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Single-layer method for quantifying the triplet exciton diffusion coefficient in disordered organic semiconductor materials

Arnout Ligthart a,b, Xander de Vries a, Peter A. Bobbert a,b, Reinder Coehoorn a,b

a Department of Applied Physics, P.O. Box 513, NL, 5600 MB, Eindhoven, The Netherlands
b Institute for Complex Molecular Systems, Eindhoven University of Technology, P.O. Box 513, NL, 5600 MB, Eindhoven, the Netherlands

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ABSTRACT

We propose an easy-to-use method for determining the triplet exciton diffusivity in disordered organic semiconductors using single-layer films containing a small concentration of Ir-cored guest molecules. The carefully selected guest molecules are used to create in a time-resolved photoluminescence (PL) experiment triplet excitons that are initially located on the guest molecules and that as a result of weak triplet confinement subsequently diffuse through the host material, thereby enhancing the PL efficiency loss resulting from triplet-triplet annihilation (TTA). The diffusion coefficient is obtained using a simple analytic model that takes all contributions to the enhanced TTA-rate into account. The model is validated using Kinetic Monte Carlo simulations. We demonstrate the method by application to four materials that are frequently used as a host in the emissive layer of organic light-emitting diodes. By combining these materials with chemically different emitter molecules, the consistency of the method is shown. The observed strong material dependence of the diffusion coefficient is explained qualitatively from the triplet exciton transition density distributions on the molecules studied that are obtained from Density Functional Theory calculations.

1. Introduction

In phosphorescent organic light emitting diodes (OLEDs) triplet exciton diffusion plays an important role in determining the shape of the emission zone ([11–23]) and the efficiency loss due to triplet-triplet annihilation (TTA) and triplet-polaron quenching (TPQ). TTA is the process of energy transfer from one triplet to another, after which the higher-exciton decays non-radiatively to the lowest triplet state. TPQ is the process of energy transfer from a triplet to a polaron (electron or hole), followed by thermal decay to the lowest-energy polaron state. As the likelihood of both processes depends in part on the encounter rate between the two interacting species, the TTA ([4–22]) and TPQ [9] rates increase with increasing exciton diffusion.

Commonly used methods for quantifying triplet exciton diffusion in organic semiconductors probe the diffusion length \( \bar{L} \) from the exciton transition density distribution on the molecules studied that are obtained from Density Functional Theory calculations.

\[ \bar{L} = \sqrt{D\tau} \]

Here, \( D \) is the exciton diffusion coefficient (diffusivity). An overview of the experimental methods used for obtaining \( \bar{L} \) and their relative degree of ease has recently been given by Mikhenko et al. [10]. The most direct method is a measurement of the size of the photoluminescent emission zone around a small region in a material in which the excitons are optically generated. This method is only suitable for materials with an exciton diffusion length in the order of micrometers, such as anthracene and tetracene single crystals ([11,12]). Secondly, one may use a phosphorescent OLED in which a thin layer of emissive phosphorescent dopants is placed a distance \( L \) from the exciton generation zone. The diffusion length is then derived from the emission intensity of the dopant layer as function of \( L \). However in this method special care needs to be taken to accurately describe the light outcoupling from the microcavity and the role of TTA and TPQ processes ([3,13–22]). A third and somewhat similar method is using a bilayer structure of a pure semiconductor layer within which the excitons are optically generated and a layer that is doped with phosphorescent sensing molecules. The exciton diffusion length can then be derived from the measured fluorescence and delayed phosphorescence, using a complex analysis method in which the TTA rate, the triplet transfer rate and the initial triplet density are taken into account ([4,19–22]). \( \bar{L} \) may also be determined using photocurrent [23] and microwave conductivity measurements, or by measuring the time-dependence of the absorption spectrum of triplet-excited materials [24–27]. As summarized in detail in Ref. [10], the experimental procedures that are involved in each of

* Corresponding author.
E-mail address: a.ligthart@tue.nl (A. Ligthart).
these methods present difficulties related to the ease of sample preparation, measurement or data analysis. As a result, the experimental values of $L_D$ as obtained using these various methods can vary multiple orders of magnitude. For the commonly used hole-transporting material CPB (4,4’-N,N’-dicarbazole-biphenyl), e.g., values in the range of 8.3–300 nm have been reported [13,15,19,20]. Furthermore, a measurement of $L_D$ does not directly provide the diffusion coefficient, which is a more fundamental quantity that is related to the intermolecular exciton transfer rate, as that would require knowing the exciton lifetime. For non-phosphorescent materials, accurately measuring the triplet exciton lifetime can be a challenge.

