

Triplet exciton formation and decay in polyfluorene light-emitting diodes

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We study the triplet excitons in poly (9,9-dioctylfluorene-2,7-diyl) light-emitting diode using infrared induced absorption. The infrared absorption is exclusively due to the triplet excitons and there is no spectral overlap with any other species. A strong suppression of the triplet exciton density relative to the singlet by voltage is observed. Through an unique independent measurement on the triplet exciton lifetime it is shown that the suppression solely comes from triplet exciton quenching by current injection. The triplet-to-singlet exciton formation ratio is independent of voltage as well as temperature, implying a spin-independent exciton formation.

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In organic semiconductors the lowest excited states are one spin singlet exciton and three spin triplet excitons. One of the most important questions in the electroluminescence (EL) of organic semiconductors is whether the formation rates of all four excitons depend on their total spin. If the formation is spin independent, the triplet-to-singlet formation ratio will be three based simply on multiplicity. Since only the singlet excitons decay radiatively, the theoretical limit for the internal quantum efficiency (photon per electron) will be 1/4 for spin-independent exciton formation. For small-molecule organic light-emitting diodes (LED) it has been established that the triplet-to-singlet ratio is indeed three.¹ The key consequence is that the LED efficiency can be raised four times by adding phosphorescent dopants.² On the other hand for conjugated polymer LED the situation is much less clear. Many theoretical models have been proposed for spin-dependent exciton formation, including interchain charge transfer effect^{3,4} and phonon bottleneck.^{5,6} There are also many experimental works suggesting that the exciton formation ratio is not three in polymer LED.^{7,8} However none of these experiments are done in a working LED with typical electroluminescent polymer, so they are unable to give a decisive answer to this question. Recently triplet excitons in a working poly(phenylene vinylene) (PPV) LED is directly measured,^{9–13} the triplet signal is however mixed with polaron signal. In this work we perform an unambiguous determination of the formation and decay of the triplet excitons in poly(9,9-dioctylfluorene-2,7-diyl) (PFO) LED. It is found that there is a strong suppression of the triplet exciton relative to the singlet as the voltage increases. This suppression turns out to be completely due to the quenching of the triplet excitons by polarons. The formation process itself might be in fact spin independent. Our result indicates that there is actually no difference between small molecule LED and polymer LED in terms of the exciton formation process and the importance of harvesting triplet energy by phosphorescent dopants.

The triplet excitons in conjugated polymers are detected by their infrared induced absorption under photoexcitation (PA) or electrical excitation (EA).¹⁴ In addition to triplet ex-

citons, polarons also contribute to the infrared absorption. Moreover, there is an interaction between these two species in a working polymer LED.^{12,13} Unfortunately, for PPV the induced absorption spectra for triplet exciton, electron polaron, and hole polaron are both peaked around 1.47 eV and there is a strong overlap among these signals.^{12,15} PA and EA for PPV become a superposition of triplet exciton and polaron spectra. Even though these overlapping signals can be separated in principle by the difference in frequency responses,¹⁴ the coincidence in the infrared spectrum implies that PPV is not a good material to start with. It turns out that the other commonly used polymer polyfluorene is a much better candidate for this purpose due to the absence of overlap.¹⁶ PA of PFO film is shown in Fig. 1. The spectral shape and the frequency response are identical to the previous report on the PFO triplet exciton.¹⁶ The same spectrum is also observed in EA of 50 nm thick PFO LED after the turn-on voltage. The results at 14 K are shown in Fig. 2. As the voltage increases the induced absorption spectrum maintains a fixed line shape with increasing amplitude. The spectra for various voltages are normalized in the inset of Fig. 2. They are identical as a

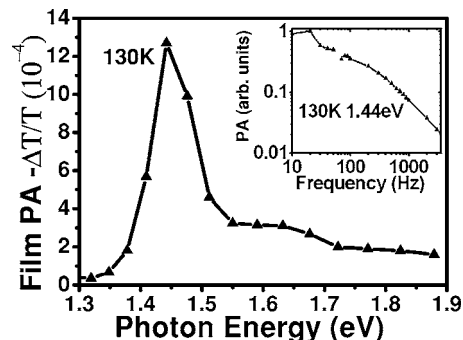


FIG. 1. Relative transmission spectrum for photoinduced absorption (PA) of PFO film is shown at 130 K with 100 Hz lock-in modulation. The dependence on modulation frequency is shown in the inset. The peak at 1.44 eV is due to triplet exciton. The power of the 405 nm CW excitation laser is 15 mW with focus area around 4 mm².

