Exciton Management in Organic Light Emitting Diodes

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
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Abstract

Over the last few decades, there has been great interest in the further development of OLEDs for practical applications. They are currently commercially-viable for low-brightness applications, such as in displays for mobile phones and televisions. However, efficiency roll-off and short device lifetimes at high luminance have restricted its progress into the lighting industry. The focus of this thesis is to study and address the major challenges that OLEDs currently face. First, energy transfer mechanisms in two-dopant sensitized fluorescence OLED systems is investigated. As most organic emitters have narrow emission bands, a combination of different coloured emitters is needed in order to achieve broadband white emission. Energy transfer mechanisms are key to ensure a balanced emission from all the colours. A model to quantify the competition between Förster and Dexter energy transfer is presented. Next, a highly simplified white OLED based on a single-emission-layer architecture is presented. This three-organic-layer device was able to achieve a low turn-on voltage of 2.7V, an external quantum efficiency of 18.9% and power efficiency of 30lm/W at practical brightness levels for lighting applications. Additionally, it exhibited good colour quality with minimal colour shifting. The origin of the improved colour shifting in the simplified device is examined. Finally, a platform for improving the device lifetime of blue OLED devices is proposed. This technique involves the introduction of a dopant to enhance the singlet to triplet ratio of excitons initially formed on the blue emitter. A high efficiency blue device was achieved with external quantum efficiency greater than 20% and the device lifetime was extended by 20-fold compared to the standard blue device without the dopant. Detailed investigation into the working mechanism of this strategy for improved device lifetime will be discussed.
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<th>Meaning</th>
</tr>
</thead>
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<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>ARL</td>
<td>Average rate life</td>
</tr>
<tr>
<td>CCT</td>
<td>Colour correlated temperature</td>
</tr>
<tr>
<td>CE</td>
<td>Current efficiency</td>
</tr>
<tr>
<td>CIE</td>
<td>Commission Internationale de L’Éclairage</td>
</tr>
<tr>
<td>CRI</td>
<td>Colour rendering index</td>
</tr>
<tr>
<td>EBL/HBL</td>
<td>Electron/hole blocking layer</td>
</tr>
<tr>
<td>EIL/HIL</td>
<td>Electron/hole injection layer</td>
</tr>
<tr>
<td>EL</td>
<td>Electroluminescence</td>
</tr>
<tr>
<td>EML</td>
<td>Emissive layer</td>
</tr>
<tr>
<td>EOD</td>
<td>Electron-only device</td>
</tr>
<tr>
<td>EPA</td>
<td>Electron-polaron annihilation</td>
</tr>
<tr>
<td>EQE</td>
<td>External quantum efficiency</td>
</tr>
<tr>
<td>ETL/HTL</td>
<td>Electron/hole transport layer</td>
</tr>
<tr>
<td>HOD</td>
<td>Hole-only device</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>ISC</td>
<td>Intersystem crossing</td>
</tr>
<tr>
<td>JVL</td>
<td>Current density-voltage-luminescence</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest occupied molecular orbital</td>
</tr>
<tr>
<td>MEL</td>
<td>Multiple-emission layer</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic light emitting diode</td>
</tr>
<tr>
<td>PE</td>
<td>Power efficiency</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>PLQY</td>
<td>Photoluminescence quantum yield</td>
</tr>
</tbody>
</table>
QCM  Quartz crystal microbalance
RISC  Reverse intersystem crossing
SEL   Single emitting layer
SPA   Singlet-polaron annihilation
STA   Singlet-triplet annihilation
TADF  Thermally activated delayed fluorescence
TCSPC Time correlated single photon counting
TPA   Triplet-polaron annihilation
TTA   Triplet-triplet annihilation
UV    Ultraviolet

$\eta_{ex}$  EQE
$\eta_{b}$  Charge balance factor
$\phi_{eff}$  Effective radiative efficiency of the emitter
$\eta_{out}$  Outcoupling efficiency
$\eta_{int}$  Internal quantum efficiency
$\Phi_{PL}$  Photoluminescence quantum yield
$k_{F}$  Rate constant for Förster energy transfer
$R_{0}$  Förster radius
$\tau$  Exciton lifetime
$\phi_{F}$  Efficiency of Förster energy transfer
$\phi_{D}$  Efficiency of Dexter energy transfer
$k_{D}$  Rate constant for Dexter energy transfer
$R$  Donor-acceptor separation distance (for energy transfer)
$L$  Sum of the effective van der Waals radii of donor and acceptor (for Dexter energy transfer)
$N_{tot}$  Total number of excitons captures (sensitized fluorescence)
\[ E_{ph,av} \] Average photon energy emitted
\[ h \] Plank’s constant
\[ c \] Speed of light
\[ f(\lambda) \] EL spectrum as function of wavelength, \( \lambda \)
\[ \Delta V \] Change in voltage
\[ k_r \] Rate constant for radiative decay
\[ k_{nr} \] Rate constant for non-radiative decay
\[ k_{ISC} \] Rate constant for ISC
\[ k_{RISC} \] Rate constant for RISC
\[ \Phi_R \] Quantum yield for Rubrene
\[ \Phi_{Ir} \] Quantum yield for Ir(ppy)\textsubscript{2}(acac)
\[ n_R \] Number excitons that decayed radiatively on Rubrene
\[ n_{Ir} \] Number excitons that decayed radiatively on Ir(ppy)\textsubscript{2}(acac)
\[ q(V) \] Ratio of charge carrier trapped versus transported through EML
\[ D \] Charge carrier diffusion coefficient
\[ \mu \] Charge carrier mobility
\[ V_{0,eff} \] Effective injection voltage
\[ d \] Emissive layer thickness
\[ L_T \] Average distance a charge travels before reaching a trapping center
\[ n_S \] Singlet exciton population density
\[ n_T \] Triplet exciton population density
\[ n_{T,d} \] Triplet exciton population density on the dopant (Chapter 6)
\[ \gamma \] Fraction of exciton formed on dopant (Chapter 6)
\[ J \] Current density
\[ e \] Elementary charge
\[ W \] Width of recombination zone
\[ k_{SS} \] Rate constant for SSA
\[ k_{ST} \] Rate constant for STA
\[ k_{TT} \] Rate constant for TTA
\[ k_{SP} \] Rate constant for SPA
\[ k_{TP} \] Rate constant for TPA
\[ \phi_{S/T} \] Efficiency of energy transfer to singlet/triplet state (Chapter 6)
\[ \phi_{PF} \] Efficiency of prompt fluorescence
\[ n_p \] Portion of excitons to undergo prompt fluorescence
Chapter 1
Introduction

In this chapter, a brief summary of the major research and commercial milestones for organic light emitting diodes (OLEDs) is presented. The basic operational principles and current status of the technology as well as the motivation for this thesis is discussed.

1.1 Brief overview of OLEDs

Organic light emitting diodes have attracted considerable attention over the last few decades in both academic and commercial settings. An OLED is a device made of thin films of organic material that is capable of emitting light in response to an electric current. The phenomenon of light emission from an organic material in response to electrical excitation was first demonstrated in 1965\(^1\,\text{2}\). However, no practical applications were envisioned for these devices due to high operating voltages on the order of 100V. In 1987, Tang et al. demonstrated the first efficient organic electroluminescent device, which could emit light at voltages below 10V\(^1\). This device was based on a simple heterostructure consisting of a bilayer of organic materials sandwiched between two metal electrodes, as shown in Figure 1a. Ideally, when a bias is applied across the device, four processes occur. Firstly, there is charge carrier injection from the electrodes into the device. Holes are injected from the anode into the highest occupied molecular orbital (HOMO) of one of the organics while electrons are injected from the cathode to the lowest occupied molecular orbital (LUMO) of the other organic material. Next, the charge carriers move through their respective organic layer towards the interface where they form an electron-hole pair known as an exciton. This exciton can then undergo recombination on the electroluminescent material, resulting in the emission of a photon.
Figure 1 a) Simple bilayer OLED structure first introduced by Tang et. al in 1987. b) Complex OLED architecture often used in modern OLED devices.

Over the years, the device architecture has become increasingly complex in order to facilitate these four processes, as shown in Figure 1b. Extra layers can be added to improve charge injection by minimizing energy barriers at interfaces and specific transport layers for holes and electrons are often used. Additionally, electron and hole blocking layers are sometimes added to confine the charge carriers and/or exciton to the emissive layer. Common layers included in modern OLED devices and their functions are summarized in Table 1. Furthermore, modern OLEDs often use a host-dopant system, as proposed by Tang et al. in 1988, in which the emissive material is doped at low concentrations into a bipolar host material. This is done as electroluminescent materials generally have better radiative efficiency at low concentrations.

Table 1 Summary of the typical layers used in modern OLED devices and their functions

<table>
<thead>
<tr>
<th>Layer</th>
<th>Abbreviation</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron/hole transport</td>
<td>EIL or HIL</td>
<td>Used to facilitate charge carrier injection by providing better alignment of electrode work function to the HOMO or LUMO of the organic material; often metal oxides used (e.g. LiF, MoO&lt;sub&gt;3&lt;/sub&gt;)</td>
</tr>
<tr>
<td>Electron/hole transport</td>
<td>ETL or HTL</td>
<td>High electron/hole carrier mobility material to facilitate the movement of injected carriers towards the EML; Similar electron mobility in ETL as hole mobility in HTL to balance carriers in EML</td>
</tr>
</tbody>
</table>
It’s clear that in order to create efficient OLED devices, many factors must be considered, such as carrier mobility, energy barriers and intrinsic properties of the emitter material used. An important metric used to gauge these factors is the external quantum efficiency (EQE), which is the number of photons emitted per pair of charge carrier injected into the device. The EQE is also given by:

\[
\eta_{ex} = \eta_{b}\chi \phi_{eff} \eta_{out} = \eta_{int} \eta_{out}
\]

(1.1)

where \(\eta_{b}\) is the charge balance factor, \(\chi\) is the fraction of excitons that are captured by the emitter molecules, \(\phi_{eff}\) is the effective radiative efficiency of the emitter and \(\eta_{out}\) is outcoupling efficiency. The effective radiative efficiency of the emitter is an intrinsic property of the emitter material used. It is a combination of the spin-orbital factor and the photoluminescence quantum yield of a molecule. The outcoupling efficiency is the fraction of photons emitted that escape the device and can be detected. Reflections at the layer interface can trap emitted light and reduce the perceived efficiency. The internal quantum efficiency (IQE), \(\eta_{int}\), is the efficiency in the absence of optical effects.

Another significant development in OLED research is the use of phosphorescent emitters, which was first used by Forrest et al.\(^4\) in 1998. Phosphorescent dopants can harvest all the excitons formed through electroluminescence while fluorescent emitters are generally limited to 25% due to spin statistics (\(\phi_{eff} \leq 0.25\)). The exact mechanism for this as well as other emitter types will be discussed in more detail in Chapter 2. Therefore, phosphorescent-based OLEDs can potentially achieve 100% IQE\(^5\). Currently, the best performing red, green and blue OLEDs utilize phosphorescent emitters and are summarized in Table 2.
Table 2 Summary of the current state-of-the-art phosphorescent OLEDs reported in literature

<table>
<thead>
<tr>
<th>Colour</th>
<th>Peak wavelength (nm)</th>
<th>Power Efficiency (lm/W)</th>
<th>EQE (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue</td>
<td>473</td>
<td>66</td>
<td>30.3</td>
<td>6</td>
</tr>
<tr>
<td>Green</td>
<td>524</td>
<td>142.5</td>
<td>32.3</td>
<td>7</td>
</tr>
<tr>
<td>Red</td>
<td>605</td>
<td>66.2</td>
<td>35.6</td>
<td>8</td>
</tr>
</tbody>
</table>

Extensive research in the field has yielded high efficiency commercially viable devices through careful material design and synthesis\(^4\)\(^-\)\(^11\) as well as device architecture optimization\(^12\)\(^-\)\(^14\). This has led to the successful commercialization of OLEDs, particularly for small-area flat panel displays. The first commercially available OLED display was produced by Pioneer in the late 1990s and was used for car audio systems, as shown in Figure 2\(^15\). Now OLED displays can be found in most modern smart phones due to their high efficiency and contrast ratio.

Figure 2 Photographs showing the evolution of commercial OLED displays: a) The first commercially available OLED display produced by Pioneer in 1997; a monochrome display based on fluorescent small molecule organic material and fabricated by vacuum deposition. b) Samsung 55” curved OLED TV released in 2013. c) prototype of LG’s 6-inch flexible OLED display

However, the more stringent requirements needed for general lighting has limited the commercial availability of OLED-based lighting. Lighting requires much higher brightness levels
 (>1,000 cd/m\(^2\)) than display applications (~100 cd/m\(^2\)), where OLED devices are currently not as efficient. The first white OLED was reported by Kido et al. in 1994\(^{16}\). Utilizing three different fluorescent emitters, this device was able to achieve a broadband emission spectrum, as shown in Figure 3, and a power efficiency of 0.83 lm/W. Presently, commercial OLED lighting panels are available but are very costly with efficiencies that are just beginning to compete with compact fluorescent light bulbs. In research, the first breakthrough white OLED with power efficiencies comparable to fluorescent light sources was reported by Karl Leo in 2009\(^{17}\). Without outcoupling techniques, a power efficiency of 90 lm/W was achieved at 1,000 cd/m\(^2\) and 74 lm/W at 5000 cd/m\(^2\). Now, many white OLEDs with power efficiencies greater than 100 lm/W have been reported in literature\(^{18–20}\). However, there are further complications associated with the colour quality and device lifetime of white OLEDs, as will be discussed in Chapter 2. Further research is needed for OLEDs to be a competitive option for general lighting, but the current state of the field indicates that OLEDs have great potential to help reduce our carbon footprint. In addition, the low processing temperature required for organic materials gives rise to the potential of low-cost manufacturing processes and flexible OLEDs for unique lighting form factors and wearable electronics. When mature, in addition to reducing energy consumption, OLED lighting can offer warm diffuse lighting, large area manufacturing and unique form factors\(^{21}\).

**Figure 3** Electroluminescent spectrum and device structure with molecular structure of the three emitter molecules for first reported white OLED by Kido et al. in 1994\(^{16}\)
1.2 Motivation

Despite extensive research in the area, there are still major challenges that prevent the use of OLEDs for solid state lighting. As mentioned previously, often a trade-off between high efficiency and colour quality is observed. Moreover, increasingly complex device architecture is generally required to achieve high efficiency, which complicates the manufacturing process for commercialization. In addition to requiring extra layers for charge carrier and exciton confinement, multiple emitter molecules are needed in the host-guest system as organic emitters commonly have a narrow emission band. This necessitates the use of a combination of emitters in order to achieve a broadband emission for high quality white light. Energy transfer mechanisms, which will be described in detail in Section 2.4, are thus important in order to distribute excitons to the different color emitters. The distribution of excitons amongst the different emitters can change at different driving voltages, thus causing colour shifting and affecting degrading the colour of the light. Although major breakthroughs have been achieved over the years in device efficiency, much of the device physics and mechanisms causing poor performance is still unknown.

The purpose of this thesis is to advance white OLEDs towards practical application in lighting. The focus is on designing practical device structures that can better harvest excitons. This work begins by trying to gain a better understanding of excitons dynamics within complicated multi-dopant devices. Exciton energy transfer mechanisms are studied in a simpler two-dopant system and simple model for quantifying the processes using straightforward electroluminescence spectra is developed. The next focus was to design a white OLED device that is capable of meeting both high efficiency and colour quality at practical brightness levels, while maintaining a simple device architecture. Studies on how different layers affect the colour stability were conducted. Finally, the last criteria for lighting is addressed; device lifetime. As blue emitters have inherently short lifetimes and present the limiting factor in white OLEDs, the focus was shifted to designing a long lifetime blue device.