In this paper we propose a simple method for determining the triplet exciton diffusivity in amorphous organic semiconductors. Advantageously, only a single organic layer is required. We focus on fluorescent small-molecule materials, such as those that are used as host materials in the emissive layers of evaporation-deposited phosphorescent OLEDs. In order to be able to optically generate triplet excitons, a small concentration of iridium-cored phosphorescent guest molecules is added. These guest molecules are carefully selected, such that their triplet energy $E_{T,G}$ is only slightly smaller than the energy $E_{T,H}$ of triplets on the host material. In previous work [5], we have shown using transient photoluminescence (PL) measurements that for confinement energies $\Delta E_T \approx (E_{T,H} - E_{T,G})$ below 0.2 eV significant deconfinement occurs of the triplets from the guest molecules to the host material. This is evident from an increase of the effective triplet lifetime that is obtained from a transient PL measurement at a small laser fluence, and from an increase of the TTA rate coefficient that is obtained from transient PL measurements at a relatively large laser fluence. The TTA rate enhancement results from host-mediated exciton diffusion, which gives rise to enhanced Förster-type TTA due to interactions between two triplets on a phosphorescent dye molecule and to Dexter-type TTA between an exciton on the host material and a second exciton on a host or guest molecule. We deduce the diffusivity from a quantitative analysis of the lifetime and TTA rate enhancement, using a simple but accurate analytical model that is applicable in the limit of weak triplet confinement and relatively strong exciton diffusion.

Fig. 1 gives a schematic overview of the exciton diffusion and TTA processes in the four physical regimes that may be distinguished. Light absorption leads to singlet formation on the host. Due to Förster transfer to the guest molecules, followed by fast intersystem crossing to the triplet state, already very soon after time $t = 0$ all excitons reside as triplets on the guest molecules. The experimental details will be discussed in section 2. Subsequently, deconfinement to the host and diffusion via the host can take place. Our method is applicable in regime I. As a result of the weak exciton confinement and large diffusion coefficient, the time-averaged triplet exciton density on the host material is then essentially uniform. In the figure, one of the processes that gives rise to a TTA rate enhancement (exciton encounter on the host, process C) is highlighted. The other three mechanisms that contribute to the TTA efficiency loss, indicated by capital letters in the figure, are discussed in section 2.2. Measurements in regime IV (using guest molecules with a smaller triplet energy) are used as a reference. The general methodology presented in this paper would also be applicable to systems with weak host-mediated diffusion, so that the average diffusion distance of the deconfined excitons is small as compared to the average distance between the sites at which the excitons reside at $t = 0$ (regime II). However, the analysis should then employ numerical simulations using a Kinetic Monte Carlo (KMC) approach. In this work, we use KMC simulations as a means to validate the simple analytical method that is applicable in regime I.

We apply the method to four organic semiconductors that are often used in OLEDs:

- TPBi ($2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole)$),
- TPD ($N,N'-bis(3-methylphenyl)-N,N'-diphenylbenzidine$),
- $\alpha$-NPD ($N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)-2,2'-dimethylbenzidine$), and
- NPB ($N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine$).

The validity of the method is cross-checked by combining these materials with various Ir-cored guest molecules, so that in total 9 systems have been studied. Interestingly, Wu et al. have found a tendency towards longer triplet exciton diffusion lengths for naphtyl-based materials than for phenyl-based materials [19]. Our study indeed reveals a significantly larger triplet exciton diffusion coefficient for $\alpha$-NPD and NPB than for TPBi and TPD.

The paper is structured as follows. In section 2, we discuss the experimental method, the analytic model that is used to analyze the experimental results and the KMC simulations that are used to validate the model. In section 3, we give an overview of the experimental results and their analysis. Section 4 contains a discussion of the observed differences between the diffusivities for the four materials studied in terms of the triplet exciton density on each of the molecules as obtained from density functional theory calculations. Section 5 contains a summary, conclusions and outlook.

2. Experimental and analysis methods

2.1. Experimental approach

As a first step, we have carefully selected for each of the four materials studied one or more Ir-cored emitters with a slightly smaller triplet energy than that for the host material. We will show below that the triplet confinement energy should be in the range 0–0.2 eV, and preferably not larger than about 0.1 eV. TPBi is combined with
Overview of the measurement and analysis results. The second column gives the confinement energy $\Delta E_{\text{spec}}$ that follows from the spectroscopically determined peak energies of the triplet spectrum for the host, taken from the literature, and for the guest, measured for each of the host-guest systems studied in this work (see the first column of the table). The values in between the parentheses are the references values, as obtained for the emitter molecules in TCTA.

