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Förster-type triplet-polaron quenching in disordered organic semiconductors

R. Coehoorn,^{1, a)} P.A. Bobbert,¹ and H. van Eersel²

¹⁾*Department of Applied Physics and Institute for Complex Molecular Systems, Eindhoven University of Technology, P.O. Box 513, NL-5600 MB Eindhoven, The Netherlands*

²⁾*Simbeond B.V., P.O. Box 513, NL-5600 MB Eindhoven, The Netherlands*

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Triplet-polaron-quenching (TPQ) is a major cause of the efficiency loss at large current densities in phosphorescent organic light-emitting diodes (OLEDs). The nature of the interaction process is presently not well understood. In this paper, we study TPQ due to Förster-type triplet-polaron interactions in energetically disordered organic semiconductors with a Gaussian polaron density of states. A continuum theory, which neglects the spatial inhomogeneity and energetic disorder, is from a Kinetic Monte Carlo approach shown to correctly predict that the effective steady-state TPQ rate coefficient, $k_{\text{TPQ,eff}}$, depends only sensitively on the polaron diffusion in a rather narrow range of diffusion coefficients. However, in this regime, significant discrepancies between the two approaches are found, in particular for realistic values of the TPQ-Förster radius, around 3 nm, and for systems with strong energetic disorder. Both approaches show that $k_{\text{TPQ,eff}}$ is not constant, but can depend on the polaron density and the electric field. Various methods for deducing the TPQ mechanism from experiment are discussed, including an approach which utilizes the shape of the time-dependent photoluminescence after pulsed illumination.

I. INTRODUCTION

Exciton-polaron quenching is one of the excitonic interaction processes that give rise to a reduction of the internal quantum efficiency of organic optoelectronic devices such as organic light-emitting diodes (OLEDs). For phosphorescent OLEDs, within which the emission originates from triplet excitons, several studies indicate that triplet-polaron quenching (TPQ) is the major cause of the observed efficiency roll-off with increasing luminance, at least at relatively low luminance levels.¹⁻³ TPQ may be viewed as a process in which first the energy of the excited emitter molecule is transferred to the positively or negatively charged polaron, followed by fast thermal relaxation of the acceptor molecule upon which the excess energy is lost. Alternatively, the energy of a triplet-excited emitter molecule may be lost by energy transfer to another triplet-excited emitter molecule, followed by non-radiative relaxation of the acceptor molecule to the triplet ground state (“triplet-triplet annihilation”, TTA). Kinetic Monte Carlo (KMC) simulations have shown that there is in OLEDs a subtle interplay between the efficiency loss due to TPQ and TTA, and that within a realistic range of parameters describing both processes either TPQ or TTA could be predominant in application-relevant devices.⁴

Quantitative models describing the rate of TPQ processes in organic semiconductors have been developed at various levels of refinement. Conventionally, the TPQ rate r_{TPQ} is assumed to be proportional to the local polaron volume density, n_p , so that (under steady-state conditions)

$$r_{\text{TPQ}} = k_{\text{TPQ,eff}} n_p, \quad (1)$$

with $k_{\text{TPQ,eff}}$ a material-specific effective steady-state rate coefficient that is in general different for quenching at holes or electrons. This formalism has been used to analyze the contribution of TPQ to the roll-off,¹ using rate coefficients as obtained typically from transient and steady state photoluminescence (PL) studies of unipolar metal/semiconductor/metal sandwich-type devices.⁵⁻⁷ Within such analyses, it is assumed that the rate coefficient is independent of the local polaron density and the local electric field. However, we have recently shown that for the specific case of TPQ occurring immediately when a polaron has diffused to a nearest-neighbour (NN) site of the triplet, the effective rate coefficient can show in organic materials a distinct carrier density and electric field dependence.⁸ Such an immediate NN-type TPQ mechanism may be viewed as resulting from a Dexter-type short-range quantum-mechanical tunneling process. From Kinetic Monte Carlo simulations for prototypical green and red emitting OLEDs, it was found that assuming this process (which does not introduce a new parameter) provides good agreement with the experimental roll-off curves. Nevertheless, it would be important to establish whether this mechanism more generally yields an appropriate description of the efficiency roll-off. This is urged by experimental evidence that in green and blue emitting OLEDs TPQ is actually a more long-range process, due to Förster Resonant Energy Transfer (FRET) resulting from a triplet-polaron dipole-dipole interaction.⁹ The distance (R) dependent quench rate is then given by

$$r_{\text{TPQ}}(R) = \frac{1}{\tau} \left(\frac{R_{\text{F,TPQ}}}{R} \right)^6. \quad (2)$$

For a donor-acceptor distance equal to the TPQ Förster-radius, $R_{\text{F,TPQ}}$, the quench rate is equal to the effective decay rate $1/\tau$. Support for a Förster-type

^{a)}Electronic mail: r.coehoorn@tue.nl

mechanism has furthermore been obtained from an analysis of the phosphorescent green and red emission in white OLEDs.¹⁰ By analyzing the measured efficiency roll-off using KMC simulations, a value of $R_{\text{F,TPQ}} \cong 3$ nm for triplet-polaron quenching was estimated. $R_{\text{F,TPQ}}$ depends on the overlap of the donor emission and the acceptor extinction spectra¹¹. For FRET to a neutral chromophore, such analyses have been carried out intensively.¹² However, accurately measuring the extinction spectra of positively or negatively charged molecules is more difficult. Recently, Young *et al.* developed for that purpose an electrochemical method, applicable to dissolved ions.⁹ Positively charged 4,4'-bis[1-naphthyl(phenyl)amino]-1,1'-biphenyl (α -NPD), was found to show strong optical absorption with a peak around a wavelength of 480 nm, explaining the occurrence of strong roll-off for blue phosphorescent OLEDs utilizing α -NPD as a hole-transporting layer in direct contact with the emissive layer. The question now arises to what extent it would be possible to distinguish NN-type and Förster-type TPQ using the more conventional approach of measuring PL quenching in unipolar devices based on solid films, and to what extent in the case of Förster-type TPQ such experiments could be analyzed assuming a rate coefficient description (Eq. (1)) with a constant value of k_{TPQ} .

