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Clarifying the mechanism of triplet-triplet annihilation in phosphorescent organic host-guest systems: a combined experimental and simulation study

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Abstract

At high brightness, triplet-triplet annihilation (TTA) reduces the efficiency of organic light-emitting diodes. Triplet diffusion may considerably enhance this effect, which is otherwise limited by the rate of long-range interactions. Although its role can be clarified by studying the emissive dye concentration dependence of the TTA loss, we demonstrate here the practical applicability of a more direct method, requiring a study for only a single dye concentration. The method uses transient photoluminescence yield measurements, for a wide initial excitation density range. The analysis is applied to an iridium complex and is supported by the results of kinetic Monte Carlo simulations.

Keywords:

Triplet-Triplet Annihilation, transient photoluminescence, kinetic Monte-Carlo simulations, organic semiconductors, organic light-emitting diodes

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1. Introduction

Understanding and ultimately manipulating the exciton dynamics plays an essential role in the development of modern organic optoelectronic devices, such as organic light emitting diodes (OLEDs) and organic photovoltaics (OPVs)

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5 [1–6]. The internal quantum efficiency (IQE) is reduced due to exciton-charge quenching and exciton-exciton annihilation. Such processes are particularly important for triplet excitons, which are in general relatively long-lived. For phosphorescent OLEDs, nearly 100% internal quantum efficiency can be obtained by making use of enhanced spin-orbit coupling in dye molecules containing a heavy
 10 atom [6]. Exciton states with predominant triplet character have then also some singlet character, making them emissive [2, 6]. Nevertheless, their radiative lifetime is usually still of the order of one microsecond, so that at high luminance levels, at which the triplet and polaron volume densities are relatively large, an efficiency drop (roll-off) is observed, resulting from triplet-polaron quenching
 15 (TPQ) and triplet-triplet annihilation (TTA) [1, 7–10].

In recent studies, the effective TTA rate in host-guest systems as used in phosphorescent OLEDs is described as being controlled either by the rate of direct long-range Förster-type triplet-triplet interactions [11–13], or by the rate of a more indirect process of exciton diffusion followed by a relatively short-
 20 range capture step [14–16]. The relative role of both processes is a subject of current debate [11–18]. The diffusion-controlled picture is consistent with the conventional phenomenological description of TTA as a bimolecular process which modifies the time dependence of the triplet volume density, $T(t)$, in a manner as described by the last term in the expression

$$\frac{dT}{dt} = G - \frac{T}{\tau} - f k_{\text{TT}} T^2, \quad (1)$$

25 with G a triplet generation term, τ the triplet emissive lifetime, f a coefficient which is equal to 1/2 (1) if upon each TTA process one of the two (both) excitons involved is (are) lost, and k_{TT} a phenomenological triplet-triplet interaction rate coefficient. If Eq. (1) is valid, the time-dependent photoluminescence (PL) response $I(t)$ after optical excitation to an initial exciton density T_0 is given by

$$\frac{I(t)}{I(0)} = \frac{1}{(1 + f T_0 k_{\text{TT}} \tau) \exp(t/\tau) - f T_0 k_{\text{TT}} \tau} . \quad (2)$$

30 Time-dependent PL experiments would then yield the quantity fk_{TT} , which
 may be employed to obtain the exciton loss due to TTA under any operational
 condition, and hence e.g. the IQE roll-off due to TTA [1]. However, this often-
 used approach is not always valid. In host-guest systems as used in OLEDs, the
 role of triplet diffusion decreases with decreasing dye concentration. In prac-
 35 tical systems, the dye concentration is limited to values typically less than 15
 mol% in order to limit concentration quenching [19, 20]. From kinetic Monte
 Carlo (kMC) simulations, it has been shown that when the direct process be-
 comes dominant, Eq. (2) no longer properly describes the time-dependent PL
 response, showing a faster-than-expected initial drop [18]. The physical expla-
 40 nation is that for weak or no diffusion TTA processes quickly deplete the density
 of nearby excitons around the “surviving” excitons. The resulting non-uniform
 distribution of pair distances gives rise to a slowing-down of the TTA rate in the
 later stage of the process. The validity of Eq. (2) may be probed by deducing
 from the transient PL data (i) the time at which half of the total emission has
 45 occurred, and (ii) the total exciton loss [18]. The values of k_{TT} which would
 follow from such analyses, $k_{\text{TT},1}$ and $k_{\text{TT},2}$, respectively, are expected to be
 equal when Eq. (2) is valid, i.e. when TTA is a diffusion controlled multiple
 step process. However, when the direct process prevails, the ratio

