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Citation for published version (APA):

Ligthart, A., Nevels, T. D. G., Weijtens, C. H. L., Bobbert, P. A., & Coehoorn, R. (2021). Mechanistic description of the efficiency loss in organic phosphorescent host–guest systems due to triplet-polaron quenching. *Organic Electronics*, 91, [106058]. <https://doi.org/10.1016/j.orgel.2020.106058>

Document license:
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DOI:
[10.1016/j.orgel.2020.106058](https://doi.org/10.1016/j.orgel.2020.106058)

Document status and date:
Published: 01/04/2021

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

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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Mechanistic description of the efficiency loss in organic phosphorescent host–guest systems due to triplet-polaron quenching

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ARTICLE INFO

Keywords:

Organic semiconductors
Triplet-polaron quenching
Field-induced dissociation
Roll-off
Organic light-emitting diodes
Kinetic Monte Carlo simulations

ABSTRACT

In this study we demonstrate how a mechanistic description can be obtained of the interplay of all processes that give rise to the efficiency loss due to triplet polaron quenching (TPQ) in phosphorescent host-guest systems such as used in organic light-emitting diodes (OLEDs). We study unipolar devices with an emissive layer consisting of m-MTDATA:Ir(ppy)₃(acac), in which excitons on the phosphorescent Ir(ppy)₃(acac) molecules are quenched by holes on the m-MTDATA host. The final TPQ-process is disentangled from all other relevant processes, such as polaron and exciton diffusion and field-induced exciton dissociation, by carrying out a combination of electrical, photoluminescence (PL) and field-induced dissociation experiments. The analysis is supported by carrying out kinetic Monte Carlo simulations. We find that a conventional approach, within which the loss is phenomenologically quantified using a rate coefficient, cannot consistently describe all experimental results. For a wide temperature range a fair mechanistic description of all results is obtained when using a TPQ Förster radius of 3.8 nm and a triplet exciton binding energy of 0.9 eV.

1. Introduction

Phosphorescent organic light emitting diodes (OLEDs) show a strongly reduced internal quantum efficiency at high luminance levels. The main loss processes that contribute to this efficiency roll-off are triplet-triplet annihilation (TTA) and triplet-polaron quenching (TPQ). Both TTA and TPQ are bimolecular interactions. TTA is the process of energy transfer between a donor and acceptor triplet exciton, in which one or both of the excitons are lost. TPQ is the result of energy transfer from a triplet exciton to a polaron. Subsequently, the excited polaron decays non-radiatively to its ground state, upon which the excitation energy is lost. As the molecules are highly excited during TTA and TPQ events, the probability of the breaking of a bond during such an event is strongly enhanced, even though it is for each single event for commonly used materials still very small. The resulting degradation probability is largest when blue phosphorescent emitters are involved [1–3].

For a long time, there has been an intensive discussion in the literature about the relative contributions of TTA and TPQ to the efficiency roll-off [4–9]. To accurately quantify both contributions it is necessary

to describe the processes involved in a mechanistic manner. The relative contributions of TTA and TPQ result from a subtle interplay with many other processes, such as exciton diffusion and field-induced exciton dissociation [10–13]. In previous work we disentangled the final TTA rate from the rates of all other processes that influence the overall loss by affecting the triplet exciton density, such as guest-guest exciton diffusion and host-mediated diffusion [14–16]. In the present study we provide a mechanistic description of the interplay of all processes that determine the efficiency loss due to TPQ in a selected phosphorescent organic semiconductor host-guest system. In particular, we disentangle the roles of the direct TPQ loss process and field-induced exciton dissociation.

When studying phosphorescent host-guest systems, important research subjects are the relative roles of quenching by polarons on the host and the guest molecules [17], the relative roles of quenching by hole and electron polarons [18,19], and ultimately the development of molecular-scale understanding of the TPQ mechanism. Triplet-polaron quenching studies typically make use of either photoluminescence (PL) experiments, electroluminescence (EL) experiments or combinations of the two, depending on whether unipolar or bipolar devices are

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studied [5,17–25]. Correctly disentangling the roles of hole and electron quenching requires the use of unipolar devices, studied using a PL experiment. An important challenge in the analysis of any experiment is obtaining accurate information on the polaron density profile across the thickness of the device. Ideally, the density is uniform across the thickness of the zone from which the emission takes place. In PL experiments, also the light-incoupling and light-outcoupling efficiencies across the device thickness must be accurately known, in particular when the emission occurs from a zone within which these efficiencies are strongly non-uniform. In that case, also the emitter orientation must be accurately known [26]. The analysis should furthermore take a possible enhancement of the radiative decay rate by micro-cavity effects (Purcell effect) into account [5]. As pointed out by Wehrmeister et al. [5], the TPQ rate is unaffected by micro-cavity effects. Finally, the analysis should include the possible effects of field-induced exciton dissociation [22,23,25]. We will address this issue more extensively below.

Based on these considerations, we have chosen to focus this study on TPQ in host-guest systems containing 4,4',4''-tris[3-methylphenyl(phenyl)amino]triphenylamine (m-MTDATA) as the host material and

bis[2-(2-pyridinyl-N)phenyl-C](acetylacetonato)-iridium(III) ($\text{Ir}(\text{ppy})_2(\text{acac})$) as the phosphorescent guest molecule, using unipolar (hole-only) devices with the layer and energy level structure that is shown in Fig. 1(b). The molecular structures are shown in Fig. 1(a). The selection of the contact and injection layers will be motivated in Section 2. This carefully selected host-guest system utilizes an idea that was first proposed and demonstrated by Hertel et al. for a polymer system [27], viz. to select a host material with a HOMO energy that is higher (less negative) than that of the guest. Advantageously, that simplifies the development of an accurate mechanistic model for the hole transport and the hole density throughout the device, independent of the concentration of guest molecules, as a first step to a mechanistic description of the TPQ process. The resulting near-uniformity of the hole density across the thickness of the doped layer and the relatively large distance to the metal (Al) electrode will be shown to make the analysis quite insensitive to microcavity effects. The difference of the energy of triplets on m-MTDATA (~ 2.62 eV [28,29]) and $\text{Ir}(\text{ppy})_2(\text{acac})$ (~ 2.38 eV) is larger than the minimum value of ~ 0.2 eV that we found from previous work to be required for good exciton confinement to the phosphorescent emitters [16]. An unavoidable consequence of the use of a host material

