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Bimolecular Annihilation Processes in OLEDs

Department of Materials Engineering

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This thesis investigates the physical limitations and efficiency roll-off of organic light-emitting diodes (OLEDs) at high brightness levels. Due to the low dielectric constant of organic semiconductors, tightly bound excitons are formed, which at high current densities trigger bimolecular loss mechanisms such as triplet–triplet annihilation (TTA) and triplet–polaron annihilation (TPA). These phenomena reduce device efficiency and generate heat as well as high-energy excited states, which cause chemical damage to the materials and shorten the operational lifespan of the device.

The study demonstrates that these losses can be managed by restricting exciton diffusion through host–guest systems or by accelerating radiative recombination using optical microcavities. The development of OLED devices requires a constant balance between high efficiency, durability, and manufacturing complexity. Future research should focus particularly on improving the stability of blue emitters and developing more precise kinetic models to ensure the reliability of mass-produced devices.

Keywords: OLED, Triplet–Triplet Annihilation (TTA), Triplet–Polaron Annihilation (TPA), Efficiency Roll-off, External Quantum Efficiency (EQE), Host–Guest Systems

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Tämä tutkielma selvittää orgaanisten valodiodien (OLED) fysikaalisia rajoitteita ja hyötysuhteen laskua (efficiency roll-off) suurilla kirkkaustasoilla. Orgaanisten puolijohteiden pieni dielektrisyysvakio johtaa tiukasti sitoutuneiden eksitonien muodostumiseen, jotka suurilla virrantiheyksillä aiheuttavat bimolekulaarisia häviömekanismeja, kuten tripletti–tripletti- (TTA) ja tripletti–polaroni-annihilaatiota (TPA). Nämä ilmiöt heikentävät laitteen tehokkuutta ja synnyttävät hukkalämpöä sekä korkeaenergiatiloja, jotka vaurioittavat materiaaleja kemiallisesti ja lyhentävät laitteen käyttöikää.

Tutkielmassa osoitetaan, että häviöitä voidaan hallita rajoittamalla eksitonien diffuusiota isäntä–vieras-järjestelmillä tai nopeuttamalla niiden säteilevää rekombinaatiota mikrokaviteettien avulla. OLED-laitteiden kehitys vaatii jatkuvaa tasapainottelua valotehon, kestävyyden ja valmistusmonimutkaisuuden välillä. Tulevaisuuden tutkimuksen on keskityttävä erityisesti sinisten emitterien kestävyyteen ja tarkempaan kineettiseen mallintamiseen massatuotannon laadun varmistamiseksi.

Avainsanat: OLED, Tripletti-Tripletti Annihilaatio (TTA), Tripletti-Polaroni Annihilaatio (TPA), Ulkoinen kvanttihyötysuhde (EQE), Isäntä-vieras-systeemi

Abbreviations:
OLED – Organic Light–Emitting Diode
PHOLED – Phosphorescent Organic Light–Emitting Diode
HOMO – Highest Occupied Molecular Orbital
LUMO – Lowest Unoccupied Molecular Orbital
ETL – Electron Transport Layer
HTL – Hole Transport Layer
EML – Emissive Layer
TTA – Triplet–Triplet Annihilation
TPA – Triplet–Polaron Annihilation
EQE – External Quantum Efficiency
IQE – Internal Quantum Efficiency
TADF – Thermally Activated Delayed Fluorescence
RISC – Reverse Intersystem Crossing

Symbols:
L_D – Exciton diffusion length
τ – Exciton lifetime
S_1 – Lowest excited singlet state
T_1 – Lowest excited triplet state
S_0 – Singlet ground state
ϵ_r – Dielectric constant
E_g – Optical band gap

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1 Introduction

Organic Light-Emitting Diodes (OLEDs) have become essential for modern displays and lighting, currently used in the majority of smartphones. Unlike Liquid Crystal Displays (LCDs), OLEDs are self-emissive, removing the need for a separate backlight. Their pixels, made from organic materials, emit red, green, and blue light. This structure allows individual pixels to be completely deactivated, resulting in an exceptional contrast ratio and “true blacks”. Because the structure of an OLED is based on ultrathin organic layers, devices can be made highly flexible and transparent, expanding the possibilities for device design. Despite these advantages, OLEDs face significant physical limitations when operated at high brightness levels. [1]

Achieving high brightness requires driving a large electrical current through the device. This leads to a high density of excited states, known as excitons, within the emissive layer. At these high concentrations, excitons undergo bimolecular annihilation processes. These interactions generate unwanted heat that degrades the organic materials and shortens the device’s lifespan. Furthermore, they cause a severe drop in the device’s efficiency, a phenomenon referred to as efficiency roll-off. Understanding these physical phenomena is essential for developing brighter and more durable displays. [2]

