

# Exciton Quenching due to Hole Trap Formation in Aged Polymer Light-Emitting Diodes

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Polymer light-emitting diodes based on two poly(*p*-phenylene vinylene) derivatives are aged at a constant current density, leading to the formation of hole traps. Time-resolved photoluminescence spectroscopy (TRPL) measurements show that the degraded polymer light-emitting diodes (PLEDs) also demonstrate a decrease in exciton lifetime. The amount of nonradiative exciton quenching sites in the aged devices is quantified by Monte Carlo simulations. It is found that the number of hole traps obtained from electrical charge transport measurements matches the number of newly formed nonradiative quenching sites determined from the TRPL experiments. The results reveal the origin for the apparent different behavior of the electroluminescence and photoluminescence upon PLED degradation. The decrease of the electroluminescence is governed by recombination of free electrons with trapped holes, whereas the photoluminescence is reduced by nonradiative quenching processes between excitons and hole traps.

causes for PLED degradation a decrease of charge carrier mobility, the formation of charge traps, and reduced charge carrier injection by electrodes due to, e.g., chemical impurities have been suggested.<sup>[2–5]</sup> A remarkable observation is that although the electroluminescence of a PLED strongly decreases under aging the photoluminescence efficiency seems to hardly be affected.<sup>[4,6]</sup> From this it has been concluded that the majority of the polymer molecules is not affected by the current stress. Apparently, only a small volume of the polymeric semiconductor seems to be affected, like the polymer–electrode interface. A decrease of the charge injection as a result of a damaged interfacial region would then lead to a decrease of the electroluminescence due to imbalanced transport as well as to a rise of the driving voltage at constant current.

## 1. Introduction

The device operation of polymer light-emitting diodes (PLEDs) has been extensively studied in the last two decades. It has been demonstrated that the hole transport is trap-free and space-charge limited, whereas the electron transport is severely limited by trapping.<sup>[1]</sup> Furthermore, the recombination is governed by a combination of bimolecular Langevin recombination and nonradiative recombination of free holes with trapped electrons. The combination of these results provides an excellent quantitative description of the current density–voltage and light–output–voltage characteristics of PLEDs.<sup>[1]</sup> Far less attention was paid to the degradation of PLEDs under current stress. The degradation of a PLED stressed at a constant current is characterized by a decrease of the electroluminescence and an increase of the driving voltage.<sup>[2]</sup> As possible

In a recent study, numerical simulations on pristine and degraded PLEDs were performed to discriminate between the various proposed degradation mechanisms.<sup>[7]</sup> It was found that the formation of hole traps is the only mechanism consistent with the observed increase of driving voltage and the decrease of the electroluminescence in the PLED. Formation of electron traps during degradation was inconsistent with the observed voltage increase; since PLEDs are hole-dominated devices, formation of additional electron traps would have negligible effect on the driving voltage, in contrast with experiment. The additional nonradiative recombination process of free electrons with trapped holes is then responsible for the loss of light output and device efficiency with aging time. The knowledge that hole trap formation is responsible for the increase of the PLED driving voltage then enabled us to study its dynamics as function of aging time. We demonstrated that in the first few hours the hole trap concentration increases linearly with aging time, followed by a square-root dependence on longer times.<sup>[8]</sup> The decrease of the PLED light-output as function of aging time could then be predicted from the voltage increase, taking into account the additional nonradiative radiation between free electrons and trapped holes. The agreement between measured and predicted light-output as function of aging time once more confirmed that hole trap formation is the main mechanism for PLED degradation. Furthermore, the degradation characteristics of PLEDs with various thicknesses confirmed that hole traps are being formed in the bulk of the semiconductor. The observed dynamics of hole trap formation also provided information about the origin

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of hole trap formation: The observed linear increase on short times and square-root behavior at longer times are consistent with hole trap formation via exciton–polaron interactions.<sup>[8]</sup> Here, the energy of the exciton is transferred to the hole, which subsequently is excited to higher energetic states. While the majority of excited holes decay to the ground state via internal energy conversion, some of these “hot molecules” can lead to bonds breaking via direct dissociation route to dissociated products,<sup>[9]</sup> which may act as hole traps themselves or interact with adjacent molecules by forming hole traps. What is not straightforward and not understood so far is why the formation of hole traps in the bulk of the polymer would not strongly affect the photoluminescence efficiency as well.

