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Kinetic Monte Carlo modeling of the efficiency roll-off of a multilayer white OLED

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Triplet-triplet annihilation (TTA) and triplet-polaron quenching (TPQ) are processes in OLEDs that can lead to a roll-off of the internal quantum efficiency (IQE) with increasing current density J . We present a kinetic Monte Carlo modeling study of the IQE and the color balance as a function J of a multilayer hybrid white OLED that combines fluorescent blue with phosphorescent green and red emission. We investigate two models for TTA and TPQ involving the phosphorescent green and red emitters: short-range quenching and long-range Förster-type quenching. Short-range quenching predicts roll-off to occur at much higher J than measured. Taking long-range quenching with Förster radii for TTA and TPQ equal to twice the Förster radii for exciton transfer leads to a fair description of the measured IQE- J curve, with the major contribution to the roll-off coming from TPQ. The measured decrease of the phosphorescent vs. fluorescent component of the emitted light with increasing J is correctly predicted by the modeling. A proper description of the J -dependence of the relative contributions of red and green phosphorescent emission needs further model refinements.

The introduction of phosphorescent emitters in white organic light-emitting devices (OLEDs) has gained much interest due to the possibility of obtaining a very high internal quantum efficiency (IQE).¹⁻³ The significant spin-orbit coupling of the heavy metal atoms in phosphorescent emitters allows not only singlet, but also triplet excitons to decay radiatively. However, the triplet excitons still have a lifetime that is considerably longer than that of singlet excitons. As a consequence, they are more vulnerable to quenching. Three exciton-quenching mechanisms have been identified:⁴⁻⁶ (1) triplet-triplet annihilation (TTA) (2) triplet-polaron quenching (TPQ), and (3) field-induced exciton dissociation. Exciton quenching will increase in importance when the current density and the brightness level of the OLED increase, since the densities of charge carriers and excitons as well as the electric field are then higher. The drop in the efficiency with increasing current density as a result of exciton quenching is known as the efficiency roll-off. A better understanding of the factors that determine this roll-off is crucial, because in practice one would like to use white OLEDs for lighting at the highest possible brightness level. Moreover, exciton-quenching processes may also be a source for material degradation, because the involved high excitation energies may lead to breaking of chemical bonds and hence to loss of functionality of the used semiconducting molecules.

Complicating aspects in the analysis of exciton quenching are that the dominant quenching process may depend on the particular system and that a predictive description of quenching processes is presently lacking. Reineke *et al.*⁶ argue that field-induced dissociation does not play an important role in state-of-the-art OLEDs. Baldo *et al.*⁴ claim that TTA is the only process responsible for efficiency roll-off in the case of Ir(ppy)₃ and PtOEP dyes.

On the other hand, Kalinowski *et al.*⁷ claim that field-induced dissociation and TPQ are the main mechanisms behind the efficiency roll-off.

In previous work⁸ we modeled the electronic processes that lead to electroluminescence in a hybrid multilayer white OLED by kinetic Monte Carlo (kMC) simulations. The stack structure and the energy-level scheme of the OLED are given in Figures 1(a) and (b), respectively. The hybrid character of this OLED lies in the combined use of a fluorescent blue emitter (Spiro-DPVBi) with phosphorescent green (Ir(ppy)₃) and red (Ir(MDQ)₂(acac)) emitters. Hybrid OLEDs are commercially important, since as yet no sufficiently stable blue phosphorescent emitter for OLEDs exists. The suboptimal efficiency due to the use of a blue fluorescent emitter is taken for granted. An important role is played in the OLED of Figure 1 by the interlayer in between the blue and green emitting layers. This interlayer, consisting of a mixture of an electron (TPBi) and hole (TCTA) transporter, should allow passage of electrons and holes in opposite directions, while blocking triplet excitons from transferring from the green emitter to the energetically lower-lying triplet level in the blue fluorescent layer.

