Clear Distinction Between Triplet-Polaron Quenching (TPQ) and Triplet-Triplet Annihilation (TTA) in OLEDs via Combined Characterization and Simulation

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Abstract

The performance of an OLED is often marred by an efficiency drop at high brightness. This efficiency roll-off is primarily caused by exciton quenching. Here, we introduce an innovative methodology for exploring exciton quenching in OLEDs, combining characterisation and simulation. Through multitarget optimization, we can effectively distinguish between triplet-polaron quenching (TPQ) and triplet-triplet annihilation (TTA) and investigate their relative contributions during operation.

Keywords

OLED; exciton quenching; efficiency roll-off; MPLS; recombination profile; TTA; TPQ.

1. Introduction

Organic Light-Emitting Diodes (OLEDs) are characterised by their self-emissive nature, flexible structure, and vibrant colours. They are extensively used in commercial applications such as smartphones, tablets, and TVs. Despite the significant improvements in OLED technologies over the past two decades, continued enhancements are necessary. While these devices have achieved a certain level of maturity in peak efficiency and stability, the OLED luminous efficacy tends to diminish at higher current densities. This phenomenon, commonly called the efficiency roll-off, has been mainly assigned to exciton quenching occurring during the electrical excitation of the device. These mechanisms, such as triplet-triplet annihilation (TTA) and quenching by polarons (TPQ), involve the interaction of excited states in the OLED materials, leading to a reduction in the device's efficiency. The quenching probability is highly dependent on the density of excitons and polarons, as much as the charge's recombination profile. [1] [2]

Here, we present a comprehensive and innovative approach to investigating exciton quenching in OLEDs, combining characterization and device simulation. We performed modulated photoluminescence spectroscopy (MPLS) experiments on a phosphorescent OLED and collected several device characteristics, such as electroluminescence (EL), current-voltage (IV), and capacitance-voltage (CV). Additionally, we simulated both the EL and the photoluminescence (PL) roll-off and fitted the experimental results. Thanks to the performed multitarget optimization, we could investigate exciton quenching and differentiate between TPQ and TTA even at biases below the turn-on voltage, increasing the extracted parameters' accuracy.

2. Methods

Device Structure: The devices analyzed were provided by the Institut für Angewandte Photophysik from the Technical University of Dresden (TUD) and possess the following structure: ITO/ Spiro-TTB:F6:TCNNQ (30 nm)/ NPB (10 nm)/ NPB:Ir(MDQ)$_2$(acac) (90:10 %, 20 nm)/ BAlq$_3$ (10 nm)/ Bphen:Cs (30 nm)/ Ag. Each sample contains four OLEDs with an active area of 6.62 mm^2 each. [3]

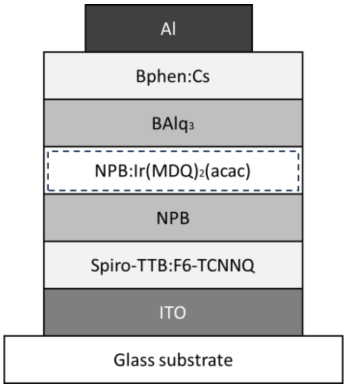

Figure 1: Structure of the OLED used in this study.

Electro-optical Characterization: The electro-optical measurements were performed with the all-in-one measurement system Paios. [4] The MPLS measurements are inspired by previously reported methods. [5] [6] [7] Paios was used as a source of constant device voltage while the current was recorded. The voltage sweep was performed from -2 to 6 V with a step size of 0.2 V, with a settle time of 0.5 s. The devices were optically excited with a 9.8mW (min) Thorlabs' M365FP Fiber-Coupled LED (Nominal Wavelength = 365 nm, Bandwidth = 9 nm). The Fiber-Coupled LED has been controlled by Paios, modulating its intensity at 500 Hz. The amplitude of the light signal was not found to significantly impact the magnitude of PL quenching. The devices under measurement were masked accurately to prevent excitation outside the device area. The lock-in detection technique has been used to exclude any background of electroluminescence (reject the baseline EL signal) from the PL measurement.

Device Simulations: The electro-optical simulations were performed using the software Setfos 5.4. [8] External post-processing procedures were necessary to obtain the bias-dependent PL simulations shown.

