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Citation for published version (APA):

Document license:
TAVERNE

DOI:
10.1002/adfm.201804618

Document status and date:
Published: 27/12/2018

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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Download date: 10. Jun. 2022
Effect of Triplet Confinement on Triplet–Triplet Annihilation in Organic Phosphorescent Host–Guest Systems

Arnout Ligthart, Xander de Vries, Le Zhang, Mike C. W. M. Pols, Peter A. Bobbert, Harm van Eersel, and Reinder Coehoorn

The efficiency of phosphorescent organic light-emitting diodes (OLEDs) shows a decrease with increasing luminance (“roll-off”). One of the contributions to the roll-off is triplet–triplet annihilation (TTA). TTA is the process of energy transfer from one triplet exciton to another, after which the excited exciton decays nonradiatively to the lowest triplet state. In this study, the TTA-rate is measured for a large number of emissive materials consisting of a small concentration of phosphorescent “guest” molecules, with emission colors across the entire visible range, embedded in various host materials. It is found that the TTA-rate does not only depend on the direct interaction rate between the excitons on the guest molecules, but also on the difference in triplet energy \( \Delta E_T \) of the host and guest molecules: when \( \Delta E_T \) is smaller than about 0.20 eV, diffusion of excitons via the host molecules leads to a significant enhancement of the TTA-rate. By varying the guest concentration and using kinetic Monte Carlo simulations, the roles of the direct interaction, guest-mediated diffusion, and host-mediated diffusion are disentangled.

1. Introduction

The internal quantum efficiency (IQE) of phosphorescent organic light-emitting diodes (OLEDs) is determined by the probability that the triplet excitons formed on the emissive metal–organic dye molecules will decay radiatively. When the charge carriers and triplet excitons are well-confined in the emissive layer (EML), the main potential loss processes are intrinsic nonradiative decay, concentration quenching, and triplet–triplet annihilation (TTA) and triplet–polaron quenching (TPQ). TTA and TPQ are due to bimolecular interactions, and give rise to an efficiency roll-off at high brightness. In addition, these loss processes can trigger degradation events.

The main cause of the efficiency roll-off has been a subject of debate. Studies of various different types of devices suggest that the predominant mechanism depends on the detailed structure of the emissive layer. Simulation results of phosphorescent OLEDs suggest that TPQ is the predominant mechanism at small current densities, but that the relative contribution due to TTA becomes larger at high current densities. Furthermore, simulations have revealed a subtle interplay between TPQ and TTA: decreasing the contribution of one process can increase the contribution of the other process, so that the roll-off is not significantly reduced. The overall IQE reduction is not only determined by the encounter-distance-dependence of the rate with which the final TPQ and TTA processes take place, but also by the triplet exciton diffusivity. In order to accurately quantify the relative contributions from TTA and TPQ, it will be necessary to develop a mechanistic description of the direct triplet–triplet and triplet–polaron interaction rates and of the exciton diffusion processes. That will allow disentangling all contributions, and will support the development of predictive simulations as a route toward reduced OLED roll-off.

In this paper, we demonstrate how time-resolved photoluminescence studies of the efficiency loss due to TTA can be used to sensitively probe triplet exciton diffusion processes in organic semiconductor host–guest systems. The analysis provides not only a mechanistic description of the direct annihilation process, but also of the guest–guest and host-mediated diffusion processes that can contribute to the overall TTA rate, as well as to the TPQ rate in full OLEDs. In particular, we focus on investigating host-mediated triplet diffusion. In state-of-the-art phosphorescent OLEDs, this contribution to the diffusion is limited by selecting host materials with a sufficiently high triplet energy. However, this design rule should not be followed too rigorously. First, obtaining a long device lifetime requires that the dye concentration is not too small. Second, a large host triplet energy implies in general also a large fundamental energy gap, so that electron and/or hole injection in the host material occurs only at a relatively high voltage, giving rise to
a reduction of the power efficiency. It is therefore of interest to determine the conditions required for good triplet exciton confinement on the guest molecules.

The importance of good triplet exciton confinement is well known from studies of the host triplet exciton energy dependence of the IQE in phosphorescent OLEDs based on small-molecule[21–29] or polymer[30–33] host materials, and in third-generation OLEDs utilizing thermally assisted delayed fluorescence (TADF).[34–36] Triplet confinement near interfaces with hole-transport layers was studied in ref. [36]. A key parameter is the triplet confinement energy $\Delta E_T \equiv E_{T,h} - E_{T,g}$, with $E_{T,big}$ the triplet energy on the host and guest molecules, respectively. However, it is presently not clear whether, as a rule, $\Delta E_T$ should exceed a certain minimum value in order to guarantee sufficient triplet confinement. Most studies carried out so far focus on the effect of a variation of the host material type on the external quantum efficiency (EQE) of OLEDs. As discussed by Swensen et al.,[28] such studies are often at best qualitative: the EQE can also be affected by various other loss processes such as exciton transfer to the electron and hole transport layers and (more indirectly) by the change transport properties. For OLEDs based on the sky-blue emitter bis[2-(4,6-difluorophenyl)pyridinato-C$_2$N](picolinato)iridium(III) (FIrpic, $E_T = 2.7$ eV), e.g., replacing a higher triplet-energy host material ($E_T = 2.8$ eV) by a lower triplet-energy host material ($E_T = 2.6$ eV) was even found to lead to a slight increase of the EQE, to almost 18% in the low-current-density limit.[28] Neglecting (for the moment) the possible role of energetic disorder, the confinement energy $\Delta E_T$ properly determines the thermodynamic equilibrium stability of triplet excitons on the guest molecules. However, the effects of triplet deconfinement on the IQE will also be determined by the kinetics of the host–guest and host–host triplet exciton transfer processes. It is therefore of interest to study to what extent kinetic effects could give rise to a system-to-system variation of the dependence of exciton deconfinement on the confinement energy.