OLED materials are traditionally categorized into three generations based on their emission mechanisms. First-generation OLEDs rely on fluorescence. While they are cost-effective and have long operational lifetimes, their Internal Quantum Efficiency (IQE) is limited. Second-generation OLEDs utilize phosphorescence, achieving high efficiency, but they rely on expensive and rare heavy metals like iridium. Third-generation technology, Thermally Activated Delayed Fluorescence (TADF), aims to maintain high efficiency without such metals. While the display industry currently relies on a combination of fluorescent and phosphorescent emitters, the transition toward TADF systems remains a significant area of development. [3]

This thesis investigates the mechanisms behind these exciton interactions, their impact on device degradation and the structural strategies employed to suppress them. Three key research questions are addressed:

1. What physical phenomena cause bimolecular annihilation in organic semiconductors?
2. How do these annihilation processes impact the efficiency and operational lifespan of OLEDs at high brightness?
3. What structural strategies can be used to prevent these interactions?

The study is a literature review based on peer-reviewed scientific articles, physics journals, and foundational textbooks. The scope is limited to the internal physics of OLED devices, excluding other optoelectronic applications, manufacturing or chemical synthesis. Furthermore, the analysis focuses primarily on the behavior of long-lived triplet excitons, as singlet excitons typically decay before significant annihilation occurs [2]. This work aims to provide comprehensive overview of the factors driving the efficiency roll-off and material degradation in OLED devices.

Artificial Intelligence (Gemini 1.5 Pro) was used to improve clarity and flow of the thesis. Additionally, AI (Gemini 1.5 Pro and SciSpace) was used to screen source materials for relevance and identify key themes to speed up the review process. All suggestions provided by the AI were critically evaluated by the author.

2 Physics of Organic Semiconductors

Organic semiconductors are carbon-based materials that form the active layers of OLED devices. They differ fundamentally from traditional inorganic semiconductors, such as silicon, in terms of their chemical bonding and structural order. While inorganic semiconductors are composed of atoms bound by strong covalent bonds into a crystalline structure, organic solids consist of discrete molecules held together by weak Van der Waals forces. [4]

This difference in bonding leads to two significant physical consequences. First, organic materials are often amorphous, which limits the mobility of electrical charges. Second, due to the weak intermolecular interactions, organic materials have a low dielectric constant ($\epsilon_r \approx 2 - 3$) [5] compared to inorganic semiconductors ($\epsilon_r \approx 11$) [4]. Because this low dielectric constant cannot effectively screen electric fields, the electrostatic attraction between charge carriers is strong. Consequently, electron–hole pairs form tightly bound states known as excitons. These properties (slow charge transport and high exciton binding energy) explain why excitons accumulate and undergo annihilation in OLED devices. [4]

2.1 Electrical Conductivity of Organic Semiconductors and OLED Working Principle

The electrical conductivity and optical properties of organic materials are based on the π-conjugation of carbon atoms. In typical organic molecules, electrons are tightly bound between atoms, making them electrical insulators. However, in conjugated materials, carbon atoms are linked by alternating single and double bonds. While single bonds hold the molecular structure together, the delocalized electron cloud from the double bonds acts as a pathway, allowing to move within the molecule and carry electrical current. [6]

This delocalization creates two primary frontier molecular orbitals, known as HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital). The HOMO is analogous to the valence band, while the LUMO is analogous to the conduction band found in inorganic semiconductors. The energy difference

between these levels (E_g) defines the optical band gap and therefore the color of the emitted light. When an electron transitions from the LUMO back to the HOMO, the excess energy is released as a photon (or a phonon, i.e., heat.) [6]

An OLED typically consists of a thin-film multilayer structure placed between two electrodes with a total thickness of approximately $100\ \mathrm{nm}$. A standard structure includes the following layers [7]:

1. Anode: A positive electrode (typically transparent Indium Tin Oxide, ITO) for hole injection.
2. HTL (Hole Transport Layer): Enables the transport of holes.
3. EML (Emissive Layer): The central layer where light generation occurs.
4. ETL (Electron Transport Layer): Enables the transport of electrons.
5. Cathode: A negative electrode (typically a low work-function metal) for electron injection.

This multilayer heterostructure is designed to optimize charge injection and confine charge carriers within the emissive layer through organic layers' energy level alignment [7]. The structure of an OLED is illustrated in Figure 1.