1.3 Outline

This thesis consists of seven chapters. This chapter presented a quick introduction to OLEDs and its history. Chapter 2 provides a more detailed background on OLEDs, which include
types of emitters, energy transfer mechanisms and performance evaluation for white OLEDs. Chapter 3 discusses the experimental methods involved such as the device design, fabrication and characterization. Chapter 4 details the analysis of energy transfer mechanisms in multi-dopant OLEDs. A simple white OLED that meets the basic efficiency and colour quality requirements for lighting is discussed in Chapter 5, with an emphasis on studying the colour stability in the device. Chapter 6 presents a brief discussion of factors affecting device lifetime in OLEDs and then demonstrates a concept to improve the lifetime in blue OLEDs. Chapter 7 is the summary of the thesis and proposed future work.
Chapter 2
Theoretical background

Chapter 2 will present all the necessary theoretical background on OLED device physics. This includes excitonic differences between organic and inorganic semiconductors, the photophysics of organic molecules, energy transfer mechanisms and performance metrics for white OLEDs.

2.1 Organic vs. inorganic semiconductors

The vastly different electrical properties observed in organic and inorganic semiconductors originates from the difference in bonding. In solid-state, traditional inorganic semiconductors, such as silicon and gallium arsenide, are highly crystalline structures comprised of atoms held together by a strong network of primary bonds. In contrast, organic semiconductors are made of molecules bonded together by weak secondary bonds, namely van der Waals interactions. Consequently, inorganic semiconductors typically have high dielectric constants allowing charges to be effectively screened from one another in the material while organic materials have low dielectric constant. This results in different types of excitons that can be formed in the two materials. An exciton is a bound excited state of an electron and hole pair. In inorganic materials, a large separation distance (40-100Å) exists between the electron and hole as the material is able to effective screen the charges. Excitons thus have low binding energy and are generally easily disassociated at room temperature. This type of excitons is known as a Wannier-Mott exciton. Small-radius excitons where the electron and hole exist on the same or on adjacent molecules is known as a Frenkel or charge-transfer exciton, respectively. These are commonly found in organic semiconductors and large binding energies are associated with them. The different types of excitons are illustrated in Figure 4. The material structure in solid state also affects the charge carrier mobility. Organic semiconducting materials are amorphous resulting in a distribution of energy levels within the material. This leads to small energy level differences from one molecule to the next and the charge carrier are highly localized due to the disorder. Carriers are thus transported by an inter-molecular thermally-activated hopping mechanism where they must overcome a small energy barrier from one molecule to another. This leads to lower hole and electron mobility in organic materials compared to inorganic semiconductors, where intra-molecular band transport occurs between atoms.
There are two types of electroluminescent materials commonly used in OLEDs; they are fluorescent and phosphorescent molecules. The two materials differ in the type of exciton that is capable of efficient radiative decay. Excitons exist in either a singlet state, where the unpaired electron in the HOMO and LUMO have antiparallel spin, or a triplet state, where they have parallel spin. In electroluminescence, singlet and triplet excitons are formed in a 1:3 ratio. The radiative decay of singlet state excitons to the ground state, known as fluorescence, is quantum mechanically allowed and occurs at fast timescales. In contrast, the radiative decay of a triplet state to the ground state, called phosphorescence, is not kinetically favourable and does not occur readily in most materials. This process requires a spin flip so that the resulting ground state electron pair has antiparallel spin. Phosphorescent materials, in which this process can occur efficiently, exhibit strong spin-orbital coupling, typically due to the present of some heavy metal atom, such as platinum and iridium\textsuperscript{4,24}. The difference between the two processes as well as the chemical structure of commonly used fluorescent and phosphorescent organic molecules is shown in Figure 5.

**Figure 4** Schematic of the different types of excitons: a) Wannier-Mott exciton b) Charge-transfer exciton, and c) Frenkel exciton

### 2.2 Radiative decay mechanisms and types of emitters

There are two types of electroluminescent materials commonly used in OLEDs; they are fluorescent and phosphorescent molecules. The two materials differ in the type of exciton that is capable of efficient radiative decay. Excitons exist in either a singlet state, where the unpaired electron in the HOMO and LUMO have antiparallel spin, or a triplet state, where they have parallel spin. In electroluminescence, singlet and triplet excitons are formed in a 1:3 ratio. The radiative decay of singlet state excitons to the ground state, known as fluorescence, is quantum mechanically allowed and occurs at fast timescales. In contrast, the radiative decay of a triplet state to the ground state, called phosphorescence, is not kinetically favourable and does not occur readily in most materials. This process requires a spin flip so that the resulting ground state electron pair has antiparallel spin. Phosphorescent materials, in which this process can occur efficiently, exhibit strong spin-orbital coupling, typically due to the present of some heavy metal atom, such as platinum and iridium\textsuperscript{4,24}. The difference between the two processes as well as the chemical structure of commonly used fluorescent and phosphorescent organic molecules is shown in Figure 5.
Figure 5 Illustrating the fluorescence and phosphorescence decay mechanisms and the chemical structure of a commonly used fluorescent emitter, Tris(8-hydroxyquinolinato)aluminium (Alq₃), and phosphorescent emitter, Bis(2-phenylpyridine)(acetylacetonate)iridium(III) (Ir(ppy)₂(acac)).

In all electroluminescent materials, both fluorescence and phosphorescence could technically occur. However, what is practically observed depends on the timescale at which the two processes occur in a material. A faster decay mechanism can better compete with alternate mechanisms and will thus be the dominant decay pathway. Materials that are considered “fluorescent” generally possess weak spin-orbital interaction and so the radiative decay of triplet excitons is unlikely. Phosphorescence could occur given long enough timescales but generally the triplet state excitons will decay through other non-radiative mechanisms beforehand. For this reason, fluorescent materials can effectively only harvest singlet excitons. This limits the spin-orbital factor and thus the EQE of fluorescent-based OLEDs to 25%. In contrast, phosphorescent materials can theoretically achieve 100% IQE. The strong spin-orbital coupling in phosphorescent materials not only allows for the radiative decay of triplet state excitons but also enables excitons to transition between the singlet and triplet states. This process, known as intersystem crossing, allows singlet state excitons to be converted to the lower energy triplet state where they can decay radiatively. Generally, this process is fast enough to convert all excitons to the triplet state. Thus, phosphorescent emitters are capable of harvesting all excitons created through electroluminescence.
Recently a new type of decay mechanism has emerged known as thermally activated delayed fluorescence (TADF). This mechanism is efficient in molecules where the HOMO and LUMO are localized on separate constitutes. This is generally accomplished by separating the electron donating and electron-accepting group in a molecule. The localization of the HOMO and LUMO results in a small energy level difference between the triplet and singlet states. Using thermal energy, even at room temperature, triplet state excitons can be efficiently up-converted to the singlet state, where they decay radiatively through fluorescence, as shown in Figure 6. As TADF emitters can harvest both singlet and triplet excitons, similar to phosphorescent emitters, they can theoretically achieve 100% IQE. High EQEs have been achieved using TADF molecules for blue, green and red OLEDs.

Figure 6 TADF decay mechanism and the chemical structure of blue TADF emitter, 10,10’-(4,4’-Sulfonylbis(4,1-phenylene))bis(9,9-dimethyl-9,10-dihydroacridine) (DMAC-DPS). The electron donating and accepting moieties of the structure is labelled and the HOMO and LUMO energy level localization is shown.

2.3 Non-radiative decay mechanisms and efficiency roll-off

Excitons can also undergo many non-radiative decay mechanisms, where the energy that would have been released in the form of a photon is instead lost through other forms, such as heat. These mechanisms compete with the radiative pathways and generally become more significant at high brightness levels, thus resulting in lower efficiencies. The phenomenon of decreasing efficiency at high luminance is known as efficiency roll-off. Two significant non-emissive decay
mechanisms that contribute to this problem are triplet-triplet annihilation (TTA) and exciton-polaron annihilation (EPA)\textsuperscript{32}.

Once an exciton is formed, this quasiparticle is capable of moving from one molecule to another through energy transfer processes. These processes will be further explored in section 2.3.1. The exciton can migrate through the OLED device and interact with other species. In TTA, two adjacent triplet excitons can interact resulting in a ground state molecule and a singlet state exciton. This process can be beneficial in fluorescent materials as some non-emissive triplets are converted into singlets, which can then be harvested. However, TTA can be greatly detrimental in phosphorescent OLEDs, as two emissive excitons are converted into a single particle that can emit light. It becomes particularly significant at high brightness levels when a high density of triplet states is created, thus making TTA more probable.

In EPA, a trapped or free charge carrier is responsible for quenching the exciton. This can occur for both singlet and triplet excitons. However, this process tends to occur more frequently with triplet states due to their long lifetimes. The longer timescales required for phosphorescence to occur makes it more likely for triplet excitons to undergo other non-desirable pathways. This is why efficiency roll-off tends to be more prominent in phosphorescent-based OLEDs.

2.4 Energy transfer mechanisms

Energy transfer processes allow excitons to travel from one molecule to another. This can be accomplished through two main processes; Förster energy transfer and Dexter energy transfer. Both processes involve the non-radiative transfer of an exciton from one molecule, called the donor, to another, called the acceptor. These processes also compete with the emissive and non-emissive pathways.

Förster energy transfer is due to dipole-dipole interaction\textsuperscript{33}. The non-emissive relaxation of an exciton into the ground state induces the formation of an exciton on a neighbouring molecule. This is considered a long-range process, which can range up to 100Å for some materials. The Förster radius, $R_0$, is used to characterize the distance at which Förster energy transfer occurs efficiently. $R_0$ is the donor-acceptor distance at which Förster transfer occurs with 50% efficiency. This parameter depends on the quantum yield of the donor and the integral overlap between the
donor emission spectrum and the acceptor absorption spectrum. The rate constant, $k_F$, and efficiency, $\phi_F$, of Förster energy transfer is often given in terms of $R_0^{34}$:

$$k_F = \frac{1}{\tau} \left(\frac{R_0}{R}\right)^6 = k \left(\frac{R_0}{R}\right)^6$$  

(2.1)

$$\phi_F = \frac{k_F}{k_F + k} = \frac{1}{1 + \left(\frac{R}{R_0}\right)^6}$$  

(2.2)

where $k = 1/\tau$ is the decay rate constant of the donor in the absence of energy transfer and $R$ is the donor-acceptor separation distance. Förster energy transfers is predominately observed for singlet excitons in fluorescent materials as the electronic transition of triplet excitons to the ground state is highly unlikely in these materials. Triplet excitons will generally be transferred through Dexter energy transfer.

Dexter energy transfer is through electron exchange between the donor and acceptor. This requires significant wavefunction orbital overlap between the molecules and so Dexter energy transfer often occurs over shorter distances than Förster transfer. The rate constant for Dexter energy transfer is exponentially related to the donor-acceptor separation$^{33}$:

$$k_D = A \exp\left(-\frac{2R}{L}\right)$$  

(2.3)

where $A$ is a constant related to the spectral overlap between the donor and acceptor molecules and $L$ is the sum of their effective van der Waals radii. This process can occur for both singlet and triplet excitons in fluorescent and phosphorescent materials.

It is also possible for excitons to be transferred through a radiative process. In this case, the exciton decays radiatively, either through fluorescence or phosphorescence. The resulting photon is reabsorbed by a nearby molecule, thus exciting the formation of a new exciton. However, this process is not significant in OLED systems. The thin layers in OLEDs makes it unlikely for emitted photons to be absorbed by another molecule in the device. Figure 7 illustrates the three possible energy transfer mechanisms.
Excitons are able to move through an organic material through successive energy transfer processes. Their movement is generally described as a “random walk” that’s driven by a gradient in the exciton concentration within a material or by an exciton energy difference between two organic materials. The diffusion of excitons can generally be modelled using Frick’s 2nd law\textsuperscript{35}.

2.5 White OLEDs requirements for lighting

There are three main criteria that must be satisfied for OLEDs to become a viable lighting option. They are high efficiency, colour quality and device lifetime. This section will outline the metrics for quantifying these standards and then conclude with an overview of the current lighting market.

2.5.1 Efficiency

As mentioned previous, the EQE is typically used to evaluate OLED performance. However, for lighting purposes, the power or luminous efficiency is more appropriate, and it is already a standard measurement in the industry. This quantity measures the amount of visible light emitted to the power inputted in lumens per Watt (lm/W). The amount of light is adjusted to reflect the sensitivity of the human eye, which peaks at 555nm (green light) and has no sensitivity for wavelengths outside visible light. The standard photopic luminosity function, as defined by the
Commission Internationale de L’Éclairage (CIE), for the human eye is shown in Figure 8. The EQE is not adjusted for human eye and higher efficiencies can be recorded for light emitted outside the visible spectrum.

![Photo of a diagram](image)

**Figure 8** a) CIE photopic luminosity function for the human eye b) Typical power efficiency vs. luminance curve for an OLED

It’s also important to consider the power efficiency at brightness levels high enough for lighting applications. Similar to the EQE, the power efficiency tends to decrease when biased at higher voltages and hence at high luminance. Generally, a luminance of at least 1,000 cd/m² is needed for lighting and subsequent performance metrics will be compared at this level.

### 2.5.2 Colour Quality

There are three quantities that will be discussed in terms of colour quality; they are the CIE coordinates, the correlated colour temperature (CCT), and the colour rendering index (CRI).

The chromaticity of the light can be defined using the colour space defined by the CIE in 1931, shown in Figure 9. The CIE coordinates of \((0.33, 0.33)\) on this colour space is perceived as “colourless” white light. However, the coordinates \((0.448, 0.408)\) marks the chromaticity of tungsten incandescent lamps, which are widely accepted being the most comfortable artificial light sources\(^{35}\). For this reason, many light sources attempt to mimic this warm white light.
Figure 9 CIE 1931 chromaticity colour space with the Planckian locus showing the colour temperature associated with blackbody radiators. Lines normal to the Planckian locus are drawn to illustrate how the CCT is determined for colour chromaticity close to blackbody radiators.

It is also common to express the chromaticity of light using its colour temperature. As a blackbody radiator emits light of a specific chromaticity depending the temperature at which its heated, the absolute temperature can be used to characterize the colour of other light sources. The colour temperature expresses the chromaticity of light by the temperature in Kelvin that a blackbody radiator must be heated to in order to produce light of the same chromaticity. The Planckian locus is achieved by plotting the chromaticity points for a series of colour temperatures of a blackbody radiator, as illustrated on the CIE colour space in Figure 9. Since blackbody radiators cannot achieve all possible colours, the correlated colour temperature is used. The CCT is the colour temperature of a blackbody radiator that is closest to the radiation. It can be defined by drawing a line from the point of interest that crosses the Planckian locus at a right angle. Only chromaticity points within 0.05 units from the Planckian locus can be associated with a CCT. A lower CCT, such as tungsten incandescent lamps which have a CCT of 2856K, is considered “warm” white light, while more blue-ish light with CCT of 4000-5000K is described as “cold” white light.
Visible radiation composed on narrow emissions of blue, green and red light can be perceived by a human observer as a similar white light to a broad emission spectrum covering all visible wavelengths. However, objects will be illuminated differently by the two sources since the colour of objects depends on the wavelengths of the light source that it reflects. The CRI is used to characterize the effect of a light source on the colour of objects it illuminates. It measures the ability of light to accurately render the colour of an object in comparison to a natural light source. Black body radiators, such as incandescent lights, which emit a broad spectrum that covers the entire visible light spectrum, have a maximum CRI of 100 and are used as the reference source. The CRI is calculated from the arithmetic mean of eight special colour indices, $R_i$. The special indices are based on eight colour samples. The colour coordinates of the samples under the light source of interest and the reference light source is measured and the difference between the two points in the color space, $\Delta E_i$, is calculated. The specific colour index for each sample can then be computed by $R_i = 100 - 4.6\Delta E_i$. If the spectral reflectance of the colour samples and the spectral distribution of the reference source is known, then only the spectral distribution of the test source is needed to calculate the CRI $^37$.

Another factor that should be considered is the colour stability of the white light. Colour shifting is often observed in white OLEDs as the distribution of excitons among the different emitters can change with increasing bias (and brightness). This can lead to a change in CRI and CIE coordinates. Generally, a CIE coordinate change ($\Delta x, \Delta y$) of less than 0.005-0.01 is considered acceptable$^38$. An extreme case of colour shifting is shown in Figure 10 where at ~8V white light is observed but only blue or red light is emitted at high and low voltages, respectively.

