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Reverse bias measurements of the photoluminescent efficiency of semiconducting organic thin films

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Abstract

Photoluminescent (PL) efficiency measurements are an essential component of the characterization of high efficiency organic light emitting devices. We demonstrate that a reverse bias technique for measuring PL efficiency possesses several advantages. Using a two-tone synchronous detection scheme, it is found that nonlinearities in the reverse bias photoresponse are a probe for the presence of charge transfer states that may confuse the interpretation of PL data. Compared to alternative techniques, reverse bias measurements are also relatively unaffected by photoinduced changes in material properties.

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1. Introduction

Photoluminescent (PL) efficiency is not only an important manifestation of exciton formation processes in an organic material, but also an essential component of the characterization of a material for potential applications, such as high efficiency organic light-emitting diodes (OLEDs). For example, PL efficiency measurements are used to quantify the maximum possible electroluminescent (EL) efficiency of an OLED, and they have also been used to calculate singlet and triplet population statistics [1–4].

PL efficiency is measured by generating excited singlet excitons S^* with an optical pump and collecting the fluorescence from relaxed singlet excitons, S. The measured efficiency, however, may be less than the maximum, or ideal, PL efficiency if excited singlet excitons decay to non-emissive charge transfer (CT) states rather than relaxed singlet excitons [5–7]. The fraction of excited singlet excitons, S^*, that form relaxed singlet excitons, S, is termed the branching ratio, [5] and a determination of the ideal PL efficiency requires knowledge of this ratio. The branching ratio is often assumed to be unity, corresponding to no CT formation, but measurements have shown that as few as 50% of excited singlet states directly form the relaxed singlet state in certain polymers [5,6], and also that the branching ratio may be dependent on pump energy [5,7].

It is desirable, then, to use a PL measurement technique that also indicates whether the branching ratio is unity in a particular film. We demonstrate that a reverse bias technique [2] for measuring PL efficiency will produce a non-linear

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characteristic when the branching ratio is substantially below unity. In addition, organic thin films are often fragile and may be susceptible to chemical degradation and laser-induced morphological changes that can corrupt PL measurements. We demonstrate that reverse bias measurements of PL efficiency are relatively unaffected by transient changes in thin film properties, such as changes in absorption.

The effect of CT states on reverse bias measurements is determined in Section 2, and experimental data showing linear and non-linear photoresponses as a function of pump wavelength is described in Section 3. In Section 4, we compare the reverse bias technique to conventional methods and present data showing changes in absorption and photoluminescence for a polymer thin film in a low-oxygen environment. We also discuss the implications for measurements of the singlet-triplet ratio in polymers that compare EL to PL efficiencies.

2. Theory of reverse bias PL efficiency measurement

Fig. 1(a) shows a model for exciton formation after optical or electrical excitation of an organic material [2]. The electrical excitation is assumed to occur under forward bias in an OLED heterostructure, so that injected charges are confined [8]. The model considers five discrete states of a possible continuum of states: the excited singlet exciton S*, the relaxed singlet and triplet excitons S and T, and singlet and triplet CT states. Each of these states consists of an electron–hole pair, and is classified by the symmetry of its spin wavefunction under particle exchange. Each state has three triplet spin-symmetric configurations, and one singlet spin-antisymmetric configuration.

Excitons are highly localized and consist of a hole and electron situated on one molecule or polymer chain. CT states are bound electron–hole pairs that are not confined to a single molecule or polymer chain, and are precursors to exciton for-