$$r \equiv \frac{k_{\text{TT},2}}{k_{\text{TT},1}} \quad (3)$$

is much larger than 1. In that case, $k_{\text{TT},1}$ and $k_{\text{TT},2}$ should be viewed as auxiliary
 50 parameters only. A full description of the TTA process requires then a micro-
 scopic theory, in which exciton diffusion in the disordered material is included as
 well as the Förster-type triplet-triplet interaction. The description of the time-
 dependence of the photoluminescence, obtained from such a theory, should be
 consistent with the values of $k_{\text{TT},1}$ and $k_{\text{TT},2}$ obtained. Within such a micro-
 55 scopic theory, the TTA process is no longer described using a phenomenological
 coefficient k_{TT} , but using microscopic interaction parameters describing the dis-
 tance dependent exciton transfer rates (leading to diffusion) and the distance

dependent triplet-triplet interaction rates (leading to TTA). Advantageously, an analysis along these lines can already be applied to a single sample with one
60 doping concentration, not requiring a series of samples with different doping concentrations. We note that the ability to disentangle the relative contributions of the direct and indirect contributions to TTA would also be important in other types of systems, e.g. fluorescent OLEDs with an enhanced efficiency due to TTA-induced delayed fluorescence as well as photovoltaic devices [21–23].

65 In this paper, we demonstrate that it is indeed possible to clarify the mechanism of the TTA process from a study for only one doping concentration. The sample used in the present study is a 50 nm thick film with 3.9 wt% of the green emitter bis(2-phenylpyridine)(acetylacetonate)iridium(III) ($\text{Ir(ppy)}_2(\text{acac})$) doped into the host material 4,4'-bis(carbazol-9-yl)biphenyl (CBP), which is widely
70 used in high-efficiency OLEDs [24–26]. The doping concentration is chosen to avoid on the one hand guest molecule aggregation effects observed at high doping concentration (> 8 wt%), and on the other hand a dopant saturation effect at high excitation intensities (expected below 2 wt%) [20, 27], so that a direct comparison with kMC simulation results assuming a random emitter distribu-
75 tion may be made. From a careful experimental study combined with the kMC simulations, we show that the r -ratio based analysis method proposed in Ref. 18 can be made even more convincing by extending the time-resolved PL experiments to a wide range of initial triplet densities T_0 , from 10^{22} m^{-3} to over 10^{25} m^{-3} . We demonstrate (i) that indeed a significant deviation from Eq. (2) can
80 occur, and (ii) that the method proposed in Ref. 18 for making a distinction between both contributions to the TTA process can indeed be applied successfully. Furthermore, we find at high initial triplet densities ($T_0 > 10^{24} \text{ m}^{-3}$) an increase of the r -ratio and show that this is consistent with the results of the kMC simulations.