<table>
<thead>
<tr>
<th>System</th>
<th>$\Delta E_{\text{spec}}$ (eV)</th>
<th>$c_g$ (mol%)</th>
<th>$R_{\text{T,T,spec}}$ (nm)</th>
<th>$\tau_{\text{eff}}$ (μs)</th>
<th>$\beta$</th>
<th>$k_{\text{TT}}$ (10^{-18} m^3 s^{-1})</th>
<th>$\Delta E_{\text{f}}$ (eV)</th>
<th>$D_{\text{max}}$ (10^{-12} m^2 s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPBI, $E_2$ = 2.66 ± 0.02 eV</td>
<td>3.06 ± 0.02</td>
<td>3.46</td>
<td>3.4</td>
<td>6.94 (1.30)</td>
<td>0.41 (0.85)</td>
<td>1.5 (0.87)</td>
<td>0.05</td>
<td>19</td>
</tr>
<tr>
<td>Ir(pppy)$_3$, $E_2$ = 2.38 eV</td>
<td>3.06 ± 0.02</td>
<td>3.31</td>
<td>3.4</td>
<td>4.82 (1.05)</td>
<td>0.52 (0.89)</td>
<td>1.69 (0.80)</td>
<td>0.06</td>
<td>22</td>
</tr>
<tr>
<td>TPD, $E_2$ = 2.39 ± 0.08 eV</td>
<td>3.06 ± 0.02</td>
<td>3.31</td>
<td>3.4</td>
<td>3.3 (1.30)</td>
<td>0.37 (0.88)</td>
<td>4.2 (1.0)</td>
<td>0.01</td>
<td>12</td>
</tr>
<tr>
<td>Ir(pppy)$_3$, $E_2$ = 2.38 eV</td>
<td>3.06 ± 0.02</td>
<td>3.33</td>
<td>3.5</td>
<td>5.2 (1.37)</td>
<td>0.48 (0.95)</td>
<td>1.8 (0.65)</td>
<td>0.07</td>
<td>33</td>
</tr>
<tr>
<td>TEG, $E_2$ = 2.37 eV</td>
<td>2.02 ± 0.02</td>
<td>2.09</td>
<td>3.4</td>
<td>3.4 (1.05)</td>
<td>0.42 (0.88)</td>
<td>4.2 (2.1)</td>
<td>0.09</td>
<td>50</td>
</tr>
<tr>
<td>NPB, $E_2$ = 2.31 ± 0.06 eV</td>
<td>3.06 ± 0.02</td>
<td>3.21</td>
<td>3.4</td>
<td>1.47 (1.3)</td>
<td>0.82 (0.91)</td>
<td>3.64 (0.99)</td>
<td>0.15</td>
<td>730</td>
</tr>
<tr>
<td>Ir(BT)$_2$(acac), $E_2$ = 2.23 eV</td>
<td>0.08 ± 0.02</td>
<td>2.36</td>
<td>4.5</td>
<td>6.16 (9.3)</td>
<td>0.96 (0.92)</td>
<td>0.67 (0.17)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>α-NPD, $E_2$ = 2.23 ± 0.06 eV</td>
<td>0.08 ± 0.02</td>
<td>3.35</td>
<td>4</td>
<td>1.38 (1.3)</td>
<td>0.77 (0.91)</td>
<td>1.7 (0.99)</td>
<td>0.17</td>
<td>480</td>
</tr>
</tbody>
</table>

2.2. Analytic model

Here we present a simple model to describe the TTA and the lifetime enhancement as a function of the triplet confinement energy and the diffusivity, which are applicable in the strong diffusion limit. When assuming for simplicity equal host and guest exciton disorder energies, the lifetime enhancement is from Ref. [5] given by

$$I(t) = I(0) \exp \left[ -\frac{t}{\tau_{\text{eff}}} \right],$$

with $\tau^*$ the 1/e lifetime and $\beta$ an stretching exponent that is equal to unity for the case of strong confinement and decreases with decreasing confinement energy. The effective lifetime that we use in this study is defined as $\tau_{\text{eff}} \equiv (f_t/2\ln(2))$, with $f_t$ the time at which the emission intensity has decreased to $I(0)/2$.

The delayed emission decay is measured using a correlated single-photon counting setup (CSPC), using a 400 nm excitation pulse with a 5 ns width and a measurement window of 25 μs in the low fluence regime (initial triplet volume density $N_0 < 10^{14}$ m⁻³).
We therefore express each of the four terms in Eq. (3). In the next section, we validate this approach for each of the material systems studied using the results of KMC simulations.

For large confinement energies, when almost all excitons are located on guest molecules, the first term in Eq. (3) is the dominant contribution. The interaction between two triplets on a guest molecule is described as a Förster process with a Förster radius \( R_{\text{F},TT} \). The rate coefficient in the no-diffusion limit and for the small initial triplet densities \( T_0 \) used in this study is from Ref. [33] to an excellent approximation given by

\[
k_{\text{TT},\text{nl}} \approx \frac{4\pi^2}{3} \left( \frac{R_{\text{F},TT}^3}{T_0} \right)
\]

where \( \tau_{\text{eff},0} \) is the triplet lifetime in the case of excellent triplet confinement. The effective rate coefficient given by Eq. (4) takes into account that in the absence of exciton diffusion the decrease of the TTA rate with time is not only due to the decrease of the overall triplet density, but also to the development of a spatially correlated distribution of the remaining (non-annihilated) excitons. The average distance to the first nearest neighbour is larger than would be expected for the case of a spatially random distribution [33].

