Phosphorescence as a probe of exciton formation and energy transfer in organic light emitting diodes

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The development of highly efficient phosphorescent molecules has approximately quadrupled the quantum efficiency of organic light emitting devices (OLEDs). By harnessing triplet as well as singlet excitons, efficient molecular phosphorescence has also enabled novel studies of exciton physics in organic semiconductors. In this review, we will summarize recent progress in understanding exciton formation and energy transfer using phosphorescent molecular probes. Particular emphasis is given to two topics of current interest: energy transfer in blue phosphorescent OLEDs, and quantifying the formation ratio of singlet to triplet excitons in small-molecular weight materials and polymers.

1 Introduction

Semiconducting organic materials have found an important application in organic light emitting devices (OLEDs). Brightly emissive across the visible spectrum, OLEDs may be fabricated on glass or flexible plastic substrates, and they are Lambertian sources, producing color independent of viewing angle. Based on these advantages, it is envisaged that OLEDs will provide a platform for the next generation of video displays. But if they are to compete with alternative display technologies, OLEDs must be efficient, converting as many injected charges into photons as possible.

OLEDs are typically constructed of thin films of a molecular or polymeric amorphous organic semiconductor. Electronic states are localized in OLEDs because the energetic and positional disorder in the constituent amorphous organic semiconductors overwhelms relatively weak intermolecular interactions. Thus, when an electron and hole combine within the emissive layer of an OLED, a localized excited state with a binding energy as high as 1 eV is formed. This excited state, or 'exciton', possesses a spin. In fluorescent materials, only excitons with total spin $S = 0$ may emit light, while in phosphorescent materials, excitons with total spin $S = 1$ also luminesce, allowing these typically dark states to be harnessed and studied [1].

The chemistry and detailed performance of phosphorescent materials in OLEDs has been reviewed in detail elsewhere [2]. This review is concerned with phosphorescent studies of the crucial exciton processes that start with the formation of an exciton from injected charge. An overview of exciton formation and triplet energy transfer in guest-host systems is described in Section 2. Experimental studies that have employed phosphors to directly study the spin dependence of exciton formation are discussed in Section 3. In Section 4, phosphorescent studies of exciton diffusion and triplet energy transfer in phosphorescent blue OLEDs are described. We summarize the results of phosphorescent studies of triplet excitons in Section 5.

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2   Phosphorescence, the spin dependence of exciton formation
     and triplet energy transfer

In an OLED, the conversion of electrical energy into light is mediated by excitons, whose properties are the primary determinant of the overall luminescent efficiency. Excitons may be thought of as two-electron systems: one electron is excited into an unfilled orbital of a given molecule or polymer, while the second remains in a partially filled ground state. The total spin of a two-electron system is either $S = 0$, or $S = 1$. The $S = 0$ spin wavefunction is antisymmetric under particle exchange:

$$\sigma_- = \frac{1}{\sqrt{2}}\left\{\uparrow(1)\downarrow(2) - \downarrow(1)\uparrow(2)\right\} \tag{1}$$

where $\uparrow$ and $\downarrow$ represent the possible spin states of each electron. The electrons are signified by (1) and (2), and σ is the spin wavefunction. There are three possible spin wavefunctions with $S = 1$, all symmetric under particle exchange:

$$\begin{aligned}
\sigma_+ &= \frac{1}{\sqrt{2}}\left\{\uparrow(1)\downarrow(2) + \downarrow(1)\uparrow(2)\right\} \\
\sigma_+ &= \uparrow(1)\uparrow(2) \\
\sigma_+ &= \downarrow(1)\downarrow(2)
\end{aligned} \tag{2}$$

The degeneracy of each state is reflected in its title: the $S = 0$ state is known as a singlet, and the $S = 1$ is a triplet. If the excited state is formed from the combination of two uncorrelated electrons, then in a completely random formation process the relative degeneracies of the singlet and triplet states result in a 1:3 singlet:triplet ratio, *i.e.* the fraction of singlet excitons is $\chi_S = 0.25$.

Exciton spin is crucially important because it determines whether an exciton can efficiently emit light in a fluorescent material. The ground state of most molecules is a singlet state, and because the emission of a photon conserves the symmetry of the spin wavefunction, typically only singlet excited states can efficiently decay to the ground state and emit light. Radiative singlet decay is termed 'fluorescence'. Radiative triplet decay is termed 'phosphorescence'. But the probability of luminescence from triplet states is generally so low that almost all their energy is lost to non-radiative processes. Thus, the excitonic singlet-triplet ratio imposes a fundamental limit, χ_S, on the efficiency of fluorescent organic materials. It follows that $1/\chi_S$ expresses the gain to be achieved if luminescence from triplets can be harnessed as well.