Photoexcitation measurements allow a direct way to investigate exciton properties in organic semiconductors. Upon photon absorption a singlet exciton is generated at an arbitrary energy site within the high-energy tail of the density of (excitonic) states (DOS) that is well described by a Gaussian energy distribution. The created exciton subsequently migrates toward lower energy sites by means of energy transfer.<sup>[10–14]</sup> The so-called downhill migration or spectral diffusion results in a redshift of the emission spectrum, and typically occurs in PPV derivatives in the time range of 100 ps.<sup>[15]</sup> When the exciton approaches quasi-equilibrium at  $-\sigma^2/kT$  below the center of the DOS with variance  $\sigma$ , thermally activated hopping takes over at room temperature, where balanced downward and thermally activated upward hopping occurs.<sup>[12]</sup> Therefore, the exciton diffusion in conjugated polymers can be described as hopping process between conjugated chain segments, which are distributed in size and energy.<sup>[16,17]</sup> During the hopping process excitons can reach a conjugated chain segment containing recombination centers, where it can decay either radiatively or nonradiatively, and/or it can reach a trap site. At these traps, the excitons can be quenched via electron transfer. Exciton quenching has been reported at defects and impurities,<sup>[18]</sup> such as carbonyl groups or hydrated oxygen defects due to photooxidation,<sup>[19–22]</sup> halogen ions,<sup>[23]</sup> metals,<sup>[24,25]</sup> polarons,<sup>[26]</sup> and electron acceptor materials, such as PCBM molecules.<sup>[27]</sup>

Herein, we investigated the degradation of PLEDs based on SuperYellow copolymer (SY-PPV, Merck) and BEH-PPV (poly[2,5-bis(2'-ethylhexyloxy)-1,4-phenylene vinylene]) by using time-resolved photoluminescence (TRPL) spectroscopy. These two materials exhibit different rates of degradation under stress conditions,<sup>[8]</sup> so we considered them as two exemplary models to study the role of hole-trap formation on photoluminescence properties. We combine the TRPL results with Monte Carlo simulations to calculate the number of nonradiative exciton quenching sites in the devices. The amount of exciton quenchers is then compared with the hole trap density obtained from the voltage increase. Our results show that the number of generated hole traps  $P_t$  calculated from electrical measurements is equal to the concentration of nonradiative quenching sites  $c_0$  retrieved from the TRPL experiments. This indicates that hole traps formed during PLED degradation quench excitons via an additional nonradiative decay process, leading to a shorter exciton lifetime. The apparent contradiction of strong electroluminescence decrease with nearly unaffected photoluminescence efficiency upon aging is the result of different physical mechanisms. The electroluminescence decay under current

stress is governed by the trap-assisted recombination between free electrons and trapped holes (Shockley–Read–Hall recombination), which leads to an additional nonradiative recombination process in PLEDs that compete with the radiative Langevin recombination. In contrast, the exciton decay time and photoluminescence efficiency are governed by the diffusion of excitons toward the hole traps formed under degradation, which is a relatively slow process in PPV derivatives.

