Recombination kinetics in wide gap electroluminescent conjugated polymers with on-chain emissive defects

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We analyze the experimental dependence of temporally and spectrally resolved electroluminescence (EL) from polyfluorene-based light-emitting diodes on electric field and temperature. The blue band in the EL spectrum is caused by emission from the polymer backbone, while the low-energy green emission results from on-chain keto defects, which act as traps for electrons. Although the time and temperature dependencies of the blue and green emission could be explained by the kinetics of redistribution of trapped holes and electrons in energy and space, the increase of the blue-to-green delayed emission ratio with increasing field strength appears to result from a difference in the nature of recombination. We propose that the formation of blue-emitting singlet excitons from close electron–hole pairs after turn-off is impeded by an energy barrier, in contrast to the formation of green-emitting excitons. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1566091]

I. INTRODUCTION

Conjugated polymers are subject to wide investigations in device and material physics. These materials are becoming increasingly important for technological applications, such as light-emitting diodes (LEDs) and lasers.[1] In particular, an investigation of the dynamic response of electrically driven LEDs is of great interest for the understanding of charge transport and recombination in polymers. Most of the previous research has focused on spectrally integrated studies.[2–4] Recently, time-gated spectroscopy has been found to be a powerful tool for investigation of delayed photoluminescence (PL) from conjugated polymers[5,6] and was also applied to the investigation of delayed electroluminescence (EL)[7,8] in LEDs. It was demonstrated that this technique is highly sensitive and can map out delayed emission components over 1000 times weaker than the cw luminescence.

Poly(2,7-(9,9-bis(2-ethylhexyl)fluorene)) (PF) is an example of a conjugated polymer with possible applications in LEDs and lasers due to highly efficient blue emission.[9] However, this emission is often accompanied by a broad green band, which turns the emission color to an undesired blue-green. The green emission is especially strong in the case of EL.[9] Recently, the green emission band was identified in PL spectra of both solid-state PF and of dilute PF solutions,[6] and cannot therefore be attributed to aggregate or excimer states.[10,11] The origin appears to be the recombination of charge carriers on defect sites, which are formed in PF due to oxidation.[9,12]

In this article, we present an analysis and theoretical modeling of microsecond-gated spectra of delayed EL from PF-based LEDs. The delayed emission spectra are found to exhibit a range of dynamical processes, which are totally masked in the cw operation.[7] In particular, variations of peak heights of blue (430 nm) and green (525 nm) EL emission bands with delay time and temperature allow us to estimate densities and parameters of distributions of localized states for holes and electrons. We have attributed the observed increase of the intensity of the delayed blue EL peak relative to the green EL peak with increasing electric field strength inside the LED to the kinetic delay of the final step of radiative recombination on backbone states leading to blue emission. Such a delay is absent for defect recombination leading to green emission. The reason is that the energy of the singlet ''blue'' exciton is higher than the Coulombic binding energy of a close electron–hole (e–h) pair, and hence the charge carriers have to overcome an energy barrier, which can be reduced by an external electric field. Otherwise, recombination is nonradiative. At the same time, ''green'' excitons are formed by holes and electrons, which are trapped on deep states originating from chemical defects, and hence energies of these excitons are typically lower than the Coulombic binding energy of an e–h pair. The present discussion therefore provides important insight into the influence of a small concentration of emissive defects on the operation of polymer LEDs.

II. EXPERIMENT AND EXPERIMENTAL RESULTS

The experimental method of gated EL and the main observations are discussed in detail elsewhere.[7] Approximately 100-nm-thick films of PF were spin-coated onto ITO anodes covered by a layer of poly(3,4-ethylenedioxythiophene)/poly(styrene)-sulfonate 50 nm), facilitating injection of holes. Calcium cathodes, 15 nm thick and 4 mm^2 in area, capped by an aluminum layer (150 nm), were thermally evaporated on top of the polymer films. The spectra of the delayed EL were detected by an EG&G intensified, red-enhanced gated diode array coupled to a 0.3-m monochro-