Fig. 1. (a) The molecular structures of $\text{Ir}(\text{ppy})_2(\text{acac})$ and m-MTDATA. (b) The energy level diagram of the studied hole-only devices used for the TPQ experiments (device type A). The HOMO levels were measured using UPS and the LUMO levels were obtained using measured exciton energies and estimated exciton binding energies, as discussed in the text [28, 31,33–35]. The 10 nm MoO_x layer is contacted by a 100 nm Al layer. (c) Energy level diagram of device type B, in which the MoO_x and CBP layers are replaced by a 3 nm LiF layer, which is again contacted by a 100 nm Al layer. This device, where hole injection is prevented when a positive voltage is applied to the LiF electrode, is used for the field-induced dissociation experiments.

with a HOMO energy that is higher (less negative) than that of the guest is that the activation energy for dissociation of triplet excitons on the guest to a charge-transfer type exciton with the hole on a neighboring host molecule is reduced. It is well known that field-induced dissociation can affect the efficiency of OLEDs. For phosphorescent host-guest systems this effect was extensively studied by Kalinowski et al. [25], Reineke et al. [22] and Haneder et al. [23]. We note that in well-designed OLEDs exciton dissociation plays no *direct* role in the efficiency roll-off, as dissociated excitons will reform in time when the charge carriers are confined to the emissive layer (EML). However, the effect plays an *indirect* role, by leading to enhanced TPQ due to an increased local polaron density.

As a first step towards a mechanistic model in which all contributions to the roll-off are disentangled we develop an accurate charge transport model, based on an analysis of the measured current-voltage characteristics of neat m-MTDATA films using kinetic Monte Carlo (kMC) simulations. Next, we study the efficiency roll-off and the decrease of the effective radiative lifetime with increasing current density using time-resolved PL experiments, in a wide temperature range. The finding of a discrepancy at room temperature between the efficiency and lifetime roll-off, and the disappearance of that discrepancy at low temperature, provides clear evidence of the role of thermally-activated field-induced dissociation. We therefore study that effect independently under low-polaron-density conditions. As a final step, we use kMC simulations to demonstrate that all results can be consistently described assuming a Förster-type TPQ process, and deduce from the experiments the Förster radius and the triplet exciton binding energy.

2. Experimental and analysis methods

2.1. Efficiency roll-off measurements

The layer and energy level structure of the unipolar (hole-only) m-MTDATA:Ir(ppy)₂(acac) devices is shown in Fig. 1(b). We label this structure as “Device A”. The HOMO levels for m-MTDATA and Ir(ppy)₂(acac) were measured using ultraviolet photon spectroscopy (UPS) and were found to be −5.1 eV and −5.2 eV, respectively. The LUMO levels of m-MTDATA and Ir(ppy)₂(acac) were estimated by adding the experimental singlet and triplet energy, respectively, and an estimated value of 1 eV for the singlet and triplet binding energies to the HOMO energies. The estimated exciton binding energy is consistent with the values found by Yoshida et al. [30] from UPS and Low-Energy Inverse Photoemission Spectroscopy (LEIPS) for various organic materials. For Ir(ppy)₃ Yoshida et al. found an exciton binding energy of 1.03 eV, which is close to the value of the triplet binding energy of Ir(ppy)₂(acac) deduced in this work from exciton dissociation experiments (see below). In view of the large difference between the LUMO energies for the host and guest materials, triplets on a guest are not expected to show field-induced dissociation to a charge transfer (CT) state with the electron on a host. The final results of our study are therefore not sensitive to the precise values of the LUMO energies.

Devices of type A were fabricated by first spin-coating a 20 nm PEDOT:PSS layer, which for positive voltages over the device functions as a cathode, on a glass(120 nm indium-tin oxide) (ITO) substrate. Subsequently, the following layers were evaporated: a 50 nm hole transport layer (HTL) consisting of m-MTDATA, an EML consisting of co-evaporated m-MTDATA doped with 7 wt% (~9 mol%) of Ir(ppy)₂(acac), and another 100 nm of m-MTDATA. This stack design, with a relatively large distance of the emissive layer to the electrode layers, was chosen to prevent a large Purcell effect on the radiative decay rate of the excitons, such that a uniform exciton radiative lifetime can be assumed across the thickness of the EML [5,26,31]. The second contact, which for positive voltages serves as an anode, was fabricated by evaporating a 7 nm CBP layer, a 10 nm MoO_x layer and a 100 nm Al layer. Kotadiya et al. [32] have shown that by using a thin interlayer with a high ionization energy, such as the CBP layer used in our study with from UPS a HOMO energy

of −6.1 eV, an effectively Ohmic contact can be achieved between a MoO₃ electrode layer and an organic semiconductor with a relatively low ionization energy, such as m-MTDATA. We used a CBP layer thickness of 7 nm, for which the highest current density was achieved. For comparison, also undoped devices of type A with the same total (200 nm) layer thickness were fabricated. The current density-voltage $J(V)$ characteristics for the doped and undoped hole-only devices are presented in Fig. 2. The figure shows as expected no significant effect of the doping. The $J(V)$ characteristics of the devices at various temperatures are shown in the Supporting Information, see Fig. S1.

To study TPQ, the experimental approach introduced by Wehrmeister et al. [5] was adopted. Using a wavefunction generator a sequence of square voltage pulses was applied, with widths of 100 μ s, to ensure steady-state conditions, and a time interval between the pulses of 100 ms, to minimize the temperature increase at large applied voltages. Halfway each voltage pulse the devices are photo-excited using a pulsed nitrogen laser with a wavelength of 337 nm and a peak width of 3.5 ns (Stanford Research Systems, NL100). To obtain a uniform intensity profile and to ensure that only the active area was excited, a 1 mm² circular aperture was used. The initial triplet exciton density T_0 is estimated to be about $5 \times 10^{23} \text{ m}^{-3}$, which is sufficiently low to minimize the TTA loss. The resulting time-dependent photoluminescence was measured using a fast photodiode (MenloSystems, FPD 510-FV). Simultaneously, the photoluminescence was spectrally resolved using a gated CCD camera, with a delay of 2 ns and a measurement window of 20 μ s. Both measurements were performed under an angle of 30° with respect to the direction normal to the sample, enabling convenient alignment of the setup.