![Figure 10](image_url)  
**Figure 10** Spectral distribution of a white OLED showing colour shifting with increasing voltage
2.5.3 Operational Lifetime

This section focuses on the current state of OLED device lifetime compared to commercially available lighting options and how the device lifetime for light sources is determined. Presently, the lifetime of white OLEDs is very short compared to other lighting options. This is primarily due to the short lifetime of blue organic emitters, particular phosphorescent emitters\textsuperscript{39}. The potential causes and mechanisms leading to shorten lifetime in blue materials in particular will be discussed in further detail in Chapter 6. The lifetime of incandescent, fluorescent and LED light sources is on the order of $10^2$-$10^3$ hours, $10^3$-$10^4$ hours, and $10^4$-$10^5$ hours, respectively\textsuperscript{40}. Comparing the lifetimes to that of monochrome OLEDs from Figure 11, it’s clear that the red and green emitters are able to meet the current industry standards.

The lifetime of conventional lights is measured using the Average Rate Life (ARL), which is the time for 50\% of a test batch to fail. This is because light sources such as incandescent and fluorescent light bulbs fail through predictable modes that lead to burnout\textsuperscript{41}. Conversely, solid-state light lights will not burnout but instead tend to dim over time. For this reason, the lifetime of LED and OLED light sources are determined by monitoring the luminance, at constant applied current, over time. The time required to reach one-half of the initial luminance is termed the half-life, $t_{50}$ and it is used to gauge the lifetime of the light source. Other metrics such as the time to reach 95\% or 80\% of the initial luminance are also sometimes reported but the half-life will be used in this work since it is most commonly reported in literature. The steady-state luminance decay of an OLED can generally by modelled by the stretch exponential function\textsuperscript{42}:

$$L = L_0 \exp \left( \frac{t}{\tau} \right)^\beta$$ \hspace{1cm} (2.4)

where $L_0$ is the initial luminance, $\tau$ is the decay time constant and $\beta$ is the stretch factor. By fitting the luminance versus time data, the $t_{50}$ can be extracted by $t_{50} = (0.693)^{1/\beta} \cdot \tau$. The decay will occur more rapidly when the device is biased to a higher initial brightness level, as shown in Figure 11. The standard is to monitor the luminance decay for an initial luminance of $1,000\text{cd/m}^2$. 
Figure 11  a) Device lifetime for different colour and emitter types for OLEDs$^{43-45}$ b) Typical luminance decay over time for an OLED device at different initial luminance.
Chapter 3
Experimental methods

This chapter outlines the device fabrication and characterization process as well as provides a detail list of the materials and general device structures used in experiments for this thesis.

3.1 Device fabrication

All devices were fabricated by thermal evaporation in either the Kurt J. Lesker Cluster tool or the SKY PVD-200 system, both shown in Figure 12. The experiments studying exciton energy transfer mechanisms discussed in Chapter 4 were conducted using the Cluster tool while subsequent experiments discussed in Chapters 5 and 6 were completed on the newer Sky system. Both systems have different chambers for metal and organic deposition. The organic chambers operate at a base pressure of ~10^{-6} Pa while the metal chambers are at ~10^{-5} Pa. The metal chamber is generally at higher pressure as it is exposed to atmosphere daily. Aluminum was used as the cathode for all the devices and the Al crucible must be refilled after each deposition.

![Figure 12](image)

**Figure 12** a) Kurt J. Lesker cluster tool system used to fabricate OLED devices for studying exciton energy transfer mechanisms b) Sky PVD-200 system used for white OLED and lifetime experiments

The devices were fabricated on glass substrates that have been pre-patterned with ITO strips, purchased from Zhuhai Kaivo Optoelectronic Technology Co., Ltd.. Prior to use, the substrate is cleaned using Alconox soap, acetone and methanol, with sonication in each solvent. The sample is then dried using N\textsubscript{2} gas and subjected to ultraviolet (UV) ozone treatment for 15
minutes before being mounted onto a substrate holder and loaded into the vacuum system. Thin film layers are deposited onto the sample by carefully heating the organic material in boron nitride (BN) crucibles using electrical current until it sublimes. When the vapours hit the cooler substrate, they condense back into solid state forming a uniform thin film. The thicknesses and rate of deposition is monitored using a quartz crystal microbalance (QCM) that was calibrated using profilometry (KLA-Tencor P16+). The target rate of deposition for organic materials was limited between 0.5-1.0 Å/s. The injection layers require higher temperatures for deposition and were thermally evaporated from alumina-coated boats.

A total of 32 OLED devices can be fabricated on a single 5cm x 5cm substrate, each with an active area of 2.2 mm². Up to eight different device structures can be created on a single substrate by using the 2x4 shadow mask shown in Figure 13. A mask with any one or more of the eight openings on the mask covered can be used to prevent deposition on that area. This allows very controlled experiments to be conducted where only small changes are made between devices on the same substrate so that the performance of the devices can be compared directly. The general layout of a substrate with devices deposited on it is pictured in Figure 13.

**Figure 13** a) 2x4 shadow mask with top four positions open and the bottom four closed, thus prevent deposition on the bottom half of the substrate b) substrate in substrate holder which would sit on top of the shadow mask. Black box shows where organics would be deposited if the mask from part a) were used.
3.2 Organic materials and device structure

All organic materials were purchased from Luminescence Technology Corporation and used as received with the exception of \( \text{Ir(fpt)}_3 \), which was synthesized and sublimated by researchers from Peking University. The details of the synthesis can be found in reference 46. The Al pellets for the cathode and the injection layers were purchased from Sigma-Aldrich. A summary of the materials used, their purpose, and chemical structures is provided in Table 3.

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Abbreviation</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,4'-Bis(carbazol-9-yl)biphenyl</td>
<td>CBP</td>
<td>HTM/Host</td>
</tr>
<tr>
<td>2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole)</td>
<td>TPBi</td>
<td>ETL</td>
</tr>
<tr>
<td>Bis(2-phenylpyridine)(acetylacetonate)iridium(III)</td>
<td>Ir(ppy)$_2$(acac)</td>
<td>Green phosphorescent emitter</td>
</tr>
<tr>
<td>5,6,11,12-Tetraphenyl-9H-pyrene</td>
<td>Rubrene</td>
<td>Yellow fluorescent emitter</td>
</tr>
<tr>
<td>Bis[2-(diphenylphosphino)phenyl] ether oxide</td>
<td>DPEPO</td>
<td>EBL</td>
</tr>
<tr>
<td>1,3-Bis(N-carbazolyl)benzene</td>
<td>mCP</td>
<td>HTM/EBM</td>
</tr>
<tr>
<td>10,10'-(4,4'-Sulfonylbis(4,1-phenylene))bis(9,9-dimethyl-9,10-dihydroacridine)</td>
<td>DMAC-DPS</td>
<td>Blue TADF emitter</td>
</tr>
<tr>
<td>3,3',3''-[Borylidynetris(2,4,6-trimethyl-3,1-phenylene)]tris[pyridine]</td>
<td>3TPYMB</td>
<td>ETM</td>
</tr>
<tr>
<td>tris(5-(4-fluorophenyl)-1,3-dimethyl-1H-1,2,4-triazolyl)iridium</td>
<td>Ir(fdpt)$_3$</td>
<td>Blue phosphorescent emitter</td>
</tr>
<tr>
<td>Bis(2-methylbenzo[f,h]quinoxaline)(acetylacetonate)iridium(III)</td>
<td>Ir(MDQ)$_2$(acac)</td>
<td>Red phosphorescent emitter</td>
</tr>
<tr>
<td>Molybdenum(VI) oxide</td>
<td>MoO$_3$</td>
<td>HIL</td>
</tr>
<tr>
<td>Lithium Fluoride</td>
<td>LiF</td>
<td>EIL</td>
</tr>
</tbody>
</table>

Most the OLED structure presented in this thesis will consist of the typical structure: ITO/MoO$_3$(1nm)/HTL/EML/ETL/LiF(1nm)/Al(100nm). The transport and emission layer thicknesses are optimized for the specific device. A typical hole and electron transport material that’s typically used together is CBP and TPBi, respectively, because they provide a good balance of hole and electron mobility. The green phosphorescent standard device use for baseline and on
which many of the devices are based on is: ITO/MoO$_3$(1nm)/CBP(35nm)/CBP:7wt.% Ir(ppy)$_2$(acac) (15nm)/TPBi(60nm)/LiF(1nm)/Al(100nm). Its energy diagram is shown in Figure 14.

![Figure 14](image)

**Figure 14** Schematic a) of device structure and b) energy diagram for standard green OLED

Single carrier devices were also fabricated for some experiments and were used to study the effect of dopants on the charge transport properties. Single carrier devices are designed with a large injection barrier for one type of charge carrier (electron or hole) to impede its injection into the device, thus making the other carrier type the dominant charge carrier. The most basic single carrier device structure consists of the organic layer to be studied sandwiched between two electrodes. Additional interface layers can be added to improve carrier injection on one end and to introduce an energy barrier to prevent carrier injection at the opposite electrode. The device structure used for hole-only devices is ITO/MoO$_3$(1nm)/CBP(10nm)/X(100nm)/CBP(10nm)/MoO$_3$(1nm)/Al, and the structure for electron-only devices is ITO/TPBi(10nm)/X(100nm)/TPBi(10nm)/LiF(1nm)/Al, where X is the organic layer to be studied. CBP is a hole transport material and TPBi is an electron transport material. They were added to help facilitate the injection and transport of holes or electrons, respectively.

### 3.3 Device Characterization

Following fabrication, the current density-voltage-luminance (JVL) characteristics of OLED devices were measured in ambient conditions using the HP4140B picoammeter and a Minolta LS110 Luminance meter. The EQE are measured using an integrating sphere and a silicon photodiode with NIST traceable calibration. The EL spectrum was capture using the Ocean Optics
USB4000 spectrometer. Measurements were taken on multiple devices of the same type to ensure accuracy of results. The general measurement setup is shown in Figure 15.

![Setup for IVL measurement showing the Minolta LS-110 Luminance Meter over the sample](image)

**Figure 15** Setup for IVL measurement showing the Minolta LS-110 Luminance Meter over the sample

Lifetime measurements were conducted under an inert atmosphere of nitrogen using a glovebox attached to the Sky System, as shown in Figure 16. This ensures that the degradation in luminance of the device was due to electrical excitation and exciton dynamics during operation and not caused by extrinsic factors such as moisture exposure leading to dark-spot generation. The change in the voltage needed to maintain a constant current in the device is monitored over time using the Keithley 2400 Source Meter. The current is set to achieve an initial luminance of 1,000 cd/m². The change in luminance over time is monitored using a Si diode and the Keithley 2410 Source Meter. The setup is covered with a blackout curtain to prevent other light sources from contributing to the luminance measurement.

Photoluminescence (PL) measurements were done in atmosphere. Thin film samples were fabricated in the Cluster Tool on 1x1 cm² quartz substrates that were cleaned using the same procedure as outlined for the ITO-patterned glass substrates.
Figure 16 Picture showing the glovebox attached to the sky system
Chapter 4
Quantifying inter-dopant exciton processes in organic light emitting diodes

This chapter will present a simple method, based on electroluminescence spectra, to study and quantify the energy transfer mechanisms in a two dopant (triplet-singlet) system. Through a combination of experimental spectra obtained from a collection of donor-acceptor separations and theoretical simulations of spectral variations, key physical parameters such as the Dexter van der Waals radii and the Förster radius can be quantified. The content of this chapter was published in J. Phys. Chem. C, 121, 6, 3304-3309 (2017). Other contributing authors for this paper were Dr. Grayson Ingram (G.I.) and Professor Zheng-Hong Lu (Z.H.L). All the OLED devices were fabricated and characterized by me and I developed the model to study the energy transfer mechanisms. G.I. contributed to the initial design of the experiments and provided feedback on the model. Z.H.L. supervised the project and the data analysis.

4.1 Introduction

Organic emitters commonly have a narrow emission band, so that a combination of emitters is needed in order to achieve a broadband emission for high quality white light. Energy transfer mechanisms are thus important in order to distribute excitons to the different color emitters. Additionally, white OLEDs still struggle with maintaining high efficiencies at the high brightness levels needed for lighting. A better understanding of excitons dynamics within complicated multi-dopant devices is needed for the design of high efficiency white OLEDs. This work presents a method for quantifying energy transfer in a two-dopant system consisting of a green phosphorescent material and a yellow fluorescent emitter. This is known as a sensitized fluorescence system, where the phosphor can transfer triplet excitons into the singlet state of the fluorophore, thereby increasing the efficiency of fluorescence.

Several studies have investigated energy transfer processes in OLEDs by observing changes in the intensity of electroluminescent (EL) spectra. These studies only present qualitative information on how a factor affects energy transfer efficiency and it is often limited to studying only either Dexter or Förster transfer. Additionally, relative energy transfer efficiency are often deduced based on spectral overlap and triplet/singlet energy levels of the donor and acceptor materials. A large overlap between the emission spectrum of the donor and the absorption
The spectrum of the acceptor is needed to facilitate energy transfer. Another method involving time-correlated single photon counting (TCSPC) technique has been used on doped organic films in order to measure the energy transfer efficiency based on the transient decay time of the donor emission\textsuperscript{54}. This method does not distinguish between Förster and Dexter energy transfer. In this work, we present a method that can quantify the amount of Förster and Dexter energy transfer occurring between the two dopant in an OLED as well as study the behavior of the two competing processes with changing dopant concentrations.

4.2 Theory

4.2.1 Sensitized fluorescence system

In sensitized fluorescence, a fluorescent material is used as the emitter while a phosphorescent material serves as the second dopant. This type of system was first demonstrated in OLEDs by Baldo et al. in 2000\textsuperscript{47,48}. In addition to capturing more excitons, the phosphorescent dopant acts as a sensitizer by helping the fluorescent emitter harvest triplet excitons through Förster energy transfer. As the electronic transition of triplet state excitons to the ground state is allowed in phosphorescent materials, excitons can be transferred from the triplet state of the sensitizer to the singlet state of the neighbouring fluorophore.

In order for this process to occur efficiently, optimal spatial proximity between emitter and sensitizer molecules is needed. Dexter energy transfer between the sensitizer and emitter is considered a lost mechanism as excitons maintain their spin multiplicity. Triplet excitons transferred via Dexter will remain triplet state excitons on the fluorophore where its radiative decay is not permitted. As Dexter transfer is most efficient over short ranges, it’s important to keep emitter and sensitizer molecules at a distance from one another. However, they must still exist within the Förster radius for the pair of materials to ensure efficient Förster transfer. There should theoretically be some optimal spatial separation between the materials which best promotes sensitized fluorescence. This separation distance can be controlled through the dopant concentrations of the two materials. Figure 17 illustrates the ideal processes in sensitized fluorescence, as well as the lost mechanisms.
In the following experiments, Ir(ppy)$_2$(acac) is used as the sensitizer and a yellow fluorescent emitter, Rubrene, in a CBP host. Ir(ppy)$_2$(acac) was chosen as sensitizer for its high photoluminescence quantum efficiency ($\Phi_{PL} = 0.94$) and its excellent exciton trapping ability demonstrated in CBP\textsuperscript{47}. As significant overlap between the emitter absorption spectrum and the sensitizer emission spectrum is also needed to promote Förster transfer, the fluorescent emitter was chosen to satisfy this criterion. The energy diagram for the sensitized OLED is shown in Figure 18. It differs from the standard devices, discussed previously, only by the addition of Rubrene in the emission layer.

\textbf{Figure 17} Schematic illustrating possible energy transfer processes in sensitized fluorescent systems (Dashed lines indicated Dexter transfer, solid lines are Förster transfer)\textsuperscript{48}
4.2.2 Model for quantifying energy transfer mechanisms

It is desirable for the higher energy dopant to capture all the excitons first in order to allow subsequent energy transfer to lower energy emitters. Generally, excitons will not transfer from a lower energy dopant to a higher energy one. The concentration of Rubrene is varied in order to change the average distance between Rubrene and Ir(ppy)$_2$(acac) molecules, thus affecting the energy transfer efficiency between the two materials. The efficiency of either energy transfer process, $\phi_j$, can be calculated as the rate constant of that process over the sum of the rate constants for all competing processes. This can be expressed as:

$$\phi_j = \frac{k_j}{\sum_i k_i}$$  \hspace{1cm} (4.1)

By analyzing the EL spectra from the two-dopant OLEDs and fitting the extracted data to Equations 2.1, 2.2 and 4.1, we will demonstrate in the following text a method to extract values for $R_0$ and $L$. Furthermore, this EL spectra data analysis method enables us to study the competition between Förster and Dexter transfer mechanisms in the devices.

