On the Role of Molecular Structure on the Lifetime of Organic Light-Emitting Devices

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Dedications

To my family and friends, for supporting all my endeavors
Abstract

Organic light-emitting devices (OLEDs) are an established technology in mobile and large format display technologies due to their improved dark contrast and efficiency. The ability to create long-lived devices for lighting or high-brightness applications relies on understanding the degradation mechanisms inherent to excitonic organic semiconductor systems. This work discusses procedures and methods to characterize and understand the degradation in OLEDs, with emphasis on devices containing a phosphorescent light-emitter. Two structurally similar hosts, 4,4'-bis(N-carbazolyl)-1,1'-biphenyl (CBP) and 4,4'-bis(carbazole-9-yl)-2,2'-dimethylbiphenyl (CDBP) are investigated as hosts in phosphorescent OLEDs, as a stark 10x difference in operational lifetime is observed despite their similarities. Using accelerated aging tests, molecular fragment analysis, and low-temperature phosphorescence spectroscopy, the reduced lifetimes of devices containing CDBP are correlated with the formation of triplet excimer states. These findings suggest that candidate host molecules should be screened for excimer formation, as host excimers may aggravate device degradation and lower device stability.
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CHAPTER 1 – ORGANIC SEMICONDUCTORS AND LIGHT-EMITTING DEVICES

1.1 Basics of Organic Semiconductors

1.1.1 Molecular Orbitals and Excitons

Organic semiconductors are carbon-based molecules that exhibit enhanced conduction because of delocalized \( \pi \)-bonding in their conjugated double and single bond structures. Linear combination of atomic orbitals (LCAO) shows that conjugation of double and single bonds leads to sp\(^2\) hybridized bonding. \( \pi \)-orbitals of adjacent carbon atoms can become highly delocalized in extended conjugated networks of carbon.\(^1\)\(^-\)\(^3\) These delocalized orbitals are referred to as molecular orbitals. The energy of the molecular orbitals is determined by the precise elemental makeup and structure of the molecule. Wide varieties of structural and elemental configurations enable an assortment of electronic properties applicable to a broad range of electronic applications. The challenge for researchers is to engineer the structures and elemental compositions to achieve a desired set of properties.

Organic semiconductors are broadly classified in two categories: small molecule (\( M_w < 1 \text{kg/mol} \)), and polymer organic semiconductors composed of long chains of repeating units.\(^3\) In this thesis the emphasis is on small molecule organic semiconductors, but most of the properties discussed below are relevant to both families of organic semiconductors.
The difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is known as the electronic band gap ($E_g$) of an organic semiconductor. Figure 1 illustrates how the electronic gap of an organic semiconductor can be tuned via molecular design, in this case, by increasing the length of the acene chain. An energy gap enables semiconductor properties such as absorption and emission of light. This work will discuss the use of organic semiconductors in organic light-emitting devices (OLEDs).

An electron can be promoted from the HOMO to the LUMO via optical excitation, leaving a hole in the HOMO and forming a molecular excited state. Similarly, under electrical excitation, electrons and holes may be injected directly the LUMO and HOMO. In organic semiconductors, the electron-hole pair is bound as an exciton since the low dielectric constant of the material frustrates screening of the electrostatic interaction.\(^1\) The exciton binding energy reduces the effective bandgap of the organic semiconductor. Therefore, the excitonic bandgap describes the energy required to form an exciton as the electronic bandgap minus the binding energy. An exciton is energetically favored to return to the ground state, which can occur by radiative or non-radiative recombination over timescales ranging from hundreds or picoseconds to hundreds of microseconds. A photon is emitted during radiative recombination, while non-radiative recombination results in emission of a phonon (vibrational energy).\(^1,2,4\) Whether or not an excited state recombines

Figure 1: Illustration of HOMO and LUMO in a series of acenes with increasing number of benzene rings. The bandgap of the molecules decreases with increasing number of benzene rings.
radiatively depends on competing excitonic processes and is a result of the quantum mechanical rules in excitonic systems.

1.1.2 Spin Statistics

![Diagram of electron-hole pairs with differing spin configurations]

Figure 2: Vector representation of electron-hole pairs with differing spin configurations. The singlet has no net spin angular momentum, while the triplets have spin of 1 in one of three possible configurations corresponding to \( m_s = -1, 0 \) or 1.

The tendency of an organic material to decay radiatively or non-radiatively is dictated by the nature of the spin state. Quantum mechanics dictates that an excited state can form spin 0 and spin 1 states, with either singlet of triplet degeneracy.\(^4\) Spin can be represented as a vectoral quantity and the differences between singlets and triplets is illustrated in Figure 2.\(^3\)\(^-\)\(^5\) Singlet states readily recombine by emission of a photon. Triplets are forbidden from radiative recombination due to their unpaired spin, as spin must be conserved during radiative recombination. Thus, triplet states must undergo processes that change their spin state in order to recombine. Since additional processes are involved in recombination of triplet states, radiative recombination of triplets is significantly slower (microseconds to hours) than singlet recombination (nanoseconds)\(^1\)\(^,\)\(^3\)\(^,\)\(^4\)
Spin statistics dictate that triplets and singlets are formed in a 3:1 ratio upon excitation. As a result of this, the type of exciton harvested in an OLED will determine the ultimate efficiency a device can achieve.

1.1.3 Exciton Electronic Transitions in Organic Semiconductors

The excitation of an electron changes the electronic and vibrational states of the host molecule. The Born-Oppenheimer approximation helps simplify the picture of excitation by assuming that the comparatively fast electronic transitions can be treated separately from the relatively slow nuclear rearrangements molecules undergo after changes in electronic states. This allows for simplified computational calculations of the electronic and vibrational states in a molecule.

Figure 3 illustrates the excitonic states in an organic semiconductor, alongside potential exciton conversion mechanisms. The ground state singlet is denoted as $S_0$, the first excited singlet state $S_1$, and the first excited triplet state $T_1$. Fluorescence and phosphorescence are radiative
transitions from \( S_1 \) and \( T_1 \) to the ground state respectively. Higher excitonic states \( S_n \) and \( T_n \) may exist in a given molecule. Each state \( (S_0, S_1, T_1, \text{etc.}) \) is composed of a manifold of vibronic states, which can be defined as \((0,1,2\ldots)\), and are denoted as a second subscript \( S_{0,1} \). Vibronic states refer to the combination of electronic and geometrical/vibrational arrangements in the molecule.

