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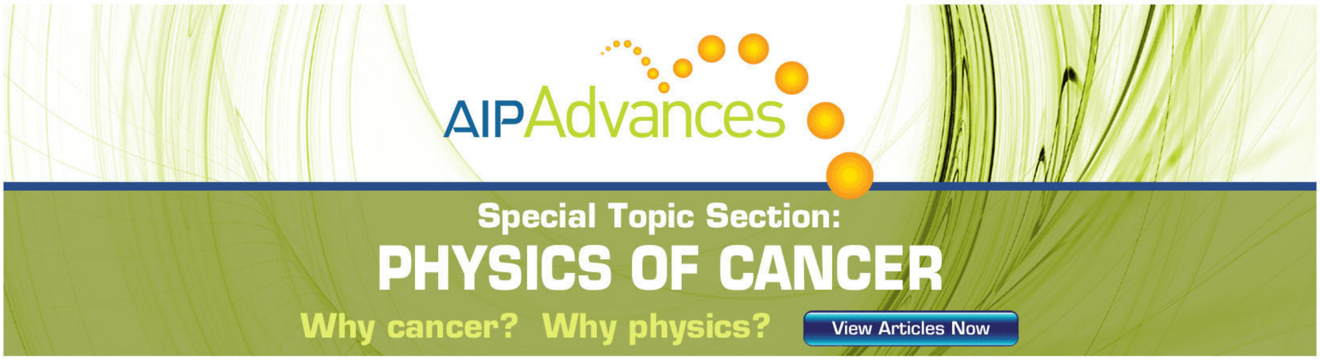

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The contribution of triplet–triplet annihilation to the lifetime and efficiency of fluorescent polymer organic light emitting diodes

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We demonstrate that the fast initial decay of a prototypical fluorescent polymer based organic light emitting diode device is related to the contribution that triplet–triplet annihilation makes to the device efficiency. We show that, during typical operating conditions, approximately 20% of the device efficiency originates from the production of singlet excitons by triplet–triplet annihilation. During prolonged device operation, the triplet excitons are quenched much more easily than the emissive singlets; thus, the contribution to the efficiency from triplet–triplet annihilation is lost during the early stages of the device lifetest. The fast initial decay of the device luminance can be removed by incorporating a triplet quenching additive into the active layer to remove any effect of triplet–triplet annihilation; this yields an increase in the device lifetime of greater than 3× and an even more significant improvement in the initial luminance decay. © *2011 American Institute of Physics*. [doi:10.1063/1.3561430]

I. INTRODUCTION

The lifetime and efficiency of conjugated polymer based organic light emitting diodes (P-OLEDS) are reaching a level, where commercialization is becoming possible, with reports of over 8 cd/A efficiency and lifetimes in excess of 18 000 h for fluorescent blue devices.[1] However, the device lifetime (T50—defined as the time taken for current efficiency to drop to half the initial value) and in particular the rapid initial degradation (e.g., T90) remain an issue.

Improvements in performance have been made possible through understanding the fundamental processes governing the efficiency[2–4] and degradation of electrical contacts or of the conjugated polymers within P-OLED devices.[5–8] In the model devices considered in this study, the primary cause of efficiency loss during electrical stressing has been shown to be the buildup to photoluminescence quenching sites in the emissive layer rather than the decay of the charge injecting contacts.[9] Although there have been some recent reports on the contribution that triplet states can make to the efficiency of a fluorescent small molecule OLED,[10,11] there has been little published research on the consequences of high triplet densities on the operational lifetime of the devices. This paper will report on the effect of triplet–triplet annihilation (TTA) on the device lifetime and efficiency of P-OLEDS. We show how the careful control of the triplet states can lead to significant ($\sim 3\times$) increases in the device lifetime (T50) and even more dramatic improvements ($\sim 5\times$) in the rapid initial decay (T90).