Although radiation from triplet states is rare, the process can be quite efficient in some materials [2]. For example, the decay of the triplet state is partially allowed if the excited singlet and triplet states are mixed such that the triplet gains some singlet character [2]. Typically, singlet-triplet mixing and efficient phosphorescence is achieved in molecules with large spin-orbit coupling due to the presence of heavy metal atoms such as Pt or Ir [2]. To exploit an efficiently phosphorescent material in an OLED, we require the transfer of both singlet and triplet excitons from the charge transport layer (henceforth called the host) to the phosphorescent guest [2].
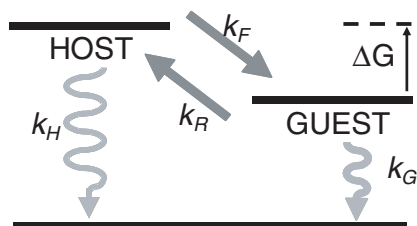
Fig. 1   Triplet dynamics in a guest-host system: the rates of forward and back transfer, k_F and k_B, respectively, are determined by the free energy change (ΔG) and the molecular overlap; also significant are the rates of decay from the guest and host triplet states, labeled k_G and k_H, respectively. Adapted from Ref. [24].

Since the initial studies of Tang, et al. [3] OLED designers have found it advantageous to separate the functions of charge transport and luminescence within the emissive layer of an OLED. One method for achieving this is to mix a small concentration of a highly luminescent phosphorescent guest into a host material with suitable charge transport abilities. This technique confines excitons onto phosphorescent molecules and therefore has the ancillary advantage of minimizing exciton quenching [4] by other excitons in the emissive material, by charges in the emissive material, and by metallic contacts. Four processes determine the overall efficiency of energy transfer between a host and a guest molecule as shown in Fig. 2: the rates of exciton relaxation on the guest and host, k_G and k_H, respectively; and the forward and reverse triplet transfer rates between guest and host, k_F and k_R, respectively.

Host-to-guest triplet energy transfer is exothermic when $\Delta G < 0$, and endothermic when $\Delta G > 0$. In fluorescent materials, endothermic energy transfer is very inefficient and results in a large population of excitons remaining confined on the host, where they rapidly decay via fluorescent or non-radiative processes. But, as described below, endothermic energy transfer may be successfully employed in phosphorescent devices since the decay of excitons in the host is retarded by spin conservation, i.e. $k_G \gg k_F \gg k_H$.

The triplet energy difference ΔG can be estimated by measuring the relaxed triplet state energies of both the donor and acceptor molecules from the highest-energy transition observed in their phosphorescent spectra, taken at low temperature to minimize non-radiative transitions [5]. Alternately, the triplet energy levels of a molecule can be determined using pulse radiolysis [6] by mediating triplet-triplet energy transfer from a solvent to the molecule with an energy acceptor of a known energy. Triplet populations in the molecule of interest are monitored using photoabsorption, and will be significant only when the energy level of the acceptor is greater than the molecular triplet energy level [6].

Triplet energy transfer is a hopping process known as Dexter transfer and follows

$$^3D* + {}^1A \rightarrow {}^1D + {}^3A*, \tag{3}$$

where D is the donor and A, the acceptor. Triplet and singlet states are represented by superscript 3 and 1, respectively, and the asterisk signifies an excited state. Singlet energy transfer follows

$$^1D* + {}^1A \rightarrow {}^1D + {}^1A*. \tag{4}$$

Host singlet states may transfer to guest singlet states via Dexter transfer, except when guest-host singlet spectral overlap is strong, in which case long-range dipole-dipole or Förster energy transfer predominates [7]. The triplet state of the donor may also Förster transfer to the singlet state of the acceptor, following:

$$^3D* + {}^1A \rightarrow {}^1D + {}^1A*. \tag{5}$$

This process is known as sensitized fluorescence when it results in the transfer of triplet excitons to the singlet state of a fluorescent dye. It may be very efficient if the donor is phosphorescent [7, 8].