In this paper, we address these questions by studying Förster-type TPQ using Kinetic Monte Carlo simulations. We focus on energetically disordered organic semiconductors with a Gaussian density of states (DOS). The analysis is restricted to systems with a negligible exciton diffusion. From studies of the dependence of the TTA rate on the phosphorescent emitter concentration, this is known to be a good approximation for host-guest systems used in OLEDs within which the triplet-emitting dye (guest) molecules are present at a concentration smaller than approximately 5 mol%.¹³ From theoretical and simulation studies on Förster-type donor-acceptor exciton transfer^{11,14,15} one may expect that for energetically ordered systems (with a constant polaron diffusion coefficient) k_{TPQ} depends only in a restricted diffusivity-range on the precise value of the polaron diffusivity. In the two regimes outside this range, k_{TPQ} is essentially equal to the value obtained in the no-diffusion limit or in the limit of an infinite diffusion coefficient. We find that this picture applies as well to TPQ in disordered organic semiconductors. That is a distinct difference with NN-type TPQ. We study in which of the three resulting physical regimes Förster-type TPQ in energetically disordered semiconductors falls, and find that k_{TPQ} can only be viewed as a constant under conditions of small disorder and a small polaron density.

The paper is organized as follows. In Section II, Förster-type TPQ in spatially uniform (continuum) materials with a constant polaron diffusion coefficient is discussed. In Section III, the effects of energetic disorder are studied using KMC simulations. The analysis includes an overview of the dependence of the effective steady-state

value of k_{TPQ} on material properties such as the Gaussian DOS width and the exciton lifetime and on measurement conditions such as the polaron volume density and the electric field. In Section IV, we discuss various experimental methods for investigating the contribution of polaron diffusion to the TPQ efficiency loss. In Section V, a summary and conclusions are given.

II. FÖRSTER-TYPE TPQ IN A SPATIALLY UNIFORM MATERIAL

In this Section, we discuss the TPQ rate for the case of polaron diffusion in a spatially uniform material. Within the continuum model used, the description of the diffusion process is not complicated by the discreteness of the molecular site positions and by the energetic disorder, and the diffusion coefficient is independent of the polaron density. The analysis will serve as a reference for the KMC simulation results for the case of polaron hopping between discrete energetically disordered molecular sites, presented in Section III, and will help to distinguish various mechanisms using the results of time-resolved PL experiments. In such an experiment, absorption from a delta-shaped light pulse creates at time $t = 0$ a spatially uniform initial triplet volume density $n_{\text{T}}(0)$. We focus in this paper on TPQ with a single type of carrier, and take for the sake of definiteness the quench rate proportional to the hole volume density, n_{h} . Furthermore, we assume that TTA may be neglected. The triplet volume density decreases then with a rate

$$\frac{dn_{\text{T}}(t)}{dt} = -(k_{\text{TPQ}}(t)n_{\text{h}} + 1/\tau)n_{\text{T}}(t), \quad (3)$$

with $k_{\text{TPQ}}(t)$ an effective time-dependent TPQ rate and $1/\tau \equiv 1/\tau_{\text{rad}} + 1/\tau_{\text{nr}}$, where τ_{rad} and τ_{nr} are the radiative and non-radiative decay time, respectively, so that

$$n_{\text{T}}(t) = n_{\text{T}}(0) \exp\left(-\frac{t}{\tau} - \int_0^t k_{\text{TPQ}}(t')n_{\text{h}}dt'\right). \quad (4)$$

Due to TPQ, the total photoluminescence quantum yield (PLQE, η_{PL}) is thus reduced by a factor

$$\frac{\eta_{\text{PL}}}{\eta_{\text{PL},0}} = \frac{1}{\tau} \int_0^\infty \frac{n_{\text{T}}(t)}{n_{\text{T}}(0)} dt = \frac{\frac{1}{\tau}}{\frac{1}{\tau} + k_{\text{TPQ,eff}}n_{\text{h}}}, \quad (5)$$

where $\eta_{\text{PL},0}$ is the PLQE in the absence of TPQ. The time-independent quantity $k_{\text{TPQ,eff}}$ in the right-hand side of the expression is the effective TPQ rate coefficient that follows from the time-integrated yield observed in a transient PL experiment or from a steady-state PL experiment. The theory of Förster-type TPQ is fully analogous to the theory of Förster-type donor-acceptor energy transfer.¹¹ After discussing the results for the no-diffusion and strong-diffusion limits in subsection A, we present in Subsection B a general theory of diffusion-mediated Förster-type TPQ that has been obtained by adapting an approach developed by Gösele *et al.*¹⁴ and Butler and Pilling.¹⁵

A. No-diffusion and strong-diffusion limits

The TPQ rate $k_{\text{TPQ}}(t)$ is in general time-dependent because after creating at a time $t = 0$ an ensemble of excited molecules, the probability density

$$n'_h(R, t) = u(R, t)n_h \quad (6)$$

of finding at time t a hole at a distance R from a *remaining* excited molecule decreases for small R : on average, excitons with a hole at a relatively short distance are quenched first, so that for the population of remaining excitons the average distance to the nearest holes becomes gradually larger. This "depletion" process is most important in the absence of hole diffusion; in the strong-diffusion limit, the effect does not occur. The depletion process is thus *not* a result of any influence of the presence of excitons on the presence and diffusional motion of the polarons, but simply a consequence of the fact that when time proceeds the average distance between a remaining exciton and the most nearby polarons increases. From the analogy with donor-acceptor systems,¹¹ the TPQ rate in the no-diffusion (nd) limit decreases then with time as

$$k_{\text{TPQ,nd}}(t) = \frac{2\pi^{3/2}}{3} R_F^3 \left(\frac{1}{\tau t} \right)^{1/2}. \quad (7)$$

The divergence of the rate in the $t = 0$ limit is due to a neglect of a minimal distance between the molecular sites, occurring in realistic materials. This does not significantly affect the effective TPQ rate coefficient when the Förster radius is at least a factor of two larger than the minimal intermolecular distance. In subsection B, this effect will be included.

