Research paper

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

L. Zhang [a], H. van Eersel [b], P.A. Bobbert [a], R. Coehoorn [a,*]

[a] Department of Applied Physics and Institute for Complex Molecular Systems, Eindhoven University of Technology, P.O. Box 513, NL-5600 MB Eindhoven, The Netherlands
[b] Simbeyond B.V., P.O. Box 513, NL-5600 MB Eindhoven, The Netherlands

ABSTRACT

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

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1. Introduction

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

In recent studies, the effective TTA rate in host–guest systems as used in phosphorescent OLEDs is described as being controlled either by the rate of direct long-range Förster-type triplet–triplet interactions [11–13], or by the rate of a more indirect process of

exciton diffusion followed by a relatively short-range capture step [14–16]. The relative role of both processes is a subject of current debate [11–18]. The diffusion-controlled picture is consistent with the conventional phenomenological description of TTA as a bimolecular process which modifies the time dependence of the triplet volume density, $T(t)$, in a manner as described by the last term in the expression

$$\frac{dT}{dt} = G - \frac{T}{\tau} - fk_{TT}T^2, \qquad (1)$$

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

$$\frac{I(t)}{I(0)} = \frac{1}{(1 + fT_0 k_{TT}\tau)\exp(t/\tau) - fT_0 k_{TT}\tau}. \qquad (2)$$

Time-dependent PL experiments would then yield the quantity fk_{TT}, which may be employed to obtain the exciton loss due to TTA under any operational condition, and hence, e.g. the IQE roll-off due to TTA [1]. However, this often-used approach is not always valid. In host–guest systems as used in OLEDs, the role of triplet diffusion decreases with decreasing dye concentration. In practical systms, the dye concentration is limited to values typically less than 15 mol% in order to limit concentration quenching [19,20]. From

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* Corresponding author.
  E-mail address: r.coehoorn@tue.nl (R. Coehoorn).

kinetic Monte Carlo (kMC) simulations, it has been shown that when the direct process becomes dominant, Eq. (2) no longer properly describes the time-dependent PL response, showing a faster-than-expected initial drop [18]. The physical explanation is that for weak or no diffusion TTA processes quickly deplete the density of nearby excitons around the "surviving" excitons. The resulting non-uniform distribution of pair distances gives rise to a slowing-down of the TTA rate in the later stage of the process. The validity of Eq. (2) may be probed by deducing from the transient PL data (i) the time at which half of the total emission has occurred and (ii) the total exciton loss [18]. The values of k_{TT} which would follow from such analyses, $k_{TT,1}$ and $k_{TT,2}$, respectively, are expected to be equal when Eq. (2) is valid, i.e. when TTA is a diffusion controlled multiple step process. However, when the direct process prevails, the ratio

$$r \equiv \frac{k_{TT,2}}{k_{TT,1}} \tag{3}$$

is much larger than 1. In that case, $k_{TT,1}$ and $k_{TT,2}$ should be viewed as auxiliary parameters only. A full description of the TTA process requires then a microscopic theory, in which exciton diffusion in the disordered material is included as well as the Förster-type triplet–triplet interaction. The description of the time-dependence of the photoluminescence, obtained from such a theory, should be consistent with the values of $k_{TT,1}$ and $k_{TT,2}$ obtained. Within such a microcopic theory, the TTA process is no longer described using a phenomenological coefficient k_{TT}, but using microscopic interaction parameters describing the distance dependent exciton transfer rates (leading to diffusion) and the distance dependent triplet–triplet interaction rates (leading to TTA). Advantageously, an analysis along these lines can already be applied to a single sample with one doping concentration, not requiring a series of samples with different doping concentrations. We note that the ability to disentangle the relative contributions of the direct and indirect contributions to TTA would also be important in other types of systems, e.g. fluorescent OLEDs with an enhanced efficiency due to TTA-induced delayed fluorescence as well as photovoltaic devices [21–23].

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

2. Experimental results

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

Typical transient PL decay curves and the corresponding integrated cumulative PL yield curves obtained for increasing initial triplet densities T_0 are shown in Figs. 2(a) and (b), respectively. It may be seen that for the cumulative PL curves the noise level is greatly suppressed, especially at long delay times. This will be exploited when extracting the rate coefficient $k_{TT,1}$ as discussed below. For sufficiently small T_0 ($< 0.5 \times 10^{24}$ m^{-3}), the transient PL curves exhibit to an excellent approximation a monoexponential decay from which the triplet lifetime τ can be estimated. Obtaining τ with good accuracy is found in this study to be key to analyzing the TTA process in terms of the two possible mechanisms. From more than 40 transient PL curves measured at low T_0, an average lifetime $\tau_{av} = 1.39 \pm 0.04$ μs is obtained. This value is within the range of values reported in the literature (1.22–1.56 μs [15,31,32]).
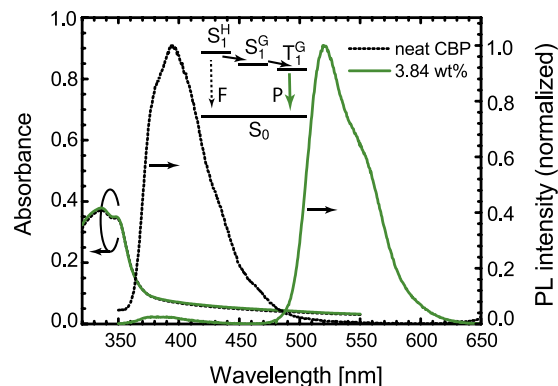

Fig. 1. Absorbance spectra and normalized PL intensity spectra (excitation at 337 nm; normalization to the PL peak intensity) of a neat CBP film and a CBP:3.9 wt % Ir(ppy)$_2$(acac) film (thickness 50 nm, on quartz). The absorbance spectra of the two samples are almost identical. In the inset, the energy transfer diagram is given. The arrows in the inset indicate the very weak fluorescent (F) emission from host (H) singlets (dashed), the main exciton transfer processes and the phosphorescent (P) decay process from the guest (G) triplets (full).