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Analysis of the phosphorescent dye concentration dependence of triplet-triplet annihilation in organic host-guest systems

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Abstract

Using a novel method for analyzing transient photoluminescence (PL) experiments, a microscopic description is obtained for the dye concentration dependence of triplet-triplet annihilation (TTA) in phosphorescent host-guest systems. It is demonstrated that the TTA-mechanism, which could be a single-step dominated process or a diffusion-mediated multi-step process, can be deduced for any given dye concentration from a recently proposed PL intensity analysis. A comparison with the results of kinetic Monte Carlo simulations provides the TTA-Förster radius and shows that the TTA enhancement due to triplet diffusion can be well described in a microscopic manner assuming Förster- or Dexter-type energy transfer.

Keywords:

triplet-triplet annihilation, transient photoluminescence, kinetic Monte-Carlo simulations, organic semiconductors, organic light-emitting diodes

1. Introduction

Triplet excitons play a crucial role in modern organic optoelectronic devices, such as organic light-emitting diodes (OLEDs) and organic photovoltaic

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Already in the 1960s, photoluminescence (PL) experiments on single crystal anthracene have been used to study exciton formation and triplet-triplet annihilation (TTA), which in these materials gives rise to delayed fluorescence [5]. More recently, TTA-induced delayed fluorescence has been exploited as a means to increase the internal quantum efficiency (IQE) of the fluorescent OLEDs beyond the theoretical spin-statistical limit of 25% [6, 7]. To overcome this limit, it is required that both singlets and triplets are harvested [8]. Phosphorescent OLEDs, which make use of the enhanced spin-orbit coupling in dye molecules containing a heavy atom, have shown an IQE close to 100% [9, 11]. For the newly developed class of high-efficiency OLEDs based on thermally activated delayed fluorescence (TADF) materials, fast triplet-to-singlet reverse intersystem crossing plays an important role [12, 13]. Many types of OLEDs thus successfully explore either direct emission from triplets or emission following processes in which triplets are present in the intermediate excitonic stages preceding radiative decay. However, due to their long emissive lifetime, e.g. around one microsecond in typical high-efficiency phosphorescent dyes, the triplet density is sensitive to bimolecular loss processes such as TTA and triplet-polaron quenching (TPQ) at high luminance levels [14, 17]. In phosphorescent OLEDs, these processes give rise to an efficiency drop (roll-off) with increasing current density [11]. Developing detailed microscopic-scale understanding of the triplet dynamics is necessary in order to rationally improve the OLED device performance.

In this paper, we focus on the development of a quantitative microscopic-scale description of the mechanism of TTA in phosphorescent host-guest systems such as used in high-efficiency OLEDs [18, 20], using the results of transient PL experiments. In practical systems, the emissive dye concentration is typically in the range 3 – 10 mol%. In this concentration range, the role of triplet exciton diffusion varies strongly. At high dye concentrations, the small average distance between the dye molecules facilitates exciton diffusion. Already at small exciton densities the PL efficiency can then be decreased due to concentration quenching [21], whereas at large densities exciton diffusion can give
rise to an additional efficiency loss due to TTA. In that case, TTA is thus a multi-step process: diffusion followed by an interaction process between two triplets upon which annihilation of one of the triplets takes place. The interaction leading to TTA can be a Förster-type dipole-dipole process, which is quantum-mechanically allowed due to the small mixed-in singlet-character in the predominantly triplet-type states. In contrast, at low dye concentrations, where the role of exciton diffusion is limited, the TTA process is predominantly a single-step process, with a rate determined almost entirely by the rate of the direct interaction process \[22\,24\]. We note that also a Dexter-type interaction could contribute to the annihilation process. In a previous publication, we have proposed a method to distinguish the TTA mechanism (single-step or multiple step) from a cumulative PL yield analysis as measured in a time-resolved PL experiment \[25\]. Using kinetic Monte Carlo (kMC) simulations, it was shown how this can be already accomplished by carrying out a study for only a single emissive dye concentration. The method is based on measurements of the total (time-integrated) efficiency loss as a function of the initial triplet volume density, combined with a measurement of the time at which the cumulative PL yield has reached half of its total value. We recently demonstrated the validity of the method for the case of a host-guest system in which 3.9 wt% of the often-used green emitter bis(2-phenylpyridine)(acetylacetonate)iridium(III) (Ir(ppy)_2(acac)) is doped into the host material 4,4'-bis(carbazol-9-yl) biphenyl (CBP) \[26\]. An analysis which was supported by kMC simulations led to the conclusion that for this system the Förster radius \(R_{F,TT}\) describing the TTA rate is in between 3 and 5 nm, and that diffusion plays no significant role. This study did not yet establish whether the novel analysis method could also be applied successfully for a wide range of dye concentrations, including values at which strong diffusion takes place.