We disentangle the roles of the confinement energy and of the host-mediated triplet diffusion by studying in total 22 systems, based on combinations of five Ir-based emitter molecules and seven host molecules. The confinement energy $\Delta E_T$ varies from about $-0.1$ to $+0.8$ eV. By making use of various host materials, also the effect of a variation of the host-mediated diffusion is probed. We find that only for $\Delta E_T \lesssim 0.20$ eV, the effective TTA rate coefficient is significantly enhanced due to triplet deconfinement. For selected systems, experiments have been carried out for a variable guest concentration and temperature. Figure 1 shows the various regimes that are probed: in the case of strong confinement and small guest concentrations, TTA is predominantly due to a single-step direct quenching process (Figure 1a). For large guest concentrations, TTA is a more indirect multistep process (Figure 1b). And in the case of weak confinement, host-mediated diffusion can give rise to an additional loss (Figure 1c). Using an analysis method proposed by van Eersel et al.,[37] and applied already to bis[2-(2-pyridinyl-N)phenyl-C$_{-}$C$_{\text{acetylatedenato}}$]iridium(III) (Ir[ppy]$_2$acac), embedded in a 4,4$^\text{-}$N,N$^\text{-}$dicarbazole-1,1$^\text{-}$biphenyl (CBP) host,[21,22] as well as the results of kinetic Monte Carlo (KMC) simulations, we find that it is possible to establish a microscopic description that is able to describe all strongly confined systems studied, with only slightly different material-dependent parameters. Within the model, TTA is described as a Förster type process. Guest–guest exciton diffusion is described as either a thermally activated Dexter or Förster process, with rates that are affected by the random disorder in the triplet energies. For weakly confined systems, the complexity of the interplay of all processes related to triplet guest–host or host–guest transfer, triplet-diffusion on the host, and possible quenching processes on the host obviously precludes at present developing a mechanistic model with predictive quality. Nevertheless, we argue that for the systems studied our approach provides realistic constraints to the parameters describing triplet transfer and annihilation rates.

2. Experimental and Analysis Methods

Table 1 gives an overview of the systems studied. The molecular structures are shown in Figure 2. Five phosphorescent emitters were used

- bis[2-(4,6-difluorophenyl)pyridinato-C$_2$N](picolinato)-iridium(III) (FIRpic, sky-blue),

Figure 1. Schematic overview of the relevant processes leading to TTA in phosphorescent host–guest systems. a) In systems with a low concentration of guest molecules and a large triplet confinement energy $\Delta E_T$, only TTA due to a direct (single step) TTA process is possible. In the figure, this process is depicted as a Förster-type process. b) For systems with a high concentration of guest molecules, guest-to-guest triplet exciton diffusion can enhance the TTA rate. c) The TTA rate is also enhanced when as a result of weak triplet confinement (small $\Delta E_T$) host-mediated diffusion occurs. Empty black and red spheres denote host and guest molecules in the ground state. Filled red spheres denote triplet-excited guest molecules. The dashed circles indicate the region within one TTA-Förster radius around each triplet. The arrows indicate possible diffusion paths.
Table 1. Host–guest systems studied in this paper. In parentheses, the host and guest triplet energies as obtained from the peak energy in the PL spectra are given (unit: eV), as displayed in Section S2 (Supporting Information) for the guest molecules and as obtained from the literature for the host molecules. For each system included, the triplet confinement energy $\Delta E_T$ (top entry, unit: eV) and the experimental value of $k_{TT}$ and its uncertainty range (bottom entry, unit: $10^{-18}$ m$^3$ s$^{-1}$) are given.