The concentration of Rubrene in the EML was varied between 0.2wt% and 16wt%, with the Ir(ppy)$_2$(acac) concentration held at ~7wt%. Figure 19a displays the normalized EL spectrum for sensitized OLED devices as well as pure emission from Ir(ppy)$_2$(acac) and Rubrene, which have a peak emission at ~520nm and ~560nm, respectively. The emissive layer composition of
each device is summarized Table 4. In the sensitized system, there are emission bands from both dopants. The EL spectrum can be resolved into its Ir(ppy)$_2$(acac) and Rubrene emission components, as shown in Figure 19b. There is a clear trend of decreasing green emission and increasing yellow emission at higher Rubrene concentration. This indicates more efficient energy transfer occurring from the phosphor to the lower energy fluorophore.

Figure 19 a) Normalized EL spectra for select devices tested in this study biased at 7V (EML of devices are summarized in table below spectra) b) Non-normalized EL spectrum of Device B resolved into its Rubrene and Ir(ppy)$_2$(acac) emission components, biased at 7V

<table>
<thead>
<tr>
<th>Device</th>
<th>Emissive Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (standard)</td>
<td>7wt.% Ir(ppy)$_2$(acac) in CBP</td>
</tr>
<tr>
<td>B (sensitized)</td>
<td>0.2wt.% Rubrene/7wt.% Ir(ppy)$_2$(acac) in CBP</td>
</tr>
<tr>
<td>C (sensitized)</td>
<td>0.6wt.% Rubrene/7wt.% Ir(ppy)$_2$(acac) in CBP</td>
</tr>
<tr>
<td>D (sensitized)</td>
<td>2wt.% Rubrene/7wt.% Ir(ppy)$_2$(acac) in CBP</td>
</tr>
<tr>
<td>E (sensitized)</td>
<td>10wt.% Rubrene/7wt.% Ir(ppy)$_2$(acac) in CBP</td>
</tr>
<tr>
<td>F (standard)</td>
<td>2wt.% Rubrene in CBP</td>
</tr>
<tr>
<td>G (neat layer)</td>
<td>Neat layer of CBP</td>
</tr>
</tbody>
</table>

This model assumes that Rubrene has little effect on exciton formation compared to a standard device consisting of only 7wt.% Ir(ppy)$_2$(acac) in CBP. The validity of assumptions made for this model will be addressed in Section 4.4. Under these assumptions, the total number of
excitons captured in the sensitized system by Ir(ppy)$_2$(acac) can be extracted from the emission spectra of 7wt.% Ir(ppy)$_2$(acac) in CBP as the exciton formation mechanism should be similar in the two systems. Excitons on Ir(ppy)$_2$(acac) will primarily be triplets due to the high intersystem crossing rate (ISC) in the phosphor. The ISC rate for Ir(ppy)$_2$(acac) has been calculated to be $\sim 10^{12}/s$ while fluorescence rates for Ir-based phosphors are generally around $10^7/s$ and energy transfer rates are on the order of $10^7-10^8/s$. Due to the many orders of magnitude difference, singlets on the iridium compound will be quickly converted to the triplet state rather than be energy transferred to a Rubrene molecule. In the sensitized system, the triplet excitons can either decay radiative on the Ir(ppy)$_2$(acac) or be energy transferred, through Dexter or Förster mechanism, to a nearby Rubrene molecule. Dexter transfer will result in non-emissive triplets on the fluorophore, as the spin must be conserved in this process, while Förster transfer leads to singlet state excitons that can decay radiatively on the Rubrene. The emission from Rubrene can thus be related to the amount of Förster transfer occurring in the system. Subsequently, the total energy transfer efficiency can be extracted by comparing the Ir(ppy)$_2$(acac) emission to its emission in the 7wt.% Ir(ppy)$_2$(acac) in CBP standard. Any change in its peak height compared to the standard must be due to energy transfer to Rubrene. The total energy transfer is the sum of the Dexter and Förster processes.

The non-normalized EL spectrum is examined in order to extract the energy transfer efficiencies. The total optical energy output can be obtained by integrating the spectrum over the wavelength. By dividing this optical energy by the average photon energy emitted (calculated by Equation 4.2), the number of photons emitted per second is obtained. Each photon corresponds to an emissive exciton. To account for non-radiative processes, this number is divided by the photoluminescence quantum yield of the dopant being examined. By carrying out this procedure for the emission spectrum of the 7wt.% Ir(ppy)$_2$(acac) in CBP standard, we obtain the total number of excitons captured by the Ir(ppy)$_2$(acac) molecules, $N_{tot}$. As mentioned previously, this can be used as an approximation of the total number of excitons captured by Ir(ppy)$_2$(acac) in the sensitized system.

$$E_{ph,av} = \frac{\int \frac{hc}{\lambda} f(\lambda)d\lambda}{\int f(\lambda)d\lambda}$$ (4.2)
where $E_{ph,av}$ is the average photon energy emitted, $h$ is Planck’s constant, $c$ is the speed of light and $f(\lambda)$ is the EL spectrum.

For the sensitized fluorescence devices, the EL spectra must be resolved into its Rubrene and Ir(ppy)$_2$(acac) emission components, which can subsequently be used to calculate the number excitons that decayed radiatively on Rubrene, $n_R$, and Ir(ppy)$_2$(acac) molecules, $n_{Ir}$, respectively. Non-radiative processes are factored in using the photoluminescence quantum yield of the emitters at their doping concentrations. From these numbers the Förster energy transfer efficiency and total energy transfer efficiency can be calculated as follows:

$$\% \text{ Forster} = \frac{n_R/\Phi_R}{N_{tot}} \times 100\%$$

(4.3)

$$\% \text{ Total ET} = \frac{n_{tot} - n_{Ir}/\Phi_{Ir}}{N_{tot}} \times 100\%$$

(4.4)

where $\Phi_R$ and $\Phi_{Ir}$ are the quantum yield for the Rubrene and Ir(ppy)$_2$(acac) emitters at the dopant concentrations used.

The Dexter efficiency can consequently be calculated as the difference between the total energy transfer efficiency and the Förster energy transfer efficiency. These calculations were repeated for data from all the sensitized devices fabricated. The data was then fitted to theoretical models for the two transfer processes. The transfer efficiencies can be calculated as follows:

$$\phi_F = \frac{k_F}{k_D + k_F + k_r + k_{nr}} \times 100\%$$

(4.5a)

$$\phi_F = \frac{\left(\frac{R_0}{R}\right)^6}{A exp\left(\frac{-R}{B}\right) + \left(\frac{R_0}{R}\right)^6 + \frac{1}{\Phi_{Ir}}} \times 100\%$$

(4.5b)

$$\phi_D = \frac{k_D}{k_D + k_F + k_r + k_{nr}} \times 100\%$$

(4.6a)

$$\phi_D = \frac{A exp\left(\frac{-R}{B}\right)}{A exp\left(\frac{-R}{B}\right) + \left(\frac{R_0}{R}\right)^6 + \frac{1}{\Phi_{Ir}}} \times 100\%$$

(4.6b)

$$\frac{1}{\Phi_{Ir}} = 1 + \frac{k_{nr}}{k_r}$$

(4.7)

$$\phi_{Total} = \phi_F + \phi_D$$

(4.8)
where \( k_D \), \( k_F \), \( k_{nr} \) and \( k_r \) are the rate constants for Dexter transfer, Förster transfer, non-radiative and radiative decay, respectively. By substituting the expressions for the rate constants, as defined in Equations 2.1 and 2.2, and dividing through by \( k_r \), we arrive at a theoretical model that is a function of separation distance. An approximate separation distance was calculated from the Rubrene weight percentage concentration by assuming molecules are hard-spheres and distributed uniformly throughout a layer. The uniformity of the films is investigated in section 4.4.2.

### 4.3 Results and discussion

Figure 20a displays the energy transfer efficiency as a function of donor-acceptor separation distance. These numbers were calculated from the EL spectrum of devices at a current density of 60 mA/cm\(^2\). The three transfer efficiency equations are simultaneously fitted to the three sets of experimental data to obtain the unknown parameters \( L \) and \( R_0 \). \( R_0 \) is the Förster radius and, as mentioned previously, is generally on the order of 50-100Å\(^5\). \( B \) is related to the sum of the van der Waals radii of the donor and acceptor molecules by \( L = 2B \). \( L \) is generally on the order of a few angstroms\(^5\). From the curve fitting, we find \( R_0 = 40.7 \pm 2.8\) Å and \( L = 6.8 \pm 0.06\) Å, both of which are within theoretical ranges. Repeating these calculations for devices biased at different current densities resulted in similar values for \( R_0 \) and \( L \), as shown in Figure 20b. At higher current densities there is a decline in the Förster radius measured. This is due to high brightness levels at high current densities, which saturates the detector, leading to distorted EL spectra. Using PL measurements and following the method as described in \(^3\), the Förster radius for Ir(ppy)\(_2\)(acac)-Rubrene was calculated to be 43.4Å, similar to the \( R_0 \) calculated using the method described in this work.
Figure 20 a) Energy transfer efficiency as function of separation distance for sensitized OLED at a current density of 60 mA/cm$^2$ b) $R_0$ and L values extracted from experimental data for OLED biased at different current densities. Separation distances less than 1nm are shown in dashed lines as they are only theoretical since these distances are on the order of the molecular radii of the emitter molecules.

From Figure 20, it is clear that the energy transfer efficiencies for the Förster and Dexter mechanisms do not follow a simple trend of increasing or decreasing efficiency with separation distance. In the Ir(ppy)$_2$(acac)-Rubrene system, there is an optimal distance range in which Dexter transfer is the major contributor towards energy transfer. At close separation distances, its efficiency begins to drop off while the Förster transfer efficiency increases. A similar trend was observed in devices with an emissive layer consisting of Ir(ppy)$_2$(acac) and DCM$_2$. An $R_0$ and B value of 54.8 ± 1.6Å and 4.6 ± 0.1Å, respectively, was measured for this system. It is generally accepted that the Dexter mechanism is dominant at close interatomic distances, however this is not what the fitted data suggests. Whether the Förster or Dexter mechanism is dominant at any given separation distance depends on their relative rate constants. At some close enough distance the Förster mechanism becomes dominant due to its $1/R^6$ relation. However, in this Ir(ppy)$_2$(acac)-Rubrene system, it is unlikely that the Förster mechanism would actually ever overtake Dexter at small distances since the fitted data shows that this only occurs at separation distances less 1nm. This is on the order of the molecular radius of the emitters and the dopants cannot pack closer to one another than the size of the molecules. It is important to note that this is not a universal trend.
for all materials but depends on the $R_0$ and $L$ values associated with the pair of dopant molecules used.

We can see in Figure 21 that the Förster and Dexter energy efficiency behaviour as a function of concentration can change drastically with different $R_0$ and $L$ values. Figure 21a shows the effect of changing $R_0$ with $L$ held constant at 6.4Å, while Figure 21b demonstrates the effect of changing $L$ with $R_0=40.7$ bÅ. Each set of $R_0$ and $L$ simulates a different set of donor and acceptor material. Using known values for $R_0$ and $L$ for a set of materials and Equations 4.5 and 4.6, it is possible to quickly plot out the Förster and Dexter energy transfer efficiency and determine the optimal dopant concentration that favours the desired transfer mechanism.

**Figure 21** Förster energy transfer efficiency (dashed line) and Dexter energy transfer efficiency (solid line) with a) changing $R_0$ and b) changing $L$. The same coloured lines indicate the Förster and Dexter energy transfer modelling results for one set of $R_0$ and $L$ parameters. The red, blue and black lines in a) are for $R_0 = 20Å$, 40.7 Å and 60Å, respectively, with $L = 6.4Å$. The red, blue and black lines in b) are for $L = 2Å$, 6.4Å, and 4Å, respectively, with $R_0 = 40.7Å$.

### 4.4 Model assumptions

#### 4.4.1 Exciton formation mechanism

This model assumes that Rubrene has little effect on exciton formation compared to a standard device consisting of only 7wt.% Ir(ppy)$_2$(acac) in CBP. It has been demonstrated previously that direct exciton formation on the dopant is the likely mechanism for Ir(ppy)$_2$(acac)
in CBP\textsuperscript{58,59}. A previous study has also shown that Ir(ppy)$_2$(acac) acts as carrier traps and exciton formation sites in co-doped systems using CBP as the host\textsuperscript{55}. Figure 22 below shows the turn-on voltages at $L = 1\text{ cd/m}^2$ for Devices A-G. The turn-on voltage for Device G, which has a neat layer of CBP as the EML, is 3.8V. A significantly reduction in turn-on voltage is observed for Device F, with 2wt.% Rubrene in CBP, and a further reduction is seen for Device A, with 7wt.% Ir(ppy)$_2$(acac) doped into CBP. This indicates that the Ir(ppy)$_2$(acac) atoms play a significant role in carrier trapping and exciton formation in a CBP host. All the co-doped devices show the same turn-on voltage of 3V as in Device A, thus suggesting a similar exciton formation mechanism. Some excitons may still form on the Rubrene molecules but this fraction of excitons should be small enough that it is negligible.

![Figure 22](image.png)

**Figure 22** (a) Luminance vs. voltage and (b) Turn-on voltages at $L = 1\text{ cd/m}^2$ for OLED devices A-E and G

J-V plots can also provide information regarding charge transport and trapping characteristics between the different devices. Device H is the 16wt% Rubrene/7wt% Ir(ppy)$_2$(acac) device. All other devices are as described in Table 4.
Most of the co-doped devices have a similar J-V to the standard Ir(ppy)$_2$(acac) device. Only the 16% Rubrene/7% Ir(ppy)$_2$(acac) shows some deviation, which indicates there will be a higher error associated with the energy transfer efficiencies calculated from this device. The fitting done in the manuscript used data from co-doped devices using doping concentrations up to 10wt% Rubrene. This is shown in the solid lines in the figure below. Adding the measured data for the 16wt.% Rubrene/7% Ir(ppy)$_2$(acac) device onto the plot, it lies very close to the simulated model.

If there is some direct exciton trapping on the Rubrene molecules then we would expect a reduced calculated Förster efficiency and higher Dexter efficiency. This is what we observe for the calculated efficiencies of the 16wt.%Rubrene/7%Ir(ppy)$_2$(acac) device in relation to the fitted data. Even at this high of a doping concentration, there is not significant enough direct exciton formation on the Rubrene to greatly affect the simulation results. If we add the 16wt.%Rubrene/7%Ir(ppy)$_2$(acac) device into the fitting process, we still arrive at similar results of $R_0$ and L with values of $40.5 \pm 2.7\text{Å}$ and $6.4 \pm 0.03\text{Å}$, respectively. The dashed lines Figure 24 below show the results.
Figure 24 Measured and fitted energy transfer efficiency data as a function of separation distance. The solid lines show the fit to co-doped devices using Rubrene concentrations between 0.2wt% and 10wt%. Dashed lines show the fit including a co-doped device with 16wt.% Rubrene. The filled in data points are the efficiencies calculated from the co-doped 16wt.% Rubrene device.

Colour shifting in the electroluminescence spectrum can also be used to determine if Rubrene is acting as a significant a recombination center in the co-doped system. Colour stability indicates that excitons are primarily formed on the high energy molecules (the host or green dopant) and then subsequently energy transferred to the yellow emitter because energy transfer is a voltage-independent process. If more high energy emission is observed at higher voltage, then it indicates that Rubrene is acting as a charge trapping and direct recombination centre. At low bias, charge trapping occurs on the low energy dopant leading to more yellow emission. De-trapping occurring at higher voltages would lead to more emission from the higher energy dopant, thus leading to colour shifting in the EL spectrum with changing voltages. The EL spectra of Device H (16wt% doped Rubrene), in Figure 1a below, shows only emission from Rubrene for all the voltages studied. Quick energy transfer from Ir(ppy)$_2$(acac) to Rubrene at this high concentration of Rubrene may not allow us to observe emission from the Ir-dopant and no change in the EL spectrum can be observed. For this reason, we look at the EL spectrum of Device E, which shows some green emission from Ir(ppy)$_2$(acac). Figure 25b shows almost no colour shifting from 6V to 10V. The closeup of the green emission peak, in the figure inset, shows a very small increase in the green emission peak with voltage. This corresponds to a minimal change in CIE coordinates of (0.0057, 0.0052). The change in the calculated energy transfer efficiency at 6V and 10V are summarized in Table 5 below. The minimal change in the calculated values demonstrates that
direct recombination on Rubrene is negligible in the system. Even less direct charge trapping on Rubrene would be expected for the other devices with even lower Rubrene dopant concentrations.