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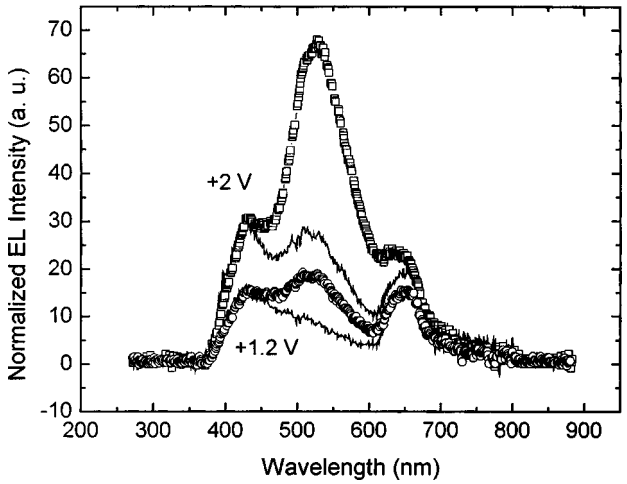

FIG. 1. Delayed El spectra recorded in a 40-μs time window at two different bias offsets at a delay of 30 μs after turnoff of a 40-μs, 5-V pulse. The curves without and with symbols are for the fresh and slightly aged samples, respectively. The data are normalized to the blue emission band. Respective bias offsets are shown.

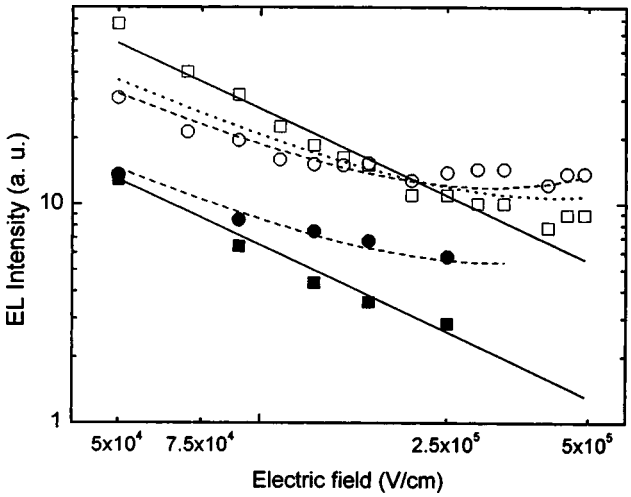

FIG. 2. Peak intensities at 430 nm (circles) and at 520 nm (squares) for the fresh (filled symbols) and oxidized (open symbols) samples as a function of reverse electric field strength. The delay time is 20 μs. The parallel solid lines show the field dependence of the Coulombic capture cross section, F^{-1}. The dashed and dotted curves are calculated from Eq. (4) with $a=0.8$ and $a=0.6$ nm, respectively.

mator with a grating of 150 lines/mm. Spectra were recorded through a slit corresponding to a spectral resolution of 10 nm after turn-off of a 5-V pulse of 40-μs duration and 10% duty cycle. Spectra were recorded in a 40-μs time window at variable delay times. The samples were mounted in a water-cooled cold-finger cryostat under rotary pump vacuum. Series of spectra were recorded at temperatures of 277, 298, 323, and 353 K. In order to probe the origin of the delayed emission spectra, a constant bias offset was applied to the voltage pulse, which varies from $+2$ to -2.4 V. The direction of the electric field inside the LED is reversed in any case due to the built-in potential $V_{bi} \approx 2.5$ V.[13]

It has recently been demonstrated that the green emission band in PF arises due to photo-oxidation of the backbone to fluorenone units.[9,12] In order to investigate the recombination kinetics on these fluorenone sites, we compare two samples with slightly different degrees of oxidation. Figure 1 shows delayed EL spectra recorded at two different bias offsets at a delay of 30 μs. Two pairs of spectra are compared, one of them corresponds to a fresh sample, while the second (which is marked by symbols in the figure) corresponds to a slightly oxidized sample in which the polymer solution was stored in the refrigerator for 48 h prior to processing. Objectively, the green feature is more pronounced in the latter case. Figure 1 shows that for both cases, the green band becomes relatively weaker with an increase in the absolute value of field strength $F=(V_{bi}-V)/L$ (that is, with decreasing offset voltage V), where L is the thickness of the PF layer. The red feature seen in all specta at 650 nm results from doping of PF with the dye 2,3,7,8,12,13,17,18-octaethyl-21H, 23H-porphyrin platinum[7] and is beyond the scope of this article. The dependencies of the green emission intensity (squares) and the blue emission intensity (circles) on the field strength at a fixed delay time are plotted in Fig. 2 for the cases of fresh (filled symbols) and slightly more oxidized (open symbols) samples. These intensities were determined by fitting of the respective spectral shapes with Gaussian curves and subsequent integration. It can be seen that the field dependencies of the blue and green emission differ considerably, while the respective intensities behave similarly for the two samples with different levels of oxidation. The intensity of the green emission follows a F^{-1} law (solid lines), while the decrease in blue emission with increasing F is weaker and the delayed blue EL becomes field independent at strong fields.

