

## Singlet energy transfer and singlet-singlet annihilation in light-emitting blends of organic semiconductors

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Excitation energy transfer from host to guest is studied in spin-cast blends of 4,4'-bis(*N*-carbazolyl)biphenyl (CBP) and a phosphorescent *fac*-tris(2-phenylpyridyl)iridium(III)-cored dendrimer using time resolved fluorescence. The kinetics of energy transfer are consistent with homogeneous dispersion of the dendrimers in the CBP host. Diffusion-controlled singlet-singlet exciton annihilation is observed in the CBP host at moderate excitation densities, similar to those encountered in high brightness light-emitting devices and organic lasers. The results are important for organic lighting and the understanding of exciton diffusion in guest-host systems for electrophosphorescence. © 2009 American Institute of Physics. [doi:10.1063/1.3253422]

Organic guest-host systems offer a promising route to make inexpensive light-emitting diodes (LEDs) with high efficiency and brightness<sup>1-10</sup> and low-threshold organic lasers.<sup>11,12</sup> Increasing the distance between light emitting guest chromophores helps to reduce concentration quenching<sup>13-15</sup> and losses associated with exciton dissociation, exciton-exciton annihilation, and exciton-charge interactions, which occur at high electric fields and high current densities.<sup>11,15-20</sup> A particularly widely used host for organic LEDs is the organic semiconductor 4,4'-bis(*N*-carbazolyl)biphenyl (CBP).<sup>2-9</sup> CBP is also of current interest as a host for laser gain media, with the potential for low threshold or even electrical pumping.<sup>11,12</sup> Given the widespread use of guest-host systems it is important to understand the energy transfer process from host to guest and the role of exciton-exciton annihilation in the host material. The issues are even more important at high excitation densities as would be encountered in high brightness LEDs and lasers. Triplet exciton diffusion and triplet-triplet annihilation has been studied in CBP films,<sup>21</sup> but no such study has been reported for singlet excitons.

In this work, we have studied singlet excitation transfer in blends of CBP with a phosphorescent *fac*-tris(2-phenylpyridyl)iridium(III)-cored dendrimer (IrG1), which have been used previously to make efficient solution-processable LEDs.<sup>7,8</sup> The results show that IrG1 dendrimers can form uniform blends with CBP without any significant phase separation. We also report a study of singlet-singlet exciton annihilation in CBP films and discuss the implications for LEDs and lasers.

Neat and blended films were spin coated onto fused silica substrates from chloroform solutions at a concentration of 20 mg/ml and using a spin speed of 1000 rpm. The absorption coefficient and the refractive index of the IrG1 film

were measured using variable-angle spectroscopic ellipsometry on a J. A. Woollam, Inc. M-2000DI instrument. Time-resolved photoluminescence (PL) was measured using 100 fs light pulses at 330 nm with a repetition rate of 5 kHz for excitation and a Hamamatsu synchroscan streak camera with a spectrograph for detection. The excitation spot size was 250  $\mu\text{m}$  (at  $1/e^2$  of the maximum intensity). The fluorescence quantum yield of the CBP film was measured in an integrating sphere using a previously described method<sup>22</sup> under a flowing nitrogen atmosphere.

Figure 1(a) shows the absorption coefficient of an IrG1 film and the PL spectrum of a CBP film. There is good spectral overlap between the CBP emission and IrG1 absorption, which implies the possibility of radiation-less energy transfer by dipole-dipole interaction. This is confirmed by the steady state PL spectrum of the IrG1:CBP (20:80 wt %) blend [Fig. 1(b)], which shows only IrG1 emission with a peak at 520 nm. The transient PL spectrum recorded in the time window from 10 to 20 ps after excitation shows a weak emission between 400 and 450 nm, which is assigned to CBP fluorescence because the IrG1 fluorescence has been reported to have much shorter (<70 fs) decay time in this spectral window.<sup>23</sup> It also shows strong IrG1 emission implying that energy transfer to IrG1 occurs predominantly within 10 ps.

Figure 2 shows the decay of CBP fluorescence in the same blend, which represents the kinetics of energy transfer to IrG1. The energy transfer rate  $k$  in the weak dipole-dipole coupling limit can be calculated using the Förster formula,<sup>24</sup>  $k=(R_0/R)^6/\tau$ . Here  $\tau=0.5$  ns is the CBP fluorescence decay time,  $R$  is a distance between donor and acceptor transition dipoles, and  $R_0$  is the Förster radius, which can be calculated using  $R_0^6=(9000\kappa^2\phi \ln 10)/(128\pi^2n^4N_A)\int_0^\infty F_D(\lambda)\epsilon_A(\lambda)\lambda^4d\lambda$ , where  $\kappa^2=2/3$  in the case of random dipole orientation,  $F_D(\lambda)$  is the donor's fluorescence normalized by area,  $\phi$  is the fluorescence quantum yield of the donor,  $\epsilon_A(\lambda)$  is the molar decadic extinction coefficient of the acceptor,  $n$  is the refractive index of the medium,  $N_A$  is Avogadro's number,

