Applied Physics Letters

RESEARCH ARTICLE | APRIL 21 2009

Highly phosphorescent organic mixed films: The effect of aggregation on triplet-triplet annihilation

Sebastian Reineke; Gregor Schwartz; Karsten Walzer; Meiken Falke; Karl Leo

Check for updates

Appl. Phys. Lett. 94, 163305 (2009)
https://doi.org/10.1063/1.3123815

View Online
Export Citation

09 June 2025 16:36:26

AIP Publishing
Applied Physics Letters
Special Topics Open for Submissions
Learn More

AIP Publishing

SDC EX. 1032 - 1/4

Highly phosphorescent organic mixed films: The effect of aggregation on triplet-triplet annihilation

Sebastian Reineke,[1,a] Gregor Schwartz,[1] Karsten Walzer,[1] Meiken Falke,[2] and Karl Leo[1]
[1]*Institut für Angewandte Photophysik, Technische Universität Dresden, George-Bähr-Str. 1, 01062 Dresden, Germany*
[2]*Institut für Physik, Technische Universität Chemnitz, Reichenhainer Str. 70, 09107 Chemnitz, Germany*

(Received 4 December 2008; accepted 2 April 2009; published online 21 April 2009)

The efficiency roll-off at high brightness levels is a key factor limiting the application of organic light emitting diodes. We investigate triplet-triplet annihilation in an archetype phosphorescent host-guest system. We show that the currently used host-guest systems are not at the physical limit set by intrinsic annihilation, but have an increased roll-off due to aggregate formation. The existence of these aggregates is directly proven by transmission electron microscopy. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3123815]

Organic semiconductors have recently gained considerable attention due to the many physical phenomena involved and due to interesting applications, such as organic light emitting diodes (OLEDs). Recently, the efficiencies of white OLEDs have surpassed those of incandescent bulbs and are approaching the efficiency of fluorescent tubes.[1,2] OLEDs are thus a promising candidate for next-generation lighting due to advantages such as high efficiency, flexibility, and low cost. For lighting applications, high brightness levels, ideally at a few thousand $\mathrm{cd/m^{-2}}$, are required. However, OLEDs suffer from a strong reduction in efficiency at higher intensities that is due to the long radiative lifetime τ of the emitting species. This effect is particularly pronounced for phosphorescent emitter dyes, where the emission originates from triplet excitons, which have been employed to quadruple the device efficiency as a result of simple spin statistics.[3,4] Therefore, many researchers have recently addressed the quenching processes which cause the reduction in the efficiency. Among the various processes, triplet-triplet annihilation (TTA)

$$^3D^* + {}^3A^* \rightarrow [k(t)] \rightarrow {}^1D + {}^3A^*, \tag{1}$$

with a rate $k(t)$, is considered to be dominant at high excitation levels.[5–7] Here, D and A represent donor and acceptor states, the superscript is the corresponding multiplicity, and the star is an excited state. TTA of mixed systems comprising *fac*-tris(2-phenylpyridine) iridium [$\mathrm{Ir(ppy)_3}$], the archetype phosphorescent emitter in OLED applications, have been widely investigated. Despite these many studies, a key question remains open: Staroske *et al.*[8] estimated the Förster radius R_F for the triplet energy transfer of $\mathrm{Ir(ppy)_3}$ in a solid mixed film, $^3D^* + {}^3A^* \rightarrow [k(t) \propto R_F^3] \rightarrow {}^1D + {}^3A^{**}$, to be $R_F = 2.9$ nm, where $^3A^{**}$ is a higher excited triplet state (T_n) of the acceptor upon energy absorption.[8] Estimations of the impact of TTA based on these results strongly differ from experimental data, i.e., the critical current density j_c of an $\mathrm{Ir(ppy)_3}$-based OLED, where TTA occurs solely via single-step long range Förster transfers, should be at least *one order of magnitude higher* than experimentally observed.[6,8] This discrepancy calls for further investigations to fully understand these mechanisms, in order to reach the physical limits in OLED devices.

In this letter, we demonstrate that the strong differences in TTA observed in previous data can be explained by an aggregation of the emitter molecules, a fact that has been suggested earlier, but which has never been proven.[9] We apply different TTA models to experimental data and show that the Förster-limit is not reached for $\mathrm{Ir(ppy)_3}$-based mixed films. Using aberration (Cs) corrected scanning transmission electron microscopy (STEM), we prove the emitter dopant aggregation, leading to increased TTA.