The purpose of the present paper is threefold: (i) to verify whether the method developed in ref. 25 for deducing the TTA mechanism from transient PL measurements can be applied successfully for any dye concentration, (ii) to establish an accurate description using a single set of microscopic parameters to
quantify the TTA and diffusion rates in the full guest concentration range, and
(iii) whether it is then possible to deduce the type of diffusion process (Förster
or Dexter-type) from the analysis. In the literature, both types of processes
have been argued to be relevant [21–30]. For this purpose, we extend the study
carried out in ref. 26 to CBP:Ir(ppy)$_2$(acac) host-guest systems with a guest
concentration which is varied in small steps from 1.0 wt% to 16.4 wt%.

The experimental results show a clear variation of the efficiency loss due to
TTA with respect to the guest concentration and confirm the wide applicability
of the method developed in ref. 25. We provide a quantitative analysis of the
experimental data using an extensive set of kMC simulations, assuming either
Förster or Dexter-type diffusion of triplet excitons. In addition, the analysis
demonstrates the important role of properly taking into account the percolative
nature of the exciton diffusion process in these positionally disordered materi-
als. With the optimized parameters, kMC simulation results assuming either
Förster- or Dexter-type diffusion are both found to provide a fair explanation of
the experimental results. Therefore, making a clear distinction between these
two triplet diffusion mechanisms would be difficult on the basis of the present
analysis. However, the optimized values of the microscopic parameters provide
already useful information and insight into theories and simulation models of
exciton diffusion.

2. Experimental results and analysis

The details of the CBP:Ir(ppy)$_2$(acac) sample fabrication and transient PL
measurement methods have been discussed in detail in ref. 26. All films are
prepared by co-evaporation on pre-cleaned quartz substrates and encapsulated
in a glove box. The thickness of the films is 50 nm.

Figure 1(a) shows the absorbance and normalized PL emission spectra of
the doped samples and, as a reference, of a neat CBP film prepared in the same
way. All absorption spectra coincide, implying that the incident light is almost
exclusively absorbed by the host CBP molecules. Figure 1(b) shows that the
averaged absorbance at 337 nm (the wavelength of the nitrogen laser used in the transient PL measurements) is indeed independent of the guest concentration. At high guest concentrations almost all singlets created transfer quickly to the guest Ir(ppy)$_2$(acac) molecules, and convert subsequently to triplets due to efficient intersystem crossing [9, 31, 32]. At very low guest concentrations, residual emission from the host CBP is observed. This is quantified in Fig. 1(b), which includes the guest concentration dependence of the PL emission ratio, defined as the ratio of the peak area of the guest PL spectrum and the spectrally integrated PL intensity. The PL emission ratio reveals the efficiency of the exciton transfer processes, and has been used for calculating the initial triplet density ($T_0$) in a manner discussed already in ref. 26. A small redshift of the main PL peak at 520 nm and a gradual smearing out of the shoulder structure at 560 nm might be due to the increasing statistical probability that emitters are paired, or to aggregation at high guest concentrations [21, 33, 34].