1.1.4 Intermolecular Excited States

Excitons whose electron-hole pairs are confined within a single molecule are called “monomer” excitons. However, electrons and holes located on adjacent molecules can still form shared excited states called excimer states.\(^1\),\(^6\),\(^7\) Shared excited states between dissimilar molecules are called exciplex states. Both states can radiatively recombine, returning to an unbound ground state in the process. Intermolecular states have defining emission features, but no absorption features since the excited state forms from the monomer excited states.\(^1\),\(^5\)–\(^8\) Excimer states are important because they change the energetic landscape in an organic molecule and potentially, its overall optoelectronic behavior. Indeed, this thesis will examine how the formation of excimers can strongly impact the stability of OLEDs.
1.2 Principles of Organic Light-Emitting Devices

1.2.1 Basic OLED principles

OLEDs are electroluminescent (EL) devices, meaning light is emitted by applying an electrical input. The fundamental goal in OLED design is to optimize the transport, injection, and emitter layers to create efficient devices with low operating voltages and long lifetimes at a desired output color. OLEDs emit light through radiative recombination of excitons formed via charge injection into an emissive layer (EML). Charges are injected from an anode and a cathode and travel through subsequent electron and hole transport layers (ETL, HTL) to recombine in the EML. This arrangement, known as a bottom emitting diode because it emits from the glass substrate side, is shown in Figure 4. Figure 4 also shows an illustration of the energy levels in an OLED. Transport and injection barriers of the layers leading up to the emissive layer of the OLED determine the balance of electrons and holes in the emissive layer, which in turn, determines the profile of exciton formation in the EML. The region where excitons are formed is known as the recombination zone (RZ) of the emissive layer.
1.2.2 Evolution in OLED architecture

Practical fluorescent OLEDs were first demonstrated by Tang and Van Slyke\textsuperscript{9} using a bilayer structure of 8-hydroxyquinoline aluminum (Alq\textsubscript{3}) and a diamine with ITO and Mg/Ag electrodes. This first practical demonstration had an electron-to-photon conversion efficiency of 1% with a relatively low driving voltage. Subsequent development of doped Alq\textsubscript{3} OLEDs, where the dopant acted as the emitting molecule, expanded the known capabilities of fluorescent OLED devices and laid the groundwork for future OLED design.\textsuperscript{9} In the context of OLEDs, doped emissive layers refer to mixed host-guest layers, where a small amount (< 20%) of the emitting guest is added to a wider bandgap host. The purpose of the host is direct and confine charges and excitons on the emitter to enhance the efficiency of emission compared to a neat film of emissive material.\textsuperscript{10-12}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Figure 5: (a) Red emitter platinum octaethylporphyrin (PtOEP). (b) Green emitter Ir(ppy)\textsubscript{3} (c) Blue emitter Bis[2-(4,6-difluorophenyl)pyridinato C\textsuperscript{2},N](picolinato)iridium(III) (Firpic). These phosphors share a common organometallic structure.}
\end{figure}

Despite the advances in fluorescent OLEDs, fluorescent emitters continued to be restricted to harvest only 25% of generated excitons, while 75% of “dark” triplet excitons remained unexploited. Attention turned to the idea that high spin-orbit coupling in a molecule increases the intersystem crossing rate, and effectively mixed the singlet and triplet states to allow radiative recombination from all available excitons. Successful demonstrations of OLEDs utilizing this concept were achieved through the use of phosphorescent emitters with organometallic
complexes. These emitters are able to efficiently harvest triplet excitons at room temperature due to the large mass of the coordinating metal atom, which increases the spin-orbit coupling as $Z$. An archetypical green phosphor used extensively in this work is tris[2-phenylpyridinato-C2,N]iridium(III) (Ir(ppy)$_3$). Figure 5 shows the structure of Ir(ppy)$_3$, along with two common red and blue organometallic phosphors. In fully assembled devices, External Quantum Efficiencies (EQE) over 25% have been achieved in Red, Blue and Green devices, demonstrating the efficiency improvement of phosphorescent devices. The concept of EQE is described in chapter 2 in detail.

This thesis focuses on the role of intermolecular excimer states on the lifetime of OLEDs based on host-guest emissive layers with the archetypal phosphorescent emitter Ir(ppy)$_3$. Chapter 2 introduces the OLED assembly and characterization methods used in this study. Chapter 3 and 4 then discusses the experiments performed to elucidate the discrepancy in lifetime of two structurally similar OLED host materials.
CHAPTER 2 – EXPERIMENTAL METHODS

2.1 Vacuum Thermal Evaporation

In this work, organic semiconductor thin films are grown via high vacuum thermal evaporation.\textsuperscript{19} The general setup for vacuum thermal evaporation is shown in Figure 6. Solid powder of the desired organic semiconductor material is placed in a metal crucible and is sublimed via resistive heating at a temperature above the sublimation temperature of the source material, but below the decomposition temperature. The crucible is designed to allow the sublimed material to escape in the direction of the substrate, which typically in placed at a throw distance of 0.5-1 m from the sources. The deposition chamber is evacuated with a cryogenic pump and maintained at pressures of $10^{-7}$ Torr to realize long vapor mean free paths for the sublimed material. Deposition of thin films is typically performed at rates of 0.1-5 Å/s.\textsuperscript{19} Film thickness is monitored during deposition with quartz crystal microbalances. Several crucibles are used to realize multi-layer deposition without breaking vacuum.

**Figure 6:** Illustration of vacuum thermal evaporation chamber. Source material is placed inside a sublimation crucible, and the crucible is heated resistively. Sublimed material travels away from the crucible, condensing on the substrate as a thin film. Deposition is monitored with a quartz crystal monitor.
2.2 Device Fabrication

The OLED architecture used in this thesis is similar to that of Figure 4. Pre-patterned indium-tin-oxide (ITO) thin films coated onto a 2-mm-thick glass slide are used as the substrate and anode, respectively. Substrates are first sonicated in Tergitol, distilled water, acetone, and then washed in boiling isopropanol to eliminate contaminants that may negatively affect device performance. Substrates are placed under a UV-ozone lamp for 15 minutes to enhance hole injection from the ITO to the transport layer. Devices are transferred to a N₂ glovebox, and coated with a layer of the proprietary hole-injector layer AQ-1250. This layer also planarizes the sharp edges of the ITO to prevent contact with the top aluminum cathode in the final step of deposition.

Samples are loaded into an Angstrom Engineering thermal evaporation chamber along with all organic source materials. The organic layers (HTL, EML, ETL) are first deposited using a patterned metal mask to define the active device area, followed by the cathode composed of 0.5 nm of LiF and 100 nm Al using a cathode-specific mask. The emissive layer, 10 nm thick, is composed of a carbazole-based host with Ir(ppy)₃ doped at 6 vol%. The electron and hole transport layers in this work are both 40 nm thick and are composed of tris(4-carbazoyl-9-ylphenyl) amine (TCTA), and 2,2',2"-(1,3,5-benzenetriyl)-tris(1-phenyl-1-H-benimidazole (TPBi), respectively. The ETL and HTL materials are selected to have wider bandgaps than the emissive layer host, which confines excitons to the emissive layer.