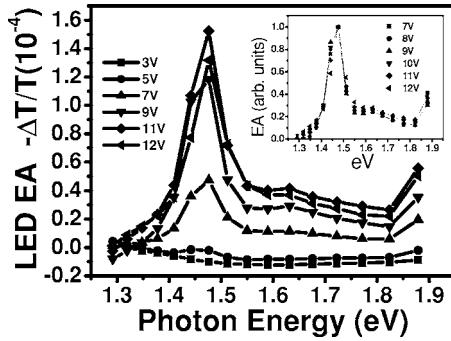


FIG. 2. Electroluminescence-induced absorption (EA) spectrum for PFO LED is shown for various voltage at 14 K. The modulation frequency is 1 kHz. The spectra at different voltages can be normalized to one single line shape as shown in the inset. The LED structure is indium-tin-oxide/PEDOT:PSS/PFO/Ca/Al. PEDOT:PSS is poly(3,4-ethylenedioxythiophene) doped with polystyrene sulphonated acid

proof that there is only one species in this spectral region, and this species has been confirmed to be the triplet exciton in PA. Such identical normalized EA curves can never be observed in PPV. Below we take EA as its peak value at 1.47 eV. The line shape remains the same for whatever voltage, modulation frequency, and temperature.

The most striking feature of Fig. 2 is that the growth of the amplitude of the spectrum with voltage is strongly suppressed at higher voltage. The amplitude of the spectrum is proportional to the average triplet exciton density N_T in the LED. In Fig. 3 N_T is plotted against voltage V . After an initial rapid growth N_T starts to saturate. It is to be compared with the average singlet exciton density N_S and the current density J . N_S is proportional to the EL intensity emitted from the LED. All the curves are normalized to one at their respective maxima. N_S and J are almost proportional to each other meaning a fixed conversion efficiency (CE) from electrical current to singlet excitons as is also shown in the inset of Fig. 3. Unlike the singlet exciton, the density of the triplet exciton is not correlated with the injected current at all. At high voltage while the current increases fast with voltage the

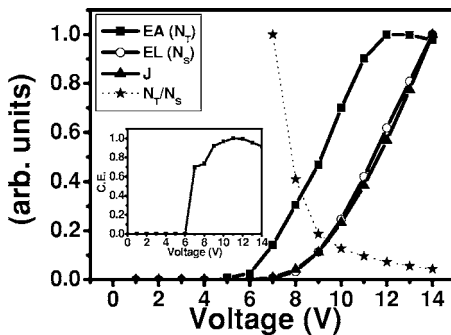


FIG. 3. Voltage dependence of EA (proportional to triplet exciton density N_T), EL (proportional to singlet exciton density N_S), and the current density J are plotted. The ratio N_T/N_S are also shown. The EL conversion efficiency (CE) N_S/J are shown in the inset. For absolute scale, the maximal current density J at 14 V is 966 mA/cm².

triplet exciton is suppressed. In order to stress this remarkable difference between the voltage dependence of the singlet and triplet excitons, their ratio N_T/N_S is shown as a function of voltage. The ratio drops for more than an order of magnitude as the voltage increases. Such a dramatic variation of the ratio between excitons with different spin would lead to a possible interpretation as the strong suppression of triplet exciton formation cross section by the electric field. If this were true due to whatever mechanism, the exciton formation would be spin dependent and the triplet-to-singlet exciton formation rate must not be a fixed number of three in polymer LED. However, the suppressed formation is not the only possibility to explain the behaviors in Fig. 3. The triplet exciton density N_T is a product of its formation rate and its lifetime. Either the suppression of the formation rate or the lifetime can lead to the drop of N_T/N_S with voltage. Assuming γ is the triplet-to-singlet exciton formation ratio and G is the average singlet exciton formation rate per unit volume, the exciton densities are

$$N_S = G\tau_S, \quad N_T = \gamma G\tau_T. \quad (1)$$

Dividing these two relations we have

$$\frac{N_T}{N_S} = \gamma \frac{\tau_T}{\tau_S} \propto \gamma \tau_T. \quad (2)$$

τ_S and τ_T are the singlet and triplet exciton lifetimes. Here we assume that τ_S is independent of voltage and other conditions in the experiment because of the fast radiative decay. The similarity of N_S and J curves in Fig. 3 suggests that G is in fact roughly proportional to the current density. N_T/N_S can be experimentally measured as shown in Fig. 3 as a function of voltage V . Now we need to find out whether its strong V dependence comes from γ or τ_T according to Eq. (2). If it comes from γ , field dissociation of triplet exciton is probably the main reason. Exciton-polaron interaction might be the cause if it turns out to come from τ_T .