In Ref. 8, a two-step procedure was followed in the simulations by decoupling charge and exciton dynamics. First, the dynamics of electrons and holes, and the formation of excitons was simulated. The emitter sites in the green and red emitting layers at which excitons were generated were recorded. Next, the excitons were released at the recorded emitter sites and their dynamics and final radiative or non-radiative decay was simulated. The resulting simulated emission profile and color balance were found to agree well with experiment. Because of the decoupling of charge and exciton dynamics, exciton quenching could not be investigated. In the present Letter we

Figure 1. (a) Layer structure of the studied hybrid OLED (surface area: 2.7×2.5 mm). From bottom to top: glass, indium tin oxide, p-doped hole-injecting layer of NHT5 with 4 mol% NDP2 (materials supplied by Novaled), hole-transporting layer of α -NPD, red-emitting layer of α -NPD with 5 mol% Ir(MDQ)₂(acac), green-emitting layer of TCTA with 8 mol% Ir(ppy)₃, interlayer of the hole transporter TCTA with 33 mol% of the electron transporter TPBi, blue-emitting layer of Spiro-DPVBi, electron-transporting layer of NET5, and n-doped electron-injecting layer of NET5 with 4 mol% NDN1 (materials supplied by Novaled). (b) HOMO and LUMO energies of the materials in the OLED in (a) as used in the simulations, in each case defined as the energy at the top of a nearly Gaussian density of states with standard deviation $\sigma = 0.1$ eV. The horizontal arrows indicate the work functions used for the doped hole- and electron-injecting layers. See Ref. 8 for further details.

consider exactly the same OLED of Figure 1, but treat charge dynamics, exciton dynamics and exciton quenching in a fully integrated way. We recently performed such integrated simulations for prototype monochrome OLEDs.^{9–11} This is the first time that such simulations are applied to a realistic multilayer white OLED.

The details of the kMC simulation procedure were described in Ref. 8. We repeat here only the most important aspects. The molecular sites in the organic layers are modeled as a cubic lattice with a lattice constant of 1 nm, corresponding to the typical intermolecular distance. In the charge transport, the highest molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are given energies according to Figure 1(b), with the addition of a random energy as obtained from a correlated disorder model with a standard deviation $\sigma = 0.1$ eV. Emitter sites in the green and red layer are randomly assigned according to their known concentrations. Electron trap sites in the electron transporting layer (NET5) and the blue emitting layer are randomly assigned and given an energy drawn from an exponential distribution, according to model studies of electron transport in these layers. The electron- and hole injecting n- and p-doped layers are modeled as sheets of metallic-like sites with energies given in Figure 1(b). They can inject or collect an arbitrary number of charges. Coulomb interactions and image charge effects are included. Site-to-site hopping of charges occurs by a Miller-Abrahams

hopping rate, with a prefactor chosen such that measured or assumed electron and hole mobilities of the different materials in the stack at room temperature, low electric field and low carrier concentration, are reproduced. The use of Marcus hopping rates would be more appropriate, but introduces as new parameters the reorganization energies of all the materials in the stack. In the limit of low electric field the difference in mobility functions following from Miller-Abrahams and Marcus hopping rates was shown to be small.¹²

In Ref. 8, exciton formation was assumed to be always an irreversible energetically downward process. Here, we add a refinement by taking into account the binding energy of an exciton and allowing also exciton dissociation. An exciton is then modeled as an electron-hole pair at a site with an energy equal to the HOMO-LUMO energy difference minus the exciton binding energy. Charge carriers generated from dissociated excitons can again participate in exciton formation. In the blue fluorescent layer we take an exciton binding energy of 0.5 eV, corresponding to a typical singlet binding energy, whereas in the interlayer and in the green and red phosphorescent layers we take an exciton binding energy of 1.0 eV, corresponding to a typical triplet binding energy. We checked that this refinement does not have a noticeable influence on the results presented below, demonstrating that exciton dissociation is not an important process in this OLED under the investigated conditions.