The overlap between the ITO pattern and the cathode pattern defines an active device area of 25 mm². Devices are taken outside the vacuum chamber after deposition, and into a separate glovebox for encapsulation with a 1” glass slide and UV-cured epoxy. Devices are tested following the encapsulation process by performing 3 IV sweeps (1-10 V) while measuring the brightness of the device.
2.3 Optical Characterization

The energies of the singlet and triplet states of the emitting guest are typically tuned through molecular design and define the color of an OLED. Characterization of the spectral shape of OLED emission is carried out using a spectrometer. To measure the efficiency of an OLED, and to compare OLEDs which emit in different wavelengths, it is necessary to quantify the output of the device. The External Quantum Efficiency (EQE) of an OLED is defined as the number of photons that escape the device divided by the number of charges injected into the device. This considers photons that may be generated, but do not escape the device due to total internal reflection or waveguided modes.\(^{23}\)

For display and lighting applications, it is necessary to account for the sensitivity of the human eye towards specific wavelengths. The emission of an OLED can be scaled by the photopic response curve (CIE 1931 color space), which is curve centered about 550 nm.\(^{23}\) The scaled optical output is termed “Luminous Flux”, measured in Lumens (lm), and is a better representation of the perceived brightness of the device. Figure 7 shows the photopic response curve which is used to scale the optical power output of an OLED.

![Figure 7: Photopic response curve used to normalize the optical power to luminous flux.](image)

Further normalization of the luminous flux by the solid angle of emission measured quantifies the output per unit solid angle of emission and is termed Candela (cd). Normalizing this
by the unit area of emission of the device results in the “nit” unit, expressed in units cd/m². This term is used to refer to the “brightness” or luminance of a device.

### 2.4 OLED Efficiency

The efficiency of an OLED is typically expressed as the ratio of emitted photons to injected charges. It is characterized by measuring the brightness of the device as a function of current density and voltage. This efficiency can be represented as current efficiency (cd/A), power efficiency (lm/watt), or external quantum efficiency (%). EQE values are useful to determine overall efficiencies as a function of brightness and can yield important information about non-ideal behaviors.

It is possible to define the external quantum efficiency of a device by the component efficiencies of intermediate processes required for emission to occur. Previous work\textsuperscript{14,20,22} has introduced several parameters to define the external quantum efficiency of an OLED ($\eta_{eqe}$):

$$\eta_{eqe} = \eta_{PL} \eta_{EF} \eta_\tau \chi \eta_{OC}$$  \hspace{1cm} \text{Eqn 1}

Where $\eta_{PL}$ is the photoluminescence (PL) efficiency of the emissive layer, $\eta_{EF}$ is the exciton formation (EF) efficiency, $\eta_\tau$ is the fraction of excitons that relax via natural recombination, and $\eta_{OC}$ is the fraction of photons that escape the OLED structure and is determined by total internal reflection or waveguided modes. $\eta_{EF}$ describes the efficiency of exciton formation from injected charges. $\chi$ is the fraction of excitons that can recombine and is defined by spin statistics and the type of emitter (fluorophore vs phosphor).\textsuperscript{20} Fluorescent molecules are limited to singlet emission, leading to $\chi = 0.25$, while phosphors have a value of unity. This representation of efficiency is particularly useful when studying OLED lifetimes because it can provide insight about the relative contribution of each component efficiency to the degradation of the device.
2.5 Operation and Lifetime of OLEDs

OLEDs are operated by applying a constant current corresponding to a desired output brightness. While occurring at different rates, the EL output of all OLEDs degrades over time. Figure 8 shows the dependence of EL intensity as a function of time for a green OLED based on Ir(ppy)₃. Figure 8 also shows a common way to describe lifetime, the $t_{50}$, where $t_{50}$ represents the time at which the device reaches 50% of its initial intensity. It is possible to fit the EL degradation of an OLED by using a stretched exponential function. This allows a basic characterization of degradation but does not provide insight about the mechanisms of degradation in the device.

A more thorough method involves simultaneously probing the $\eta_{\text{EL}}, \eta_{\text{PL}}$, and $\eta_{\text{EF}}$ of devices relative to their starting efficiency. Previous work has demonstrated how to perform such measurements in OLEDs. In this setup, the EL of an OLED is measured while the device degrades under constant current. Intermittent pauses in EL operation allow PL measurements of the degraded region via laser excitation. The electrical excitation is the primary form of degradation in this experiment, while the optical excitation is meant only to assess the change in PL efficiency due to electrically-driven degradation. Since the EL signal of a device is proportional to the external quantum efficiency (EQE or $\eta_{\text{EQE}}$), it is possible to express the ratio of $\eta_{\text{EQE}}$ at time $t$ to $\eta_{\text{EQE}}$ at $t=0$:  

---

**Figure 8:** (a) Example of the EL decay of an electrophosphorescent device with the architecture shown in (b).
\[
\frac{\eta_{EQE}}{\eta_{EQE,0}} = \frac{\eta_{PL} \eta_{EF} \eta_{\tau} \eta_{OC}}{\eta_{PL,0} \eta_{EF,0} \eta_{\tau,0} \eta_{OC,0}}
\]  
Eqn 2

By assuming that both \( \eta_{\tau} \) and \( \eta_{OC} \) remain constant throughout the test,\textsuperscript{20,22} it is possible to extract the ratio of exciton formation:

\[
\frac{\eta_{EF}}{\eta_{EF,0}} = \frac{\eta_{PL} \eta_{EQE,0}}{\eta_{PL,0} \eta_{EQE}}
\]  
Eqn 3

EL, PL and EF efficiencies are therefore quantified relative to their initial values as a function of time. PL and EF efficiencies can be plotted as a function of percent EL degradation to determine relative contributions of PL and EF to the total EL degradation. In this way, the general EL measurement can be decoupled into the degradation of the emitter PL efficiency and the ability of the device to form excitons.

There are several challenges to interpret these extracted efficiency losses. A primary concern is whether the RZ in the device overlaps the region probed by PL. Analysis of changes in EL, PL and EF must consider potential changes in the RZ position and width as a function of degradation. Potential error can be reduced by decreasing the thickness of the emissive layer, which reduces potential RZ migration effects, and by optimizing the architecture of the device to ensure uniform PL excitation.

Changes in PL efficiency reflect changes in emitter efficiency, usually due to degradation of the emitter or to an increase in quenching sites.\textsuperscript{22,26} Changes in exciton formation can reflect changes in transport due to carrier traps or an increase in pathways for non-radiative exciton recombination. Overall, with appropriate knowledge of the RZ width, this technique enables the analysis of the EF and PL efficiencies in OLEDs, which can help pinpoint the mechanisms of degradation in the device.
It is important to note that OLEDs can also degrade via extrinsic failure mechanisms that are not related to excitonic processes in the emissive layer, such as moisture damage or shorts.\textsuperscript{24} This work will only discuss exciton degradation processes that occur in the EML of the device.

