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Triplet exciton diffusion in *fac*-tris(2-phenylpyridine) iridium(III)-cored electroluminescent dendrimers

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We have studied triplet-triplet annihilation in neat films of electrophosphorescent *fac*-tris(2-phenylpyridine) iridium(III) [Ir(ppy)$_3$]-cored dendrimers containing phenylene- and carbazole-based dendrons with 2-ethylhexyloxy surface groups using time-resolved photoluminescence. From measured annihilation rates, the limiting current densities above which annihilation would dominate in dendrimer light-emitting devices are found to be >1 A/cm^2. The triplet exciton diffusion length varies in the range of 2–10 nm depending on the dendron size. The distance dependence of the nearest-neighbor hopping rate shows that energy transfer is dominated by the exchange mechanism. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1867571]

Exciton diffusion is an important physical process in the operation of organic light-emitting diodes (OLEDs). It can lead to excitons migrating out of the intended emissive layer, quenching by diffusion to contacts, and quenching by exciton-exciton annihilation.[1–7] Exciton annihilation occurs when two excitons meet and form a single higher excited state, thus leading to the loss of an exciton.[7] Exciton annihilation depends on the concentration of excitons: At high concentrations, excitons will meet more frequently, leading to faster decay. It also depends on the diffusion constant of the excitons: Faster diffusion will lead to excitons meeting more frequently and faster decay. We show that measurements of time-resolved luminescence at a range of excitation densities provide a useful way of studying this process, and deducing the diffusion constants of excitons. Exciton-exciton annihilation is a particular issue in phosphorescent materials because of the longer exciton lifetime, and leads to a decrease of electroluminescence (EL) efficiency at high current densities.[3–6]

In this letter, we report the intensity dependence of time-resolved photoluminescence (PL) in films of *fac*-tris(2-phenylpyridine) iridium (III) [Ir(ppy)$_3$]-core dendrimers. The intermolecular distance is altered by changing the size of the dendron. We measured triplet-triplet annihilation constants and estimated limiting current densities for the dendrimer OLEDs. We show that the exciton hopping rate between nearest neighbors decreases exponentially with distance, thus it is dominated by the exchange (Dexter) interaction in neat dendrimer films.

Three dendrimers were studied: The first-generation (Ir-G1) and the second-generation (Ir-G2) dendrimers consist of an Ir(ppy)$_3$ core, phenylene-based dendrons, and 2-ethylhexyloxy surface groups, while first-generation Ir(ppy)$_3$ carbazole dendrimer (Ir-Carb) contains a Ir(ppy)$_3$ core, carbazole-based dendrons, and 2-ethylhexyloxy surface groups (see inset in Fig. 1). Dendrimer films were made by spin coating from chloroform solution onto fused silica substrates at typical concentrations of 20 mg/ml and a spin speed of 800 rpm. The PL kinetics were measured by time-correlated single-photon counting. Excitation was tuned in the range of 375–400 nm by using the second harmonic of a femtosecond Ti-sapphire laser. No dependence on excitation wavelength was observed. An acousto-optic pulse picker was used to reduce the repetition rate to 100 kHz. The excitation spot size was measured with a beam profiler to be 20 μm (full width at half maximum). The emitted light was dispersed in a monochromator with an entrance slit corresponding to a bandwidth of 25 nm and detected with a cooled Hamamatsu microchannel plate photomultiplier tube RU-3809U-50. Measurements were performed at room temperature in a vacuum of ~10^{-6} mbar.

Figure 1 shows the absorption and PL spectra of Ir-G1, Ir G2, and Ir-Carb neat ~80 nm thick films. Absorption in the 330–450 nm spectral region is due to a singlet-singlet

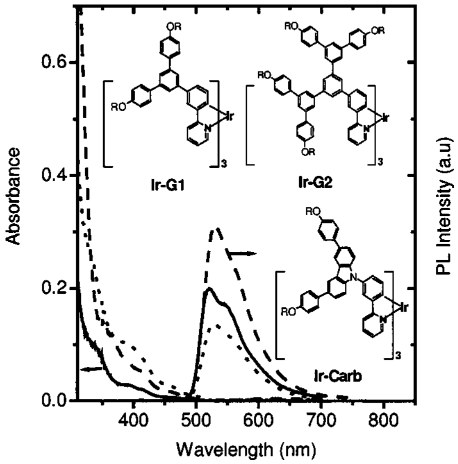

FIG. 1. Absorption and PL spectra of 80 nm thick neat films of the Ir-G1 (dotted lines), Ir-G2 (solid lines), and Ir-Carb dendrimer (dashed lines). Inset shows the chemical structures of Ir-G1, Ir-G2, and Ir-Carb dendrimers. R =2-ethylhexyl.