Figure 25 Normalized EL spectrum showing little colour shifting in a) Device H and b) Device E. The inset of b) shows a closeup at the green emission peak

<table>
<thead>
<tr>
<th></th>
<th>6V</th>
<th>10V</th>
<th>%Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Energy Transfer</td>
<td>99.4%</td>
<td>98.4%</td>
<td>-1.01%</td>
</tr>
<tr>
<td>Forster Energy Transfer</td>
<td>28.1%</td>
<td>28.0%</td>
<td>-0.36%</td>
</tr>
<tr>
<td>Dexter Energy Transfer</td>
<td>71.3%</td>
<td>70.4%</td>
<td>-1.26%</td>
</tr>
</tbody>
</table>

4.4.2 Film Uniformity

Previous papers have used the assumption of uniformly distributed dopants in a host to calculate interatomic distances\(^\text{47,60}\) as well as in modeling to find good fit to experimental data\(^\text{61}\). One experimental method that has been used to study the uniformity of thin films is measuring the steady-state PL on different spots of the thin-film\(^\text{62}\). Non-uniform films will have a distribution of PL intensities as varying dopant concentrations can lead to red-shifting in the PL spectra and different PL efficiencies. Repeating this type of experiment using Rubrene:CBP thin films has shown similar PL intensity and spectra at different points of the film. The results are shown in Figure 26. The average maximum PL intensity for the 10 points was 206.8 a.u. with a standard deviation of 1.8 a.u. and the average of the corresponding peak wavelength was 562nm ± 0.6nm. Little red-shifting and change in PL efficiency was observed along the film. This result
demonstrates uniformity in the thin film on the macroscale. In terms of Rubrene aggregation on the nanoscale, a previous study has shown that there is insignificant Rubrene aggregation in mCP:Rubrene films, even at high doping concentrations\(^{63}\). Aggregation of guest molecules results in changes in the EL spectrum with temperature. Minimal temperature dependence of EL spectra of Rubrene:mCP films indicated that there was little guest aggregation.

**Figure 26** PL spectra for 10 different spots on a 2wt.% Rubrene:CBP thin film. Inset shows a close-up of the spectra near the emission peak

### 4.4.3 Evidence that Ir(ppy)\(_2\)(acac) acts as sensitizer

Triplet excitons generally cannot decay radiatively on traditional fluorescent emitters. The relative orientation of the spins of the unpaired electrons in the HOMO and LUMO determine whether an exciton in a singlet or triplet. If the spins are parallel then it is a triplet state and if it is anti-parallel then it is a singlet. In order for a triplet exciton to decay radiatively, a spin flip is necessary in order to have an electron pair with opposite spin in the ground state. This process is highly unlikely in fluorophores and the excited state is more likely to be deactivated through other non-radiative mechanisms. Their internal quantum efficiency is thus limited to 25% in electrical excitation as singlet and triplets are generally formed in a 1:3 ratio\(^{64}\). Table 6 below summarizes the EQE for the OLED devices, which have been broken down into their Rubrene and Ir(ppy)\(_2\)(acac) components. When comparing the 2wt% Rubrene (Device F) and 2wt.% Rubrene co-doped with 7wt% Ir(ppy)\(_2\)(acac) (Device D), there is a greater than 2-fold increase in the EQE associated with the yellow dopant, just through the addition of the green emitter in the co-doped device. This shows that excitons are being energy transferred from the green dopant to the yellow...
The increase in EQE associated with the Rubrene molecules is due to the sensitization effect, in which triplet state excitons can be harvested by phosphor and subsequently transferred through Förster mechanism to the singlet state of the Rubrene\textsuperscript{47}. This allows the fluorophore to utilize more of the excitons generated through electrical excitation, rather than only 25% of the excitons that are in singlet state. It’s generally accepted that the theoretical EQE limit for traditional fluorescent-based OLED is 5%, after considering a light outcoupling efficiency of ~20% for devices\textsuperscript{65,66}. EQEs greater than 5% observed for Rubrene further confirms that energy transfer must be occurring between the green and yellow emitters.

**Table 6** EQE associated with Rubrene and Ir(ppy)\textsubscript{2}(acac) in the OLED devices at \( J = \sim0.03\text{mA/cm}^2 \)

<table>
<thead>
<tr>
<th>Device</th>
<th>EQE due to Rubrene</th>
<th>EQE due to Ir(ppy)\textsubscript{2}(acac)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B (sensitized)</td>
<td>5.80%</td>
<td>6.18%</td>
</tr>
<tr>
<td>C (sensitized)</td>
<td>5.62%</td>
<td>1.11%</td>
</tr>
<tr>
<td>D (sensitized)</td>
<td>4.26%</td>
<td>0.03%</td>
</tr>
<tr>
<td>E (sensitized)</td>
<td>3.14%</td>
<td>0.02%</td>
</tr>
<tr>
<td>F (standard)</td>
<td>1.70%</td>
<td>N/A</td>
</tr>
</tbody>
</table>

**4.4.4 Device lifetime**

The change in the electroluminescence spectrum and driving voltage to maintain a constant current density of 0.1mA/cm\(^2\) was measured for Ir(ppy)\textsubscript{2}(acac) only, Rubrene-only and co-doped Ir(ppy)\textsubscript{2}(acac)/Rubrene devices. The results are shown in Figure 27. After 2 hours, the percent change in the maximum of the EL spectrum is ~11% and ~12% for the Rubrene and Ir(ppy)\textsubscript{2}(acac) devices, respectively. Significantly faster degradation of one dopant over the other, in ambient conditions, would greatly affect the energy transfer efficiency calculations since they’re based on the emission spectra. However, the two dopants have shown roughly similar degradation over time. A change in driving voltage over time can also indicate degradation of the devices. Over the typical timescale of a measurement (<10 minutes), a slightly faster increase in the voltage in observed in the Ir(ppy)\textsubscript{2}(acac) device but the percent change remains less than 2% for both devices.
Figure 27 Electroluminescence spectra between 0-120 minutes for a) 7wt.% Ir(ppy)2(acac), c) 2wt.% Rubrene, and e) co-doped 7wt.% Ir(ppy)2(acac)/2wt.% Rubrene devices. The insets show the percent change in the maximum electroluminescence as a function of time. Plots b), d) and f)
show the percent change in the voltage needed over time to maintain a current density of $1 \times 10^{-4}$ A/cm$^2$.

4.5 Conclusions

In summary, we have demonstrated a simple method for quantifying energy transfer efficiency in a two-dopant system using EL emission spectra. This study allowed Dexter and Förster mechanisms to be studied individually as a function of separation distance in a sensitized fluorescence system. In an Ir(ppy)$_2$(acac)-Rubrene system, a Förster radius of 42.7Å was calculated and we demonstrated a very different Förster and Dexter energy transfer efficiency profile than what is expected when the two mechanisms occur independently. We expect that this work can be used towards designing stable white OLEDs with a single emissive layer for use in general lighting applications.
Chapter 5
Simple single-emitting layer hybrid white organic light emitting OLED with high colour stability

This chapter will focus on designing a simple white OLED capable of meeting the basic efficiency and colour quality requirements at high enough brightness for solid-state light applications. Here, we report a highly simplified three-layered white OLED that achieves a low turn-on voltage of 2.7V, an external quantum efficiency of 18.9% and power efficiency of 30lm/W at 1,000cd/cm². This simple white OLED also shows good color quality with a Color Rendering Index (CRI) of 75, CIE coordinates (0.42, 0.46) and little color shifting at high luminance. The origin of the stable white colour will be examined in detail. The contents of this chapter have been published in J. Appl. Phys., 122, 134503 (2017). Z.H.L supervised the project and provided counselling and feedback regarding the project direction. I fabricated and characterized the OLEDs and analyzed the data.

5.1 Introduction

White organic light emitting diodes have shown great promise for application in next-generation solid-state lighting. They have the potential to provide warm diffuse lighting, large-area manufacturing, thin form-factor and eventually low-cost production. Intense research in the field has led to the development of highly efficient white OLEDs. Hybrid devices using a combination of a blue fluorophore and lower energy phosphors are generally employed due to the low lifetime and instability of blue phosphors. However, this often requires complicated device structures in order to separate singlet and triplet excitons and ensure all singlet excitons are captured by the blue fluorophore while the triplets are funneled to the phosphor. To achieve this, multiple emission and spacer layers are needed with materials carefully chosen to have appropriate singlet and triplet energies to trap singlet and triplet excitons in desired regions.

Recently, the development of high efficiency blue thermally activated delayed fluorescence emitters (TADF) has presented a great opportunity to simplify white OLEDs while maintaining high efficiency. By careful designing fluorophores with separated donor and acceptor moieties, a small energy splitting between the singlet and triplet exciton states can be achieved. This thermally accessible energy gap allows triplets to undergo reverse intersystem crossing (RISC) into the singlet state where the exciton can then be harvested through fluorescence. As
TADF molecules are capable of accessing triplet excitons, complicated device architectures utilizing multiple emissive zones and spacer layers are no longer needed to prevent triplet loss on the fluorophore. Furthermore, many TADF emitters have shown high photoluminescence quantum yield (PLQY) as a neat undoped layer and their ambipolar nature can make them ideal host materials. These properties make blue TADFs a good candidate for use as both a host and blue emitter in single-emissive layer white OLEDs.

Single-emitting layer (SEL) white OLEDs are desirable for their simpler device architecture that streamlines device fabrication. All the emitters are co-doped into a single host layer where excitons are ideally formed on the higher energy emitter and can successively be energy transferred to lower energy dopants through Dexter or Förster mechanism. Both processes are highly dependent on the separation distance between the two interacting molecules. This can be fine-tuned by adjusting the dopant concentrations to achieve balanced emission from the different colors and ultimately the desirable warm white light. It is also possible for excitons to be formed directly on the dopants by charge trapping. However, there has been difficulty in simultaneously achieving high efficiency and high color quality at the luminance level needed for lighting applications. Additionally, color shifting is often observed in SEL white OLEDs, with enhanced emission from higher energy emitters often observed at higher voltages. In multiple-emission layer (MEL) white OLEDs, the different colour emitters can be doped into different host materials. Colour shifting can occur in these devices due to the changing position of the recombination zone at higher driving voltages. The general device architecture for both types of white OLEDs are shown in Figure 28.

**Figure 28** Schematic of device architecture for typical a) SEL and b) MEL white OLEDs
This chapter presents a device that avoids the common pitfalls associated with SEL white OLEDs. This highly simplified SEL hybrid white OLED demonstrates no color shifting, an EQE of 18.9%, power efficiency of 30 lm/W and CRI of 75 at 1000 cd/m². The maximum EQE, power efficiency (PE) and current efficiency (CE) for the device are 20.3%, 51 lm/W and 43.8 cd/m², respectively. This highly simplified device requires no exciton blocking layers and only uses CBP and TPBi as the hole and electron transporting materials, respectively. The blue TADF emitter, 10,10'-((4,4'-sulfonylbis(4,1-phenylene))bis(9,9-dimethyl-9,10-dihydroacridine)) (DMAC-DPS), has demonstrated a high PLQY of 0.88 and 0.80, in doped and neat films, respectively, and an EQE of ~20% OLED devices. It is used as the host material for the green and red emitting phosphors, Bis(2-phenylpyridine)(acetylacetonate)iridium(III) (Ir(ppy)₂(acac)) and Bis(2-methyl dibenzo[f,h]quinoxaline)(acetylacetonate)iridium(III) (Ir(MDQ)₂(acac)), respectively. Although DMAC-DPS has been used previously in multi- and single emission layer hybrid white OLEDs, the device structure presented achieves a balance of device efficiency and color quality while further simplifying the device architecture.

5.2 Results and discussion

5.2.1 Blue OLED devices

Ideally, a cascade energy transfer scheme is desired, where excitons are formed on the highest energy dopant, in this case the DMAC-DPS, followed by subsequent energy transfer to the lower energy dopants. In order to achieve this, it is important to optimize the neat blue OLED device structure. This ensures that the maximum number of excitons can be captured by the blue dopant first.

DMAC-DPS was first reported by the Adachi group where it was doped into the large bandgap and high triplet energy host Bis[2-(diphenylphosphino)phenyl]ether oxide (DPEPO). This device achieved a maximum EQE of 19.5% with a small roll-off to 16.0% at 1000 cd/m². However, a complex device architecture was needed with blocking layers on the electron and hole sides as well as multiple layers on the hole side to facilitate hole injection. A simplified device based on a neat DMAC-DPS emission layer was later reported, which only used 1,3-Bis(N-carbazolyl)benzene (mCP) and DPEPO as the hole and electron transport layers, respectively. A maximum EQE of 19.5% with a roll-off to 14.6% was achieved at 1000 cd/m² but high driving voltages were required. The device turned on at 4.3 V and required ~10 V to reach 1000 cd/m². This
is likely due to the poor energy level matchup between the charge transport layers and their respective injection layers/electrodes.

To optimize the device structure towards achieving an efficient simple device structure with good electrical characteristics, we first looked at the electron transport side. DPEPO was likely chosen as the transport layer for its high triple energy ($T_1 = 3.3\text{eV}$), which helps confine excitons to the neat emissive layer. However, it does not provide optimal electron transport properties. Simply changing the electron transporting layer (ETL) to TPBi, a well-established and cost-effective material, while keeping a thin 10nm DPEPO blocking layer leads to significant improvements to the IVL characteristics. The turn-on voltage for this device is 2.7V and it reaches 1000cd/m$^2$ at ~5V and the two devices achieved similar efficiencies. Removal of the DPEPO layer entirely leads to improve device turn-on but reduced device efficiency due to exciton quenching by the TPBi layer. Subsequently looking at the hole transport side, CBP has superior hole mobility than mCP and it is commonly used with TPBi$^{88,89}$. However, it has low triplet energy of 2.6eV compared to the 3.0eV that has been reported for mCP. The triplet energy of DMAC-DPS is 2.9eV and so exciton transfer to the hole transporting layer (HTL) may be a loss mechanism when using CBP. For this reason, devices using a 10nm blocking layer (BL) of mCP were tested. Contrary to expectations, the devices using a BL had inferior performance compared to CBP without a BL, which had comparable device efficiency to the mCP HTL device. This indicates that the exciton generation zone is far away from the HTL. It is likely at the recombination zone is at the emissive layer (EML)/ETL interface due to the larger energy barrier on the electron transport side and lower electron mobility in TPBi than hole mobility in CBP. The excitons are efficiently harvested in the EML before they can reach the HTL and be quenched by CBP. The energy levels of the various materials discussed as well as the device IV and efficiencies for the blue optimization are shown in Figure 29. The device structures are detailed in Table 7. The optimized blue device achieves a max EQE of 20.1% with a turn on voltage of ~2.9V and it only requires one additional layer compared to Adachi’s neat DMAC-DPS device$^{76}$. 