<table>
<thead>
<tr>
<th>Host</th>
<th>Guest</th>
<th>$\Delta E_T$ (eV)</th>
<th>$k_{TT}$ (a)</th>
<th>$k_{TT}$ (b)</th>
<th>$k_{TT}$ (c)</th>
<th>$k_{TT}$ (d)</th>
<th>$k_{TT}$ (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPB (2.30 eV)$^a$</td>
<td>Ir(MDQ)$_2$(acac)</td>
<td>0.07</td>
<td>3.63 ± 0.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N,N′-bis(naphthalen-1-yl)-N,N′-bis(phenyl)-benzidine (NPB)</td>
<td>Ir(BT)$_2$(acac)</td>
<td>0.07</td>
<td>3.63 ± 0.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPD (2.40 eV)$^a$</td>
<td>Ir(pppy)$_2$(acac)</td>
<td>0.06 ± 0.05</td>
<td>1.74 ± 0.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CBP (2.56 eV)$^a$</td>
<td>Ir(BT)$_2$(acac)</td>
<td>0.01 ± 0.05</td>
<td>1.40 ± 0.10</td>
<td>1.91 ± 0.14</td>
<td>4.2 ± 0.2</td>
<td></td>
<td>−0.06</td>
</tr>
<tr>
<td>Ir(ppy)$_2$(acac)</td>
<td>Ir(BT)$_2$(acac)</td>
<td>0.02</td>
<td>0.02 ± 0.05</td>
<td>1.05 ± 0.06</td>
<td>1.10 ± 0.09</td>
<td>1.08 ± 0.09</td>
<td></td>
</tr>
<tr>
<td>Ir(MDQ)$_2$(acac)</td>
<td>Ir(BT)$_2$(acac)</td>
<td>0.03</td>
<td>0.03 ± 0.05</td>
<td>1.05 ± 0.06</td>
<td>1.10 ± 0.09</td>
<td>1.08 ± 0.09</td>
<td></td>
</tr>
<tr>
<td>Ir(ppy)$_3$</td>
<td>Ir(BT)$_2$(acac)</td>
<td>0.04</td>
<td>0.04 ± 0.05</td>
<td>1.02 ± 0.16</td>
<td>1.57 ± 0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TCTA (2.84 eV)$^a$</td>
<td>Ir(MDQ)$_2$(acac)</td>
<td>0.05 ± 0.09</td>
<td>0.09 ± 0.10</td>
<td>0.65 ± 0.06</td>
<td>1.05 ± 0.09</td>
<td>0.85 ± 0.07</td>
<td></td>
</tr>
<tr>
<td>mCP (2.90 eV)$^a$</td>
<td>Ir(MDQ)$_2$(acac)</td>
<td>0.06 ± 0.05</td>
<td>0.06 ± 0.15</td>
<td>0.62 ± 0.05</td>
<td>0.65 ± 0.15</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Refs. [36,39]; $^b$Ref. [40]; $^c$Refs. [3,36,39,41]; $^d$Refs. [3,24,28,36]; $^e$Refs. [42,43]; $^f$Refs. [27,39,42,44]; $^g$Refs. [24,28,34].

The following host materials were used:

a) N,N′-bis(naphthalen-1-yl)-N,N′-bis(phenyl)-benzidine (NPB),
b) N,N′-bis[naphthalen-1-yl]-N,N′-bis(phenyl)-2,2′-dimethylbenzidine (α-NPD),
c) N,N′-bis[3-methylphenyl]-N,N′-diphenylbenzidine (TPD),
d) 4,4′-N,N′-dicarbazole-1,1′-biphenyl (CBP),
e) 2,2′, 2″-(1,3,5-benzenetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi),
f) tris(4-carbazoyl-9-ylphenyl)amine (TCTA),
g) 1,3-bis(N-carbazolyl)benzene (mCP). The triplet energies of all molecules, as obtained from the peak energy in the phosphorescence (PL) spectra, and the triplet confinement energy for each host–guest system studied are included in Table 1.

The systems studied are 50 nm thick host–guest films, coevaporated on pre-cleaned quartz substrates and encapsulated in a glove box under nitrogen conditions. For all host–guest systems, films containing 3.85 weight percent of guest molecules were studied, while for selected systems a full study of the guest concentration dependence was carried out. The transient PL experiments were carried out using a pulsed nitrogen laser with a wavelength of 337 nm. A 1 mm$^2$ aperture is used to form a uniform intensity profile. The light is focused using a lens on a fast-response photodiode. Absorbance measurements (Section S1, Supporting Information) are done to determine the initial triplet volume density, $N_0$, which is varied in 25 steps using optical density filters. To get sufficient statistics, each measurement is repeated on four spatially different spots. In ref. [21], a more extensive description of the experimental method is given. Although almost all absorption occurs on the host molecules, it is assumed that the transfer from the host to the guest is 100% efficient, as a result of singlet diffusion on the host, followed by transfer to the guest molecules and subsequent fast intersystem crossing on the guest molecules. Steady state PL measurements (Section S2, Supporting Information) indeed show that for all systems studied the transfer is very efficient, as the contribution from the host in the PL spectrum is found to be negligible.

