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Triplet exciton formation ratio in poly(*p*-phenylene-vinylene) light-emitting diode

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Abstract

The triplet to singlet exciton formation ratio in a poly(2-methoxy-5(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) light-emitting-diode is measured by comparing the triplet induced-absorptions with optical and electric excitations at 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-statistics value 3 at intermediate field but is reduced to about 1 for higher field.

Key words: triplet exciton, light-emitting-diode
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In this work we report the first 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). 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 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. For EL we have $N_S^{EL} = G\tau_S$, $N_T^{EL} = \gamma G\tau_T$ For PL we have $N_T^{PL} = N_S^{PL}\frac{\tau_T}{\tau_{isc}}$. G is the steady-state generation rates for the singlet exciton in an LED. τ_S and τ_T are the lifetimes for the singlet and triplet excitons, reapectively. τ_{isc} is the intersystem crossing lifetime from the singlet to the triplet exciton, which is

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identified as the only source of triplet exciton in PL. Assuming that the singlet exciton densities N_S^{EL} and N_S^{PL} are made equal, we have $\gamma = \frac{N_T^{EL}}{N_T^{PL}} \frac{\tau_S}{\tau_{isc}}$. The triplet exciton ratio N_T^{EL}/N_T^{PL} can be determined by comparing the EL-induced triplet absorption (EA) and the PL-induced triplet absorption (PA). τ_S is determined by time-resolved PL, and τ_{isc} can be measured by time-resolved PA[1].

A 400 Å hole-transport PEDOT:PSS layer is coated on cleaned ITO glass first. The MEH-PPV solution in chloroform is then spin-coated to form the active layer. Ca/Al cathode is evaporated on top of it to complete a LED. 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 850 nm (1.46 eV)[2]. A mask with a opening of 1 mm^2 is used to select a region with highly uniform EL. The intensity profile of the pump beam is found to change for less than 10 percent within the mask size. 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. 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. Our measurement on γ is limited to bias with saturated CE only.

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 set of data fall on the same curve, as seen in Fig.1. V_{bi} is the built-in voltage determined by the onset of CE, and d is the MEH-PPV thickness. γ is much larger than 3 in for intermediate bias and smaller than 3 for high bias. We use singlet exciton lifetime $\tau_S = 0.64$ ns obtained by time-resolved PL of our MEH-PPV film. We use τ_{isc} =4 ns[1].

In conclusion, γ is larger than three in the intermediate field region, and is reduced by more than five times as field further increases. Harvest of triplet electron-pairs is justified for intermediate bias but not necessary for high bias of a LED. The field dissociation of higher triplet exciton is proposed to explain this behavior.

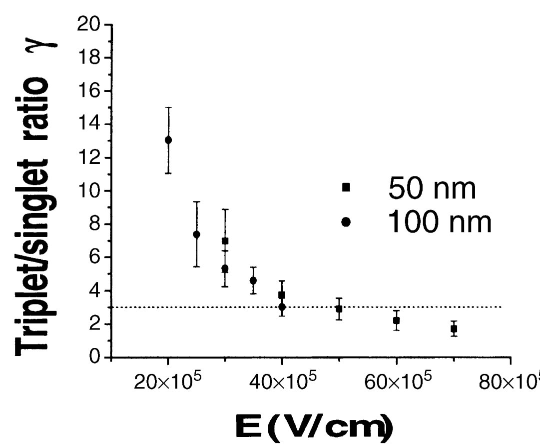

Fig.1

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