2.6 Measurement Methodology

![Diagram of a simultaneous EL/PL system. The laser (either 405nm or 473nm) is turned on every 10 min for PL measurements. (1) Device Photodiode (2) Laser Reference Photodiode (3) 50/50 optical splitter (4) Device mount (5) Device slide]

Previous work from the Holmes group developed the equipment necessary for this measurement.\textsuperscript{20,22} A diagram of this setup is shown in Figure 9. A device is placed on a holder at a 45° angle to a laser source. A photodiode placed directly in front of the device measures both EL during electrical operation and PL during optical excitation with the laser. A standard test cycle consists of a 10-minute block of EL operation, followed by a PL measurement under no electrical excitation. Cycles are repeated until the EL signal reaches a user defined threshold (a percentage of the initial EL signal). All instrumentation is controlled via a Python interface, with several tunable parameters and capability to measure several devices at once using parallel channels. Additional information about the setup, including specific details regarding laser power and operation are available in Appendix A.
2.7 Understanding OLED Degradation

Several electronic processes occur simultaneously during the operation of an OLED device. This work focuses on the processes that occur in phosphorescent OLEDs. During device operation, charges are injected from the cathode and anode into the organic semiconductor layers. Each charge inherently causes the surrounding molecules to rearrange due to Coulombic forces. The collection of charge and re-arranged surroundings is referred to as a polaron and the term associates each charge with a localized energetic state in the organic semiconductor. “Electrons” and “Holes” will therefore be referred to as polarons or charges in this work.

Opposite charges that encounter each other can recombine to form excitons, which can subsequently recombine radiatively or non-radiatively. The lifetime of an exciton $\tau_e$, is described by the inverse sum of the rates of radiative and non-radiative recombination,$^{1,27}$

$$\tau = \frac{1}{k_r + k_{nr}}$$

Eqn 4

The exciton lifetime depends on several factors, including the character of the exciton (singlet or triplet), and the properties of the surrounding molecules. The density of excitons and polarons within the emissive layer has been modeled previously to interpret device efficiency and luminance degradation.$^{28-30}$ Models describing exciton and polaron density are relevant for this work since exciton and polaron densities are known to affect both the efficiency and lifetime of OLEDs. In phosphorescent systems, where triplets dominate the exciton population, the exciton density can be described as$^{30}$:

$$\frac{dn_{ex}}{dt} = G_{nex} - \frac{n_{ex}}{\tau} - \frac{1}{2} k_{tt} n_{ex}^2 - k_{tp} n_{ex} p$$

Eqn 5

Where $n_{ex}$ represents exciton density, $G_{nex}$ represents exciton generation rate, $k_{tt}$ and $k_{tp}$ represent triplet-triplet annihilation and triplet-polaron quenching rate constants, and $p$ is polaron density. $G_{nex}$, $n_{ex}$, and $p$ are functions of position in EML and time. The first two terms describe exciton
generation and natural exciton decay (both radiative and non-radiative). The third and fourth term in Eqn 5 describe bimolecular processes. These processes occur when two energetic states, either two excitons, or an exciton and a polaron, interact and form a single, high energy exciton. These events are known as triplet-triplet annihilation (TTA) and triplet-polaron quenching (TPQ).

Bimolecular quenching processes result in higher energy excitons. In cases where the triplet energy is already high, the energetic states resulting from bimolecular events can have energies higher than bond-dissociation energies, increasing the chances for bond scission in OLEDs. TTA and TPQ are therefore considered the primary degradation mechanisms of the EML in phosphorescent OLEDs. It is worth noting that where the degradation rate of the device typically correlates with the energy of the emitted photon, and is particularly evident in Red, Green, and Blue OLEDs. Also notable from Eqn 5 is that high exciton densities, which are required for high luminance applications, inherently result in accelerated device degradation due to increased bimolecular events. A defect generation rate can be modeled in an OLED by assuming that a fraction of TTA and TPQ events lead to defect generation:

\[
\frac{df}{dt} = k_{\text{ta}} n_{\text{ex}}^2 + k_{\text{tpq}} p n_{\text{ex}}
\]

\[\text{Eqn 6}\]

\(k_{\text{ta}}\) and \(k_{\text{tpq}}\) here represent also the probability of forming a fragment and are different from those shown in Eqn 5.

### 2.8 Molecular Fragmentation in OLEDs

The composition and energetic levels of generated fragments in OLEDs will determine the role of the fragment in the device after degradation, and whether the PL or EF is ultimately affected. In particular, the HOMO and LUMO of the remaining fragment can be calculated to assess whether the molecules will behave as exciton quenchers, polaron, or exciton traps. For example, a fragment that acts as a polaron trap ultimately affects transport and exciton formation in the device. It is not uncommon for the operating voltage of an OLED to rise during operation. In some cases,
this increase in voltage can be attributed to the increase in concentration of traps due to bimolecular quenching events.\textsuperscript{26,29}

While decoupled EL/PL testing can elucidate the component efficiency losses in OLEDs and provide insight into degradation mechanisms, this technique does not provide further insight about bond cleavage and the composition of fragments. Understanding the molecular structure of the fragments provides additional insight into bond degradation and the behavior of fragments in the device. Therefore, the ability to determine the composition of fragments is paramount to understanding device degradation.

\subsection*{2.9 Fragment Characterization}

There are several methods of characterizing fragment formation in OLEDs. Fragments of molecules can retain optical properties that can be probed if the concentration and PL efficiency of the fragments is sufficiently high.\textsuperscript{28} Alternatively, mass spectrometry (MS) can measure both fragment mass and the relative concentrations of fragments. Examples of commonly used MS techniques include High Performance Liquid Chromatography (HPLC MS), and laser-desorption/ionization time of flight mass spectrometry (LDI-TOF-MS).\textsuperscript{24,31–38} Since the relative abundance of fragments in these devices can be extremely low, it can be difficult to detect them using HPLC. LDI-TOF-MS, on the other hand, is particularly suited for mass characterization in degraded OLED devices, as has been previously shown in several OLED degradation studies.\textsuperscript{28,31,32,35,39}
2.10 LDI-TOF-MS

LDI-TOF-MS can be used to characterize the mass distribution of laser desorbed molecules from an OLED device. Figure 10 illustrates the LDI-TOF-MS instrument. A laser with a wavelength of 332nm is used to desorb and ionize molecules. An electric field accelerates the desorbed ionized material towards a detector. Masses are separated by their mass/charge ratio and are differentiated by the time they take to reach the detector. Laser desorbed molecules are imparted different amounts of kinetic energy during desorption. For small molecules analysis, the instrument is setup in reflector mode to reduce the spread of kinetic energies and increase mass resolution.