The role of guest-mediated diffusion can be judged by analyzing the transient PL response using a method first proposed by van Eersel et al.[37] and experimentally demonstrated by Zhang et al. for CBP:Ir(ppy)$_2$(acac) systems.[21,22] Conventionally, the efficiency of TTA on the triplet volume density $T(t)$ in an organic semiconductor is described by the expression

$$\frac{dT}{dt} = G - \frac{T}{\tau} - f k_{TT} T^2$$

(1)

with $G$ the generation rate, $\tau$ the effective triplet radiative lifetime, $k_{TT}$ the effective triplet–triplet interaction rate coefficient, and $f$ a coefficient indicating the fraction of excitons that are lost in the TTA process. Typically, one exciton is assumed to be

...
lost upon the encounter of two excitons, so that \( f \) is generally assumed to be equal to \( 1/2 \). When Equation (1) is applicable, the response \( I(t) \) of the system in a transient-photoluminescence (PL) experiment is given by

\[
I(t) = I(0) \left( 1 + T_0 \frac{k_{TT,1} \tau}{T} \right) \exp \left( \frac{-t}{\tau} \right) - T_0 \frac{k_{TT,1} \tau}{T}
\]

with \( T_0 \) the initial triplet density and \( I(0) \) the initial PL intensity. However, this description of TTA breaks down when applied to systems with little or no diffusion. The exciton density becomes then spatially nonuniform when time proceeds, so that Equation (2) is no longer valid. Within the refined analysis method developed in refs. [21,22,37], the measured time at which half of the emission has taken place is used to deduce, for any value of \( T_0 \), a first effective rate coefficient \( k_{TT,1} \), assuming that Equation (2) is applicable. Accurately deducing \( k_{TT,1} \) requires determining \( \tau \) with high accuracy. The lifetime is determined in the very low \( T_0 (<10^{-24} \text{ m}^{-3}) \) region in which TTA is negligible. A second effective rate coefficient, \( k_{TT,2} \), is obtained from the measured decrease of the total PL efficiency, relative to the PL efficiency in the zero-fluence limit, again assuming that Equation (2) is applicable. In the limit of strong diffusion, the conventional analysis method is applicable, and the ratio

\[
r = \frac{k_{TT,1}}{k_{TT,2}}
\]

is equal to 1. In the absence of guest-mediated diffusion, when TTA is due to a single-step Förster-type process, the \( r \)-ratio can be well above 2. The role of guest-mediated diffusion can thus already be deduced from an analysis of the PL response for a single material. For CBP:Ir(ppy)_2(acac) systems, \( k_{TT,1} \) and \( k_{TT,2} \) have been found to become \( T_0 \)-dependent for values of \( T_0 \) above \( 10^{24} \text{ m}^{-3} \), in a manner as expected from KMC simulations within which TTA is described as a long-range Förster-type process. The effect was found to occur when \( T_0 \) exceeds the value at which on average one triplet is present within a sphere with a radius equal to the triplet–triplet interaction Förster radius, \( R_{F,TT} \). In this paper, we focus on the low-triplet density regime \( (T_0 < 10^{-24} \text{ m}^{-3}) \), in which \( k_{TT,1} \) and \( k_{TT,2} \) are independent of \( T_0 \). A more detailed discussion of the analysis method is given in ref. [21].

In the case of weak triplet confinement, resulting in delayed emission after host-mediated exciton diffusion and potentially trapping on the host, the decay is not monoexponential. In Section 3, the decay is from correlated single-photon-counting (CSPC) experiments shown to be well-described by a stretched-exponential function, \( I(t) = I(0) \exp[-(t/\tau')^\beta] \), with \( \tau' \) an effective \( 1/e \) lifetime and with \( \beta \) an exponent that decreases with decreasing triplet confinement.

Figure 2. Structure of the host and guest molecules included in this study.
3. Experimental Results and Analysis

In this section, we first present the results of an in-depth study of the system TCTA:Ir(ppy)$_2$(acac). For this system, the triplet confinement energy is large ($\Delta E_T = 0.46$ eV), so that deconfinement to the host plays no role. From this study, we motivate why for studying triplet deconfinement effects materials with a guest concentration of $3.85 \text{ wt\%}$ were selected. Subsequently, we show that for all systems included in Table 1 good triplet confinement requires that $\Delta E_T$ is larger than $0.20$ eV. The role of triplet diffusion is further investigated by studying for selected systems the temperature dependence of the TTA loss.

3.1. Strong Confinement—TCTA:Ir(ppy)$_2$(acac)

Figure 3a shows the measured dependence of $k_{TT,1}$ and $k_{TT,2}$ on the average guest–guest distance $a = c_g^{-1/3}$ and guest concentration, $c_g$ (top axis of the figure), for the system TCTA:Ir(ppy)$_2$(acac). The analysis has been based on the measured lifetime, deduced from the emission in the low-fluence limit, which decreases from 1.36 $\mu$s for small $c_g$ to 1.14 $\mu$s for $c_g = 18$ mol\%. Such a decrease (indicative of concentration quenching) is quite generally observed for phosphorescent host–guest systems (see, e.g., ref. [1]), and can result from diffusion followed by quenching at defects or from a finite nonradiative decay probability upon repeated Förster-type triplet transfer between adjacent molecules ("dampening"[2]). The method used to deduce $k_{TT,1}$ and $k_{TT,2}$ from the experimental data is explained in detail in Section S3 (Supporting Information).