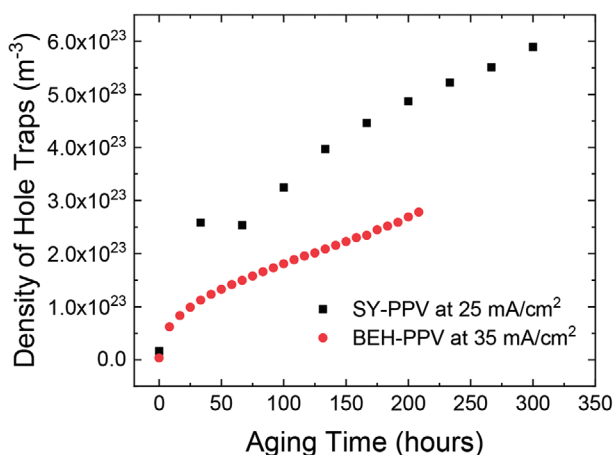
## 2. Experimental Section

The copolymer SY-PPV has been purchased from Merck KGaA (PDY-132), and BEH-PPV was synthesized in-house.<sup>[28]</sup> The device fabrication was as follows: Both PPVs were dissolved in toluene and spin-coated on a glass/ITO/PEDOT:PSS substrate. The layer thickness of SY-PPV and BEH-PPV amounts to 100–120 and 200 nm, respectively, as determined by using a surface profilometer (Bruker, DektakXT). Then the cathode (Ba 5 nm/Al 100 nm) was thermally evaporated on top of the PPV layer (chamber pressure  $10^{-7}$  mbar). All devices were measured with a Keithley 2400 source meter and stressed in nitrogen atmosphere. Due to the above noted different rates of degradation, the stressing conditions were adjusted to ensure that similar degrees of degradation were seen. Accordingly, the SY-PPV PLED was stressed at 25 mA  $\text{cm}^{-2}$  for 328 h, and the BEH-PPV PLED was stressed at 35 mA  $\text{cm}^{-2}$  for 211 h. After stressing, the degraded PLED devices were transferred into a home-made air-tight sample holder, which maintains the inert nitrogen atmosphere during the optical measurements. The unstressed samples were measured from the same substrate and at the same time as the stressed samples.

For the time-resolved photoluminescence measurements, the samples were excited with an excitation wavelength of 400 nm with the frequency-doubled output from a Ti:Sapphire laser (Coherent, Libra HE 3.5 mJ) supplying 100 fs pulses with a repetition rate of either 1 kHz (10 ns time window, 0.12 ns instrument response) or 80 MHz (2 ns time window, 14 ps instrument response). The PLED was photoexcited through the glass/ITO/PEDOT:PSS side of the device. The fluorescence emission was detected by streak camera (Hamamatsu C5680) and the PL decay was collected at the polymer luminescence maximum (540–560 nm for SY-PPV and 560–580 nm for BEH-PPV). The laser fluence was  $<1 \mu\text{J cm}^{-2}$ . The decay lifetimes are fit to either a monoexponential (BEH-PPV) or biexponential (SY-PPV) function. For biexponential decays, the average exciton lifetime is determined from

$$\tau_f = \langle t \rangle = \frac{\int_0^\infty tI(t)dt}{\int_0^\infty I(t)dt} = \frac{\sum_i a_i \tau_i^2}{\sum_i a_i \tau_i} \quad (1)$$

where  $I(t)$  is the luminescence intensity,  $a_i$  is the pre-exponential factor, and  $\tau_i$  is the time constant of multiexponential decays. Monte Carlo simulations were used to determine the concentration of exciton quenching sites, as described previously,<sup>[29,30]</sup> and the software can be downloaded from the Internet.<sup>[31]</sup> Briefly, the scheme models the PL decay in emitter–quencher mixtures in order to extract the exciton diffusion parameters, is based on the exciton-diffusion-limited quenching model at



**Figure 1.** Density of hole traps (symbols) formed during degradation of SY-PPV and BEH-PPV PLEDs as a function of aging time.

nonradiative quenchers. Excitons and quenchers are placed in a cubic simulation box of  $50 \times 50 \times 50$  nm length as balls of 1 nm diameter. The diffusion is modeled as a random walk with constant exciton hopping distance (“hop size”). For each time iteration  $\delta t$  every exciton is moved in a random 3D direction for a fixed distance  $\delta s$ , which correlates with the exciton diffusion coefficient as follows:  $D = \delta s^2 / 6 \delta t$ . Radiative recombination is assumed if an exciton has not been quenched after time  $t_r$ , which is fixed at the beginning of the simulation. The concentration of hole traps was determined by using drift-diffusion numerical simulations.<sup>[7,8]</sup>

### 3. Results and Discussion

#### 3.1. Hole Trap Formation

In an earlier study, the current–voltage ( $J$ – $V$ ) and luminescence–voltage ( $L$ – $V$ ) characteristics of degraded PLEDs could be modeled by the formation of hole traps.<sup>[7,8]</sup> **Figure 1** shows the evolution of the hole trap concentration for the SY-PPV and

**Table 1.** Hole trap concentration in stressed PLEDs found in this study using electrical modeling ( $P_t$ ) and the optical studies with Monte Carlo simulations ( $c_0$ ).