2.2. Field-induced dissociation measurements and analysis

The time dependence of the triplet exciton volume density $T(t)$, modified by triplet-polaron quenching in the absence of triplet-triplet annihilation, is often described by the following empirical rate equation:

Fig. 2. Room-temperature (295 K) current density-voltage ($J(V)$) characteristics for devices with an electrode structure such shown in Fig. 1(b). Full curves: experimental $J(V)$ characteristics for single-layer devices with a 150 (black), 200 (red) and 250 nm (blue) m-MTDATA layer, obtained from steady-state and pulsed measurements at low and high current densities, respectively. Dashed curve: experimental $J(V)$ characteristic for a 200 nm three-layer type-A device (see Fig. 1(b)), with a central m-MTDATA host layer containing 7.2 wt% Ir(ppy)₂(acac). Squares: kMC simulation results, obtained using the parameter values discussed in Section 2.3. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

$$\frac{dT}{dt} = G - \frac{T}{\tau} - k_{\text{TPQ,h}} n_h T - k_{\text{TPQ,e}} n_e T \quad (1)$$

with G the triplet generation rate, τ the effective triplet lifetime, $n_{h(e)}$ the hole (electron) densities, and $k_{\text{TPQ,h(e)}}$ the triplet-polaron quenching rate coefficients. Although this approach has didactic value, it ceases to be valid when (as discussed already in the Introduction) at large internal fields field-induced dissociation occurs. From Eq. (1), it would be expected that the decrease of the efficiency with increasing current density that follows directly from the relative time-integrated PL yield, $\eta_{\text{PL,rel}}(J)$, is equal to the decrease of the efficiency that is expected from the decrease of the relative lifetime, $\eta_{\tau,\text{rel}}(J)$:

$$\eta_{\text{PL,rel}}(J) \equiv \frac{\eta_{\text{PL}}(J)}{\eta_{\text{PL}}(J=0)} = \frac{1}{1 + \frac{r_{\text{TPQ}}(J)}{k_{\text{rad}} + k_{\text{nr}}}} = \frac{\tau(J)}{\tau(J=0)} \equiv \eta_{\tau,\text{rel}}(J) \quad (2)$$

with $r_{\text{TPQ}}(J) = k_{\text{TPQ,h}} n_h(J) + k_{\text{TPQ,e}} n_e(J)$. However, Reineke et al. [22] and Haneder et al. [23] observed that there can be a discrepancy between $\eta_{\text{PL,rel}}(J)$ and $\eta_{\tau,\text{rel}}(J)$, and attributed that to field-induced triplet exciton dissociation.

When developing a mechanistic description of the roll-off due to TPQ, it is thus important to develop as well an experimentally validated method for quantifying the process of field-induced exciton dissociation. A key parameter is the triplet exciton binding energy, $E_{\text{T,b}}$. In principle, $E_{\text{T,b}}$ follows from the difference between the fundamental energy gap E_g (the difference between the ionization energy and the electron affinity) and the triplet energy. As already mentioned before, Yoshida et al. [30] determined E_g from a combined photoemission and Low-Energy Inverse Photoemission Spectroscopy (LEIPS) study for tris(2-phenylpyridinato) iridium(III) ($\text{Ir}(\text{ppy})_3$), and deduced from the measured triplet energy, E_{T} , an exciton binding energy of $E_{\text{T,b}} \equiv E_g - E_{\text{T}} = 1.03 \pm 0.05$ eV. However, accurate LEIPS measurements of the electron affinity are not available for other Ir-cored emitters. Alternatively, $E_{\text{T,b}}$ can be deduced from measurements of the field-induced reduction of the PL efficiency in devices, as demonstrated e.g. in Ref. 14, where for the blue emitter tris(1-cyanophenyl-3-methylbenzimidazol-2-ylidene-C,C^{2'}) ($\text{Ir}(\text{cnbic})_3$) a value $E_{\text{T,b}} \approx 0.9$ eV was found. At present, it is not clear to what extent the triplet exciton binding energy varies between different Ir-cored emitters.

We quantify the exciton loss due to field-induced dissociation using Device B, shown in Fig. 1(c), and deduce $E_{\text{T,b}}$ from an analysis of the experimental results using kMC simulations (see Section 2.3). In this device the hole injection layers (CBP/MoO_x) are replaced by 3 nm LiF, which due to its low work function results in a large injection barrier for holes. That prevents the injection of holes when the Al|LiF electrode is used as the anode.

We remark that the neglect of field-induced dissociation is not the only reason why Eq. (1) is often an oversimplification when applied to application-relevant systems. In general, the rate-equation model assumes that the exciton and polaron density gradients are sufficiently small and that the interacting species are positionally uncorrelated. The former assumption is often invalid in practical OLEDs where the emission takes place in a narrow zone close to one of the blocking layers. The latter assumption can become invalid in the case of weak exciton and polaron diffusion during the exciton lifetime. Concerning TPQ, kMC simulations show that for a given system the rate coefficient is not constant, but dependent on the carrier density, the electric field, and (in a time-resolved experiment) on the time [11,13]. The extent to which k_{TPQ} is not just constant depends on material-specific details such as the emissive lifetime and the energetic disorder of the frontier orbital states, and the interaction type (short-range Dexter-type or longer-range Förster-type TPQ). These complications provide an additional motivation for analysing the quenching and field-induced dissociation experiments using a mechanistic model.