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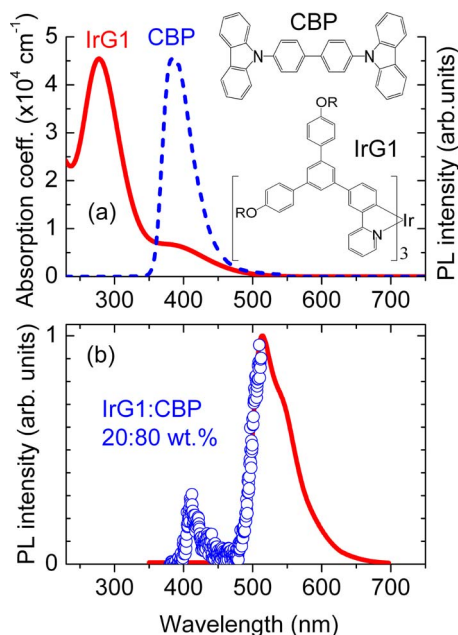


FIG. 1. (Color online) (a) Absorption coefficient of IrG1 film (solid line) and photoluminescence spectrum of CBP film (dashed line). The inset shows chemical structures of CBP and IrG1, where R=2-ethylhexyl. (b) Steady state PL spectra of IrG1:CBP (20:80 wt %) blend (solid line) and the transient PL spectrum of the same blend in the time interval from 10 to 20 ps (circles), emission at wavelengths shorter than 400 nm is absorbed by a cutoff filter.

and  $\lambda$  is the wavelength. We used the absorption coefficient  $\alpha(\lambda)$  of IrG1 film obtained from ellipsometry [Fig. 1(a)] to determine  $\varepsilon_A(\lambda) = \alpha(\lambda) / (c \ln 10)$ . Here  $c$  is the concentration of dendrimers in the film calculated as  $c = 1000\rho / M_w$ , where  $\rho = 1.1 \text{ g/cm}^3$  is the density of the film measured by neutron reflectivity and  $M_w = 2109 \text{ g/mol}$  is the molecular weight of IrG1. From the spectra in Fig. 1(a) and using the measured values of  $\phi = 0.5$  and  $n = 1.7$  we calculated  $R_0 = 2.8 \text{ nm}$  for energy transfer from CBP to IrG1 in film.

The number of IrG1 dendrimers in  $1 \text{ cm}^3$  of the blend was calculated to be  $N_d = 6.3 \times 10^{19} \text{ cm}^{-3}$  using  $N_d = f \cdot \rho \cdot N_A / M_w$ , where  $f = 0.2$  is the fraction of IrG1 in the blend. We have modelled our results in two limiting cases: energy transfer to the dendrimer (without exciton diffusion), and exciton diffusion to the dendrimer. We assume that the IrG1 dendrimers are homogeneously dispersed in the CBP

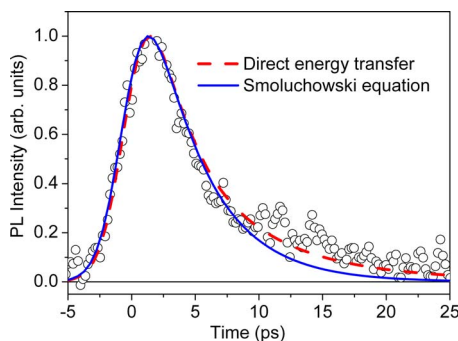


FIG. 2. (Color online) PL decay of CBP in IrG1:CBP (20:80 wt %) blend detected in the spectral window between 390 and 460 nm (circles). The dashed line shows the simulated kinetics using the Förster formula for a direct energy transfer and the solid line is a fit to the data using the Smoluchowski equation, which gives  $D = 0.003 \text{ cm}^2 \text{ s}^{-1}$ . The fits are convolved with the instrument response function.

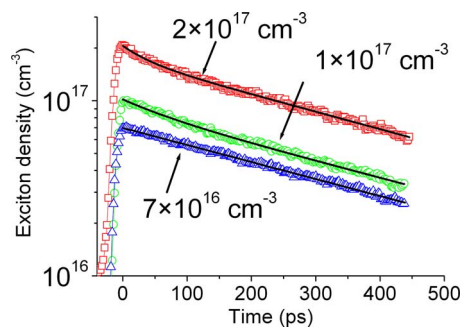


FIG. 3. (Color online) PL decays of the CBP neat film at different initial excitation densities. The solid lines are fits with a time-independent annihilation constant  $\gamma = 6 \times 10^{-9} \text{ cm}^3/\text{s}$ .

host at a molecular scale, which was inferred in a previous study of triplet-triplet annihilation.<sup>15</sup> In this case the average center-to-center distance between IrG1 dendrimers is  $N_d^{-1/3} = 2.5 \text{ nm}$ . We have modeled the direct energy transfer in the blend assuming a cubic unit cell with a point dipole of the acceptor molecule located in the center of the cube. The length of a side of this cube is set to the average distance between IrG1 dendrimers of 2.5 nm. Approximating the dendrimer as a sphere, the radius of IrG1 is 0.9 nm, which is close to the measured hydrodynamic radius of 1.0 nm (Ref. 25). In the model, the CBP part of the unit cell is initially populated with singlet excitons, and the subsequent energy transfer to the dendrimers at the center of the unit cell and at the center of nearest neighbor unit cells was calculated. The result was convolved with the instrument response function to compare with experiment. Figure 2 shows that the simulated decay is close to the measured PL decay.