Since EA can only determine the variation of the product of γ and τ_T , it will be helpful to study a situation where one of the two are known to be fixed. For this purpose we perform a unique PA measurement for a LED under constant voltage bias. In the EA measurement discussed above, the voltage is square-wave modulated at a frequency which is used as the reference frequency for the lock-in amplifier for the infrared induced absorption. In the PA for LED, the LED is simultaneously excited by a modulated pump laser (405 nm) and a dc voltage bias. The pump laser modulation frequency is used as the lock-in reference while the voltage does not change with time. Even though both the photoexcitation and electrical current injection cause triplet exciton formation, only the photoexcited triplet excitons are detected by the lock-in amplifier as the PA signal. The basic idea here is that for photoexcitation the triplet exciton completely comes from the intersystem crossing from the photoexcited singlet exciton, so the triplet exciton formation is independent of the voltage V . The triplet exciton density N_T^{PA} in this measurement is therefore proportional to τ_T only as V

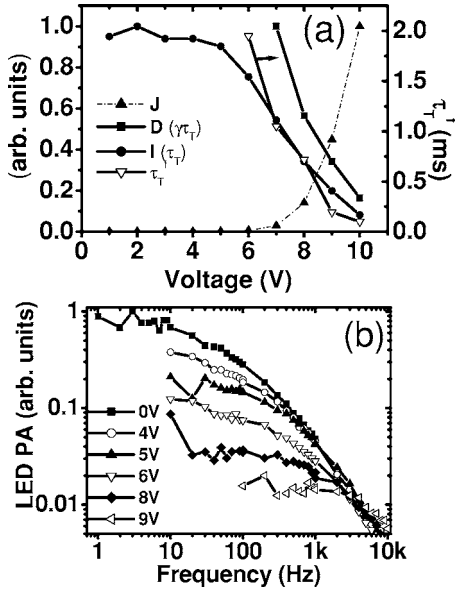


FIG. 4. Triplet lifetime τ_T is obtained from PA/PL [see Eq. (3)], measured at 14 K with 100 Hz optical pump modulation. $\gamma\tau_T$ is obtained from EA/EL [see Eq. (2)]. The frequency response of PA due to photoexcited triplet excitons measured in LED is shown to depend on the applied dc voltage in (b). The fitted lifetime τ_T^f from (b) is plotted as a function of voltage V in (a). Note that $\gamma\tau_T$, τ_T and τ_T^f share the same voltage dependence. The fitting is done by drawing a line with slope minus one to fit the high-frequency part and a horizontal line (slope zero) from the low frequency limit. The crossing of these two lines determines the lifetime.

changes. Because there might be some slight dependence of the photoexcited singlet exciton density N_S^{PA} on V , it is more precise to write

$$\frac{N_T^{\text{PA}}}{N_S^{\text{PA}}} \propto \tau_T. \quad (3)$$

N_S^{PA} is determined by the photoluminescence (PL) intensity. We are now free from the coupling of γ and τ_T occurred in EA. Since the LED is under voltage bias as in EA, the photoexcited triplet exciton will experience the same environment as in EA in terms of field and polaron density, etc. The lifetime should therefore be the same function of V . PA/PL, i.e., $N_T^{\text{PA}}/N_S^{\text{PA}} \propto \tau_T$, is plotted versus V in Fig. 4(a) together with EA/EL, i.e., $N_T/N_S \propto \gamma\tau_T$. Equations (2) and (3) are used. It turns out that they are *the same* function of V . It implies that $\gamma\tau_T$ and τ_T have the same V dependence. In other words, the triplet-to-singlet exciton formation ratio γ is independent of V . The suppressed EA in Fig. 3 comes solely from the suppression of τ_T by voltage which occurs after about 6 V. Interestingly this onset of suppression coincides with the onset of the large current injection as shown in Fig. 4. This implies that the suppression of the triplet lifetime is due to polarons instead of electric field. We also measure $N_T^{\text{PA}}/N_S^{\text{PA}}$ in the reverse bias and found that there is no significant voltage dependence. Since the field is large in the reverse bias, this confirms that field alone is not the reason for the suppression. Current injection and polarons must be involved in the mechanism.¹³ Independent evidence for trip-