85 2. Experimental results

The details of the sample fabrication and transient PL measurement methods are given in the Supplementary Material. Figure 1 shows the absorbance and normalized PL emission spectra of the doped sample and, as a reference, of a neat CBP film prepared in the same way. It may be concluded that most of the incident photons are absorbed by CBP molecules (excitation to the singlet state, S_1^H), then quickly transferred to a guest $\text{Ir(ppy)}_2(\text{acac})$ molecule (singlet state, S_1^G , the metal-ligand singlet charge transfer state $^1\text{MLCT}$ at 2.99 eV), and subsequently due to fast intersystem crossing converted to guest triplet states (T_1^G , 2.3 eV) [25]. These triplet states are well confined to the guest molecules due to the high energy barrier to the host material (T_1^H , 2.60 eV) [28]. The competing processes, radiative decay (with $\lambda_{PL} \sim 400$ nm) and non-radiative decay of S_1^H , are slower in this host-guest system [25, 29]. The high efficiency of the host-guest singlet energy transfer process is confirmed by the PL emission spectrum, which exhibits a main contribution from $\text{Ir(ppy)}_2(\text{acac})$ peaked at 520 nm with a shoulder at 560 nm [25], and only a very small contribution from the CBP host. The energy transfer diagram is given as an inset in Fig. 1. The proposed exciton transfer process has been confirmed from similar experiments on samples with doping concentrations from 0.78 to 11.6 wt%, which reveal a negligible variation in absorption but a systematic variation in host contribution to the PL emission spectra (not shown here). From these spectra, and using the PL quantum yield of CBP (0.60, [30]) and $\text{Ir(ppy)}_2(\text{acac})$ (0.94, [26]), the film-averaged initial triplet density T_0 is calculated. Although the initial triplet density is actually non-uniform across the film thickness, we find by solving Eq. (1) for a non-uniform density that for the very thin layers studied this will not significantly affect the transient PL response. We henceforth assume a uniform density.

Typical transient PL decay curves and the corresponding integrated cumulative PL yield curves obtained for increasing initial triplet densities T_0 are shown in Figs. 2(a) and (b), respectively. It may be seen that for the cumulative

Figure 1: Absorbance spectra and normalized PL intensity spectra (excitation at 337 nm; normalization to the PL peak intensity) of a neat CBP film and a CBP:3.9 wt% Ir(ppy)₂(acac) film (thickness 50 nm, on quartz). The absorbance spectra of the two samples are almost identical. In the inset, the energy transfer diagram is given. The arrows in the inset indicate the very weak fluorescent (F) emission from host (H) singlets (dashed), the main exciton transfer processes and the phosphorescent (P) decay process from the guest (G) triplets (full).

115 PL curves the noise level is greatly suppressed, especially at long delay times. This will be exploited when extracting the rate coefficient $k_{TT,1}$ as discussed below. For sufficiently small T_0 ($< 0.5 \times 10^{24} \text{ m}^{-3}$), the transient PL curves exhibit to an excellent approximation a mono-exponential decay from which the triplet lifetime τ can be estimated. Obtaining τ with good accuracy is found in
120 this study to be key to analyzing the TTA process in terms of the two possible mechanisms. From more than 40 transient PL curves measured at low T_0 , an average lifetime $\tau_{av} = 1.39 \pm 0.04 \text{ } \mu\text{s}$ is obtained. This value is within the range of values reported in the literature (1.22 to $1.56 \text{ } \mu\text{s}$ [15, 31, 32]).

3. Analysis and discussion

125 With increasing T_0 , the transient PL curves for $T_0 > 0.5 \times 10^{24} \text{ m}^{-3}$ show a gradual enhancement of the initial triplet exciton decay rate, which is indicative of the occurrence of TTA. As a first step, these transient PL curves are fitted using Eq. (2), i.e. following the conventional approach, assuming that one triplet is lost upon the TTA process ($f = 1/2$). Figure 3 gives the values of

Figure 2: (a) Measured transient PL intensity decay curves for various initial triplet densities and a fit to Eq. (2) (red curves). The inset (data for $T_0 = 20.2 \times 10^{24} \text{ m}^{-3}$) shows that the fits are not only imperfect for late times, but also for early times. (b) The corresponding cumulative PL yield curves and a fit to Eq. (4) (red curves). The lowest two curves are in the low- T_0 region ($< 0.5 \times 10^{24} \text{ m}^{-3}$), in which the decay is essentially mono-exponential, so that $t_{1/2} = \tau \ln 2 \approx 0.94 \mu\text{s}$ (downward pointing arrow).