Like in Ref. 8, we assume that 25% of the excitons formed in the blue fluorescent layer are singlets, emitting a photon by immediate radiative decay. The 75% triplet excitons formed are assumed to be lost. Excitons formed at traps (an insignificant fraction) are also assumed to be lost. In the green- and red-emitting layers, excitons are either formed directly on the emitters, or on the host molecules (TCTA and α -NPD, respectively), followed by immediate transfer to an emitter in their neighborhood. Excitons formed in the interlayer (a significant fraction) and in all other layers (a negligible fraction) are assumed to be lost.

The mixing in of singlet character by the iridium spin-orbit coupling, in addition to the predominant triplet character, allows for radiative decay as well as Förster transfer of excitons in between the phosphorescent emitters, including transfer from green to red emitters. The transfer rate between two emitters i and j is¹³

$$k_{ij} = \frac{1}{\tau_{r,i}} \left(\frac{R_{0,ij}}{R_{ij}} \right)^6, \quad (1)$$

where $\tau_{r,i}$ is the radiative lifetime of emitter i , R_{ij} the distance between the two emitters, and $R_{0,ij}$ the Förster radius for transfer from i to j . The Förster radius accounts for the spectral overlap between the emission spectrum of i and the absorption spectrum of j . Excitons can decay radiatively with a rate $k_{r,i} = 1/\tau_{r,i}$, or non-radiatively with a rate $k_{nr,i} = 1/\tau_{nr,i}$. These rates are related to the radiative decay probabilities $\eta_{r,i}$ by $\eta_{r,i} = k_{r,i}/(k_{r,i} + k_{nr,i})$. The parameters used in the

exciton dynamics are taken from literature. For the green-emitting Ir(ppy)₃ we take $k_r = 0.816 \mu\text{s}^{-1}$ and $k_{nr} = 0.249 \mu\text{s}^{-1}$,¹⁴ leading to a radiative decay probability $\eta_r = 0.77$, which agrees with the value $\eta_r = 0.76$ given in Ref. 15. For the red-emitting Ir(MDQ)₂(acac) we take $k_r = 0.588 \mu\text{s}^{-1}$ ¹⁶ and $k_{nr} = 0.112 \mu\text{s}^{-1}$ as obtained from $\eta_r = 0.84$.¹⁵ A typical value of $R_0 = 1.5 \text{ nm}^{13}$ is taken for transfer in between green or red emitter molecules, while for the transfer from a green to a red emitter we take $R_0 = 3.5 \text{ nm}$, according to the estimate in Ref. 17. Transfer from red to green emitters should play no role and is therefore neglected.

No sufficiently detailed knowledge is as yet available about the molecular-scale mechanisms of TTA and TPQ. We investigate two possible scenarios, already explored by us in prototype monochrome OLEDs:^{9–11} (1) immediate quenching of one triplet exciton when two triplet excitons or a triplet exciton and a charge appear on nearest-neighboring sites (short-range quenching);^{9,10} (2) quenching by Förster transfer of a triplet exciton to a site where another triplet exciton or a charge resides (long-range quenching).¹¹ In the latter scenario the question is what to take for the Förster radius R_0^Q of the “quenching transfer”. The simplest choice is to take $R_0^Q = R_0$, but this ignores the difference in the absorption spectrum of an excited emitter hosting a triplet exciton or a charge and an unexcited emitter. Since further exciting an already excited emitter is much easier than exciting an unexcited emitter, we will actually have $R_0^Q > R_0$. We choose to take $R_0^Q = \gamma R_0$ for all possible quenching transfers, with $\gamma > 1$ an adaptable overall enhancement factor. This simplifying assumption ignores differences in γ between TTA and TPQ, and between different emitters, but does provide a way to systematically investigate the influence of this enhancement of exciton quenching transfer on the IQE.

