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Citation for published version (APA):

van Eersel, H., Bobbert, P. A., Janssen, R. A. J., & Coehoorn, R. (2016). Effect of Förster-mediated triplet-polaron quenching and triplet-triplet annihilation on the efficiency roll-off of organic light-emitting diodes. *Journal of Applied Physics*, 119(16), 1-12. [163102]. <https://doi.org/10.1063/1.4947457>

DOI:

[10.1063/1.4947457](https://doi.org/10.1063/1.4947457)

Document status and date:

Published: 28/04/2016

Document Version:

Accepted manuscript including changes made at the peer-review stage

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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- The final published version features the final layout of the paper including the volume, issue and page numbers.

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Effect of Förster-mediated triplet-polaron quenching and triplet-triplet annihilation on the efficiency roll-off of organic light-emitting diodes

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We report the results of a systematic study of the interplay of triplet-polaron quenching (TPQ) and triplet-triplet annihilation (TTA) on the efficiency roll-off of organic light-emitting diodes (OLEDs) with increasing current density. First, we focus on OLEDs based on the green phosphorescent emitter tris[2-phenylpyridine]iridium (Ir(ppy)_3) and the red phosphorescent dye platinum octaethylporphyrin (PtOEP). It is found that the experimental data can be reproduced using kinetic Monte Carlo (kMC) simulations within which TPQ and TTA are due to a nearest-neighbor (NN) interaction, or due to a more long-range Förster-type process. Furthermore, we find a subtle interplay between TPQ and TTA: decreasing the contribution of one process can increase the contribution of the other process, so that the roll-off is not significantly reduced. Furthermore, we find that just analyzing the shape of the roll-off is insufficient for determining the relative role of TPQ and TTA. Subsequently, we investigate the wider validity of this picture using kMC simulations for idealized but realistic symmetric OLEDs, with an emissive layer containing a small concentration of phosphorescent dye molecules in a matrix material. Whereas for NN-interactions the roll-off can be reduced when the dye molecules act as shallow hole and electron traps, we find that such an approach becomes counterproductive for long-range TTA and TPQ. Developing well-founded OLED design rules will thus require that more quantitative information is available on the rate and detailed mechanism of the TPQ and TTA processes.

I. INTRODUCTION

The ultimate performance of organic optoelectronic devices like organic light-emitting diodes (OLEDs), organic lasers, organic photovoltaic devices and light-emitting field-effect transistors is determined by exciton physics. Processes like exciton generation, dissociation and (non)radiative decay, but also interactions with charge carriers and other excitons govern the gain and loss mechanisms. The large probability of such interactions at high excitation levels poses a challenge for the development of high-brightness OLEDs and electrically-pumped organic lasers, due to roll-off of the efficiency with increasing current density. Considerable effort has been made to study the rate of the individual quenching processes thought to contribute to the roll-off in phosphorescent OLEDs: triplet-polaron quenching (TPQ) and triplet-triplet-annihilation (TTA).^{1–6} However, due to the complex interplay of the various processes and the spatial non-uniformity inherent to organic semiconductor materials and devices, it has been difficult to link the results of individual experiments to actual device performance.

TPQ and TTA can be Dexter-mediated, i.e. due to Dexter transfer⁷ of an exciton to a site occupied by a carrier or an exciton, and/or Förster-mediated, i.e. due to transfer of the exciton energy to an occupied site by

the Förster mechanism.⁸ In the case of Förster transfer, care should be taken that the proper Förster radius is used to describe the process: it is different for exciton transfer to a molecule in an ionized state (TPQ), in a triplet excited state (TTA), or in the ground state (exciton diffusion). This picture is reasonably well established in the literature for Förster-mediated TTA. For example, for the well-studied phosphorescent emitter molecules platinum octaethylporphyrin (PtOEP) and tris[2-phenylpyridine]iridium(III) (Ir(ppy)_3), spatially separated pump-probe measurements of thin films have yielded TTA Förster radii of 2.7 and 3.1 nm, respectively,⁹ while values of 3.6 and 2.9 nm have been deduced from transient absorption measurements in solution.¹⁰ A recent kinetic Monte Carlo study of the roll-off in multilayer white OLEDs has revealed a fair agreement with experiment when using TPQ and TTA Förster radii describing the quenching of excitons on Ir(ppy)_3 and bis(2-methyldibenzo[f,h]quinoxaline)(acetylacetonate)-iridium(III) ($\text{Ir(MDQ)}_2(\text{acac})$) of 3.0 nm.¹¹ The possible additional role of more short-range Dexter-type TTA has so far not been established. We note that in the case of fluorescent emitters, for which Förster-mediated TTA is not possible, Dexter-type TTA is non-negligible at high triplet densities, giving rise to delayed fluorescence.¹² Whereas various studies have provided evidence for a significant contribution of TPQ to the roll-off of OLEDs,^{3,5,13,14} and whereas effective TPQ rate coefficients have been determined for various host-guest systems,¹ the underlying mechanism (Dexter-type and/or Förster-type?) and interaction

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range have not yet been established. A complication is that the effective TPQ rate is not only determined by the TPQ Förster-radius, but also by the polaron diffusion coefficient. Both quantities are in general different for electrons and holes. Furthermore, also exciton diffusion affects both the TTA and TPQ rates (see Ref. 15).

