Triplet-to-Singlet Exciton Formation in poly(*p*-phenylene-vinylene) Light-Emitting Diodes

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The triplet to singlet exciton formation ratio in a MEH-PPV light-emitting diode is measured by comparing the triplet-induced absorptions with optical and electric excitations at the same singlet exciton density. The ratio is a strong universal decreasing function of the averaged electric field. Using 4 ns for singlet to triplet intersystem crossing time, the ratio is significantly larger than the spin-independent value 3 at intermediate field but is reduced to about 2 for higher field.

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The triplet to singlet exciton formation ratio γ is one of the most important issues regarding the electroluminescence (EL) of conjugated polymers. Because EL results exclusively from the decay of singlet excitons, $1/(1+\gamma)$ can be considered as the theoretical limit for the internal quantum efficiency η for a polymer light-emitting diode (LED). Simple spin statistics predicts $\gamma = 3$, but there have been some theoretical works which suggest that the exciton formation process is spin dependent and γ is not fixed at 3 [1,2]. Using magnetic resonance techniques Wohlgenannt and co-workers [3] showed that the capture cross section for the polaron pairs is indeed spin dependent. Direct measurement on γ for a LED based on Pt-containing conjugated polymer has been performed by Wilson and co-workers [4]. They showed that γ is only about 0.75. We believe that such low γ is because the strong spin-orbital coupling and resulting intersystem crossing introduced by the Pt ion make the recombination highly spin dependent. Because of the requirement of heavy atoms on the backbone, their approach is inherently limited to polymers with very low photoluminescence (PL) and EL quantum yield, and cannot be applied to highly luminescent polymers, e.g., poly(*p*-phenylene vinylene) (PPV), polyfluerene, and their derivatives, which are the promising materials for a practical LED. Therefore, one central question still remains: What is the value of γ in an operating LED of highly electroluminescent conjugated polymers? The direction for further improvement of the quantum yield depends critically on its value. Recently Dhoot *et al.* studied the triplet exciton formation in an efficient polymer LED based on OC1C10-PPV [5]. They obtain the ratio γ by dividing the generation rates for the singlet and triplet excitons. This approach, however, requires the absolute values of many quantities including the singlet and triplet exciton densities which are difficult to determine without complicated and indirect interpretations. Uncertainties on γ therefore remain.

In this Letter we report a new and much simpler approach for a direct measurement on the triplet to singlet exciton formation ratio γ in a LED of poly(2-methoxy-5(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV), which is one of the most commonly used polymers for LED. It is found that γ is not a constant but is a strong decreasing function of the electric field. γ is obtained by comparing the triplet exciton densities when the LED is electrically excited (EL) and optically excited (PL), provided the singlet excitons are maintained at the same density for both of the excitations. Let N_S^{EL} and N_T^{EL} be the singlet and triplet exciton densities for EL. Similarly, N_S^{PL} and N_T^{PL} are the exciton densities for PL. In steady state, the exciton densities are related by simple rate equations. The exciton formation and decay are shown in Fig. 1. For EL we have

$$N_S^{\mathrm{EL}} = G\tau_S, \qquad N_T^{\mathrm{EL}} = \gamma G\tau_T. \tag{1}$$

For PL we have

$$N_T^{\mathrm{PL}} = N_S^{\mathrm{PL}}\frac{\tau_T}{\tau_{\mathrm{isc}}}. \tag{2}$$

G is the steady-state generation rate for the singlet exciton in a LED. τ_S and τ_T are the lifetimes for the singlet and triplet excitons, respectively. τ_{isc} is the intersystem

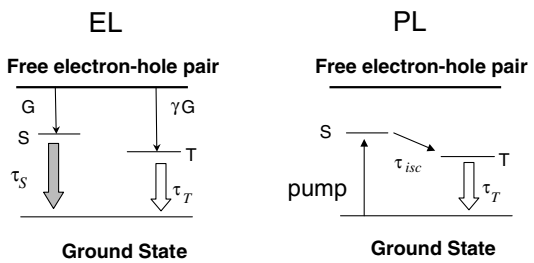

FIG. 1. The exciton formation and decay processes are shown for both optical (PL) and electric (EL) excitations. In the PL triplet excitons result from the intersystem crossing of the singlet excitons. In the EL triplet excitons are formed from capture of triplet electron-hole pairs. γ is the triplet formation ratio relative to the singlet in EL.

crossing lifetime from the singlet to the triplet exciton, which is identified as the only source of triplet exciton under PL. Assuming that the singlet exciton densities N_S^{EL} and N_S^{PL} are made equal, Eq. (1) and (2) gives

$$\gamma = \frac{N_T^{\mathrm{EL}}}{N_T^{\mathrm{PL}}} \frac{\tau_S}{\tau_{\mathrm{isc}}}. \tag{3}$$

The triplet exciton ratio $N_T^{\mathrm{EL}}/N_T^{\mathrm{PL}}$ can be determined by comparing the EL-induced triplet absorption (EA) and the PL-induced triplet absorption (PA) [6]. τ_S is determined by time-resolved PL, and τ_{isc} can be measured by time-resolved PA [7].