The second term in Eq. (3) describes the enhancement of the TTA rate between excitons on the guest molecules due to triplet diffusion via the host. As a result of this diffusion process, the distribution of triplets over the guest molecules remains more spatially random, leading to an enhanced time-integrated loss due to TTA. In Ref. [33], a somewhat similar situation was studied, viz. exciton diffusion due to Förster-type transfer between the guest molecules. This was to a good approximation found to give rise to a guest-diffusion contribution \( k_{\text{TT},\text{gd}} \) to the TTA rate that could be described using a capture radius formalism: \( k_{\text{TT},\text{gd}} \approx 8\pi (R_{\text{F},TT} - R_0)D \), with \( D \) the effective diffusion coefficient and \( R_0 \) an empirical cutoff value of \( R_0 \approx 1.8 \text{ nm} \). In the case of host-mediated diffusion, two modifications to this expression are expected:

(i) When taking \( D \) equal to the diffusion coefficient for triplets on the host, \( D \), a reduction factor equal to the probability \( P_{\text{host}} = (1 - P_{\text{guest}}) \) must be included,

(ii) The reduced triplet density on the guest molecules reduces the TTA rate by a factor \( P_{\text{guest}}^2 \). On the other hand, it enhances the radiative decay time by a factor \( 1/P_{\text{guest}} \). This enhances the time-integrated loss due to TTA, and hence the rate coefficient. The net effect on the rate coefficient is a factor \( P_{\text{guest}} \).

We therefore express \( k_{\text{TT},\text{gd}} \) as

\[
k_{\text{TT},\text{gd}} = P_{\text{host}} P_{\text{guest}}^2 8\pi R_{\text{gd}} D = \frac{8\pi (R_{\text{F},TT} - R_0)D}{2 + \frac{1}{\gamma} \exp \left( \frac{-\Delta E}{k_B T} \right) + \frac{1}{\gamma} \exp \left( -\frac{\Delta E}{k_B T} \right)}.
\]

We will also describe the contribution to the TTA loss due to triplet encounter processes on the host using the capture radius formalism. The rate coefficient must now be proportional to the square of the triplet density on the host, i.e. to \( P_{\text{host}}^2 \), and (due to the enhanced radiative decay time, see above) to a factor \( 1/P_{\text{guest}} \). The overall expression is therefore

\[
k_{\text{TT},\text{hh}} = P_{\text{host}}^2 P_{\text{guest}}^2 8\pi R_{\text{hh}} D = \frac{1 + \frac{1}{\gamma} \exp \left( \frac{-\Delta E}{k_B T} \right)}{2 + \frac{1}{\gamma} \exp \left( \frac{-\Delta E}{k_B T} \right)} \times 8\pi R_{\text{hh}} D,
\]

with \( R_{\text{hh}} \) the capture radius for this process.

Finally, the capture radius formalism is used to obtain a description of the TTA loss due to the interaction between diffusing excitons on the host and fixed excitons on the guest molecules. The rate coefficient is proportional to the triplet concentration on the host, and therefore to \( P_{\text{host}} \). However, it does not depend on \( P_{\text{guest}} \), as the increase of the rate coefficient (by a factor \( 1/P_{\text{guest}} \)) due to the longer effective triplet lifetime is cancelled by the decrease due to the proportionality of the rate with the guest concentration (factor \( P_{\text{guest}} \)). The resulting expression for \( k_{\text{TT},\text{hh}} \) is therefore

\[
k_{\text{TT},\text{hh}} = P_{\text{host}} 4\pi R_{\text{hh}} D = \frac{4\pi R_{\text{hh}} D}{1 + \frac{1}{\gamma} \exp \left( \frac{-\Delta E}{k_B T} \right)}
\]

with \( R_{\text{hh}} \) the capture radius for this process. The proportionality factor \( 4\pi \) is a factor 2 smaller than in the expressions for \( k_{\text{TT},\text{gd}} \) and \( k_{\text{TT},\text{lh}} \), as now one of the excitons that is involved in the TTA process does not diffuse.

### 2.4. Kinetic Monte Carlo simulations

In order to validate the analytic model that has been proposed in the previous subsection and to deduce the values of the capture radii \( R_{\text{cc,hh}} \) and \( R_{\text{cc,hg}} \), we have performed KMC simulations using the simulation tool Bumblebee [34]. In the KMC simulations the TTA process is assumed to be a Förster process with a Förster radius \( R_{\text{F},TT} \) that is derived from TTA measurements of the emitter in the well confining host material TCTA, with a triplet energy \( E_T = 2.84 \text{ eV} \) ([35–37]). The experimental values are contained in Table 1. The table gives in between parentheses also the effective radiative lifetime \( \tau_{\text{eff},0} \), which is taken equal to the measured effective lifetime in TCTA. The exciton lifetime on the host is assumed to be infinite.