the rate coefficient, $k_{\text{TT},0}$, which would follow from such a fit when assuming various fixed values of τ , including the value $\tau = \tau_{\text{av}} = 1.39 \mu\text{s}$. It may be seen that for small T_0 the value of $k_{\text{TT},0}$ can be quite sensitive to τ . A result of analyzing the data using an incorrect value of τ would thus be an unphysical dependence of $k_{\text{TT},0}$ on T_0 . This sensitivity has not been addressed in previous studies [15, 27, 28, 33–36]. The T_0 dependence obtained for small T_0 vanishes when assuming $\tau = 1.36 \mu\text{s}$, a value within the estimated uncertainty interval for τ_{av} . We will use this refined value $\tau = 1.36 \mu\text{s}$ for all subsequent analyses. Figure 2(a) reveals that for large T_0 ($> 5 \times 10^{24} \text{ m}^{-3}$) the fit quality is not satisfactory. For smaller values of T_0 , inaccuracies of the fit are less visible due to the noise. We remark that the fit results shown in Fig. 3 are obtained for the transient PL plotted on a linear scale. A slightly different result would be obtained when fitting to the PL intensity plotted on a log scale (as in Fig. 2(a)), because of the different effective weights of the data points. The result is also sensitive to the time-range included in the fit [13].

Figure 3: Initial triplet density (T_0) dependence of $k_{\text{TT},0}$, assuming various lifetimes from 1.30 to 1.48 μs . The dashed lines are guides to eyes. For $T_0 < 3 \times 10^{24} \text{ m}^{-3}$, the value of $k_{\text{TT},0}$ is quite sensitive to the assumed lifetime. The error bars in $k_{\text{TT},0}$ are the standard deviation obtained from four independent measurements. The uncertainty in T_0 is smaller than the symbol size.

145 The ambiguities in the conventional fit process, mentioned above, and the sensitivity to noise at longer delay times have led in Ref. 18 to the proposal to make use of the cumulative PL yield, shown in Fig. 2(b). Following Ref. 18, we fit the data using Eq. (4) under the constraint of a fixed value of $\tau = 1.36 \mu\text{s}$, such that at the time $t_{1/2}$ at which half of the total PL (the cumulative PL for
150 $t = \infty$) has been obtained the fitted and measured cumulative PL coincide. The cumulative PL yield is given by integrating Eq. (2):

$$Y(T_0, t) \equiv \int_0^t I(t) dt = \frac{2I(0)}{k_{\text{TT},1}T_0} \left\{ \ln \left[\frac{1}{2} \exp(t/\tau)(2 + k_{\text{TT},1}T_0\tau) - \frac{k_{\text{TT},1}T_0\tau}{2} \right] - \frac{t}{\tau} \right\}. \quad (4)$$

The fit parameters are the effective TTA rate coefficient $k_{\text{TT},1}$ and the initial PL intensity $I(0)$. From Fig. 2(b), it may be seen that the fit quality is quite good over the full time scale and for the entire T_0 range, although it is not
155 perfect. The $t_{1/2}$ points are indicated with arrows. The T_0 dependence of $k_{\text{TT},1}$ is shown as open circles in Fig. 4(b). From a comparison with Fig. 3, it may be seen that for small T_0 , the values of $k_{\text{TT},0}$ and $k_{\text{TT},1}$ are not significantly different, whereas for large T_0 deviations occur: while $k_{\text{TT},0}$ shows a slight increase with increasing T_0 , $k_{\text{TT},1}$ shows a slight decrease. Figure 4(a) shows
160 that for small T_0 the fitted intensity $I(0)$ (open squares) varies approximately linearly with T_0 , as would be expected from Eq. (1). However, an increasing deviation occurs with increasing T_0 , which may be attributed to the emergence of the emitter saturation effect [27].

The quantity $k_{\text{TT},1}$ provides a measure of the temporal characteristics of
165 the cumulative PL curve, indicating how fast the triplets are lost via TTA. As suggested first in Ref. 18, it is also useful to introduce another effective rate coefficient, $k_{\text{TT},2}$, which depends on the total fraction of triplets lost via TTA. It provides distinct and complementary information on the TTA process. The value of $k_{\text{TT},2}$ is evaluated from the relative PL efficiency $\eta_{\text{PL,rel}}(T_0)$, which is a
170 dimensionless quantity defined as the ratio between the PL efficiency at T_0 and that for $T_0 \rightarrow 0$, so that $\eta_{\text{PL,rel}}(T_0 \rightarrow 0) = 1$:

Figure 4: (a) Closed circles: T_0 -dependence of the relative PL efficiency, $\eta_{\text{PL,rel}}$. Full curve: fit for small T_0 to Eq. (6). Open squares: initial PL intensity $I(0)$ as obtained from a fit of the cumulative PL in Fig. 2(b) to Eq. (2). Dashed line: linear fit to $I(0)$ for small T_0 . (b) T_0 -dependence of the TTA rate coefficients $k_{\text{TT},1}$ and $k_{\text{TT},2}$ (symbols) and their average for small T_0 (dashed lines) and (c) T_0 -dependence of the r -ratio $k_{\text{TT},2}/k_{\text{TT},1}$. The dashed line gives the average for $T_0 < 5 \times 10^{24} \text{ m}^{-3}$ (2.4 ± 0.4).

$$\eta_{\text{PL,rel}}(T_0) \equiv \lim_{T'_0 \rightarrow 0} \frac{\eta_{\text{PL}}(T_0)}{\eta_{\text{PL}}(T'_0)} = \lim_{T'_0 \rightarrow 0} \frac{T'_0}{T_0} \frac{Y(T_0, t = \infty)}{Y(T'_0, t = \infty)}, \quad (5)$$

with $\eta_{\text{PL}}(T_0)$ the absolute PL quantum efficiency. By making use of the relative PL efficiency, the analysis is insensitive to geometrical factors and calibration error. The right hand part of the equation expresses that the relative PL efficiency is proportional to $Y(T_0, t = \infty)/T_0$, which readily follows from the fits shown in Fig. 2(b). The quantity of $k_{\text{TT},2}(T_0)$ is then defined as the value of k_{TT} which follows the expression

$$\eta_{\text{PL,rel}}(T_0) = -\frac{2 \ln(\frac{2}{2+k_{\text{TT},2}T_0\tau})}{k_{\text{TT},2}T_0\tau}. \quad (6)$$

It may be seen from Eq. (4), in the strong-diffusion limit, when Eqs. (1) and (2) are valid, $k_{\text{TT},2}$ is equal to $k_{\text{TT},0}$ and $k_{\text{TT},1}$. However, in the absence of diffusion, Eq. (2) is invalid and $k_{\text{TT},2}$ is much larger than $k_{\text{TT},1}$ [18]. In practice, obtaining accurate absolute values of $\eta_{\text{PL,rel}}$ is hampered by the limited signal-to-noise ratio for low-fluence measurements. As will be shown below, a fluence leading to $T_0 < 10^{23} \text{ m}^{-3}$ would be needed to approach the limit of $\eta_{\text{PL,rel}} = 1$ within 4%, whereas the experimental uncertainty of the total PL yield is then already of the order of 10%. We therefore determine an optimized value of $k_{\text{TT},2}$ by normalizing the $\eta_{\text{PL,rel}}$ data in such a way that for $T_0 < 2 \times 10^{24} \text{ m}^{-3}$ an optimal fit can be obtained using Eq. (6). We thus assume that for sufficiently small T_0 the value of $k_{\text{TT},2}$ does not depend on T_0 . We will validate that approach below by showing from kMC simulations that $k_{\text{TT},2}$ is indeed expected to be independent of T_0 , until a critical value of T_0 beyond which also $k_{\text{TT},1}$ shows a T_0 dependence. Figure 4(b) confirms this picture, and shows that this critical concentration occurs outside the range for which we have assumed that $k_{\text{TT},2}$ is independent of T_0 . In Fig. 4(a), the full curve shows the decay of $\eta_{\text{PL,rel}}$ for the optimal normalization of the data and the optimal value of $k_{\text{TT},2}$ ($1.0 \times 10^{-18} \text{ m}^3\text{s}^{-1}$). In the Supplementary Material, we show that a 5% different normalization already leads to a significantly worse agreement with a

fit for adapted optimal values of $k_{\text{TT},2}$. From a sensitivity analysis, we conclude that the uncertainty in the value of $k_{\text{TT},2}$ at small T_0 is at most 20% and that the critical value $T_0 \approx 3 \times 10^{24} \text{ m}^{-3}$ above which $k_{\text{TT},2}$ becomes T_0 -dependent
200 is not very sensitive to the precise normalization used.