For all guest concentrations, the transient PL intensity $I(t)$ as obtained after excitation by a 337 nm N$_2$ laser has been measured as a function of the initial triplet density $T_0$, in the range $5 \times 10^{22} - 3 \times 10^{25}$ m$^{-3}$, in a manner discussed in detail in ref. 26. An overview of the experimental data for two typical guest concentrations is given in the Supplementary Material. Conventionally, from a fit to the emission intensity a TTA rate coefficient, $k_{\text{TT}}$, is derived, assuming that the contribution to the decrease of the triplet volume density $n_T$ due to TTA is given by $dn_T/dt = -fk_{\text{TT}}n_T^2$, with $f = 1/2$ if upon a triplet-triplet interaction process one of the two excitons is lost [32, 35, 36]. However, this assumption is only valid in the limit of strong diffusion, when the distribution of triplets remains spatially random. In the case of weak or no diffusion, the triplets which “survive” longest are most likely those which are relatively isolated with respect to other triplets, so that in the course of the PL decay process the triplet distribution becomes spatially correlated. As proposed first in ref. 25 and as demonstrated in ref. 26, the mechanism of the TTA process is revealed by deducing from the PL intensity two auxiliary parameters, $k_{\text{TT},1}$ and $k_{\text{TT},2}$, which are equal in the case of strong diffusion.
Figure 1: (a) Absorbance spectra and normalized PL intensity spectra (excitation at 337 nm; normalization to the PL peak intensity) of a neat CBP film and of selected doped films (thickness 50 nm, on quartz). All absorbance spectra coincide. (b) Guest weight concentration \( c_D \) dependence of the absorbance at 337 nm and the PL emission ratio, which is defined as the ratio of the PL intensity in the range 475 – 650 nm (emission from \( \text{Ir(ppy)}_2(\text{acac}) \)) and the total PL intensity in the range 360 – 650 nm. Solid curves are guides-to-the-eye.
(multi-step TTA), but different in the case of weak diffusion (predominantly single-step TTA. The ratio $r \equiv k_{TT,2}/k_{TT,1}$ is then significantly larger than 1).

The auxiliary parameter $k_{TT,1}(T_0)$ is obtained from the time $t_{1/2}$ at which the cumulative PL yield $Y(T_0, t)$ has reached half of the final ($t = \infty$) value, using the analytical expression for $Y(T_0, t)$ that would be exact in the strong-diffusion limit [25]. The cumulative PL yield is defined as $Y(T_0, t) = \int_0^t I(t')dt'$. The value of $k_{TT,1}$ obtained from the analysis is quite sensitive to the value of lifetime used. Using a procedure discussed in ref. 26, the lifetime is carefully evaluated. At low guest concentrations ($< 7$ wt%), it is almost constant and equal to the value of $1.36 \pm 0.02$ µs reported in ref. 26 for 3.9 wt% systems. The lifetime decreases gradually with increasing guest concentration, to $1.15 \pm 0.02$ µs for 16.4 wt% materials (see the Supplementary Material). Such a dependence of the triplet lifetime on the guest concentration has been observed earlier and ascribed to concentration quenching [21]. The analysis is also sensitive to the value of $T_0$ assumed. Ideally, $I(0)$ should be linearly proportional to the value of $T_0$. However, at very small guest concentrations $I(T_0)$ is found to saturate for large nominal values of $T_0$, as shown in Fig. 2(a) for the case of 1 wt% systems. This saturation effect can be used to cross-check the guest concentration [37, 38].

In our case, assuming a molar molecule density of $10^{27}$ m$^{-3}$, the saturation value of $T_0$ (approximately $10^{25}$ m$^{-3}$) observed for the 1 wt% systems is quite consistent with the nominal guest concentration. A weight percentage equal to $c_D = 1$ wt% corresponds therefore to a molar concentration very close to $x_D = 1$ mol%. For our present set-up, $T_0$ is limited to $3 \times 10^{25}$ m$^{-3}$, implying that no saturation will be observed for samples with a guest concentration larger than approximately 4 wt%. As an example, Fig. 2(a) shows that indeed a fully linear dependence of $I(0)$ on $T_0$ is found for the 16.4 wt% case.