One of the fundamental limits to the efficiency of a fluorescent OLED is the ratio of emissive singlet excitons to nonemissive triplet excitons formed during device operation. From simple spin statistics, one would expect that 25% of the excitons formed are singlets. However, there have been a number of recent publications in which the singlet yields have been measured to be greater than the statistically expected value, often around 40%–50%. Although, there are a number of suggested mechanisms for this phenomenon, there is no consensus formed.[12–15] In small molecule OLEDs, it is reported that triplet–triplet annihilation can boost the singlet yield in the device by converting triplet excitons into singlets.[10,11]

This study focuses on a single prototypical P-OLED structure, consisting of an ITO anode, a solution processable hole injection layer (35 nm), a conjugated polymer interlayer (15 nm), a conjugated polymer emissive layer (70 nm), and a shallow work function cathode. The materials used for the interlayer and emissive layer are the commonly studied F8-TFB (poly-{9,9-dioctylfluorene-N-[4-(2-butyl)phenyl]-diphenylamine}) (50:50) copolymer (1) and F8-PFB {poly-[9,9′-dioctylfluorene-co-bis-N, N′-(4-butylphenyl)-bis-N,N′-phenyl-1,4-phenylenediamine]} (95:5) copolymer (2), respectively, as shown in Fig. 1(a). In addition, we have made devices where the emissive layer has been blended (1% mol ratio) with a triplet quenching additive DPVBi (4,4′-bis(2,2′-diphenylvinyl)-1,1′-biphenyl) (3). This material was chosen as the triplet quenching additive because not only does it have a triplet energy below that of the polyfluorene triplet[16,17] but it also has a high singlet energy (3.2 eV) compared to the luminescent polymer, ensuring that the emissive singlet states are not affected by the additive.

In this study, the dynamics of the singlet and triplet excitons have been probed using time resolved electroluminescence (EL) as well as quasi-cw and time resolved excited state absorption. The polyfluorene triplet state has been well characterized with these techniques and is known to show a

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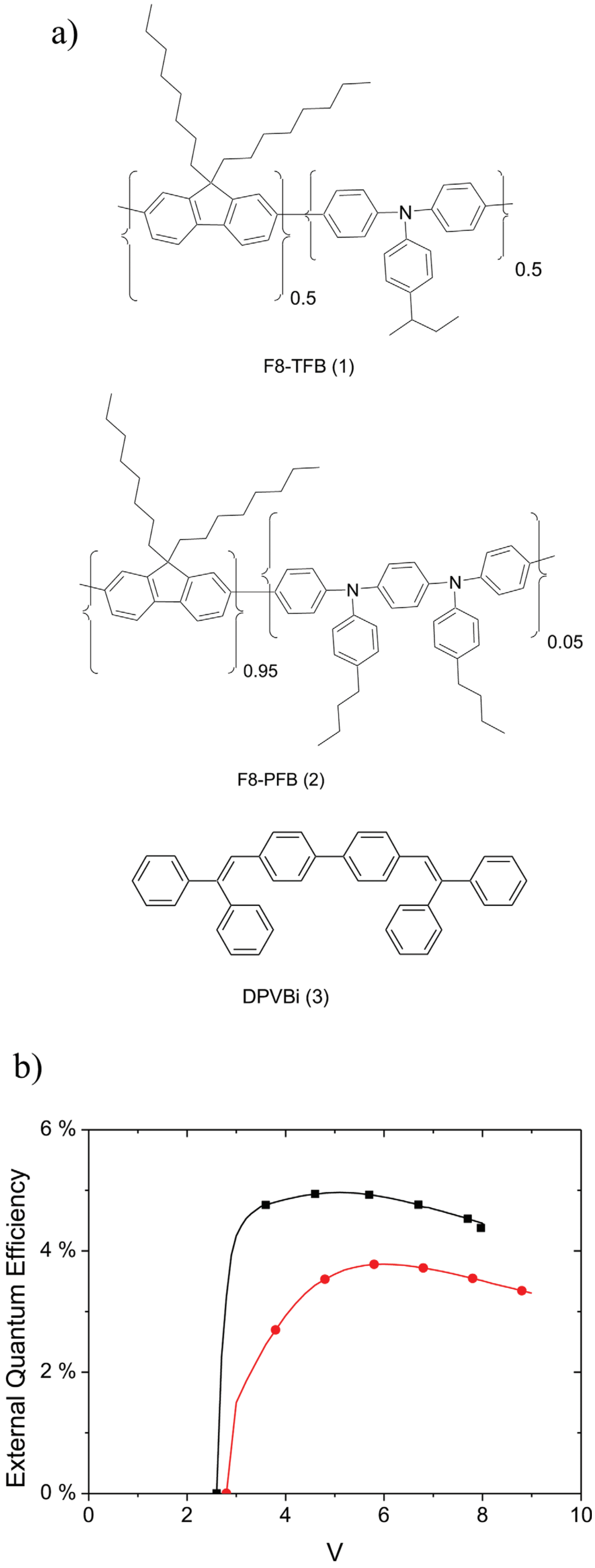

