Temperature dependence of electronic energy transfer from a polymer host to a triplet emitter in light emitting diode materials

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Abstract

We investigate the temperature dependence of electronic energy transfer between a polymer host, poly(N-vinylcarbazole) blended with 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole, and the triplet emitter tris[9,9-diethyl-2-(phenyl-4′-(pyridin-2″-yl))fluorene] iridium(III) (Ir(DPPF)3). The photophysics of the blend are similar to those of neat poly(N-vinylcarbazole), with two emitting species corresponding to shallow and deep excimer traps. When the blend is doped with Ir(DPPF)3, the deep trap emission is preferentially quenched. This quenching cannot be explained by simple Förster energy transfer to the dopant. Instead, the data are consistent with a rapid, temperature-dependent partitioning of the energy between the two host species and the Ir(DPPF)3, each of which decays independently.

1. Introduction

Light-emitting diodes based on organic semiconducting polymers have improved steadily in both efficiency and stability, and have now reached the stage of commercialization. A major advance in the field occurred when it was realized that the fraction of triplet excitons created by charge recombination could be harvested by strongly emitting triplet energy acceptors [1]. Since the original demonstration of highly efficient triplet harvesting by Forrest and coworkers [2], a number of other groups have demonstrated efficient electrophosphorescence in a variety of organic-based materials [3–5]. Recent work by Gong et al. [6–8] has shown that the combination of iridium complexes (tris[9,9-diethyl-2-(pyridinyl-2′) fluorene] iridium (III) (Ir(DPPF)3), tris[9,9-diethyl-2-(phenyl-4′-(pyridin-2″-yl)) fluorene] iridium(III) (Ir(DPPF)3) and tris[2,5-bis-2′-(9,9′-diethylfluorene) iridium] (Ir(HFP)3)
in a blend of poly(N-vinylcarbazole) (PVK) and 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) can result in highly efficient electroluminescence in the green and red. For all these materials, there are several ways in which electrical energy, in the form of separated electrons and holes, can be converted into phosphorescence from a triplet emitter. These include charge recombination directly on the triplet acceptor, charge recombination in the host material to form a triplet exciton which undergoes Dexter energy transfer to the acceptor, and finally charge recombination in the host to form a singlet exciton which transfers its energy via long-range Förster transfer.

In this Letter we investigate the dynamics of host–guest energy transfer for Ir(DPPF)₃ doped into the PVK–PBD blend material in more detail by measuring the photoluminescence (PL) dynamics at various temperatures. The highly efficient emission of this material has been attributed to Förster energy transfer from the excited host PVK–PBD blend to the Ir(DPPF)₃ due to the overlap of their respective emission and absorption spectra [8]. From our data, it appears that this energy transfer process is more complicated than simple Förster transfer. In the PVK–PBD blends studied here, we find that photoexcitation leads to the formation of two types of states whose broad emission spectra overlap but which have different lifetimes. Following previous work on neat PVK, we attribute the short-lived emission to a shallow trap state which dominates at lower temperatures, while the long-lived emission belongs to a deep trap whose formation is favored at high temperatures. When the PVK–PBD blend is doped with the triplet emitter Ir(DPPF)₃, we find that the deep trap emission is suppressed. By studying the temperature dependence of both the host and guest emission, we show that the deep trap and the dopant directly compete for the initial excitation energy, with the Ir(DPPF)₃ being the favored acceptor on the sub-nanosecond timescale. We find that another, slow (microsecond) energy transfer process contributes to the phosphorescence as well, although as a relatively small channel. The fact that the Ir(DPPF)₃ selectively displaces the deep trap may help explain why it is so efficient at harvesting energy from its polymer host.

2. Experimental

The synthesis of Ir(DPPF)₃ was reported elsewhere [9]. Poly(vinylcarbazole) (PVK) and 2-tert-butylphenyl-5-biphenyl-1,3,4-oxadiazol (PBD) were purchased from Aldrich. Their molecular structures were shown in the inset of Fig. 1. The thin film was prepared by spin-casting from the solution (dichloroethane as the solvent) on quartz substrates for spectroscopy measurements. Two kinds of solid films were made. One is Ir(DPPF)₃ doped into poly(methyl methacrylate) (PMMA) with the ratio of Ir(DPPF)₃/PMMA = 1 wt%; another is Ir(DPPF)₃ doped into PVK–PBD with the ratio of Ir(DPPF)₃/PVK–PBD (40 wt%) = 1 wt%. The film quality was high and all films had approximately the same thickness (for direct comparison of the emission intensities).