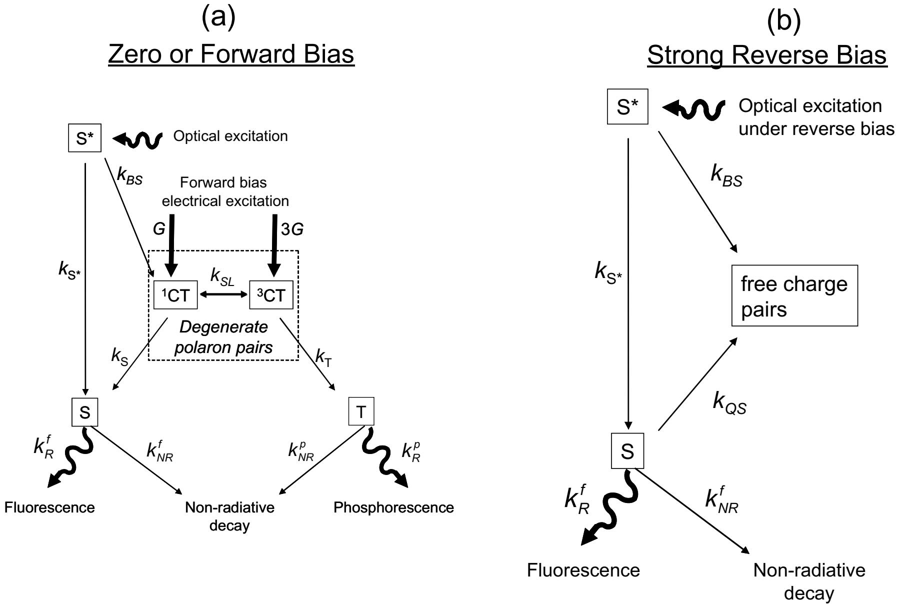


Fig. 1. (a) A rate model of exciton formation considering five states: the excited and relaxed singlet states S* and S, the relaxed triplet state T, and the singlet and triplet CT states. The efficiency of formation of S from S* is described by the branching ratio b_0 at zero electric field (Eq. (3)) and b_F (Eq. (5)) at non-zero electric field. Electrical excitation is assumed to occur under forward bias in an OLED heterostructure. Adapted from [2]. (b) A rate model of exciton formation in the presence of a reverse bias electric field. CT states are assumed to dissociate to charge with unity probability.

mation. Exchange interactions are strongest in excitons, lowering the energy of the triplet exciton with respect to the singlet exciton. CT states, on the other hand, experience weak exchange interactions and are assumed to have degenerate singlet and triplet states. Mixing between these degenerate CT states is facilitated by spin lattice interactions, with mixing rate k_{SL}, which is assumed to be large [9], i.e. $k_{SL} \gg k_S, k_T$. Here k_S and k_T are the rates of formation of relaxed singlet and triplet excitons from singlet and triplet CT states respectively.

Electrical excitation forms singlet CT states at some rate G, and triplets at $3G$. Excited singlet excitons, S^*, form relaxed singlet excitons, S, at a rate k_{S^*} and CT states at a rate k_{BS}. Fluorescent singlet excitons decay radiatively and non-radiatively at rates k_R^f and k_{NR}^f respectively, and phosphorescent triplet excitons, T, decay radiatively and non-radiatively at rates k_R^p and k_{NR}^p, respectively. In most fluorescent materials with weak spin-orbit coupling, the phosphorescent rate k_R^p and the intersystem crossing rates from the singlet to triplet manifolds are small, and they are neglected here.

From Fig. 1(a), the ideal PL efficiency η_{PL} is given by

$$\eta_{PL} = k_R^f/(k_R^f + k_{NR}^f). \tag{1}$$

The ideal PL efficiency is the upper limit of the EL efficiency and of the measured PL efficiency,

$$\eta_{PL}^{\text{measured}} = b_0\eta_{PL}, \tag{2}$$

where the branching ratio in the absence of an applied electric field $b_0 \leqslant 1$ is a measure of the efficiency of formation of the relaxed singlet state from the excited singlet state [5]. From Fig. 1(a), the branching ratio is [2]

$$b_0 = \frac{\chi_S k_{BS} + k_{S^*}}{k_{S^*} + k_{BS}}, \tag{3}$$

where $\chi_S = k_S/(k_S + k_T)$ is the fraction of CT states which relax into singlet excitons.

The reverse bias technique of measuring the PL efficiency involves optically exciting a luminescent organic thin film inside an OLED under reverse bias [2]. The reverse bias establishes an electric field that dissociates CT states and some singlet excitons into free charge pairs. In contrast with forward bias, where charges are confined by the heterostructure, in reverse bias the charge is swept out of the OLED as photocurrent. Fig. 1(b) presents a model for exciton formation and dissociation after optical excitation under reverse bias. The probability of dissociation of a CT state under strong reverse bias is assumed to be unity, and the rate k_{BS} now describes the dissociation of excited singlet states into free charge pairs [3]. The dissociation rate of relaxed singlet excitons under reverse bias is k_{QS}. Both the rates k_{QS} and k_{BS} will be dependent on electric field strength.