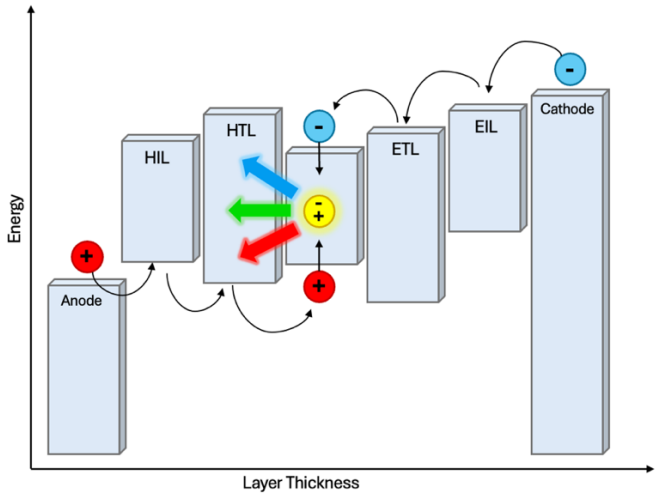

Figure 1. Schematic energy level diagram and working principle of a multilayer OLED. The arrows illustrate the process of charge injection from the electrodes, charge transport through the functional layers (HIL (Hole Injection Layer), HTL, ETL, EIL (Electron Injection Layer)), and the final formation of excitons within the Emissive Layer (EML). The alignment of the energy levels is designed to confine charge carriers and excitons effectively within the EML to maximize radiative recombination. (Modified from Pols et al. [8])

The working principle of an OLED is based on electroluminescence, which can be described as a four-step process [7]:

1. Charge injection: When an external voltage is applied, electrons are injected from the cathode into the LUMO of the organic material, while holes are injected from the anode into the HOMO.

2. Charge transport: The charge carriers drift through the transport layers (HTL and ETL) and are driven by an electric field toward the center of the device.

3. Exciton formation: Electrons and holes meet within the Emissive Layer (EML). Due to the low dielectric constant of the organic material, the opposing charges attract each other strongly via the Coulombic interaction, forming a bound state called an exciton.

4. Radiative recombination: The exciton decays as the electron relaxes to the ground state. The excess energy is released as a photon, resulting in light emission.

2.2 Polarons and Hopping Mechanism

In organic semiconductors, the behavior of charge carriers conducting electrical current differ significantly from the free electrons and holes found in inorganic materials. These materials typically have a low dielectric constant, meaning the material cannot effectively screen electric charges. Consequently, when an excess charge is injected, its electric field induces a strong local polarization and structural distortion of the surrounding molecules. [5]

A charge (an electron or a hole) with its surrounding molecular distortion known as a polaron [5]. Because interactions in organic materials are short-range, this polarization effect is limited to the nearest neighboring molecules and is often referred to as a small polaron [9]. Polarization causes the charge to localize and “self-trap” at the molecular unit, and its effective mass increases significantly because it must carry the polarization energy as it moves [5].

Due to the weak intermolecular bonds and structural disorder, organic energy levels (HOMO and LUMO) are highly localized rather than forming the continuous energy bands typical of crystalline silicon. Therefore, instead of flowing freely as delocalized waves (band transport), charge carriers move through a process called incoherent hopping. [5]

The primary consequence of the hopping mechanism is a significantly reduced charge carrier mobility (μ). Because every jump is a discrete, energy-dependent event, the overall movement is slow, typically three to six orders of magnitude lower than in inorganic semiconductors. For the operation of OLEDs, this low mobility can lead to accumulation of charges within the emissive layer. [5]

2.3 Excitons

When an electron meets a hole within the emissive layer (EML) of an OLED, their opposite charges attract through electrostatic forces. Together, they form an electrically neutral, bound electron–hole pair known as an exciton. In organic semiconductors, this pair is referred to as a Frenkel exciton. This means that the electron and hole are localized, typically staying on the same molecule or immediately adjacent ones. Consequently, a Frenkel exciton has a small physical radius (approximately 1 nm), typically on the order of the dimensions of a single molecule. [5]

Frenkel exciton state is a direct consequence of the material's electronic properties. As discussed in previous sections, organic materials have a low dielectric constant. Because the surrounding material cannot effectively screen the electric field between the two charges, the electrostatic Coulomb attraction remains strong. This results in a high binding energy, typically ranging from $0.5 - 1.0\ \mathrm{eV}$. Since this is significantly greater than the thermal energy at room temperature, Frenkel excitons are stable under ambient conditions. [5]

This behavior differs fundamentally from traditional inorganic semiconductors. Inorganic crystals have high dielectric constants that effectively screen the electric field, resulting in loosely bound electron–hole pairs known as Wannier-Mott excitons. These excitons have a large radius extending across thousands of atoms and a low

binding energy, often less than $10\ \mathrm{meV}$. Wannier-Mott excitons easily dissociate into free charges and are typically stable only at low temperatures. [5]

2.3.1 Singlet and Triplet States

Both electrons and holes have a quantum mechanical property known as spin, which can be oriented either “up” or “down”. When these carriers meet to form an exciton, their individual spins combine according to quantum mechanics, resulting in four possible spin configurations. [5]

One combination result in an antisymmetric spin state, forming a singlet exciton (S_1). The other three combinations result in parallel symmetric spins, forming triplet excitons (T_1). Because charge injection in an OLED is statistically random, these excitons form in a 1:3 ratio: 25% are singlets and 75% are triplets. The T_1 state always resides at a lower energy level than corresponding S_1 state due to the electron exchange interaction. [6]

This 1:3 ratio significantly impacts device efficiency. In most organic molecules, the ground state (S_0) is a singlet state. For a singlet exciton, the transition back to the ground state $(\mathrm{S}_1 \rightarrow \mathrm{S}_0)$ is spin allowed, occurring rapidly (typically on a nanosecond timescale) and releasing energy as a photon through fluorescence.