The value of the auxiliary parameter $k_{TT,2}(T_0)$ is derived from the relative PL efficiency, which is a dimensionless quantity defined as

$$
\eta_{PL,rel}(T_0) = \lim_{T' \to 0} \frac{T'}{T_0} \times \frac{Y(T_0, \infty)}{Y(T', \infty)}
$$

(1)
Figure 2: Analysis of the initial triplet density dependence of the transient PL intensity for CBP:Ir(ppy)$_2$(acac) systems with a 1.0 and 16.4 wt% guest concentration. (a) The initial PL intensity shows a saturation effect for the low-concentration system (see the main text). (b) The relative PL efficiency (symbols) and the $T_0$ dependence expected from the value of $k_{TT,2}$ as obtained in this work for small values of $T_0$ assuming fully diffusion controlled TTA (full curves). From the measured values of $\eta_{PL,rel}$ for large $T_0$, this assumption is clearly invalid for the 1.0 wt% system. (c) The values of $k_{TT,1}$ and $k_{TT,2}$ for both 1.0 and 16.4 wt% guest concentrations. If no error bars are shown, the uncertainty is smaller than or approximately equal to the symbol size.
In the absence of TTA, the total cumulative PL yield is proportional to $T_0$, so that then $\eta_{PL,\text{rel}}(T_0) = 1$. As shown by Fig. 2(b), the measurements reveal a decrease of $\eta_{PL,\text{rel}}(T_0)$ with increasing $T_0$, in a manner which depends on the guest concentration. The decrease is initially larger for high-concentration systems than for low-concentration systems, revealing an increase of the TTA efficiency loss with increasing dye concentrations. This effect may be quantified by a parameter $k_{TT,2}(T_0)$, which is equal to the value of $k_{TT}$ which would give rise to the measured value of $\eta_{PL,\text{rel}}(T_0)$ in the case of strong diffusion. The value of $k_{TT,2}$ may be derived using an analytical expression for $\eta_{PL,\text{rel}}(T_0)$ (see ref. 25).

Figure 2(c) gives an overview of the $T_0$ dependence of $k_{TT,1}$ and $k_{TT,2}$, for two concentrations. At low guest concentrations, both parameters are quite different, and depend significantly on $T_0$ beyond an initial triplet density $T_0 \cong 3 \times 10^{24}$ m$^{-3}$. In Fig. 2(b), this is visible as a clear deviation of the measured values of $\eta_{PL,\text{rel}}(T_0)$ from the curve which is expected when assuming that $k_{TT,2}(T_0)$ is constant and given by the value obtained for $T_0 < 2 \times 10^{24}$ m$^{-3}$. For large guest concentrations, the difference between $k_{TT,2}$ and $k_{TT,1}$ is small, and quite independent of $T_0$. As discussed already in ref. 26, an increase of $k_{TT,2}$ and a decrease of $k_{TT,1}$ beyond a certain critical value of $T_0$ is expected in the case of single-step Förster-type TTA, as a result of a cross-over to a regime in which on average more than one triplet is present within a sphere around each triplet with a radius equal to the TT interaction Förster radius, $R_{F,TT}$. Consistent with that interpretation, this $T_0$ dependence disappears for large guest concentrations, when TTA is predominantly due to the diffusion controlled multi-step mechanism. We note that the exciton dynamics at high excitation densities, which is complicated and still under intense study in view of e.g. the development of organic lasers [39][41], is beyond the scope of the present study. Therefore, we limit our analysis to the low-$T_0$ regime ($< 2 \times 10^{24}$ m$^{-3}$), where $k_{TT,1}$ and $k_{TT,2}$ are both $T_0$-independent.