3 Phosphorescent studies of exciton formation

Quantifying the fraction of singlet excitons formed in OLEDs is an active area of research. A simple model for interpreting experimental studies of χ_S is shown in Fig. 2. It assumes that the precursors to excitons, charged encounter complexes, relax into singlet and triplet excitons at different rates, k_S and k_T, respectively. In the absence of a process that mixes the spin of the encounter complex, a quarter of excitons form as singlets, regardless of the relative formation rates of singlets and triplets. But if a mixing process is present, then either singlet or triplet formation will dominate, depending on which is fastest.

It has been suggested both that $k_S > k_T$ [9–11], and $k_S < k_T$ [12]. Tandon et al. [13] have critically reviewed theoretical estimates of k_S and k_T. They model these rates in polymers using parallel interacting chains and argue that electron correlations between delocalized states can account for $\chi_S > 0.25$ in polymers. In contrast, analyses of the magnetic field dependence of photoconductivity in polymers suggest that $k_S < k_T$ [12]. But it is important to note that differences in exciton formation rates only influence the
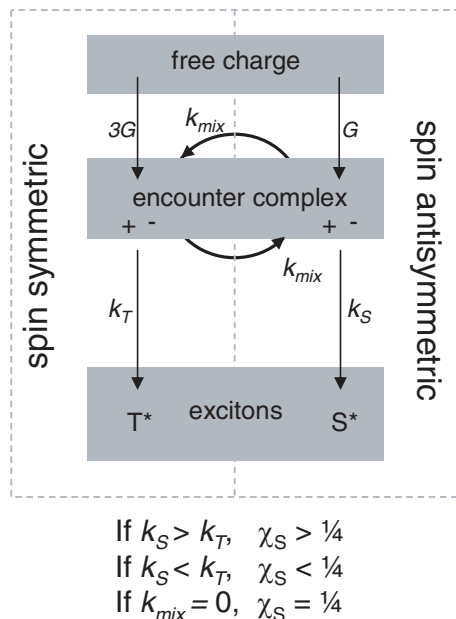
Fig. 2 A model of exciton formation. The formation rates of triplet and singlet excitons are k_S and k_T, respectively. The mixing rate at room temperature is k_{mix}. G is a constant determined by the formation rate of encounter complexes. In the absence of mixing the singlet fraction $\chi_S = 0.25$ irrespective of the spin-dependent exciton formation rates.

If $k_S > k_T$, $\chi_S > \tfrac{1}{4}$
If $k_S < k_T$, $\chi_S < \tfrac{1}{4}$
If $k_{mix} = 0$, $\chi_S = \tfrac{1}{4}$

ultimate singlet fraction, χ_S, if there is significant mixing of singlet and triplet precursors to excitons. Quantification of this mixing rate must remain a major objective of ongoing studies of exciton formation.

By acting as a probe for the normally dark triplet states, phosphorescence provides an important experimental tool for the determination of χ_S. Here we discuss three techniques used in phosphorescent investigations of the spin dependence of exciton formation:

3.1   Comparison of OLED efficiencies with fluorescent or phosphorescent guest molecules

Perhaps the first measurement [14] of χ_S in a small molecular weight organic semiconductor used fluorescent and phosphorescent guest molecules to capture singlet and triplet excitons formed in a host film of tris(8-hydroxyquinoline) aluminum (Alq$_3$). Captured singlets were identified by fluorescence and triplets by phosphorescence. By comparing the ratio of phosphorescence to fluorescence, the singlet-to-

$\chi_S \sim$ fluorescence/phosphorescence
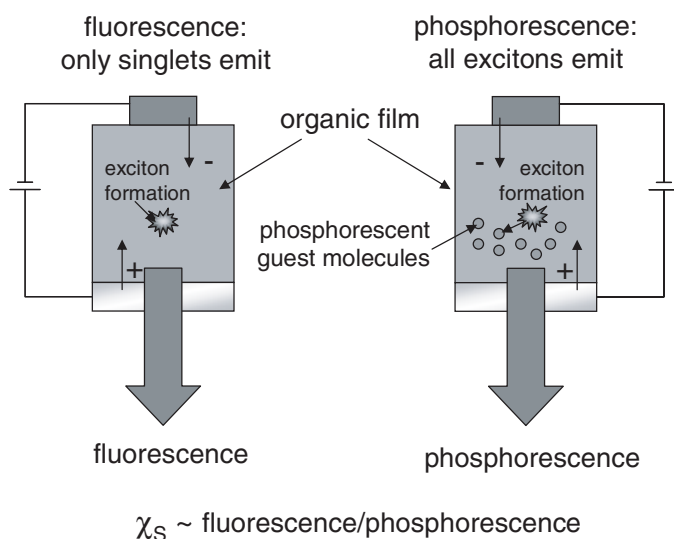
Fig. 3 Phosphorescent guest molecules can be used to sense triplets. After correcting for photoluminescent efficiency, comparing fluorescence and phosphorescence then gives the singlet fraction. Note that the intersystem crossing rate in phosphorescent molecules is very high, converting nearly all singlet excitons to triplets prior to luminescence. Adapted from Ref. [14].