The symbols in Fig. 3 show the decay of the green EL with increasing delay time, where the variable parameter is the temperature. The decay becomes faster with increasing temperature and the law of decay is a power law rather than an exponential function of time.

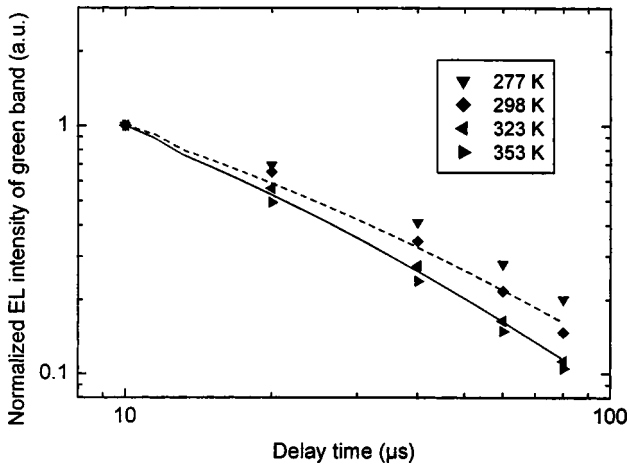

FIG. 3. Intensity of green delayed EL detected with a 40-μs gate as a function of delay time for different temperatures (symbols). The solid and dashed lines are the results of calculations with Eq. (2) for temperatures of 353 and 277 K, respectively. The following parameters were used for the calculations: $\sigma=0.06$ eV, $N/\gamma^3=0.001$, $\nu_0=10^{13}$ s^{-1}, $F\approx -2.5\times10^5$ V/cm due to the built-in field. All curves are normalized to the delay time 10 μs.

III. DISCUSSION

On the basis of time-of-flight experiments,[13,14] I–V measurements[13] and time-resolved EL,[3] the transport of holes in PF is known to be nondispersive and characterized by weak field and temperature dependencies of mobility of holes: $\mu_h \approx 10^{-4}$ cm^2/V s. This suggests that hole transport is controlled by a density of states with weak energetic disorder, similar to another well-investigated conjugated polymer, methyl-substituted ladder-type poly(paraphenylene) (MeLPPP).[15] In contrast, electron transport in PF is known to be dispersive,[14] and the effective electron mobility was estimated as $\mu_e \leqslant 10^{-8}$ cm^2/V s.[3] On the other hand, the electron current injected from the Ca electrode appears to be space-charge limited (SCL),[3] while the hole current is injection limited.[3,13] To estimate the SCL area density of electrons in the PF layer, we assume $N_e \cong \varepsilon\varepsilon_0(V_0 - V_{\rm bi})/eL \geqslant 10^{16}$ cm^{-3}, where $V_0 = 5$ V is the cw voltage, $L = 100$ nm is the thickness of PF, and $\varepsilon \approx 3$ is the dielectric constant. Estimation of the cw electron current density $J_e \approx eN_e\mu_e(V_0 - V_{\rm bi})/L$ yields a value that is three orders of magnitude lower than the measured current density, $J_{\rm cw} \approx 10^{-2}$ A/cm^2, and hence the cw current is dominated by holes. The cw density of holes can be estimated as 10^{15} cm^{-3}, which is consistent with barrier-limited injection.