A 400 Å poly(3,4-ethylenedioxythiophene) doped with polystyrene sulphonated acid (PEDOT:PSS) is coated on cleaned indium-tin-oxide glass first as the hole-transport layer. MEH-PPV solution in chloroform is then spin coated to form the polymer layer with variable thickness. Ca/Al is evaporated as the cathode. The singlet exciton is detected by a Si photodiode through their radiative decay. The photodetector signal is proportional to the singlet exciton density $N_S^{\mathrm{EL,PL}}$. A 5 mW 409 nm blue diode laser with a tunable attenuator is used as the pump for PL. The triplet exciton is detected by its induced absorption at around 1.5 eV. The probe spectrum, measured by a halogen lamp and 960–500 nm monochromator, is shown as the inset of Fig. 2. The shape and peak position are consistent with the spectrum reported earlier [6]. The measurement on γ is obtained by using a 850 nm (1.46 eV) semiconductor diode laser as the probe. The probe beam is first focused then incident on the LED at room temperature from the glass side and reflected by the metal electrode. Induced absorption inside the active layer reduces the reflection R of the probe beam. The relative change in reflection $\Delta R/R$ is proportional to the triplet exciton density $N_T^{\mathrm{EL,PL}}$. A preamplifier and a lock-in amplifier is used to resolve $\Delta R/R$ of the probe induced by both EL and PL with square-wave modulation. Special care is undertaken to ensure the uniformity of exciton densities in both EL and PL. A mask with an opening of 1 mm^2 is used to select a region with highly uniform EL. The EL uniformity is checked by scanning the probe position across the open region, and the probe-induced absorption changes by less than 1% for one mask, and the difference between different masks in the same LED is within 5%. As for PL, the pump beam is expanded by a beam expander to achieve uniform optical excitation in the opening of the same mask as EL. We mapped the intensity profile of the expanded beam and found that it changes for less than 10% within 1 mm, i.e., the size of the opening. For given bias V, EL and EA are recorded first. The intensity of the pump laser is then tuned such that PL is as strong as EL and PA is recorded. Since both of the excitations cause uniform singlet exciton density in the same open region, the same level of the photodetector signals correspond to the same singlet exciton density.

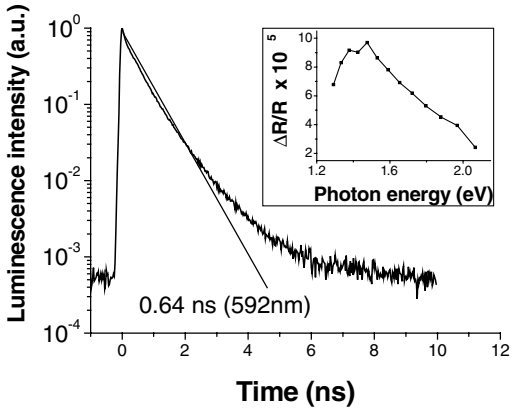

FIG. 2. The time-resolved PL of MEH-PPV film. The data can be fit by a single exponential with lifetime 0.64 ns. The inset is the EA spectrum.

The probe signals EA and PA are divided to obtain the ratio $N_T^{\mathrm{EL}}/N_T^{\mathrm{PL}}$ as a function of V. This procedure is repeated for several masks with different shapes with the same results as expected, further verifying the uniformity of excitations. The ratio is finally substituted into Eq. (3) to get γ. τ_S and τ_{isc} are assumed to be independent of the bias [4]. So the dependence of the ratio $N_T^{\mathrm{EL}}/N_T^{\mathrm{PL}}$ is a direct consequence of the dependence of γ on V.