FIG. 1. (Color online) (a) Chemical structures of the materials under study. (b) External quantum efficiency of a prototypical PLED device comprising an F8-PFB LEP and a TFB interlayer, without (■) and with (●) the addition of the triplet quenching additive (3).

strong excited state absorption feature peaking at 780 nm.[18,19] In this study, all probes of the polyfluorene triplet population are performed at 780 nm. In our setup, the steady state population of triplets is probed by exciting a device electrically with a modulated current. The modulation of the reflectivity of the device at the probe wavelength (780 nm) is then measured with a lockin amplifier referenced to the frequency of the modulation current. The magnitude of the modulated signal is therefore the change in reflectivity of the device due to the excited states formed in the active layer. This change in transmissivity of the laser through the active area is related to the excited state population by Eq. (1) given below. In the time resolved steady state absorption experiment, the change in transmission of the probe is detected and recorded by a p-i-n photodiode coupled to a 30 GHz digital oscilloscope giving an overall time resolution for the system of <2 ns. These excited state absorption techniques have been described in more detail elsewhere.[18,20]

II. RESULTS AND DISCUSSION

Figure 1(b) shows the external quantum efficiency (EQE) of the prototypical polymer light emitting diode (PLED) both with and without the addition of the triplet quenching additive (3). The device with the triplet quenching additive shows an approximately 20% reduction in the EQE at high voltage, for example, at 6.5 V, the EQE drops from 5% to 3.8% on the addition of the triplet quenching additive. The photoluminescence intensity under constant UV irradiation from both of these devices is similar. In addition, the loss of efficiency occurs without any change to the electroluminescence spectrum of the device. As would be expected from the relative singlet energies of the light emitting polymer (LEP) (2) and additive (3), we conclude that the additive is neither quenching the singlet excitons nor taking part in the emission of the device.

The density of triplet excitons on the polymer backbone is measured using quasi-cw excited state absorption as outlined above. Figure 2 shows the density of triplets on the polymer backbone both including and excluding (3). In the device with the additive, the density of triplets on the fluorene backbone is reduced by approximately a factor of 10, demonstrating the efficiency of DPVBi as a triplet quencher at all drive voltages in this system. Literature values for the cross section of the triplet excited state absorption in conjugated polymers range[21] from 10^{-16} to 10^{-15} cm^2. The Beer–Lambert law for excited state absorption [Eq. (1)] is used, where n is the concentration of absorbing species, σ is the absorption cross section, and l is the thickness of the sample (in our case the recombination layer width), which is estimated at 10–50 nm.

$$dT/T = n\sigma l. \tag{1}$$

This gives a triplet density of 10^{16}–10^{17} cm^{-3} in the standard device at typical drive currents of 50 mA cm^{-2}. The consequence of such a high density of triplet excited states in conjugated polymers has been studied previously, where it was found that the triplet decay is dominated by their mutual