In previous work,¹⁶ we demonstrated how advanced molecular-scale kinetic Monte Carlo (kMC) simulations including charge transport, exciton diffusion and quenching can be employed to elucidate the cause of the efficiency roll-off in prototypical green and red-emitting small-molecule OLEDs based on Ir(ppy)₃ and PtOEP, respectively. As this study clearly revealed various non-idealities, the study was extended to idealized but potentially realizable symmetric OLED stacks. For these stacks, design rules were established, providing guidelines for optimally choosing the dye trap depth with respect to the matrix energy levels. We also studied the role of TPQ on the degradation of OLEDs.¹⁷ In both cases, we assumed both TPQ and TTA to be instantaneous nearest-neighbor (NN) processes. Under this assumption, we find TPQ to be the dominant contribution to the roll-off. However, assuming an instantaneous nearest-neighbor process may overestimate the interaction rate for small distances, and may underestimate the rate for large distances. For example, there are experimental indications that not every encounter of a triplet exciton and a polaron gives rise to quenching.^{18,19}

In this paper, we use kMC simulations to investigate and quantify the effect of the interaction strength and range of TPQ and TTA on the efficiency roll-off and to investigate the interplay between both processes. We focus first on the prototypical green and red-emitting OLEDs, studied in Ref. 16. The emissive layer (EML) consists of 5 mol% Ir(ppy)₃ or PtOEP, respectively, embedded in a matrix consisting of 4,4'-bis[N-carbazolyl]-1,1'-biphenyl (CBP). The EML is sandwiched in between electron and hole transport, injection and blocking layers. The electrodes consist of indium tin oxide (ITO) and lithium fluoride/aluminum (LiF/Al). The layer structure, the materials used and the energy levels assumed in the simulations are shown in Figure 1(a). The simulation results are compared to the experimental data presented by Giebink and Forrest.⁴ The simulations extend the work presented in Ref. 16 by showing how for a fixed value of the Förster radius for TTA, taken equal to 3.5 nm (close to the experimental values, discussed above), a variation (in the 0–3.5 nm range) of the less well-known value of the Förster radius for TPQ affects the roll-off. Surprisingly, we find that such a variation has only little effect on the overall internal quantum efficiency (IQE) loss, even when the TPQ contribution is quite dominant. The efficiency loss thus cannot be viewed as a simple sum of two independent contributions. Instead, there is a subtle interplay between both loss processes. We also find that a simple analysis of the shape of the roll-off curve is insufficient for determining the relative roles of TPQ and TTA.

Since the results of Ref. 16 showed that these devices

are far from optimal – most excitonic events happen close to the interface with the hole transport layer (HTL) – we compare these devices with idealized but potentially realizable symmetric OLEDs, with a variable dye trap depth Δ . The layer and energy level structure is shown in Figure 1(b). In Ref. 16, it was shown that by varying Δ the emission profile as obtained at small voltages can be varied from being double-peaked (emission near the interfaces with the hole and electron transport layers), *via* quite uniform across the EML for Δ close to 0.2 eV, to being more confined to the EML center for large Δ . This analysis is here generalized by studying the effects of a variation of the TPQ Förster radius as well as the TTA Förster radius in the 0–3.5 nm range. Whereas we found in Ref. 16 that for the case of nearest neighbour TTA and TPQ a uniform emission profile is optimal for obtaining a small roll-off, we find here that the optimal trap depth of the dye molecules depends strongly on the range of the TPQ and TTA processes, in particular for TPQ. It thus follows that for developing proper OLED design rules, it will be necessary to determine the TTA and TPQ interaction ranges.

FIG. 1. (a) Energy level and layer structure of the green and red OLEDs studied. The phosphorescent EML is sandwiched in between materials facilitating hole and electron injection, transport and blocking: CuPc (copper phthalocyanine), α -NPD (4,4'-bis[N-(1-naphthyl)-N-phenyl-amino] biphenyl), BCP (2,9-dimethyl, 4,7-diphenyl, 1,10-phenanthroline) and Alq₃ (tris [8-hydroxyquinoline] aluminum). (b) Energy level and layer structure of the idealized OLED, here for a dye trap depth Δ of 0.3 eV.

The paper is organized as follows. In Section II, we

describe the parameters and simulation method used in more detail. The results for the red and green device are presented in Section III using five scenarios. In addition to the reference case using instantaneous TPQ and TTA at nearest neighbors only, similar to the situation in Ref. 16, we study four TPQ scenarios using a fixed TTA Förster radius of 3.5 nm for both Ir(ppy)₃ and PtOEP devices. TPQ is either not included, described as an instantaneous nearest-neighbor process, or described as a longer-range process with Förster radii of 1.5 nm and 3.5 nm. The 1.5 nm value used is similar to the Förster-radius describing triplet diffusion.²⁰ We regard this value as a lower bound for the actual Förster radius for TPQ. Results for the idealized symmetric devices are presented in Section IV, in which these four TPQ scenarios are combined with the four analogous TTA scenarios. For these 16 scenarios, we also study the effect of the dye trap depth on the roll-off. Section V contains a summary, conclusions and outlook.