Within the simulations, the molecules are taken to be randomly distributed on a cubic lattice with an intersite distance \( a_0 = 1 \text{ nm} \). In refs 5 and 27, we have shown that triplet exciton guest-host diffusion starts playing a role when using a guest concentration larger than 5 mol%. As the guest concentrations used in this work are below 5 mol% (see Table 1), we therefore assume that there is no guest-guest diffusion. An excitonic Gaussian disorder energy (standard deviation) of \( \sigma_T = 40 \text{ meV} \) is assumed for all materials. Host-mediated exciton diffusion is assumed to be due to thermally activated Dexter-type processes, characterized by a wavefunction decay length \( \lambda = 0.3 \text{ nm} \), by a transfer rate \( k_{\text{DD}} \) between nearest-neighbour molecules with equal triplet energies, and by a Miller-Abrahams type dependence of the rate on the difference \( \Delta E = (E_T - E_l) \) between the final and initial state triplet exciton energies. The distance \( R \) and \( \Delta E \) dependence of the transfer rate is thus given by

\[
k_{\text{DD}} = k_{\text{DD}0} \exp \left( -\frac{2(R - a_0)}{\lambda} \right) \exp \left( -\frac{\Delta E}{2k_BT} - \frac{\Delta E}{2\sigma_T^2} \right).
\]

For simplicity, the rate is assumed to be identical for host-host and host-guest transfer.

For the materials studied in this work, \( D \) may be expressed as

\[
D = a_R^2 \alpha \gamma D_{\text{D}0}.
\]

Here \( \alpha \) and \( \gamma \) are an enhancement factor due to Dexter transfer to more remote neighbours and a reduction factor due to excitonic disorder, respectively. In the absence of excitonic disorder and for the case of transfer to only nearest neighbour sites, both factors are equal to unity. For the materials studied in this work, with \( \lambda / a_0 = 0.3 \) and \( \sigma_T = 0.04 \text{ eV} \), it follows from KMC simulations that \( \alpha = 1.295 \) (see the Supporting Information section 3 IV in Ref. [31]) and \( \gamma = 0.239 \). Table SI of the Supporting Information gives the dependence of \( \gamma \) on the disorder energy. Within the KMC simulations, we describe TTA due to the encounter of two triplet excitons on host molecules and due to the encounter of a triplet on a host molecule and a triplet on a guest molecule as a Dexter-type process with the same rate as Dexter-type diffusion. As both processes are described in an equal manner, the corresponding capture radii \( R_{\text{cd,hh}} \) and \( R_{\text{cd,hg}} \) are expected to be equal. In order to obtain the capture radius, we have carried out KMC simulations within which only these two processes are included. As may be seen in Fig. S2 of the Supporting
Information, the capture radius is only weakly dependent on the Dexter prefactor $k_\text{p,1}$ (and hence on the diffusivity), and is found to be in range of 0.6–0.7 nm. The finding of such a small value of the capture radius, of the order of the intersite distance, is consistent with the very short range of the Dexter-type TTA process that is assumed. When applying the analytic model, we will use a fixed value $R_{c,hb} = R_{c,hg} = 0.65\text{ nm}$. This will be shown to provide excellent descriptions of the full KMC simulation results.

3. Results

In this section, we demonstrate for the four selected organic semiconductors the method introduced in this work for determining the triplet exciton diffusivity. The experimental and analysis results are summarized in Table 1. For all but two of the host-guest systems studied, the tabulated data show a clear increase of the effective lifetime $\tau_{\text{eff}}$ and $k_{\text{T,T}}$ with respect to the values (in between parentheses) obtained for the case of strong exciton confinement. Qualitatively, it is then already evident that host-mediated diffusion plays a significant role in all systems. The deviating response that is found for the systems containing Ir(nppy)$_2$(acac) will be discussed in the last paragraph of this section.