The origin of the green band in EL spectra seems to result from recombination of holes with electrons that have been captured on deep defect states, which most probably originate from oxidation of the monomer units of the polymer backbone.[7,9] The latter is in agreement with the results in Fig. 1 (the green emission is weaker for the less oxidized sample). The energy depth of these traps can be estimated from the EL spectra to be no less than 0.5 eV, and hence the respective electrons are immobile on the time scale of interest. The intensity of the green emission at a time t after switching off the driving voltage can be calculated as

$$J_{\rm EL}^{\rm green}(t) = \varphi^{\rm green}(e\Sigma_e^{\rm green}/\varepsilon\varepsilon_0 F) J_h(t), \tag{1}$$

where $\varphi^{\rm green}$ is the probability of radiative recombination in the green band, $\Sigma_e^{\rm green}$ is the area density of deeply trapped electrons in the zone of most effective recombination (the factor in the brackets is the recombination probability), and $J_h(t)$ is the current density of residual holes. After the switch-off of the driving voltage, the direction of the electric field inside the LED inverses and holes flow back to the anode. Since the time of flight of holes across the LED is less than 1 μs, only holes trapped within the deep tail of localized states can remain inside the polymer after the delay time $t_d \gg 1$ μs. The release of holes from these relatively deep states is the rate-limiting step for the delayed current of holes, and hence the latter is determined by the depletion rate of the area density of holes: $J_h(t) \approx -d\Sigma_h(t)/dt$. The latter is a product of the density at $t = 0$, Σ_{h0}, and the relative density of the deep states for holes $N_d(t)/N$, where N is the total density of localized states for holes. It is assumed that these states are randomly distributed in space, featuring a Gaussian distribution in energy with a variance σ: $g(E) = (N/\sqrt{2\pi\sigma^2})\exp(-E^2/2\sigma^2)$.[15] A localized state is referred to as deep if the release of a carrier, localized at $t = 0$, from this state is still improbable at a given time t. It should be noted that the measured value is the EL intensity, which is integrated within the time window Δt starting from the delay time t_d. Finally, by the use of Eq. (1), one obtains

$$\langle J_{\rm EL}^{\rm green}\rangle(t_d) = \int_{t_d}^{t_d+\Delta t} J_{\rm EL}^{\rm green}(t)dt = \varphi^{\rm green}(e\Sigma_e^{\rm green}/\varepsilon\varepsilon_0 F) \times (\Sigma_h(t_d) - \Sigma_h(t_d+\Delta t)], \tag{2}$$

where $\Sigma_h(t) = \Sigma_{h0}N_d(t)/N$. It is clear that the density of carriers on deep states $N_d(t)$ decreases with time. A method of calculating this value was described in the Ref. 16, in which it was shown that the release of holes from deep states can determine the law of asymptotic decay of delayed PL in MeLPPP. The decay of time-gated EL in PF, as calculated from Eq. (2), is compared with experimental results in Fig. 3 for the case of $T = 353$ K (solid line) and $T = 277$ K (dashed line). The results are in fairly good agreement. The decay of the green emission with time becomes faster with increasing temperature due to acceleration of the release of holes. The model includes two parameters of localized states, in addition to σ: the attempt-to-hop frequency ν_0 in the Miller–Abrahams formula for hopping between two localized states, and the density of states relative to the inverse localization radius γ, N/γ^3.[15,16] It should be noted that the numerical values of these parameters, namely, $\nu_0 = 10^{13}$s^{-1} and $N/\gamma^3 = 0.001$, used in this calculation, are very close to the values used in the modeling of spectra of thermally stimulated PL in MeLPPP[15] ($\nu_0 = 10^{13}$s^{-1}, $N/\gamma^3 = 0.0006$). The variance σ of the Gaussian density of states used for holes is $\sigma = 0.06$ eV, which slightly exceeds the values of 0.054 eV[16] and 0.055 eV[15] from previous modeling of MeLPPP. This can be understood as a result of reduced rigidity and hence increased disorder of the PF backbone in comparison to MeLPPP.