The photocurrent, I_{ph}, from dissociated excitons and CT states under reverse bias is

$$I_{ph} = q\phi(b_F\eta_{QS} + 1 - b_F), \tag{4}$$

where ϕ is the incident photon flux, q is the electron charge, η_{QS} is the probability of dissociation of a relaxed singlet exciton under reverse bias, and b_F is the branching ratio under a reverse bias electric field. From Fig. 1(b), $\eta_{QS} = k_{QS}/(k_R^f + k_{NR}^f + k_{QS})$, and

$$b_F = k_{S^*}/(k_{S^*} + k_{BS}). \tag{5}$$

The change in PL under application of a reverse bias electric field is, from Fig. 1,

$$\begin{aligned}\Delta PL &= PL_0 - PL_F \\ &= -hv\phi\eta_C\eta_{PL}[b_0 - b_F + b_F\eta_{QS} + \chi_S(1 - b_0)],\end{aligned} \tag{6}$$

where η_C is the output coupling efficiency and hv is the photon energy. The observed quantity in reverse bias measurements of the PL efficiency is $\Delta PL/I_{ph}$, which is, from Eqs. (4) and (6),

$$\frac{\Delta PL}{I_{ph}} = -\frac{hv}{q}\eta_C\eta_{PL}\left(\frac{b_0 - b_F + b_F\eta_{QS} + \chi_S(1 - b_0)}{b_F\eta_{QS} + (1 - b_F)}\right). \tag{7}$$

The quantity $q/hv(-\Delta P_{PL}/I_{ph})$ therefore underestimates the out-coupled PL efficiency unless $b_0 = b_F = 1$.

If a CT formation pathway exists (i.e. $S^* \rightarrow CT$), the rate of CT formation is expected to increase with electric field, with a corresponding decrease in the branching ratio. Conversely, an electric-field-independent branching ratio implies there is no pathway $S^* \rightarrow CT$ and hence $b_0 \sim 1$. This is the basis for the capability of the reverse bias technique to detect the presence of CT states. Eq. (7) shows that an electric field dependence of the branching ratio, b_F, must cause an electric field dependence in the measured quantity $\Delta PL/I_{ph}$ and a non-linear reverse bias characteristic. A reverse bias characteristic which is measured to be linear, therefore, requires b_F to be independent of electric field, so that that $b_0 \sim b_F \sim 1$, and, from Eq. (7),

$$\eta_C \eta_{PL} = q/h\nu(-\Delta P_{PL}/I_{ph}). \tag{8}$$

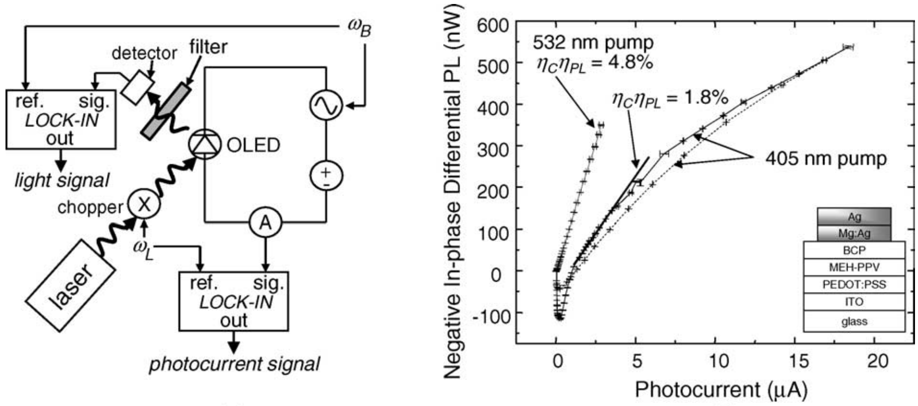
This limit applies to many polymers excited at their absorption edge and has been considered elsewhere [2].

Note that a non-linear reverse bias characteristic $\Delta PL/I_{ph}$ does not itself require $b_0 < 1$. A reverse bias characteristic that is only non-linear at high pump energies, however, strongly suggests the formation of CT states and $b_0 < 1$. Such a characteristic is presented in the next section.

In addition to acting as a probe for CT states, the reverse bias method offers two other important advantages. First, because the PL efficiency is obtained by a comparison of ΔPL to I_{ph}, the strength of absorption of pump light by the organic material does not affect the result. Second, the EL and PL efficiencies can be measured using the same device and in the same experimental geometry, so that the out-coupling efficiency η_C does not need to be determined in experiments comparing EL to PL efficiencies [2].

3. Reverse bias PL efficiency measurements

Reverse bias measurements of the PL efficiency of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) in OLED structures were performed using the two-tone synchronous detection technique, with the experimental setup shown in Fig. 2(a). The reverse bias PL efficiency experiment measures photocurrent and photoluminescence as a function of bias. The total measured current, however, will include reverse bias leakage current, and, along with measured photoluminescence, will be affected by random source pump fluctuations and extraneous light sources.