From Eq. (4), the time-dependence of the triplet density is then given by

$$n_{\text{T,nd}}(t) = n_{\text{T}}(t) \exp \left[-\frac{t}{\tau} - 2\gamma \left(\frac{t}{\tau} \right)^{1/2} \right], \quad (8)$$

with

$$\gamma = \frac{2\pi^{3/2}}{3} R_F^3 n_h. \quad (9)$$

so that from Eq. (5), the reduction of the PLQE due to TPQ is given by:

$$\frac{\eta_{\text{PL}}}{\eta_{\text{PL},0}} = 1 - \sqrt{\pi\gamma^2} \exp(\gamma^2) \text{erfc}(\gamma), \quad (10)$$

with $\text{erfc}(x)$ the complementary error function. The effective TPQ rate coefficient is then given by

$$k_{\text{TPQ,eff,nd}} = \frac{1}{\tau n_h} \left[\frac{1}{1 - \sqrt{\pi\gamma^2} \exp(\gamma^2) \text{erfc}(\gamma)} - 1 \right]. \quad (11)$$

For small hole densities (small γ), the rate coefficient may be expanded in n_h as

$$k_{\text{TPQ,eff,nd}} \cong \frac{2\pi^2}{3} \frac{R_F^3}{\tau} \left[1 + \left(\frac{\pi}{2} - 1 \right) \frac{4\pi}{3} R_F^3 n_h + O(n_h^2) \right]. \quad (12)$$

Beyond a certain carrier density, when the probability that within a radius around a triplet equal to R_F there is more than one polaron present becomes significant, the TPQ rate becomes thus enhanced. That may be viewed as a result of a "competition" between polarons that can each quench the nearby triplet. An analogous effect has been theoretically predicted¹⁶ and experimentally found^{13,17} for the case of TTA at high initial triplet volume densities and from a KMC simulation study of NN-type TPQ.⁸

In the strong-diffusion (sd) limit, the polaron density around the remaining triplets does not decrease ($u(R, t) = 1$ for all R and t), so that the rate coefficient is time-independent. For the case of a spatially uniform material, it is given by

$$k_{\text{TPQ,sd,cont}} = \int_{R_0}^{\infty} \frac{1}{\tau} \left(\frac{R_F}{R} \right)^6 4\pi R^2 dR = \frac{4\pi}{3} \frac{R_F^6}{\tau R_0^3}, \quad (13)$$

with R_0 the smallest possible triplet-polaron distance. Within the KMC simulations used in this study, the triplets and polarons are located on the sites of a simple cubic lattice with a lattice constant $a = 1$ nm (see Section III). The rate is then obtained by a summation over all possible lattice distances, leading to

$$k_{\text{TPQ,sd}} \cong \kappa \frac{R_F^6}{\tau a^3}, \quad (14)$$

with $\kappa = 8.402$.

B. General theory

Within a general theory of the effect of diffusion on Förster-type TPQ in a spatially uniform material with a minimum encounter distance R_0 , the rate coefficient is given by

$$k_{\text{TPQ}}(t) = \int_{R_0}^{\infty} \frac{1}{\tau} \left(\frac{R_F}{R} \right)^6 u(R, t) 4\pi R^2 dR, \quad (15)$$

where the function $u(R, t)$, defined by Eq. (6), gives the time-dependent shape of the depleted region. Gösele *et al.*¹⁴ and Butler and Pilling¹⁵ studied the analogous case of energy transfer in donor-acceptor systems, and argued that $u(R, t)$ is the solution of the differential equation

$$\frac{\partial u(R, t)}{\partial t} = \frac{D}{R} \frac{\partial^2 u(R, t)}{\partial R^2} - \frac{1}{\tau} \left(\frac{R_F}{R} \right)^6 u(R, t), \quad (16)$$

where the rate of change of $u(R, t)$ is expressed as a sum of contributions due to polaron diffusion with a diffusion

coefficient D and exciton quenching. The initial condition is

$$u(R, t = 0) = 1 \text{ for all } R > R_0, \quad (17)$$

and the outer boundary condition is

$$u(R = \infty, t) = 1 \text{ for all } t. \quad (18)$$

In Refs 14 and 15, this approach was used to study the effect of diffusion on donor-acceptor transfer due to a Förster-type interaction process *and* due to immediate quenching when due to diffusion the donor-acceptor distance becomes equal to the minimal encounter distance R_0 . Although the validity of the inner boundary condition used for that purpose in Ref. 14,

$$u(R = R_0, t) = 0 \text{ for all } t, \quad (19)$$

was debated in Ref. 15, a numerical study using a refined approach provided support for the main outcomes of the work presented in Ref. 14.

In our study, we focus on TPQ that is due to Förster-type quenching only. The inner boundary condition is then

$$\left. \frac{\partial u(R, t)}{\partial R} \right|_{R=R_0} = 0 \text{ for all } t. \quad (20)$$

As a first step, we calculate the shape of the depleted region in the infinite-time limit, $u_{\text{inf}}(R)$. Using a transformation of the differential equation introduced in Ref. 14, we find

$$u_{\text{inf}}(R) = \frac{2^{3/4}}{\Gamma(1/4)} z(R)^{1/4} (K_{1/4}(z(R)) + p \cdot I_{1/4}(z(R))), \quad (21)$$

with

$$z(R) = \frac{1}{2R^2} \sqrt{\frac{R_F^6}{D\tau}}, \quad (22)$$

and with (from Eq. (17))

$$p = \frac{K_{3/4}(z(R_0))}{I_{-3/4}(z(R_0))}. \quad (23)$$

$K_n(x)$ and $I_n(x)$ are modified Bessel functions of order n and $\Gamma(x)$ is the Euler gamma function.

As an example, Fig. 1(a) shows for a typical material, with $R_F = 3$ nm, $\tau = 1$ μ s and $R_0 = 1$ nm, the shape of the depleted region in the infinite-time limit for various values of D . For very small D , the shape of the depleted region is independent of D , although its size decreases when D increases. Around a certain value of D , a regime change takes place: the depleted region widens, and at a distance $R = R_0 = 1$ nm there is still a significant remaining polaron density. A second regime change takes place when for even larger diffusion coefficients the depleted region essentially vanishes. The boundaries between the three regimes may be obtained

as follows. From Eq. (21), it follows that in the weak-diffusion regime, a characteristic value of the size of the depleted region is $R_{\text{char}} \equiv (R_F^6/(D\tau))^{1/4}$. A characteristic value of the time needed to fully develop the depleted region is then $t_{\text{char}} \equiv R_{\text{char}}^2/D = R_F^3/(D\tau)^{3/2} \times \tau$. The intermediate-diffusion regime is reached when t_{char} becomes smaller than τ and the strong-diffusion regime is reached when R_{char} becomes smaller than R_0 :

$$D \ll \frac{R_F^2}{\tau} \text{ (weak-diffusion regime)}, \quad (24)$$

and

$$D \gg \frac{R_F^6}{R_0^4 \tau} \text{ (strong-diffusion regime)}. \quad (25)$$

For the example given, the regime transitions are then expected to occur around $D \cong 10^{-11}$ m²/s and $D \cong 10^{-9}$ m²/s, consistent with the results shown in the figure. Whereas the transition between the weak-diffusion and intermediate regime was already properly treated in earlier studies,^{11,14,15} the use of the boundary condition given by Eq. (20) leads also to a proper treatment of the full intermediate-diffusion regime and the transition to the strong-diffusion regime.