In contrast, for a triplet to return to ground state $(T_1 \rightarrow S_0)$, the electron would have to reverse its spin orientation. This process is quantum mechanically “spin-forbidden”, meaning triplet excitons cannot easily decay by emitting light. If a triplet exciton does decay radiatively, the emission is referred to as phosphorescence. Consequently, they possess long lifetimes, ranging from microseconds to milliseconds. [6]

The long lifetime of triplets makes them problematic, particularly at high brightness levels. Because triplets are generated in large numbers and cannot decay quickly, they accumulate in the emissive layer. As these triplet excitons diffuse through the material, they are likely to interact with one another or with slow-moving polarons. These interactions lead to non-radiative energy losses known as Triplet–Triplet Annihilation (TTA) and Triplet–Polaron Annihilation (TPA). [2]

2.3.2 Diffusion of Excitons

Unlike polarons, which are driven by an external electric field, an exciton is electrically neutral. Consequently, their movement is not directed by an electric field but is instead driven by concentration gradients. This process is known as diffusion, which can be described as a random walk, where the exciton transfers its energy from one molecular site to an adjacent one. [2]

In solid organic materials, this energy transfer occurs by one of two mechanisms, long-range Förster transfer or short-range Dexter transfer. Förster Resonance Energy Transfer (FRET) allows an exciton to transfer its energy through space to a neighboring molecule without physical contact, but its efficiency decreases strongly with distance. FRET requires a spin-allowed optical transition, making it efficient for singlet excitons. [2]

In Dexter Energy Transfer electrons exchange between neighboring molecules, requiring their electronic wavefunctions (electron clouds) to physically overlap. This interaction is limited to shorter distances. While both singlets and triplets can utilize this mechanism, it is the primary mode of transport for triplet excitons due to their spin-forbidden nature. [2]

The dynamics of the random walk are characterized by the exciton diffusion coefficient (D), which describes how fast the exciton spreads through the material. The total distance an exciton travels during its lifetime (τ) is defined by its diffusion length $(\mathrm{L_D})$, which can be expressed as [2]:

$$\mathrm{L_D} = \sqrt{\mathrm{D}\tau}\,. \tag{1}$$

As discussed previously, triplet excitons have long lifetimes because their decay to the ground state is spin forbidden. Even though triplets move only short distances per hop via Dexter mechanism, their long lifetimes allow them to make a vast number of hops, potentially leading to significant diffusion length. However, $\mathrm{L_D}$ is highly sensitive to the material's morphology. In disordered or loosely packed materials, excitons can become localized at low energy molecular states which significantly limits their ability to diffuse. [2]

3 Bimolecular Annihilation Mechanisms

The accumulation of polarons and excitons leads to high particle densities, which in turn results in frequent bimolecular interactions. These annihilation processes are often referred to as “quenching” in the literature, as they typically result in the non-radiative loss of excitation energy. [10]

During an annihilation event, the energies of the two interacting particles combine. One particle is destroyed, while the surviving particle is promoted to a highly excited state. From this high-energy state, the particle rapidly relaxes back to its lowest excited level through internal conversion, releasing the excess energy as heat. This process is damaging to the device’s performance, as it results in the loss of an exciton that was originally intended to emit a photon. [11]

The probability of these interactions is diffusion-limited, meaning it depends heavily on the ability of excitons to move through the organic material. A longer exciton diffusion length (L_D) allows a particle to sample a larger volume during its lifetime, which significantly increases the statistical probability of encountering another particle. [2] Depending on the specific particles involved, these annihilation processes can be divided into two main categories.

3.1 Exciton–Polaron Annihilation

Exciton-polaron annihilation occurs when an electrically neutral exciton interacts with a charged polaron, such as a hole or an electron. While this mechanism can involve short-lived singlets (Singlet-Polaron Annihilation, SPA), Triplet–Polaron Annihilation (TPA) is more significant challenge due to the high density and long lifetimes of triplet excitons. [10]

In TPA, the triplet exciton transfers its energy to a nearby charge carrier. The polaron absorbs the energy and is promoted to a higher excited state, while the exciton is quenched to the ground state (S_0). The excited polaron then undergoes rapid relaxation, releasing the excess energy as heat. [10] In addition to reducing the device’s External Quantum Efficiency (EQE), TPA critically drives device degradation [12]. The energy

released during the relaxation of high-energy polaron can exceed the dissociation energy of organic chemical bonds, resulting in irreversible molecular damage [13].