Figures 3(a) and 3(b) give the dependence of $k_{TT,1}$ and $k_{TT,2}$, averaged over the entire low-$T_0$ regime, and the $r$-ratio, respectively, on the average guest-guest
distance, $a = x_D^{-1/3}$. In order to obtain an improved accuracy, in each case four independent measurements were carried out. Figure 3(a) shows that there are two distinct regimes. At large guest-guest distances, corresponding to a guest concentration below 7 mol%, $k_{TT,1}$ and $k_{TT,2}$ are nearly constant. The role of diffusion is then almost negligible. Consistent with this view, also the large $r$-ratio is indicative of a single-step dominated TTA process. The relatively large error bars in this regime are due to the weak PL intensity obtained from the low guest concentration samples. The uncertainties are largest for $k_{TT,1}$, which depends strongly on the early evolution of the cumulative PL yield \[25\]. As a result, the increase of the $r$-ratio at large guest-guest distances, which might be suggested by Fig. 3(c), is not statistically significant. For guest concentrations above 7 mol% a gradual increase of $k_{TT,1}$ and $k_{TT,2}$ is observed, implying an enhanced TTA rate. In addition, $k_{TT,1}$ exhibits a steeper dependence on the guest distance, resulting in a decrease of $r$-ratio as shown in Fig. 3(b). Such a dependence of the $r$-ratio on the guest distance implies an increasing importance of triplet-diffusion. The observation that even at 16 mol% the $r$-ratio is significantly larger than 1 implies that for these materials single-step TTA still plays a role. In order to quantify the interplay between direct TTA and diffusion, a microscopic description is needed. In the following section, the experimental data are analyzed using the results of kMC simulations.

3. Refined analysis using kinetic Monte-Carlo simulations

For obtaining a quantitative microscopic-scale picture of triplet-diffusion mediated TTA, we have performed kMC simulations for pure Förster-type diffusion and pure Dexter-type diffusion, using the Bumblebee simulation tool \[12\]. All simulations were carried out for an initial concentration $T_0 = 1.0 \times 10^{-24}$ m$^{-3}$, i.e. for the low-$T_0$ regime. As a first step, simulations were carried out without diffusion. The inset in Fig. 4 shows the calculated value of $k_{TT,2}$ as a function of the triplet-triplet interaction Förster radius $R_{F,TT}$. From a comparison with the experimental value for the smallest dye concentration considered,
Figure 3: The values of $k_{TT,1}$ and $k_{TT,2}$ (a) and of the ratio $r = k_{TT,2}/k_{TT,1}$ (b), as obtained from the analysis in Section 2, as a function of the average guest-guest distance $a$ (lower scale) or the guest concentration (upper scale).

$k_{TT,2} = (0.95 \pm 0.15) \times 10^{-18}$ m$^3$s$^{-1}$, it would follow that $R_{F,TT} = 4.6 \pm 0.2$ nm. Consistent with this finding, we have studied the effect of diffusion using a fixed value of $R_{F,TT} = 4.5$ nm. We note that this value is larger than the value of about $3.0 - 3.6$ nm which has been deduced spectroscopically [1, 28].

3.1. TTA enhancement due to Förster-type diffusion

The values of $k_{TT,2}$ and $k_{TT,1}$ as obtained from simulations assuming a pure Förster-type diffusion, with a distance ($R$) dependent guest-guest triplet exciton transfer rate equal to

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

are shown in Fig. 4(a) and (b), respectively. It may be seen from the figure that a fair fit to the experimental results for high dye concentrations is obtained for $R_{F,\text{diff}} = 2.0 \pm 0.2$ nm. This value is close to (although slightly larger than) the range of values (1.5 – 1.8 nm) obtained by Kawamura et al. [21] from the
Figure 4: Dependence of the values of (a) $k_{TT,2}$ and (b) $k_{TT,1}$ on the average guest-guest distance, as obtained from kMC simulations in which triplet diffusion is described as a Förster-type process with Förster-radii equal to 1.5, 2.0 and 2.5 nm and a fixed value $R_{F,TT} = 4.5$ nm. The starred symbols indicate the experimental results. The inset shows the dependence of $k_{TT,2}$ as obtained from kMC simulations as a function of $R_{F,TT}$ in the absence of diffusion; the horizontal dashed line is the experimental value for 1.0 wt% concentration, and the vertical dashed line gives the value of $R_{F,TT}$ used in the subsequent analysis. The upper scale gives the guest concentration.
overlap of the extinction and emission spectra for various Ir-containing phospho-
resent dyes. We note that the simulation data shown in the figure have been
obtained for a fixed value of $\tau = 1.36 \mu s$, equal to the value measured for low
guest concentrations. It is presently not clear how the concentration quenching
effect, which as discussed above leads to an approximately 18 % decrease of
the lifetime for the 16 mol% system to $\sim 1.15 \mu s$, should be included in the
analysis. Repeating the kMC simulations for this smaller lifetime would lead to
18 % larger values of $k_{TT,1}$ and $k_{TT,2}$. From Fig. 4, it may be seen that the
best fit value $R_{F,TT}$ would then be only slightly larger, viz. approximately 2.1
nm. In the analysis, the concentration quenching effect should thus preferably
be included in a physically consistent microscopic manner. However, this is
beyond the scope of the present study.