2.3. Kinetic Monte Carlo simulations

We use kMC simulations to develop a charge transport model and to disentangle the various contributions to the exciton dynamics in the studied devices. The simulations were performed using the simulation tool Bumblebee [36]. In the Supporting Information we give a brief overview of the steps involved in the kMC simulations. In previous work we have shown how kMC simulations can be used to describe and disentangle the excitonic processes involved in losses in phosphorescent host-guest systems due to TTA, as probed using time-resolved photoluminescence experiments [16,37]. The findings from these earlier studies concerning the description of the triplet energy distribution and intermolecular transfer rates will be used here as input for the simulations.

Charge transport. In the simulations, the host and guest molecules are taken to be randomly distributed on a cubic lattice with an intersite distance $a_0 = 1$ nm, with a spatially uncorrelated Gaussian energy distribution with a width (standard deviation) σ . The dependence of the polaron hopping rates on the initial and final state energies and the distance is described using the Miller-Abrahams model. To study triplet-polaron quenching it is crucial to be able to deduce the polaron density throughout the devices, using a charge transport model that consistently describes the $J(V)$ curves for the wide range of layer thicknesses and temperatures included in our experimental study. An excellent description of all $J(V)$ characteristics is obtained using the following parameters: a disorder energy $\sigma = 0.10$ eV, a hopping attempt rate to the first nearest neighbor $\nu_1 = 4.6 \times 10^{10} \text{ s}^{-1}$, and a wavefunction decay length $\lambda = 0.3$ nm. The resulting mobility in the limit of zero charge carrier density and zero field is then equal to $\mu_0 = 3 \times 10^{-9} \text{ m}^2/\text{V}$. The symbols in Fig. 2 indicate the kMC simulation results, which are in good agreement with the experimental results. From Fig. S1 (see the Supporting Information), it may be seen that this set of parameters also yields at 5 and 10 V a good description of the measured temperature dependence of the current density of the 250 nm devices.

PL quenching. kMC simulations mimicking the time-resolved PL experiments were carried out by introducing triplet excitons randomly on $\text{Ir}(\text{ppy})_2(\text{acac})$ molecules in a system with a layer structure as shown in Fig. 1, after convergence at a selected current voltage was achieved. The simulations were typically done for five nominally equal $50 \times 50 \text{ nm}^2$ devices, with different disorder configurations. If needed to achieve the statistical level of the efficiencies of a few percent, shown in the figures, simulations for more devices were done. Triplet-triplet annihilation was not included in the simulations. The value of the initial concentration of triplets in the host:guest layer was typically 10^{-3} triplets per site. Variations of this concentration by a factor 0.5–2 were not found to affect the efficiency roll-off curves. For all excitonic states Gaussian disorder with a disorder energy (standard deviation) of 0.04 eV is assumed. The radiative lifetime of the triplet excitons was taken equal to the measured effective lifetime at zero voltage. The non-radiative decay rate was taken equal to zero. That assumption is of no consequence to the analysis, as non-radiative decay does not affect the current density dependence of the normalized PL efficiency curves. The effective triplet exciton lifetime is obtained from the calculated time-dependent cumulative decay intensity, and is defined as $\tau_{\text{eff}} \equiv \tau_{1/2}/(\ln 2)$, where $\tau_{1/2}$ is the time at which 50% of the total emission has taken place.

TPQ is assumed to be a Förster-type process, with a rate r_{TPQ} given by

$$r_{\text{TPQ}} = \frac{1}{\tau} \left(\frac{R_{\text{F,TPQ}}}{R} \right)^6 \quad (3)$$

with τ the exciton lifetime, $R_{\text{F,TPQ}}$ the TPQ Förster radius and R the distance between the donor and the acceptor. In the simulations, we have used the measured lifetime at $V = 0$ V. The experimental value increases from 1.20 μs at 295 K to 1.39 μs at 190 K. This slight increase may be explained from the zero-field splitting of the triplet manifold [38]. In previous work we have shown that exciton diffusion due to

transfer between Ir(ppy)₂(acac) molecules starts to play a role for Ir(ppy)₂(acac) concentrations larger than 5 mol % [15,16]. As for the systems studied the guest concentration is larger, viz. 9 mol %, a Förster-type diffusion process with a Förster radius for guest-guest transfer equal to 2.7 nm is included [16]. Host-mediated diffusion is not included, because the triplet exciton confinement energy is larger than 0.2 eV [16].

Field-induced exciton dissociation. When a triplet exciton on an Ir(ppy)₂(acac) molecule dissociates, the hole will transfer to a neighboring m-MTDATA molecule whereas the electron will stay on the Ir(ppy)₂(acac) molecule, resulting in the formation of a CT state. Due to the Coulomb attraction the hole is limited in its movement away from the electron. After some time the geminate pair can generate again an exciton on the Ir(ppy)₂(acac) molecule. The resulting delay of the radiative decay gives rise to an increase of the emissive lifetime. By increasing the electric field, the energy difference between the local and charge transfer exciton states decreases, resulting in a further enhancement of the lifetime. However, increasing the applied field also increases the probability of complete dissociation of the electron and hole. Whether the effective lifetime decreases or is enhanced depends therefore on the balance between the rates of exciton dissociation, (re) generation and complete dissociation. Just like the rates of all other thermally-activated processes that are included in the kMC simulations, the rate of exciton dissociation due to transfer of a hole from a donor (D) site *i* to an acceptor (A) site *j* is assumed to be given by a Miller-Abrahams type expression:

$$r_{\text{dis}}(i, j) = \sqrt{\nu_{1,D} \nu_{1,A}} \exp\left(-\frac{2R_{ij}}{\lambda}\right) \exp\left(-\frac{|\Delta E_{\text{dis},ij}| + \Delta E_{\text{dis},ij}}{2k_B T}\right) \quad (4)$$