The analysis shows that the ratio r between $k_{\text{TT},2}$ and $k_{\text{TT},1}$ is significantly larger than 1, viz. about 2.4 ± 0.4 for small values of T_0 and increasing for $T_0 > 6 \times 10^{24} \text{ m}^{-3}$; see Fig. 4(c). In Ref. 18, it was argued on the basis of kMC simulations that around $r = 2$ a cross-over occurs between the multiple-
205 step diffusion-dominated regime ($1 < r < 2$) to the regime in which TTA is predominantly due to direct (single-step) TTA ($r > 2$). The r -value found would thus imply that in the systems studied the multiple-step contribution to TTA is relatively small, and that single-step (direct) processes dominate. In view of the relatively low guest concentration, this seems reasonable.

An analysis of the variation of the quantities $k_{\text{TT},1}$ and $k_{\text{TT},2}$ with T_0 , using
210 the results of kMC simulations, provides more quantitative information about the TTA Förster radius, $R_{\text{F,TT}}$. This radius determines the distance (R) dependence of the rate $r \equiv (1/\tau)(R_{\text{F,TT}}/R)^6$ of the triplet-triplet interaction which gives rise to annihilation. Figure 5 shows the T_0 dependence of $k_{\text{TT},1}$ and $k_{\text{TT},2}$
215 as calculated from kMC simulations using the method described in Refs. 4 and 18 and outlined briefly in the Supplementary Material, under the assumption that exciton diffusion may be neglected, for $\tau = 1.36 \text{ } \mu\text{s}$ (the value for the present system) and for $R_{\text{F,TT}} = 3$ and 5 nm. The simulations are based on the kMC device simulation tool Bumblebee [37]. Figure S3 in the Supplementary
220 Material gives as an example the simulation data and the analysis for the case of $R_{\text{F,TT}} = 5$ nm. Just like the steady-state values [18], $k_{\text{TT},1}$ and $k_{\text{TT},2}$ are to a reasonable first approximation found to be proportional to $R_{\text{F,TT}}^3$. The simulation results show good qualitative agreement with the experimental results, also included in Fig. 5: $k_{\text{TT},1}$ and $k_{\text{TT},2}$ are constant at small T_0 , and $k_{\text{TT},1}$
225 decreases while $k_{\text{TT},2}$ increases when T_0 is sufficiently large with increasing T_0 .

The value of $k_{\text{TT},2}$, which is a measure of the total loss under transient PL conditions, is for all values of T_0 smaller than the effective steady-state TTA

rate coefficient. For the case of $R_{F,TT} = 5$ nm, this is shown in Fig. S4 of the Supplementary Material. The difference is due to the continuous addition under
230 steady-state conditions of new excitons at random positions. That counteracts the slowing-down of the TTA rate occurring under transient conditions in the absence of diffusion. The increase of $k_{TT,ss}$ above a certain critical value of T_0 occurs for triplet densities for which there is on average more than one other triplet present within a distance equal to $R_{F,TT}$, so that a competition
235 arises between annihilation processes of a triplet exciton with a number of other triplet excitons [18]. We explain the increase of $k_{TT,2}$ with T_0 in a similar way. The effect is less pronounced than under steady-state conditions, as during a transient PL experiment the triplet density decreases quickly. For small T_0 , $k_{TT,1}$ is smaller than $k_{TT,2}$ as a result of the slower-than-expected decrease of
240 the triplet density in the later stages in the process due to depletion of the triplet density close to each “surviving” triplet. For large T_0 , $k_{TT,1}$ decreases further due a similar reason: because in the very early stage of the process TTA is then much faster than expected, the time-dependent emission resembles results for a much smaller value of T_0 , characterized by a larger value of $t_{1/2}$.