3.2 Exciton–Exciton Annihilation

In exciton-exciton annihilation, two electrically neutral excitons encounter each other, typically leading to the non-radiative decay of one of them. In the context of long-lived excited states, the primary loss mechanism in modern OLEDs is Triplet–Triplet Annihilation (TTA). [10]

When two triplet excitons interact, the outcome depends heavily on the specific properties of the emissive material. In phosphorescent OLEDs (PHOLEDs), TTA acts purely as a loss mechanism. One triplet returns to the ground state, while the other is promoted to a higher triplet state (T_n), eventually losing the excess energy as heat. [2]

However, TTA presents a dual nature in fluorescent devices. In a process known as TTA-upconversion, the collision of two triplets can result in a single light-emitting singlet state (S_1). This allows certain fluorescent OLEDs to exceed the traditional 25% internal quantum efficiency (IQE) limit by recycling non-radiative triplets into delayed fluorescence. [14] However, within the scope of this thesis, TTA is examined as a severe loss mechanism that contributes to efficiency roll-off at high brightness [15].

3.3 Kinetic Modeling of Annihilation Processes

To evaluate the impact of annihilation on device performance, it is essential to use kinetic modeling. The annihilation rate defines the frequency and probability of these bimolecular interactions. The rate can be described as the frequency at which interactions occur within a given volume and on the number of excitons. A higher rate indicates that excitons are more likely to undergo non-radiative annihilation before radiative decay can occur. By using this approach, the energy that is lost to heat can be quantified, providing insight into why OLED efficiency declines as the brightness increases. [7]

In this analysis, the focus is specifically on TTA. Given that triplet excitons have significantly longer lifetimes than singlets, TTA serves as the primary energy loss mechanism in high-performance OLED devices [16]. The effective TTA rate $(\mathrm{k_{TTA}})$ in the emissive layer can be expressed as [7]:

$$\mathrm{k_{TTA}} = \frac{8\pi \mathrm{DR[T]}}{\mathrm{V}} \quad . \tag{2}$$

The interaction radius (R) defines the critical distance at which the probability of annihilation becomes significant [7]. In organic semiconductors, this parameter is controlled by the wavefunction overlap between the two excitons [5]. For an annihilation event to occur, these wavefunctions must physically overlap via Dexter energy transfer, a process that is extremely sensitive to distance [10]. As the distance between two triplet excitons exceeds the molecular radii, the overlap and interaction probability decrease exponentially. [17]

As shown in the Equation (2), the loss rate depends on both exciton diffusion coefficient (D) and the interaction radius (R) [7]. As opposed to the original equation $(8\pi \mathrm{DR})$ [7], this effective rate includes the triplet density $\left(\frac{[\mathrm{T}]}{\mathrm{V}}\right)$ within the given rate $\left(\frac{1}{\mathrm{s}}\right)$, showing how the total annihilation probability increases as the exciton density increases within the emissive layer [10].

The effect of these parameters is illustrated in Figure 2, where scenarios (a) and (b) occupy the same volume (V). In scenario (a), both the interaction radius and diffusion

length are small, and the triplet density $\left(\frac{[T]}{V}\right)$ is low, resulting in fewer interactions. Scenario (b) demonstrates how an increase in these values enhances the probability of exciton overlap. Since $[T]$ increases proportionally with electrical current, these losses become the dominant factor in efficiency roll-off at high brightness levels [16].

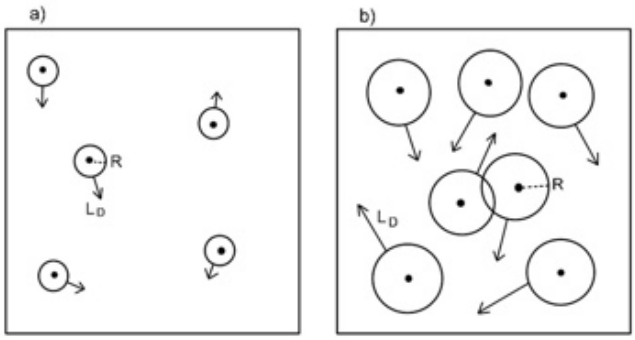

Figure 2. Schematic representation of the physical parameters governing Triplet–Triplet Annihilation (TTA) and fixed volume (V). (a) Low exciton density with small interaction radius (R) and a limited diffusion length (L_D), resulting in a low probability of interaction. (b) High exciton density where the increased diffusion length (L_D) allows excitons to sample a larger volume during their lifetime. This enhanced mobility, combined with a larger interaction radius (R), significantly increases the statistical probability of wavefunction overlap and annihilation. (Image by author)

4 Impact on Device Performance

While the previous chapters examined excitons and polarons at the molecular level, this chapter addresses the macroscopic consequences of these effects on device behavior. Understanding these molecular interactions is fundamental to the optimization of high-performance OLEDs.