For time-resolved PL decay measurements, the samples are mounted in a compressed helium cryostat under argon filled glove bag to avoid air-exposure. Excitation pulses at 325 nm are gener-
ated by using a home-built non-collinear optical parametric amplifier (NOPA) with the 800 nm output of a 40 kHz regenerative amplifier (Spectra Physics, Spitfire). Continuum seed pulses are generated by focusing the 800 nm beam in a 2 mm sapphire plate and amplified in a 1 mm BBO (31°, Type I phase-matching) pumped by the 400 nm pumping beam. In this experiment, 650 nm pulses are selected by an interference filter (10 nm FWHM, Andover) and amplified. Then the 650 nm NOPA output is frequency doubled using 0.1 mm BBO and remaining 650 nm pulses are removed with two UG11 filters. Picosecond time-resolved fluorescence spectra are measured using a streak camera (Hamamatsu, streak scope C4334) [10]. The samples are excited with the beam coming in at an angle of about 20° from the sample surface normal. The emission is collected normal to the sample surface, collimated, filtered with a long-wave pass filter (400 nm cut-off, Andover) and focused into a spectrometer (Spectra-Pro-150) with a 150 grooves/mm grating to disperse the spectrum before the streak camera. The excitation fluence is kept below 1 μJ/cm² to avoid high fluence effects such as the amplified spontaneous emission [11,12]. The instrumental response time of this measurement is about 50 ps in a 5 ns sweep window. Steady-state photoluminescence (PL) spectra of thin films were measured on an Ocean Optics S-2000 spectrometer with the same 325 nm excitation pulses.

3. Results and discussion

In Fig. 1 we show the temperature dependent emission spectrum of the Ir(DPPF)₃/PVK–PBD after excitation at 325 nm, which is near the absorption peak of both the blend and the complex. At the 1% doping level used in these experiments, the ratio of PVK–PBD absorption to Ir(DPPF)₃ absorption is approximately 40. The broad excimer-like emission centered at 420 nm corresponds to what is seen in the PVK–PBD blend by itself, and does not change as the temperature increases from 4 to 290 K. This contrasts with the behavior of the undoped blend, where the 420 nm emission increases by a factor of two over the same temperature range. The Ir(DPPF)₃ emission peaks at 548 nm and has the well-defined vibronic peaks commonly seen for these organometallic compounds. As the temperature increases from 4 to 50 K, the amount of Ir(DPPF)₃ emission remains fairly constant. From 50 to 290 K, however, the integrated emission in this spectral region increases by a factor of 8. In addition, we see some spectral broadening, most likely due to an increase in the homogeneous linewidth with temperature. In summary, no largescale spectral shifts or shape changes are observed as the temperature is varied, but the relative quantum yield of the guest molecules increases by a factor of 8 from 50 to 290 K.

The increase in quantum yield in the PVK–PBD blend is accompanied by a change in the host emission decay dynamics. This can be seen in Fig. 2a, where the fluorescence decay of the 420 nm emission is plotted for 50, 100, and 290 K. Following earlier treatments of excimer dynamics in neat PVK [13–15], we fit the data using a bi-exponential decay