LDI-TOF-MS is not particularly suited for absolute quantitative analysis of molecular abundance due the sensitivity of the measurement to factors such as absorption, intermolecular forces, and potential fragmentation during ionization. However, by comparing degraded devices to pristine undegraded devices, it is possible to compare the differences in abundance of specific fragments, enabling more concrete conclusions about the generation of fragments in the OLED during operation. Knowledge of the composition of fragments can yield important information about the degradation mechanisms in the device, as well as enabling DFT calculations of the energetic levels of the fragments.

Figure 10: Diagram of a LDI-TOF-MS system. The sample device is irradiated with a pulsed 332nm laser. Desorbed material is accelerated through a column and reflected towards the detector in reflector mode.
2.11 LDI-TOF-MS for OLEDs

OLEDs that have degraded are opened by removing the encapsulating cover slide. The Al cathode is removed by peeling the layer with scotch tape. The organic layers beneath remain in place as they have higher adhesion to the glass substrate than the aluminum. The device slides are mounted on the LDI-TOF-MS plate (SCIEX 5800 TOF) and are placed under vacuum for analysis. The laser ionizes the material, which is accelerated under vacuum and reaches a detector. The output of this measurement is mass/charge (m/z) vs intensity. The user defines the number of laser pulses per scan and the area that is ablated in each scan. Additional information on data processing and experimental design can be found in Appendix B.

LDI-TOF-MS was used in the study presented in Chapter 3 to differentiate the degradation mechanisms of devices assembled with two distinct host materials. This technique allowed the identification of molecular fragments formed during device degradation due to electrical excitation.
CHAPTER 3 – ROLE OF HOST AGGREGATION IN DEGRADATION

3.1 Main Properties of Carbazole Hosts

The properties of the EML host are a principal contributor to the efficiency and lifetime of the device. In the case of OLEDs, hosts with high triplet energies are desired to prevent excitons from populating the host molecule, enhancing exciton confinement on the emitter. In addition, good electron and hole transport is desired to achieve a wide recombination zone that translates into low exciton densities. In this regard, hosts that contain the carbazole moiety have been studied extensively as hosts due to their high triplet energies and ambipolar transport.\textsuperscript{11,12,16,41–49}

3.2 Properties of Devices with CBP and CDBP Hosts

Figure 11 shows the molecular structures and triplet energy levels of CDBP, CBP and emitter Ir(ppy)\textsubscript{3}.

Figure 11: Molecular structures and triplet energy levels of CDBP, CBP and emitter Ir(ppy)\textsubscript{3}

\begin{itemize}
  \item \textbf{CDBP}:
    \begin{itemize}
      \item Monomer T\textsubscript{1}:
      \begin{itemize}
        \item 3.0 eV
      \end{itemize}
      \item Excimer T\textsubscript{1}:
      \begin{itemize}
        \item 2.6 eV
      \end{itemize}
    \end{itemize}
  \item \textbf{CBP}:
    \begin{itemize}
      \item Monomer T\textsubscript{1}:
      \begin{itemize}
        \item 2.55 eV
      \end{itemize}
    \end{itemize}
  \item \textbf{Ir(ppy)}\textsubscript{3}:
    \begin{itemize}
      \item Monomer T\textsubscript{1}:
      \begin{itemize}
        \item 2.42 eV
      \end{itemize}
    \end{itemize}
\end{itemize}

4,4′-bis(N-carbazolyl)-1,1′-biphenyl (CBP) and 4,4′-bis(carbazole-9-yl)-2,2′-dimethylbiphenyl (CDBP) are two carbazole containing hosts that differ by two methyl groups. CDBP, however, has a higher singlet and triplet energy. From an energetic standpoint, as shown in

\textsuperscript{1} A portion of the results shown in this section are under submission to Applied Physics Letters
Figure 11, CDBP should have a longer lifetime due to the higher triplet energy, as excitons are less likely to transfer back to the host molecule. As Figure 12 shows, when CDBP is used as host instead of CBP, the lifetime of Ir(ppy)$_3$ based devices suffers a nearly ten-fold decline when run at 3000 cd/m$^2$. Differences in the efficiency of these devices do not account for the difference in lifetime of these hosts, suggesting the existence of alternative degradation mechanisms.

![Figure 12](image)

**Figure 12:** (a) Lifetimes of CBP and CDBP devices at three different initial luminances. Power law acceleration factors extracted from the data are -1.51 ±0.02 and -1.42 ±0.06 for CBP and CDBP respectively. (b) Illustration of device architecture

Figure 12 also shows the lifetime trends of CBP and CDBP based devices as a function of initial luminance (acceleration factors). This trend correlates with increasing exciton and polaron densities in the device. EL $t_{50}$ and PL $t_{90}$ refer to the time required for EL and PL signal to reach 50% and 90% of the initial intensity respectively. In this case, the slopes of both CBP and CDBP are statistically similar, indicating that the same power law behavior and acceleration factor is observed for both systems. This result suggests that the underlying degradation mechanism for both carbazole hosts is similar or is at least equally dependent on the density of excited and charge states. It is important to note that CBP exhibits slightly higher PL degradation across the board, but this effect a reflection of rapid PL degradation at short times only.
Knowing that the degradation mechanism for both hosts is similar, LDI-TOF-MS analysis was performed on degraded and undegraded CBP and CDBP devices in order to assess fragment formation in the EML of both systems. Figure 13 shows the degraded and undegraded peak intensities of the fragments of the parent host molecule. The primary fragments forming from device operation consist of molecules with broken C-N bonds. In both CBP and CDBP, the difference in fragment abundance between degraded and undegraded devices is large enough to determine that the fragments indeed form during degradation. In addition, the CDBP fragments appear to form more than CBP fragments at the same level of EL degradation. These results suggest

Figure 13: LDI-TOF-MS data of CBP and CDBP degraded and undegraded devices. (A) CBP fragments and (B) CDBP fragments.
that CDBP suffers from lower molecular stability, despite having larger singlet and triplet energy than CBP.

Calculation of BDE for both CBP and CDBP were performed by the DuPont Korea Group*, using B3LYP package basis set (6-31G*), utilizing program Gaussian 16 28,52,53 in order to assess molecular stability of CDBP through its Bond Dissociation Energy. Calculated values for BDE are shown in Table 1, and diagrams depicting bond breakage locations are shown in Figure 14.

<table>
<thead>
<tr>
<th>BOND DISSOCIATION ENERGY</th>
<th>CBP</th>
<th>CDBP</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-N BOND</td>
<td>81.75 kcal/mol</td>
<td>81.28 kcal/mol</td>
</tr>
<tr>
<td>CENTER C-C BOND</td>
<td>112.46 kcal/mol</td>
<td>107.7 kcal/mol</td>
</tr>
<tr>
<td>SIDE C-C BOND</td>
<td>n/a</td>
<td>95.72 kcal/mol</td>
</tr>
</tbody>
</table>

Table 1: Bond Dissociation Energy Calculations for CDBP/CBP

Figure 14: (A) (B) CBP bond cleavage at C-N and C-C locations respectively. (C)(D)(E) CDBP bond cleavage at center C-C bond, side C-C bond, and C-N bond respectively.