In the weak-diffusion regime, the depletion process continues until a time that strongly exceeds the lifetime τ . In Figure 1(b), this is shown for the case $D \cong 10^{-13}$ m²/s. Figure 1(c) shows that at a time $t = \tau$, the shape of the depleted region is for such a small value of D independent of the precise value of D . Its size, taken as the radius at which $u(R, \tau) = 1/2$, is then approximately equal to $R_F = 3$ nm. The figure also shows how in the intermediate-diffusion regime the size of the depleted region for $t = \tau$ decreases with increasing D , until it vanishes when the strong-diffusion regime is reached.

Figure 2 shows for this system the time-dependent TPQ rate, for various values of the diffusion coefficient, as calculated using Eq. (15). Initially, the rate is equal to the strong-diffusion value $k_{\text{TPQ, sd}}$, given by Eq. (13). Quenching starts to give rise to a depleted region at a time

$$t_1 = \frac{\pi}{4} \left(\frac{R_0}{R_F} \right)^6 \tau, \quad (26)$$

which follows from the condition that $k_{\text{TPQ, sd}} = k_{\text{TPQ, nd}}(t_1)$. Subsequently, the rate coefficient decreases, until at a time $t_2 \sim t_{\text{char}}$ the size of the depleted region does not increase anymore. The rate is then equal to the rate coefficient for infinite time, $k_{\text{TPQ, inf}}$, which follows from Eqs (15) and (21) (dashed lines in the figure). When $R_F \gg R_0$ and for small D , the intermediate time-range is very wide ($t_{\text{char}} \gg t_1$) and the rate within this range is equal to $k_{\text{TPQ, nd}}(t)$, given by Eq. (7). We find that for arbitrary R_F and D the rate is for $t < t_1$ to a fair approximation given by

$$k_{\text{TPQ}}(t) \cong k_{\text{TPQ, sd}}, \quad (27)$$

and for $t \geq t_1$:

$$k_{\text{TPQ}}(t) \cong k_{\text{TPQ,inf}} + (k_{\text{TPQ,sd}} - k_{\text{TPQ,inf}}) \sqrt{\frac{t_1}{t}}. \quad (28)$$

The result is exact in the no-diffusion limit ($k_{\text{TPQ,inf}} \rightarrow 0$) and in the strong-diffusion limit ($k_{\text{TPQ,inf}} \rightarrow k_{\text{TPQ,sd}}$). For the example given, $t_1 = 1.1$ ns. In the figure, the approximation is indicated by the full curves.

The effective steady-state rate coefficient $k_{\text{TPQ,eff}}$ can now be calculated using Eqs (4) and (5). Figure 3 shows the dependence of $k_{\text{TPQ,eff}}$ on the Förster radius for various values of the diffusion coefficient, for the values $R_0 = 1$ nm and $\tau = 1$ μ s also used above. The full curves show the rate in the limit of a small hole density. The dashed and dashed-dotted curves show the results for the case of $n_h = 10^{24}$ and 10^{25} m^{-3} , respectively, for $D = 1 \times 10^{-10}$ m^2s^{-1} . In particular for large R_F , a significant density dependence is thus found. We return to that issue in the next Section, where we show that the conditions for which this effect is found can occur realistically in OLEDs. The figure furthermore shows that the range of values within which $k_{\text{TPQ,eff}}$ can vary is quite limited. For $R_F = 3$ nm, e.g., the width of the range is only slightly larger than one order of magnitude. For $R_F < 1$ nm, all curves collapse to the rate obtained in the strong-diffusion limit, as then no depleted-zone formation takes place.

It is of interest to analyze the simulation results more quantitatively. Figure 3 reveals that within the intermediate-diffusion regime and for the case of a small hole density, the sensitivity of $k_{\text{TPQ,eff}}$ to a variation of R_F is quite weak and given approximately by $k_{\text{TPQ,eff}} \propto R_F^{3/2}$. This result can be understood as follows. Diffusion gives rise to a decrease of the size of the depleted region. In the intermediate-diffusion regime, the time t_{char} required for forming the depleted region has decreased to a value much smaller than τ . The TPQ rate coefficient is then essentially time-independent, and given by the value that follows from Eq. (15), evaluated for the final shape of the depleted region, $u_{\text{inf}}(R) = u(R, t \rightarrow \infty)$. When $u_{\text{inf}}(R)$ is approximated by a step function, which is equal to 0 (or 1) for R smaller (or larger) than the value of R_{char} defined above, respectively, Eq. (15) yields for the intermediate-diffusion regime:

$$k_{\text{TPQ,eff}} \cong \frac{4\pi}{3} \frac{R_F^{3/2}}{\tau} (D\tau)^{3/4}. \quad (29)$$

This expression is found to be precise within a factor of about two, the actual rate being larger. Eq. (29) also explains the observed 3/4-power scaling of the rate with the diffusion coefficient.

III. EFFECTS OF GAUSSIAN DISORDER

A. Method

As a next step, we investigate the effects of Gaussian energetic disorder on the rate coefficient for Förster-type TPQ. The rate coefficient was calculated by simulating a steady-state photoluminescence (PL) experiment, applied to an organic semiconductor within which a hole current flows, using the kinetic Monte Carlo tool Bumblebee.¹⁸ The approach has been described extensively in Ref. 8. In short, the systems considered are $100 \times 100 \times 100$ nm^3 boxes in which the molecular sites reside on a simple cubic lattice with a lattice constant $a = 1$ nm. The total site density, N_t , is thus equal to 10^{27} m^{-3} . Periodic boundary conditions are used in all three directions. The site energies are in a spatially uncorrelated way drawn from a Gaussian distribution with a width (standard deviation) $\sigma = 0.05, 0.10$ or 0.15 eV, corresponding at the simulation temperature $T = 298$ K employed to disorder parameters $\sigma/(k_B T)$ close to 2, 4 and 6, respectively. The hole transport is described using Miller-Abrahams hopping rates,¹⁹ including only nearest-neighbor (NN) hops. The NN hopping attempt rate is taken equal to $\nu_1 = 3.33 \times 10^{10}$ s^{-1} . This is a typical value for hole transport in disordered semiconductors based on small organic molecules such as α -NPD.² The Coulomb interaction between the holes was switched off. Unless stated otherwise, the simulations were carried out for a low uniform electric field, $F = 1 \times 10^7$ V/m. By carrying out the simulations at a small but finite field, the simulations also provide the hole mobility, from which the hole diffusion coefficient can be deduced. Table I in Ref. 8 contains an overview of the dependence of the diffusion coefficient on the disorder parameter and the carrier density.