II. METHOD

The simulations are based on the kinetic Monte Carlo device simulation tool Bumblebee.²¹ More details on the method can be found in Refs. 15–17, and 22. We use an OLED device model within which charge transport and excitonic processes are included in an integrated manner. The complete device stack is modeled as a collection of sites on a simple cubic lattice with site density $N_t = 10^{27} \text{ m}^{-3}$, where each site represents a molecule. Charges are injected from the electrodes and hop from site to site with a rate as described within the Miller-Abrahams formalism.²³ Both the Coulomb interactions between the carriers as well as between the carriers and their image charges are included. We assume the hopping attempt frequencies to be equal for all materials and for both holes and electrons and use a typical value for the attempt frequency to the first neighbor, $3.3 \times 10^{10} \text{ s}^{-1}$ (see Ref. 16).²⁴ In Ref. 16, we have found that for the case of instantaneous nearest-neighbor TPQ and TTA, the effect of the hopping frequency on the roll-off is rather limited. In Ref. 17, we have shown that under simplified ‘uniform density model’ conditions, charge carrier transport in an energetically highly disordered emissive layer will indeed give rise to only a limited dependence of the roll-off on the hopping attempt frequency. We take a Gaussian density of states (DOS) with width 0.1 eV, based on the energy levels shown in Figure 1. The energy levels are spatially uncorrelated. As discussed in Ref. 16, the highest occupied molecular orbital (HOMO) energies were obtained using ultraviolet photoelectron spectroscopy, and the lowest unoccupied molecular orbital (LUMO) was obtained by adding the measured optical gap. We note that the efficiency roll-off, if expressed as a function of the current density, is insensitive to an overall shift of hole or electron energy levels. The wavefunction decay length was assumed to be 0.3 nm for all charge

transfer and Dexter-type exciton transfer processes.

Excitons are generated upon a hop of a carrier to a site occupied by a carrier of the opposite sign, and can dissociate by the reverse mechanism, both taking into account a triplet exciton binding energy of 1.0 eV, as motivated in Ref. 16, and may be deduced for the case of Ir(ppy)₃ from recent work of Yoshida and Yoshizaki.²⁵ We assume instantaneous intersystem crossing. Therefore, only triplet excitons are considered. Excitons can decay radiatively (non-radiatively), with rates $\Gamma_{r(nr)} = 1.0(0.3) \mu\text{s}^{-1}$ and $\Gamma_{r(nr)} = 0.010(0.051) \mu\text{s}^{-1}$, for Ir(ppy)₃ and PtOEP respectively. The maximum possible IQE is equal to the photoluminescence (PL) efficiency which follows from these rates, viz. 0.77 and 0.164, respectively. The PL efficiency used for Ir(ppy)₃ is close to the value of 0.766 obtained in Ref. 26 for Ir(ppy)₃ in 4,4',4''-tris(N-carbazolyl)-triphenylamine (TCTA), and intermediate between the values of 0.62 or 0.70 for 4 wt% (3 mol%) Ir(ppy)₃ in CBP reported in Ref. 27 and the value of 0.92 for 6 wt% Ir(ppy)₃ in CBP reported in Ref. 28. The PL efficiency used for PtOEP (0.164) is very close to the value of 0.16 reported in Ref. 27 for a film of 4 wt% PtOEP in CBP, fabricated by spin-coating and studied under ambient conditions. In an earlier study of the same authors a PL efficiency of 0.37 was reported for similar films, studied under vacuum conditions, and a value of 0.54 was reported for PtOEP in polystyrene, fabricated by spin-coating and studied under vacuum conditions.²⁹ These observations are indicative of the sensitivity of the PL efficiency of PtOEP to the film fabrication and measurement conditions, and to the matrix material used.

The simulation includes Förster-type exciton diffusion⁸, with a transfer rate

$$r_{F,diff} = \Gamma \left(\frac{R_{F,diff}}{R} \right)^6, \quad (1)$$

where $\Gamma = \Gamma_r + \Gamma_{nr}$ is the overall exciton decay rate, $R_{F,diff}$ is the Förster radius and R is the distance between donor and acceptor, and Dexter-type exciton diffusion⁷, with a transfer rate

$$r_{D,diff} = k_{D,0} \exp \left(-\frac{2R}{\lambda} \right), \quad (2)$$

where $k_{D,0}$ is the Dexter prefactor and λ is the exciton wavefunction decay length. As motivated in Ref. 16, $R_{F,diff}$ is taken equal to 1.5 nm, and $k_{D,0}$ is such that for Ir(ppy)₃ the Dexter contribution to the diffusion rate is equal to the Förster contribution for transfer over 1.443 nm, close to $R_{F,diff}$. For shorter distances, the diffusion is thus assumed to be a predominantly Dexter-type process, whereas it is predominantly due to Förster transfer for larger distances. The exciton energies are assumed to be energetically disordered, as described by with a Gaussian distribution with a width of 0.1 eV. Analogous to the Miller-Abrahams formalism used for charge

transport, the rate of energetically upward exciton transfer is reduced by an Arrhenius factor $\exp[-\Delta E/(k_B T)]$, with ΔE the energy level difference, k_B the Boltzmann constant and T the temperature. We find that for the small dye concentrations considered, the contribution of exciton diffusion to the TPQ and TTA rates is limited.