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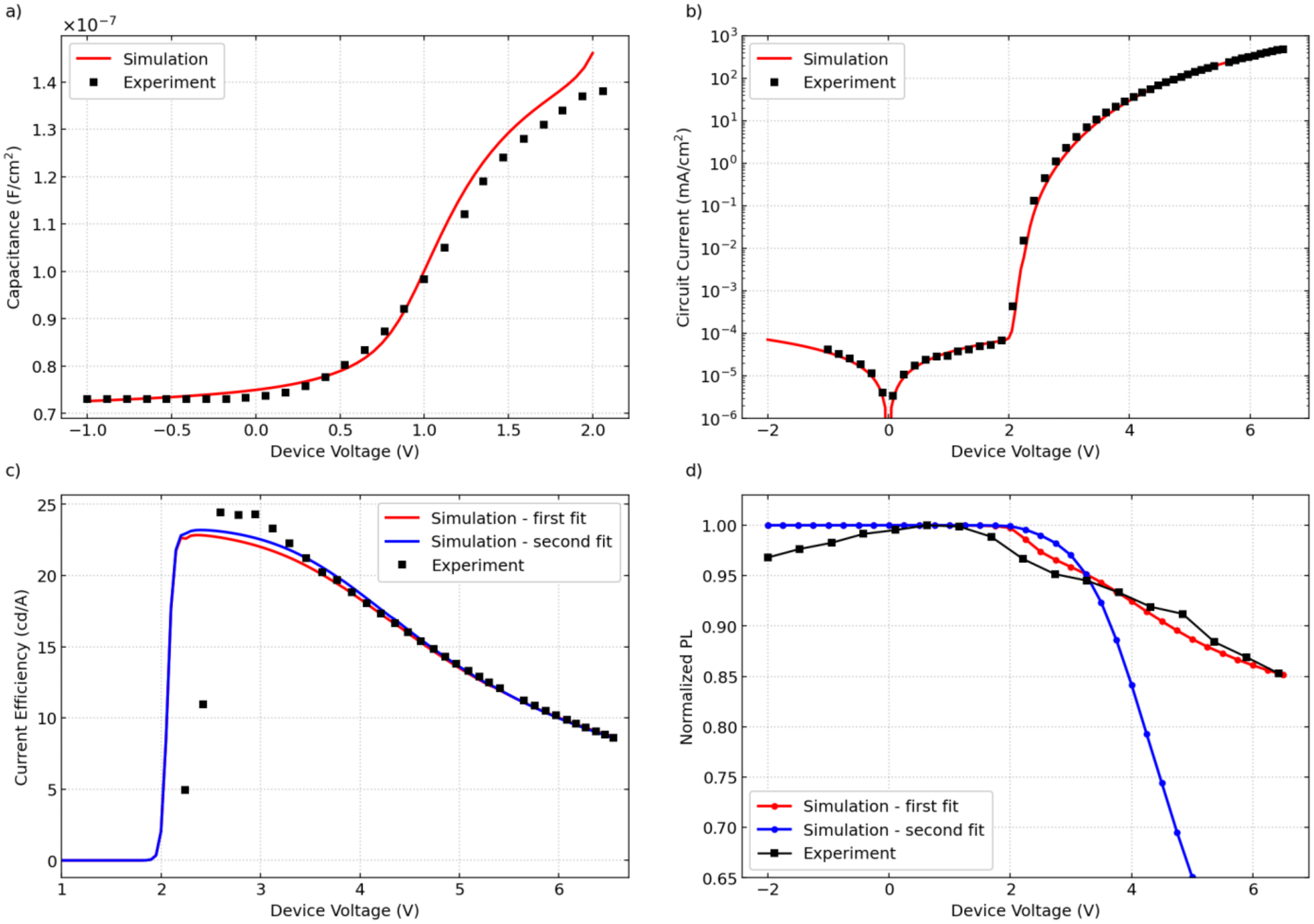

Figure 2: Opto-electrical measurements and simulations of the OLED under investigation. (a) Experimental CV and (b) IV characteristics (solid lines) and simulations (symbols). (c) Current Efficiency (d) Normalized PL as a function of the applied bias.