Many commercial OLED applications, such as televisions and smartphones, require devices to operate at high brightness levels [1]. To achieve this, a higher current density must be driven through the device, which directly increases the exciton density within the emissive layer [16]. This high density leads to a significant loss in efficiency, known as efficiency roll-off [18], as well as irreversible degradation of the organic materials [13].

4.1 Efficiency Roll-off

Efficiency roll-off is one of the most critical limitations in modern OLED technology [16]. To analyze this effect, External Quantum Efficiency (EQE) is used as a metric. It is defined as the ratio of the number of photons emitted into free space to the number of charge carriers injected into the device. In an ideal scenario, the EQE would remain constant regardless of the brightness level. However, in practical devices, the efficiency declines as the current density increases. [7]

In an ideal OLED, every injected electron–hole pair would form an exciton that decays radiatively. In such case, the exciton population would increase linearly with the current density (J), maintaining a stable EQE across all luminance levels [7]. At low injection leves, the triplet density $\left(\frac{[\mathrm{T}]}{\mathrm{V}}\right)$ is approximately proportional to the current $\left(\frac{[\mathrm{T}]}{\mathrm{V}} \propto \mathrm{J}\right)$. As the current density increases, triplets accumulate in the emissive layer. [16] Since TTA involves the interaction of two particles, the time derivative of this process depends on the square of density, $\left(\frac{[\mathrm{T}]}{\mathrm{V}}\right)^2$. Consequently, at high current densities, the triplet population no longer increases linearly but sub-linearly $\left(\frac{[\mathrm{T}]}{\mathrm{V}} \propto \sqrt{\mathrm{J}}\right)$ [16]. This non-linear relationship is the primary cause of efficiency roll-off [18].

The practical impact of these losses is demonstrated in Figure 3, which shows a typical EQE versus current density plot for phosphorescent OLED [19]. As shown in the logarithmic plot, EQE peaks at very low current densities (approximately at $0.02\ \frac{\mathrm{mA}}{\mathrm{cm}^2}$) and declines steeply as the injection levels approach $100\ \frac{\mathrm{mA}}{\mathrm{cm}^2}$, falling from over 10% to nearly 0.1% [19].

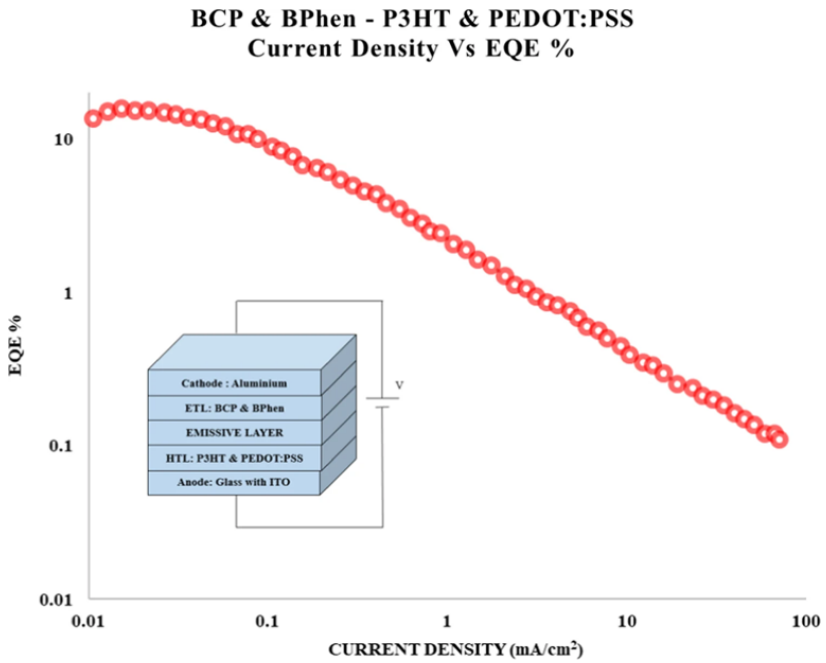

Figure 3. External Quantum Efficiency (EQE) as a function of current density for a PHOLED. The figure displays the device structure, including the specific materials used for the transport and emissive layers. The logarithmic plot illustrates a significant efficiency roll-off, where the EQE declines from a peak of approximately 15% to nearly 0.1% as the current density increases, primarily due to bimolecular annihilation processes. (Image reproduced with permission from Springer Nature [19]).