TTA is either described as an instantaneous nearest-neighbor process, or as a process with a distance-dependent rate consisting of a Dexter (electron-exchange) contribution and, for the phosphorescent dyes, a Förster (dipole-dipole interaction) contribution. In the simulations, we describe TTA as a single Monte Carlo step in which one triplet is lost. The excitation is assumed to happen randomly on one of the two dye molecules involved. The Dexter contribution may be viewed as resulting from the formation of a spatially bound triplet-triplet complex, followed by energy relaxation via internal conversion. The intermediate-state spin-structure depends on the spin-spin coupling, and the relaxation process to the final state can depend on interactions with the local nuclear hyperfine field and with an external magnetic field.³⁰ In principle, the relaxation process can give rise to singlet, triplet and quintet excited states. However, the formation of a quintet excited state on one molecule is energetically unlikely. If the relaxation process gives rise to a singlet excited state, fast intersystem crossing on the phosphorescent emitters will almost immediately give rise to a triplet state. The Dexter contribution to the TTA rate is assumed to be equal to the Dexter exciton diffusion rate, given by Eq. (2). The Förster contribution involving two triplet excitons on phosphorescent dye molecules results from the small admixture of singlet character in their triplet wavefunctions. The distance dependence is described in a manner analogous to Eq. (1), with a Förster radius $R_{F,TTA}$. We note that this Förster radius is in general different from the Förster radius for exciton diffusion due to energy transfer between the dye molecules. For diffusion, the rate depends on the overlap of the dye emission spectrum and the absorption spectrum of the (non-excited) dye molecule, whereas the TTA rate depends on the overlap of the dye emission spectrum and the triplet exciton extinction spectrum.³¹

The TPQ process may be viewed as the transfer of a triplet exciton to a site at which a polaron resides, followed by fast non-radiative de-excitation of the polaron. In the simulations, this is described as a single-step process in which the exciton is lost. The polaron is not displaced. Analogous to the description of TTA, TPQ is either described as an instantaneous nearest-neighbor process, or as a process with a distance-dependent rate consisting of a Förster (dipole-dipole interaction) contribution with a Förster radius $R_{F,TPQ}$ (equal for electrons and holes) and a Dexter (electron-exchange) contribution with a rate as given by Eq. (2). In the case of Förster-type TPQ, only TPQ due to polarons on dye molecules was included. $R_{F,TPQ}$ depends on the overlap of the dye emission spectrum and the extinction spectrum of a neg-

atively or positively charged molecule. We note that it cannot be excluded that in a certain fraction of the cases the polaron is transferred to the site at which the exciton resides. Making such a distinction would be relevant when using the simulations to predict the OLED lifetime, assuming that the degradation is a result of the dissipation of the excess energy resulting from the TPQ process.¹⁷

III. RESULTS – RED AND GREEN DEVICES

In this section, we study the effect of the range of TPQ and TTA on the shape and composition of the roll-off for green- and red-emitting devices, based on Ir(ppy)₃ and PtOEP, respectively. A comparison with experimental results presented by Giebink and Forrest⁴ will allow us to investigate which sets of parameter values can reproduce the actual roll-off measurements. Five scenarios are considered:

- (I) instantaneous NN-TTA and NN-TPQ,
 - (II) $R_{F,TTA} = 3.5$ nm and instantaneous NN TPQ,
 - (III) $R_{F,TTA} = 3.5$ nm and no TPQ,
 - (IV) $R_{F,TTA} = 3.5$ nm and $R_{F,TPQ} = 1.5$ nm,
 - (V) $R_{F,TTA} = 3.5$ nm and $R_{F,TPQ} = 3.5$ nm,
- as motivated in Section I.

We find that for these five scenarios the current-voltage ($J(V)$) characteristics are essentially identical, i.e. equal to the result already shown for scenario I in Ref. 16. Apparently, excitonic effects such as exciton dissociation do not influence the $J(V)$ curve. Figure 2 summarizes the results from the simulations for the roll-off, for the five scenarios studied. The experimental IQE curves have been obtained from the experimental external quantum efficiency given in Ref. 4, assuming 20% light outcoupling efficiency. This neglects a possible change of the light outcoupling efficiency due to a shift of the emission profile with increasing voltage. For the two devices studied, these shifts were found to be very small. For both devices, the emission profile is peaked strongly near the anode-side of the EML, with a tail which extends to the cathode side of the EML. For the Ir(ppy)₃ (PtOEP) devices approximately 80% and 65% (65% and 60%) of the emission occurs in the 5 nm zone adjacent to the HTL at 4 V and 10 V, respectively. In view of the quite optimal distance of the peak in the recombination profiles with respect to the cathode, near the maximum in the light-outcoupling efficiency from the microcavity at a distance of approximately one-quarter of the internal emission wavelength, such small emission profile shifts will only marginally affect the light-outcoupling efficiency (see e.g. Ref. 32). As may be seen, for the green device, the experimental roll-off is well described by the simulations. For the red device the experimental roll-off is slightly underestimated by the simulations for scenarios I–IV, whereas the roll-off is well reproduced by scenario V.