3.2. TTA enhancement due to Dexter-type diffusion

Also Dexter-type triplet transfer can contribute to exciton diffusion. The
triplet transfer rate is then given by

$$r_{D,\text{diff}}(R) = k_{D,0} \exp \left( -\frac{2R}{\lambda} \right) \tag{3}$$

with $k_{D,0}$ the Dexter hopping rate in the zero distance limit and $\lambda$ an effective
exciton wavefunction decay length, which is related to the electron and
hole wavefunction decay lengths. The approach which has been used to obtain
optimal values of $k_{D,0}$ and $\lambda$, assuming pure Dexter-type exciton transfer, is
explained in detail in the Supplementary Material. The $\lambda$-value is varied from
0.2 to 1.2 nm. The result of the optimized combinations of $k_{D,0}$ and $\lambda$ values is
shown as an inset of Fig. 5(a) for the 6.0 mol% guest concentration. With the
optimized parameters, the guest concentration is varied from 1 to 20 mol% to
investigate the effect of diffusion on TTA. Figures 5(a) and (b) show a compar-
ison between the experimental and kMC simulation results for $k_{TT,2}$ and $k_{TT,1}$,
respectively, as a function of the average guest-guest distance. A quite good
fit to the experimental data is obtained using $\lambda \approx 0.3$ nm and $k_{D,0} \approx 2 \times 10^{11}$
The kMC simulations then successfully describe the average guest distance dependence of both $k_{TT,2}$ and $k_{TT,1}$ in the full guest concentration range, especially for $k_{TT,2}$.

Figure 5: Dependence of the values of (a) $k_{TT,2}$ and (b) $k_{TT,1}$ on the average guest-guest distance, as obtained from the kMC simulations in which triplet diffusion is described as a pure Dexter-type process with various values of the exciton wavefunction decay length $\lambda$, combined with the values of $k_{D,0}$ as given in the inset of (a), for a fixed value $R_{E,TT} = 4.5$ nm and at guest concentration 6.0 mol%. The stars indicate the experimental results. The upper scale gives the guest concentration.

The value $\lambda \approx 0.3$ nm, which follows from the analysis, is equal to the value for the electron, hole and exciton wavefunction decay lengths employed in recent kMC simulations of the roll-off and degradation of phosphorescent OLEDs [43]. However, it is much smaller than the value of 1.7 nm which has been extracted by Zhang and Forrest for CBP:Ir(ppy)$_2$(acac) systems from the slope of a plot of the quantity $\ln(k_{TT,0}/a^2)$ versus $a$, with $k_{TT,0}$ the TTA rate coefficient which would follow from a conventional analysis of time-resolved PL experiments [28]. This approach assumes diffusion-controlled (multi-step) TTA for all concentrations, and it assumes that $k_{TT}$ is then proportional to the exciton diffusion coefficient, given by $a^2 k_{D,eff}(a)$. However, using our novel analysis method, we
have demonstrated that for the systems studied the TTA mechanism is in no case fully diffusion-controlled, and at low concentrations actually close to the single-step limit [26]. Furthermore, we find from the kMC simulations that due to the positional disorder of the dye molecules the dependence of the exciton diffusion coefficient on the average guest-guest distance is not simply equal to $a^2 k_{D,\text{diff}}(a)$. Exciton diffusion is non-uniform (percolative) [44]. For similar reasons the $a$-dependence of $k_{TT}$ in the case of Förster-type diffusion (Section 3.1) is not simply proportional to $a^{-6}$, as would be expected for fully diffusion-controlled TTA in the absence of positional disorder. A detailed discussion of the dye concentration dependence of the exciton diffusion process will be given in a forthcoming paper.