triplet ratio was estimated [14] to be $(22 \pm 3)\%$; see Fig. 3. Although it is apparently straightforward, this technique has several disadvantages. First, it is necessary to correct for the differing photoluminescent efficiencies of the fluorescent and phosphorescent guest molecules. Secondly, the efficiency of energy transfer to both guest materials must be determined to ensure that radiative emission accurately reflects the number of excitons formed within the device. Thirdly, the impact of quenching phenomena must be calculated for both singlet and triplet excitons. Finally, when applied to polymeric systems, it is especially important to ensure that excitons are formed on the polymeric host and not on the small molecular weight phosphorescent guest.

3.2 Sensitized fluorescence

As discussed in Section 3, phosphor-sensitized fluorescence is a technique that uses a phosphorescent material to transfer energy from triplet excitons to the singlet state of a guest molecule; see Fig. 4 [8]. To determine χ_S using this method two OLEDs must be built, one with and one without the phosphorescent sensitizer. In the absence of the sensitizer, only singlet excitons luminesce, but singlets *and* triplets are detected when the sensitizer is included. In both cases, radiation is emitted from the same fluorescent guest molecule, thereby eliminating errors in comparisons of fluorescence and phosphorescence due to differing radiative efficiencies, or quenching phenomena [8, 15]. This technique yielded a singlet fraction of $(22 \pm 2)\%$ in the material 4,4′-N,N′-dicarbazole-biphenyl (CBP). The technique may, however, overestimate the singlet fraction if triplets form directly on the fluorescent guest rather than on the host or sensitizer. Thus, the most accurate measurements [15] employ very low concentrations (~0.2%) of the fluorescent dye and high concentrations (~8%) of the phosphorescent sensitizer.

3.3 Simultaneous measurement of fluorescence and phosphorescence

Wilson and co-workers [16] proposed that χ_S can be readily measured in materials that simultaneously fluoresce from their singlet states and phosphoresce from their triplet states. If the intersystem crossing
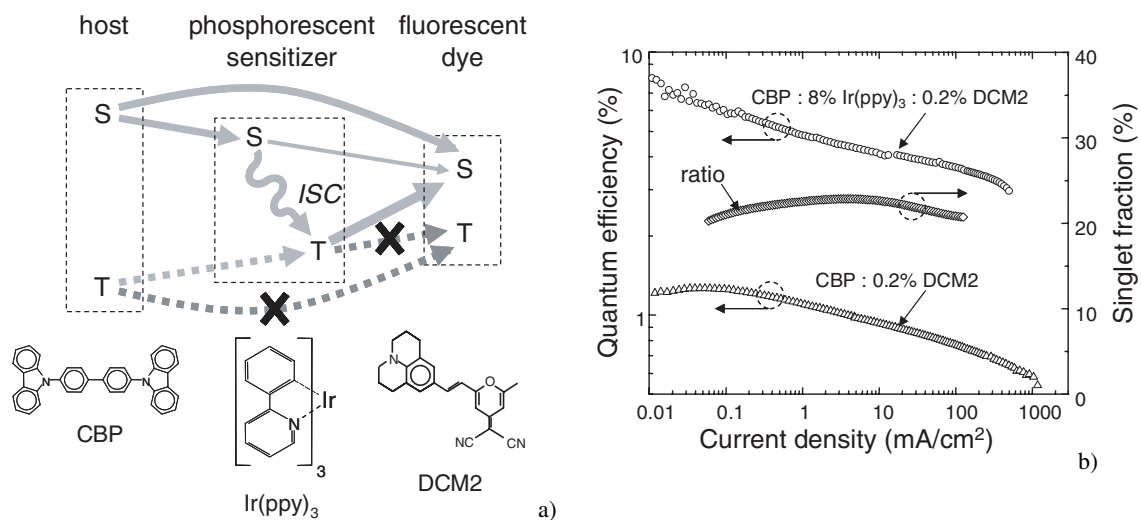
Fig. 4 a) Energy transfer mechanisms in phosphor sensitized fluorescence and the materials used to demonstrate the principle. Non-radiative dipole-dipole transfers are represented by solid lines and hopping transfers by dotted lines. The presence of the phosphorescent sensitizer redirects triplets to the singlet state of the fluorescent dye, where they may emit. b) The external quantum efficiencies of the fluorescent dye DCM2 with and without phosphorescent sensitization by tris-(2-phenylpyridine) iridium (Ir(ppy)$_3$). The host material is 4,4′-N,N′-dicarbazole-biphenyl (CBP). The ratio between sensitized and unsensitized emission gives $\chi_S = (22 \pm 2)\%$. From Refs. [8, 34] and [18].