4.2 Thermal Loss and Morphological Stability

The energy dissipated through bimolecular annihilation processes does not simply vanish, but is released as non-radiative heat within the organic layers [20]. This continuous internal heating poses a severe threat to the physical structure of the device, as organic emissive layers are typically composed of soft, amorphous thin films. The morphological stability of these layers is primarily governed by their glass transition temperature ($\mathrm{T_g}$). [21]

High current densities and heat generated by bimolecular annihilation (TTA and TPA) causes the internal temperature of the device to rise significantly [7]. If this local heating

reaches or exceeds the T_g of the emissive layer, the molecules gain enough thermal energy to overcome intermolecular forces and move from their fixed positions [21]. Such molecular mobility can lead to irreversible morphological changes, such as crystallization or phase separation, which drastically impair the device performance and operational lifespan [22].

As these crystallized regions become rough and uneven, the emissive layer loses its ideal physical contact with adjacent layers. This can block charge flow and results in the formation of non-emissive regions, commonly referred to as “dark spots” [23]. To prevent such structural failures, OLED layers must be engineered for high thermal resistance. Utilizing mixed-host emissive layers, for example, can prevent molecular crystallization and significantly extend the device’s operational stability [24].

4.3 Chemical Degradation and Trap Formation

In addition to morphological damage, the high-energy states generated by annihilation processes can lead to direct chemical destruction of the organic molecules [13]. As discussed in Chapter 3, during a bimolecular annihilation, the surviving particle absorbs the energy of both participants, promoting it to a highly excited state [11]. The energy of these “hot excitons” or “hot polarons” can exceed 6 eV, which can surpass the bond dissociation energy of the organic molecules [25]. This results in the cleavage of chemical bonds, causing the molecule permanently lose its electroluminescent properties [25]. This event is particularly problematic in blue-emitting OLEDs, where triplet energies are already exceptionally high [12].

When a molecule is chemically broken, its fragments remain in the emissive layer and can form new electronic defect states, known as charge traps. These trap states are directly driven by TPA. [26] They capture injected electrons and holes, disrupting the electrical balance of the device and acting as non-radiative recombination centers [27]. The progressive accumulation of non-radiative centers results in a permanent, uneven loss of brightness, a phenomenon widely known as screen burn-in [28]. Consequently, controlling bimolecular interactions is not only a matter of maximizing efficiency but is fundamental to ensuring the long-term reliability of organic displays.

5 Management and Optimization Strategies

To prevent efficiency roll-off and device degradation, exciton dynamics must be precisely controlled within the OLED structure. This chapter introduces two primary strategies for suppressing annihilation: physically isolating excitons to prevent interactions and accelerating their radiative decay to limit the time available for annihilation to happen.

5.1 Host–Guest Systems

The implementation of host–guest systems within the emissive layer is a standard approach to reduce efficiency-roll off and material degradation. A well-designed host–guest system effectively traps excitons on specific molecular sites, restricting their mobility and preventing high local exciton densities. [29]

This strategy involves doping a small concentration of guest molecules into a wider-bandgap host matrix. Maintaining a low dopant concentration ensures physical separation between the emissive guest molecules, thereby minimizing non-radiative energy loss caused by intermolecular proximity. If the concentration is too high, the molecules are forced too close together, leading to unwanted energy transfer and heat instead of radiative emission. [29]

The host material is selected to have energy levels (HOMO and LUMO) that straddle those of the guest, thereby confining exciton movement. When excitons form on or transfer to the guest molecules, their surrounding high-energy host acts as a potential barrier. This prevents the exciton from diffusing back into the host matrix. Crucially, the rapid energy transfer from the host to the guest ensures that the host's excited states are deactivated faster than they can undergo bimolecular interactions. [30]

The operation of a host–guest system is based on the precise alignment of the materials' energy levels. Effective exciton confinement requires the host triplet energy level (T_1) to exceed that of the guest, which enables the exciton transfer within the guest molecules. In third generation Thermally Activated Delayed Fluorescence (TADF) systems, the small energy gap between the guest's T_1 and S_1 states allow for reverse

intersystem crossing (RISC). This converts non-radiative triplets into radiative singlets, as illustrated in the Jablonski diagram in Figure 4. [31]