**Figure 29** a) Energy level diagram for the optimized blue device (left side) and for other materials used in this study (right side) b) JV for blue OLED devices c) EL spectrum of blue devices d) Power efficiency and current efficiency for blue devices

**Table 7** Device structure for blue OLED optimization

<table>
<thead>
<tr>
<th>Device</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>mCP(35nm)/DMAC-DPS(30nm)/DPEPO(40nm)</td>
</tr>
<tr>
<td>2</td>
<td>mCP(35nm)/DMAC-DPS(30nm)/DPEPO(10nm)/TPBi(30nm)</td>
</tr>
<tr>
<td>3</td>
<td>CBP(35nm)/mCP(10nm)/DMAC-DPS(30nm)/DPEPO(10nm)/TPBi(30nm)</td>
</tr>
<tr>
<td>4</td>
<td>CBP(35nm)/DMAC-DPS(30nm)/DPEPO(10nm)/TPBi(30nm)</td>
</tr>
<tr>
<td>5</td>
<td>CBP(35nm)/DMAC-DPS(30nm)/TPBi(40nm)</td>
</tr>
</tbody>
</table>
5.2.2 SEL white OLED

Neat undoped DMAC-DPS has an emission peak at 492nm, as shown in Figure 30a. The two lower energy phosphors used for the white OLED were green-emitting Ir(ppy)$_2$(acac) and red-emitting Ir(MDQ)$_2$(acac), which have emission peaks at 517.5nm and 612nm, respectively, in dichloromethane. The absorption spectrum of both Ir(ppy)$_2$(acac) and Ir(MDQ)$_2$(acac) (Figure 30a) show considerable overlap with the emission spectrum of DMAC-DPS, indicating that there should be efficient energy transfer from DMAC-DPS to the phosphors. Additionally, there is good overlap between the emission spectrum of Ir(ppy)$_2$(acac) and the absorption spectrum of Ir(MDQ)$_2$(acac). Thus, energy transfer from the green to the red phosphor should also occur effectively. Figure 30b shows the emission spectrum for Ir(ppy)$_2$(acac) doped into DMAC-DPS at different concentrations. There is clearly very efficient energy transfer from DMAC-DPS to Ir(ppy)$_2$(acac) with only green emission observed at 5wt% doping. Additionally, increased energy transfer with higher dopant concentrations leads to less blue emission from DMAC-DPS. A similar trend is observed for Ir(MDQ)$_2$(acac) in DMAC-DPS (Figure 30c).

Figure 30 a) Normalized photoluminescence (solid lines) and absorption (dashed lines) spectra for relevant materials in dichloromethane solvent. EL emission spectra of DMAC-DPS with different b) Ir(ppy)$_2$(acac) and c) Ir(MDQ)$_2$(acac) doping concentrations at 7V.

To obtain white light emission, Ir(ppy)$_2$(acac) and Ir(MDQ)$_2$(acac) were co-doped into the DMAC-DPS emission layer. Low concentrations of both dopants were needed to achieve optimal simultaneous emission from the three emitters; DMAC-DPS at 492nm, Ir(ppy)$_2$(acac) at 517nm and Ir(MDQ)$_2$(acac) at 590nm. The thickness of the ETL was optimized at 65nm for the white device. This thickness affects the electron and hole balance in the device as well as the out-coupling for the different colors, thus affecting the emission spectrum of the device. Blue emission
is enhanced for devices with thinner ETL while red emission is favored for a thicker ETL layer. The best electrical properties and efficiency were seen for the 65nm ETL. This device demonstrated a max EQE of 22.1%, power efficiency of 37.5lm/W and currently efficient of 40.4 cd/m$^2$. These values roll off to 18.8%, 19.2lm/W, and 30.3cd/m$^2$ at 1000cd/m$^2$, respectively (Figure 31a and 30b). The EL spectrum, shown in Figure 31c, displays some color shifting with CIE coordinates ranging from (0.44, 0.47) at 5V to (0.40, 0.46) at 10V. The device demonstrates a turn-on voltage of 2.9V and reaches 1000cd/m$^2$ at 5V.

**Figure 31** The a) J-V-L and b) efficiency plots for the SEL white OLEDs. The emissive layer is composed of DMAC-DPS co-doped with Ir(ppy)$_2$(acac) and Ir(MDQ)$_2$(acac) doped at 0.4wt% and 0.7wt.%, respectively. The EL spectra at different biases for the white devices c) with and d) without the DPEPO blocking layer.

Examining the energy level diagram (Figure 29a), it is clear that the 0.7eV offset between the DPEPO and TPBi LUMO is a significant contributor to the driving voltage needed to achieve 1000cd/m$^2$. Upon removal of the blocking layer, the turn-on voltage and the driving voltage at
1000cd/m$^2$ is reduced to 2.5V and 4V, respectively. Furthermore, slightly superior device performance is observed at 1000cd/m$^2$ with an EQE, power efficiency and current efficiency of 18.9%, 30lm/W, and 37.8cd/m$^2$, respectively. This is an unexpected result as the triplet energy of TPBi ($T_1$=2.6eV) is 0.3eV below that of DMAC-DPS, thus triplet quenching by TPBi would be expected as seen in the blue devices. With the removal of the DPEPO layer, electrons are able to more easily penetrate into the EML layer, thus allowing excitons to be formed on the DMAC-DPS away from the EML/ETL interface. Additionally, the dopants change the charge transport characteristics of the EML by acting as charge traps and subsequently resulting on direct exciton formation on the dopants. Excitons that form on the lower triplet energy phosphors cannot be energy transferred to TPBi molecules. Triplet excitons that form on the DMAC-DPS near the TPBi layer must also compete with energy transfer to the phosphors as well as reverse intersystem crossing to the singlet state of the DMAC-DPS. Poor spectral overlap between the emission of DMAC-DPS and the absorption of TPBi (Figure 29) suggests poor energy transfer to the ETL. The slow transfer rate cannot compete with the harvesting of excitons by other mechanisms and thus does not present a major quenching pathway. Quenching by TPBi does still occur since there is a slight decrease in the maximum EQE for the white OLED without a blocking layer ($\text{EQE}_{\text{max}} = 20.3\%$) compared to with one ($\text{EQE}_{\text{max}} = 22.1\%$). However, at 1000cd/m$^2$ the EQEs are basically identical as the more narrow recombination zone in the DPEPO device causes more significant roll-off due to the higher exciton density in the narrow region, while superior power efficiency is observed in the blocking-layer free device.

In addition to simplifying the device structure, the removal of the blocking layer further improves the color stability. The EL spectrum in Figure 31d shows almost no change between 5V and 10V. The CIE coordinates range from (0.40, 0.46) at 4V to (0.39, 0.45) at 10V with CRI of 75 to 78, respectively. We investigated this improved color stability by first examining and identifying the source of color shifting in the white device with the DPEPO blocking layer.

5.2.3 Colour stability

A common explanation for changing EL spectrum is the shifting and broadening of the recombination zone$^{90-93}$. This changes the distance between the emissive zone and the reflective cathode and thus alters the outcoupling efficiency of the different wavelengths. In the case with the DPEPO blocking layer, the large energy barrier causes electrons to accumulate at the
DPEPO/TPBi interface. As a larger bias is applied, more electrons can penetrate into the EML and shifts the recombination zone towards the hole-transport side. If this was the case then enhanced red-emission at higher voltages would be expected. There is an increasing distance between the emissive zone and the cathode as the recombination zone shifts towards to the HTL. Red-emission tends to favored at longer distances while shorter wavelengths are more prominent at shorter distances\(^{38}\), as was observed when varying the TPBi layer thickness. However, enhanced blue and green emission is actually observed at higher bias (Figure 31c). This indicates that recombination zone shifting is not the major cause of the color instability in the device with the DPEPO blocking layer.

Another theory for the origin of color shifting, which was proposed by Meerholz et. al\(^{38}\), is the competition between charge carrier trapping and charge transport through the emissive layer. At lower voltages, there is more red emission due to charge carrier trapping by the dopants. At higher electric fields, the unperturbed charge transport through the host layer becomes more dominant leading to reduced red emission and subsequently allows more excitons to be formed on the blue emitter. Energy transfer from the higher energy emitter to the lower ones is electric field independent and therefore color shifting is not observed at higher voltages. The energy levels of the dopants (Figure 29a) would suggest that both Ir(ppy)\(_2\)(acac) and Ir(MDQ)\(_2\)(acac) can act as charge carrier traps due to the deeper HOMO and LUMO levels compared to DMAC-DPS. To examine the effect of the dopants on the charge transport characteristics, hole-only devices with a structure ITO/MoO\(_3\)(1nm)/CBP(10nm)/X(100nm)/CBP(10nm)/MoO\(_3\)(1nm)/Al and electron-only devices with a structure ITO/TPBi(10nm)/X(100nm)/TPBi(10nm)/LiF(1nm)/Al were fabricated, where the X layer is either neat DMAC-DPS or DMAC-DPS co-doped with the two phosphors. Figure 32 clearly shows a difference in the current density for both electrons and holes, with reduced current density in the case of the co-doped DMAC-DPS. The reduced hole and electron mobility observed confirms that the dopants act as both hole and electron traps.
Figure 32 The JV curves for the hole-only (blue) and electron-only (black) single-carrier devices

We can examine the color shifting more quantitatively by defining $R_{R/B}$ and $R_{G/B}$ as the ratio of the peak red emission intensity at 590nm and green emission at 519nm to the peak blue emission at 492, respectively. The ratios as a function of applied voltage are shown in Figure 33. Both the $R_{R/B}$ and $R_{G/B}$ ratio initially decline with voltage before leveling off towards some constant value. Meerholz et al. observed a similar trend and they modeled the competition between charge carrier trapping and charge transport by the following equation:

$$q(V) = \frac{D}{\mu} \left( \frac{d}{L_T} \right)^2 \frac{1}{V - V_{0,\text{eff}}} + \frac{d}{L_T},$$

(5.1)

where $D$ is the charge carrier diffusion coefficient, $\mu$ is the mobility, $d$ is the emissive layer thickness, and $L_T$ is average distance a charge travels before reaching a trapping center. $V_{0,\text{eff}}$ is an effective injection voltage; a term that will be discuss later in this section. This ratio should be proportional to $R_{R/B}$ and $R_{G/B}$. The fit of $q(V)$ to the experimental $R_{R/B}$ data is shown in Figure 33a. The good fit indicates that charge carrier trapping is likely the main origin of color shifting in the white OLED with a DPEPO blocking layer. Repeating this process, we find that this model also fits well with the white device without DPEPO (Figure 33b). However, the $R_{R/B}$ ratio as a function of voltage levels off much sooner and color stability is achieved for a broader brightness range.
Figure 33 Ratio of the peak emission intensity from the red and green dopants to the blue emitter for the white devices a) with DPEPO and b) without the DPEPO blocking layer. Part c) shows a close up of the experimental data points of the device without DPEPO. In part a) the $V_{0,\text{eff}}$ value extracted from the fit for $R_{\text{R/B}}$ and $R_{\text{G/B}}$ are 4.66V and 4.59V while the values from part b) are 3.72V and 3.69V, respectively. The EL spectrum for both devices at 10V is shown in d)

The original model proposed by Meerholz et al. was applied to a simple device consisting of a single polymer emissive layer sandwiched between two electrodes. In this case, $V_{0,\text{eff}}$ measured the built-in voltage, $V_0$. The fits found a $V_0$ value that was very close to the threshold current injection. A previous study\(^94\) has used this model on a more complex device structure and assumed that the electric field mainly dropped across the emissive layer. In our multi-layered device, there should be added voltage drops across interface barriers, particularly in the DPEPO device, that need to be overcome before carriers can move through the emissive layer. The built-
in voltage and interfacial injection voltages are combined into the $V_{0,\text{eff}}$ term. A $V_{0,\text{eff}}$ of 4.66V and 4.59V is found for fitting the $R_{R/B}$ and $R_{G/B}$ ratios, respectively, in the white devices with DPEPO while a smaller $V_{0,\text{eff}}$ of 3.72V and 3.69V were extracted for the white device without DPEPO. Due to the larger $V_{0,\text{eff}}$ in the DPEPO device, which should be due to the large injection barrier at the TPBi/DPEPO interface, the effective electric field across the EML is less than in the blocking-layer free device. The rate of charge carrier trapping depends on the electric field across the emissive layer. Higher applied voltages are thus required to achieve a stable EL spectrum. As shown in Figure 33c, the EL spectrum of the white OLED with DPEPO approaches that of the device without DPEPO at high voltages when the field is sufficient enough to inject electrons across the DPEPO barrier and transport through the host layer becomes dominant over charge trapping becomes dominant. Additionally, at high voltages, the green to blue and red to blue ratios approach similar values. Similar results regarding color stability were found for white OLED devices using mCP as the HTL instead of CBP.

**mCP as HTL for SEL white OLED**

**Device Structure:** ITO/MoO$_3$(1nm)/mCP(35nm)/DMAC-DPS:Ir(ppy)$_2$(acac):Ir(MDQ)$_2$(acac) (30nm)/TPBi(65nm)/LiF(1nm)/Al(100nm)

In terms of color stability, similar effects should be observed as long as the new HTL does not introduce any unnecessary energy barriers. We’ve demonstrated this by using mCP as the HTL instead of CBP. mCP has similar energy levels as CBP so that there is a cascade energy level formed between ITO/MoO$_3$ and DMAC-DPS. Slightly higher efficiency is observed in this system. This can be attributed to the higher triplet energy of mCP, which helps trap exciton in the emissive layer. This device also shows a different emission spectrum with less blue emission. This is due to the different charge transport properties in mCP that can affect the recombination zone. In this case, lower hole mobility in mCP compared to CBP$^{95-97}$ would shift the recombination zone towards the HTL side and subsequently increase the distance between the emission zone and the anode. As previously reported$^{38}$, blue emission is enhanced for smaller distances while longer wavelengths are favored for shorter thicknesses.

Reduced color shifting is observed in the case of mCP without DPEPO compared to with the blocking layer as shown in the Figure 34a. However, more color shifting is seen with mCP as HTL versus CBP as HTL despite their similar HOMO levels (-6.1eV). There is a change in CIE
coordinates of (0.04, 0.01) from 4V to 10V compared to a change of (0.01, 0.01) with CBP. This can be attributed to slightly increased injection barrier in the mCP case. By comparing the JV curves, Figure 34b, for the CBP and mCP device, we can see that the electrical turn-on occurs at a slightly lower voltage in the case of CBP for the HTL. Additionally, when we fit the ratios \( R_{R/B} \) and \( R_{G/B} \) to Equation 5.1, we extract a larger \( V_{0,\text{eff}} \) of 4.28V and 4.14V, respectively. The injection barrier is largely determined by the energy offset between the fermi level of the metal and the energy levels of the organics however, it can also be affected by the interfacial morphology and interfacial states formed between the organics and MoO\(_3\)^{98,99}. A previous study\(^{100}\) has shown different surface morphology through atomic force microscopy (AFM) images of mCP and CBP thin films. Although, this study showed more surface roughness in CBP than mCP for the substrate used, this does not indicate that mCP should form a better interface with MoO\(_3\). The point is that despite their similar structure, when deposited on the same surface, CBP and mCP do not pack or interact with the underlying layer in the same manner. In the case of MoO\(_3\), the evidence suggests that CBP creates a more favorable interface for charge injection as reflected in the lower electrical turn-on and smaller fitted \( V_{0,\text{eff}} \) parameter than with mCP.
Figure 34 Ratio of the peak emission intensity from the red and green dopants to the blue emitter for the white device with mCP as HTL and no DPEPO layer. the $V_{0,eff}$ value extracted from the fit for $R_{R/B}$ and $R_{G/B}$ are 4.28V and 4.14V (shown by the dashed lines). b) JV curve of white devices using CBP and mCP as the HTL. Part c) and d) show the EL spectrum of white devices using mCP as the HTL without and with the DPEPO blocking layer.

5.3 Conclusions

In summary, a highly simplified three-layered white OLED with a single emission layer consisting of a high energy TADF host doped with two lower energy phosphors was presented. Table 8 summarizes the performance of current state of the art white hybrid and all phosphorescent SEL white OLEDs at a luminance of 1000cd/m$^2$. The device presented in this paper can achieve efficiencies comparable to the highest performing devices while achieving improved color stability. Furthermore, a less complicated device structure with no blocking layers is required. It
was shown that the removal of the blocking layer did not lead to significant quenching by the transport layers. The elimination of significant energy barriers presented by blocking layers brought about improved color stability with little change to the CIE coordinates from 4V to 10V.

**Table 8** Summary of performance of representative SEL white OLEDs at 1000cd/m². A device was considered to exhibit color stability if its change in CIE coordinates (ΔCIE) over the range of reported voltages is less than (0.02, 0.02).