with $\sqrt{\nu_{1,D} \nu_{1,A}}$ the geometric mean of the nearest-neighbor hopping attempt rates for a hole in the pure donor material and in the pure acceptor material [39], R_{ij} the intersite distance, λ the wavefunction decay length (taken equal to 0.3 nm, see above), k_B the Boltzmann constant and T the temperature. $\Delta E_{\text{dis},ij} = E_{\text{HOMO},i} - E_{\text{HOMO},j} + E_{\text{T},b} - E_{\text{CT},b}$ is the energy difference between sites *i* and *j*, where $E_{\text{T},b}$ is the local triplet exciton binding energy and $E_{\text{CT},b}$ is the binding energy of the charge transfer exciton. The binding energy of the charge transfer exciton with an electron on site *i* and a hole on site *j* is given by $E_{\text{CT},b} = \frac{1}{4\pi\epsilon_0\epsilon_r} \frac{e^2}{R_{ij}}$, with ϵ_0 the vacuum dielectric permittivity, e the elementary charge and $\epsilon_r = 3$ the relative dielectric constant assumed in the simulations. We have used the hole transport parameters for m-MTDATA given above, and have used the same parameters for Ir(ppy)₂(acac). The value of $E_{\text{T},b}$ for Ir(ppy)₂(acac) is not well known. We will therefore treat it as a free parameter, to be determined from a fit to the experimental results. Triplet-polaron quenching was not included in the field-induced dissociation simulations, as the experiments are carried out at very small laser fluences.

Role of microcavity effects. In general, the normalized PL efficiency should be determined by weighing the position-dependent internal quantum efficiency $\eta_{\text{IQE}}(x, J)$ as obtained from the kMC simulations by the position-dependent light-incoupling and light-outcoupling efficiencies:

$$\eta_{\text{PL,rel}}(J) = \frac{\int_0^L \eta_{\text{in}}(x) \eta_{\text{out}}(x) \eta_{\text{IQE}}(J, x) dx}{\int_0^L \eta_{\text{in}}(x) \eta_{\text{out}}(x) \eta_{\text{IQE}}(0, x) dx} \quad (5)$$

where the integration extends over the 50 nm thick host-guest layer. However, for the studied devices we found that $\eta_{\text{IQE}}(J, x)$ does not depend significantly on the position *x*, so that no weighing is required.

3. Experimental results

3.1. Photoluminescence yield and emissive lifetime roll-off

Fig. 3 shows the results of the voltage-dependent PL measurements of device A. Fig. 3(a) gives the voltage dependence of the time-integrated but spectrally resolved PL intensity. The figure shows the characteristic emission profile of Ir(ppy)₂(acac), with an emission peak at 518 nm. The time-integrated PL yield decreases with increasing applied voltage. Fig. 3(b) shows the time-resolved spectrally-integrated PL intensity. The intensity decay is to a good first approximation mono-exponential. As expected, the triplet decay rate increases with increasing applied voltage. The large initial peak is attributed to the singlet emission from the 100 nm and 50 nm neat m-MTDATA layers.

Fig. 4(a) shows the current density dependence at 295 K of the relative efficiency deduced directly from the time-integrated PL yield, $\eta_{\text{PL,rel}}(J)$ (full symbols) and as deduced from the lifetime, $\eta_{\tau, \text{rel}}(J)$ (open symbols). As defined in Eq. (2), both quantities are taken relative to the values at zero current density. The figure shows clearly that the two normalized efficiencies are not equal. Apparently, Eq. (2) is not valid at 295 K. The measured value of $\eta_{\text{PL,rel}}(J)$ starts to decrease at current

Fig. 3. (a) Time-integrated PL intensity for device A at 295 K, for voltages in the range 0–16 V. (b) Spectrally integrated time-dependence of the PL intensity for device A.

Fig. 4. (a) The decrease of the efficiency at 295 K as determined from the PL yield (full) and the lifetime (open), normalized to the values obtained at zero voltage, as a function of the current density. (b) The relative decrease of these efficiencies at 190 K. The full curves are guides-to-the-eye. At $V = 0$ V, the lifetime is 1.20 μ s at 295 K and 1.39 μ s at 190 K.

densities of the order of 10 A/m². In contrast, $\eta_{\tau,rel}(J)$ starts to decrease around 100 A/m², i.e. one order of magnitude later.

Fig. 4(b) shows that this discrepancy disappears when decreasing the temperature to 190 K. At this temperature $\eta_{PL,rel}(J)$ and $\eta_{\tau,rel}(J)$ are equal. This observation indicates that the process underlying the discrepancy between both quantities at 295 K is thermally activated. We show below that the set of measured voltage and temperature dependent efficiencies can be explained consistently by taking the combined effects of TPQ and field-induced dissociation into account.

3.2. Field-induced dissociation

To quantify the exciton loss due to field-induced dissociation, additional measurements were performed using device B (Fig. 1(c)), in which the MoO_x/CBP layers were replaced by LiF. This replacement prevents the injection of holes from that electrode, resulting in current densities that are even at voltages of 32 V still smaller than 10⁻² A/m². We have found from impedance measurements that these devices can then be viewed as ideal capacitors, with $\epsilon_r = 3.2 \pm 0.1$ at a frequency of 100 Hz.

In Fig. 5 the relative PL efficiency (normalized to the value at $V = 0$ V) and the effective exciton lifetime is given as a function of the voltage. The PL efficiency decreases with increasing voltage, but, surprisingly, the effective lifetime remains constant at 1.20 ± 0.05 μ s. A similar observation was reported by Reineke et al. [22] and Haneder et al. [23] for TCTA:Ir(ppy)₃ and Ir(dpbc)₃:Ir(cnbic)₃ host:guest systems, respectively. In an attempt to explain why the effective triplet lifetime does not decrease these authors attributed the efficiency loss to the dissociation

Fig. 5. Voltage dependence of the normalized PL efficiency (left axis, black squares) and the effective emissive lifetime (right axis, red squares), measured at 295 K for device B (see Fig. 1(c)). The full curves are a guide-to-the-eye. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

of non-thermalized precursor excitons (i.e. singlet excitons on the host). However, we find in the PL spectra no m-MTDATA singlet contribution. That shows that the characteristic time $\tau_{transfer,hg}$ for the transfer of singlets from m-MTDATA to the guest molecules is much shorter than the effective (radiative and non-radiative) decay time τ_{eff} of singlets on m-MTDATA and the charge transfer state formation time τ_{CT} , so that this transfer occurs with almost 100% efficiency.