For this study, we prepared 20 nm thick mixed films of $\mathrm{Ir(ppy)_3}$ doped into 4,4′,4″-tris(*N*-carbazolyl)-triphenylamine (TCTA) with approximately 0.1 and 1 mol % by coevaporation under high vacuum ($\sim 10^{-7}$ mbar) onto quartz glass substrates. These samples were investigated in time-resolved photoluminescence experiments with different laser excitation densities, carried out as previously reported.[7] In general, the time evolution of the triplet exciton density n can be expressed as

$$\frac{dn}{dt} = -\frac{n}{\tau} - fk(t)n^2, \tag{2}$$

with $f = i \cdot 1/2$ and $i \in \{1,2\}$, depending on the relaxation of the acceptor excited state $^3A^{**}$. We assume $i=1$, i.e., one triplet exciton remains on the product side of the process ($^3A^{**} \rightarrow {}^3A^*$). For an estimation of the initial $\mathrm{Ir(ppy)_3}$ triplet exciton density n_{Ir}, we analyzed samples with higher concentration (~ 1 mol %). The host emission of both samples was completely quenched by $\mathrm{Ir(ppy)_3}$ molecules, indicating that the host-guest energy transfer $k_{H\rightarrow G} = 1$. We assumed that the intersystem crossing (ISC) k_{ISC} to the $\mathrm{Ir(ppy)_3}$ triplet (T_1) state is unity.[7,10] n_{Ir} was calculated for minimal pump exciton density n_p by assuming $k_{H\rightarrow G} = 1$, thus, $n_{\mathrm{Ir}} = k_{H\rightarrow G} k_{\mathrm{ISC}} n_p$, which gave at the end a calibration factor C between photodiode (PD) signal, i.e., phosphorescence, and n_{Ir}, i.e., $n_{\mathrm{Ir}} = C(U - U_0)_{\mathrm{PD}}$. Here, U is the measured PD voltage and U_0 is the corresponding dark signal.

Figure 1 plots n_{Ir} versus n_p, i.e., the host singlet exciton density upon laser absorption. One can see that n_{Ir} scales linearly with the pump power at low excitation levels and then starts to saturate with increasing intensity. This saturation nicely agrees with the calculated guest density in the

[a]Electronic mail: sebastian.reineke@iapp.de.

 © 2009 American Institute of Physics

09 June 2025 16:36:26

SDC EX. 1032 - 2/4

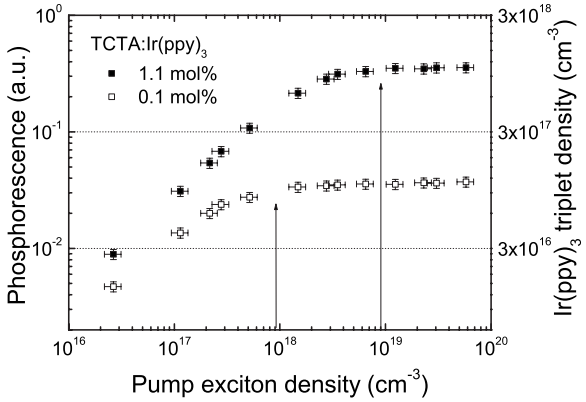

FIG. 1. n_{Ir} vs the pump exciton density n_p created on the host TCTA. Arrows indicate the calculated guest density. As a function of n_p, the phosphorescence increases linearly until n_{Ir} reaches the density of the phosphor. Upon further increase in n_p, the phosphorescence intensity remains constant, indicating a saturation of the phosphor sites.

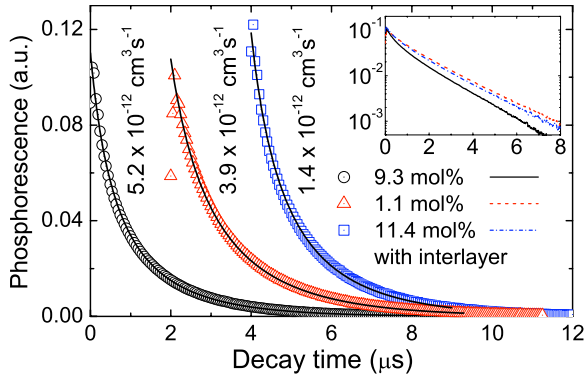

FIG. 3. (Color online) Photoluminescence transients of TCTA:$\mathrm{Ir(ppy)_3}$ mixed films with different composition. Solid lines: hopping-based fit calculations (with derived k_{TT}) Inset: data in semilogarithmic plot. Transients are separated in time for better visibility. The heterostructure with interlayers shows the smallest TTA rate constant.

mixed films, indicated by the arrows in Fig. 1 and therefore corresponds to the saturation of the phosphor.