3. Results and Discussion

This study aimed to set up a reliable electro-optical model able to differentiate between the different exciton quenching processes taking place in the phosphorescent OLED under examination. We started investigating the IV and CV characteristics of the OLED to determine reliable electrical model parameters. Subsequently, we studied the excitonic parameters of the device, analyzing EL and PL characteristics.

Electrical Characteristics: As stated above, we first started investigating the electric properties of the OLED by collecting its capacitance-voltage (CV) and current-voltage (IV) characteristics. These curves are shown as black squares in Figures 2a and 2b, together with their respective simulated best fit (shown as solid red lines). The presence of a polar layer in the stack induces an injection of charges into the device at biases below the built-in voltage, altering the electron injection from the cathode and shifting the position of the recombination zone. This is shown by the CV curve, where the injection of charges starts at around 0.5 V, while the IV curve shows a built-in voltage of 2.1 V. [9]

To obtain the correct electrical model parameters, we simulated the device's CV and IV characteristics. Figures 2a and 2b show a good agreement between simulation and experimental data, confirming the accurate set of model parameters. A global CV-IV fit was necessary to increase the reliability of the material parameters.

Excitonic Characteristics: EL and PL measurements provide a valuable understanding of the exciton processes occurring within OLEDs. Specifically, EL provides insights into the performance and efficiency of the device when an external current is applied. As both electrons and holes need to be injected and then recombine inside the device, the EL analysis is limited to voltages above the turn-on. On the other hand, PL examines light emitted by the OLED when it is excited by an external light source and thus allows one to understand excitonic processes even below the device's turn-on.

In our study, we performed a bias-dependent PL measurement, i.e. MPLS, to characterize exciton quenching mechanisms as a function of the applied bias. The measurement consists of detecting the PL emission signal using a lock-in upon excitation of the EML with a modulated LED at a fixed wavelength. The specific wavelength (λ=365 nm) is chosen to excite Ir(MDQ)2(acac) selectively, focusing solely on examining the relative emitter's photoluminescence efficiency. The lock-in is used to exclude any background of EL from the PL measurement. This allows us to isolate any relative PL change due to exciton quenching even at biases below turn-on. This mechanism has already been used to quantify efficiency roll-off mechanisms in light-emitting devices based on quantum dots and metal-halide perovskite. [5]

The emissive characteristics of the device are evaluated from the current efficiency (CE) and MPLS measurements. In particular, the device shows a peak CE of 24.4 cd/A at 2.6 V. Increasing the current, the OLED exhibits an efficiency roll-off. In fact, as observable from Figure 2c, the luminous efficacy is experiencing an abrupt drop, reaching 70% of its initial value at 4.2 V. This is in line with the 30% EL drop at 4 V, as shown previously by Murawski et al. on a very similar stack. [3]

Figure 2d shows the dependence of the normalized PL intensity on the applied voltage. The normalized PL signal obtained is characterized by a drop under reverse biases, possibly due to quenching from leakage current or exciton dissociation [3]. As the voltage increases above +0.6 V, the device shows a decline in performance, reaching 85% of its starting value at 6.4 V. The PL drop below the device turn-on has been attributed to the exciton polaron quenching with holes that accumulate at the HTL/EML interface as a result of the polar characteristics of the EML. [10] Notably, the PL starts to drop at +0.6 V, matching the threshold voltage seen in CV. After the built-in voltage has been reached, the exciton density increases. Consequently, the triplet-triplet annihilation process appears to have a fundamental role in the PL roll-off. It is clear how the density of charges, their accumulation and the recombination profile of the OLED play a critical role in the device's performance.

Starting from the electrical material parameters found in the previous analysis, we used the same electro-optical model to investigate the OLED excitonic characteristics, fitting both the EL and PL curves. As in the previous scenario, a multitarget fitting procedure was carried out, but this time, it was made to obtain a distinct set of excitonic parameters.

We first fitted the EL roll-off and observed that two different sets of excitonic parameters could correctly reproduce the experimental data shown in Figure 2c (Table 1). However, simulating the normalized PL roll-off with the parameters value listed in Table 1 shows that only the first set of parameters (red line) leads to a good agreement with the measured PL roll-off (see Figure 2d), while the second set (blue line) leads to a more pronounced quenching. Therefore, only one set of excitonic parameters can correctly reproduce the PL roll-off behavior.