The time-gated intensity of the blue emission, $\langle J_{\rm EL}^{\rm blue}\rangle(t)$, is described by Eq. (2) substituting $\varphi^{\rm green} \to \varphi^{\rm blue}$ and $\Sigma_e^{\rm green} \to \Sigma_e^{\rm blue}$. To be rigorous, one has to analyze an additional term, describing recombination of shallow trapped and hence more mobile electrons on the backbone with immobile residual holes, which are trapped relatively deeply. This term is $\varphi^{\rm blue}(e/\varepsilon\varepsilon_0 F)\langle\Sigma_h(t)J_e(t)\rangle \approx (e\Sigma_e^{\rm blue}/\varepsilon\varepsilon_0 F)\Sigma_h(t_d)[\mu_e F\Delta t/l_{\rm rec}]$, where $l_{\rm rec} \ll L$ is the thickness of the zone of most efficient recombination. This expression is similar to Eq. (2) except for the factor in the square brackets. The latter is much less than unity even for the strongest field strength, $F \approx 5\times 10^5$ V/cm, assuming $\Delta t = 40$ μs,[7] $\mu_e \leqslant 10^{-8}$ cm^2/V s, and $l_{\rm rec} \approx 10$ nm.[3]

Consequently, even electrons responsible for the blue emission can be considered as immobile to a first approximation, and hence the measured green-to-blue emission ratio can be expressed as

$$\langle J_{\rm EL}^{\rm green}\rangle/\langle J_{\rm EL}^{\rm blue}\rangle = (\varphi^{\rm green}/\varphi^{\rm blue})[\Sigma_e^{\rm green}/\Sigma_e^{\rm blue}]. \tag{3}$$

The ratio $\langle J_{\rm EL}^{\rm green}\rangle/\langle J_{\rm EL}^{\rm blue}\rangle$ can, however, be varied with time even if the transport of electrons over distances of more than 10 nm is unlikely to occur due to a redistribution of electrons in energy, providing that thermal equilibrium is still not

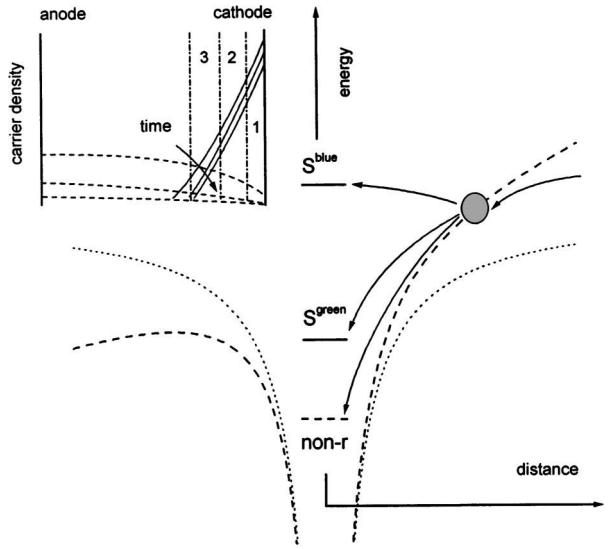

FIG. 4. Schematice of the final step of the recombination processes, which leads to the formation of radiative singlet excitons emitting in blue or green bands of the spectra, or alternatively to nonradiative recombination. Dotted and dashed lines show the profiles of the electric potential for the case of zero and nonzero external fields, respectively. An increase of external field strength reduces the energy barrier for the formation of blue excitons and hence the probability of radiative recombination in the blue band increases. The inset shows the schematics of the time evolution of electron (solid lines) and hole (dotted lines) spatial densities in an LED with increasing time after the end of the driving pulse. The region of quenched radiative recombination (1) and the regions of most effective recombination at short (2) and long (3) times after the reversal of the field direction inside the LED are also shown schematically.

achieved, in accord with the dispersive nature of electronic transport. Indeed, Ref. 7 reported a small decrease ($\sim$20%) of the green/blue EL ratio during the first 10 μs (room temperature), while at a longer time scale ($t_d = 10-140$ μs), this ratio increases by a factor which varies from 1.2 ($T=263$ K) to 1.6 ($T=323$ K), approaching the cw level at long times. The short-time feature can be understood by taking into account the spatial redistribution of holes inside the LED just after inversion of the electric field, as indicated in the inset of Fig. 4. At $t<0$, the zone of most effective recombination (2) is located near to the cathode next to the zone of quenching (1).[4] In the first few microseconds after switch-off, however, most of the holes leave the zone 2, but are recaptured on shallow states further inside the device (zone 3). This zone acts as an efficient recombination zone at longer times, because a subsequent shift of the recombination zone towards the anode is limited by the sharp decrease in electron density. Although the steady-state shape of the EL spectrum is established at $t<0$ within 40 μs, requiring electrons to be in equilibrium within zone 2, this may not be the case within zone 3 (i.e., at larger distances from the cathode). Consequently, the relative number of deeply trapped electrons involved in the recombination decreases, and hence the relative weight of the green emission in the EL spectrum decreases as the recombination zone shifts immediately after turn-off. At longer times, electrons inside zone 3 finally equilibrate, and hence the redistribution of electrons towards deeper states results in a relative increase of the green peak in delayed EL. This effect becomes stronger with increasing temperature within a given time interval[7] due to the acceleration of electron thermalization. One has to keep in mind that the absolute value of the measured blue EL decreases with delay time, as does that of the green EL, due to the escape of holes from the LED, as discussed for Fig. 3. The redistribution of electrons in energy and to second order in space results in deviations of up to 50% from the proposed decay law.