At small voltages, the IQE of the green devices is significantly reduced in comparison with the maximum possi-

FIG. 2. Simulated and experimental roll-off curves of the (a) Ir(ppy)₃ and (b) PtOEP device, for all five scenarios (see section III and the top part of Figure 3). Experimental data from Ref. 4. For both devices, the experimental IQE curve is obtained from the experimental external quantum efficiency assuming 20% light outcoupling efficiency. The dashed lines indicate the IQE at small current densities, expected from the PL efficiency of the emitter molecules.

ble value of ~ 0.77 which would be expected from the PL efficiency. As reported already in Ref. 16, this is caused by charge carrier and triplet exciton loss to the α -NPD hole transport layer. Up to high voltages, this effect is the dominant cause of the IQE loss. That is one of the reasons why in this case the dependence of the roll-off on the scenario type is very weak. For the red devices, the efficiency loss to the hole transport layer is seen to be rather insignificant. However, also for this case the sensitivity of the roll-off to the specific scenario is limited, albeit that it is more pronounced than for the green devices. This surprisingly weak sensitivity indicates that the TPQ and TTA contributions to the efficiency loss are non-additive. For example, for the red devices the roll-off increases only slightly from scenario III (no TPQ) to scenario V ($R_{F,TPQ} = 3.5$ nm). That could (erroneously) be viewed as evidence that TTA is also for scenario V the predominant loss process. Instead, we show below that TPQ is then under all conditions studied the major loss factor.

A full quantitative overview of all contributions in the EML to the efficiency loss within all scenarios is given by Figure 3. Firstly, we note that, as mentioned above, also loss processes outside the EML, for example the loss to the α -NPD layer can play a role (see Ref. 16). That this

loss to the HTL depends strongly on the scenario can be seen from the comparison between the almost identical roll-off curves (Figure 2) and the varying fractions of radiative decay in Figure 3. Secondly, in particular for the red devices, the figure shows that the contributions to the roll-off are indeed non-additive: an increase of the TPQ contribution, e.g. from scenario III to V, results in a decrease of the TTA contribution. Thirdly, we find that at low voltages TPQ is always the dominant process, except for scenario III within which TPQ is not included. The contribution of TTA increases with increasing voltage. However, in the voltage range studied it only becomes the dominant process for scenario IV. Finally, we find that introducing Förster-mediated TTA with $R_{F,TTA} = 3.5$ nm (scenario II) significantly increases the TTA contribution as compared to the NN-TTA reference case (scenario I), while (as shown already in Figure 2) the roll-off curves are essentially identical. The non-additivity of the contributions of TTA and TPQ can be explained as follows: if the interaction strength for one of the quenching mechanisms increases, the triplet density in the device will decrease, so that the role of the other quenching mechanism will be less prominent.

Overall conclusions are that (i) there is thus a subtle interplay between the TPQ and TTA processes, (ii) losses of charge carriers or excitons to the transport layers can play a role, and (iii) it is therefore in general not possible to deduce the predominant roll-off mechanism just from the shape of the roll-off curves. For obtaining further refined insight into the origin of the roll-off, dedicated studies determining the molecular-scale details of the TPQ process will therefore be required.

IV. RESULTS – IDEALIZED DEVICES

In order to investigate to what extent the findings obtained above may be generalized, we study the effect of varying the TPQ and TTA rate on the roll-off for the idealized but potentially realizable devices, with an EML consisting of a single matrix material and 5 mol% Ir(ppy)₃ guest molecules. The energy level structure is shown in Figure 1(b). In this architecture, which was introduced in Ref. 16, the losses due to imperfect electron blocking and exciton charge transfer to the HTL, are eliminated. Furthermore, the shape of the emission profile is optimized by carefully tuning the energy difference, Δ , between the phosphorescent dye and the embedding matrix (“dye trap depth”). Charge carrier trapping at the guest sites prevents that the exciton formation is confined to narrow interfacial zones near the HTL and ETL. This is illustrated by Figure 4, which gives an overview of the voltage and trap depth dependence of the triplet density profile as well as the electron and hole density profiles in the absence of TPQ and TTA, with Δ in the range 0–0.5 eV. An overview of the trap depth dependence of the $J(V)$ curves was given in Ref. 16.

For the case of immediate NN-TPQ and NN-TTA, we

FIG. 3. The different excitonic contributions in the EML to the roll-off for the five scenarios indicated in the top part of the figure, for both dyes. The device structures are as shown in Fig. 1(a). As mentioned in the main text, for the green devices part of the efficiency loss at small current densities and part of the roll-off with increasing current density is also due to charge and exciton loss to the α -NPD hole transport layer. For scenario II, a breakdown of all excitonic processes which includes these losses is given in Figure 1(d) of Ref. 16.

found in Ref. 16 that $\Delta \sim 0.3$ eV provides an optimum between the reduction of the roll-off due to a more uniform emission profile and the increase of the overvoltage due to the increasing dye trap depth. In this section, we aim to refine and generalize this design rule by including scenarios where longer-range excitonic interactions play a role. In total 16 scenarios are considered, combining NN-TPQ, no TPQ, and TPQ due to Förster-type processes with a Förster radius of 1.5 or 3.5 nm with the analogous TTA processes. These scenarios thus include scenarios I–V studied in the previous section.