The two sets of parameters can lead to the same current efficiency characteristic while affecting the PL characteristic differently. Therefore, the global fit of EL and PL is crucial to obtaining reliable exciton quenching parameters. In other words, investigating the EL roll-off is not sufficient to unambiguously determine the device's excitonic characteristics.

The mismatch in the PL roll-off at low voltages (between 1.15 V and 2 V) is probably related to the fact that non-local quenching events are not considered in the current simulation. In fact, there is an accumulation of holes in the HTL at the HTL/EML interface that are – in the simulation - not affecting the excitons in the EML and thus not contributing to TPQh. In the experiment, non-local TPQ events are likely happening, leading to an earlier PL roll-off. These model refinements are part of ongoing investigations.

Table 1: Excitonic parameters used in our model.

Excitonic parameter	**First Fit**	**Second Fit**
Radiative decay rate	0.8 us^{-1}	0.8 us^{-1}
Non-radiative decay rate	0.2 us^{-1}	0.2 us^{-1}
Diffusion constant	0.002 nm^2/ns	0.1 nm^2/ns
TTA	4.8 x 10^{-13} cm^3/s	2.5 x 10^{-12} cm^3/s
TPQ-e	1 x 10^{-14} cm^3/s	1 x 10^{-13} cm^3/s
TPQ-h	4 x 10^{-13} cm^3/s	1 x 10^{-13} cm^3/s

Analysis of the Excitonic Loss Mechanisms: To analyze the impact of the excitonic model parameters extracted from the global fit on the OLED performance, we draw our attention to the loss diagram. Figure 3 shows the relative contribution of the different exciton loss mechanisms at different operating voltages. In the low-voltage regime, the only loss mechanism is the non-radiative decay. Increasing the voltage above turn-on, leads to a contribution of exciton polaron and exciton-exciton annihilation mechanisms. In particular, it's possible to observe that around 2 V, both exciton polaron quenching mechanisms start to contribute, though at a different magnitude. At around 2.5 V, TTA sets in and due to its scaling nature, this quenching mechanism will dominate with increasing voltage. Indeed, TTA is scaling quadratically with the exciton density, while TPQ mechanisms are scaling linearly.

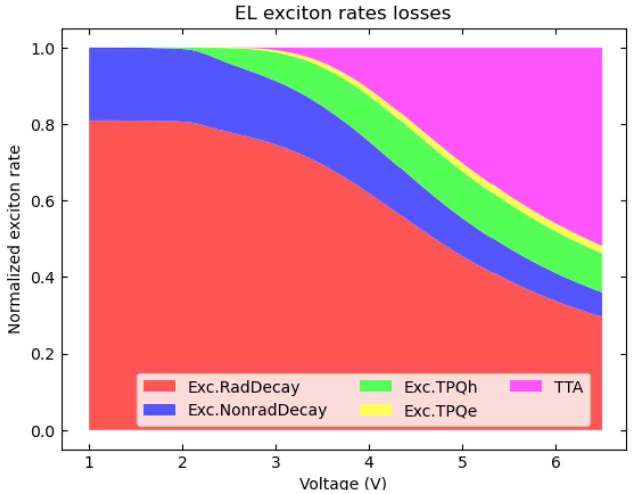

Figure 3: Exciton rate losses diagram for electroluminescence analysis.

4. Conclusions

In this work, we analyzed and quantified the exciton quenching processes under normal operating conditions of a phosphorescent OLED. In addition to the traditional EL roll-off, we exploited the MPLS technique to investigate excitonic processes below turn-on.

We showed that studying the EL alone is not enough to accurately distinguish between the different exciton processes. Instead, we proposed evaluating both EL and PL data to find a unique set of exciton parameters that can quantitatively reproduce both PL and EL roll-off measurements in the simulation.

Thanks to our multitarget optimization, we could not only differentiate between triplet-polaron quenching (TPQ) and triplet-triplet annihilation (TTA) processes but also investigate their relative contributions during normal OLED operations.

5. Acknowledgements

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