rate in the material is large, the singlet fraction is obtained from the ratio of fluorescence to phosphorescence in both electroluminescence (EL), which is luminescence resulting from an electrical pump, and photoluminescence (PL), which is luminescence resulting from an optical pump:

$$\chi_S = \left(\Phi_f \middle/ \Phi_p \right)_{EL} \middle/ \left(\Phi_f \middle/ \Phi_p \right)_{PL} . \tag{6}$$

Here the fluorescent and phosphorescent radiation intensity is given by Φ_f and Φ_p, respectively. The singlet exciton formation fraction in a Pt-containing monomer was determined to be $\chi_S = (0.22 \pm 0.01)$. This technique has the advantage that it does not require any absolute measurements of fluorescent or phosphorescent quantum efficiencies. It may be necessary, however, to determine whether quenching phenomena affect triplets and singlets identically in electroluminescence and or photoluminescence. It is also necessary to ensure that significant numbers of photoexcited excitons do not dissociate into charges, as this can lead to erroneously large measured values of χ_S.

The leading phosphorescent study of exciton formation in polymers was also reported by Wilson, et al. [16] From a simultaneous measurement of fluorescence and phosphorescence in a Pt-containing polymer, these workers measured $\chi_S = (0.57 \pm 0.04)$, consistent with predictions [9] that the singlet fraction should be higher in polymeric materials. But overall, experimental results concerning exciton formation in polymeric materials remain contradictory. In a study similar to that of Wilson et al. [16], measurements of the EL and PL spectra of polymers containing phosphorescent iridium complexes grafted onto a polyfluorene backbone do not show $\chi_S > 0.25$ [17]. Furthermore, a comparison [18] of EL and PL efficiencies in MEH-PPV yielded only $\chi_S = (0.20 \pm 0.04)$, and photo-absorption detected magnetic resonance (PADMR) studies [10, 11] that suggest $\chi_S > 0.25$ in polymers appear to be contradicted by electroluminescent-detected magnetic resonance (ELDMR) studies that show only small resonant changes in EL [19, 20].

Conclusive evidence for $\chi_S > 0.25$ in polymers may come from measurements of external EL quantum efficiencies. At present the external quantum efficiency of fluorescent polymer devices appears to be limited to 4−6% [21, 22]. Given the high PL efficiencies of some polymers, it might be expected that measurements of $\chi_S > 25\%$ should be reflected in polymeric EL fluorescent quantum efficiencies that approach the $\approx 20\%$ observed in phosphorescent small molecular weight materials [18]. Thus, pending significant advances in the quantum efficiency of fluorescent polymers, achieving high efficiency electroluminescence will continue to require the harnessing of triplet excitons using phosphorescence. Phosphorescence will also continue to be an attractive experimental probe of χ_S in new materials.

4   Energy transfer in blue phosphorescent OLEDs

Perhaps the best example of the importance of triplet energy transfer is the development of highly efficient blue phosphorescent OLEDs, one of the most challenging applications for phosphorescent materials. In most small molecular weight phosphors, exchange interactions typically lower the triplet excited state by approximately 1 eV relative to the singlet state. Thus relative to blue fluorescent devices, blue phosphorescent OLEDs must be capable of generating charge encounter complexes that are higher in energy by approximately 1 eV [23]. This complicates energy transfer in these devices. Here we examine three techniques, endothermic energy transfer, exothermic energy transfer and charge trapping, as they are applied to blue phosphorescent devices.

