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Lifetime of triplet excitons in organic LEDs based on thermally activated delayed fluorescence

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Organic light-emitting diodes (OLEDs) based on thermally activated delayed fluorescence (TADF) are currently limited by their operational stability and a decreased efficiency at high brightness, both of which are strongly related to the interactions between triplet excitons and other quasiparticles. Here, an expression for the lifetime of triplet excitons in TADF OLEDs is derived, which correlates with the efficiency roll-off. The triplet lifetime in a TADF OLED intriguingly can be well approximated by the delayed-fluorescence lifetime of the TADF emitter, enabling facile quantification of the triplet population in a working OLED for investigating triplet-related loss processes, such as the efficiency roll-off and degradation.

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Thermally activated delayed fluorescence (TADF) is currently among the most promising routes for harvesting triplet excitons in organic light-emitting diodes (OLEDs) [1]. In contrast to phosphorescent emitters, no heavy metals are required. However, despite the achievement of very high external quantum efficiencies in TADF OLEDs, two major issues remain, which are the operational stability [2,3] and the efficiency roll-off [4]. The efficiency roll-off quantifies the decrease of the charge-to-photon efficiency at high brightness. While the exact origins of the stability and efficiency roll-off may vary, it is established that fundamentally, the annihilation effects between triplet excitons and other quasiparticles, such as other triplet excitons, polarons, and singlet excitons play a major role [2,4]. In TADF emitters, a continuous cycling between singlet and triplet excited states occurs [5], resulting from (reverse) intersystem crossing processes, complicating the assessment of the steady-state triplet population in an OLED. Therefore, it was recently proposed that the efficiency roll-off in TADF OLEDs could be linked to a figure of merit that considers the radiative decay rate and the dynamic equilibrium between singlet and triplet excitons [4]. This result was put in contrast with phosphorescent OLEDs, in which the triplet lifetime is easily determined from a transient photoluminescence (PL) measurement. Considering that triplets are both heavily involved in the operational stability and the efficiency roll-off, it is crucial to know how the triplet lifetime is related to the TADF rate constants and how it can be assessed experimentally.

Here, an expression of the triplet-exciton lifetime in TADF OLEDs is formulated. The triplet lifetime enables direct quantification of the steady-state triplet population and is the driving force behind the efficiency roll-off. Additionally, it is derived that the triplet lifetime in an OLED—to a very good approximation—intriguingly corresponds to the delayed-fluorescence lifetime of the TADF emitter, such that the triplet concentration in an OLED directly follows from a simple PL experiment, drawing a striking parallel between phosphorescent and TADF OLEDs and providing easy access to the key determinant of the efficiency roll-off and degradation.

As the efficiency roll-off and the operational stability of TADF OLEDs are related to interactions between triplet excitons and other quasiparticles, it is useful to consider the triplet population in an operational OLED. The electrically generated triplet density $[T_1]$ in a TADF OLED in steady state for an exciton-generation rate G per unit volume per unit time reads [4]

$$[T_1] = \frac{3\left(k_{\mathrm{r}}^S + k_{\mathrm{nr}}^S\right) + 4k_{\mathrm{ISC}}}{4k^S\left(k_{\mathrm{r}}^T + k_{\mathrm{nr}}^T\right) + 4k_{\mathrm{RISC}}\left(k_{\mathrm{r}}^S + k_{\mathrm{nr}}^S\right)} G. \tag{1}$$

Here, k_{r}^S, k_{nr}^S, k_{r}^T, and k_{nr}^T are the rates for radiative and nonradiative singlet and triplet decay, respectively, $k_{(\mathrm{R})\mathrm{ISC}}$ is the rate for (reverse) intersystem crossing, and k^S is the sum of k_{ISC}, k_{r}^S, and k_{nr}^S. The generation rate G is determined by the current density $J = qGL$ through the OLED, with q the elementary charge and L the emissive layer thickness.

For ideal TADF emitters, there is only radiative singlet decay, and thus k_{nr}^S, k_{r}^T, and k_{nr}^T are equal to zero. In this case, one can derive the lifetime of triplet excitons in a TADF OLED, before annihilation effects, as

$$\tau_T^{\mathrm{OLED}} = \frac{[T_1]}{G} = \frac{3k_{\mathrm{r}}^S + 4k_{\mathrm{ISC}}}{4k_{\mathrm{r}}^S k_{\mathrm{RISC}}}. \tag{2}$$

In a similar fashion, one can derive the lifetime of singlet excitons in a TADF OLED, which simply equals $1/k_{\mathrm{r}}^S$ for ideal emitters. The triplet lifetime is a useful quantity for evaluating annihilation processes that involve triplet excitons, which are believed to be mainly responsible for the efficiency roll-off and operational stability.