The best fit value $k_{D,0} \approx 2 \times 10^{11} \text{s}^{-1}$ corresponds to a hop rate to a first nearest neighbor site at a distance $a_0 = 1 \text{ nm}$ equal to $k_{D,1} = k_{D,0} \exp(-2a_0/\lambda) \approx 2.6 \times 10^8 \text{s}^{-1}$. This value is two orders of magnitude smaller than the electron or hole hopping attempt frequency assumed typically [25, 45]. The difference could be in part due to the neglect of excitonic energetic disorder [25, 46, 47]. From the emission spectrum, we deduce a Gaussian width (standard deviation) of the triplet density of states equal to approximately 50 meV. Assuming that width, and thermally activated Dexter-type diffusion, we find that a two orders of magnitude larger value of $k_{D,0}$ ($2 \times 10^{13} \text{s}^{-1}$) would be consistent with the experimental results (not shown).

On the basis of the analysis given in this section, we cannot decide whether the diffusion process is predominantly due to Förster- or Dexter-type transfer, or perhaps due to a combination of both. This is due to the rather long-range nature of the Förster-type triplet-triplet interaction, so that diffusive exciton transfer only affects the triplet loss due to TTA for relatively small average intersite distances. The analysis probes most sensitively the role of diffusion in a relatively small guest concentration range, corresponding to an average intersite distance in the range $1.7-2.3 \text{ nm}$. Consistent with this view, the exciton transfer rates $r_{F,\text{diff}}(R)$ and $r_{D,\text{diff}}(R)$ which provide a best fit to the measured data are equal for an intersite distance $R \sim 1.8 \text{ nm}$ (see the Supplementary Material).
4. Summary and conclusions

In this paper, we have shown that a novel method for analyzing the results of transient PL experiments, which probe the efficiency loss due to TTA in phosphorescent host-guest OLED materials, provides a consistent view on the mechanism of the TTA process in a wide range of guest concentrations. For the CBP:Ir(ppy)$_2$(acac) systems studied, TTA is for small concentrations due to a single-step dipole-dipole interaction mechanism, characterized by a Förster radius $R_{F,TT} \approx 4.5$ nm. For concentrations above approximately 7 mol%, TTA is enhanced due to triplet diffusion, and becomes a multi-step process. This is evident from an observed increase of the two auxiliary parameters, $k_{TT,1}$ and $k_{TT,2}$, with increasing guest concentration, and an observed decrease of the ratio $r$ between both quantities (= $k_{TT,2}/k_{TT,1}$). We find that even for the largest guest concentrations included in our study (16 mol%), the $r$-ratio is still larger than 1, implying that the fully diffusion controlled limit has then not yet been reached.

As to the diffusion mechanism, using the results of kinetic Monte Carlo simulations, a quantitative analysis shows that the diffusion contribution can be quite well described as a dipole-dipole energy transfer process with a Förster-radius $R_{F,\text{diff}} = 2.0 \pm 0.2$ nm or as a result of Dexter-type exciton transfer with an exciton wavefunction decay length $\lambda \simeq 0.3$ nm and a prefactor $k_{D,0} = 2 \times 10^{11}$ s$^{-1}$. From the quality of the fit, no distinction between both mechanisms can be made. The value of $R_{F,\text{diff}}$ is consistent with typical values as obtained spectroscopically for similar materials, and the value of $\lambda$ is equal to the value employed earlier in studies of charge and exciton transport.

The analysis given in this paper provides a first step towards a fully microscopic picture of the TTA mechanism. In contrast to the conventional description, in terms of a rate coefficient $k_{TT}$, the microscopic description provides an explanation for the observed increase of the TTA loss at high initial exciton densities (see ref. 26) and a proper prediction for the TTA loss under steady-state conditions (see ref. 25). Future studies are required to resolve the discrepancy...
of the value of $R_{F,TT}$ obtained from our study and the (somewhat smaller) spectroscopic value, and to deduce the mechanism of the diffusion process. These studies should include a systematic variation of the type of host and guest material, so that the relative roles of the direct and multi-step TTA mechanism can be varied and the possible effects of non-ideal exciton confinement are probed.

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