This method, however, can be reliably used only when the LED has reached its full efficiency. The reason is that when the LED is just turned on (low bias) the recombination zone is close to the metal cathode due to the low electron mobility, and the singlet excitons are quenched by the metal plasma modes [8]. The singlet exciton lifetime is therefore shorter than τ_S measured by time-resolved PL. The V dependence of the conversion efficiency (CE), defined as the ratio between EL intensity and electric current, is used to monitor the metal quenching. As shown in Fig. 3, CE rises rapidly after turn-on then saturates, beyond which the metal quenching is no

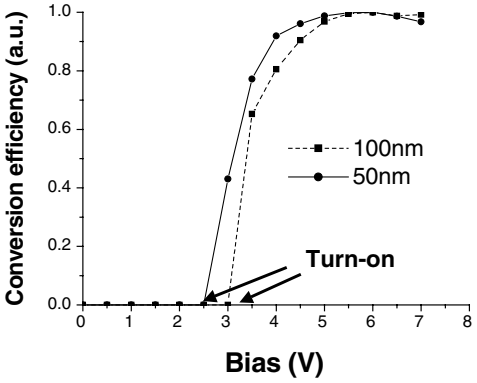

FIG. 3. The conversion efficiencies CEs for 50 and 100 nm LEDs are shown as a function of the bias V. CE rises rapidly as the recombination zone is pushed away from the metal cathode due to enhanced electron mobility at higher field.

longer important. Our measurement on γ is limited to bias with saturated CE only.

The relative triplet and singlet exciton densities are shown in Fig. 4. For PL, N_T^{PL} is basically proportional to N_S^{PL} as expected. But for EL surprisingly N_T^{EL} (measured by EA) changes little with N_S^{EL} as V increases after turn-on. EA can be detected even before EL is turned on with peak position still at 1.5 eV. Evidence that EA is not complicated by other species (polaron, bipolaron) is provided by the same responses of EA and PA to modulation frequency shown in Fig. 5, with triplet exciton lifetime τ_T identified around 100 μs consistent with a previous report [9]. EA before turn-on implies that triplet excitons are not quenched even when they are generated very close to the metal cathode. The consequence of the nonlinear EA/EL relation is that γ decreases dramatically as the bias V increases. Moreover, when we plot γ for 500 and 1000 Å LEDs as a function of the averaged electric field $E \equiv (V - V_{bi})/d$, the two sets of data fall on the same curve, as seen in Fig. 6. V_{bi} is the built-in voltage determined by the onset of CE, and d is the MEH-PPV thickness. Voltage drop in the PEDOT layer is negligible because of its high conductivity. γ is much larger than 3 for intermediate bias, and is reduced by more than 5 times to become about 2 in the high bias region. It implies that triplet exciton formation is no longer such a severe limit for the efficiency of a LED operated under high bias. We use singlet exciton lifetime $\tau_S = 0.64$ ns in Eq. (3). It is obtained by time-resolved PL of our MEH-PPV film on glass without the electrodes as shown in Fig. 2. As for τ_{isc} we use the value 4 ns reported by Frolov and co-workers [7] for PPV films. Despite some uncertainty on the exact value of τ_{isc}, many experiments have indicated that it is a few ns [7,10,11] for conjugated polymers. Therefore, our result that γ is larger than 3 in the intermediate field region (still with CE saturation) holds even with this uncertainty. In fact, a γ lower than 3 would require τ_{isc} larger than 20 ns, which is quite unlikely.

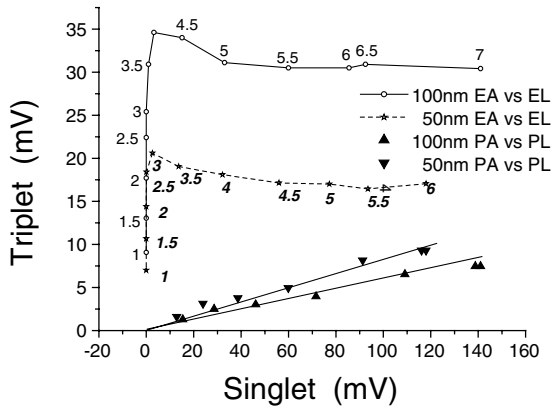

FIG. 4. The triplet exciton density (EA) is plotted against the singlet exciton density (EL) as the bias of an LED is changed. The curve is highly nonlinear and nearly flat after the LED is turned on. Linear relation between triplet and singlet exciton densities for PL is also shown. PL vs PA is extrapolated to some extent to match EL because of the limited pump intensity after beam expansion. The triplet exciton densities (in mV) for EL and PL at the same singlet exciton density are directly divided to give γ. The data are shown in raw voltages recorded by the lock-in amplifier.