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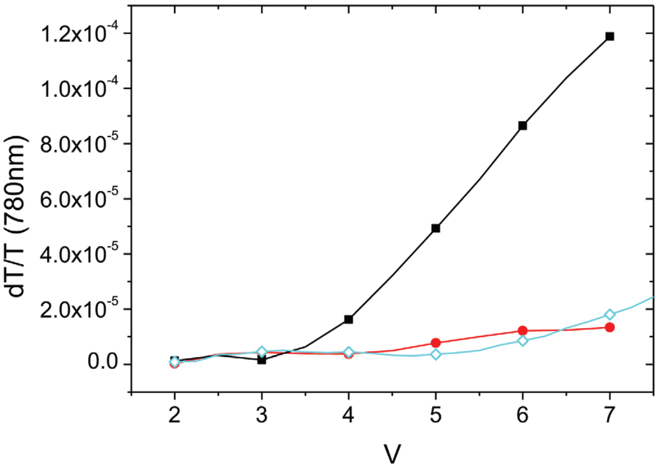

FIG. 2. (Color online) Quasi-cw current induced excited state absorption curves of the prototypical PLED without (■) and with (●) the addition of the triplet quenching additive (3). Also shown is the prototypical PLED driven to half the initial luminance (□).

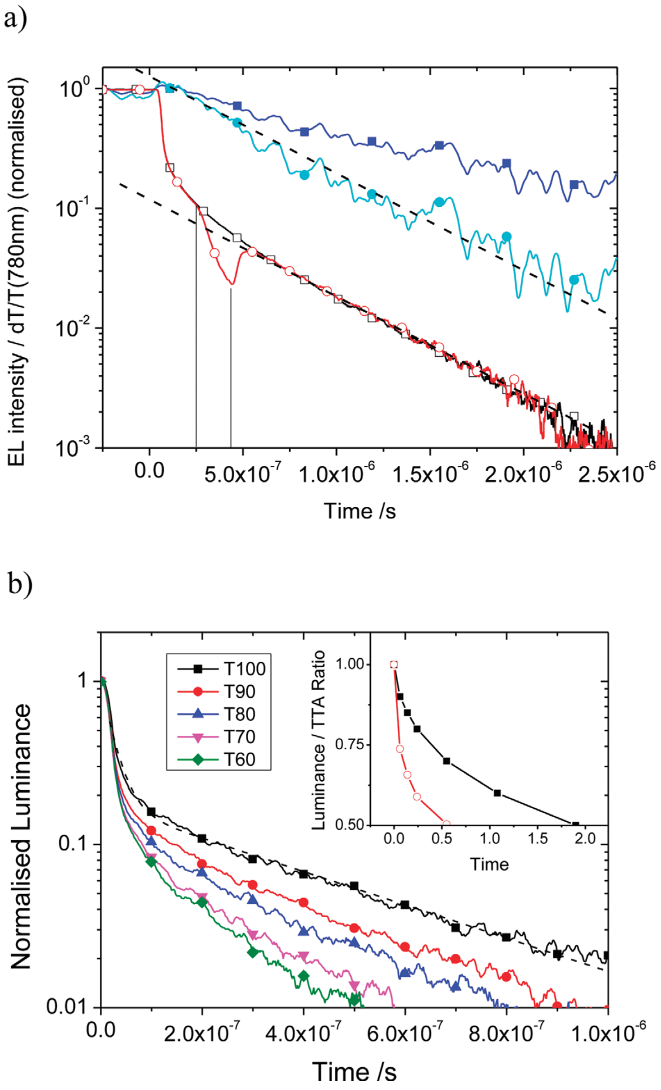

FIG. 3. (Color online) (a) Electroluminescence turn off of the prototypical device (□) compared with the time resolved transient triplet absorption (■) and its square (●). The dotted lines are of the same slope. Also shown is the effect on the electroluminescence turn off when a reverse bias pulse of −10 V for 200 ns duration is applied to the device 250 ns after the device current is switched off (○). (b) Electroluminescence turn off transients for an undriven device (T100) and devices driven to different relative luminance (e.g., T90 is driven to 90% of starting luminance). Also shown in the inset is the normalized luminance decay of the device (■) compared to the normalized contribution that TTA singlets make to the device efficiency (○).

bimolecular annihilation (TTA),[22,23] resulting in the production of emissive singlet excitons.

