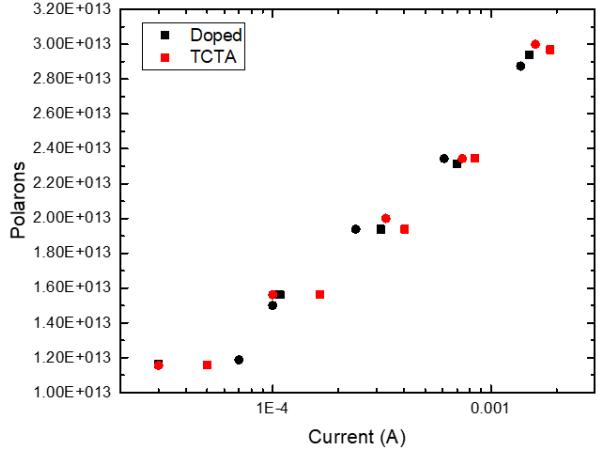


Figure C.4: Polaron population as a function of current for the devices in Figure C.3a

Appendix D

Out-Coupling Code

D.1 Transfer Matrix Model

The following is code to implement a transfer matrix model for calculating absorption and electric field profile within a thin film stack, as described by Pettersson.¹¹¹

transfer.m

```
1 function transfer
2
3 global q
4 global d
5 global n
6
7 %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
8 %
9 % Model Setup
10 %
11 %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
12
13 % Layers. Must match names in lookup table
14 layers = {'SiO2' 'ITOorizon' 'PEDOT' 'P3HTPCBBlendDCB' 'Ca' 'Al'};
15
16
17
18 % layer thicknesses. First value is unused
19 % but placeholder so indices match
20 d = [
21     0
```

```

22    110
23    35
24    220
25    7
26    200
27    ];
28
29 % angle of incidence
30 phi_0 = 0;
31
32 %%%%%%
33 %
34 % Test Parameters
35 %
36 %%%%%%
37
38 % resolution in nm
39 res = 1;
40 %% note: You should try to make this an even division of the layer
41 %% thicknesses. If not, the first output will always be at the left edge
42 %% of the layer,sampling at each res step. This could result in an uneven
43 %% spacing between the last sample of j and the first of j+1.
44
45 % Wavelengths to test
46 waves = [400];
47
48
49 %%%%%%
50 %
51 % Generation
52 %
53 %%%%%%
54
55 %% Load in index of refraction for each material and each wavelength
56 ntable = zeros(size(layers,2),size(waves,2));
57 for index = 1:size(layers,2)
58     ntable(index,:) = LoadRefrIndex(layers{index},waves);
59 end
60
61
62

```

```

63 % calculating array size for preallocation
64 numSteps=0;
65 x = [];
66 depth = 0;
67 for l = 1:length(d)-1
68     numSteps=numSteps+(ceil(d(l+1)/res)-1)*res+1;
69     steps = 0:res:(ceil(d(l+1)/res)-1)*res;
70     x = [x (steps+depth)];
71     depth = depth + d(l+1);
72 end
73 specs = zeros(numSteps, size(waves,2));
74
75 % hard work begins
76 for iter = 1:size(waves,2)
77     lambda = waves(iter);
78     n=ntable(:,iter);
79     q = (n.^2-n(1)^2*(sin(phi_0))^2).^(1/2);
80     % ! ! ! ! ! ! ! ! ! ! ! ! !
81     % T_glass=abs(4*1*n(1)/(1+n(1)).^2);
82     R_glass=abs((1-n(1))/(1+n(1))).^2;
83     S=scattering(1,lambda);
84     R=abs(S(2,1)/S(1,1))^2; %JAP Vol 86 p.487 Eq 9 Power Reflection from layers other than
85     % substrate
86     T=abs(2/(1+n(1)))/sqrt(1-R_glass*R); %Transmission of field through glass substrate
87     Griffiths Electrodynamics 9.85 + multiple reflection geometric series
88     % ! ! ! ! ! ! ! ! ! ! ! ! !
89
90
91     spec = [];
92
93     for l = 1:length(d)-1
94         steps = 0:res:(ceil(d(l+1)/res)-1)*res; % this is inefficient
95         % x = [x (steps+depth)];
96         spec = [spec pstm(steps,l,lambda)];
97         % depth = depth + d(l+1);
98     end
99
100    % ! ! ! ! ! ! ! ! ! ! ! ! !
101    spec = T * spec;
102    % ! ! ! ! ! ! ! ! ! ! ! ! !