With respect to the efficiency roll-off, recently, a figure of merit was proposed that relates the efficiency roll-off in TADF OLEDs to the product of the radiative decay rate of singlet

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excitons k_r^S and the equilibrium ratio between the singlet and triplet concentration $[S_1]/[T_1]$ in steady state, and is given by [4]

$$k_r^S \frac{[S_1]}{[T_1]} = \frac{4k_r^S k_{RISC}}{3k_r^S + 4k_{ISC}}, \tag{3}$$

under the assumption that there is no nonradiative singlet exciton decay and that the rate for triplet-exciton decay equals zero, i.e., the case of ideal TADF emitters. The figure of merit defined in Eq. (3) showed a good positive correlation with the efficiency roll-off in TADF OLEDs reported in recent literature [4].

However, it does not seem intuitive that the *ratio* of singlet to triplet excitons would be responsible for the efficiency roll-off, as one would assume that the absolute (triplet) exciton concentration quantifies the number of annihilation events. This apparent incongruity can be resolved by comparing Eqs. (2) and (3) and realizing that, for the case of only radiative singlet decay,

$$k_r^S \frac{[S_1]}{[T_1]} = \frac{G}{[T_1]}, \tag{4}$$

or, in other words, the figure of merit in Ref. [4] simply equals the inverse of the triplet lifetime in a TADF OLED in steady state. This can be understood as follows: the ratio of the singlet and triplet population equals the ratio of the singlet and triplet lifetime. Since the singlet lifetime equals $1/k_r^S$ for ideal emitters, this term is factored out in Eq. (4), leaving only the triplet lifetime. As a result, it can be inferred that the roll-off in TADF OLEDs is correlated with the triplet lifetime. Reducing the triplet lifetime directly results in a decreased triplet population in an OLED at a given driving current, rationalizing the results in Ref. [4].

To derive the triplet lifetime from directly measurable quantities, it is useful to consider how the rate constants for TADF relate to the parameters extracted directly from a time-resolved PL experiment. Typically, in such an experiment, a TADF emitter exhibits a biexponential PL decay, which can be fitted with the function $A_1 \exp(-t/\tau_{PF}) + A_2 \exp(-t/\tau_{DF})$, with the prompt- and delayed-fluorescence lifetime τ_{PF} and τ_{DF}, and the prefactors A_1 and A_2, with $A_1 + A_2 = 1$ for fitting a normalized PL decay characteristic. For a three-level system and with the only assumption of the absence of triplet decay to the ground state, the kinetic rates are exactly given by [6]

$$\begin{aligned} k_{RISC} &= \frac{A_2}{\tau_{PF}} + \frac{A_1}{\tau_{DF}}, \\ k_{ISC} &= \frac{\frac{\tau_{PF}}{\tau_{DF}}\left(\frac{\tau_{DF}}{\tau_{PF}} - 1\right)^2}{\frac{\tau_{DF}}{A_1} + \frac{\tau_{PF}}{A_2}}, \\ k_r^S &= \frac{\Phi_{PL}}{A_1\tau_{PF} + A_2\tau_{DF}}. \end{aligned} \tag{5}$$

For $k_{nr}^S = 0$, the PL quantum yield (Φ_{PL}) can here be considered unity. Inserting these rate constants in Eq. (2), yields

$$\tau_T^{OLED} = \frac{3\tau_{PF}\tau_{DF} + 4A_1A_2\tau_{PF}^2\left(\frac{\tau_{DF}}{\tau_{PF}} - 1\right)^2}{4(A_1\tau_{PF} + A_2\tau_{DF})}, \tag{6}$$

which for $\tau_{DF} \gg \tau_{PF}$ and $A_1 \approx 1$ can be approximated by

$$\tau_T^{OLED} = \frac{(3\tau_{PF} + 4A_2\tau_{DF})\tau_{DF}}{4\tau_{PF} + 4A_2\tau_{DF}} \approx \begin{cases} \tau_{DF} & \text{if } A_2\tau_{DF} \gg \tau_{PF} \\ \frac{3}{4}\tau_{DF} & \text{if } A_2\tau_{DF} \ll \tau_{PF}. \end{cases} \tag{7}$$

Fascinatingly, the lifetime of triplets in a TADF OLED in steady state is thus almost equal to the delayed-fluorescence lifetime, implying that the triplet concentration can be directly inferred from τ_{DF}. It should be noted that this only applies to triplets under electrical excitation, whereas under photoexcitation the triplet concentration may be considerably lower. It has been found experimentally that delayed fluorescence under electrical excitation indeed has a higher yield than in a PL experiment, which stems from the high (75%) initial triplet population [7]. Interestingly, a good correlation between the efficiency roll-off and τ_{DF} was also found by Diesing *et al.* [4], which is no coincidence, as is here rationalized with the above derivations of the triplet lifetime being close to the delayed-fluorescence lifetime.