The figure shows that beyond $c_g \approx 4$ mol\%, $k_{TT,1}$ and $k_{TT,2}$ increase with increasing guest concentration. The effect can be attributed to guest-mediated triplet diffusion, consistent with the decrease of the $r$-ratio with increasing guest concentration shown in Figure 3b. For $c_g$ larger than 20 mol\%, the $r$-ratio approaches 1 and the conventional (strong-diffusion) model (Equation (2)) is well-obeyed. Similar results were found for TCTA:Ir(ppy)$_3$ systems, for which the exciton confinement is also excellent (Section S4, Supporting Information). This motivates using a guest concentration of 3.85 wt\% when studying in the next subsection the effects of deconfinement, so that no host-mediated diffusion occurs whereas the transfer of excitons from the host (where most absorption takes place) to the guest molecules is still very efficient.

We note that qualitatively similar results were obtained by Zhang et al. for CBP:Ir(ppy)$_2$(acac) systems. However, for those systems the measured values of $k_{TT,1}$ and $k_{TT,2}$ are significantly larger than for TCTA:Ir(ppy)$_2$(acac), viz. by a factor 1.4 and 1.8, respectively, for systems with $c_g \approx 4$ mol\%. This indicates that in CBP:Ir(ppy)$_2$(acac) systems, with $\Delta E_T = 0.17$ eV, triplet diffusion via the host gives rise to a significant contribution to the efficiency loss due to TTA, consistent with the results shown in the next subsection.

3.2. Effect of Triplet Confinement

Figure 4 shows the dependence of $k_{TT,2}$ on the exciton confinement energy for all host–guest systems studied, measured at a temperature $T = 298$ K, at a guest concentration of 3.85 wt\%. This corresponds to molar-concentrations in the range 2.3–4.7 mol\%, depending on the system (Section S5, Supporting Information). The numerical values and experimental uncertainties are included in Table 1. The fraction of excitons lost, from which $k_{TT,2}$ has been deduced, is for all systems given in Section S6 (Supporting Information). The figure shows that for small confinement energies a significant enhancement of $k_{TT,2}$ is found, up to a factor of 4, as compared to the value

![Figure 3](image3.png)

**Figure 3.** Dependence on the average guest–guest distance of a) the rate coefficients $k_{TT,1}$ and $k_{TT,2}$ and b) the ratio $r = k_{TT,2}/k_{TT,1}$, for the system TCTA:Ir(ppy)$_2$(acac). The dashed curves are a guide-to-the-eye. The upper axis shows the guest concentration; 1 mol\% corresponds to 0.82 wt\%.

![Figure 4](image4.png)

**Figure 4.** The dependence of $k_{TT,2}$ on the triplet confinement energy (the difference between the host and guest triplet energies), measured at 298 K, for systems based on five different phosphorescent guest molecules (colored symbols, as indicated) and seven different host molecules. In Table 1, the numerical values are given. All systems have a guest concentration of 3.85 wt\%.

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obtained for confinement energies larger than about 0.20 eV. We interpret this result as a consequence of host-diffusion mediated TTA, giving rise to an enhanced energy loss. Interestingly, for all five emitter molecules $k_{TT,2}$ is quite similar when embedded in a well-confining host, viz. in the range (0.5–1.1) $\times 10^{-33}$ m$^3$ s$^{-1}$.

Triple deconfinement to inert host triplet states (at which no radiative or nonradiative decay takes place) is expected to give rise to an increase of the effective lifetime. However, deconfinement would lead to a reduced effective lifetime if strong quenching would occur upon diffusion on the host. Experimentally, we find an increase of the lifetime, up to a factor larger than 30, for systems with $\Delta E_T < 0.1$ eV, as shown in Figure 5. The figure gives the effective (1/e) lifetime $\tau_{\text{eff}}$ as measured from CSPC experiments relative to the lifetime $\tau_0$, as a function of the confinement energy. Interestingly, the confinement energy below which a significant lifetime enhancement is expected in the limit of very fast guest–host and host–host exciton transfer.

Figure 5. Effective emission lifetime in the zero-fluence limit for the 3.85 wt% host–guest systems studied.

It is not a priori clear how the host-mediated diffusion contribution to the TTA loss could be best described. The diffusion could either be due to an incoherent triplet hopping process such as depicted in Figure 1, or it could be due to a coherent host-mediated (superexchange like) coupling between guest sites, such as found to be relevant in the charge transport of organic semiconductor host–guest systems.[45] Incoherent excitation transfer is a thermally activated process, although the precise description is a subject of current debate,[46,47] whereas in as far as known to us for the case of coherent transfer no theoretical model giving the temperature dependence is available. In order to further explore the nature of the host-mediated diffusion contribution to TTA, we have carried out measurements at 200 K of $k_{TT,2}$ for 3.85 wt% Ir(ppy)$_2$(acac) in TCTA, CBP, and TPD. We find that $k_{TT,2}$ shows no significant temperature dependence for Ir(ppy)$_2$(acac) in TCTA, CBP, and TPD. In contrast to a coherent transfer, host-mediated diffusion is thus indeed a thermally activated process.
4. Quantitative Analysis—KMC Simulations