```

```

102     specs(:,iter)=spec;
103 end
104
105 %%%%%%
106 %
107 % Plotting
108 %
109 %%%%%%
110 specs=(abs(specs)).^2;
111 plot(x,specs(:,1))
112 hold all
113 for iter = 2:size(waves,2)
114     plot(x,specs(:,iter))
115 end
116 title('PEDOT / P3HTPCBM Device')
117 xlabel('depth (nm)')
118 ylabel('|E|^2')
119 legend(strtrim(cellstr(num2str(waves)))')
120
121 % vertical lines for layers
122 axislimit1=axis;
123 for matindex=2:length(d)
124     line([sum(d(1:matindex)) sum(d(1:matindex))],[0 axislimit1(4)]);
125 end
126
127 hold off
128
129
130 %%%%%%
131 %
132 % Helper Functions
133 %
134 %%%%%%
135
136 % layer matrix
137 function [L] = layer(l,lambda) % indices match paper
138     global q
139     global d
140     xi = (2*pi/lambda) * q(l+1);
141
142     L = [ exp(-1i*xi*d(l+1)) 0 ; 0 exp(1i*xi*d(l+1)) ];

```

```

143
144 % interface matrix
145 function [I] = interface(l,k) % indices match paper
146 global q
147 r_TE = (q(1+1)-q(k+1))/(q(1+1)+q(k+1));
148 t_TE = (2*q(1+1))/(q(1+1)+q(k+1));
149 % switch to these for TM transmission
150 % r_TM = (-n(k+1)^2*q(j+1)+n(j+1)^2*q(k+1))/(n(k+1)^2*q(j+1)+n(j+1)^2*q(k+1));
151 % t_TM = (2*n(j+1)*n(k+1)*q(j+1))/(n(k+1)^2*q(j+1)+n(j+1)^2*q(k+1));
152
153 I = 1/t_TE*[1 r_TE ; r_TE 1];
154
155 % scattering matrices
156 function [S_jp, S_jpp] = scattering(l,lambda)
157 global d
158 S_jp = eye(2);
159 for v = 1:(l-1)
160     S_jp = S_jp * interface(v-1,v) * layer(v,lambda);
161 end
162 S_jp= S_jp * interface(l-1,l);
163
164 S_jpp = eye(2);
165 for v = (l+1):(length(d)-1) %%
166     S_jpp = S_jpp * interface(v-1,v) * layer(v,lambda);
167 end
168 %S_jpp= S_jpp * interface(length(d)-2,length(d)-1); %%
169
170 % partial system transfer matrix. E(x) for single layer
171 function [tm] = pstm(x,l,lambda)
172 global q
173 global d
174 [s_jp,s_jpp] = scattering(l,lambda);
175
176 xi = 2*pi/lambda * q(1+1);
177
178 tm = (s_jpp(1,1)*exp(-1i*x*(d(1+1)-x))+s_jpp(2,1)*exp(1i*x*(d(1+1)-x))) ./ ...
179 (s_jp(1,1)*s_jpp(1,1)*exp(-1i*x*d(1+1))+s_jp(1,2)*s_jpp(2,1)*exp(1i*x*d(1+1)));
180
181
182
183 function ntotal = LoadRefrIndex(name,wavelengths)

```

```

184 %Data in IndRefr , Column names in IndRefr_names
185 [IndRefr,IndRefr_names]=xlsread('Index_of_Refraction_library.xls');
186
187 % Load index of refraction data in spread sheet, will crash if misspelled
188 % file_wavelengths=IndRefr(:,strmatch('Wavelength',IndRefr_names));
189 file_wavelengths=IndRefr(:,strncmp('Wavelength',IndRefr_names,10));
190 % n=IndRefr(:,strmatch(strcat(name,'_n'),IndRefr_names));
191 n=IndRefr(:,strncmp(strcat(name,'_n'),IndRefr_names,length(name)+2));
192 % k=IndRefr(:,strmatch(strcat(name,'_k'),IndRefr_names));
193 k=IndRefr(:,strncmp(strcat(name,'_k'),IndRefr_names,length(name)+2));
194
195 % Interpolate/Extrapolate data linearly to desired wavelengths
196 n_interp=interp1(file_wavelengths, n, wavelengths, 'linear', 'extrap');
197 k_interp=interp1(file_wavelengths, k, wavelengths, 'linear', 'extrap');
198
199 %Return interpolated complex index of refraction data
200 ntotal = n_interp+1i*k_interp;