According to Eq. (7), the average lifetime of triplet excitons in an OLED approaches $\frac{3}{4}\tau_{DF}$ for $A_2\tau_{DF} \ll \tau_{PF}$, which is the case of low delayed-fluorescence quantum yields and short delayed-fluorescence lifetimes. This situation corresponds to high k_r^S/k_{ISC} ratios and high k_{RISC} rates. Under electrical excitation, this means that the triplet concentration in the OLED is dominated by the $\frac{3}{4}$ fraction of initially generated triplets, whereas intersystem crossing of the remaining singlet fraction is inefficient. Therefore, for low delayed-fluorescence

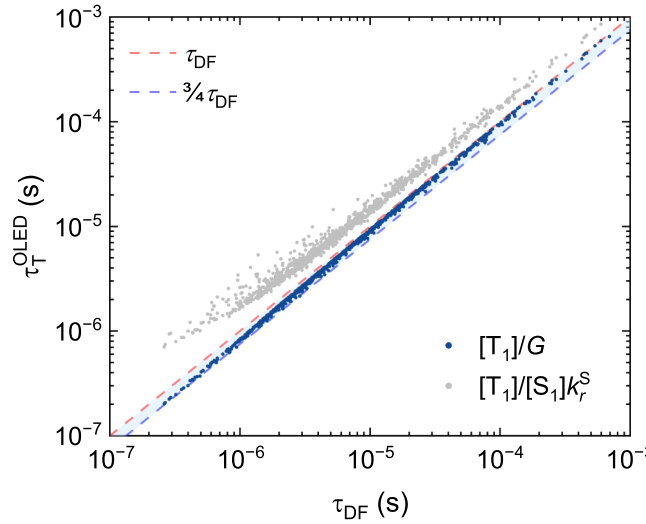


FIG. 1. Dependence of the triplet lifetime in an OLED on the delayed-fluorescence lifetime. $[T_1]/G$ (blue circles) and $[T_1]/[S_1]k_r^S$ (gray circles) were evaluated for random combinations of rate constants, calculating the electrically generated exciton densities exactly ($k_{nr}^T \neq 0$) for a PL quantum yield of 0.7. The rate constants k_{RISC}, k_{ISC}, and k_r^S were varied randomly from 10^3 to $10^6\ s^{-1}$, from 10^3 to $10^7\ s^{-1}$, and from 10^3 to $5 \times 10^6\ s^{-1}$, respectively, while k_{nr}^T was adjusted [9] to obtain a Φ_{PL} of 0.7 for all random combinations. Combinations returning negative k_{nr}^T or $A_2 > 0.2$ were excluded. The delayed lifetime was calculated from the kinetic rates using the exact expression from Ref. [7].

quantum yields, $[T_1]$ in an OLED approaches $\frac{3}{4}\tau_{DF}G$. For small A_2 and τ_{DF}, Eq. (5) gives $k_{RISC} \approx \frac{1}{\tau_{DF}}$. Inserting this into Eq. (2) and assuming $k_r^S \gg k_{ISC}$ indeed yields $[T_1]/G \approx \frac{3}{4}\tau_{DF}$. Conversely, for $k_{ISC} \gg k_r^S$, the triplet concentrations under electrical and optical excitation become almost equal, meaning that $[T_1] \approx \tau_{DF}G$.

In the above derivations, no nonradiative losses were assumed. To evaluate how the triplet lifetime correlates with the delayed-fluorescence lifetime for nonideal emitters, these quantities were calculated for different random combinations of rate constants, with τ_{DF} calculated from the exact expressions for a three-level system [8]. Figure 1 shows that even in the presence of nonradiative triplet decay, the triplet lifetime in a TADF OLED is very well approximated by the delayed-fluorescence lifetime, within the upper and lower boundaries as defined by Eq. (7).

In the preceding, for ideal emitters, it was realized that the recently proposed figure of merit for the efficiency roll-off [4] is equal to the inverse of the triplet lifetime [Eq. (4)]. However, when removing the assumption that nonradiative losses are absent (i.e., when $\Phi_{PL} \neq 1$), these quantities start to diverge. The simplest example is for the case of the presence of losses only due to nonradiative singlet decay. This will neither affect the equilibrium between the singlet and triplet population, nor the triplet density, as k_{nr}^S and k_r^S are always summed in the respective expressions. However, the figure of merit [Eq. (3)] will decrease due to a reduction in the radiative singlet decay rate. As the efficiency roll-off is related to the exciton densities, this reduced figure of merit will not be accompanied by an increased roll-off. By contrast, the triplet lifetime $[T_1]/G$ is not affected by nonradiative singlet decay and therefore retains its correlation with the efficiency roll-off. Furthermore, as displayed in Fig. 1, the correlation between the triplet lifetime in an OLED and τ_{DF} even holds for nonradiative triplet losses, whereas Eq. (3) (in its exact form) deviates from $G/[T_1]$ by at least a factor equal to the PL quantum yield and diverges further in the desired region of short triplet lifetimes.

To conclude, it was demonstrated that the lifetime of triplet excitons in a TADF OLED is well approximated by the delayed-fluorescence lifetime of the emitter. Therefore, the triplet concentration in a working OLED can be directly inferred from a PL experiment, enabling facile quantification of triplet-related interactions in TADF OLEDs, such as the efficiency roll-off and degradation phenomena. For both TADF and phosphorescent OLEDs, minimizing the PL lifetime is key for long-lived OLEDs with increased efficiency at high brightness.

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