Material	SY-PPV, 25 mA cm <sup>-2</sup> , 328 h	BEH-PPV, 35 mA cm <sup>-2</sup> , 211 h
$P_t$ [cm <sup>-3</sup> ] (electrical modeling)	$6.3 \times 10^{17}$ cm <sup>-3</sup>	$2.8 \times 10^{17}$ cm <sup>-3</sup>
$c_0$ [cm <sup>-3</sup> ] (optical studies)	$4.8 \times 10^{17}$ cm <sup>-3</sup>	$4.4 \times 10^{17}$ cm <sup>-3</sup>

BEH-PPV PLEDs employed in this study. The concentration of hole traps formed in SY-PPV after being stressed at 25 mA cm<sup>-2</sup> for 328 h amounts to  $6.2 \times 10^{17}$  cm<sup>-3</sup> and in BEH-PPV stressed at 35 mA cm<sup>-2</sup> for 211 h is  $2.8 \times 10^{17}$  cm<sup>-3</sup> (also summarized in **Table 1**).

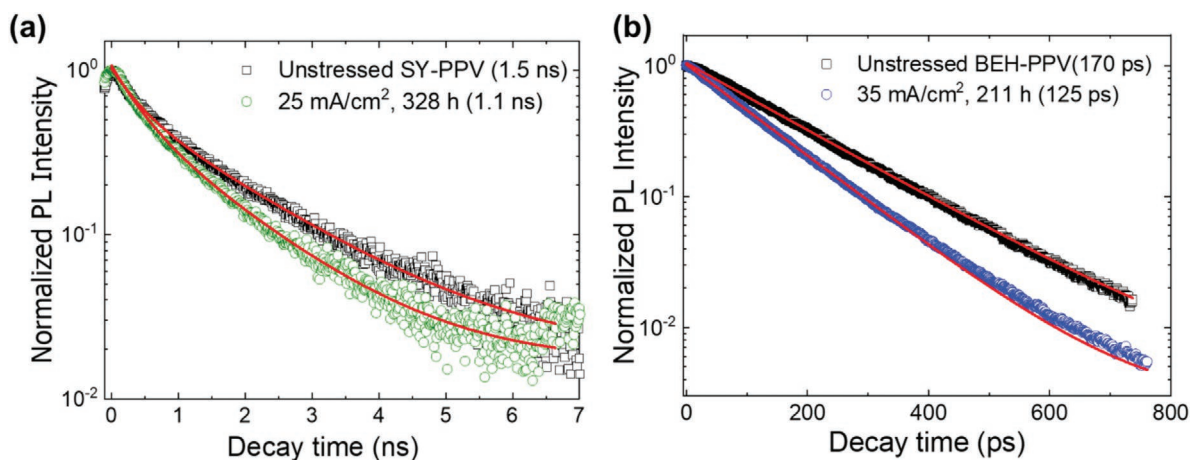
#### 3.2. Exciton Lifetime

**Figure 2a,b** shows the PL decay times of unstressed and stressed SY-PPV and BEH-PPV PLEDs. The aged devices demonstrate faster PL decay relative to the unaged sample. The exciton lifetime ( $\tau_f$ , shown in brackets) decreases upon stressing the device, going from 1.5 to 1.01 ns in SY-PPV and from 170 to 125 ps in BEH-PPV. The exciton lifetime of the unaged devices is slightly shorter as compared to pristine thin films (1.9 ns for SY-PPV and 180 ps for BEH-PPV),<sup>[32]</sup> due to the presence of charge transfer/exciton quenching at the electrode interface in the PLED structure.<sup>[33]</sup>

We recently reported that the exciton lifetime  $\tau_f$  in thin conjugated polymer films is governed by the diffusion of excitons toward nonradiative quenching sites and can be expressed by the following equation<sup>[32]</sup>

$$\tau_f = 1 / (k_{\text{rad}} + k_{\text{nonrad}} + k_{\text{diff}}) \quad (2)$$

where  $k_{\text{rad}}$  and  $k_{\text{nonrad}}$  are the radiative and nonradiative decay rates, and  $k_{\text{diff}}$  is the nonradiative decay rate originating from exciton quenching at defect sites due to exciton diffusion. Therefore, the measured exciton lifetime represents the time



**Figure 2.** Normalized PL decay curves (scatter symbols) of PLEDs measured at the PL maximum. The exciton lifetime, noted in brackets, has been determined by using fits to exponential functions, indicated by the solid red lines.

an exciton needs to find a quenching site.<sup>[32]</sup> Since the decay rates  $k_{\text{rad}}$  and  $k_{\text{nonrad}}$  are intrinsic numbers and considered to remain constant during the SY-PPV PLED device aging process, the only parameter that influences the exciton lifetime is  $k_{\text{diff}}$ .