4.1. Strong Confinement—Guest–Guest Diffusion

Making use of KMC simulations it is possible to obtain a quantitative microscopic picture of guest–guest exciton diffusion in systems for which the triplet confinement is strong. The KMC simulations were done using the Bumblebee simulation tool,\[48\] for an initial triplet density of $10^{24}$ m$^{-3}$, i.e., within the low-$T_0$ region considered in the experiments. A realistic Gaussian disorder in the triplet energy levels of $\sigma_T = 0.05$ eV (standard deviation) was taken into account. TTA is assumed to be due to a Förster-type process,\[49\] with a distance ($\lambda$) or using (for Dexter-type diffusion) a distance-dependent rate between equienergetic sites given by

$$R_{TT} = R_{F,TT} (2\pi/\hbar)^2 \sigma_T^2$$

For TPD:Ir(BT)$_2$(acac), we find indeed a small decrease of the effective lifetime with decreasing temperature. However, we find that for the very weakly confined systems TPBi:Irpic and TPD:Ir(ppy)$_2$(acac) the effective lifetime actually increases with decreasing temperature. We attribute this surprising result to the decrease of the diffusion over the host with decreasing temperature. The final effect is determined by a delicate balance between two opposing effects, viz. the decrease in the escape rate and the decrease of the diffusion rate on the host with decreasing temperature. The experimental results are shown in Section S9 of the Supporting Information. In Section 4.2, we analyze this effect using KMC simulations.

Figure 6. Experimentally determined parameters $k_{TT1}$ (black) and $k_{TT2}$ (red) for TCTA:Ir(ppy)$_2$(acac) as function of the distance between guest molecules. The final annihilation process is assumed to be a Förster-type process with a triplet-triplet interaction radius $R_{TT} = 3.5$ nm. a) KMC simulations results (open symbols) obtained using pure Förster-type diffusion with $R_{F,TT} = 2.7$ nm and a constant lifetime of 1.36 $\mu$s, b) The KMC results assuming a pure Dexter-type diffusion using a wavefunction decay length $\lambda = 0.35$ nm and a nearest neighbor hopping attempt frequency $k_{D,1} = 1.4 \times 10^8$ s$^{-1}$. with $R_{TT}$ the Förster radius for TTA. The value of $R_{TT}$ can be determined spectroscopically. In the literature values in the range of 3.0–3.6 nm are found for various Ir-based phosphorescent emitters.\[7,19\] We focus here on the system TCTA:Ir(ppy)$_2$(acac), with $\Delta E_T = 0.46$ eV. For systems with a guest concentration below $\approx 4$ mol%, guest–guest diffusion is not yet significant (see Figure 3). Figure 6 shows that an excellent fit to the measured values of $k_{TT1}$ and $k_{TT2}$ is obtained from KMC simulations with $R_{TT} = 3.5$ nm. From the narrow range of values of $k_{TT2}$ in the strong-confinement regime, observed in Figure 4, it follows immediately that for the emitters studied $R_{TT}$ varies only little, from about 3.4 nm for Ir(MDQ)$_2$(acac) to about 3.8 nm for Ir(ppy)$_2$.\[90\] We note that from the available data, we cannot exclude that for Flirpic a study with a more strongly confining host than mCP would lead to a value of $R_{TT}$ that is slightly smaller than 3.4 nm.

It is not known whether guest–guest triplet diffusion is most properly described as a Förster or Dexter process, or by a combination of both. As shown in Figure 6, we find from KMC simulations that for TCTA:Ir(ppy)$_2$(acac) a good description of the experimental data can be obtained assuming either process, using a Förster radius for diffusion equal to $R_{F,TT} = 2.7$ nm (Figure 6a) or using (for Dexter-type diffusion) a distance-dependent rate between equienergetic sites given by

$$r_{TT} = k_{D,1} \exp \left[ -\frac{2(R-a)}{\lambda} \right]$$

with $k_{D,1} = 1.4 \times 10^8$ s$^{-1}$ the Dexter hopping rate to the nearest neighbor at a distance $a = 1$ nm and with $\lambda = 0.35$ nm the exciton wavefunction decay length (Figure 6b). The effect of energetic disorder has been included by treating both processes as thermally activated, in a manner as described by the Miller–Abrahams formula.\[51\] We note that $R_{TT}$ is not expected to be equal to $R_{F,TT}$ as the absorption spectrum for an excited guest molecule is different than that for a nonexcited guest. If no disorder is included, a good fit assuming Förster-type diffusion is obtained with $R_{F,TT} = 2.0$ nm. This value is equal to the value obtained by Zhang et al.\[21\] for Förster-type guest–guest diffusion in the system CBP:Ir(ppy)$_2$(acac) under the assumption of no excitonic disorder. From measurements of the overlap of the extinction and emission spectrum for various Ir-containing emitter molecules Kawamura et al.\[53\] found values for $R_{F,TT}$ in the range of 1.5–1.8 nm.\[2\] The value for $R_{TT}$ found in the simulations with energetic disorder is almost a factor of two higher, and even the value when neglecting disorder is slightly larger. In as far as the Förster process is concerned, a microscopic approach that is consistent with the results of analyses based on a more macroscopic and ensemble-averaged spectral overlap approach is thus still to be developed. Concerning the Dexter mechanism, we note that the value of $\lambda$ obtained is close to the value of 0.3 nm used for the electron, hole and exciton wavefunction decay lengths in recent studies for charge transport and efficiency roll-off simulations.\[10,20\] However, the value obtained for $k_{D,1}$ is an order of magnitude lower than the value typically assumed for electron and hole hopping rates in these studies. We note that, although for Ir(ppy)$_2$ in TCTA a similar concentration dependence of $k_{TT2}$ as for Ir(ppy)$_2$(acac) was found (Section S4,
Supporting Information), preliminary results obtained for various other Ir-based emitters reveal that the role of guest–guest diffusion is quite molecule-specific.