As an alternative scenario, we have considered diffusion of the excitons to the dendrimer. In this case we have fitted the data with a nondispersive exciton diffusion coefficient  $D$  using the Smoluchowski equation  $k = 4\pi DR_c N_d (1 + R_c / \sqrt{\pi Dt})$ , where  $R_c$  is the exciton capture radius and set to 0.9 nm, which is the radius of IrG1 dendrimer and  $N_d$  is the concentration of IrG1 dendrimers calculated as described above assuming that dendrimers are homogeneously dispersed. The best fit gives a value  $D = (3.0 \pm 0.5) \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ , which is similar to  $D = (4 \pm 1) \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$  obtained from the measured exciton diffusion length in a CBP film.<sup>26</sup> Hence our PL decay measurements can be explained either by energy transfer (without diffusion) or by exciton diffusion. This means that the value for the diffusion coefficient we obtain is an upper limit. The important point, however, is that the very rapid decay of the PL from CBP implies that the IrG1 dendrimers are fully dispersed through the CBP host material. If there were aggregation of the dendrimers in the films studied here, the measured decay would be much slower.

Exciton-exciton annihilation, which occurs at high exciton densities, is detrimental to operation of high brightness light-emitting devices and organic lasers.<sup>17-21</sup> Figure 3 shows the PL kinetics measured in a CBP neat film at different excitation pulse energies, which taken together with the fraction of light absorbed and the size of excitation spot allows us to determine the initial exciton density assuming that one absorbed photon generated one exciton. When the excitation density increases, the PL decays become faster due to exciton-exciton annihilation. The PL intensity is proportional

to the density of singlet excitons  $N(t)$ , which in the case of a short excitation pulse and a time-independent annihilation constant  $\gamma$  can be described by<sup>15,17</sup>  $N(t)=[N_0 \exp(-t/\tau)]/\{1+\gamma\cdot\tau\cdot N_0[1-\exp(-t/\tau)]\}$ , where  $N_0$  is the initial excitation density and  $\tau=0.5$  ns is the decay time in the absence of annihilation. The results in Fig. 3 fit well with a single value of  $\gamma=(6\pm 1)\times 10^{-9}$  cm<sup>3</sup>/s, which indicates that the annihilation is diffusion-controlled. In this case<sup>15,17</sup>  $\gamma=4\pi DR_a$ , where  $R_a$  is the annihilation radius. The diffusion coefficient  $D$  in the neat CBP film is expected to be the same as in the blend because the diffusion occurs by incoherent hopping and is therefore insensitive to scattering effects. Using the measured  $\gamma$  value and our upper limit for  $D$  of  $3\times 10^{-3}$  cm<sup>2</sup>/s we obtain a lower limit for the annihilation radius  $R_a$ , of 1.6 nm. This value is larger than the exciton capture radius  $R_c=0.9$  nm used in the Smoluchowski equation, which suggests that the spectral overlap of the CBP emission with its excited state absorption is larger than with the ground state absorption of IrG1.

Our results have the following implications for solution-processed light emitting devices. The energy transfer kinetics show that there is an essentially homogeneous dispersion of IrG1 dendrimer in the CBP. This is a desirable morphology for capture and recombination of electrons and holes on phosphorescent emitters in organic LEDs, and for avoiding concentration quenching. It also helps to reduce field-induced dissociation of phosphorescent excitons and their quenching by injected charges. An optically pumped field effect transistor structure using CBP as a host showed amplified spontaneous emission with a threshold of  $2.5\ \mu\text{J cm}^{-2}$ , which corresponds to the pump intensity at which optical gain exceeds losses.<sup>12</sup> This is equivalent to a singlet exciton density of about  $10^{18}$  cm<sup>-3</sup>, at which the singlet-singlet annihilation in CBP molecules will be much more pronounced than at the lower densities used in Fig. 3. Our results show that exciton-exciton annihilation would compete with energy transfer to the laser dye, which is dispersed in CBP at a concentration of typically 6 wt %. Accordingly the optimal concentration of the guest molecule under such conditions may be higher.

In conclusion, we have studied singlet energy transfer from photoexcited CBP molecules to a phosphorescent iridium(III) complex-cored dendrimer. Very fast energy transfer is observed, which shows that the IrG1 dendrimers are homogeneously dispersed in the CBP host at a molecular scale. Exciton diffusion controls the singlet-singlet exciton annihilation rate in CBP, which has to be taken into account when modeling organic lasers.

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