The field suppression of the triplet exciton formation leading to $\gamma < 3$ is consistent with the smaller capture cross section of the triplet electron-hole pair [3]. As an electron and hole with triplet spin configuration encounter each other in a conjugated segment, they will form a higher triplet exciton state first. Theoretical calculations using both model Hamiltonian and *ab inito* methods have established a higher T2 triplet exciton above the lowest T1 triplet exciton. Once the triplet electron-hole pair relaxes to T2, there are two possibilities for the next step. The first is further relaxation to T1, and the second is field dissociation back into a free electron-hole pair. The rate for the first possibility is small because the large energy splitting between T2 and T1 is around 1 eV [12], which is much larger than the optical phonon energy, approximately 0.17 eV. There is therefore probably a phonon bottleneck for triplet exciton relaxation [2]. On the other hand, T2 exciton has only a small binding energy around 0.1 eV [13] so the rate of its field dissociation is expected to be large under high electric field. The consequence of the dominance of the dissociation over further relaxation is that only a small fraction of the electron-hole encounter in the triplet spin configuration result eventually in a bound state. This manifests effectively as a field-suppressed cross capture cross section for the triplet. As for the singlet electron-hole pair, the energy splitting between the lowest S1 exciton and higher S2 exciton is only about 0.3 eV [12] so there is no phonon bottleneck. Therefore, all singlet electron-hole encounters in spin singlet configuration result in a singlet exciton, corresponding to a larger capture cross section.

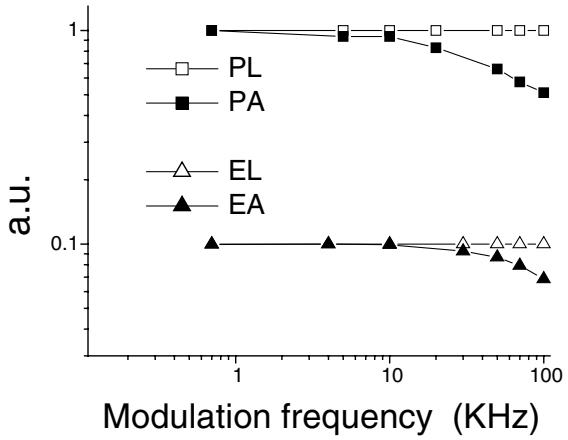

FIG. 5. The frequency dependence of the EA and PA are shown to be the same. Triplet lifetime can be identified to be about 100 μs.

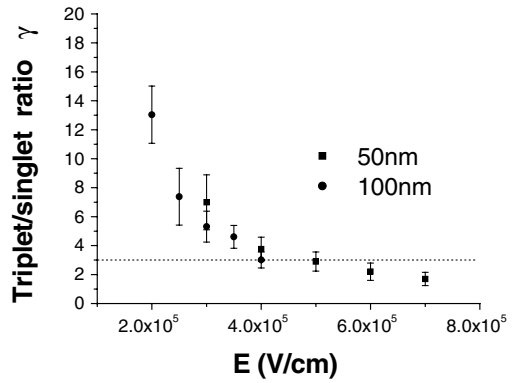

FIG. 6. The triplet exciton formation ratios γ for two LEDs with 500 and 1000 Å MEH-PPV film thickness are shown. The error bars are determined by the values obtained from different LEDs and different masks (see text). They are the same function of electric field within experimental error.

The microscopic origin for γ larger than 3 at the intermediate field is not clear so far. In this work we follow the analysis of Blom *et al.* [8] that the possibility of a higher singlet exciton quenching rate by the metal cathode than by the triplet can be ruled out once CE is saturated, as discussed above. On the other hand, Becker *et al.* reported quenching of PL even for excitons 50–100 nm away from the cathode [14]. Assuming this long-range quenching does exist and taking the average distance between excitons and cathodes as 50 nm, τ_S should be reduced by a factor of 3 to 0.21 ns [14]. γ would then need to be divided by 3 in Fig. 6 and its highest values become only around 4, which is consistent with the criterion of $\gamma < 3$ considering the uncertainty of τ_{isc}. Direct generation of triplet excitons due to impact ionization or another process is also a possible reason for $\gamma > 3$. In a typical local field of 1.5×10^6 V/cm and conjugation length of 10 nm, the carriers can acquire kinetic energy of 1.5 eV, just enough to create a triplet exciton through impact ionization. In fact, the earlier onset of EA than the EL further supports the existence of sources for triplet excitons other than electron-hole recombination.

In conclusion, the triplet formation ratio γ in a MEH-PPV LED is found to be not a constant, but a strong universal function of electric field. γ is larger than 3 in the intermediate field region, and is reduced by more than 5 times as field further increases. The combined effect of phonon bottleneck and field dissociation of higher triplet exciton is proposed to explain these behaviors.

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