We checked that without taking into account exciton quenching, the simulated room-temperature emission profile at a bias voltage $V = 3.6 \text{ V}$ is within the error bars equal to that displayed in Figure 2(b) of Ref. 8. The simulated room-temperature J - V curve is plotted in Figure 2, together with the curve of the non-integrated simulation approach from Ref. 8. Also these results are essentially the same. We note that, apart from the neglect of exciton dissociation, the non-integrated approach also neglects the fact that a charge and an exciton, or two excitons, cannot occupy the same site. Apparently, neither has a significant influence on the simulation results. Figure 2 also shows a remeasured J - V curve, together with the original measurement from Ref. 8. At high voltage the current density has decreased somewhat, pointing at a possible slight degradation. In addition, J - V data obtained with a pulsed approach are given. Using such an approach, it is possible to reach higher voltages and current densities than with a dc approach, because the effects of heating are suppressed. The pulsed measurements were performed in three voltage regions with a duty cycle of 1% and with different pulse durations:

Figure 2. Previous⁸ and new measured and simulated current density-voltage characteristics, with results from pulsed measurements added (see main text for details). The errors in the simulated data were estimated from simulations for different disorder configurations and are smaller than the displayed symbols.

for $V < 4 \text{ V}$ pulses of 1 s were used, for $4 < V < 6 \text{ V}$ pulses of 0.1 s and for $V > 6 \text{ V}$ pulses of 50 μs . Since all data connect smoothly, we can conclude that relaxation effects due to the use of pulses are small. In a broad voltage range there is a good agreement between simulated and experimental results. The disagreement at high voltage ($> 6 \text{ V}$) might be due to the use of Miller-Abrahams instead of Marcus hopping rates. The discrepancy at low voltage could be due to an underestimation of the trapping of holes by Ir(MDQ)₂(acac) in the red emitting layer.⁸ The J - V curves of the simulations in which exciton quenching is included are not displayed, since these are indistinguishable from the J - V curve without exciton quenching. From this we can conclude that exciton quenching has in our case no significant influence on the current density.

Results for the IQE, defined as the fraction of generated excitons decaying radiatively, are plotted as a function of J in Figure 3 and compared to the experimental IQE. The experimental IQE was obtained by dividing the luminescence as measured by a photodiode perpendicular to the OLED pixel by the current density and scaling the result such that at a bias of 3.6 V the IQE is $25 \pm 5\%$, corresponding to the measured external quantum efficiency (EQE) of $5 \pm 1\%$ and the light-outcoupling efficiency of $20 \pm 1\%$, as reported in Ref. 8. In the high current density region $J > 500 \text{ A/m}^2$, the IQE was obtained using the pulsed measurements. The transition can be observed in Figure 3, but results in only a small discontinuity. The simulated results plotted in Figure 3 correspond to no quenching (squares), short-range quenching (diamonds), long-range quenching with $R_0^Q = R_0$ ($\gamma = 1$, downward-pointing triangles), and long-range quenching with $R_0^Q = 2R_0$ ($\gamma = 2$, upward-pointing triangles).

Figure 3. Measured and simulated internal quantum efficiency as a function of current density. Black discs: experimental results, obtained by dividing the measured luminescence by the current density and scaling such that at a bias of 3.6 V the external quantum efficiency of $5 \pm 1\%$ reported in Ref. 8 is reproduced with an outcoupling efficiency of $20 \pm 1\%$. There is an overall uncertainty in these results of $\pm 5\%$. Blue squares: simulated results without quenching. Green diamonds: short-range quenching by triplet-triplet annihilation (TTA) and triplet-polaron quenching (TPQ). Orange downward-pointing and red upward-pointing triangles: long-range quenching by TTA and TPQ with Förster quenching radius $R_0^Q = R_0$ and $2R_0$, respectively. The error in the simulated results is of the order of the symbol size. Inset: the same, but with only TTA switched on.