4.2. Weak Confinement–Host-Mediated Diffusion

We have used KMC simulations to explore the effects of host-mediated diffusion under the constraint that no guest–guest diffusion takes place (as in the experiments for 3.85 wt% systems presented in Section 3.2), for systems with a $c_g = 5$ mol% guest concentration. Additional simulations for 3 mol% systems (Section S10, Supporting Information) reveal that the sensitivity of the main simulation results to such a change of $c_g$ is only minor. Guest–guest TTA is described as a Förster process, with $R_{F,TT} = 3.5$ nm, the excitonic disorder energy is assumed to be $\sigma_T = 0.05$ eV, $\tau = 1$ µs, $T_0 = 10^{-24}$ m$^{-3}$, and $T = 300$ K. In the absence of more detailed information, guest–host, host–host, and host–guest exciton transfer are treated as a thermally activated Dexter process with the same (varying) value of $k_D$ and with $\lambda = 0.30$ nm, and possible guest–host and host–host TTA are described as an immediate nearest-neighbor process. Possible quenching or nonradiative decay processes on the host are not included.

Figure 7a shows the dependence of $k_{TT,2}$ on $k_{D,1}$ for values of $\Delta E_T$ in the range $-0.05$ eV to $+0.30$ eV. In Section S11 of the Supporting Information, the simulated relative PL efficiency from which $k_{TT,2}$ has been evaluated is given. The figure shows that there are two regimes: for weak host-mediated diffusion $k_{TT,2}$ is decreased, because part of the excitons reside on the host so that guest–guest TTA is reduced, whereas for strong host-mediated diffusion $k_{TT,2}$ is increased, because the fusing excitons create already within the radiative decay time $\tau$ new closely spaced excited guest molecules. In the $k_{D,1}$-range studied, a significant enhancement of $k_{TT,2}$ is only obtained for values of $\Delta E_T$ below 0.2 eV, consistent with the experimental results (Figure 4). The largest observed enhancement, by about a factor 4, would for the parameters assumed and taking $\Delta E_T = 0$ eV be expected to result from a value $k_{D,1} \approx 3 \times 10^7$ s$^{-1}$.

Figure 7b shows the enhancement of the PL lifetime ($\tau_{eff} = 1/2/\tau_{eff}$, i.e., as defined in Figure 5), as obtained from KMC simulations carried out in the zero-fluence limit (no TTA) for the same $k_{D,1}$ and $\Delta E_T$ range. For large $k_{D,1}$, the enhancement approaches the values given by Equation (4). For a given confinement energy, the enhancement is largest for intermediate values of $k_{D,1}$, for which the excitons diffuse on the host but quickly reach a guest at which radiative decay can take place. The figure shows that an enhancement by a factor 30–40, as obtained for systems with $\Delta E_T = 0$ eV (Figure 5), would be consistent with values of $k_{D,1}$ in almost the entire range considered. The figure thus suggests that measurements of the lifetime enhancement can be a sensitive probe of triplet confinement, but are a less sensitive probe of the detailed diffusion rates. Consistent with the experimental findings, the KMC simulations also show a significantly stretched decay, with average lifetimes that are a factor 4–6 larger than the (already enhanced) effective lifetime $\tau_{1/2}/\ln 2$ shown in Figure 7b for weakly confined systems ($\Delta E_T < 0.1$ eV) with $k_{D,1}$ around $3 \times 10^8$ s$^{-1}$ (see Section S12 in the Supporting Information). Giving a discussion of the detailed shape of the decay, which is not in all cases well-described by a stretched-exponential function, is beyond the scope of the paper.

In Section 3.3, the surprising observation of an increase of the effective PL lifetime with decreasing temperature, measured for TPBi:Flrpic and TPD:Ir(ppy)$_2$(acac) was attributed to decreasing diffusion on the host. The effect can outbalance the decrease of the thermally activated deconfinement rate. The results of KMC simulations are consistent with this view. The effect is found for quite weakly confined systems ($\Delta E_T < 0.1$ eV) for which the Dexter rate coefficient $k_{D,1}$ is relatively small, around and below $10^8$ s$^{-1}$. We note that also in Figure 7b the contours of equal lifetime enhancement become then dependent on $k_{D,1}$. An overview of the simulation data is given in Section S13 of the Supporting Information.