```

D.2 Out-Coupling (Power Dissipation)

The following model implements an out-coupling calculation by calculating the power dissipation as a function of the normalized in-plane wavevector, u . This is an implementation of the method outlined by Furno *et al.*^{4,5}

PowerDissipationModel.m

```

1
2 function [] = PowerDissipationModel
3 %TE=s
4 %IM=p
5 clear
6
7 %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
8 % -----
9 % Model Parameters %%%
10 % -----
11 %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
12
13
14 % Layers. Must match names in lookup table
15 materials = {'SiO2' 'ITOzorizon' 'TCTA' 'Bphen' 'Irppy' 'Al' 'Air'};

```

```

16
17 % Wavelengths to test
18 waves = 1E-9*510; % freespace wavelengths
19
20 %% start u initiation and nreftable fetching
21 %#####
22 % Dipole inplane wave vectors %#
23 u_range = cat(2,0:.005:.999,1.001:.005:pi/2); %#
24 %#
25 % Load in index of refraction for each material and each wavelength %#
26 nreftable = zeros(size(materials,2),size(waves,2)); %#
27 for index = 1:size(materials,2) %#
28     nreftable(index,:) = LoadRefrIndex(materials{index},waves*1E9); %#
29 end %#
30 %#####
31 %% end u initiation and nreftable fetching
32
33 % Save u
34 % u_r = u_range';
35 % save('u.txt','u_r','-ascii')
36
37 %construct layer matrix
38 ntable(1,:) = nreftable(1,:); % glass
39 ntable(2,:) = nreftable(2,:); % ITO
40 ntable(3,:) = nreftable(3,:); % neat TCTA
41 ntable(4,:) = (nreftable(3,:)+nreftable(4,:))/2; % MEML
42 ntable(5,:) = nreftable(4,:); % neat bphen
43 ntable(6,:) = nreftable(6,:); % Al
44 ntable(7,:) = nreftable(7,:); % air
45
46 % layer thicknesses.
47 d(1) = 0; % Sio2
48 d(2) = 150; % ito
49 d(3)=20; %tcta
50 d(4)=60; %MEML
51 d(5)=20; %bphen
52 d(6) = 100; % Al
53 d(7) = 0; % air
54 d = d * 1E-9; % convert to nm
55
56 for thick_iter=1:60

```

```

57 % Emitter Matrix
58 % [layer    location_p(nm)    weight]
59 emitters = [
60     4 thick_iter 1
61 ];
62 emitters(:,2)=emitters(:,2)*1E-9;
63
64 %% Start main work loop
65 %#####
66 % -----
67 % Generation
68 % -----
69 %%%%%%%%%%%%%%
70 %#
71 % initialize power array
72 K_TMv = zeros(size(u_range));
73 K_TMh = zeros(size(u_range));
74 K_TEh = zeros(size(u_range));
75 K_TMvp = zeros(size(u_range));
76 K_TMhp = zeros(size(u_range));
77 K_TEhp = zeros(size(u_range));
78
79 % hard work begins
80 for wavelength_iter = 1:size(waves,2)
81     for wavenumber_iter = 1:size(u_range,2)
82         u = u_range(wavenumber_iter);
83
84
85         lambda = waves(wavelength_iter); % free space lambda
86         n=ntable(:,wavelength_iter);
87
88         K_TMv(wavenumber_iter)=0;
89         K_TMh(wavenumber_iter)=0;
90         K_TEh(wavenumber_iter)=0;
91         K_TMvp(wavenumber_iter)=0;
92         K_TMhp(wavenumber_iter)=0;
93         K_TEhp(wavenumber_iter)=0;
94
95         for emitter = 1:size(emitters,1)
96             q= (n.^2-((n(emitters(emitter,1)).*u)).^2).^(1/2);
97