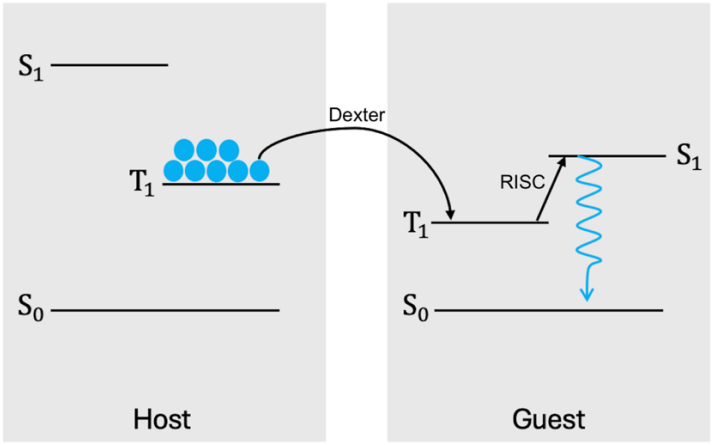

Figure 4. Jablonski diagram of a TADF-based host–guest system, where the blue icons illustrate the accumulation of triplet excitons at the host's T_1 level, transferring via Dexter mechanism to the guest. The small energy gap between the guest's T_1 and S_1 states enable upconversion via reverse intersystem crossing (RISC) and radiative emission. (Image by author)

While basic host–guest systems confine excitons effectively, high current densities can still create a bottleneck if excitons accumulate within a narrow recombination zone [30]. To prevent this, the recombination zone can be broadened to distribute excitons over a larger volume [32]. This is often achieved by using mixed-host systems, which balance the transport of electrons and hole to widen the area of exciton generation, lowering the local density [33].

Although the host–guest systems are effective in suppressing annihilation, they increase manufacturing complexity. Precise doping requires complex techniques, such as co-evaporation, which can elevate production costs. Consequently, developing doping-free alternatives has become a significant focus in recent research to simplify device engineering. [34]

5.2 Exciton Lifetime Management

An alternative strategy for reducing annihilation is to shorten the exciton lifetime. Since the probability of interaction increases with the time an exciton spends in the excited state, shortening their lifetime reduces the opportunity for interaction. [35] As discussed in Chapter 5.1, third-generation TADF technology achieves this by RISC, which transfers triplet excitons into shorter-lived radiative singlets, reducing the opportunity for TTA and TPA to occur [34].

Another approach for shortening the lifetime of excitons involves using optical microcavities. A microcavity is constructed by placing the organic layers between a highly reflective mirror (cathode) and a semi-transparent electrode (anode) [35]. When the total thickness of the organic layers is precisely tuned to the emission wavelength, optical resonance occurs. This resonant environment enhances the Purcell factor, which describes the acceleration of the spontaneous emission rate due to the surrounding cavity. [36]

A high Purcell factor forces the exciton to decay into a photon significantly faster than in non-resonant environment. Because the excitons decay into light rapidly, their random walk through the material is cut short, drastically reducing the probability of encountering other excitons or polarons. This effectively reduces both TTA and TPA. [37]

Despite these benefits, microcavities introduce a significant optical drawback. The resonance effect forces the emitted light into a narrow, highly directional beam. While this increases the brightness looking straight at the device, it severely restricts the viewing angles and can cause noticeable color shifts when the display is viewed from the side. [35]

6 Conclusions

This thesis has examined the physical mechanisms that cause efficiency loss and chemical degradation in organic light-emitting diodes, focusing on the role of long-lived triplet excitons. By analyzing the dynamics of TTA and TPA, it is clear that while these interactions can be controlled, they remain a significant limitation of organic semiconductors [2]. The low dielectric constant of organic materials ensures that excitons stay tightly bound as excitons [4]. This makes interactions and annihilation almost unavoidable when current density and exciton populations increase at high brightness levels [2].

The optimization strategies discussed, such as host–guest systems and the use of microcavities, offer effective ways to suppress annihilation but do not provide a total solution. For instance, while host–guest systems limit exciton diffusion and isolate guest molecules, they increase manufacturing complexity and production costs due to the need for precise doping [34]. Similarly, using microcavities can reduce annihilation by accelerating radiative decay through the Purcell effect, but they simultaneously restrict viewing angles and can cause unwanted color shifts [35]. Therefore, optimizing an OLED is a constant balance between achieving high brightness and maintaining practical characteristics of the display.

The accuracy of kinetic modeling is limited by its reliance on averages, which fail to account for the disorder within amorphous organic films. In a real-world device, molecular impurities and structural defects created during mass production cause variations from ideal kinetic behavior. Since calculating the exact position and interaction of every single molecule is computationally prohibitive, these kinetic models must be understood as sufficiently good approximations of the complex environment within the emissive layer.

The transition toward third-generation TADF technology represents a significant shift in how annihilation is managed. By converting non-radiative triplets into radiative singlets, TADF changes the role of triplet accumulation [34]. Controlling annihilation events is essential for preventing both efficiency roll-off and irreversible chemical degradation.

Future research could focus on third-generation OLEDs, particularly blue emitters, where high triplet energies accelerate chemical bond dissociation [12]. Additionally, the development of more advanced computational models that account for material defects and impurities is needed to better understand how mass-produced devices behave in real-world conditions. Finally, exploring new doping-free structures could help solve the constant need to balance high efficiency, low cost and long operational lifespan.

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