Interestingly, the system CBP:Flrpic shows a lifetime enhancement as expected for a system with $\Delta E_T$ close to 0 eV, but only a relatively small enhancement of $k_{TT,2}$ (by a factor
of about 2, see Figure 4). The relatively small TTA-induced loss could explain, at least in part, the finding of a fairly large external quantum efficiency (EQE) of OLEDs based on this system with endothermic host–guest transfer,[3] although a further increase of the EQE can be obtained from mCP:FIrpic based OLEDs with exothermic host–guest transfer.[2]

From Figure 7a, it would follow that the weak TTA-loss for CBP:FIrpic could be a result of weak host-mediated diffusion, with $k_{D,1}$ about one order of magnitude smaller than for TPD or NPB hosts. From density functional theory (DFT) calculations, it is known that for CBP and TPD the triplet wavefunction is localized on the central biphenyl part of the molecule,[3] whereas we find from DFT calculations that for NPB and α-NPD the triplet wavefunctions are localized on the more exterior parts of the molecules (Section S14, Supporting Information). Interestingly, these calculations also show a clear difference between the degree of localization of the triplet wavefunctions on the two latter molecules, which could be related to the significantly different values of $k_{T,T}$ for systems containing Ir(BT)$_3$(acac). It would be of interest to establish from a comparison with explicit molecular-scale exciton transfer calculations to what extent the experimental results presented in our work also provide a sensitive probe to exciton diffusion in host materials.

5. Summary and Conclusions

In this paper, we have used time-resolved photoluminescence experiments to disentangle the processes involved in triplet–triplet annihilation in phosphorescent host–guest systems based on a large number of host–guest combinations with varying host–guest triplet confinement energy $\Delta E_T$ and varying guest concentration. A significant enhancement of the TTA-rate coefficient is observed for systems with $\Delta E_T \leq 0.2$ eV, up to a factor of 4 in, e.g., TPD:Ir(ppy)$_3$. The enhancement is found to be a thermally activated process, as it decreases with decreasing temperature. For $\Delta E_T \leq 0.1$ eV, we also find a strong increase of the effective emissive lifetime, up to a factor of 30–40, and stretched-exponential instead of monoexponential decay, with some cases rather small stretching exponents. These effects are attributed to host-mediated diffusion in which the triplets escape from the guest and diffuse over the host, thereby effectively increasing the interaction radius of the triplets.

For the prototypically strongly confined system TCTA:Ir(ppy)$_3$(acac), a mechanistic microscopic description of the direct TTA process and the guest–guest diffusion contribution has been given using a recently proposed analysis method of the time-resolved emission, combined with the results of kinetic Monte Carlo simulations. The direct TTA process is well described by a Förster type process with $R_{F,T} = 3.5$ nm. Similar values are found for the four other Ir-based phosphorescent emitters studied. For this system, diffusion enhances the TTA-loss when the guest concentration $c_g > 6$ mol%. However, even for the highest guest concentration considered, $c_g = 18$ mol%, the strong-diffusion limit has not yet been reached. The effect of diffusion can be well described assuming either a Förster mechanism with $R_{F,diff} = 2.7$ nm, a value that is significantly larger than literature values as deduced from the overlap of emission and extinction spectra, or a Dexter mechanism with a wavefunction decay length $\lambda = 0.35$ nm and a hopping attempt rate to the first nearest neighbor $k_{D,1} = 1.4 \times 10^8$ s$^{-1}$. Refined studies will thus be required to elucidate the transfer mechanism.

Making use of the observed TTA-Förster radius, KMC simulations have been used to explore for systems with negligible direct guest–guest diffusion the dependence of the enhancement of the TTA rate and the emissive lifetime on $\Delta E_T$ and on the host–guest and host–host triplet transfer rates. The comparison with the experimental results suggests that the host–host hopping rates can be quite molecule-specific. When describing host-mediated transfer as a Dexter-type process with a wavefunction decay length $\lambda = 0.3$ nm, values of $k_{D,1}$ in the range $10^6$–$10^8$ s$^{-1}$ are obtained. Interestingly, these values are much smaller than the values obtained in Section 4.1 for Dexter-type host–guest–guest diffusion. In particular, for CBP as a host for FIrpic, the experiments suggest a quite small diffusion rate. We conclude that these experiments do not only sensitively probe the TTA-induced efficiency loss as a function of the exciton confinement energy, but potentially also the rate of host-mediated triplet diffusion.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors thank Heidi Thomas, Felix Fries, and Sebastian Reineke (Technische Universität Dresden) for making available measured PL spectra of NPB and α-NPD. This work was supported by the Horizon-2020 EU project MOSTPHOS (Project No. 646259, A.L., X.d.V., P.A.B., R.C.), and by the Dutch-German project MODEOLED, funded on the Dutch side by the Dutch Technology Foundation (STW, Project No. 12200, L.Z.), which is part of the Dutch Science Foundation (NWO).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

exciton confinement, exciton diffusion, kinetic Monte Carlo simulations, organic light-emitting diodes, triplet–triplet annihilation

Received: July 5, 2018
Revised: September 18, 2018
Published online: November 12, 2018