```

```

98 % reflection coefficients                                     %#%
99 [r_TMP,t_TMP,~] = reflection_neg(emitters(emitter,1),lambda,0,n,d,q);    %#%
100 [r_TMn,~,~] = reflection_pos(emitters(emitter,1),lambda,0,n,d,q);      %#%
101 [r_TEp,t_TEp,~] = reflection_neg(emitters(emitter,1),lambda,1,n,d,q);    %#%
102 [r_TEn,~,~] = reflection_pos(emitters(emitter,1),lambda,1,n,d,q);       %#%
103                                                               %#%
104 k=2*pi*n(emitters(emitter,1))/lambda;                         %#%
105 z_p = emitters(emitter,2);                                     %#%
106 z_n = d(emitters(emitter,1))-z_p;                            %#%
107 a_TMP = r_TMP*exp(2*j*k*sqrt(1-u.^2).*z_p); % Furno A4      %#%
108 a_TMn = r_TMn*exp(2*j*k*sqrt(1-u.^2).*z_n); % Furno A5      %#%
109 a_TEp = r_TEp*exp(2*j*k*sqrt(1-u.^2).*z_p); % Furno A4      %#%
110 a_TEn = r_TEn*exp(2*j*k*sqrt(1-u.^2).*z_n); % Furno A5      %#%
111                                                               %#%
112 % Radiated Power Density                                    %#%
113 K_TMv(wavenumber_iter) = K_TMv(wavenumber_iter) + emitters(emitter,3).*3/4*real(   %#%
114 u.^2./sqrt(1-u.^2).*(1+a_TMP).*(1+a_TMn)./(1-a_TMP.*a_TMn)); % Furno A1      %#%
115 K_TMh(wavenumber_iter) = K_TMh(wavenumber_iter) + emitters(emitter,3).*3/8*real(   %#%
sqrt(1-u.^2).*(1-a_TMP).*(1-a_TMn)./(1-a_TMP.*a_TMn)); % Furno A2      %#%
116 K_TEh(wavenumber_iter) = K_TEh(wavenumber_iter) + emitters(emitter,3).*3/8*real(   %#%
(1./sqrt(1-u.^2).*(1+a_TEp).*(1+a_TEn)./(1-a_TEp.*a_TEn)); % Furno A3      %#%
117                                                               %#%
118 % Transmission of the top half-stack                      %#%
119 T_TMP = abs(t_TMP).^2*(n(1)/n(emitters(emitter,1)))*sqrt((1-(u*n(emitters(   %#%
emitter,1))/n(1))^2)/(1-u^2)); % Furno A12
120 T_TEp = abs(t_TEp).^2*(n(1)/n(emitters(emitter,1)))*sqrt((1-(u*n(emitters(   %#%
emitter,1))/n(1))^2)/(1-u^2)); % Furno A13
121                                                               %#%
122 % Power radiated into the substrate                        %#%
123 K_TMvp(wavenumber_iter) = K_TMvp(wavenumber_iter) + emitters(emitter,3).*3/8*(u   %#%
.^2./sqrt(1-u.^2).*(abs(1+a_TMn)).^2./(abs(1-a_TMP.*a_TMn)).^2)*T_TMP; % Furno A8
124 K_TMhp(wavenumber_iter) = K_TMhp(wavenumber_iter) + emitters(emitter,3).*3/16*(   %#%
sqrt(1-u.^2).*(abs(1-a_TMn)).^2./(abs(1-a_TMP.*a_TMn)).^2)*T_TMP; % Furno A9
125 K_TEhp(wavenumber_iter) = K_TEhp(wavenumber_iter) + emitters(emitter,3)   %#%
.*3/16*(1./sqrt(1-u.^2).*(abs(1+a_TEn)).^2./(abs(1-a_TEp.*a_TEn)).^2)*T_TEp; % Furno A10
126                                                               %#%
127 end % emitter                                         %#%
128 end % wavenumber                                       %#%
129 end % wavelength                                       %#%