The single-step long range Förster-type transition (cf. Ref. 8) in a specific mixed film is the limiting mechanism because it solely depends on the photophysical properties of the compounds, i.e., the phosphorescent lifetime τ and the spectral overlap between the phosphorescent emission and the $T_1 \rightarrow T_n$ absorption band of donor and acceptor, respectively.[8] Therefore, we analyze the data with respect to the contribution of Förster-type transitions to the overall TTA. Since it is not possible to distinguish between the different mechanisms leading to TTA, an upper limit of R_F is derived as a first step. Therefore, the photoluminescence transient of the highly diluted sample is analyzed, which shows purely monoexponential decay. The low emitter concentration assures that the guest molecules are spatially separated. The corresponding data for TCTA:$\mathrm{Ir(ppy)_3}$ are shown in Fig. 2. Additionally, fits based on the single-step Förster model are included, showing a variation in $R_F \in \{3,6,9,12\}$ nm.[8] The bimolecular term in Eq. (2) follows $k(t)=2/3\pi R_F^3\sqrt{\pi/(\pi t)}$. An increasing deviation from the experimental data is observed when R_F is increased while $R_F=3$ nm still follows the monoexponential decay. With $R_F=6$ nm, the differences become distinct. Therefore, from these data, $R_F=6$ nm is found as upper limit for the ${}^3D^*+{}^3A^* \rightarrow {}^1D+{}^3A^{**}$ transition, which is in good agreement with $R_F=2.9$ nm determined by Staroske *et al.*[8] For comparison,

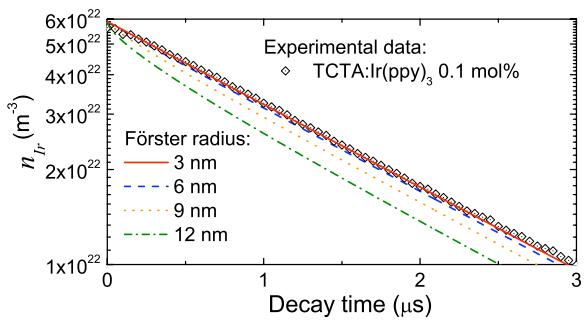

FIG. 2. (Color online) Photoluminescence transient of a 0.1 mol % TCTA:$\mathrm{Ir(ppy)_3}$ mixed film with maximum pump intensity while at the same time revealing solely monoexponential decay. Lines: fits (Förster model) under a variation in R_F. An increase in R_F shows a deviation from the experimentally observed photoluminescence decay.

Kawamura *et al.*[9] determined a Förster radius for the triplet energy transfer to a ground state acceptor, ${}^3D^*+{}^1A \rightarrow {}^1D+{}^3A^*$, to $R_F=1.4$ nm for a CBP:$\mathrm{Ir(ppy)_3}$ blend. The single-step Förster model is applied as a next step to all photoluminescence transients of the TCTA:$\mathrm{Ir(ppy)_3}$ samples with 1.1 and 0.1 mol %, under a variation in the pump intensity. The data can only be fitted with $R_F=(10\pm1)$ nm which by far exceeds the above-determined limit of 6 nm. This difference in R_F cannot be explained with an error in the determination of n_0, since it then must change roughly one order of magnitude to compensate ΔR_F. This gives further evidence that other mechanisms must be present in host:$\mathrm{Ir(ppy)_3}$ systems, leading to strong TTA.