<table>
<thead>
<tr>
<th>Reference</th>
<th>PE (lm/W)</th>
<th>EQE (%)</th>
<th>CRI</th>
<th>Color Stability</th>
<th>V&lt;sub&gt;1000&lt;/sub&gt;</th>
<th>Number of Layers (EML composition)</th>
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<tr>
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<td>38.7</td>
<td>19.6</td>
<td>48</td>
<td>✓</td>
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<td>6 (B host, R dopant)</td>
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<tr>
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<td>31.3</td>
<td>18.3</td>
<td>67*</td>
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<td>14.8</td>
<td>76</td>
<td>x</td>
<td>8.5V</td>
<td>6 (co-host B exciplex, RG dopants)</td>
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<tr>
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<td>21.7</td>
<td>9.7</td>
<td>52*</td>
<td>x</td>
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<td>x</td>
<td>-</td>
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<td>68*</td>
<td>x</td>
<td>3.5V</td>
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<td>This work(a)</td>
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<td>19.2</td>
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<td>69</td>
<td>x</td>
<td>5V</td>
<td></td>
<td>4 (B host, RG dopant)</td>
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</table>

(a) hybrid white OLED (b) all-phosphor white OLED *calculated based on EL spectrum presented in paper. B = blue, R = Red, G = Green, O = Orange
Chapter 6
Lifetime of blue OLEDs

This chapter will discuss the challenges associated with developing OLEDs with long operational lifetime. We present a platform for improving the device stability of a blue thermally activated delayed fluorescent emitter through the introduction of a dopant that can increase the initial distribution of singlet to triplet excitons on the blue emitter above the typical 1 to 3 ratio observed in electrical excitation. For the materials studied, EQE modelling showed that as more excitons were formed on the dopant at high dopant concentrations, they primarily underwent Förster energy transferred to the singlet state of the blue host emitter. This resulted in more excitons undergoing prompt fluorescence and reduced the long-lived exciton population that is more likely to undergo undesirable processes that degrade the organic materials and ultimately shorten the device lifetime. The content of this chapter is to be published.

6.1 Introduction

Although great strides have been made in the development of high efficiency organic light emitting diodes (OLEDs), their short operational lifetime, particularly in blue devices, continues to present a significant challenge preventing its practical application in displays and lighting. As blue emitters are the limiting factor, the following study will redirect its focus towards blue OLEDs. As mentioned in Chapter 5, since blue phosphorescent emitters suffer most severely from short device lifetimes, white OLEDs tend to be made from a hybrid of a blue fluorophore and lower energy phosphors in order to meet basic lifetime requirements, even for display applications\textsuperscript{35}. This consequently limits the energy efficiency of white OLEDs. With the introduction of TADF molecules, there is an opportunity to overcome the limitations of phosphors and traditional fluorophores. Presently, there are limited reports in literature on the lifetime of TADF-based devices and on methods of enhancing its devices lifetime. Although, there is some work showing short device lifetimes, the research into the design and synthesis of TADF molecules is not yet as developed as in phosphors. Better molecular and device design criteria are being developed\textsuperscript{104–106}, leading to improved device lifetimes that are comparable to phosphorescent and even fluorescent emitters for lower energy emitters\textsuperscript{107–109}. As the study of TADF molecules matures, it has the potential to provide a new path for designing high efficiency and long-lived white OLEDs.
Short device lifetime can be attributed to either material or device-related degradation mechanisms. All organic materials are sensitive to some degree to photodecomposition through photo-oxidation or photocleavage\textsuperscript{110}. Materials with high bond dissociation energy are desirable to minimize degradation when inevitably exposed to UV-visible light. The materials chosen should also be resistant to electrochemical degradation. They often undergo multiple successive oxidation and reduction processes during charge carrier transport. The formation of charged polarons have been shown to cause instability in materials that are otherwise stable. The design and synthesis of organic materials resistant to degradation by these factors is highly desirable. Details on strategies for the improving the chemical stability of organic materials can be found in reference \textsuperscript{111}.

This work will focus on device engineering to improve the lifetime of TADF-based devices. Long exciton lifetimes are generally associated with more severe device-related degradation mechanisms\textsuperscript{39}. When excited-state species, such as excitons and polarons, interact with one another through exciton-exciton or exciton-polaron annihilation processes, there is an exchange of energy from one species to the other. This results in one molecule relaxing to the ground state while the other is excited into a higher energy-state that can bring about chemical bond dissociation in the host or emitter material. This process is illustrated in Figure 35. Blue emitters tend to have shorter device lifetimes due to its higher energy states (and the higher energy host material required) that are more likely to cause damage to the organic material. The long triplet lifetime of blue phosphors, in particular, makes these annihilation processes more likely leading to the degradation of the organic materials and subsequently shorter device lifetimes. It’s widely accepted that triplet-triplet annihilation (TTA) and triplet-polaron annihilation (TPA) are the most prominent in phosphorescent OLEDs\textsuperscript{112–114}. Only a couple of studies have looked into TADF molecules; some showed that TTA and singlet-triplet annihilation (STA) are dominant\textsuperscript{115,116} while another work indicated that TPA is the most significant mechanism\textsuperscript{117}. However, these works did not look into the effects on device lifetime.
Studies on device lifetime of TADF-based OLEDs has been found to be strongly dependent on the host material used. This was either due to the instability of the high energy host material\textsuperscript{107,109} or to the better carrier charge balance provided by certain types of hosts\textsuperscript{118}. In the latter case, the better balance of charge carriers shifted the recombination zone towards the centre of the emissive layer and reduced the local exciton density at an interface leading to reduced annihilation processes. This can also be achieved by altering the dopant concentration\textsuperscript{108}. In order to eliminate the effect of the host material and to focus the study on the TADF molecule, we look to studying a blue TADF that has shown high photoluminescent quantum efficiency (PLQY) and high device performance when used as a neat undoped layer: DMAC-DPS\textsuperscript{76}.

In this work, a concept is proposed to improve the lifetime of neat blue TADF devices through the introduction of a dopant. The purpose of the dopant is two-fold: to cause charge trapping and to allow energy transfer to and emission from the blue TADF material. In order to do this, the dopant must have energy levels within the bandgap of DMAC-DPS as well as a higher triplet energy to enable efficient energy transfer. The iridium-based compound, tris(5-(4-fluorophenyl)-1,3-dimethyl-1H-1,2,4-triazolyl)iridium (Ir(fdpt)\textsubscript{3}), was chosen to meet these criteria\textsuperscript{46}. From modelling of the external quantum efficiency data, we found that the STA process is dominant in this material and that the dopant altered the initial distribution of exciton in the singlet and triplet state of DMAC-DPS. At higher dopant concentrations, more singlets are initially

![Diagram of a common device-related degradation mechanism in OLEDs involving high energy exciton species. The triplet-triplet annihilation process leads to high energy excitons that induces chemical bond dissociation in the organic material.](image-url)

**Figure 35** Illustration of a common device-related degradation mechanism in OLEDs involving high energy exciton species. The triplet-triplet annihilation process leads to high energy excitons that induces chemical bond dissociation in the organic material.
formed on DMAC-DPS, thus increasing the fraction of excitons having short lifetime and undergoing prompt fluorescence. Both improved lifetime and efficiency were observed with increasing Ir(fdpt)$_3$ dopant concentration in DMAC-DPS. Through this strategy, the device lifetime was lengthened by 20 times compared to the undoped DMAC-DPS device.

6.2 Results and Discussion

6.2.1 Performance of Blue TADF OLED

Figure 36 shows the optimized device structure and energy level diagram for the blue TADF devices studied in this work as well as the chemical structure of the materials used. DMAC-DPS served as both a 35nm-thick hole transport layer and the host material in the 30nm-thick emission layer with 3,3′,3″-[Borylidynetris(2,4,6-trimethyl-3,1-phenylene)]tris[pyridine] (3TPYMB) used in the 30-nm electron transport layer. The Ir(fdpt)$_3$ dopant concentrations tested were 0wt.%, 5wt.%, 7wt.%, 10wt.%, 13wt.% and 20wt.%. To clearly show the trend, only select dopant concentrations are shown in plots (0wt%, 7wt%, 13wt% and 20wt%).

![Energy level diagram for blue OLED devices and chemical structure of organic materials](image)

**Figure 36** Energy level diagram for blue OLED devices and chemical structure of organic materials

The current density-voltage-luminance, current efficiency, lifetime data and electroluminescence spectra are shown in Figure 37. Table 9 summarizes the efficiency and lifetime performance of the devices. From the JV and EL spectra, we can see that the dopant satisfies the two basic requirements. The shifting of the JV curve to higher voltages suggests charge trapping while emission from only DMAC-DPS, even at higher concentrations of Ir(fdpt)$_3$
indicates efficient energy transfer from the dopant to the host. From the CE and lifetime plots, a clear trend of increasing performance and lifetime is observed. The doped devices demonstrate high efficiencies for blue devices with maximum current efficiencies and EQEs above 40cd/A and 20%, respectively. The 20wt% doped device has a lifetime that is 20 times longer than the undoped DMAC-DPS device.

**Figure 37** Performance of blue OLED devices (a) Current density-voltage (left) and luminance-voltage (right) plots (b) current efficiency vs. luminance (c) EL emission spectra (d) Normalized luminance versus time (initial luminance, $L_0 = 1000$cd/m$^2$)

**Table 9** Summary of the performance and lifetime of blue TADF devices

<table>
<thead>
<tr>
<th>Dopant Concentration</th>
<th>Maximum current efficiency (cd/A)</th>
<th>Maximum EQE (%)</th>
<th>$T_{50}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0wt%</td>
<td>32.52</td>
<td>18.2</td>
<td>10.8s</td>
</tr>
<tr>
<td>7wt%</td>
<td>38.16</td>
<td>20.5</td>
<td>18.6s</td>
</tr>
<tr>
<td>13wt%</td>
<td>43.10</td>
<td>21.6</td>
<td>32s</td>
</tr>
</tbody>
</table>
6.2.2 Charge carrier transport and the recombination zone

As mentioned previously, there have already been studies showing how dopants can affect the carrier mobilities through the emission layer\textsuperscript{108}. This can lead to a broadening of the recombination zone thus reducing the exciton density across the EML and subsequently decreasing the rate of annihilation processes that shorten device lifetime. To further study the conduction mechanisms and to verify that the improved lifetime is not solely due to a broadening of the emission zone, single-carrier devices were fabricated. The JV curve for the hole-only (HOD) and electron-only devices (EOD) are shown in Figure 38.

![Figure 38](image)

**Figure 38** Current density-voltage characteristics for HOD (closed markers) and EOD (open markers)

The significant reduction in the current density of the HOD indicate trapping of holes leading to reduce hole transport through the emission layer. The electron transport characteristics, on the other hand, are unaffected by the presence of the dopant. This can be explained by looking at the energy diagram of Ir(fdpt)\textsubscript{3} compared to DMAC-DPS. The deeper HOMO of the dopant would trap holes while the higher energy LUMO would have little effect on the electron conduction, which would occur primarily on the DMAC-DPS. Since the transport of holes is slowed through the EML, electrons can penetrate deeper into the EML, consequently reducing the
local exciton density at the EML/ETL interface. The results from the single carrier devices confirms that a shifting and broadening of the recombination zone does play a part in the improved lifetime observed. However, when further increasing the dopant concentration, there isn’t a continued significant reduction in the hole conduction. If better charge balance is the only cause of improved device lifetime then there should be a trend of reduced hole current density with dopant concentration. This is not observed and suggests that there is another mechanism that also plays a role in lengthening the lifetime, particularly as the dopant concentration is increased. There is actually a slight increase in the hole density with dopant concentration as the holes are better able to move between dopant molecules at higher concentrations, which would lead to a poorer hole and electron mobility balance. No significant change in the current density for the EODs was found at any of the tested concentrations.

6.2.3 Degradation mechanism: effect of singlet and triplet state exciton distribution

In general, not considering any annihilation processes, the rate equation for the singlet, \( n_S \), and triplet, \( n_T \), exciton population in the undoped DMAC-DPS devices under electrical excitation can be written as:\(^{119}\):

\[
\frac{d n_S}{d t} = -(k_R + k_{ISC}) n_S + k_{RISC} n_T + \frac{J}{4eW}
\]

(6.1)

\[
\frac{d n_T}{d t} = -(k_{nr} + k_{RISC}) n_T + k_{ISC} n_S + \frac{3J}{4eW}
\]

(6.2)

where \( k_R, k_{ISC}, k_{nr} \) and \( k_{RISC} \) are the rate constants for radiative decay from the singlet state, intersystem crossing, non-radiative decay from the triplet state and reverse intersystem crossing for DMAC-DPS. These values have been previously reported in references 107 and 112. \( J \) is the current density, \( e \) is the elementary charge and \( W \) is the thickness of the recombination zone, in this case, assumed to be approximately the EML thickness. Additional terms can be added to account for annihilation mechanisms such as STA, TTA, TPA and singlet-polaron annihilation (SPA). The expanded equations can be found at the end of this section. The equations were solved simultaneously at steady state and fitted to the EQE data using the equation, \( EQE = EQE_{max} n_S/n_{S0} \), where \( EQE_{max} \) is the maximum experimental EQE and \( n_{S0} \) is the singlet population in the absence of any annihilation processes. Figure 39 shows the fit to the EQE data for the different models. STA and TTA have been demonstrated previously to be dominant in TADF-based OLEDs\(^{115,116}\). The model including only the STA process was found to provide the
best fit for the device studied here. The rate constant for the STA process, $k_{ST}$, was found to be $3.7 \pm 0.08 \times 10^{-11} \text{cm}^2 \text{s}^{-1}$ in the neat DMAC-DPS device. In the cited references that found TTA and STA to be dominant, the TADF material was used as the host or dopant material with a traditional fluorescent material. With the fluorescent material, the triplets cannot be utilized for radiative decay and are more readily available to participate in the TTA degradation process. In the case where a TADF and phosphorescent material is used, triplet excitons formed on the host and the dopant can be utilized towards radiative decay. This extra competitive pathway would make TTA less significant in these systems.

![Figure 39 EQE versus current density plot for the neat DMAC-DPS device. The square data points are the measured experimental EQE values while the solid lines correspond to the calculated EQE based on models accounting for different annihilation processes. In the model considering STA and SSA together, the fit resulted in a rate constant for SSA of 0.](image)

Once the dopant is added, these equations must be altered to account for exciton formation on the Ir-complex and how excitons can either be transferred to the singlet or triplet state of the DMAC-DPS. Since the dopant is a phosphorescent emitter, any singlet excitons on the complex will be quickly transferred to the triplet state through ISC. For this reason, only the triplet exciton population on the dopant, $n_{T,d}$ will be considered. The rate equations are now adjusted to:
\[
\frac{dn_S}{dt} = -(k_r + k_{ISC}) n_S + k_{RISC} n_T + k_F n_{T,d} - k_{ST} n_S n_T + \frac{j}{4eW} (1 - \gamma) \tag{6.3}
\]

\[
\frac{dn_T}{dt} = -(k_{nr} + k_{RISC}) n_T + k_{ISC} n_S + k_D n_{T,d} + \frac{3j}{4eW} (1 - \gamma) \tag{6.4}
\]

\[
\frac{dn_{T,d}}{dt} = \frac{j}{eW} \gamma - k_F n_{T,d} - k_D n_{T,d} \tag{6.5}
\]

where \( \gamma \) is the fraction of excitons formed directly on the dopant and \( k_F \) and \( k_D \) are the rate constants for Förster and Dexter energy transfer, respectively. Similar to a sensitized fluorescence system, the Förster energy transfer mechanism will result in singlet-state excitons while Dexter produces triplets on the DMAC-DPS. Depending on \( \gamma \) and the relative rate constants of the two energy transfer mechanisms, the initial singlet and triplet populations on the TADF can be altered from the typical 1:3 ratio observed in electrical excitation. The exciton pathways are illustrated in Figure 40.

**Figure 40** Schematic illustration of the exciton pathways in the TADF host and phosphorescent dopant system

**Table 10** Model parameters for fitting to EQE model to the TADF OLEDs at different Ir(fdpt)₃ concentrations

<table>
<thead>
<tr>
<th>Concentration</th>
<th>( \gamma )</th>
<th>( k_{ST} ) (cm³/s)</th>
<th>( \alpha_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0wt%</td>
<td>0</td>
<td>3.71 ± 0.08 × 10⁻¹¹</td>
<td>0.25</td>
</tr>
</tbody>
</table>
The EQE fit parameters are summarized in Table 10. The $k_{ST}$ is similar at different doping concentrations, while the $\gamma$ parameter increases. The $k_F$ was calculated based the following equation:

$$k_F = k_r \left(\frac{R_0}{r}\right)^6$$  \hspace{1cm} (6.6)

where $k_r$ is the radiative decay rate of the donor (in this case the Ir-based dopant) and $R_0$ is the Förster radius, which was calculated based on the spectral overlap integral between the emission spectrum of Ir(fdpt)$_3$ and the absorption spectrum of DMAC-DPS$^{34}$. $r$ is the distance between the donor and acceptor molecules. This value is estimated by assuming the molecules are hard-spheres and uniformly distributed throughout the layer. It would not be dependent on the dopant concentration since energy transfer is occurring from the dopant to the host and there will always be a host molecule in direct contact with a dopant molecule. $k_D$ was not fixed in the fitting but similar values were found for all the different dopant concentrations, as was expected since the donor-acceptor distance should not be changing.