Figure 3(a) shows the time resolved electroluminescence during the turn off of the prototypical device. After turn off of the current, there is initially a rapid decay of the luminance on a similar time scale to the RC time constant of the device, followed by a residual signal in the EL on a time scale of a few microseconds, which accounts for about 30% of the total original electroluminescence. Generally, slow transient emissions in OLEDs are ascribed to either the recombination of charges from deep traps or interfacial charge layers or TTA.[10,24,25] In order to distinguish between the two mechanisms, the same transient electroluminescence trace has been measured with the application of a 10 V for 200 ns long reverse bias pulse 100 ns after the turn off of the device current. This pulse will remove, or at least perturb significantly, any trapped charge contribution to the decay of the luminance. Although the emission is quenched slightly during the reverse bias pulse due to the electric field quenching of the singlet excitons, the intensity of the EL after the reverse bias pulse is unchanged compared to the standard decay shape. One can therefore conclude that the recombination of trapped charge is not a significant contributor to the residual luminance signal.[26] Moreover, comparing the shape of the residual luminescence with the triplet density, shown in Fig. 3(a), there are two observations. Not only is the time scale of the decay of the triplets similar to that of the EL but also, more importantly, the approximate slope of the residual luminance decay is very similar to the slope of the square of the triplet density. This observation is strong evidence that the residual decay of the EL is due to bimolecular triplet–triplet annihilation reactions resulting in emissive singlet excitons. We note that this contribution to the efficiency from TTA is one possible reason for the higher than the expected singlet yield often measured for P-OLEDs and should be carefully considered in S:T ratio yield experiments from polymer materials. It is also notable that the triplet exciton density is not significantly quenched by the application of a 10V reverse bias pulse because the triplets are considerably more stable than singlets to the electric field due to their inherently greater exciton binding energy.[27,28] Equation (2) shows the kinetic scheme for the decay of the triplet population,

$$\frac{dT}{dt} = -k_{\mathrm{T}}T(t) - T(t)^{2}\gamma, \tag{2}$$

where T is the triplet density, k_{T} is the combined monomolecular decay rate for the triplets, and γ is the bimolecular TTA rate. The solution to the triplet population after the turn off of the device is given in Eq. (3),

$$\frac{T}{T_0} = \frac{k_{\mathrm{T}}}{(k_{\mathrm{T}} + \gamma)e^{k_{\mathrm{T}}t} - \gamma}. \tag{3}$$

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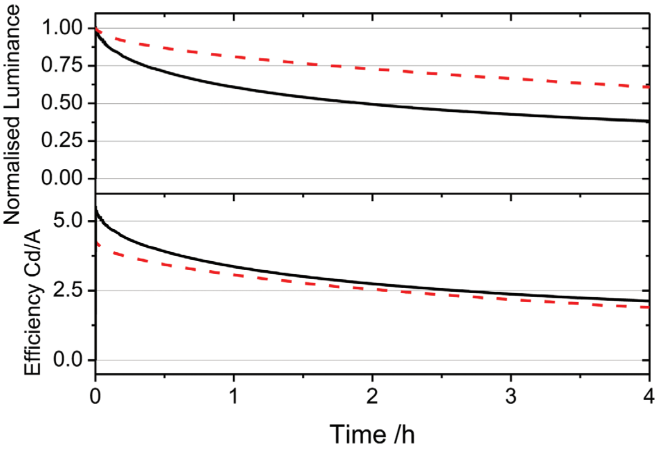

FIG. 4. (Color online) The decay of the device luminance (upper panel) with time and the change in efficiency of the device with time (lower) for a standard device (solid line) and a device containing the triplet quenching additive (dashed line). The devices were both driven from a starting luminance of 5000 cd m^{-2}.