Whenever excitons are not efficiently trapped at guest sites, they can migrate on a grid of unexcited guest or, if the energetic confinement is not given, on host molecules, mediated by individual hopping steps. Here, hopping is referred to as the triplet excited state transfer (Dexter-type) from site to site.[7] Finally, two excited states can annihilate when they reach their respective proximity. This leads to an additional, parasitic contribution to the overall TTA, ${}^3D^*+{}^3A^* \rightarrow [k(t)=8\pi\bar{a}\hat{D}=:k_{\mathrm{TT}}] \rightarrow {}^1D+{}^3A^{**}$, which is commonly represented by a time-independent rate constant k_{TT} with the critical distance $\bar{a}$ and the diffusion constant $\hat{D}$ for times much larger than the nearest neighbor hopping time, $t \gg t_{\mathrm{hop}}=\bar{a}^2/6\hat{D}$.[11] This mechanism becomes more likely when the dopant molecules form aggregates instead of being spatially separated within the host material. In order to investigate hopping-assisted TTA, two additional samples are prepared: sample I, a 20 nm TCTA:$\mathrm{Ir(ppy)_3}$ mixed film with 9.4 mol % and sample II, a sample with a layer sequence of $[A(1\ \mathrm{nm})/\mathrm{TCTA}(2\ \mathrm{nm})]_6/A(1\ \mathrm{nm})$, with A:=TCTA:$\mathrm{Ir(ppy)_3}$ and a nominal $\mathrm{Ir(ppy)_3}$ concentration of 11.4 mol % in A. In the latter, TCTA is inserted as exciton blocking layer owing its high triplet energy of $T_1=2.8$ eV.[12] Selected photoluminescence transients of those samples are shown together with data of the 1.1 mol % TCTA:$\mathrm{Ir(ppy)_3}$ in Fig. 3 for comparable initial triplet densities n_{Ir}. The solid lines in Fig. 3 correspond to fits based on the hopping model.[6,7] One can see that TTA is reduced with decreasing emitter concentration, as the deviation from monoexponential decay becomes smaller, which is reflected in the smaller k_{TT} of the 1.1 mol % sample. This concentration dependence

09 June 2025 16:36:26

SDC EX. 1032 - 3/4

in k_{TT} supports the hopping model, since a higher number of unexcited emitter molecules improves the exciton migration through the mixed film and, consequently, enhances TTA. In contrast, the single-step Förster mechanism is accompanied with a concentration independent R_F.[8] When comparing the photoluminescence transients of samples I and II, strongly reduced TTA is observed for the heterostructure sample comprising neat TCTA interlayers. Here, k_{TT} is only 27% of the value of sample I. It is taken into account that the active volume of sample II is roughly 1/3 of sample I. This results in higher n_{Ir} of sample II, necessary to obtain equal photoluminescence intensity. This decrease in k_{TT} can only be attributed to a decrease in hopping steps. By introduction of 2 nm thin neat TCTA interlayers in sample II, the excited states are efficiently hindered to migrate in one direction of space, reducing the random-walk process. In Ref. 12, we have shown that this heterostructure can be adapted to OLEDs as emission layer improving the OLED efficiency roll-off, i.e., the j_c can almost be doubled compared to a reference device. This suppression of exciton migration should also be achievable by reduction in the emitter concentration in a single mixed film down to values where the guest distance reaches values of the TCTA interlayer thickness. Assuming cubic closed packing such that every guest molecule is occupying the space of a TCTA molecule (density $\rho=1.139$ g cm^{-3}, and molar mass M=740.9 g mol^{-1}), one can compute the guest distance to 1.4 and 2.9 nm for 9.3 and 1.1 mol %, respectively. For the 1.1 mol % TCTA:Ir(ppy)$_3$ sample, the *guest distance is even greater* than the thickness of the undoped interlayers (~2 nm) of sample II. From this point of view, the homogenous sample with 1.1 mol % should have a very low k_{TT} since it should efficiently suppress exciton migration to all directions. In contrast, k_{TT} of sample II is only 36% of the value of the 1.1 mol % mixed film. As the estimation of the guest distance is based on a homogeneous distribution of Ir(ppy)$_3$, these results suggest that the preparation of mixed host:Ir(ppy)$_3$ films must be accompanied by formation of aggregates, i.e., regions of short guest-guest distance which enhance hopping-assisted TTA.[10]

To investigate possible aggregation, 50 nm TCTA:Ir(ppy)$_3$ films with a doping concentration of approximately 10 mol % were investigated by aberration (Cs) corrected STEM which were deposited onto a 2-micron hole carbon film. STEM 1 at Daresbury Laboratory equipped with a Nion Mark II Cs-corrector was operated at 100 kV accelerating voltage with a probe size of about 0.1 nm.[13] To study the iridium distribution in the film, the high angle annular dark field (HAADF) signal was used. It increases monotonously with the atomic number of the scattering atoms if the sample thickness is suitable and not changing rapidly on the length scale of interest.[14] Thus, since no other heavy element is included into the film composition, Ir atoms and agglomerates appear particularly bright in HAADF contrast. It is taken into account that the HAADF image of the Ir distribution represents a projection through a 50 nm thick film, of which the first few nanometers appear focused. Electron energy loss spectroscopy was used to prove that the bright areas are not caused by fluctuations in the amount of carbon content. Figure 4 shows the HAADF signal of a large film area. Images (a), (b), and (c) are taken with higher resolution. Iridium agglomerates of 3–4 nm [Fig. 4(a)] and few larger