4.1   Endothermic energy transfer

Endothermic energy transfer to a phosphorescent guest was demonstrated [24] and quantified [25] in transient studies of the guest:host system of Ir(ppy)$_3$:TPD, where Ir(ppy)$_3$ is *fac*-tris(2-phenyl-pyridine)iridium and TPD is *N,N*′-diphenyl-*N,N*′-bis(3-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine. As
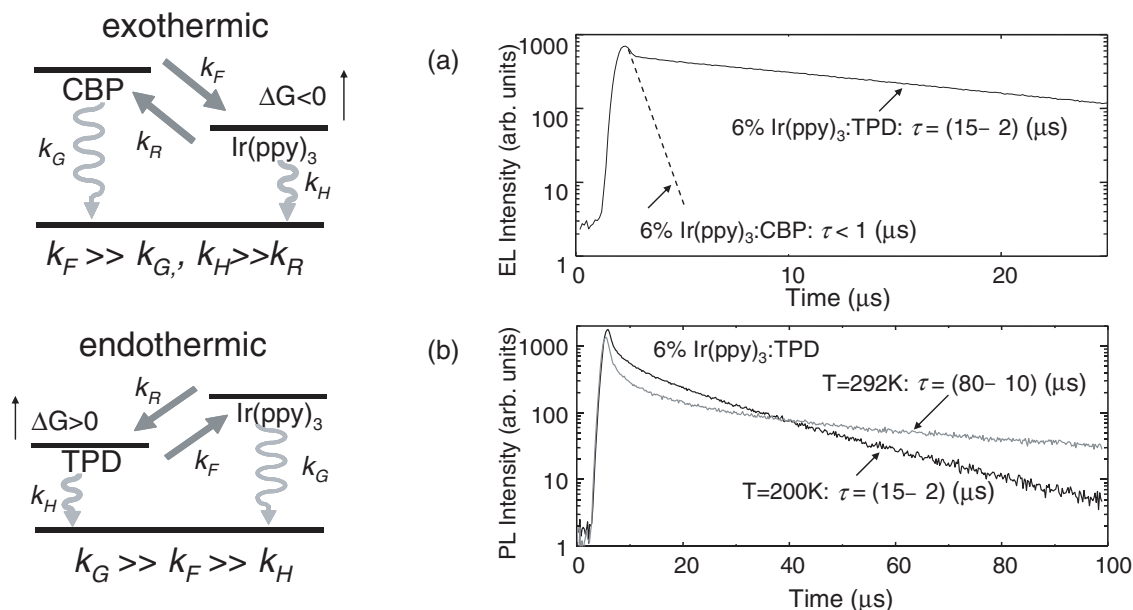
Fig. 5 a) The electroluminescent response of the endothermic system $Ir(ppy)_3$:CBP, as compared to the exother-mic system $Ir(ppy)_3$:CBP. The lifetime of $Ir(ppy)_3$ in a TPD host is significantly longer (15 μs) than the natural radiative lifetime of $Ir(ppy)_3$ (<1 μs). The initial peak in the response is principally due to fluorescence from TPD. (b) The photoluminescent response of 8% $Ir(ppy)_3$ in TPD at $T = 292$ K and $T = 200$ K. The lifetime increases at low temperatures, consistent with a thermally activated process such as endothermic energy transfer. However, unlike the EL response, the initial transient in the photoluminescent response is comprised entirely of emission from photo-excited $Ir(ppy)_3$. Adapted from Ref. [24].

noted above, triplet excitons are difficult to observe because in most materials, triplet radiative decay rates are much slower than competing non-radiative losses. Transient phosphorescence of molecules with high phosphorescent efficiencies, however, can be used to observe the diffusion of triplets within a host material, or it may give evidence for charge trapping and direct exciton formation on guest molecules within the host. Thus, it provides a convenient tool for examination of energy transfer, either from one host molecule to another, or from the host to the guest [24, 26].