Results show the similarity in BDEs for both molecules. Both CBP and CDBP share a common weakest C-N bond and similar dissociation energies. This evidence supports the first results that both hosts share a common degradation mechanism. Despite this evidence, the drastic
difference in lifetime between the two hosts suggested additional mechanisms are involved in molecular degradation.

![Molecular structure of CBP and CDBP](image-url)

**Figure 15:** Molecular structure of CBP, showing the two center phenyl groups labelled 1 and 2. Each phenyl group defines a plane and the angle between the two planes is the dihedral angle.

BDE calculations pointed to a key difference in dihedral angle in the CBP and CDBP molecules, corresponding to the angle between the two center phenyl groups, and describing the planarity of the biphenyl group. Figure 15 shows the two phenyl groups defining the dihedral angle. CBP exhibits relatively low torsion, 36° in ground state, and even less torsion, 2°, in its excited state. In comparison, CDBP shows high torsion with 90° dihedral angles. This difference in rotation was found to be consistent with several reports on the effect of bond rotation on excimer formation of CDBP.\(^{44-46,54}\) In CDBP, the extra methyl groups lead to increased C-C bond rotation which reduces the orbital coupling between the two end carbazole groups. This is argued to cause excitons to interact more strongly with neighboring excitons, leading to the formation of excimer states. In contrast, the planar nature of the biphenyl group in CBP localizes excitons in the center of the molecule, resulting in decreased excimer formation. The formation of an excimer state in CDBP decreases the effective energy levels of the triplet state.\(^{44-46,54}\) Despite speculation about the potential effect the excimer state can have on a device’s lifetime performance,\(^{46}\) the role of the excimer state CDBP on device lifetime has not been reported.

### 3.3 Excimer Formation in CDBP and Detection

Excimer state formation is inherently dependent on the concentration of the monomer and can therefore be arrested at low concentrations. It is possible to study whether low concentrations
of CDBP affect the lifetime of mixed host CBP-CDBP devices. A correlation between CDBP concentration, excimer formation and device degradation would suggest that the excimer plays a significant role in device degradation.

To understand the role of the excimer state in device degradation, it was first necessary to understand the onset of excimer formation as a function of CDBP concentration. CDBP’s excimer state has a significant triplet emission at low temperatures and is resolvable by comparing dilute and neat film emission spectra. At low temperatures, phosphorescence becomes competitive with non-radiative processes. Additionally, it is possible to resolve the phosphorescence of CDBP by filtering out the prompt (<5ms) fluorescence from the spectra. Mixed neat films of CDBP in UGH2 at different CDBP concentrations were deposited to resolve this excimer state. UGH2 acts as a transparent host and does not participate in the absorption or emission process of CDBP. This prevents any excitonic interactions between CDBP and the UGH2.

All films, at 0, 5, 10, 20, 50 and 100% CDBP, were prepared to be a minimum of 100-nm-thick to improve signal to noise ratio. Films were taken out of the deposition chamber and immediately placed in a Janis CSS-150 Optical Cryostat. The cryogenic stage was pumped to 10-15 mTorr and cooled to 10 K with liquid He. Samples were then pumped optically using a pulsed

![Figure 16](image) (left) Low temperature phosphorescence of thin films of CDBP doped in UGH2. (right) Excimer to monomer ratio, taken as ratio of intensity at 525nm to 413nm.
nitrogen laser (332 nm) operating close to 1 Hz, and spectra were taken using a FERGIE spectrometer with a delayed trigger timer, which filters out prompt fluorescence and integrates over 400ms after each laser pulse.

Figure 16 shows the low temperature phosphorescence spectra of these films. The primary monomer PL features are located at wavelengths of 412 nm and 440 nm. As the concentration of CDBP in UGH2 increases, the excimer feature at 473 nm becomes more apparent, and is predominant above 20%, while the monomer features drop dramatically as CDBP concentration increases. A ratio of excimer to monomer features, taken as the ratio of intensities at 525 nm to 413 nm, is plotted in Figure 16, and shows the excimer feature saturates above 50%. This suggests that the excimer state forms and emits primarily above 20% CDBP.

It was not possible to resolve the CDBP excimer when doped in a CBP film, as the triplet energy of CBP is lower than the CDBP excimer, and excitons likely transfer to CBP before emission occurs. Despite this, when integrated on a mixed CBP-CDBP device, the excimer state should still be populated. For subsequent analysis, it is assumed that the onset of excimer formation of CDBP in CBP is like thin films of CDBP doped in UGH2. Additionally, it is assumed that CBP will not form an exciplex state with CDBP when integrated in a device.
3.4 Excimer – Lifetime Correlation in Mixed Host Devices

Having resolved the onset of the excimer state of CDBP as a function of concentration, the following work addresses the correlation between excimer formation and reduced device lifetime. Devices with an EML consisting of a mixture of CBP and CDBP at varying concentrations with Ir(ppy)$_3$ as the emitter were assembled to test this relationship. The architectures used for these devices are identical to the previous devices, with the exception that the host is now a mixture of CBP and CDBP. Devices were grown at a range of CDBP concentrations, using the same OLED assembly procedure as previously shown.

![Figure 17](image)

**Figure 17:** (a) Representative EL curves for all concentration devices. (b) Representative voltage rise over time for the all concentration mixed CBP/CDBP devices.

Lifetime tests for the mixed host devices were carried out at 3000 cd/m$^2$. Figure 17 shows representative EL curves for each concentration of CDBP. At low concentrations, it is evident that lifetime is not significantly affected by the addition of CDBP. However, as concentration increases above 10%, the lifetime decays rapidly with CDBP concentration. Extracting the EL $t_{50}$ values confirms this trend and shows the negative effect of CDBP on the lifetime of mixed host devices.

An important note for low concentration devices is that some devices containing 5\% CDBP have better lifetime performance due to the improved efficiency in one of the deposition groups. When all devices were plotted, the variability in efficiency and lifetime of low CDBP concentration
devices becomes indistinguishable from pure CDBP devices. It is likely that the improvement observed in one run of devices is due to variations in EML thicknesses.

![Figure 18](image)

**Figure 18**: EL $t_{50}$ and Normalized excimer-monomer ratio vs CDBP concentration. The sharp decline in device lifetime correlates with the increasing number of available excimer sites.

Normalizing the excimer to monomer ratio from Figure 15 by the concentration of CDBP in the devices provides a value that is more representative of the number of active excimer sites in the host. This is more likely to correlate to device lifetime and is plotted alongside the EL $t_{50}$ values for each concentration in Figure 18. Here, a correlation between the normalized excimer-monomer ratio and the lifetime of the mixed host devices is clear. At low concentrations, low excimer formation does not affect the devices significantly, but above 10% CDBP, the onset of excimer states appears to drive the decline in device lifetime.