As a first step, we calculate for each system the dependence of $\tau_{\text{eff}}/\tau_{0,\text{D}}$ and $k_{\text{T,T}}$ on $D$ and $\Delta_{\text{T}}$, using the analytic model (Eqs (2) and (3)) and using KMC simulations. Although a nominal value of $\Delta_{\text{T}}$ is known from the triplet emission spectra ($\Delta_{\text{T,spec}}$, see Table 1), we thus treat $\Delta_{\text{T}}$ as a free parameter, to be determined from the analysis. We note that the values of triplet energies, reported in the literature, are typically obtained from measurements for neat films. As a result, the emission energy can be somewhat smaller than the value for isolated molecules, embedded in an inert matrix. Such an effect has indeed been seen for TPD, where the energy difference is approximately 0.04 eV [38]. Studies of triplet energies on isolated NPB [30] show a similar blueshift as compared to neat-film results [28]. Other contributions to the uncertainty intervals given in Table 1 are related to differences of the measurement temperature, the thin-film preparation technique, and the uncertainty in the (0-0) peak location deduced from the spectra. Considering $\Delta_{\text{T}}$ as a free parameter provides a consistence check, and allows including small deviations that might arise from complexities in the emission spectra. The only system-specific parameters that are needed to obtain the predictions are $R_{\text{p,T,T}}$ and $C_T$. As motivated in Sec. 2, the cut-off radius $R_0$ that enters Eq. (5) is taken equal to 1.8 nm and the capture radii $R_{c,hb}$ and $R_{c,hg}$ that enter Eqs. (6) and (7) are taken equal to 0.65 nm. The KMC simulations are carried out using a Dexter transfer rate as given by Eq. (8), with a value of $k_{\text{D,1}}$ that follows from $D$ using Eq. (9).

In Fig. 2, we show for seven systems contour plots of $k_{\text{T,T}}$ (upper graphs) and the lifetime enhancement (lower graphs) as a function of the excitation diffusivity and the exciton confinement energy, as obtained from the analytic model (blue curves) and from the KMC simulations (black curves). The figure shows that the simple analytic model is able to well reproduce the results of the KMC simulations of $k_{\text{T,T}}$. The discrepancy is largest for smaller values of $k_{\text{T,T}}$, i.e. for relatively strong confinement or for weak diffusion. We ascribe that to numerical uncertainties. The figure also shows that Eq. (2) somewhat underestimates the lifetime enhancement. Using the analytical model instead of the KMC simulations would lead to a slight underestimation of the diffusion coefficient. We ascribe that to numerical uncertainties. The figure also shows that Eq. (2) somewhat underestimates the lifetime enhancement. Using the analytical model instead of the KMC simulations would lead to a slight underestimation of the diffusion coefficient. We ascribe that to numerical uncertainties. The figure also shows that Eq. (2) somewhat underestimates the lifetime enhancement. Using the analytical model instead of the KMC simulations would lead to a slight underestimation of the diffusion coefficient. We ascribe that to numerical uncertainties.

In each graph in Fig. 2 a vertical red-dashed line connects the points in the upper and lower graphs for which the KMC simulation results (black curves) can simultaneously explain the measured value of $k_{\text{T,T}}$ and the lifetime enhancement. For TFBi with Ir(ppy)$_3$ and Ir(Fppy)$_3$ the analysis yields $D = 19 \times 10^{-12}\text{ m}^2\text{s}^{-1}$ and $22 \times 10^{-12}\text{ m}^2\text{s}^{-1}$, respectively, and confinement energies $\Delta_{\text{T}} = 0.05\text{ eV}$ and $0.06\text{ eV}$, respectively. The near-equality of the two values of $D$ and the excellent agreement of the values of $\Delta_{\text{T}}$ with the spectral values from the literature (see Table 1) provide strong support for the consistency of the method.

For all three systems containing TPD we find that $\Delta_{\text{T}}$ is within the confidence interval that is derived using the typical value of the TPD triplet energy found in the literature; see Table 1. The diffusivity is found to vary from $12 \times 10^{-12}\text{ m}^2\text{s}^{-1}$ to $52 \times 10^{-12}\text{ m}^2\text{s}^{-1}$. This system-dependence is possibly related to the relatively low glass temperature of TPD (333 K [39,40]), in comparison to that of TPBi (395 K [41]), which might lead to a morphology that differs for the different host-guest materials, thereby affecting the diffusivity. Ráfol-Ribé et al. [41] showed that evaporating materials on a substrate with a temperature close to their glass temperature can have a large impact on the formed morphology.

For α-NPD and NPB, Fig. 2 shows that studies with Ir(BT)$_2$(acac) lead to values of $D$ that are one order of magnitude larger than for TPBi and TPD, viz. $4.8 \times 10^{-10}\text{ m}^2\text{s}^{-1}$ and $7.3 \times 10^{-10}\text{ m}^2\text{s}^{-1}$ respectively. In section 4, we further discuss this finding, making use of a comparison of the triplet exciton wavefunctions on these molecules. The triplet exciton confinement energy for α-NPD and NPB was found to be 0.15 eV and 0.17 eV, respectively, which is just outside the confidence interval $0.08 \pm 0.06\text{ eV}$ (see Table 1). A possible explanation for this finding would be the presence of triplet quenchers, as observed for NPB by Redondo et al. [42]. However, we find that the relative PL yields obtained from Ir(BT)$_2$(acac) embedded in TCTA, CBP, TPD (no host-mediated diffusion), and α-NPD and NPB (strong host-mediated diffusion) are all essentially equal. This indicates that triplet quenching in α-NPD and NPB is insignificant. We cannot exclude that such a process would occur in other cases as well. We have therefore determined the sensitivity of the analysis to quenchers using additional KMC simulations. The results, which are given in Fig. S3 of the Supporting Information, show that already when 0.1 mol% of randomly dispersed quenchers would be present, a significant further enhancement of $k_{\text{T,T}}$ and a significant reduction of the effective lifetime are obtained. In view of this sensitivity, we thus conclude that when using the analysis method for determining the diffusion coefficient, introduced in this paper, it is important to investigate the possible effect of quenchers by measuring the PL yield, relative to that in selected reference films.