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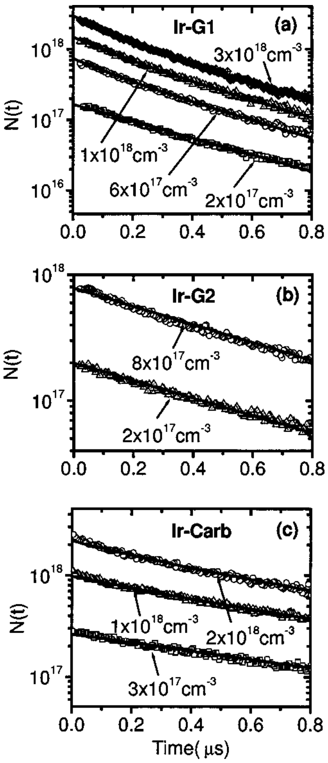

FIG. 2. Intensity dependent PL kinetics of (a) Ir-G1, (b) Ir-G2, and (c) Ir-Carb neat film. Detection wavelength were at the peak of the emission wavelengths.

metal-to-ligand charge transfer (MLCT) transition of the Ir(ppy)$_3$ core and its strength is similar in all the dendrimers studied. The higher absorption at shorter wavelengths is due to the dendrons. The PL emission has a maximum at ~530 nm in Ir-G1 and Ir-G2, whereas in Ir-Carb it is slightly redshifted due to higher electron delocalization. PL emission in these dendrimers is due to radiative decay of the triplet state (^{3}MLCT) to the ground state.[8,9] The absorption and emission spectra show very little overlap.

Figure 2 shows the intensity dependent PL kinetics of Ir-G1 neat films. The initial PL decays in Ir-G1 at excitation density of $\leqslant 2.0 \times 10^{17}$ cm^{-3} is exponential with a time constant of 0.4 μs. At higher excitation density, the initial decay becomes faster and deviates significantly from a single exponential. The reported transient EL of a 6% Ir(ppy)$_3$:CBP device[3] also shows a similar trend at excitation densities of $\sim 1 \times 10^{18}$ cm^{-3}. In both cases, the faster decay at higher excitation density is due to the triplet-triplet annihilation process.

PL intensity is proportional to the density of triplet excitons $N(t)$ as a function of time which can be described by the rate equation

$$\frac{\partial}{\partial t}N(t) = -kN(t) - \gamma N^2(t), \tag{1}$$

where k is the decay rate of excitations in the absence of the annihilation and γ is annihilation constant. The solution of Eq. (1) is

$$N(t) = \frac{N(0)\exp(-kt)}{1 + \frac{\gamma}{k}N(0)[1-\exp(-kt)]}, \tag{2}$$

where $N(0)$ is the ^{3}MLCT exciton density immediately after laser pulse excitation. The solid lines in Fig. 2 represent the fits by Eq. (2). The best fits to the experimental data are obtained using the γ values given in Table I.

Figure 2 also shows the intensity dependent PL kinetics of Ir-G2 and Ir-Carb films. The initial PL decays for Ir-G2 and Ir-Carb neat films are independent of excitation density for values up to $\leqslant 2.0 \times 10^{17}$ cm^{-3} with a time constant of 0.6 and 1 μs, respectively. At higher excitation, the initial decay becomes faster, and the γ values fitted to the data are shown in Table I. The annihilation constant for Ir-G1 is found to be the highest, and for Ir-G2 the lowest. The bigger dendrons of Ir-G2 separate Ir(ppy)$_3$ chromophores in the films and reduce the exciton diffusion rate.

Triplet-triplet annihilation in OLEDs has been considered in detail by Baldo *et al.*,[3] and in a similar way we can use the γ values to estimate a current density J_0, at which triplet-triplet annihilation leads to a halving of the EL intensity,

$$J_0 = \frac{2q \cdot d}{\gamma \cdot \tau^2}, \tag{3}$$

where q is the electron charge, d is the thickness of the exciton formation zone, and τ is the phosphorescence lifetime. J_0 can be used to quantify the relative merits of different phosphors employed in OLEDs. We have used Eq. (3) with the measured γ, τ values and assume $d \sim 25$ nm to estimate the value of J_0 for LEDs made from neat films of each dendrimer. As can be seen from Table I, we find J_0 to be >1 A/cm^2 for all three dendrimers, and this is consistent with our earlier finding in the OLEDs where external quantum efficiencies do not decrease with increasing current density over the range measured which was up to 100 mA/cm^2.[10,11] It is interesting to note that the reported values for J_0 for 8% Ir(ppy)$_3$:CBP device were much smaller (5.7 and 630 mA/cm^2) than the estimated values J_0 for our dendrimer films. A possible explanation for the more pronounced triplet-triplet annihilation could be clustering of the Ir(ppy)$_3$ in the CBP blend.[8,12,13]

From the annihilation constant, we can estimate the diffusion constant of triplet excitons in dendrimer films using the relation for three-dimensional (3D) diffusion:

TABLE I. Triplet-triplet annihilation constant (γ), center to center distance (R_{eff}), current density (J_0), diffusion coefficient (D), diffusion length (L_d), and hopping rate k_{hop} of the dendrimer films.