$$S_{420}(t) = A_1 \exp[-k_1t] + A_2 \exp[-k_2t].$$

The decay times $1/k_1 = 0.9$ ns and $1/k_2 = 14$ ns are temperature independent, but the prefactors $A_1$ and $A_2$ are allowed to vary. As can be seen from the figure, this analysis yields acceptable fits to the data. This bi-exponential decay is the result of two distinct species, whose spectra overlap and whose relative populations are controlled by a fast, thermally activated diffusion process modulated by the high degree of disorder in the polymer. The longer lived species is slightly redshifted from the shorter lived species (similar to the situation in neat PVK), and the relative weighting of the two decay components varies with wavelength. In analogy with previous work on PVK, we assign the short-lived component to a ‘shallow trap’ and the long-lived component to a ‘deep trap’ [13–15]. We note that this designation of the ‘shallow’ and ‘deep’ trap states is not rigorous in the PVK–PBD blend, and should be regarded simply as a way to put our observations in the context of what has previously been observed in PVK. The data in Fig. 2 are integrated over the wavelength range 360–530 nm to obtain the highest signal-to-noise ratio for the decays. In the Ir(DPPF)₃ doped
blend, the relative emission of long-lived component is consistently smaller than in the pure blend, as shown in Fig. 2b. We use the same fixed values of $k_1$ and $k_2$ to fit the data, again with satisfactory results, but the relative contribution of the $A_2$ component becomes smaller. It should be mentioned that the fits in Fig. 2b do not reproduce the crossover between exponentials seen at around 3 ns as well as what is seen in Fig. 3a. At 540 nm, we find that the lifetime of the Ir(DPPF)$_3$ emission remains essentially constant over the entire temperature range, and is comparable to that of the complex in PMMA, as shown in Fig. 3. Unlike Ir(DPPF)$_3$ in PMMA, however, there is a long-time non-exponential decay component present at room temperature. This long-lived component may be due to recombination of long-lived charges or may also be the result of host–guest triplet energy transfer, since both species are known to exist in PVK at room temperature for several milliseconds or more [16,17]. It is suppressed at lower temperatures, suggesting that it results from an activated process.

From our analysis of the blend decays, addition of the Ir(DPPF)$_3$ does not result in a noticeable change in the decay rates of the host emission. What this suggests is that neither species transfers its energy directly to the dopant. Rather, the partitioning of energy between the two host species and the Ir(DPPF)$_3$ appears to occur on the same short timescale as the partitioning between the two host species themselves. The surprising thing is that this partitioning occurs mainly at the expense of the long-lived, deep trap as opposed to the short-lived, shallow trap. This can be seen most clearly if we compare the temperature dependence of the change in the amount of the long-lived host emission with that of the integrated Ir(DPPF)$_3$ emission. If we assume that the excited Ir complex competes with deep trap formation, then the change in the amount of Ir emission should be proportional to the change in the relative amount of long-lived host emission, i.e.,

$$S_{\text{Ir(DPPF)}3} \propto A_2/A_1(\text{PVK–PBD}) - A_2/A_1(\text{Ir(DPPF)}_3 : \text{PVK–PBD}).$$  (2)

Fig. 4 shows a plot of both quantities as a function of temperature, and as is evident from the figure.
they are almost identical at all temperatures. As the emission from the triplet acceptor increases with temperature, it does so at the expense of the long-lived component of the host decay. This can also be surmised from Fig. 2a and b, where the increase in the long-lived component of the decay with temperature is considerably less pronounced in the Ir(DPPF)₃/PVK–PBD than in the PVK–PBD blend alone. For this analysis to be meaningful, one must assume that the amount of short-lived host species is the same for both the neat PVK–PBD and the Ir-blend. The fact that Fig. 4 shows such good correlation between the two quantities (the amount of Ir(DPPF)₃ phosphorescence and the change in blend emission) suggests that this assumption is reasonable. Other data also show that as the concentration of Ir(DPPF)₃ in the blend increases, the relative amount of the long-lived species decreases, again without a discernible change in the bi-exponential time constants [18].