The Förster and Dexter rate constants were found to be $8.9 \times 10^9 \text{ s}^{-1}$, and $2.1 \times 10^9 \text{ s}^{-1}$, respectively. Based on these two values, the faction of excitons that are transferred from the dopant to the singlet, $\phi_S$, or triplet, $\phi_T$, state of the DMAC-DPS is 0.806 and 0.194, respectively. This was calculated by:

$$\phi_{S/T} = \frac{k_{F/D}}{k_F + k_D}$$  \hspace{1cm} (6.7)

If more excitons are formed on the dopant then more excitons will initially exist in the singlet state of the host. This consequently will lead to a larger fraction of excitons undergoing prompt fluorescence and having a short exciton lifetime. A smaller number of excitons will undergo the delayed fluorescence mechanism where it’s more likely to undergo undesirable annihilation processes due to the long exciton lifetimes. We propose that this is the mechanism for improved
devices lifetime reported in this manuscript. In the presence of the dopant, the portion of excitons to in the singlet state of the TADF molecule, $\alpha_p$, is:

$$\alpha_p = [\gamma \phi_S + (1 - \gamma)0.25]$$

(6.8)

If we multiply $\alpha_p$ by $\phi_{PF} = k_F \tau_{PF}$, the fraction of excitons initially in the singlet state that undergo prompt fluorescence, which is 0.23 for DMAC-DPS\textsuperscript{44,121}, then we get the fraction of all excitons undergoing prompt fluorescence. The first term accounts for the excitons that are Förster energy transferred to the host while the second is the fraction of excitons formed directly on the host that are in the singlet state. In the undoped device, where all the excitons are formed on DMAC-DPS ($\gamma = 0$), $\alpha_p$ is just 0.25, as would be expected in the singlets to triplets ratio in electrical excitation. From Figure 41b, there’s a clear trend of increasing $\gamma$ with dopant concentration which leads to an increase in $n_p$. The reduction in the fraction of long-lived excitons would lead to a reduction in singlet-triplet annihilation processes that cause the high energy states that degrade the organic materials.

Although the $k_{ST}$ rate constants are similar for the different dopant concentration, the overall reduction in the triplet exciton population would lead to a reduced STA rate ($=k_{STnT}$). By solving Equations 5.3-5.5 as a function of time, we can calculate the triplet exciton densities as shown in Figure 41c. The $k_{ST}$ and $\gamma$ values from the EQE fittings were used for the different dopant concentrations. There’s a clear trend of reduced triplet population on DMAC-DPS with increasing dopant, further indicating the reduction of long-lived excitons. There’s a smaller reduction in the triplet population at the lower concentration with a drastic reduction at 20wt%. This corresponds well with the trend observed in the device lifetime, with only small improvements in the lifetime at the lower concentrations and 20x improvement at 20wt% doping, corresponding to a $\gamma$ value approaching unity.
The lifetime data can also be used to confirm that less organic degradation is occurring. Figure 42 shows the change in voltage ($\Delta V(t) = |V(t) - V(0)|$) with time needed to maintain a constant current density at an initial luminance of 1,000 cd/m$^2$. There is a drastic reduction in $\Delta V$ with increasing dopant concentration. A previous study by the Forrest group$^{31}$, has shown that an increase in voltage is due to the formation of trap defects that resulted from the degradation of the organic materials. The non-radiative products of the molecular dissociation of the organics create energy levels within the bandgap of DMAC-DPS, which act as traps for the charge carriers. They’re charged when filled, leading to an increase in voltage as more trap defects are formed with time. A decrease in the $\Delta V(t)$ is an indication that less organic degradation is occurring, bringing about longer-lived blue OLED devices.
**Figure 42** Time evolution of the change in voltage for an initial luminance of 1,000cd/m² at different Ir(fdpt)₃ dopant concentrations

**EQE Model - Rate equations for different annihilation processes** (Neat DMAC-DPS system)

The details for the different annihilation processes can be found in reference 32.

Triplet-triplet annihilation: \( T_1 + T_1 \rightarrow S_1 + S_0 \) or \( T_1 + S_0 \)

Since TTA can result in the formation of an excited singlet state, there’s are additional terms for the \( n_s \) and \( n_T \) rate equations:

\[
\frac{dn_s}{dt} = -(k_r + k_{ISC})n_S + k_{RISC}n_T + \frac{J}{4eW} + \frac{1}{4}k_{TT}n_Tn_T \tag{6.9}
\]

\[
\frac{dn_T}{dt} = -(k_{nr} + k_{RISC})n_T + k_{ISC}n_S + \frac{3J}{4eW} - \frac{5}{4}k_{TT}n_Tn_T \tag{6.10}
\]

Singlet-Singlet annihilation: \( S_1 + S_1 \rightarrow S_0 + S_1 \)

\[
\frac{dn_s}{dt} = -(k_r + k_{ISC})n_S + k_{RISC}n_T + \frac{J}{4eW} - \frac{1}{2}k_{SS}n_S^2 \tag{6.10}
\]
\[
\frac{d n_T}{dt} = -(k_{nr} + k_{RISC}) n_T + k_{ISC} n_S + \frac{3J}{4eW} \quad (6.11)
\]

**Triplet-Polaron annihilation:** \(T_1 + e^- \xrightarrow{k_{TP}} S_0 + e^- \) or \(T_1 + h^+ \xrightarrow{k_{TP}} S_0 + h^+\) where * denotes an excited state and \(n_p\) is the polaron population density.

\[
\frac{d n_S}{dt} = -(k_r + k_{ISC}) n_S + k_{RISC} n_T + \frac{J}{4eW} \quad (6.12)
\]

\[
\frac{d n_T}{dt} = -(k_{nr} + k_{RISC}) n_T + k_{ISC} n_S + \frac{3J}{4eW} - k_{TP} n_T n_p \quad (6.13)
\]

\[
\frac{d n_p}{dt} = \frac{J}{eW} - k_L n_p^2 \quad (6.14)
\]

\[k_L = \frac{e(\mu_e + \mu_h)}{\varepsilon_0 \varepsilon_r} \text{ (rate constant for Langevin recombination)} \quad (6.15)\]

**Singlet-Polaron annihilation:** \(S_1 + e^- \xrightarrow{k_{SP}} S_0 + e^- \) or \(S_1 + h^+ \xrightarrow{k_{SP}} S_0 + h^+\)

\[
\frac{d n_S}{dt} = -(k_r + k_{ISC}) n_S + k_{RISC} n_T + \frac{J}{4eW} - k_{SP} n_T n_p \quad (6.16)
\]

\[
\frac{d n_T}{dt} = -(k_{nr} + k_{RISC}) n_T + k_{ISC} n_S + \frac{3J}{4eW} \quad (6.17)
\]

\[
\frac{d n_p}{dt} = \frac{J}{eW} - k_L n_p^2 \quad (6.18)
\]

**Triplet-triplet annihilation and Singlet-triplet annihilation**

\[
\frac{d n_S}{dt} = -(k_r + k_{ISC}) n_S + k_{RISC} n_T + \frac{J}{4eW} + \frac{1}{4} k_{TT} n_T n_T - k_{ST} n_s n_T \quad (6.10)
\]

\[
\frac{d n_T}{dt} = -(k_{nr} + k_{RISC}) n_T + k_{ISC} n_S + \frac{3J}{4eW} - \frac{5}{4} k_{TT} n_T n_T \quad (6.10)
\]

The rate equations were solved simultaneously in steady state \(\left(\frac{d n_S}{dt} = 0, \frac{d n_T}{dt} = 0, \frac{d n_p}{dt} = 0\right)\), and the \(n_s\) is used to calculate the EQE. Analytical equations for \(n_s\) can be found for all the processes except the ones involving TTA. For TTA, numerical methods were used. The equations can be altered for the case with the dopant by adding terms to account for exciton formation on the dopant and energy transfer to the TADF host.
6.3 Conclusions

Through EQE modelling, we were able to quantitatively analyze the effect of the dopant on the initial distribution of singlet and triplet excitons on the TADF molecule. As expected, with higher dopant concentration, more excitons are formed on the Ir-complex rather than the DMAC-DPS. Since $k_F > k_D$ in the set of materials used, more excitons underwent Förster energy transfer leading to an increase in singlet excitons initially on DMAC-DPS. The device lifetime could potentially be further improved for a set of materials where $k_F >> k_D$ so that $\phi_s$ approached 1 and all excitons formed on the dopant would be transferred to the singlet state of the host. Additionally, TADF materials with a larger $\phi_{PF}$ would also further extend the device lifetime.

A paper by Fukagawa et al.\textsuperscript{122} studied devices lifetime in a system consisting of a TADF host and phosphorescent emitters. In this case, emission from occurring from the phosphorescent dopant. A strong correlation between the Förster energy transfer rate from the host to the dopant and the $t_{50}$ device lifetime was found. The Förster energy transfer rate was changed by altering the donor-acceptor separation distance through the use of different host materials. Host materials with smaller molecular radii lead to shorter donor-acceptor separation distances and thus would have faster Förster energy transfer rates. This is different than the work presented here since the Förster energy transfer rate is essentially unchanged in the proposed system where energy transfer occurs from the dopant to the host. In the typical system where energy transfer occurs from the host to the dopant, the energy transfer rate is largely dependent on the dopant concentration. Assuming dopants are distributed evenly throughout the layer, the average separation distance between the host and the dopant is reduced at higher dopant concentrations leading to faster Förster energy transfer. When energy transfer is occurring from the dopant to the host material then the donor molecule (the dopant) is always in contact with an acceptor molecule (the host), thus making the separation distance essentially equal to the interatomic distance between a dopant and host molecule packed next to one another. In our system, the Förster energy transfer rate is unchanged as the dopant concentration is increased. Therefore, improved device lifetime observed at higher dopant concentrations cannot be explained using the mechanism proposed by Fukagawa et al. Instead, it’s the increase charge trapping and exciton formation on the dopant molecule that allows more excitons to be transferred to the singlet state of the TADF host through the Förster
mechanisms and thus reduces the fraction of long-lived excitons and improve the device lifetime.

Although the device lifetimes reported are very short, we have presented a method to drastically improve the device lifetime of a blue TADF material. Ideally, as more efficient and chemically stable TADF molecules are developed, the mechanism outlined in this manuscript can be employed to achieve the long device lifetimes needed for solid-state lighting.
Chapter 7
Summary and future work

7.1 Summary

In summary, three important factors for designing white OLEDs for lighting were studied; they were energy transfer processes, colour stability and device lifetime.

In Chapter 4, energy transfer processes in two-dopant sensitized fluorescence OLED devices were studied. A technique for quantifying the competitive nature between Förster and Dexter energy transfer mechanisms using EL emission spectra was presented. From this simple model, key physical parameters could be quantified for the set of materials used. Contrary to the general thought that Dexter is dominant at close range, the data showed that it is theoretically possible for the Förster mechanism to overtake Dexter at short donor-acceptor separation distances. Furthermore, by varying the fitting parameters, we were able to simulate and study how the efficiency of the two energy transfer processes changes for different sets of materials.

In Chapter 5, the TADF molecule, DMAC-DPS, was studied for its potential to act as both the host and blue emitter in a highly simplified single-emitting-layer white OLED. The three-organic layer device utilized two lower energy phosphorescent emitters to achieve a power efficiency of 30.3 lm/W and EQE of 18.8% at 1,000 cd/m². Additionally, the device demonstrated high colour quality with CRI of 75 and little colour shifting. It was found that colour stability is greatly improved when large interfacial barriers are removed from multi-layered devices. The elimination of interfacial barriers reduced the voltage needed to enter the regime where charge transport through the emissive layer is dominant. In this regime, excitons are primarily formed on the higher energy dopant and distribution to the other coloured emitters is through energy transfer mechanisms that are voltage-independent.

Finally, in Chapter 6, the lifetime of DMAC-DPS-based TADF devices was studied. A strategy for improving its lifetime was proposed wherein an Ir-based dopant was introduced to alter the initial singlet to triplet exciton ratio on the TADF molecule. By increasing the number of singlets on the DMAC-DPS, the population of long-lived excitons was reduced thereby decreasing the annihilation processes leading to device degradation during operation. Rate equations that govern the processes occurring in this system was developed and used to quantify the effect of the
dopant concentration on the fraction of excitons undergoing prompt fluorescence. Using this approach, it was found that nearly all excitons are formed on the dopant at 20wt% doping, leading to ~80% of excitons being transferred to the singlet-state of the DMAC-DPS. In this case, ~18.3% \((= 80\% \times \phi_{PF})\) of the excitons undergo prompt fluorescence versus ~5.75% \((= 25\% \times \phi_{PF})\) in the undoped DMAC-DPS. This is a reduction of ~12.5% in the long-lived exciton population resulting in a 20-fold increase in the device lifetime. By selecting material combinations with \(k_F >> k_D\) and a TADF molecule with high \(\phi_{PF}\), the lifetime can theoretically be even further lengthened.

7.2 Future work

The platform presented for improved blue OLED device lifetime was able to greatly extend the operational lifetime of DMAC-DPS-based devices. However, the lifetimes are still very short and not even comparable to the lifetime of blue phosphorescent OLEDs\(^{44,121}\). It is currently limited by the inherently instability of the DMAC-DPS. This material was originally chosen due to its high PLQY and commercial availability. The next step would be to test this system with more chemically stable TADF emitters in order to achieve a device with efficiency that rivals phosphorescent OLEDs and with a lifetime comparable to fluorescent emitters. A large variety of blue TADF s are now readily available for purchase\(^{123}\) and many new blue TADF molecules with inherently longer device lifetimes than DMAC-DPS have been reported\(^{124}\).

Another possibility would be to work in collaboration with a materials synthesis group, in order to produce a TADF and dopant molecule combination that specifically meets criteria necessary to maximize how much the proposed platform can improve the lifetime of the blue devices. In addition to the TADF being chemically stable, it could be designed to have more efficient prompt fluorescence (i.e. higher \(\phi_{PF}\)) and a better electron and hole balance. In terms of the dopant molecule, the energy levels can be engineered to trap both holes and electrons to better induce exciton formation on the dopant. This will enable lower concentrations of the dopant to be used. Furthermore, improving the overlap between the emission spectrum of the dopant and the absorption spectrum of the TADF will increase the Förster transfer rate further above the Dexter rate, thereby maximizing the number of singlet excitons transferred to the TADF.

The next direction for the future work would be to apply the concept to improve the device lifetime in a white OLED device. The best blue TADF and dopant combination can be used in the
simplified single-emissive-layer white OLED structure presented in Chapter 5. Theoretically, the resulting white OLED system should experience less significant efficiency roll-off and thus have better efficiency performance at 1,000cd/m². The annihilation processes that lead to high energy species that degrade the organic materials are also responsible for efficiency roll-off. The reduction in the population of long-lived excitons in the optimized TADF-dopant combination should help improve both the lifetime and efficiency of the white device.

Finally, the efficiency of the resultant white OLED can be further improved to compete with the performance of current inorganic LEDs (>100m/W) by utilizing outcoupling techniques. Due to the difference in the refractive index between the organic materials, electrodes, glass substrate and atmosphere, approximately 80% of the emitted light is actually trapped within the device. This means that the efficiency of the white devices can potentially be improved by 5-fold. Simple micro-arrays have been shown to improve the out-coupling efficiency by a factor of 1.8 while more complicated optimized micro-lens arrays have improved the outcoupling efficiency by 70%. Other tactics can also be employed to further improve the out-coupling.

Together, all these strategies could potentially achieve a white OLED that meets the efficiency, colour stability and device lifetime requirements needed for solid-state lighting.
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