In order to investigate the consistency of the results for α-NPD and NPB, we extended our study to systems containing Ir(nppy)$_2$(acac), for which the triplet energy is almost identical to that of Ir(BT)$_2$(acac). We note that the emissive lifetime for this emitter is relatively long (around 9 μs) and that the TTA rate coefficient in the absence of host-mediated diffusion ($k_{\text{T,T,red}}$, Eq. (4)) is quite small. Surprisingly, we find that for these systems the shape of the PL spectrum is quite different than observed for emission from Ir(nppy)$_2$(acac) in three host materials (TCTA, mCP and TPD) with a larger triplet energy than α-NPD and NPB, and that the peak in the PL spectrum is slightly red-shifted. Fig. 3 gives an overview of the measured spectra. For Ir(BT)$_2$(acac) such a strong dependence of the spectrum on the host material was not observed (see Fig. S4 in the Supporting Information). The emission spectra from Ir(nppy)$_2$(acac) in TCTA and α-NPD do not reveal a significant temperature dependence (see Fig. S5 of the Supporting Information). This indicates that the red-shift is not due to relaxation effects. Furthermore, we find for Ir(nppy)$_2$(acac) in α-NPD and NPB a decrease of the emissive lifetime, instead of the expected increase due to host-mediated diffusion, and almost no stretching ($\beta$ close to unity, see Table 1). A first possible explanation for these observation would be the occurrence of emitter aggregation. For host-guest systems containing Ir(nppy)$_2$(acac) in neat materials aggregation has indeed been observed. The effect can result in a red shift of the PL spectra and a decrease in lifetime, and is known to depend on the type of host material [43,44]. However, so far the effect has been observed only at large emitter concentrations (> 10 mol %), whereas in our films a guest concentration smaller than 4 mol% was used. This makes the occurrence of guest-guest aggregation less likely. We therefore presently regard aggregate formation between Ir(nppy)$_2$(acac) and α-NPD and NPB as a more likely explanation. In such a case, the method
Fig. 2. Contour plots of dependence of $k_{TT}$ (in units $10^{-18}$ m$^3$/s, upper graphs) and the effective lifetime enhancement $\tau_{\text{eff}}/\tau_{\text{eff,0}}$ as a function of the diffusivity and the triplet exciton confinement energy, for host-guest systems based on TPBi, TPD, $\alpha$-NPD and NPB. The black and blue curves are obtained from KMC simulations and the analytical model presented in section 2.B, respectively. The vertical red-dashed lines connect the points at which the KMC simulation results for the TTA rate coefficient and the lifetime enhancement are both consistent with the experimental result. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
that has been presented in this work is not applicable.

4. Discussion

4.1. Exciton transition density distribution

We have found that the triplet diffusivity on α-NPD and NPB is approximately one order of magnitude larger than on TPBi and TPD. Following Wu et al. [18], who were the first to relate the triplet exciton diffusion length in organic semiconductors to the distribution of the triplet exciton density on the molecule, we investigated these distributions for TPBi, TPD, α-NPD and NPB using Density Functional Theory (DFT) calculations. As a first step, the geometries of the molecules were optimized in their ground state with DFT calculations employing the B3LYP functional with a 6–31 g basis set. The triplet exciton transition density distribution was generated using time-dependent DFT (TD-DFT), with the same basis set and functional as in the DFT calculations. All calculations were performed with the ORCA package [50].

Fig. 4 shows the transition density distributions on the four host molecules. For TPBi and TPD, the materials with a smaller diffusivity, the triplet density is mainly located in the central part of the molecule. In contrast, for NPB and α-NPD the triplet density is located more predominantly at the exterior part of the molecules. As the intermolecular wavefunction overlap (and hence the intermolecular transfer rate) is most likely smaller when the exciton is located in the central part of the molecules than when it is located at the exterior parts, these differences can explain the observed differences in the diffusivity. Furthermore, we see that on NPB the triplet density is more delocalized than on α-NPD, in which the density is solely localized on one naphtyl group due to the significant torsion angle between the methylbenzidine groups in the central part of the molecule. That may explain the finding of an approximately 50% larger diffusivity in NPB than in α-NPD.