A quantitative comparison between these three characteristic times can be made in the following way. The effective radiative lifetime of m-MTDATA at 300 K is $\tau_{eff} = 1.3$ ns [40]. However, the characteristic exciton transfer time $\tau_{transfer,hg}$ is much shorter, as may already be seen when describing this as a direct Förster transfer process. From the overlap of the absorption spectrum of Ir(ppy)₂(acac) and the normalized PL emission spectrum of m-MTDATA (see section S3 of the Supporting Information), a Förster radius for host-guest transfer of $R_{F,hg} = 2.6$ nm is found. We find from a kMC simulation of transfer with this value of $R_{F,hg}$ to randomly distributed guests in a 9 mol% system that the decrease of the number of excitons on the host is to an excellent approximation exponential, with a characteristic time $\tau_{transfer,hg} = 1.0 \times 10^{-11}$ s. This may be regarded as an upper limit, as singlet diffusion on the host and a Dexter-type contribution to the transfer process have been neglected. We find that field-induced dissociation reduces the PL efficiency in neat m-MTDATA devices and have studied this effect for undoped 200 nm devices. The experimental results and an analysis are given in section S4 of the Supporting Information. For our films, the effective lifetime is found to be slightly larger than the literature value cited above, viz. $\tau_{eff} = (1.8 \pm 0.1)$ ns. From Fig. S4, the PL efficiency is by extrapolation seen to be reduced by approximately 25% at 32 V, which is the highest voltage that is considered in this work. The effective dissociation rate is therefore around 32 V about one third of the effective decay rate, so that $\tau_{CT}(32\text{ V}) \approx 3 \times \tau_{eff} \approx 5$ ns. This characteristic time is much smaller than the value that would be expected in the absence of an activation barrier for CT state formation, which within the formalism that we have adopted in this paper is equal to the charge hopping time between equi-energetic nearest neighbor molecules, i.e. $\nu_1^{-1} = 2.2 \times 10^{-11}$ s⁻¹ (see Sec. 2.2). Even at 32 V, where the field in the 200 nm devices decreases the activation energy for dissociation to nearest-neighbor type CT-states (with a ~ 1 nm electron-hole distance) by ~ 0.16 eV, the dissociation process is thus still thermally activated. This quantitative analysis shows that $\tau_{transfer,hg}$ is indeed much smaller than the effective singlet lifetime τ_{eff} and the CT-state formation time τ_{CT} . Singlet dissociation is therefore unlikely to be responsible for the discrepancy

between the decrease in the PL efficiency and the lifetime.

In the next section, we will show using kMC simulations that a stronger decrease of the PL efficiency as compared to that of the lifetime can occur when all singlets are transferred to the guest molecules, followed by triplet formation on the Ir-emitter by fast intersystem crossing. The PLQE loss can then be due to field-induced dissociation of the triplet excitons, and partial generation of new triplets then enhances the lifetime.

4. Analysis – kinetic Monte Carlo simulations

4.1. Field-induced dissociation experiments

Before developing a mechanistic model of the PL quenching experiments, we need to develop a quantitative model that explains the results of the field-induced dissociation experiments that are shown in Fig. 5. We have for that purpose carried out kMC simulations mimicking the experiments for devices B that probe the effect of field-induced dissociation on the total PL yield and the effective lifetime, shown in Fig. 5. The binding energy of triplets on Ir(ppy)₂(acac), $E_{T,b}$, is treated as a free fit parameter.

In Fig. 6 a comparison is given between the normalized PL efficiency

Fig. 6. The normalized PL efficiency (a) and effective lifetime (b) as function of the voltage as determined from kMC simulation results for devices of type B at 295 K (closed symbols), for five values of the triplet exciton binding energies $E_{T,b}$ = 0.9 eV (black), 1.0 eV (red), 1.1 eV (blue) 1.2 eV (green) and 1.5 eV (purple). The open symbols give the 295 K experimental results, shown in Fig. 5. The full curves and the dashed curve give guides-to-the-eye. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

and the effective lifetime, determined from the kMC simulations results and from the experiments. For $E_{T,b}$ = 1.5 eV almost no dissociation is observed in the studied voltage range. With decreasing triplet exciton binding energy the kMC results show a more pronounced decrease of the $\eta_{PL,rel}$ with increasing voltage. Moreover, the simulations results for $E_{T,b}$ = 0.9 and 1.0 eV show a slightly increased but still voltage-independent lifetime.

A comparison with experimental results shows that for $E_{T,b}$ in the range 1.0–1.1 eV the PL efficiency as well as the effective lifetime agree well with the experimental results. It should be noted that the stability of the localized excitons with respect to CT-state formation scales with the difference between the HOMO energy levels of Ir(ppy)₂(acac) and m-MTDATA. If the HOMO energy of Ir(ppy)₂(acac) would actually be more negative than the value of −5.2 eV assumed in our simulations (see Fig. 1) by a difference ΔE , the value of $E_{T,b}$ that would provide a best fit to the experimental data would be ΔE larger than obtained above. We note that Yoshida et al. [30] determined an exciton binding energy of 1.03 eV for the similar molecule Ir(ppy)₃, which is comparable to the value that we find here for Ir(ppy)₂(acac).

4.2. PL quenching experiments – sensitivity to $R_{F,TPQ}$ and $E_{T,b}$

Fig. 7(a) shows the sensitivity to the triplet exciton binding energy of the efficiency roll-off of device A at 295 K, as obtained from kMC