To understand the behavior of the energy transfer in this material, we first discuss the photophysics of the PVK–PBD blend, which mirror those of neat PVK. The photoluminescence of PVK originates from two different states: the higher energy, short-lived state is assigned to a localized excimer (shallow trap), while the lower energy, longer-lived species corresponds to a second type of excimer (deep trap) [13,15]. In the blend, as in PVK, the deep trap is favored at higher temperatures, although their decay rates do not change [14]. This is because in PVK, all the branching occurs within the 100 ps after excitation, after which the individual populations decay independently. When the PVK–PBD blend is doped with Ir(DPPF)₃, the Ir(DPPF)₃ competes only with the deep traps. These observations suggest the scheme outlined in Fig. 5. Upon absorption of a photon, the excitation rapidly migrates to a shallow trap site. Depending on the available thermal energy and the local barrier height, the excitation may continue on to either a deep trap in the host or to the Ir(DPPF)₃. A similar mechanism, involving fast exciton diffusion and trapping rather than Förster transfer, has previously been invoked to explain energy transfer from PVK to various small molecule acceptors [19,20]. Thermally activated energy transfer has also been observed for singlet energy transfer in conjugated polymer blends [21]. The temperature dependence of the transfer cannot be fit in terms of a simple Arrhenius model with a single activation energy, most likely because there is a large distribution of barrier energies in this disordered system. Instead, there is a threshold for energy transfer occurring around 50 K, as can be surmised from the data in Figs. 1 and 4, which suggests that there are relatively few barriers below about 40 cm⁻¹ in this system.

The temperature-dependent, sub-nanosecond partitioning of energy between the PVK–PBD traps and the Ir(DPPF)₃, as described above, is not consistent with simple Förster energy transfer from the PVK–PBD host to the Ir(DPPF)₃ acceptor. Since none of the emission spectra undergo

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**Fig. 4.** Comparison of the integrated Ir(DPPF)₃ phosphorescence (triangles) and the relative change in the amount of the long-lived PVK/PBD emission as defined in Eq. (2) (squares) at five different temperatures. Both the integrated phosphorescence and the change in blend emission are normalized to unity at 290 K.

**Fig. 5.** Schematic mechanism of energy transfer processes in PVK/PBD/Ir(DPPF)₃ consistent with the experimental data.
spectral shifts or shape changes with increasing temperature, there is no change in spectral overlap that would cause the Förster rate to increase with temperature. Also, the spectral overlap of the two host species with the Ir(DPPF)$_3$ absorption at 340 nm are very similar [6], and if anything the blueshifted, short-lifetime species has better overlap and a larger radiative rate, based on results from PVK [22], both of which should lead to more rapid energy transfer. But from Figs. 2 and 4 we see that it is mainly the long-lived, redshifted trap that is affected by the energy transfer. Finally, the presence of the acceptor does not affect the luminescence decay rates of either species. This is in contrast to other systems where Förster transfer is the dominant mechanism. In such systems the donor’s fluorescence decay becomes more rapid, while the acceptor’s emission grows in as a function of time, and the energy transfer rates can be directly extracted from the changes in the fluorescence decay dynamics.

Our non-Förster mechanism for energy transfer from the host polymer blend to the triplet emitter has implications for the design of electroluminescent materials. Apparently, the ease of energy transfer depends on the chemical nature of the trap site. In PVK, the shallow trap is thought to involve two PVK repeat units which partially overlap, while the deep trap is due to two carbazole units which are in complete registration with each other [23]. Ir(DPPF)$_3$ may preferentially reside in or near these deep trap sites, providing a new channel for energy transfer as long as there is sufficient thermal energy. If carrier recombination is also favored at such deep trap sites, then that would explain why the electroluminescence is so efficient in these materials. To design more efficient light emitting materials, one could envision modifying the chemical structure of the host to form more deep traps, for example by restricting the rotational motion of the carbazole units.

4. Conclusion

We have measured the temperature dependent dynamics of an Ir(DPPF)$_3$/PVK–PBD blend in order to characterize the host–guest energy transfer process. By analyzing the two-component blend decay, along with the steady state emission spectra, we have determined that the energy transfer from host polymer to Ir(DPPF)$_3$ guest is a thermally activated process that directly competes with the formation of the long-lived trap species, decreasing the yield of that species by 50% at room temperature. This thermally activated energy transfer occurs rapidly after photoexcitation and does not affect the nanosecond luminescence decays, in contrast to the singlet–singlet Förster transfer observed in conjugated polymer blends. The improved design of these materials will likely require a better understanding of the dynamics and mobilities of weakly emitting charge separated states, which are in general difficult to characterize due to their transient nature and weak spectroscopic signatures.

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