The latter results provide a fair description of the whole experimental IQE- J curve. At high currents $J > 10^3$ A/m² the roll-off is somewhat underestimated. This has very likely the same origin as the overestimation of J in this region observed in Figure 2: to obtain the same J as in the experiment, a lower V is needed in the simulations than in the experiment, leading to the presence of fewer charge carriers and excitons in the OLED, and hence to less quenching. It is very gratifying to observe that not only the roll-off, but also the roll-on of the IQE at low J , i.e. the initial increase of the IQE with J , is properly described by the simulations. The explanation is that with increasing current the fraction of excitons generated in the interlayer between the green- and blue-emitting layers, which are assumed to be lost, decreases. In the case of long-range quenching with $\gamma = 2$ there is in the low- J region also some effect of exciton quenching, bringing the simulated data right on top of the experimental data. The enhancement factor $\gamma = 2$ leads to an assumed $R_0^Q = 3$ nm both for Ir(ppy)₃ and Ir(MDQ)₂(acac). This value is comparable to the reported values $R_0^Q = 3.1$ and 2.7 nm in thin films,¹⁸ and 2.9 and 3.6 nm in solution,¹⁹ for quenching by TTA in Ir(ppy)₃ and PtOEP, respectively.

To investigate the relative contributions of TTA and TPQ to exciton quenching we plot in the inset of Figure 3

the results with only TTA switched on. It is clear from these results that TTA is in our case only relevant for $J > 10^3$ A/m², which is far beyond the current density at which this OLED is typically operated (up to $J = 10^2$ A/m²). Hence, the main cause for roll-off in the present OLED appears to be TPQ. This conclusion is in line with the conclusion drawn in Ref. 9 from simulations of prototypical phosphorescent green and red OLEDs based on Ir(ppy)₃ and PtOEP, respectively.

Figure 4. Main panel: normalized measured spectra at different voltages. The arrows indicate the trends in the relative contributions of the primary colors with increasing voltage. Inset: simulated results for the generated fractions of blue (discs), green (triangles) and red (squares) photons without quenching (upper panel) and with quenching by TTA and TPQ with $R_0^Q = 2R_0$ (lower panel). The error in the simulated results is of the order of the symbol size.

To study whether also the change in color balance can be described by our modeling we display in Figure 4 (main panel) the normalized spectra of the OLED at different voltages in the range $V = 3$ -7 V, measured with a standard spectrometer perpendicular to the OLED pixel, and the fractions of the number of photons created in the red-, green- and blue-emitting layers according to the simulations (inset) without quenching (upper panel) and with long-range quenching for $\gamma = 2$ (lower panel). In agreement with our assumption that mainly triplet excitons suffer from quenching, the measured relative contribution of fluorescent blue emission increases with J at the expense of the phosphorescent red and green emission. The specific dependencies on J of the measured relative contributions of red emission (a monotonic decrease) and green emission (a decrease followed by an increase) are not accurately reproduced by the simulations. Taking somewhat different enhancement factors γ for Ir(MDQ)₂(acac) and Ir(ppy)₃ could improve the agreement. However, such fine-tuning is beyond the present study, since then also various other refinements in the modeling should be considered. For example, part of the increase of the relative contribution of blue fluorescent

emission with J may be due to singlet excitons produced by TTA of the thus far disregarded triplet excitons in this layer.

In summary, we have compared a modeling by kinetic Monte Carlo simulations of the internal quantum efficiency of a hybrid white multilayer OLED, and in particular the roll-off of this efficiency with increasing current density, with experiment. The measured roll-off behavior can be described with plausible parameters for triplet-triplet annihilation and triplet-polaron quenching. We find that triplet-polaron quenching is the dominant quenching mechanism. The observed relative increase of the blue component of the emitted light with current density is in agreement with the simulations. A proper description of the dependence of the red and green components on current density requires further model refinements.

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