The two factors that determine  $k_{\text{diff}}$  are the exciton diffusion toward nonradiative quenching sites and the concentration of these quenching sites. In the first case, a decrease in exciton lifetime can be correlated to an increase in exciton diffusion rate with a constant concentration of defect sites in the conjugated polymer. Faster exciton diffusion would then result in a higher probability of the excitons reaching a quenching energy site and, consequently, the exciton lifetime would decrease. On the other hand, the concentration of quenching sites can change, while the exciton diffusion remains unchanged. In this case, the exciton lifetime decreases with increasing concentration of trapping sites, since more nonradiative quenching sites in the conjugated polymer increase the probability of the exciton to be quenched.

We have previously shown that the exciton diffusion correlates with the energetic disorder of the conjugated polymer, as described by the width of the Gaussian DOS. Better ordered polymers have narrower DOS and this results in faster exciton diffusion and shorter exciton lifetime.<sup>[32]</sup> Considering this, enhanced exciton diffusion in the PPV based PLEDs would correlate with a decrease in energetic disorder. This energetic disorder is predominantly determined by molecular structure, and is unexpected to change upon device stressing. We thus assume that the exciton diffusion rate in the PPV PLEDs should not change with device stress. This leads us to conclude that the decrease in exciton lifetime is due to an increase in nonradiative quenching sites in the PPV-based PLEDs. With increasing number of quenching sites, the excitons can find a quenching site faster, resulting in a shorter exciton lifetime. This is consistent with diffusion-limited exciton quenching at defect sites.

However, the origin of these defect sites is not straightforward to identify, since many photophysical processes take place at the same time in conjugated polymer films. For example, time-resolved photoluminescence spectroscopy measurements have found a concentration of exciton quenchers in the range of  $10^{17}$ – $10^{18}$   $\text{cm}^{-3}$  in a series of unaged organic semiconductors.<sup>[34]</sup> Remarkably, this number of “background” exciton quenchers present in organic semiconductors is similar to the universal electron trap density that has been reported for a large range of conjugated polymers, as measured by charge transport measurements.<sup>[22]</sup> Furthermore, Mikhnenko et al. proposed that the electron traps and the exciton quenching defects share the same origin and that the excitons can be quenched at these traps via electron transfer.<sup>[34]</sup> Barbara and co-workers reported exciton quenching by holes (polarons).<sup>[26]</sup> Analogous to exciton quenching at electron traps, it is expected that excitons can be quenched at hole traps via hole transfer.<sup>[35]</sup>

Electrical measurements and numerical simulations have ascribed PLED degradation to the formation of hole traps. The question is now whether such generated hole traps will also quench excitons via an additional nonradiative decay process and are therefore responsible for the decrease in exciton lifetime, followed by how this would affect the photoluminescence efficiency of the degraded device.

### 3.3. Monte Carlo Simulation

We subsequently used the above mentioned Monte Carlo based simulation to determine the amount of nonradiative exciton quenchers (hole traps) in the aged PPV PLEDs. Details of the simulation are in the Experimental Section, and a comprehensive description of the simulation can be found elsewhere.<sup>[29,30,34]</sup> The following parameters are taken as simulation input: the measured PL decay time of the pristine semiconductor film  $\tau_i$ , the measured PL decay time of the specific semiconductor-quencher blend  $\tau$ , the volume fraction (concentration) of quencher molecules, and the sample morphology, which is represented by the relative quenching efficiency  $Q$  ( $Q = 1 - \tau/\tau_i$ ). The simulation uses the random walk model and assumes that the quenching molecules are homogeneously distributed at low concentrations.

The first step is to calculate the exciton diffusion coefficient  $D$ , which represents the spatial and temporal exciton population in the polymer. Here, the only fitting parameter is  $D$ , and the output includes the simulated PL decay kinetics. The simulation is then repeated with adjusted values of  $D$  until the modeled PL decay agrees sufficient with the experimentally determined PL decay. Therefore, the simulation output is the number of radiatively decayed excitons versus time. From previous work, fluorescence quenching experiments in thin PPV films with randomly distributed PCBM molecules were used to retrieve an exciton diffusion coefficient of  $D = 2.2 \times 10^{-4}$   $\text{cm}^2 \text{s}^{-1}$  for SY-PPV, and  $D = 2.0 \times 10^{-3}$   $\text{cm}^2 \text{s}^{-1}$  for BEH-PPV.<sup>[32]</sup>