Low temperature phosphorescent spectra give peak triplet energies of (2.3 ± 0.1) eV and (2.4 ± 0.1) eV for TPD and $Ir(ppy)_3$, respectively [24], and as shown in Fig. 5, the transient response of $Ir(ppy)_3$:TPD exhibits a phosphorescent lifetime that is much longer than that typical of $Ir(ppy)_3$ (<1 μs) [24]. Since after the initial excitation, the phosphorescent emission is entirely due to $Ir(ppy)_3$, the likely explanation for the delayed rate of phosphorescence from $Ir(ppy)_3$ is slow endothermic energy transfer from TPD. In this system, the energy barrier between host and guest forces excitons to reside primarily in the host. Thus, TPD acts as a reservoir for triplet excitons [25]. But because triplet decay to the singlet ground state in the host TPD is retarded by spin conservation, triplets decay instead by endothermic energy transfer to the guest, $Ir(ppy)_3$. The energy transfer is slow, and as shown in Fig. 5, thermally acti-vated.

The first demonstration of blue phosphorescence also employed endothermic energy transfer from the host *N,N'*-dicarbazolyl-4-4'-biphenyl (CBP) to the blue phosphorescent guest iridium(III)bis[(4,6-difluorophenyl)-pyridinato-*N*,$C^{2'}$]picolinate (FIrpic) [27]. Low temperature phosphorescent spectra ex-hibit peak triplet energies of (2.56 ± 0.1) eV and (2.65 ± 0.1) eV for CBP and FIrpic, respectively, sug-gesting endothermic energy transfer [27]. This is confirmed by the transient response of FIrpic:CBP, which exhibits reduced energy transfer at lower temperatures, consistent with the archetypal endothermic system $Ir(ppy)_3$:TPD.
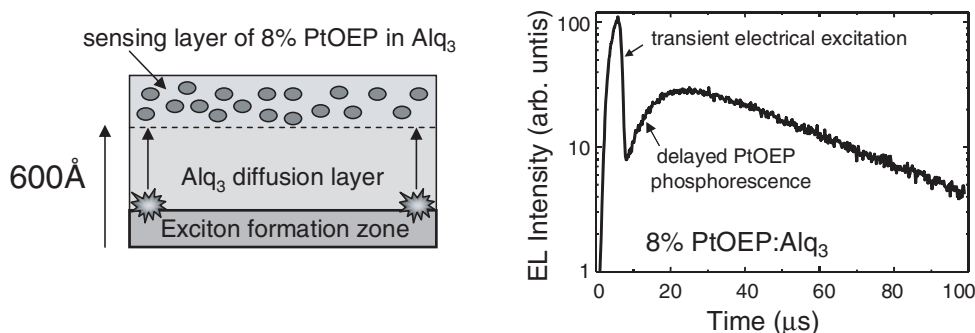
Fig. 6 Delayed phosphorescence is a signature of triplet diffusion and subsequent capture by exothermic energy transfer from an Alq_3 host matrix to the phosphorescent guest molecule PtOEP. The transient response was measured at $\lambda = (650 \pm 10)$ nm. The initial electrical pulse excites some host fluorescence and marks the formation of excitons. The triplet excitons then diffuse through a 600 Å-thick Alq_3 diffusion layer before being transferred to PtOEP. Adapted from Ref. [24].

4.2　Exothermic energy transfer

Cleave, et al. [26] introduced transient phosphorescence as a technique for studying triplet energy transfer. Their experiments conclusively demonstrated exothermic triplet energy transfer from the polymer poly[4-(*N*-4-vinylbenzyloxyethyl, *N*-methylamino)-*N*-(2,5-di-*tert*-butylphenylnaphthalimide)] (PNP) to the phosphorescent guest platinum octaethylporphyrin (PtOEP).

Similar results were subsequently obtained in studies of triplet energy transfer from the small molecular weight host Alq_3 to the phosphorescent guest PtOEP [24]. In Fig. 6, the delay in the PtOEP phosphorescence after an electrical excitation pulse is due to triplet diffusion through the Alq_3 host. The delay is observed to decrease to zero as the exciton formation zone is moved closer to the PtOEP layer, confirming that excitons are formed initially in the Alq_3 host. These experiments were used to estimate the triplet exciton lifetime in Alq_3 to be (25 ± 15) µs [24]. In both PtOEP : PNP and PtOEP : Alq_3, energy transfer is exothermic from the guest to PtOEP.