The boxes contain at any moment in time 1000 triplet excitons (so that the triplet concentration is 10^{-3}), at random sites that are not occupied by a hole. The excitons are allowed to decay with default radiative and non-radiative lifetimes $\tau_{\text{rad},0} = 1.84$ μ s and $\tau_{\text{nr},0} = 5.52$ μ s, respectively, so that the effective lifetime is $\tau_0 = 1.38$ μ s. These are realistic values for the phosphorescent orange-red emitter bis(2-methyldibenzo[f,h]quinoxaline)(acetylacetonate)-iridium(III) ($\text{Ir}(\text{MDQ})_2(\text{acac})$).²⁰ However, also the effect of varying τ , while keeping the ratio $\tau_{\text{nr}}/\tau_{\text{rad}}$ fixed, was studied. The TPQ quench rate is given by Eq. (2). The steady-state effective TPQ rate coefficient is obtained using the expression

$$k_{\text{TPQ,eff}} = \frac{1}{n_h \tau_{\text{rad}}} \frac{f_Q}{f_R}, \quad (30)$$

with f_Q and f_R the fractions of quenched and radiatively decayed excitons, respectively. The fractions used were obtained after dynamic equilibrium has been reached, i.e. under the condition of a time-stable current density and photoluminescence. In order to obtain good statistics,

an average over five up to 25 simulation boxes was used. The computational effort is kept within reasonable limits by including only TPQ with holes located within a cubic box, centered around the triplet. The box dimension is $(2N+1)$, with N equal to the smallest integer larger than $(3/2)R_F$. As a result, the simulated rate coefficients are a few percent smaller than the actual values, depending on the system.

B. Simulation results and analysis

Figure 4(a) shows the dependence of the rate coefficient on R_F for various values of the disorder parameter, for the default value of the effective lifetime, $\tau_0 = 1.38 \mu\text{s}$, and for a hole concentration $c_h \equiv n_h/N_t = 10^{-3}$. When R_F is smaller than 1 nm, the rate coefficient is for all cases given by the strong-diffusion value, as expected from the discussion in Section II. In contrast, it depends strongly on the material parameters when R_F is larger than 1 nm. For strongly disordered materials, with $\sigma/(k_B T) = 6$, $k_{\text{TPQ,eff}}$ is then very close to the no-diffusion value, given by Eq. (12). The deviation observed for larger values of R_F is due to the charge carrier density dependence of $k_{\text{TPQ,eff}}$ (see further below). For $R_F = 6$ nm, the enhancement is approximately a factor 1.5, consistent with Eq. (12). For weakly disordered materials, with $\sigma/(k_B T) = 2$, $k_{\text{TPQ,eff}}$ is for small Förster radii very close to the strong-diffusion limit. Only for large values of R_F , above about 3 nm, depleted-zone formation gives rise to a reduction of $k_{\text{TPQ,eff}}$ with respect to the strong-diffusion value. For materials with $\sigma/(k_B T) = 4$, the TPQ process falls in the intermediate-diffusion regime. Figure 4(b) shows how the loss due to TPQ then depends on the effective lifetime. The figure gives the ratio of the fractions of quenched and radiatively decayed excitons, f_Q/f_R . The figure shows, e.g., that when $\tau = \tau_0 = 1.38 \mu\text{s}$, $R_F = 3$ nm and $c_h = 10^{-3}$, the ratio of radiatively decaying to quenched triplets is approximately equal to 1:1.

Figure 5 (symbols) shows the dependence of $k_{\text{TPQ,eff}}$ on the carrier concentration for $R_F = 3$ nm (a) and 6 nm (b), as obtained from KMC simulations. The dependence increases with increasing disorder parameter and Förster radius, and can be as large as one order of magnitude over the concentration range studied. The effect is in part due to the increase of the diffusion coefficient with increasing hole density above the cross-over concentration $c_{co} = (1/2) \exp[-(1/2)(\sigma/(k_B T))^2]$, when the transport is no longer in the independent-particle (Boltzmann) regime.²¹ For $\sigma/(k_B T) = 4$, e.g., $c_{co} \cong 2 \times 10^{-4}$. This contribution is predominant for $R_F = 3$ nm. An additional contribution arises when there is on average more than one charge carrier within a sphere with a radius equal to R_F . For the no-diffusion limit, the effect is given by the higher-order terms in Eq. (12). For $R_F = 6$ nm, this second contribution is significant. In the no-diffusion limit, the total increase is over the concentration range studied then as large as one order of magnitude.

The dashed curves in Fig. 5 give the carrier concentration dependence of $k_{\text{TPQ,eff}}$ as expected from the continuum-theory developed in Section II.B. The diffusion coefficient has been deduced from the mobility μ which follows from the current density obtained from the KMC simulations, using the Einstein equation, $D = (k_B T/e)\mu$, with e the elementary charge. We note that it is not *a priori* clear whether it is more appropriate to use this classical Einstein equation, which describes self-diffusion under thermal equilibrium conditions, instead of the generalized Einstein equation, which provides the diffusion coefficient in the case of Fickian transport under the influence of a concentration gradient. In energetically disordered materials, the latter diffusion coefficient is enhanced at large carrier concentrations.²² R_0 has been taken equal to $[(4\pi)/(3\kappa)]^{1/3}a = 0.793$ nm, in order to ensure that the approach to the strong-diffusion limit is consistently treated (compare Eqs (13) and (14)). The figure shows that the continuum-theory tends to predict too large values of $k_{\text{TPQ,eff}}$, in particular for $R_F = 3$ nm in the intermediate-diffusion regime. For $R_F = 6$ nm, the agreement is much better. We view this discrepancy as a consequence of the discreteness of the cubic lattice system, employed in the KMC simulations. Consistent with the results shown in the figure, the difference is then expected to become smaller with increasing R_F (so that the depleted zone radius becomes larger), towards the no-diffusion limit (when the depleted zone is largest) and towards the strong-diffusion limit (which is appropriately treated by the choice of R_0). From the KMC simulation results, it appears that the role of diffusion is actually somewhat smaller than would be expected from the continuum theory. It is indeed possible to obtain a fair empirical description of the simulation results by re-calculating $k_{\text{TPQ,eff}}$ from the continuum-theory using for each value of R_F and $\sigma/(k_B T)$ a concentration-independent reduction of the diffusion coefficient (full curves). The reduction factors are given in the figure caption.