Considering that the delyed emission by TTA is proportional to T^2 and assuming that the non-TTA component of the device turn off is limited by the device RC time constant, a model for the turn off of the device can be derived [Eq. (4)],

$$\mathrm{EL}(t) = Ae^{-t/\tau} + (1-A)\left(\frac{k_\mathrm{T}}{(k_\mathrm{T}+\gamma)e^{k_\mathrm{T}t}-\gamma}\right)^2, \qquad (4)$$

where A gives the proportion of the device EL, which does not originate from TTA, and τ is the RC time constant for the device. Fitting the device turn off transients with Eq. (3) allows one to extract the contribution to the device EL from TTA. For the undriven device shown in Fig. 3(b), the fit to the data is shown. The contribution of TTA to the EL of 0.18 ± 0.02 is extracted for an undriven device. The device RC time constant τ is 24 ns is in good agreement with the expected value from the series resistance and capacitance of the device, giving further support to the conclusion that there is no contribution to the device turn off from the slow release of trapped charges.

Returning to the drop in device efficiency on adding the triplet quenching additive (Fig. 1), the 20% drop in EQE can be rationalized as a loss of the additional contribution to the EQE originating from TTA. When the additive is present, nearly all of the triplets are quenched from the polymer backbone. The low inclusion and short triplet lifetime of the additive means that the triplets are unable to annihilate and, therefore, there is no contribution to the EQE from TTA.

We now turn to an analysis of the stability of the triplets and the TTA process during electrical stressing and show that the proportion of singlets generated via this route is dramatically reduced during electrical stressing, in particular during the early stages of driving. In the absence of the triplet quenching additive, the triplet density drops dramatically to ~10% its initial value after driving the device to T50, as shown in Fig. 2. This drop in the triplet density is considerably greater than either the drop in electroluminescence (50%) or the decrease in the material photoluminescence quantum yield (30%), suggesting that, in this system, the triplets are quenched during driving far more efficiently than the singlets. The loss of the TTA contribution to the electroluminescence at various stages during the lifetest is plotted in Fig. 3(b), and the reduction in the contribution to the EL that TTA makes is clear. The inset of Fig. 3(b) shows that for a device with a half-life of 2 h, the half-life of the singlets generated by TTA is only 0.5 h, thus the loss of the TTA generated singlets must be making a significant contribution to the initial decay of the device.

Finally, we show how removal of the triplets from the device can significantly improve the stability of the device to electrical stress, in particular during the early stages of driving. The rapid drop in the TTA contribution to the electroluminescence dominates the crucial rapid initial decay of devices on the lifetest. Incorporating the triplet quenching additive into the luminescent polymer and hence removing the unstable TTA contribution to the device, the electroluminescence gives a significant boost to the device lifetime, particularly the initial decay. Figure 4 shows the electroluminescence decay of a device both with and without the triplet quenching additive (3). The effect on the lifetime is clear, there is an improvement in T90 of approximately 5× and an improvement of >3× to the final device lifetime. The lower panel of Fig. 4, which shows the efficiency of the devices during lifetest clearly, shows that the extra efficiency boost from the TTA contribution is lost early on in the lifetest, after which the decay of the two devices is remarkably similar.

III. CONCLUSION

We have shown that a significant proportion of the device electroluminescence in a model P-OLED device originates from the generation of emissive singlet excitons from a triplet–triplet annihilation process. Moreover, as a result of the efficient quenching of the triplet excitons by the defect sites generated in the polymer film during driving, this boost to the device efficiency is lost early on in the device lifetime and is a significant contribution to the rapid initial decay often seen in high efficiency fluorescent OLED devices. The lifetime of the device can be significantly enhanced by removing the TTA contribution to the device efficiency using a triplet quenching additive. Using this approach, a >3× improvement in the device half-life (T50) and >5× improvement in the initial decay (T90) have been realized.

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