Figure 19 shows the voltage rise and PL degradation as a function of EL degradation, revealing that despite the increase in degradation rate in CDBP, voltage and PL change similarly in all device concentrations as a function of EL degradation. This suggests that PL and EF have similar contributions to the overall degradation of the carbazole hosts and confirms that CDBP is an inherently less stable host. These results suggest that the excimer state plays a primary role in the stability of CDBP as a host.
Several theories could explain the role of the excimer state in device degradation. The lifetime of the excimer state has been shown to be longer than that of the monomer state,$^{46}$ and longer lived excited states have greater probabilities of participating in bimolecular quenching events, which are known primary causes of molecular degradation.$^{24,54}$ Since the transfer of energy from the triplet Ir(ppy)$_3$ state to the excimer state is endothermic, it is possible that the CDBP state is populated primarily by high energy excitons from bimolecular quenching processes. Although the accelerated lifetime tests in figure 12 show nearly parallel trends, the lifetimes of CDBP and CBP devices could converge at low luminances where bimolecular quenching is low. Alternatively, the localization of the excited state at the carbazole group in the excimer could increase the probability of C-N bond scission.$^{45}$

Observations from LDI-TOF-MS support the idea that CDBP is more likely than CBP to degrade, as the relative fragment signal is higher in scans of CDBP devices. Accelerated lifetime tests at high luminance show that the degradation mechanism trends equally with exciton and polaron density, thus supporting the notion that $k_{\text{sta}}$ and $k_{\text{pq}}$ in EQN 6 are higher. In other words,
the probability of forming a fragment in CDBP is higher despite potentially similar exciton and polaron densities.

The role of excimer states in the degradation of mixed CBP/CDBP devices shows how intermolecular interactions can negatively affect the lifetime of emissive devices. Thus, this work suggests careful consideration of these kinds of interactions during molecular and device design phases, particularly when carbazole moieties are present in the host molecules. In alternative architectures or operating schemes that include excimer or exciplex states, the presence of lower energy shared states can fundamentally change the excitonic landscape of the device and negatively affect the lifetime performance. While calculations of BDE can provide insight into molecular stability, intermolecular interactions such as excimer or exciplex formation must be also carefully considered.
CHAPTER 4 - CONCLUSIONS

This work made use of a variety of OLED characterization tools in order to elucidate the role of the excimer in degradation. Several other characterization methods were considered, including degradation of single carrier devices, optical degradation, impedance spectroscopy, and transient PL measurements. Techniques that were attempted in this work, but were not successful, are included in Appendix D. These additional techniques remain attractive to OLED research as they will provide additional insight into device degradation.

The formation of intermolecular states in OLED hosts was shown to play a crucial role in the degradation of phosphorescent devices. Despite having relatively similar molecular structures, CBP and CDBP exhibit drastically different lifetimes when integrated as hosts in an Ir(ppy)$_3$ based OLED. The propensity of CDBP to form excimer states, as shown via low temperature PL is linked directly to the lifetime degradation in CDBP devices. This difference in lifetime is attributed to the formation of excimer states, which reduce the effective triplet energy of the host, and likely play a role in excitonic host-guest interactions that lead to degradation.

In the case of CBP, and CDBP, the difference in excitonic properties of the hosts is rooted in the differences in molecular structure of the hosts. The simple addition of additional methyl groups enhances the probability of excimer formation in CDBP, which ultimately results in lifetime degradation. This work has shown that the intermolecular excitonic properties of the host play a large role in device lifetime and that these properties should be considered thoroughly during device design phase in addition to BDE and energy level calculations. These design criteria apply similarly to TADF, fluorescent, and white OLED systems as intermolecular states can alter the degradation processes in these different excitonic systems. Particularly close attention should be placed on excimer or exciplex based devices. In the broader context of OLED applications, the stability of
emissive devices stems from the properties of the materials that compose it and the processes that naturally occur in electronically active materials. Comprehensive understanding of all excitonic processes can help improve device design for longer OLED lifetimes.
CHAPTER 5 - BIBLIOGRAPHY


15 † Sergey Lamansky, † Peter Djurovich, † Drew Murphy, † Feras Abdel-Razzaq, † Hae-Eun Lee,


45 S.A. Bagnich, S. Athanasopoulos, A. Rudnick, P. Schroegel, I. Bauer, N.C. Greenham, P.


APPENDIX

A. EL/PL Decoupled Setup and Python Coding

The decoupled EL/PL is used extensively to measure lifetime trends in OLEDs. Key features about the setup are discussed here.

Laser filtering and power

Two lasers are available for EL/PL decoupled measurements, one emitting at 405nm, and the other at 473nm. Both are produced by OBIS. Laser selection must consider the energy levels of the materials in the OLED. Ideally, only the emissive layer should be pumped at the chosen wavelength. This prevents extraneous effects such as exciton diffusion from the transport layers to occur.

Following the laser selection, it is important to adjust the laser power accordingly by using neutral density filters. The device PL signal should be the same order of magnitude as the laser reference photodiode. The device PL corresponds to the guest emitter wavelength, which is different than the laser. Therefore, it is important to filter out any reflected laser light from the device photodiode by using a suitable long pass filter. For example, if the laser wavelength is 405nm, and the emission wavelength is centered about 500nm, a 450nm long pass filter should eliminate any laser reflections while allowing PL signal to reach the detector. The laser photodiode, on the other hand, does not need wavelength restricted filters.

Relevant to the laser and PL signal, the alignment of the device with respect to the photodiode and the laser is important to achieve maximum PL signal and to avoid potential laser reflections. For small area devices, this is particularly important. In these cases, the glass slides are masked with black masking tape so that the laser only illuminates the active OLED area. Every device is aligned with a 3D stage to maximize PL signal prior to starting the test.
Three iterations of the instrument are available to use at the Holmes Group lab, named “Box” 2, 3 or 4. Each box operated in slightly different ways, such as the number of slots available for device slides and the control methodology. In Box 4, for example, only one channel exists, limiting tests to 1 device per “run”, and data collection occurs primarily through a Keithley. In Box 3, up to 6 devices can be tested per run. An Arduino is used in conjunction with control software to switch the Keithley measurements between all devices. Box 4 is recommended for very accurate measurements with a single channel.

Efforts to improve reproducibility of the Box 3 and 4 established appropriate laser warmup times. Note that the 473nm laser is inherently less stable than the 405nm laser and requires longer warmup times. Warmup times have been soft-coded into option files used to run the software and can be changed if necessary. Despite these changes, Box 4 remains the most accurate box for measuring ultra-stable devices due to the simplicity of the single channel system.