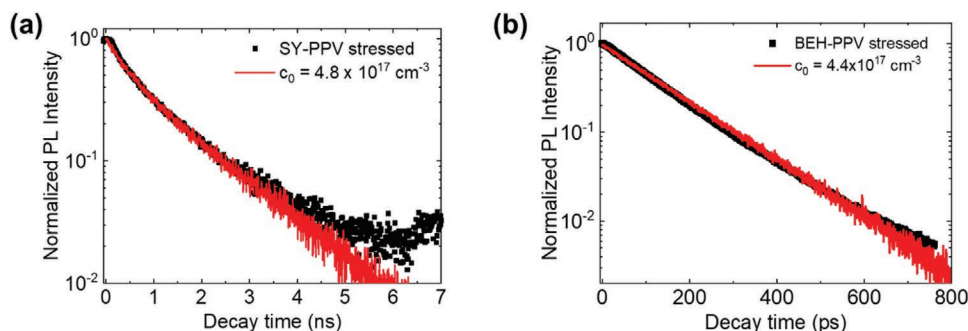
As noted above, the exciton diffusion is not expected to change upon aging of the PLEDs, but the amount of nonradiative quenchers is expected to increase. So as a next step, the exciton diffusion coefficient was kept constant, and the quencher concentration was adjusted until the simulation modeled PL decays agreed with the measured PL decays of the aged PLEDs. **Figure 3a,b** shows the simulated PL decays for SY-PPV and BEH-PPV for a specific concentration of exciton quencher (red line), which shows good agreement with the measured PL decays aged under constant current sufficient densities (black squares). From the simulated PL decays, the concentration of nonradiative quenching sites has been determined.

We note that the PL decay of the pristine PLED already includes the quenching of excitons by electron traps ( $1.0 \times 10^{17}$   $\text{cm}^{-3}$  for SY-PPV and  $1.0 \times 10^{18}$   $\text{cm}^{-3}$  for BEH-PPV, determined from the  $J$ - $V$  characteristics of electron-only devices). The reported quenching site densities here are the *additional* quenching sites formed after current stress.

Table 1 compares the density of hole traps  $P_t$  after aging determined by modeling the voltage increase of the degraded PLED,<sup>[8]</sup> and the amount of nonradiative quenching sites determined via photoluminescence measurements and Monte Carlo simulations. We find that the number of quenching sites calculated from the optical experiments matches the concentration of hole traps measured electrically.

As final step to find out how the measured amount of quenching sites will affect the photoluminescence quantum yield (PLQY), we calculated the relative photoluminescence quantum yield (rPLQY) in the stressed versus unstressed samples ( $\tau_{\text{stressed}}/\tau_{\text{unstressed}}$ ). For both samples, the stressed devices





**Figure 3.** Measured (black squares) and simulated (red solid lines) PL decays of a) SY-PPV and b) BEH-PPV PLEDs after stressing. Red lines indicate the results from the Monte Carlo simulation for the indicated quencher concentration.

exhibit 73% rPLQY. However, the electroluminescence has already dropped to about 40%. This difference is the result of different mechanisms for quenching; the electroluminescence is reduced by nonradiative recombination of free electrons with trapped holes, which is an efficient process. The PLQY on the other hand is governed by diffusion of excitons towards the newly formed hole traps. Since PPVs have a relatively low exciton diffusion coefficient due to strong energetic disorder, the excitons do not find the newly formed hole traps that easily. The result is a stronger dependence of the electroluminescence on the amount of quenching sites as compared to the photoluminescence.

#### 4. Conclusions

TRPL measurements on aged PPV based PLEDs show enhanced exciton decay relative to the unaged device. This is ascribed to increased nonradiative quenching due to hole traps that form during the aging process. The amount of nonradiative quenching sites that form during degradation are quantified from the TRPL measurements and Monte Carlo simulations and are in agreement with the concentration of hole traps determined from electrical measurements. This demonstrates that the formed hole traps are responsible for both the decrease of the electroluminescence by nonradiative recombination of free electrons with a trapped hole as well as the reduction of the photoluminescence quantum yield due to quenching of excitons. The different dependence of these mechanism on hole trap concentration explains why electroluminescence and photoluminescence behave differently during current stress of a PLED.

#### Conflict of Interest

The authors declare no conflict of interest.

#### Keywords

degradation, exciton lifetime, organic electronics, polymer light-emitting diodes

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