Sample	R_{eff}^a (Å)	γ (10^{-14} cm^3 s^{-1})	J_0 (A/cm^2)	D (10^{-9} cm^2 s^{-1})	L_d (nm)	k_{hop} (10^6 s^{-1})
Ir-G1	18.7	200	2.5	400	10	70
Ir-Carb	19.5	30	2.6	60	6	9
Ir-G2	22.8	5	44	8	~2	1

[a] Assuming density 1 g/cm^3; The uncertainty in γ, J_0, D, and k_{hop} values are ±50%. The uncertainty in L_d is ±25%.

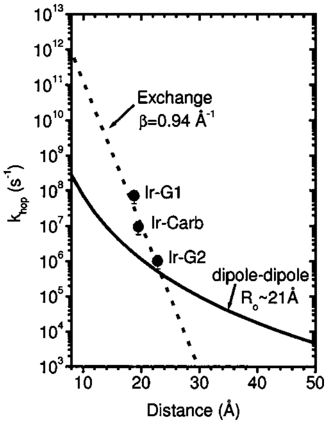

FIG. 3. Dependence of hopping rates on the distance of the closest sites of the dendrimers. Dotted line is fit with the Eq. (6) using $\beta = 0.94$ Å^{-1}. The solid line is the predicted dipole-dipole transfer rates for $R_0 = 21$ Å.

$$\gamma = 8\pi R_{\mathrm{eff}} D, \tag{4}$$

where D is the exciton diffusion constant and R_{eff} is the average lattice spacing calculated assuming a film density of ~ 1 g/cm^3 (Table I). From the diffusion constant, we obtain the diffusion length in a 3D film as, $L_d = \sqrt{6D\tau}$ (see Table I). The diffusion length decreases as the intermolecular spacing increases and is about five times smaller in Ir-G2 films. The diffusion becomes slow as intermolecular distance increases thus preventing the exciton reaching quenching sites. The small diffusion lengths (2–10 nm) provide an explanation for why exciton blocking layers are not needed in dendrimer light-emitting devices (LEDs).

Finally, we consider whether exciton diffusion occurs by a Förster or a Dexter mechanism. The nearest-neighbor hopping rates of excitation, k_{hop} in the 3D case is

$$k_{\mathrm{hop}} = \frac{6D}{R_{\mathrm{eff}}^2}. \tag{5}$$

Förster and Dexter transfer have very different scaling with spacing and, hence, a plot of k_{hop} versus R_{eff} enables us to distinguish between the two processes. The hopping rates obtained decrease exponentially with distance as shown in Fig. 3. This indicates that exciton diffusion is governed by the exchange mechanism and can be described by the following equation:

$$\ln k_{\mathrm{hop}} = \ln k_{\mathrm{hop}}^0 - \beta(r - r_0), \tag{6}$$

where β is the attenuation factor, r is the center to center distance, and k_{hop}^0 is the hopping rate at the van der Waal's distance r_0. The best fit gives $\beta = 0.94$ Å^{-1} and k_{hop}^0 $\sim 10^{12}$ s^{-1} at $r_0 = 8$ Å. Förster energy transfer involves dipole-dipole interactions and so is weak for triplet excitons. However, strong spin-orbit coupling increases the oscillator strength of the triplet-singlet transition and leads to a finite rate of Förster energy transfer. The transfer rate dependence on intermolecular distance is given by $k_{d\text{-}d} = (1/\tau)(R_0/r)^6$, where τ is the excited state lifetime of the donor dendrimers in dilute solution, taken as ~ 1.2 μs,[8,9] and R_0 is the Förster radius. From the overlap of absorption and emission spectra,[14] we get $R_0 = 21 \pm 3$ Å. The plot of the dipole-dipole transfer rate as a function of intermolecular distance in Fig. 3, indicates that the dipole-dipole energy transfer dominates at distances $\geqslant 26$ Å and its contribution at $\leqslant 26$ Å is significantly less than that of the exchange interaction.

In summary, we have measured triplet-triplet annihilation constants and exciton diffusion lengths in dendrimer films. The triplet-triplet annihilation constants are in the range of $5\text{–}200 \times 10^{-14}$ cm^3 s^{-1} and depend strongly on the dendron size. The estimated current densities for triplet-triplet annihilation to halve the efficiency of a dendrimer LED are >1 A/cm^2. The nearest-neighbor hopping rate decreases exponentially with intermolecular spacing indicating that energy migration is dominated by the exchange mechanism.

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