**B. LDI-TOF-MS Work**

Key experimental considerations

When ablating any material in the LDI-TOF-MS system, laser fluence, pulse rate, local changes in absorbance, among other factors, can contribute to the observed fragments. Laser power impacts the degree of ablation very strongly. For this work, the laser intensity was varied to understand how this would affect the quality of the mass spectra. In general, high power ablation produced higher quantities and broader distributions of mass fragments. This is undesirable in our case as excess fragments confound our analysis. Thus, when tuning laser power in the instrument, the laser power was set a point where fragments were visible, but no excess isotopic peaks or broadening were visible. At this power, all parent molecules are clearly resolved, and fragments can also be easily resolved. Laser power was then kept constant for all subsequent measurements to ensure the distribution of laser-ablated fragments would remain constant.
Comparing degraded to non-degraded devices is key to decouple the presence of laser formed fragments from fragments formed during device EL operation. Additionally, EL degradation should be performed to very low EL/EL₀ ratios to ensure the concentration of fragments in the degraded devices are high enough to resolve. In this work, samples were degraded to 10% EL₀.

LDI data analysis procedure

Section 3.2 discussed LDI-TOF-MS data for mixed CBP, CDBP host devices. Data was collected for all concentration of mixed host devices in section 3.4. The idea, early on, was to determine whether different fragments formed at different host concentrations, perhaps due to the presence of the excimer state in mixed host devices. Results, however, did not show any clear trends in fragment formation. Included here are the general procedures used to process LDI-TOF-MS data.

![Figure 20: LDI-TOF-MS scan of a CBP degraded device. Peaks below 484 are fragments, while peaks higher are the host (484), Ir(ppy)₃ and TPBi at 650, and TCTA at 742.](image)

Each scan from the LDI-TOF-MS setup yields a mass/charge vs intensity graph, and example of which is shown in Figure 20. Up to 6 scans are taken on every device tested. We identify
the masses of every peak with signal 10x above noise value. Integrals of the areas surrounding each peak are taken to quantify the relative peak intensities. Since LDI-TOF-MS is sensitive to isotopic distributions, each peak inherently carries a “tail” of C\textsuperscript{13} variants. To account for them, we integrate a window of 5amu around each peak, from mass M-1 to M+4, where M is the mass with the highest intensity (the first mass at each peak). An example of a peak of a single molecule is shown in Figure 21 and shows the peak and tail of CBP.

**Figure 21:** Portion of an LDI-TOF-MS scan of a degraded CBP device, showing only the CBP (483) molecule and its isotopic tail with higher masses. In this example, the peak integral corresponds to the area under the curve from 482 to 488. Note that the instrument is sensitive enough to detect radicals with missing hydrogen atoms. This could be relevant when studying degradation processes, as the presence of stable radicals could suggest degradation pathways.

Having identified the peaks, their corresponding masses, and intensities (integrals), we average the intensities of a single device, and then compare all the degraded and undegraded devices as a function of concentration. It is also possible to calculate the difference in average peak signal between degraded and undegraded devices, along with standard errors. To account for the changes in abundance of CBP and CDBP as the concentration of the device changes, it is also
possible to look at the ratio of the fragment peak intensity over parent molecule peak intensity. This work is performed using Jupyter notebook, a python shell, and is available in the Holmes group drive.

Multiple spectra should be taken for a same device to account for variations within a single device. In addition, multiple devices of the same condition should be measured to assess reproducibility of fragment formation across ideally “equal” devices. For this work, a target 20 spectra per condition were taken (5 per device, 4 devices per slide). Thus, a reported peak intensity corresponds to the average intensity of 20 different scans.

C. Python Information

To run the Box control software, it is necessary to first open the linux terminal and navigate to the Holmes Group “lifetime Testing” local GitHub repository. Box.py has been written as a general control software and takes two inputs to open. A “.json” file has been created for each box, and contains the necessary information (number of channels, keysight or keithley names) to correctly connect to the measuring instrumentation. Table 2 below shows the commands necessary to operate the Box control software.

<table>
<thead>
<tr>
<th>BOX NUMBER</th>
<th>COMMAND TO RUN</th>
<th>NUMBER OF CHANNELS</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOX 2</td>
<td>python3 keithleyBox.py box2.json</td>
<td>4</td>
</tr>
<tr>
<td>BOX 3</td>
<td>python3 keysightBox.py box3.json</td>
<td>6</td>
</tr>
<tr>
<td>BOX 4</td>
<td>python3 keithleyBox.py box4.json</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 2: Commands to run decoupled EL/PL software.
D. Single Carrier Device Work

Several attempts at making single carrier devices were made in an effort to study the effect of polaron density on the lifetime behavior of four carbazole hosts: CDBP, CBP, 2,2’-Bis(4-(carbazole-9-yl)phenyl)-biphenyl (BCBP), and 1,3,Bix(N-carbazolyl)benzene (mCP). Typical decoupled EL/PL lifetimes are run with current input (J) and light input (L) separately. Here, we perform optical degradation with the laser only (L), as well as optical degradation with non-EL current flow (L+J). This allows us to decouple the effect of excitons and polarons in lifetime. Devices were tested at a effective current density of 10mA/cm².

Hole only devices were fabricated from mCP, BCBP, and CDBP. The general architecture of these devices is (ITO/AQ1250/TCTA 40nm/EML 20nm (Host + Ir(ppy)₃ 5%)/TCTA 50nm/MoOx 10nm/Al). No significant emission was observed in most devices at 10V, suggesting good single carrier behavior. IV curves are shown in figure 21. Note that the IV curves do not follow exponential turn on behavior as would be expected from single carrier devices. Luminance-voltage curves are not shown because light intensity was not measurable in these devices. Example lifetimes for mCP are shown in figure 22. It is possible to observe an acceleration in degradation from the applied current.
Several attempts to assemble electron-only devices were made. However, despite several iterations in transport layers, all assembled devices exhibited EL behavior. Although some device lifetimes were tested, it was not possible to design these such that the current density was high enough to increase device degradation but not exhibit EL simultaneously. Figure 23 shows an example of mCP electron only device IVL curves built with an architecture of (non-ozone ITO/30nm 50% TPBi + 50% LiQ/10nm TPBi/20nm EML (mCP + 5% Ir(ppy)3)/40nm TPBi/LiF/Al). At 10mA/cm², the photocurrent in these devices exceeds the noise level by 2 orders of magnitude. 

**Figure 22:** (left) IV curves for hole only devices showing slight diode behavior, but no EL (luminance not shown as it is flat). (right) mCP based device lifetimes when degraded optically (L) and with an applied current during optical degradation (L+J). A slight difference in behavior can be observed by looking at the rate of degradation. These devices required a current density of $10^{-2}$-$10^{-1}$ to operate without EL emission, too small to contribute significantly to polaron density and to degradation.

![Graph](image)

**Figure 23:** JVL curves of electron only architecture devices. Devices show diode behavior and low luminances. Ideally, these should not show any EL behavior.