From these findings, one may expect that in the intermediate-diffusion regime also the precise R_F dependence of $k_{\text{TPQ,eff}}$ and the ratio f_Q/f_R , shown in Fig. 4(a) and (b), respectively, are not well-predicted by the continuum-theory. E.g., one would expect from Eqs (29) and (30) that then $f_Q/f_R \propto R_F^{3/2} \tau^{3/4}$. Fig. 4(b) shows (on the double-log scale used) indeed an approximately linear increase with R_F . However, consistent with the finding that for small R_F the actual TPQ rate is smaller than the predicted rate, the slope is found to be much larger than the expected value of $3/2$, viz. closer to 3. Furthermore, the figure indeed shows an increase with increasing τ , but even around $R_F = 6$ nm the dependence is more close to $\tau^{1/2}$ than to $\tau^{3/4}$.

From the results given in Figure 5, it is not immediately clear to which extent the discrepancy between the simulation results and the continuum-theory depends also on the disorder parameter, because of the simultaneous effect of a variation of $\sigma/(k_B T)$ on the physical

regime (near the nd-limit for $\sigma/(k_B T) = 6$, and more close to the sd-limit for $\sigma/(k_B T) = 2$). We have therefore carried out KMC simulations as a function of the emitter lifetime, for $\sigma/(k_B T) = 2, 4$ and 6 , for a fixed hole concentration $c_h = 10^{-3}$. The results are shown in Fig. 6, which shows that the discrepancy increases with increasing disorder parameter. That indicates that the discrepancy is also related to the spatial non-uniformity of the diffusivity, which from a study of the spatial uniformity of the current density is known to increase with increasing disorder parameter.²³ From Ref. 23, an even larger non-uniformity of the diffusivity is expected for the case of dipolar correlated disorder. Simulation results for the case of dipolar correlated disorder, with $\sigma/(k_B T) = 6$, show indeed a further reduction of $k_{\text{TPQ,eff}}$ for hole diffusion lengths of at least 10 nm. In the no-diffusion limit, $k_{\text{TPQ,eff}}$ is then found to be about one order of magnitude smaller than for the case of spatially random disorder.²⁴ A more detailed study of this interesting effect, which can be of importance to host-guest systems using phosphorescent dye molecules with large static dipole moments such as employed in recent work on blue OLEDs,²⁵ is beyond the scope of this paper. We cannot exclude that also the stochastic rather than time-continuous nature of the TPQ and polaron diffusion processes plays a role.

All simulation results presented so far were obtained at a small electric field, $F = 1 \times 10^7$ V/m. For the case of immediate NN-type TPQ, a significant enhancement of the rate with increasing field was found.⁸ The enhancement is due to a “polaron wind effect”, which is analogous to the effect of electric fields on the rate of diffusion-controlled reactions between ions in solution.²⁶ The effect occurs when immediately upon reaching a certain distance (“capture radius”) a reaction takes place, as in the case of NN-type TPQ. However, for Förster-type TPQ, for which the rate remains finite at any distance, a significant polaron wind effect is not expected. On the one hand, increasing the field will then increase the encounter rate. On the other hand, the time during which the distance between the exciton and hole remains small will then decrease. These opposing effects are expected to cancel or almost cancel. KMC simulation results are consistent with that picture. As an example, Fig. 7 shows the effective rate coefficient for systems with $\sigma/(k_B T) = 4$, $\tau = \tau_0$, and R_F in the range 0.6 to 4.5 nm, at a hole concentration $c_h = 10^{-3}$. The field-dependence is indeed very small, although not entirely negligible. We ascribe the dependence to the field dependence of the mobility, which is found to be approximately 60% in the field range studied. Such a field-induced increase of the mobility is well-known for systems with Gaussian disorder.²⁷ From the Einstein relation a similar increase of the diffusion coefficient is then expected. For comparison, the figure also includes the TPQ rate coefficient obtained under the condition of immediate nearest-neighbour TPQ. Due to the polaron wind effect, the field-dependence is then significantly larger.

IV. EXPERIMENTAL ANALYSIS METHODS

From the results presented in the previous Section, it follows that the effective steady-state TPQ rate coefficient is in general not just a constant. As shown in Fig. 5, $k_{\text{TPQ,eff}}$ depends for a given material on the hole concentration and on the temperature. Within a mechanistic simulation approach, such as used when carrying out KMC simulations, these effects are “automatically” included, assuming that for the material under investigation an appropriate mechanistic description of the charge transport is already available. However, it is in general not *a priori* known whether the TPQ mechanism assumed (Förster-type, NN-type, or a combination of both types, e.g.) is indeed applicable, and what value of R_F should be used in the case of Förster-type TPQ. As already mentioned in the Introduction, measurements of R_F from the overlap between donor (triplet) emission and acceptor (hole or electron polaron) absorption spectra are in practice quite difficult.

A first method for investigating the TPQ mechanism would be to use a consistent mechanistic hopping model to analyze photoluminescence experiments of dedicated unipolar devices. The effective diffusion coefficient and the value of $k_{\text{TPQ,eff}}$, deduced from the analysis and evaluated as a function of the polaron density, can then be used to determine from Fig. 3 the appropriate physical regime. Such an approach is a refinement of published studies.^{5–7} For the green phosphorescent dye fac-tris(2-phenylpyridyl)iridium (Ir(ppy)_3), embedded in various host materials, values of $k_{\text{TPQ,h,eff}}$ for triplet-hole quenching in the range $(0.1\text{--}1.1) \times 10^{-18} \text{ m}^3\text{s}^{-1}$ have been found,^{28,29} and for several blue Ir-based phosphorescent dyes values of $(0.8\text{--}1.0) \times 10^{-18} \text{ m}^3\text{s}^{-1}$ were reported.²⁵ These values could be consistent with $R_F \cong 3$ nm. It would be of interest to investigate for these cases the role of hole diffusion. A value $k_{\text{TPQ,h,eff}} = 29 \times 10^{-18} \text{ m}^3\text{s}^{-1}$ was reported for the red phosphorescent dye (acetylacetonate)bis(2-methyl-dibenzo[f,h]quinoxaline)iridium ($\text{Ir(MDQ)}_2(\text{acac})$).³ From the simulation results presented in this paper, this high value would be indicative of a value of R_F that is at least equal to 4 nm, in combination with strong polaron diffusion. Alternatively, it could be indicative of a contribution due to immediate NN-type TPQ, for which there is no upper $k_{\text{TPQ,eff}}$ -limit as was shown in Ref. 8.