```

```

130 K = (1/3*(abs(K_TMv)+2*abs(K_TMh)+2*abs(K_TEh))) ; % Forno A6      %#  

131 K = K./sum(emitters(:,3));                                %#  

132                                         %#  

133                                         %#  

134 % Transmission out of the substrate to air                %#  

135 n_g = ntable(1,1);                                         %#  

136 n_a = 1;                                                 %#  

137 u_g = u_range*ntable(emitters(1),1)/ntable(1,1);        %#  

138 cos_g = sqrt(1-u_g.^2);                                  %#  

139 cog_a = sqrt(1-(n_g./n_a.*u_g).^2);                    %#  

140 Rs = ((n_g.*cos_g-n_a.*cog_a)./(n_g.*cos_g+n_a.*cog_a)).^2;    %#  

141 T_s = 1-Rs;                                              %#  

142 Rp = ((n_g.*cog_a-n_a.*cos_g)./(n_g.*cog_a+n_a.*cos_g)).^2;    %#  

143 T_p = 1 - Rp;                                            %#  

144 % This calculation assumes a lossless interface          %#  

145                                         %#  

146 % Outcoupled Power                                     %#  

147 n = ntable(:,1);                                         %#  

148 Rc_s=zeros(1,size(u_range,2));                           %#  

149 Rc_p=zeros(1,size(u_range,2));                           %#  

150 for u_iter = 1:size(u_range,2)                         %#  

151     q= (n.^2-((n(1,1).*u_range(u_iter))).^2).^(1/2);    %#  

152     Rc_s(u_iter) = abs(reflection_neg(1,waves(1),1,ntable(:,1),d,q))^2; %#  

153     Rc_p(u_iter) = abs(reflection_neg(1,waves(1),0,ntable(:,1),d,q))^2; %#  

154 end                                                       %#  

155 K_outTMv = K_TMvp.*T_p./(1-Rp.*Rc_p); % Forno A14      %#  

156 K_outTMh = K_TMhp.*T_p./(1-Rp.*Rc_p); % Forno A14      %#  

157 K_outTEh = K_TEhp.*T_s./(1-Rs.*Rc_s); % Forno A14      %#  

158                                         %#  

159 K_out = (1/3*(abs(K_outTMv)+2*abs(K_outTMh)+2*abs(K_outTEh)));    %#  

160 K_out=K_out./sum(emitters(:,3));                          %#  

161                                         %#  

162 % Power Dissipation Spectra                            %#  

163 y=u_range.*K;                                           %#  

164 y_out=u_range.*K_out;                                    %#  

165                                         %#  

166 % critical angle from snells law                      %#  

167 u_crit = 1/real(ntable(emitters(emitter,1),1));       %#  

168 index=find(u_range<u_crit,1,'last')+1;                 %#  

169 out = trapz(u_range(1:index),y_out(1:index)); % Forno A15    %#  

170 tot = trapz(u_range,y); % Forno A7                   %#
```

```

171 %#
172 eta(thick_iter)=out/tot; %#
173 %# %#
174 % Power vs Angle %#
175 % sin_theta = u_range(1:113)/u_range(113); %#
176 % theta = asind(sin_theta); %#
177 % cos_theta = cosd(theta); %#
178 % P_out = (1/ntable(emitters(1),1)).^2.*cos_theta/pi.*K_out(1:113); % Furno A18 %#
179 %#
180 %#
181 ##### %#
182 %% End main work loop %#
183 %#
184 % End Control Loops %#
185 end %#
186 %#
187 ##### %#
188 %-----%%%
189 % Plotting %%%
190 %-----%%%
191 ##### %#
192 %#
193 %#
194 % Power Spectrum vs u %#
195 % semilogy(u_range,y) %%%
196 % xlabel('u') %%%
197 % ylabel('K*u') %%%
198 %#
199 % Power Intensity vs Angle (requires uncommenting of angle code) %%%
200 % plot(theta,P_out); %%%
201 %#
202 %#
203 %#
204 ##### %%%
205 %-----%%%
206 % Saving %%%
207 %-----%%%
208 ##### %%%
209 save('eta.txt','eta','ascii') %%%
210 %#
211