(a) (b)

Fig. 2. (a) Experimental setup for reverse bias two-tone synchronous measurement of the PL efficiency of an organic thin film placed inside an OLED [2]. Taken from [2]. This arrangement prevents corruption of the measurement by leakage current and noise. (b) Differential photoluminescence ΔPL versus photocurrent characteristics for MEH-PPV at two different pump wavelengths. The component of $-\Delta PL$ in phase with the reverse bias voltage modulation is plotted. The non-linearity and low efficiency of the $\lambda = 405$ nm characteristic are an indication of the formation of CT states, and are not due to degradation, as indicated by the similarity of the up (solid) and down (dashed) sweeps. The $\lambda = 405$ nm efficiency is taken from the slope of the data as shown. The $\lambda = 532$ nm characteristic is from [2].

Two-tone synchronous detection excludes these effects by modulating the applied reverse bias and source pump at frequencies ω_B and ω_L respectively, and measuring photocurrent and photoluminescence at frequencies ω_L and ω_B respectively [2].

Cleaned and UV-ozone treated glass slides precoated with an ITO anode were used as OLED substrates. The transparent, conductive polymer PEDOT:PSS was spun onto the slides, which were then baked at $T \sim 120$ °C for at least 30 min in an oxygen-free environment. An approximately 300-Å-thick layer of MEH-PPV was spun-cast onto the PEDOT:PSS layer, and the slides were baked again, at $T \sim 115$ °C for at least 10 h. Finally, a 150 Å-thick ETL layer of BCP, a 500 Å-thick layer of 60:1 Mg:Ag and a 500 Å-thick layer of Ag were thermally evaporated in a high vacuum of less than 10^{-6} Torr [2].

Fig. 2(b) shows the OLED device structure and two reverse bias characteristics measured in air using two different optical pumps on two different devices, immediately after each had been fabricated. One optical pump was a laser of intensity $\sim$3 W/cm^2 tuned to the absorption edge of MEH-PPV at wavelength $\lambda = 532$ nm, and the second was a laser with wavelength $\lambda = 405$ nm and intensity $\sim$0.4 W/cm^2. The two traces of the $\lambda = 405$ nm characteristic represent an upwards sweep in voltage (solid line) followed by a downwards sweep (dashed line), and their similarity indicates that the nonlinearity of the $\lambda = 405$ nm characteristic is not due to degradation of the OLED over the course of the measurement. The nonlinearity is also not a result of leakage current, since two-tone synchronous detection rejects any leakage current component in the detected photocurrent [2]. Applying Eq. (8), the out-coupled PL efficiency measured using the $\lambda = 405$ nm pump is $\eta_C\eta_{PL} < 1.8\%$. On the other hand, the $\lambda = 532$ nm characteristic is linear and produces an out-coupled PL efficiency of $\eta_C\eta_{PL} = 4.8\%$. The initial increase in PL when pumped at $\lambda = 405$ nm results from the de-trapping of photogenerated charge by the reverse bias field. This reduces singlet-polaron annihilation [10] at low bias but this effect is overwhelmed by singlet exciton dissociation at higher bias [2].

The pump wavelength dependence of the PL efficiency measurements in Fig. 2(b) is consistent with the detection of CT states by the reverse bias technique. The higher-energy pump excites CT states via higher-energy singlet exciton states, S*, causing a non-linear characteristic and a reduced PL efficiency as discussed above. The lower-energy pump excites singlets close to the absorption edge of MEH-PPV, presumably below the energy of the CT manifold in MEH-PPV, reducing the likelihood of CT state formation. From Eq. (2), then, the $\lambda = 532$ nm characteristic more accurately measures the ideal PL efficiency η_{PL}; see [2] for a full discussion. The wavelength dependence of the data in Fig. 2(b) is also observed in photoexcitation spectra of degraded PPVs [5].