A powerful second method would be a study of $k_{\text{TPQ,eff}}$ as a function of the temperature. It follows from Fig. 4 that for Förster-type TPQ with a small value of R_F , a variation of the temperature induces a relatively small variation of $k_{\text{TPQ,eff}}$, bounded by the no-diffusion and strong-diffusion limits. In contrast, for large values of R_F a large variation of $k_{\text{TPQ,eff}}$ with varying temperature would be expected.

In the remainder of this Section, we focus on a third method, based on an analysis of the time-resolved PL intensity when probing TPQ optically using narrow ex-

citation pulses. The method is analogous to an approach that we have developed theoretically and applied successfully when analyzing the results of time-resolved PL experiments of triplet-triplet annihilation in host-guest systems used in OLEDs.^{13,16,17} In the absence of diffusion, the formation of a depleted region gives rise to a distinct time-dependence of the TPQ rate, as given within the continuum theory by Eqs. (27) and (28). As a result, the PL emission intensity decreases, when plotted on a log-scale, initially faster than in a later stage of the process. In contrast, in the case of strong diffusion such depleted-region formation does not occur and the emission intensity shows a strictly exponential decrease. As an example, the inset of Fig. 8 shows the PL emission intensity for a system with $R_F = 6$ nm, $\tau = \tau_0$, $c_h = 10^{-3}$, and no diffusion (red full curve). The total PL quantum efficiency is 30.6%, so that (from Eq. (5)) $k_{\text{TPQ,eff}} = 1.65 \times 10^{-18} \text{ m}^3 \text{ s}^{-1}$. In the strong-diffusion limit, TPQ characterized by this rate coefficient would give rise to the PL intensity indicated by the black dashed line. The different shapes of both curves may conveniently be characterized by the time $t_{1/2}$ at which half of the total emission has taken place. As shown in the figure, the value $t_{1/2}$ that is deduced from the actual emission is significantly larger than the value that would be expected in the strong-diffusion limit. In that limit, it would correspond to a value of the rate coefficient given by

$$k_{\text{TPQ},1/2} = \frac{1}{n_h \tau_{\text{rad}}} \left[(\ln 2) \times \frac{\tau}{t_{1/2}} - 1 \right]. \quad (31)$$

Using the values of $k_{\text{TPQ,eff}}$ and $k_{\text{TPQ},1/2}$ that are deduced from the total PLQE and from the shape of the time-dependent PL emission, respectively, we deduce the role of diffusion from the ratio

$$r \equiv \frac{k_{\text{TPQ,eff}}}{k_{\text{TPQ},1/2}}. \quad (32)$$

If r is very close to 1, the TPQ rate is strongly diffusion-enhanced, whereas if r is significantly larger than 1, the role of diffusion is limited.

Figure 8 (main part) shows how within the continuum model developed in Section II.B the r -ratio depends on the diffusion length, for $R_F = 3$ and 6 nm and for various values of the hole concentration. In the nd-limit, the r -ratio is close to 1.66 for $R_F \gtrsim 3$ nm and for small hole concentrations. For large values of R_F , values of the r -ratio in the range 1.6 to 2.0 are then obtained in the concentration range considered. With increasing diffusion length, the r -ratio decreases. The enhancement of the r -ratio, $r - 1$, drops to approximately half of the value in the nd-limit when due to diffusion $k_{\text{TPQ,eff}}$ is approximately twice the value in the nd-limit, as may be seen from a comparison with Fig. 6, or with the detailed results taken from Fig. 5 for a range of values of the disorder parameters (symbols in Fig. 8). We expect that explicit KMC simulations will provide support of this

general picture. However, in view of the discrepancies with the continuum theory discussed in Section III.B, the dependence of the r -ratio on the diffusion length might be quantitatively somewhat different than as given by Fig. 8. Including such KMC simulations is beyond the scope of this paper. In order to assure that the charge carrier density in the devices is sufficiently uniform, we suggest that the guest molecules are only present in a relatively thin central sublayer of a (host | host-guest | host) device, and that a system is selected for which the guest ionization energy is larger than the host ionization energy, as e.g. in Ref. ? . In such a case, the presence of the guest molecules does not significantly influence the charge density profile across the active layer thickness, and does not lead to local charge accumulation.

V. SUMMARY AND CONCLUSIONS

We have studied how the effective rate coefficient $k_{\text{TPQ,eff}}$ that describes the efficiency loss in optoelectronic devices such as OLEDs due for Förster-type TPQ is enhanced by polaron diffusion. From a theoretical model within which the spatially discrete nature of the molecular system and the stochastic nature of the hopping and quenching processes are neglected, it follows that only in a relatively narrow range of diffusion coefficients their precise value affects $k_{\text{TPQ,eff}}$. The results of KMC simulations are consistent with the predicted location of this intermediate-diffusion regime, which depends on the TPQ Förster radius in a manner as given Fig. 3. The model describes how after introducing a large ensemble of triplets in the material, the average distance between a remaining triplet (not yet decayed or quenched) and the nearest polaron becomes gradually larger.

The simulations have been performed for materials with a spatially random Gaussian polaron density of states. Although the continuum theory provides a qualitatively good description of the dependence of $k_{\text{TPQ,eff}}$ on the disorder parameter $\sigma/(k_B T)$ and on the polaron density, significant quantitative discrepancies are found. As shown in Figures 4 and 5, the discrepancies are largest for systems with a small Förster radius, when the diffusion coefficient is large but still within the intermediate regime, and for materials with strong energetic disorder. Under these conditions, the size of the depleted region around the remaining excitons is relatively small, and, in particular in the presence of energetic disorder, the averaging approach used within the continuum theory is then apparently no longer precise.