```

```

212
213
214
215 %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
216 %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
217 %
218 % Helper Functions
219 %
220 %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
221 %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
222
223
224 % layer matrix -----
225 %
226 function [L] = layer(l,lambda,~,d,q)
227
228
229     xi = (2*pi/(lambda)) * q(1); % pettersson 6
230
231     L = [ exp(-1i*xi*d(1)) 0 ; 0 exp(1i*xi*d(1)) ]; % pettersson 5
232
233 % interface matrix -----
234 %
235 % o is orientation 0=TM, 1=TE
236 function [I] = interface(l,k,orientation,n,~,q)
237
238     if(orientation==1)
239         % TE light
240         r = (q(1)-q(k))./(q(1)+q(k)); % pettersson 2a
241         t = (2*q(1))./(q(1)+q(k)); % pettersson 2b
242     else
243         % TM light
244         r = (n(k)^2*q(1)-n(1)^2*q(k))./(n(k)^2*q(1)+n(1)^2*q(k)); % pettersson 3a
245         t = (2*n(1)*n(k)*q(1))./(n(k)^2*q(1)+n(1)^2*q(k)); % pettersson 3b
246
247     end
248
249     I = 1/t .* [1 r ; r 1]; % pettersson 1
250     % checks for singular matrix. If so, a small term is added to the diagonal,
251     % a common method of dealing with singular matrices.
252     % This adds in potential error, but

```

```

253 % makes the system solvable and stable. Will fail if NaN is passed
254 %if ( cond(I) > 1E8)
255 %    I = I+eye(2)*1E-5;
256 %end
257
258 % reflection coefficient Positive Direction -----
259 %
260 %Uses the Interface and layer matrices , but in the appropriate directions.
261 function [r,t,D] = reflection_pos(active_layer,lambda,orientation,n,d,q)
262
263 S_jpp = eye(2);
264 for v = (active_layer):(length(d)-2)
265     S_jpp = S_jpp * interface(v,v+1,orientation,n,d,q) * layer(v+1,lambda,n,d,q); % pettersson 13
266 end
267 S_jpp = S_jpp * interface(length(d)-1,length(d)-0,orientation,n,d,q);
268 r = S_jpp(2,1)/S_jpp(1,1); % pettersson 9
269 t = 1/S_jpp(1,1); % Pettersson 15
270
271 D=det(S_jpp);
272
273 % reflection coefficient Negative Direction -----
274 %
275 function [r,t,D] = reflection_neg(active_layer,lambda,orientation,n,d,q)
276 S_jp = eye(2);
277 % for v = (active_layer):-1:3
278 for v = (active_layer):-1:3 % Treat glass as semiinfinite
279     S_jp = S_jp * interface(v,v-1,orientation,n,d,q) * layer(v-1,lambda,n,d,q); % pettersson 13
280 end
281 S_jp = S_jp * interface(2,1,orientation,n,d,q);
282 r = S_jp(2,1)/S_jp(1,1); % pettersson 9
283 t = 1/S_jp(1,1); % Pettersson 15
284
285 D=det(S_jp);
286 %t=D*t;
287
288 % Index fetching from files -----
289 %
290 function ntotal = LoadRefrIndex(name,wavelengths)
291     %Data in IndRefr , Column names in IndRefr_names

```

```

292 [IndRefr,IndRefr_names]=xlsread('Index_of_Refraction_library.xls');
293
294 % Load index of refraction data in spread sheet, will crash if misspelled
295 file_wavelengths = IndRefr(:,strncmp('Wavelength',IndRefr_names,10));
296 n = IndRefr(:,strncmp(strcat(name,'_n'),IndRefr_names,length(name)+2));
297 k = IndRefr(:,strncmp(strcat(name,'_k'),IndRefr_names,length(name)+2));
298
299 % Interpolate/Extrapolate data linearly to desired wavelengths
300 n_interp = interp1(file_wavelengths, n, wavelengths, 'linear', 'extrap');
301 k_interp = interp1(file_wavelengths, k, wavelengths, 'linear', 'extrap');
302
303 %Return interpolated complex index of refraction data
304 ntotal = n_interp+1i*k_interp;

```

Appendix E

Lifetime Box Code

The following code outlines our implementation of lifetime setup and can be found on the Holmes Group Github page at <https://github.umn.edu/HolmesGroup/lifetimeTesting>. To implement all boxes, code is organized into separate files. *box.py* contains all general functions shared between all hardware implementations and is the main driver for lifetime. Different hardware configurations require different commands in order to control the hardware. These hardware specific implementation details are located in *keithleyBox.py*, *keithleyBox2.py*, and *keysightBox.py*. To facilitate hardware rearrangement, configuration files, such as *box1.json* coordinate hardware. Finally, each piece of hardware is uniquely named in Linux using udev rules, outlined in *85-lifetime.rules*.

```
box.py  
keithleyBox.py  
keithleyBox2.py  
keysightBox.py  
box1.json  
85-lifetime.rules
```

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