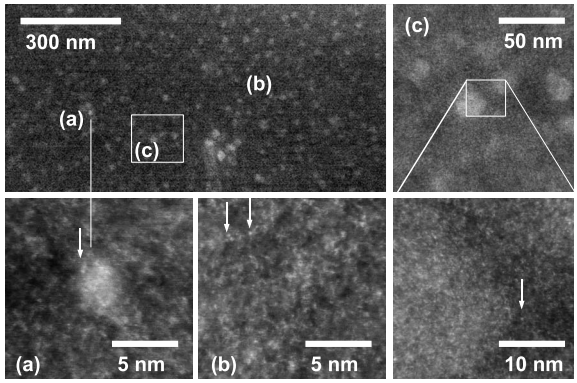

FIG. 4. HAADF images of the 50 nm TCTA:Ir(ppy)$_3$ film: small Ir agglomerates [(a) and (c)], randomly spread Ir (b).

ones of about 30 nm in diameter [Fig. 4(c)] are observed. They appear particularly bright among the otherwise evenly dustlike spread Ir [Fig. 4(b)] in the film. The small sharp bright dots in the high resolution images, marked by arrows for four examples, represent the HAADF signal of single Ir atoms in the slice of the film where the electron beam is focused. The left arrow in Fig. 4(b) points to a group of three Ir atoms. These images nicely show that mixed TCTA:Ir(ppy)$_3$ films strongly differ from films with a homogeneous emitter dopant distribution, necessary to reach the single-step Förster-limit.

In conclusion, we have shown that TTA in organic phosphorescent mixed films is strongly influenced by the emitter dopant aggregation, leading to a much stronger efficiency roll-off than expected from photophysical properties of the involved materials. To overcome this aggregation remains challenging, but bears great potential for phosphorescent OLEDs with high efficiency at very high brightness.

The authors thank for the opportunity to use the UK SuperSTEM at Daresbury Laboratory funded by the EPSRC. This work was funded by the DAAD (Project No. D/07/09995), the European Commission (Contract No. IST-2002-004607) and via the Leibniz prize of the Deutsche Forschungsgemeinschaft.

[1] Y. Sun, N. C. Giebink, H. Kanno, B. Ma, M. E. Thompson, and S. R. Forrest, Nature (London) **440**, 908 (2006).
[2] G. Schwartz, M. Pfeiffer, S. Reineke, K. Walzer, and K. Leo, Adv. Mater. (Weinheim, Ger.) **19**, 3672 (2007).
[3] M. A. Baldo, M. E. Thompson, and S. R. Forrest, Nature (London) **403**, 750 (2000).
[4] D. Tanaka, Y. Agata, T. Takeda, S. Watanabe, and J. Kido, Jpn. J. Appl. Phys., Part 2 **46**, L117 (2007).
[5] R. G. Kepler, P. Avakian, J. C. Caris, and E. Abramson, Phys. Rev. Lett. **10**, 400 (1963).
[6] M. A. Baldo, C. Adachi, and S. R. Forrest, Phys. Rev. B **62**, 10967 (2000).
[7] S. Reineke, K. Walzer, and K. Leo, Phys. Rev. B **75**, 125328 (2007).
[8] W. Staroske, M. Pfeiffer, K. Leo, and M. Hoffmann, Phys. Rev. Lett. **98**, 197402 (2007).
[9] Y. Kawamura, J. Brooks, J. J. Brown, H. Sasabe, and C. Adachi, Phys. Rev. Lett. **96**, 017404 (2006).
[10] T. Tsuboi, J. Lumin. **119**, 288 (2006).
[11] R. C. Powell and R. G. Kepler, Phys. Rev. Lett. **22**, 636 (1969).
[12] S. Reineke, G. Schwartz, K. Walzer, and K. Leo, Appl. Phys. Lett. **91**, 123508 (2007).
[13] O. L. Krivanek, N. Dellby, and A. R. Lupini, Ultramicroscopy **78**, 1 (1999).
[14] S. J. Pennycook and D. E. Jesson, Phys. Rev. Lett. **64**, 938 (1990).

09 June 2025 16:36:26