Figure 5 shows the efficiency roll-off as obtained for all scenarios. We find that also for these devices, the $J(V)$ curves are essentially independent of the scenario. To facilitate a comparison between the different scenarios, we show in Figure 6 the variation of the current densities J_{90} and J_{50} at which the efficiency is reduced to 90% and 50% of the value of radiative decay (PL) efficiency $\eta_{\text{rad}} = 0.77$. The figure shows that the use of charge carrier trapping at guest sites as a means to make the emission profile more uniform leads to a decrease of the roll-off in the case of nearest-neighbor TPQ and TTA. However, charge carrier trapping at guest sites is only weakly effective for the case of long-range TTA ($R_{F,TTA} = 3.5$ nm) and no TPQ, and is even counterproductive for the case of long-range TPQ ($R_{F,TTA} = 3.5$ nm) and no TTA. So for longer-range interactions, the sensitivity to accumulated charges and excitons in thin interfacial zones decreases apparently quickly. In the case of long-range TPQ, the trapped charges (visible as the increased charge carrier density in Figure 4) constitute a negative effect, so that elimination of charge carrier trapping is then most advisable. The design rule for minimizing the roll-off is then to make use of guest molecules which do

not give rise to charge carrier trapping. We note that this rule can only be applied under the constraint that the dye molecule triplet excitons remains well below the host triplet exciton energy. Otherwise, the resulting enhanced exciton diffusion length and longer exciton lifetime would negatively affect the roll-off.

Various authors have analyzed the roll-off of OLEDs resulting from TPQ, TTA or the interplay between both processes using the ‘uniform density model’,^{6,33} within which the charge carrier and exciton densities are assumed to be uniform across the EML thickness, d . We have used a similar approach in Ref. 17. Within this model, the reduction of the IQE due to TTA, $\eta_{\text{IQE,TTA}}$, follows from the steady-state triplet rate equation

$$\frac{dn_T}{dt} = -\frac{n_T}{\tau} - \frac{1}{2}k_{TT}n_T^2 + \frac{J}{ed} = 0, \quad (3)$$

with n_T the triplet volume density, k_{TT} an effective triplet-triplet interaction rate coefficient, and e the elementary charge. The factor 1/2 is appropriate when upon each interaction process one of the two triplets is lost. As a result,³³

$$\eta_{\text{IQE,TTA}} = \frac{J_{50}}{4J} \left(\sqrt{1 + \frac{8J}{J_{50}}} - 1 \right) \eta_{\text{rad}}, \quad (4)$$

with

$$J_{50,TTA} = \frac{4de}{\tau^2 k_{TT}}. \quad (5)$$

Analogously, the IQE roll-off due to TPQ, $\eta_{\text{IQE,TPQ}}$, follows from the triplet rate equation

$$\frac{dn_T}{dt} = -\frac{n_T}{\tau} - 2k_{\text{TPQ}}n_{\text{pol}}n_T + \frac{J}{ed} = 0, \quad (6)$$

FIG. 4. Hole (red), electron (blue) and triplet (magenta) layer-averaged concentration profiles for various trap depths and voltages, for 20–80 nm inner segments of devices as shown in Fig. 1(b), assuming no TPQ and no TTA. The layer-to-layer fluctuations reflect the statistical uncertainty related to the finite box size and the finite simulation time.

with n_{pol} the electron and hole polaron volume density (assumed to be equal), and with k_{TPQ} an effective triplet-polaron interaction rate coefficient. The polaron density may be related to the current density using the Langevin equation for the exciton generation rate. For the case of equal electron and hole mobilities which are independent of the electron and hole densities and the electric field, the roll-off is then given by^{17,33}

$$\eta_{\text{IQE,TPQ}} = \frac{\eta_{\text{rad}}}{1 + \left(\frac{J}{J_{50}}\right)^m}, \quad (7)$$

with a roll-off steepness exponent $m = 1/2$, and with

$$J_{50,\text{TPQ}} = \frac{de^2\mu}{2\varepsilon\tau^2k_{\text{TPQ}}^2}, \quad (8)$$

where μ is the mobility, and ε is the dielectric permittivity. More generally, when the mobility is polaron density dependent and given by a proportionality relation $\mu \propto n_{\text{pol}}^b$, the roll-off is given by Eq. (7) with $m = (1+b)/(2+b)$ and with J_{50} given in Table 2 of Ref. 17. As $b > 1$, one expects that m will then vary in between 1/2 and 1. Eq. (7) is often found to provide a fair phenomenological fit to the measured roll-off. From the simulations, we can now judge for a large variety of systems to what extent the uniform density model provides a good prediction of J_{50} and of the shape of the roll-off curves.