The variations of the green-to-blue emission ratio with offset voltage (i.e., electric field F at $t>0$) at a given delay time are more substantial and rather intriguing. The reduction of the delayed green emission with increasing field can be well described by a F^{-1} law (see straight lines in Fig. 2), which reflects the decrease in the Coulombic capture cross section of holes by electrons, $e/\varepsilon\varepsilon_0 F$ [see Eq. (2)]. The decrease of the blue emission is, however, considerably weaker, and hence the ratio $\langle J_{\mathrm{EL}}^{green}\rangle/\langle J_{\mathrm{EL}}^{\mathrm{blue}}\rangle$ decreases by half an order of magnitude as the field strength is increased by one order of magnitude. Apparently, the increase in electric field, which influences the redistribution of electrons in energy and space in a similar way to the temperature, cannot be responsible for the decrease of the ratio $\Sigma_e^{\mathrm{green}}/\Sigma_e^{\mathrm{blue}}$. Consequently, from Eq. (3), only a decrease of the ratio of efficiencies of radiative recombination $\varphi^{\mathrm{green}}/\varphi^{\mathrm{blue}}$ can be a reason for this effect, that is, the efficiency of blue recombination increases with increasing field relative to the efficiency of green recombination. This demonstrates that the mechanisms of recombination on polymer backbone sites and on chain defect sites are fundamentally different.

We propose that the final jump of a hole towards a trapped electron, which leads to the formation of a radiative singlet exciton on the polymer backbone, is thermally activated, and can hence be accelerated by an electric field in the case of blue emission, in contrast to the green emission, as indicated in Fig. 4. The energy difference Δ between the final and initial state of the final hole jump is given by the energies of the initial and final highest occupied molecular orbital (HOMO) levels, $E_{\mathrm{HOMO}}^{\mathrm{initial}}$ and $E_{\mathrm{HOMO}}^{\mathrm{final}}$, the binding energies of "blue" and "green" excitons, E_b^{blue} and E_b^{green}, respectively (depending on which exciton is formed in the final jump), and the Coulombic binding energy of the close e–h pair, $e^2/4\pi\varepsilon\varepsilon_0 a$: $\Delta=(E_{\mathrm{HOMO}}^{\mathrm{final}}-E_b)-(E_{\mathrm{HOMO}}^{\mathrm{initial}}-e^2/4\pi\varepsilon\varepsilon_0 a)$, where $a\leqslant 1$ nm is the typical hopping distance between neighboring sites. The energies of the HOMO levels for the formation of blue excitons may be considered to be identical ($E_{\mathrm{HOMO}}^{\mathrm{initial}}\approx E_{\mathrm{HOMO}}^{\mathrm{final}}$), at least within the characteristic interval of the energetic disorder $\pm\sigma$. This is not expected, however, for the case of the formation of green excitons, as one would expect differing HOMO levels between the polymer backbone and the keto defect. Surprisingly however, recent calculations by Zojer *et al.*[17] showed that the HOMO level of the keto defect is similar to that of the unperturbed PF chain. We also note that the binding energy of blue excitons E_b^{blue} is expected to be smaller than the Coulombic binding energy of the close e–h pair, $e^2/4\pi\varepsilon\varepsilon_0 a$ for $a\leqslant 1$ nm.[18] As the energy of the green singlet exciton state in the fluorenone defect is typically 0.5–0.6 eV lower than that of the blue exciton, it is reasonable to assume that E_b^{green} may be somewhat smaller than E_b^{blue}. The energetic barrier for recombination is therefore given by $\Delta\approx e^2/4\pi\varepsilon\varepsilon_0 a-E_b$, which can be positive

for blue exciton formation and negative (i.e., absent) for the case of green exciton formation. Thus, the final jump before exciton formation can be thermally activated and hence kinetically delayed as well as field-assisted for the case of blue emission, whereas this is not the case for the green emission. The mechanism of recombination, which is controlled by thermally activated hopping was proposed earlier by the authors of Ref. 18 for delayed fluorescence in MeLPPP. However, these authors only analyzed the effect of stabilization of long-lived geminate pairs by an electric field, and not the recombination kinetics.