The theoretical and simulation results presented reveal that $k_{\text{TPQ,eff}}$ is the result of a complex interplay between the final loss process and the effects of diffusion on a molecular scale. In the intermediate-diffusion regime, $k_{\text{TPQ,eff}}$ can depend weakly on the electric field, and strongly on the charge carrier density. It is thus not always appropriate to view $k_{\text{TPQ,eff}}$ as a constant, as is commonly assumed so far when deducing the rate

coefficient from the efficiency roll-off of OLEDs or from the current density dependence of the photoluminescence yield obtained from dedicated single-carrier devices. In Section IV, we have shown how the results of transient PL experiments can be used to investigate whether the TPQ process is in the intermediate-diffusion regime. We have successfully used an analogous approach to analyze the contribution of exciton diffusion to the triplet-triplet annihilation rate coefficient,^{13,16,17} and expect that the method will be similarly useful to study triplet-polaron quenching.

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Figure 1. (a) Shape of the depleted region in the infinite-time limit for materials with $R_F = 3 \text{ nm}$, $R_0 = 1 \text{ nm}$, and $\tau = 1 \mu\text{s}$, for values of the hole diffusion coefficient in the range $D = 1 \times 10^{-15}$ to $10^{-9} \text{ m}^2/\text{s}^{-1}$. (b) Time dependence of the shape $u(R, t)$ of the depleted zone for the case $D = 1 \times 10^{-13} \text{ m}^2/\text{s}^{-1}$. (c) Shape of the depleted zone at $t = \tau$ for various values of D .

Figure 2. Time-dependence of the TPQ rate coefficient for materials with $R_F = 3$ nm, $R_0 = 1$ nm, and $\tau = 1$ μ s, for values of the hole diffusion coefficient in the range $D = 1 \times 10^{-14}$ to 10^{-9} m^2s^{-1} . The symbols give the numerically exact results and the curves show the approximation given by Eqs (27) and (28). The dashed lines give the rate coefficients in the infinite time limit, $k_{\text{TPQ},\text{inf}}$.

Figure 3. Dependence of the effective steady-state rate coefficient for Förster-type TPQ on the Förster radius, for materials with $\tau = 1$ μ s and $R_0 = 1$ nm, and for values of the hole diffusion coefficient in the range $D = 1 \times 10^{-12}$ to 10^{-7} m^2s^{-1} . The full curves give results obtained in the limit of a small polaron density. The dashed (dashed-dotted) curves give results for hole densities $n_h = 10^{24}$ (10^{25}) m^{-3} , with $D = 10^{-10}$ m^2/s . The upper and lower lines give the values in the strong-diffusion and no-diffusion limits, respectively.

Figure 4. Results of KMC simulations of Förster-type TPQ in materials with $a = 1 \text{ nm}$ and $c_h = 10^{-3}$. (a) Dependence of $k_{\text{TPQ,eff}}$ on the Förster radius for $\sigma/(k_B T) = 2, 4$ and 6 , with $\tau = \tau_0 = 1.38 \mu\text{s}$. (b) Dependence of the ratio of the fraction of quenchings and the fraction of radiative decay processes on the Förster radius for materials with $\sigma/(k_B T) = 4$, with variable ratios τ/τ_0 . The upper and lower full lines give the expected values in the strong-diffusion and no-diffusion limits, as obtained from Eq. (14) and as obtained from Eq. (12) with $n_h = 0$, respectively.

Figure 5. Results of KMC simulations of Förster-type TPQ in materials with $\tau = 1.38 \mu\text{s}$ and $a = 1 \text{ nm}$, as a function of the hole concentration for various values of the disorder parameter, for (a) $R_F = 3 \text{ nm}$ and (b) $R_F = 6 \text{ nm}$. The symbols give the KMC simulations results. The dashed curves give the rate coefficients that follow from the continuum-theory developed in Section II.B. The full curves show an empirical fit to the simulation data that is obtained using that theory with reduced values of the diffusion coefficient. For panel (a) the reduction factors for the cases $\sigma/(k_B T) = 2, 3, 4$ and 6 are $0.30, 0.26, 0.18$ and 0.20 , respectively. For panel (b), these factors are $0.8, 0.8, 0.6$ and 0.6 , respectively. The upper and lower full lines give the expected values in the strong-diffusion and no-diffusion limits.

Figure 6. Enhancement of the effective steady-state TPQ rate coefficient with respect to the value in the no-diffusion limit for systems with $R_F = 3$ nm, $a = 1$ nm and $\sigma/(k_B T) = 2, 4$ and 6 , as a function of the hole diffusion length. The symbols, connected by curves that serve as a guide-to-the-eye, give the KMC simulation results. The dashed curve gives the rate coefficient as expected from the continuum model developed in Section II.B. The uncertainty of the simulation points is smaller than or equal to the symbol size, unless indicated by error bars.

Figure 7. Dependence of the effective TPQ rate coefficient on the electric field, F , for systems with $\sigma/(k_B T) = 4$, $c_h = 10^{-3}$, $a = 1$ nm and $\tau = 1.38$ μ s, for various values of R_F , as obtained from KMC simulations (symbols). The horizontal lines provide a reference, showing that $k_{\text{TPQ,eff}}$ depends only for large values of R_F slightly on F . The data labeled “NN” give the results obtained from simulations assuming immediate nearest-neighbour type TPQ; the curve is a guide-to-the-eye.

Figure 8. Dependence of the r -ratio, defined in Eq. (32), on the hole diffusion length, as obtained from the continuum theory, for systems with $R_F = 3$ nm (full curves) and 6 nm (dashed curves), $a = 1$ nm and for various values of the hole concentration. The three curves for $R_F = 3$ nm correspond to the same hole concentrations as used for $R_F = 6$ nm, and show also an increase of r with increasing c_h . The symbols indicate for systems with $\sigma/(k_B T) = 2$ (spheres, cyan), 3 (triangles, magenta), 4 (diamonds, blue) and 6 (squares, red) the expected values for the case $\tau = \tau_0$ using the diffusion coefficients obtained from the KMC simulations. The full (open) symbols correspond to $R_F = 3$ (6) nm. The inset shows the actual time-dependent photoluminescence expected from the model (red curve) for a system with $R_F = 6$ nm, $\tau = \tau_0$, $c_h = 10^{-3}$, $a = 1$ nm and no diffusion, and a reference line (dashed, black) that indicates the expected photoluminescence intensity for a system with the same total PL efficiency, in the strong-diffusion limit. At the $t_{1/2}$ times, the cumulative PL intensities have reached half the final value.