The applicability of Eq. (7) may be seen most easily from double logarithmic plots of the relative quench rate, defined as the ratio of the effective rate Γ_q of all TPQ and TTA loss processes and the total radiative and non-radiative decay $\Gamma = \Gamma_{\text{rad}} + \Gamma_{\text{nr}}$, versus the current density (see also Ref. 17). Γ_q is defined implicitly from the IQE: $\eta_{\text{IQE}} \equiv \Gamma_{\text{rad}}/(\Gamma_{\text{rad}} + \Gamma_{\text{nr}} + \Gamma_q)$. If Eq. (7) is valid, one expects that the relative quench rate is given by

$$\frac{\Gamma_q}{\Gamma} \equiv \frac{\eta_{\text{rad}}}{\eta_{\text{IQE}}} - 1 = \left(\frac{J}{J_{50}}\right)^m. \quad (9)$$

so that such a relative quench rate plot is then expected to provide a straight line with a slope m and an x -axis zero-crossing at $J = J_{50}$. Figure 7 gives an overview of the relative quench rate curves for all cases, including an approximation to the simulation results which is based on Eq. (7) with the values of J_{50} and m taken such that at the J_{50} and J_{90} points the curves coincide with the values obtained by interpolation from the simulations. This approximation is also shown in Figure 5. It may be seen that Eq. (7) provides in most cases a fair description, with a slope parameter in the range of 0.3–1.0 for the cases studied. For the case of the NN-TPQ and NN-TTA scenario, e.g., the figure shows that Eq. (9) is well obeyed for the entire range $\Delta = 0$ –0.5 eV, as shown in Ref. 17.

Providing a quantitative analysis of the roll-off curves is most easy for the scenario with $R_{\text{F,TTA}} = 3.5$ nm and

FIG. 5. The roll-off in internal quantum efficiency as function of the current-density for all 16 scenarios for the device shown in Fig. 1(b). In each panel, the trap depth is varied between 0.0 eV and 0.5 eV. At small current densities, the IQE is limited by non-radiative decay to 0.77. The curves give a fit with Eq. (7).

no TPQ. The observed very weak dependence of the roll-off on the trap depth indicates that the effect of the shape of the emission profile on the roll-off is only minor. When the effect of triplet exciton diffusion may be neglected, and for sufficiently small n_T , k_{TT} is given by⁸

$$k_{TT} \cong \frac{4\pi^2}{3} \frac{R_{F,TTA}^3}{\tau}. \quad (10)$$

Figure 8 (full curve) shows the relative quench rate curve which then would follow using Eq. (4). For current densities up to approximately the J_{50} value, the figure reveals good agreement between the predicted and simulated quench rate curves. However, while the uniform density model predicts a decrease of the slope of the quench rate curve, from 1 for $J \ll J_{50}$ to 1/2 for $J \gg J_{50}$, the simulation data do not reveal such an effect. We attribute that to the increasing non-uniformity of the triplet density profile with increasing current density (see Figure 4),

leading to a larger efficiency loss than as predicted from the uniform density model.

Figure 9 shows the detailed composition of the efficiency loss for devices with trap depths $\Delta = 0.0, 0.3$ and 0.5 eV, for the reference scenario I (NN-TPQ and NN-TTA) and when combining Förster-type TTA with the experimentally realistic parameter value $R_{F,TTA} = 3.5$ nm with various TPQ parameterizations (scenarios II–V). The replacement of nearest-neighbor TTA (scenario I) by Förster-mediated TTA (scenario II) increases the roll-off somewhat, especially for $\Delta = 0.3$ and 0.5 eV. At higher voltages it contains then a larger contribution due to TTA, as longer-range TTA processes are added to the TPQ-dominated roll-off. Scenario III (no TPQ) gives rise to a somewhat reduced roll-off as compared to scenario I, especially for $\Delta = 0.0$ eV, indicating that switching-off the loss due to TPQ is not completely compensated by the additional TTA. The decomposition for

FIG. 6. The J_{50} (dashed) and J_{90} (solid) current densities as function of the trap depth for all 16 scenarios, for the device shown in Fig. 1(b).

scenario IV is almost identical to that for scenario III: when $R_{F,TPQ} = 1.5$ nm, TTA is thus the dominant loss process, apart maybe for small current densities. Increasing the dye trap depth, does however add an increasing, but small contribution of TPQ, as would be expected from the increasing carrier density (see Figure 4). Scenario V shows a strong dependence of both the size of the roll-off and the composition of the roll-off on the dye trap depth. The roll-off increases significantly from $\Delta = 0.0$ to 0.5 eV, and while the roll-off is almost completely caused by TTA for $\Delta = 0.0$ eV, the opposite is true for $\Delta = 0.5$ eV. This complete reversal can be explained by the strong increase in carrier density with an increase in dye trap depth (see Figure 4) in combination with the large TPQ rate for high carrier concentrations for $R_{F,TPQ} = 3.5$ nm.