245 If triplet diffusion contributes indeed little to the TTA process, as suggested by the high r -ratio, $R_{F,TT}$ may be obtained from a comparison of the measured low- T_0 $k_{TT,1}$ or $k_{TT,2}$ values with the zero-diffusion kMC results. The experimental low- T_0 value of $k_{TT,2}$ is $(1.0 \pm 0.20) \times 10^{-18} \text{ m}^3\text{s}^{-1}$, whereas for $R_{F,TT} = 5$ nm the value obtained from the simulations is $(1.1 \pm 0.10) \times 10^{-18}$
250 m^3s^{-1} . A comparison between the experimental and simulation results would thus suggest that $R_{F,TT}$ is around or just slightly smaller than 5 nm. A similar comparison for the case of $k_{TT,1}$ would suggest a value of $R_{F,TT}$ close to 4 nm. The relatively small high- T_0 enhancement of $k_{TT,2}$ would be consistent with an even smaller value of $R_{F,TT}$. For $T_0 = 1 \times 10^{25} \text{ m}^{-3}$, e.g., the experimental
255 enhancement is approximately 10%, whereas for $R_{F,TT} = 3$ and 5 nm the enhancement which is expected from the kMC simulations is approximately 25% and 77%, respectively. This indicates that for large T_0 values a refinement of the analysis method is needed, possibly including a refined treatment of the effect of

Figure 5: Initial triplet density dependence of the transient PL rate coefficients $k_{\text{TT},1}$ and $k_{\text{TT},2}$ as obtained from kMC simulations for $R_{\text{F,TT}} = 3$ and 5 nm (full symbols), and experimental data for the CBP: Ir(ppy)₂(acac) (3.9 wt%) films studied in this paper (open symbols). The simulations were carried out assuming $\tau = 1.36 \mu\text{s}$ (the experimental value for the system studied) and neglecting triplet exciton diffusion. The uncertainty of the rate coefficients from the simulations is smaller than the symbol size.

the T_0 gradient across the layer thickness and of possible dye saturation effects.

260 4. Summary and conclusions

The mechanism of the triplet-triplet annihilation (TTA) process in a phosphorescent host-guest system with a low guest concentration, CBP:Ir(ppy)₂(acac) (3.9 wt%), has been studied by using transient photoluminescent (PL) measurements in a wide initial triplet density (T_0) range and accompanying kinetic Monte Carlo (kMC) simulations. We have demonstrated that the analysis method proposed in Ref. 18, which sensitively probes deviations from the conventionally assumed time-dependence of the PL intensity obtained from such experiments, can indeed be used to make a distinction between TTA due to single-step Förster-type interactions only and a diffusion-mediated multi-step mechanism.

We find that accurately determining the emitter lifetime τ and the cumulative PL yield for small T_0 are key to successfully applying the analysis method.

This can be achieved by making use of the finding from kMC simulations that in the small- T_0 limit the effective rate coefficients are independent of T_0 . For the system studied, TTA is found to be predominantly due to the one-step mechanism. For small T_0 , the experimentally derived rate coefficients $k_{\text{TT},1}$ and $k_{\text{TT},2}$ are consistent with the results of kMC simulations in which diffusion is neglected, with TTA Förster radii in the range 4 – 5 nm. Although the variation of the rate coefficients with T_0 suggests slightly smaller TTA Förster radii, the observed trend is qualitatively consistent with the kMC results. We therefore believe that the proposed method is useful as an efficient tool to clarify the mechanism of TTA in host-guest systems applied in e.g. OLEDs. We find from kMC simulations that in the case of TTA due to the one-step mechanism the steady-state triplet loss is larger than would be expected from the loss under transient PL conditions. This finding further emphasizes the importance of being able to describe TTA in a mechanistic manner, instead of using phenomenological rate coefficients.

Our conclusion that in the system studied here the single-step TTA mechanism prevails is at variance with the conclusions deduced in Ref. 15 that a diffusion-mediated multi-step mechanism dominates in this system. That study was, however, based on a study of the doping concentration dependence of PL transients using the conventional analysis method based on fits to Eq. (2). We remark that preliminary experimental results show that at large doping concentrations, around 16 wt%, applying the same method leads to a significantly smaller r -ratio. A study of the doping concentration dependence of the TTA mechanism, revealing the cross-over to diffusion controlled TTA, is now in progress.

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