4. Comparison with alternative techniques

Conventional measurements of PL efficiency require absolute determinations of absorption and fluorescence. Typically these measurements are performed consecutively in an integrating sphere [11]. However, many potentially interesting organic materials suffer from instabilities that may corrupt such PL measurements. Fig. 3 shows the change in

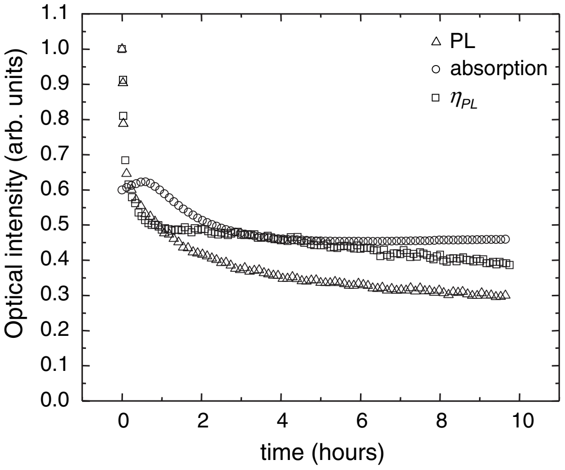


Fig. 3. Change in photoluminescence, absorption and PL efficiency of a thin film of MEH-PPV exposed to a pump laser with wavelength $\lambda = 405$ nm and intensity 0.4 W/cm^2 as a function of time. PL efficiency and fluorescence are normalized to 1.

PL and absorption of a 300 Å-thick MEH-PPV thin film with time as it is exposed to a pump laser with wavelength $\lambda = 405$ nm and intensity $\sim$0.4 W/cm^2 in an environment with less than 25 ppm oxygen. The film was spun onto a cleaned glass slide and baked at $T = 115$ °C for at least 10 h. The film was never exposed to room air. It is seen in Fig. 3 that both PL *and* absorption decrease rapidly. The decrease in PL is not fully accounted for by the decrease in absorption, suggesting that it is at least partially due to an irreversible degradation process which is expected to create defect sites that enhance the rate of exciton dissociation into CT states [5,12]. Indeed, a chemical change in the photoexcited film leading to the formation of new energetic states is evidenced by the increase in absorption for $t < 1$ h. Exposure of a second, identical, MEH-PPV thin film to a pump laser with wavelength $\lambda = 532$ nm and intensity $\sim$3 W/cm^2 produces similar rapid declines in PL and absorption. Optical micrographs of this second film demonstrate that the decrease in absorption is partly due to morphological changes, including peeling of the thin polymer film.

Conventional PL efficiency measurements must compensate for such possible changes with time of the absorption, fluorescence, and branching ratio, especially in circumstances where the organic material is necessarily fragile, for example in studies of very thin films of MEH-PPV. These photophysical changes can be caused by morphological instabilities in the film or by chemical degradation, which may occur even in a low-oxygen environment, since impurities may be incorporated during film deposition. Thus, if the organic film can be incorporated into an OLED, the reverse bias technique may be preferred, both for its insensitivity to absorption strength, and its ability to detect branching ratios below unity. Indeed, linear reverse bias characteristics were measured over time scales of approximately half an hour on thin films of MEH-PPV incorporated into OLEDs, using the same $\lambda = 532$ nm optical pump that produced rapid declines in PL and absorption as discussed above [2].

Finally, we note that measurements of PL efficiency have been critical in determining the ratio of singlet to triplet excitons formed in the electroluminescence of high efficiency polymeric OLEDs. Based on comparisons of EL and PL, several recent studies have concluded that the singlet fraction is well above the spin-degenerate limit of 25% [1,3,4]. However, as noted above, measurements of PL efficiency can result in underestimates if the branching ratio is below unity. Indeed, if $b_0 = 0$, then under the model described in Fig. 1, optical excitation is exactly equivalent to electrical excitation, yielding an apparent singlet fraction of $\chi_S = \mathrm{EL}/\mathrm{PL} \sim 100\%$. Here again, it is desirable to employ a PL measurement technique that detects the presence of a low branching ratio. Otherwise, it may be necessary to record the photoexcitation spectrum before and after each PL and EL measurement.

5. Conclusion

Knowledge of the branching ratio b_0 for the formation of relaxed singlet excitons from excited singlet excitons is necessary for measurements of the ideal PL efficiency of organic materials. Predicting the branching ratio is difficult, since it is expected to be dependent on the type and preparation of the organic material, on a variety of degradation processes, and on wavelength, even for pristine materials [5,7]. In particular, degradation under optical excitation may occur rapidly even in a low-oxygen environment. It is desirable to employ a PL efficiency measurement technique which inherently also indicates whether b_0 is substantially less than unity. The reverse bias measurement technique detects the presence of CT states formed when b_0 is less than unity, and is also insensitive to changes in absorption strength, two potentially important advantages over conventional, absolute PL efficiency measurements. Finally, measurements of high (>25%) singlet fractions in polymers under electroluminescence should be evaluated in light of the possibility that the branching ratio is substantially less than unity.

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