V. CONCLUSIONS AND OUTLOOK

We have studied the effect of the type and range of excitonic loss processes due to TTA and TPQ, and their interplay, on the efficiency roll-off of phosphorescent OLEDs by comparing experiment with kinetic Monte Carlo simulations. The rather weak sensitivity of the roll-off to the range over which TPQ and TTA occur, implies that the actual roll-off is the result of a complex interplay of both processes. A reduction of one process often leads to a larger contribution of the other process. Therefore, just reducing the TPQ or TTA rates will often only lead to a very modest reduction of the roll-off. In non-ideal OLEDs, the roll-off can be further complicated by additional loss channels, such as the transfer of triplets to the α -NPD in case of the Ir(ppy)_3 device. For these reasons, the results show that the relative contribution of TTA and TPQ to the roll-off cannot be determined from

FIG. 7. The quench rate for the device shown in Fig. 1(b) as function of the current density for all 16 scenarios. The symbols are the simulation results, the lines indicate a fit with Eq. (9). Each panel contains the curves for trap depths of 0.0 eV to 0.5 eV. The dashed lines indicate J_{50} and J_{90} .

just the shape of the roll-off curve when using simple rate equation models and analytical expressions of the roll-off such as Eqs. 4 and 7.

However, using kMC simulation studies, such as reported in this paper, it is possible to obtain all separate contributions to the triplet exciton loss under various scenarios. For the green and red devices studied in this paper, simulations were done for a restricted set of scenarios in which the most uncertain rate (that of the TPQ process) was varied. Whereas the roll-off curves were found to be quite similar for the various scenarios considered, and quite similar to the experimental roll-off curves, TPQ was found to provide at low voltages the dominant contribution to the efficiency loss in the emissive layer, unless in the simulations TPQ is switched off entirely. The use of kMC simulations as a means to reject scenarios which are inconsistent with the experimental data will be even more fruitful for OLEDs in which complications such as efficiency losses to the transport layers are avoided. This is shown by Figs. 5–7, which reveal the sensitivity of the roll-off of idealized symmetric OLEDs to the TTA and

TPQ scenario assumed.

In order to further enhance the fruitfulness of kMC simulations as a means to determine the roll-off mechanism, and in order to be able to use the simulations to develop well-founded OLED design rules, more detailed molecular-scale descriptions of the TTA and TPQ processes in emissive host-guest systems are needed. This has become particularly evident from our study of the effect of the dye trap depth on the roll-off in the idealized symmetric devices. We have found that the effectiveness of trapping charge carriers on dye molecules in order to reduce the roll-off depends strongly on the range over which the excitonic interactions take place. While an increase of the dye trapping depth flattens the triplet density profile, which is advantageous in the case of NN-TPQ and NN-TTA, the beneficial effect reduces with increasing TPQ range. The increase in carrier density, and hence in TPQ, due to an increase in the trap depth can then actually have a negative effect on the efficiency. This makes it challenging to predict the optimal stack design. Molecular-scale studies should provide a

FIG. 8. Symbols: simulated current density dependence of the relative quench rate for devices shown in Fig. 1(b) for the scenario with $R_{F,TTA} = 3.5$ nm and no TPQ, for trap depths Δ of 0.0 to 0.5 eV. The full curve shows the prediction (Eq. (4)) from the uniform density model (UDM).

view on the relative roles of nearest-neighbor and long-range Förster-type TPQ and TTA and should provide accurately measured microscopic interaction parameters such as the TTA and TPQ Förster radii (see e.g. Ref. 9 and 34). Triplet losses, leading to roll-off, are enhanced by triplet exciton diffusion.⁹ The development of a mechanistic microscopic-scale triplet exciton diffusion model, which would validate the approach used in this paper or which would provide a refined view, would therefore contribute strongly to the applicability of kMC simulations as a means to determine the most important contribution to the roll-off. Having such an experimentally validated set of microscopic interaction parameters available will also help to develop a consistent simulation-based description of the functioning of OLEDs with more complex emissive layers having more than one matrix and dye material and with varying dye concentrations.

ACKNOWLEDGMENTS

We would like to thank F.W.A. van Oost and J.J.M. van der Holst for their contributions to the Monte Carlo code, C. Weijtens for the UPS measurements and the Philips Research e-Science department for technical support. This research was supported by the Dutch nanotechnology program NanoNextNL. The work was carried out in part at the Philips Research Laboratories, Eindhoven, The Netherlands (HvE and RC).

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FIG. 9. Composition of the IQE roll-off for the idealized symmetric devices shown in Fig. 1(b) with dye trap depth $\Delta = 0, 0.3$ and 0.5 eV, for scenarios I–V.

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fraction of events

scenario I
NN-TTA
NN-TPQ

scenario II
 $R_{F,TTA} = 3.5$ nm
NN-TPQ

scenario III
 $R_{F,TTA} = 3.5$ nm
no TPQ

scenario IV
 $R_{F,TTA} = 3.5$ nm
 $R_{F,TPQ} = 1.5$ nm

scenario V
 $R_{F,TTA} = 3.5$ nm
 $R_{F,TPQ} = 3.5$ nm

non-rad.
decay
TTA
TPQ

radiative
decay

non-rad.
decay
TTA

TPQ
radiative
decay

voltage, V [V]

relative quench rate