It should be noted that the recombination constant does not need to be reduced with respect to the Langevin constant due to the kinetic delay of the last hopping jump, because close e–h pairs have no possibility of avoiding recombination. Nonradiative and thermally nonactivated recombination become, however, more probable for very close carrier pairs, and hence the efficiency of delayed blue emission is reduced. Figure 4 illustrates that the energy of charge carriers is shifted upwards (dashed line) with respect to the energy at zero applied field (dotted line), hence, the zero-field barrier for the blue radiative recombination Δ is reduced by the value of the potential drop eFa. Based on this qualitative picture, the field dependence of the blue EL intensity is estimated as

$$J_{\mathrm{EL}}^{\mathrm{blue}} \sim \exp[(-\Delta + eFa)/kT]/F, \tag{4}$$

assuming $\Delta - eFa > 0$, where $\Delta = e^2/4\pi\varepsilon\varepsilon_0 a - E_b^{\mathrm{blue}}$. In Fig. 2, the dashed and dotted curves are calculated from Eq. (4) using $a=0.8$ and $a=0.6$ nm, respectively. The second dotted curve is shifted down in order to fit the data for the less oxidized sample. We note that Δ seems to be not much more than 50 meV, otherwise $\exp(-\Delta/kT) \ll 0.1$ and the low-field efficiency of blue EL $\varphi^{\mathrm{blue}} \sim \exp(-\Delta/kT)$ would have to be unreasonably small. The condition $\Delta = 0.05$ eV requires reasonable values of $E_b^{\mathrm{blue}} = 0.35 - 0.50$ eV,[18] providing that $a = 0.8 - 0.6$ nm. As was shown earlier, these simple yet plausible assumptions lead to a good description of the temperature and field dependence of the delayed EL observed, and allow the development of a microscopic picture of the recombination mechanisms of trapped charge carriers in conjugated polymers. Varying the degree of oxidation of the sample and therefore the density of deep electron traps does not modify the underlying recombination kinetics, but simply the relative magnitudes of defect to backbone emission.

IV. CONCLUSIONS

Photo-oxidation of polyfluorenes introduces emissive on-chain defects, which act as deep traps for electrons.[6,7,9] By varying the level of oxidation and by studying the temporal evolution of the EL occurring from backbone sites and from fluorenone defects, we are able to investigate the influence of even relatively small concentrations of emissive trapping sites on the recombination kinetics. The relative increase of the delayed blue emission with increasing field strength inside the polymer layer with respect to the delayed green emission can be understood in terms of an increase of the radiative recombination efficiency in the high-energy band with electric field. Most probably, the radiative recombination in the blue band of the polymer backbone is impeded by a small energy barrier $\Delta \approx 0.05$ eV, which is caused by the difference between the Coulombic binding energy of close e–h pairs and the binding energy of the singlet exciton.[18] One has to note that $\Delta \cong \sigma$ and hence the energy barrier can originate from an energetic disorder of states for holes even for the case in which the exciton binding energy $E_b^{\mathrm{blue}} = e^2/4\pi\varepsilon\varepsilon_0 a$. Our findings reiterate the importance of reducing charge carrier trapping sites in conjugated polymers for opto-electronic applications and show how charge trapping can influence the mechanisms of recombination. This is particularly important for wide-gap polymeric semiconductors, where traps are often already introduced during synthesis.[9] In the case of emissive on-chain defects, trapping results in a reduction not only of the recombination efficiency but also of the color purity. The reduction in EL efficiency from backbone sites also provides an explanation for the previously observed large difference between EL and PL spectra of polyfluorenes, where EL spectra typically exhibit much stronger defect emission than PL.[9,10]

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