Exothermic energy transfer has also been recently demonstrated in blue phosphorescent OLEDs using the phosphorescent guest iridium(III)bis[(4,6-difluorophenyl)-pyridinato-$N,C^{2'}$]picolinate (FIrpic) and the host N,N'-dicarbazolyl-3,5-benzene (mCP) [28]. Low temperature phosphorescent spectra confirm that the triplet energy of mCP is higher than that of FIrpic [28]. Exothermic energy transfer is expected to result in higher EL phosphorescent efficiency than endothermic energy transfer. In endothermic transfer, a large population of relatively mobile triplet excitons is expected to develop in the host, increasing losses due to triplet quenching. But in exothermic transfer, triplet excitons are confined on guest molecules and the triplet density and associated quenching losses in the host are small. Consequently, the peak quantum efficiency of FIrpic : mCP is higher, $(7.5 \pm 0.8)\%$, than that of the comparable endothermic system FIrpic : CBP, $(6.1 \pm 0.6)\%$ [28].

4.3　Charge trapping

Perhaps the optimum energy transfer scheme for blue phosphorescent OLEDs is direct charge trapping on the phosphorescent guest. This mechanism was demonstrated by Lane, et al. [29] in mixtures of the polymeric host poly(9,9-dioctylfluorene) (PFO) and the phosphorescent guest PtOEP. Lane et al. [29] studied triplet populations in PFO OLEDs using photoinduced absorption. No significant difference in the PFO triplet lifetime was observed with the addition of up to 8% PtOEP, demonstrating that triplet energy transfer from PFO to PtOEP is weak. Thus, the observation of significant phosphorescence from PtOEP in PFO must be due to direct exciton formation on the phosphorescent guest.

Eliminating the host material altogether provides the most energetically efficient means for harvesting triplet excitons [30]. Several methods for eliminating the host have been demonstrated. Lupton, et al. [30] exploited residual concentrations of a Pd catalyst employed in the synthesis of a diphenyl-substituted ladder-type poly(para-phenylene) PhLPPP to demonstrate enhanced phosphorescence from PhLPPP [30]. Wang, et al. [31] employed a fluorinated variant of the archetypal [32] green phosphor Ir(ppy)$_3$, fac-tris[5-fluoro-2-(5-trifluoromethyl-2-pyridinyl)phenyl-C,N]iridium (Ir-2h) as a neat emissive layer in an OLED. Ir-2h exhibits much lower self-quenching than Ir(ppy)$_3$ allowing it to be employed successfully without dilution into a host matrix. The external quantum efficiency of devices employing Ir-2h is approximately 6% [31].

Recently, Holmes, et al. [33] demonstrated charge trapping in blue phosphorescent devices, yielding among the most efficient blue phosphorescent devices demonstrated to date. Rather than employ a neat film, which is subject to self-quenching, the blue phosphor in this work bis(4′,6′-difluorophenyl-pyridinato)tetrakis(1-pyrazolyl)borate (Fir6) was mixed into an inert matrix comprised of either diphenyldi(o-tolyl)silane (UGH1) or *p*-bis(triphenylsilyl)benzene (UGH2). The energy gaps of UGH1 and UGH2 are sufficiently large that they do not participate in electron or energy transfer within the device. The peak quantum efficiency of this device is $(8.8 \pm 0.6)\%$ [28]. Because the phosphor must perform both the roles of charge transport and luminescence, the major disadvantage of this technique is the increase in voltage necessitated by reducing the concentration of the phosphor to avoid self-quenching. Efficient, neat films of a blue phosphor have not yet been demonstrated.

5 Conclusions

Phosphorescence has provided an important probe of exciton physics and has made possible dramatic gains in the electroluminescent efficiency achievable in OLEDs. In small molecular weight materials, the realized improvement is approximately a factor of four, while in polymers the potential benefit is debated, but is probably between a factor of two to four. To fully exploit the potential benefit of phosphorescence, energy transfer in the luminescent layer must be carefully controlled to maximize the efficiency of triplet and singlet exciton transfer to the phosphorescent guest molecules, and minimize quenching of triplet excitons prior to luminescence. With a careful choice of materials, phosphorescent studies have shown that it is possible to control the lifetime of triplet excitons from $\tau > 1$s to $\tau < 500$ ns. This unique property of triplet excitons can be exploited using a variety of energy transfer schemes to enhance the performance of electroluminescent devices. For example, sensitized fluorescence reduces triplet lifetimes, minimizing triplet-triplet annihilation, and endothermic triplet transfer exploits long-lived triplets to pump a blue phosphor guest without a blue host material. Thus, the development of efficient phosphorescence has significantly enhanced our ability to observe and control the behavior of excitons in organic electroluminescent devices.

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