

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

In a recent Letter, Lin *et al.* [1] presented a method to study the triplet-to-singlet formation ratio γ in a poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) light-emitting device (LED). The spin-statistical ratio is three, while there are several recent papers showing that γ can be much lower in long-chain polymers, even below one [2–4]. We will show by extending the model presented in [1] that the measurements and results will be inconsistent with other similar measurements suggesting that the method presented in Ref. [1] cannot be used for estimating γ , the reason being that the induced absorption at 1.46 eV is not caused by triplet excitons alone.

Assuming that the induced absorption at 1.46 eV is only due to triplet excitons with a lifetime of 100 μ s [1], there will be a finite possibility for a triplet exciton-polaron reaction to occur. The possible pathway would be $T_1 + P \rightarrow S_0 + P + \text{phonons}$, where P denotes spin-half polarons in the device [5]. We can then write the rate equation for the density of triplet excitons $[T]$ as

$$\frac{d[T_{\text{EL}}]}{dt} = \gamma G - \frac{[T_{\text{EL}}]}{\tau_T} - \beta[T_{\text{EL}}][P], \quad (1)$$

where G is the (singlet) generation rate and β is the rate constant for triplet exciton-polaron reaction. By following Lin *et al.*, we can write the corrected γ_{corr} during LED operation as

$$\gamma_{\text{corr}} = \frac{[T_{\text{EL}}]}{[T_{\text{PL}}]} \frac{\tau_S}{\tau_{\text{isc}}} (1 + \tau_T \beta [P]), \quad (2)$$

where $\tau_S = 0.64$ ns is the singlet lifetime and $\tau_{\text{isc}} = 4$ ns is the intersystem crossing time [1]. Because of the space-charge-limited current-type devices used we can get a lower estimate of the carrier density by the simple formula $[P] \approx \epsilon \epsilon_0 F / ed$, where $\epsilon \epsilon_0$ is the permittivity of the material, F the applied field, e the electron charge, and d the interelectrode distance [5]. Dhoot *et al.* estimated β at 10 K to $\beta = 3 \times 10^{-14}$ cm³/s [4], which must be seen as a lower limit, since the rate constant increases strongly with increasing temperature, and it can even reach 10^{-9} cm³/s at room temperature in single crystals of anthracene [5]. In Fig. 1 we show the calculated γ_{corr} according to the values estimated from Fig. 6 of Ref. [1] and using Eq. (2).

From the more detailed analysis presented in this Comment it is clear that γ_{corr} is always much higher than the spin-statistical value of 3. For a very reasonable assumption of a room temperature $\beta = 3 \times 10^{-12}$ cm³/s, we get that $\gamma_{\text{corr}} \sim 100$, i.e., only less than 1% of the excitons would be singlets, clearly inconsistent with the high electroluminescence (EL) efficiency in these devices and with measurements performed in other groups [2–4].

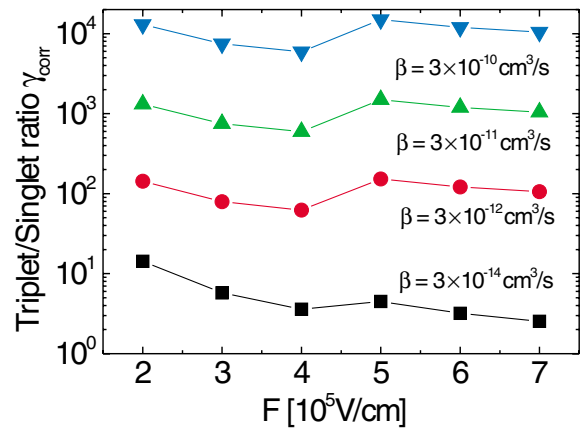


FIG. 1 (color online). Corrected triplet-to-singlet formation ratio γ calculated using the values from Ref. [1] and Eq. (2) with β given in the figure.

The possible error in the analysis of Ref. [1] is the assignment of the induced absorption peak at 1.46 eV to triplet excitons alone. The triplet absorption is strongly decreasing as a function of increasing temperature, and at room temperature no triplet signal can be observed at all [4]. It has also been shown in thin films of PPVs that at higher temperatures the peak at 1.5 eV can be attributed to charged excitations [4,6] with very similar frequency dependence as reported in [1]. Since the induced absorption peak at 1.46 eV may not be attributed to triplets alone, γ estimated using either Eq. 3 in Ref. [1] or Eq. (2) in this Comment will be incorrect. We therefore suggest that the results of Ref. [1] cannot be used as a measure of γ .

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R. Österbacka*

Department of Physics
Åbo Akademi University
Porthansgatan 3
FIN-20500 Turku, Finland

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*Electronic address: rosterba@abo.fi

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