4.2. Application to co-host systems

The proposed method can also be used to determine the triplet exciton diffusion coefficient in materials consisting of two randomly mixed organic semiconductors. That can be of interest when studying so-called “mixed-matrix” OLEDs in which the emissive layer consists of a guest and two host molecules. Usually, the two components in such a co-host system fulfill complementary roles, as the electron and hole conductive material. By varying their concentration ratio, the electron-hole mobility balance in the emissive layer can be tuned, and thereby the shape of the emission profile [9]. When one of the two materials the triplet energy is very high, so that triplet diffusion almost entirely occurs via the second material, the triplet diffusion coefficient will decrease with increasing concentration of the first material. An example would be a mixture of TPBi and TPD, studied by adding a small concentration of Ir (ppy)₃. The triplet excitons diffuse then almost only via the TPD molecules, as the triplet energy of TPBi is more than 0.2 eV larger. We find from KMC simulations that for such a system containing an inactive (high triplet energy) host, the value of $k_{TT}$ may also be obtained from the analytic model given in section 2.8, after taking into account that the dilution (i) decreases the probability $P_{host}$ that an exciton resides on a host molecule, (ii) gives rise to a decrease of the diffusion coefficient, and (iii) gives rise to a decrease of the TTA capture radii $R_{T,h}$ and $R_{T,pp}$. Each of these three factors thus gives rise to a decrease of $k_{TT}$ with increasing dilution. $P_{host}$ follows from the right-hand side of Eq. (2), when replacing $q_h$ by the mole percentage of active (low triplet energy) host molecules. In Table SII of the Supporting Information the dilution dependence of the diffusion coefficient and the capture radius, as determined from KMC simulations, are given. The decrease of the capture radius, taken equal for host-host and host-guest TTA, may be viewed as a result of the “protective” effect with respect to TTA that inactive host molecules offer to nearby excitons. Experimental validation of this model of the effect of host-dilution is beyond the scope of this paper.

5. Summary and conclusion

In summary, we have proposed a method for determining the triplet exciton diffusivity in disordered organic semiconductors using single-layer films of these materials containing a small concentration of Ir-cored guest molecules. The method involves a comparison of the TTA rate and the emissive PL lifetime for systems containing guest molecules on which the triplet excitons are well-confined and for systems containing guest molecules from which easy deconfinement to the host takes place so that host-mediated triplet exciton diffusion enhances the TTA rate and the effective lifetime. The diffusivity is determined from an analysis of the experimental data using a simple analytic model (Eqs (2)–(7)) that has been validated using KMC simulations.

The method is most suitable for material systems with a confinement energy $(E_{T,h} - E_{T,g})$ in the range of $0.0 - 0.1$ eV, as the method depends on a significant enhancement of the TTA rate and the effective lifetime. The application of the method thus requires a careful selection of the guest molecule. Fortunately, Ir-cored guest molecules with emission energies across the entire visible range, in the near UV and in the near IR range are available. A basic requirement is that the interaction between the excitonic state on the guest and the neighbouring host molecules is relatively weak, leading e.g. to PL emission spectra from the guest molecules that are independent of the host material. For two systems (Ir (ppy)₃(acac) in an NPB or α-NPD host material) this requirement was found not to be met, most likely due to host-guest aggregate formation.

We have determined the diffusivity for four organic semiconductors.

Fig. 3. Normalized steady-state PL spectra for 3.85 wt% Ir(npy)₃(acac) in five different host materials: mCP, TCTA, TPD, α-NPD and NPB. The small peak at 430 nm may be attributed to host fluorescence.

Fig. 4. Results of TD-DFT calculations of the transition density distribution for the four host molecules TPBi, TPD, NPB and α-NPD.
For TPBI and TPD the exciton diffusion coefficient is in the range $(12–52) \times 10^{-12}$ $m^2/s$, while for α-NPD and NPB the diffusion coefficient is found to be one order of magnitude larger. We relate this disparity to the different locations of the triplet exciton density on the molecules: for TPD and TPBI the triplet density is mainly located on the central part of the molecule, whereas for α-NPD and NPB it is located on the exterior parts. When the exciton is located on the exterior parts, intermolecular wavefunction overlap is more likely stronger, resulting in a larger intermolecular transfer rate and a larger exciton diffusion coefficient. The intermolecular nearest-neighbour transfer rates, $k_{0,1}$, follow from the diffusion coefficient using Eq. (9). For the materials studied in this work, we find that $k_{0,1}$ ranges from about $3 \times 10^{-11}$ s$^{-1}$ (in TPD, from experiments with Ir(ppy)$_3$) to about $2.2 \times 10^{-9}$ s$^{-1}$ (in NPB, from experiments with Ir(PT(acac))$_2$). We expect that these results will provide a valuable experimental benchmark for future first principles simulations of the intermolecular transfer rate in organic semiconductors, and that their use will enable obtaining more precise predictions of the performance of organic optoelectronic devices such as OLEDs using KMC simulations.

Declaration of competing interest

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

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Appendix A. Supplementary data

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