Fig. 7. (a) The normalized decrease with increasing current density of the efficiency at 295 K as determined from the PL yield (closed symbols) and the lifetime (open symbols), as determined from experiment and as obtained from kMC simulations for $E_{T,b}$ = 0.9 eV (red), 1.0 eV (blue) and 1.5 eV (green), assuming a Förster-type TPQ process with $R_{F,TPQ}$ = 4.0 nm. (b) kMC simulations results for Förster radii $R_{F,TPQ}$ = 3.8 nm (blue) and 4.0 nm (red) for $E_{T,b}$ = 0.9 eV. The full and dashed curves through the experimental data for $\eta_{PL,rel}$ and $\eta_{\tau,rel}$, respectively, are a guide-to-the-eye. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

simulations, for a fixed TPQ Förster radius of 4.0 nm. The figure shows that when $E_{T,b}$ is large (1.5 eV) the efficiency roll-off as obtained from the PL yield and from the lifetime are equal, inconsistent with the experimental results. However, the difference between the two quantities increases and the agreement with experiment becomes better when $E_{T,b}$ becomes smaller. For the value of the TPQ radius chosen, the previously determined binding energy of 1.0–1.1 eV is somewhat too large to describe the experimental data well. The binding energy that provides the best agreement with the roll-off of $\eta_{PL,rel}$ is approximately 0.9 eV. However, the roll-off shown by $\eta_{\tau,rel}$ is then somewhat too large. Fig. 7 (b) shows that using $E_{T,b} = 0.9$ eV a good fit to both roll-off curves is obtained for a slightly reduced value of the TPQ Förster radius, $R_{F,TPQ} = 3.8$ nm.

4.3. PL quenching experiments – temperature dependence

In order to study the validity of the analysis of the efficiency roll-off, given in Fig. 7 (b), we have extended the simulations of the PL quenching experiments to lower temperatures. From the experiments shown in Fig. 4 (b), the role of field-induced dissociation is then expected to be reduced and around 190 K even eliminated. Fig. 8 gives a comparison of the simulation and experimental results for $\eta_{PL,rel}$ and $\eta_{\tau,rel}$, studied at four values of the temperature. In the simulations the measured increase of the effective lifetime in the zero-voltage limit, from 1.20 μ s at 295 K to 1.45 μ s at 190 K, was taken into account. The figure shows that using R_F , TPQ = 3.8 nm and $E_{T,b} = 0.9$ eV a fair agreement is obtained for the entire

temperature range. The only disagreement is an increase of τ and $\eta_{\tau,rel}$ at very large current densities and electric fields, in particular at low temperatures. The simulations can well explain that $\eta_{PL,rel}$ is dependent on the temperature and that the efficiency decrease at 1000 A/m² is ~20% at room temperature but only ~6% at 190 K (Fig. 8(a)). They are furthermore consistent with the observation that $\eta_{\tau,rel}$ shows no significant change (Fig. 8(b)).

The value of $\eta_{PL,rel}$ (1000 A/m²) ≈ 0.93 that is obtained in Fig. 7 (a) at room temperature under conditions for which no field-induced dissociation occurs ($E_{T,b} = 1.5$ eV) is very close to the experimental value at 190 K, for which no or only very weak field-induced dissociation is expected. The decrease of the roll-off with decreasing temperature is therefore for this system completely due to the decreasing role of field-induced dissociation. Surprisingly, the expected decrease of the polaron diffusivity with decreasing temperature does not affect the efficiency in the absence of dissociation. This will be explained in the next subsection.

4.4. TPQ mechanism

A more detailed analysis may be made with the help of the theoretical findings that have been presented in Ref. 13 on the mechanism of Förster-type TPQ when field-induced exciton dissociation can be neglected. The analysis shows that the initial average TPQ rate, just after the creation of an exciton, can be calculated readily from the R^{-6} distance-dependent Förster formula, assuming a spatially uniform distribution of polarons. However, due to TPQ the density of polarons in the immediate neighborhood of the remaining excitons is, after some time, depleted. This effect is strongest for small values of the polaron diffusion coefficient D . As a result of this effect, three TPQ regimes can be distinguished, depending on the value of D :

- a strong-diffusion regime, in which the depletion effect can be neglected so that the effective rate coefficient k_{TPQ} is proportional to $R_{F,TPQ}^6$, independent of D .
- a weak-diffusion regime within which the polarons may be considered as essentially immobile during the triplet exciton lifetime, resulting in strong depletion and a value of k_{TPQ} that is much smaller than that in the strong-diffusion regime and proportional to $R_{F,TPQ}^3$, independent of D .
- an intermediate regime in which k_{TPQ} depends on D .

In the intermediate and weak diffusion regimes the formation of a depleted region leads to a TPQ rate coefficient that is time-dependent, so that $\eta_{\tau,rel}$ will depend on the time-range used to determine the slope of the PL intensity curve and is expected to be somewhat larger than $\eta_{PL,rel}$. As this effect could contribute to the observed difference between $\eta_{PL,rel}$ and $\eta_{\tau,rel}$, in addition to the effect of field-induced dissociation, it is of interest to establish in which regime the devices operate and whether a possible regime change takes place when decreasing the temperature.

We focus on the roll-off at a current density $J = 1000$ A/m², and analyze the role of polaron diffusion. The analysis details and an overview of the relevant parameters are given in section S5 and Table S2 of the Supporting Information, respectively. Using the average mobility in the host-guest layer that follows from the average hole density n_h and the field in that layer, and using the Einstein equation, D is found to be equal to $\sim 1.4 \times 10^{-10}$ m²/s and $\sim 0.27 \times 10^{-10}$ m²/s at 295 K and 190 K, respectively. Although D thus decreases with decreasing temperature, the decrease is relatively small. This is due to an increase of the electric field, combined with the stronger field-induced enhancement of the mobility at lower temperatures. In particular at low temperatures, the holes are therefore far from equilibrated, and relatively “hot”.