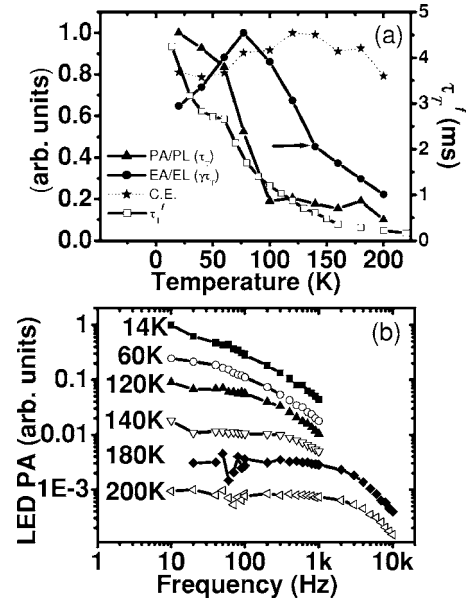


FIG. 5. In (a) $\gamma\tau_T$ and τ_T , both measured at 100 Hz modulation, are plotted as functions of T at 11 V. The EL conversion efficiency (CE) N_S/J is shown to be independent of T . The LED PA frequency response at difference T in (b) are measured without bias. Note that $\gamma\tau_T$, τ_T and τ_T^f share the same temperature dependence.

let lifetime suppression by voltage is provided by measuring the frequency response of LED PA under various dc voltages. The results are shown in Fig. 4(b). PA turns from constant to inverse frequency behavior at higher frequency as V increases. The fitted lifetime τ_T^f is also shown in Fig. 4(a). As expected it has the same voltage dependence as τ_T measured from PA. LED with thickness 100 nm shows the same features.

After knowing that γ is independent of the voltage, the next question is whether it depends on another basic parameter for a working LED, i.e., temperature T . So far T is fixed at 14 K. Here we repeat all the measurements above except T is changed and voltage fixed at 11 V. In this way we can measure the product $\gamma\tau_T$ and τ_T itself as functions of T . One would be curious to know in addition to same V dependence if they have the same T dependence as well. $N_T/N_S (\propto \gamma\tau_T)$, $N_T^{\text{PA}}/N_S^{\text{PA}} (\propto \tau_T)$, and τ_T^f from frequency response are all plotted against T in Fig. 5(a). They all have the same T dependence. The discrepancy at low temperature is due to non-steady state caused by long triplet lifetime. τ_T^f is fitted from Fig. 5(b). These results show that γ is neither a function of V nor T , i.e., a true constant. The suppression of τ_T at higher temperature also correlates well with the increasing current density J due to higher polaron mobility, consistent with the above interpretation of triplet exciton-polaron interaction.

Even though the absolute value of triplet-to-singlet formation rate γ is not determined, the fact that γ is a true constant independent of LED operation conditions strongly suggests that the exciton formation is spin independent and the constant is in fact three. γ is not three would imply that the capture cross sections for singlet and triplet electron-hole pairs are different. The electron-hole pair in spin configuration with smaller capture cross section, say triplet, would

have a higher chance to be dissociated by thermal fluctuation or electric field than the other spin configuration. In such a spin-dependent exciton formation process we would therefore expect a dependence of the formation rate on temperature, field, or current density. Since none of these parameters affect γ , we believe that the capture cross section for the singlet and triplet electron-hole pairs are the same, i.e., spin-independent exciton formation. The strong suppression of the triplet exciton lifetime is probably due to the Auger recombination where the energy of the triplet exciton is given to the kinetic energy of a free polaron accompanied with a spin flip through exchange Coulomb interaction. In addition to the triplet-polaron interaction, triplet-triplet annihilation may also contribute to the suppression of τ_T at high voltage. Even though an interesting topic by itself, the mechanism of triplet quenching by the polarons and its bimolecular rate coefficient is not the main focus of this work. The turn-on of triplet exciton in EA requires lower voltage than the singlet (Fig. 3), presumably because the singlet lifetime is suppressed by the

cathode quenching at low voltage. What is most important is that, while the decay is spin dependent, the formation rates of the four excitons are all simply proportional to the injected current density regardless of their spin. Apparently heavy-metal phosphorescent dopants are needed in order to turn the 3/4 of triplet energy into light.

In conclusion, through the direct measurement of density and lifetime of triplet exciton in a working polymer LED we show that there is a strong quenching of triplet exciton by the injected polarons at higher voltage. However the triplet-to-singlet exciton formation ratio is neither a function of voltage nor temperature. This suggests a spin-independent exciton formation in polymer LED, similar to the situation of small-molecule organic LED.

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