Using these values for D , it is possible to estimate an effective TPQ rate coefficient $k_{TPQ,eff}$ and the expected relative PL efficiency $\eta_{PL,rel} = 1/(1 + k_{TPQ,eff} n_h/k_{rad})$ from Fig. 3 of Ref. 13, which gives $k_{TPQ,eff}$ as a function of $R_{F,TPQ}$ and D . As explained in detail in section S5 of the Supporting Information, this analysis shows that in the entire

Fig. 8. The normalized decrease with increasing current density of the efficiency as determined from (a) the PL yield and (b) the effective lifetime, as obtained from experiment (open symbols) and from kMC simulations with $R_{F,TPQ} = 4.0$ nm and $E_{T,b} = 0.9$ eV (closed symbols) at 295 K (black), 250 K (red), 220 K (blue) and 190 K (green). For clarity, the 250, 220 and 190 K curves are shifted up by 0.10, 0.20 and 0.30, respectively. The absolute values of the effective lifetime are 1.2 μ s (295 K), 1.25 μ s (250 K), 1.30 μ s (220 K) and 1.45 μ s (190 K). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

temperature range the device operates in the intermediate regime, in which $k_{\text{TPQ,eff}}$ depends on D . With our experimental value $R_{\text{F,TPQ}} = 3.8$ nm, the analysis leads for both temperatures to values of $\eta_{\text{PL,rel}}$ in the range 0.93–0.95. This agrees well with the finding from kMC simulations that at 295 K and under conditions for which no field-induced dissociation occurs ($E_{\text{T,b}} = 1.5$ eV) $\eta_{\text{PL,rel}} \approx 0.93$ (Fig. 7(a)) and that at 190 K, at which no or only very weak field-induced dissociation is expected, $\eta_{\text{PL,rel}} \approx 0.94$ (Fig. 4(b)). The theoretical framework that has been developed in Ref. 13 provides thus an excellent prediction of $\eta_{\text{PL,rel}}$ when field-induced dissociation is switched off. We furthermore find that in the entire temperature range $\eta_{\text{r,rel}}$ is expected to be very close to $\eta_{\text{PL,rel}}$ when only the depletion effect is considered and field-induced dissociation is neglected (see section S6 of the Supporting Information). The analysis explains thus why, for the system studied, the difference between the values of $\eta_{\text{PL,rel}}$ at room temperature and at 190 K is almost entirely due to the effect of field-induced dissociation.

We remark that the surprising finding that for this system $\eta_{\text{PL,rel}}$ is almost independent of T if the effect of field-induced dissociation is switched off, in spite of the small but significant decrease of the polaron diffusion constant and the finding that the device operates in the intermediate regime, is due to two counteracting effects: an increase of η_{h} with decreasing T by a factor of ~ 2 , and a slight increase of the effective emissive lifetime (see Fig. S6 and Table S1 in the Supporting Information).

5. Summary and conclusions

We have studied triplet-polaron quenching in unipolar (hole-only) devices with an EML consisting of m-MTDATA: 9 mol% Ir(ppy)₂(acac). This system was selected because of the negligible effect of the presence of the guest molecules on the charge transport, as the HOMO energy of m-MTDATA is higher (less negative) than that of Ir(ppy)₂(acac). The development of an accurate charge transport model is then not affected by a possible uncertainty of the difference between the HOMO energies of the host and guest molecules. Current-voltage measurements confirm that, as expected, essentially all charge transport is due to hopping between the m-MTDATA host molecules. The TPQ process was studied using time-resolved PL experiments, which in this system probe quenching of excitons on Ir(ppy)₂(acac) by hole polarons on neighboring m-MTDATA molecules.

We find that at room temperature the roll-off as obtained directly from the PL efficiency, $\eta_{\text{PL,rel}}$, is much stronger than that obtained more indirectly from the decrease of the effective emissive lifetime, $\eta_{\text{r,rel}}$. The effect is shown to be due to field-induced dissociation, where charge transfer excitons are formed with the hole on an m-MTDATA neighbor molecule. The effective lifetime is at large current densities and electric fields on the one hand lowered due to TPQ, but on the other hand enhanced due to the temporary formation of charge transfer excitons, followed in some cases by exciton regeneration and delayed emission. We have studied the PL efficiency loss due to field-induced dissociation in the absence of polarons using devices with a large built-in voltage that are operated under reverse bias conditions. From an analysis of the results using kMC simulations we conclude that the process is well described when assuming a triplet exciton binding energy of $E_{\text{T,b}} = 1.0$ – 1.1 eV. kMC simulations of the current density dependence of $\eta_{\text{PL,rel}}$ and $\eta_{\text{r,rel}}$, measured in the 190–195 K temperature range, are found to provide a good description of the experimental data assuming a TPQ Förster radius of $R_{\text{F,TPQ}} = 3.8$ nm, and $E_{\text{T,b}} = 0.9$ eV. In view of the various uncertainties in the analysis, related to the assumed mechanistic description of the various relevant processes, we regard the agreement between the two independently determined values of the value of $E_{\text{T,b}}$ for Ir(ppy)₂(acac) as fair. We note that from photoemission and inverse photoemission studies for the similar emitter molecule Ir(ppy)₃ a value of 1.0 eV has been deduced [30]. For both materials, the fundamental (HOMO-LUMO) gap is thus significantly larger than the triplet energy. We furthermore note that the Förster radius for a specific system

depends on the PL efficiency of the donor material, as it is defined via the effective lifetime τ which is in general smaller than the radiative decay time due to non-radiative decay (Eq. (3)). When embedding Ir(ppy)₂(acac) in a different host material, with a different measured effective lifetime τ' (at zero electric field) but with the same refractive index, the TPQ Förster radius is expected to be equal to $R_{\text{F,TPQ}}(\tau') = (\tau'/\tau)^{1/6} R_{\text{F,TPQ}}(\tau)$.

In conclusion, this study has shown that it is necessary to describe TPQ in organic semiconductor host-guest systems in a mechanistic manner. A phenomenological rate equation approach can at best provide a phenomenological description of specific measurement results, and has in general only limited predictive value. In particular, such an approach does not well capture the realistic complexity of the TPQ process, including e.g. the effects of field-induced exciton dissociation. We have shown that the use of a mechanistic approach employing kMC simulations allows for disentangling and quantifying all relevant contributions to the efficiency roll-off. We expect that the methodology presented in this work will enable obtaining accurate values of $R_{\text{F,TPQ}}$ for triplets on various Ir-cored emitters that interact with holes on a given host, thereby providing a valuable experimental benchmark for future first principles calculations of $R_{\text{F,TPQ}}$, and that the use of this methodology will enable obtaining more precise predictions of the performance of organic optoelectronic devices such as OLEDs using kMC simulations.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the Horizon-2020 EU project MOSTOPHOS (project No.646259, A.L., P.A.B., R.C.).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.orgel.2020.106058>.

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