

## Stimulated emission depletion of triplet excitons in a phosphorescent organic laser

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(Received 24 May 2006; accepted 28 August 2006; published online 3 October 2006)

Triplet formation is investigated in an optically pumped polymer laser by detecting the phosphorescence emission after excitation. A clear correlation is observed between the onset of lasing and a saturation of phosphorescence intensity due to stimulated emission depletion of the singlet state and the resulting reduction in intersystem crossing. The results are consistent with intersystem crossing constituting the dominant triplet formation pathway in conjugated polymers. Excitation at different wavelengths has no effect on the triplet saturation behavior, which allows the authors to exclude singlet fission or breaking as the origin of triplet formation. The method constitutes an implementation of a highly nondegenerate excitonic switch. © 2006 American Institute of Physics. [DOI: 10.1063/1.2357023]

Weak spin orbit coupling along with a huge exchange splitting means that organic semiconductors can support primary excitations of both singlet and triplet configurations.<sup>1-3</sup> While this is particularly relevant to the operation of organic light-emitting diodes, where harvesting triplet excitations which are generally not dipole coupled to the ground state holds the key to maximizing device efficiency,<sup>4</sup> triplet accumulation effects also play a prominent role in organic lasers. Triplet saturation, for example, is a well known phenomenon in organic dye lasers, which are therefore subject to constant solution exchange. Such a scheme is not viable in solid state organic lasers, for which organic semiconductors hold great promise. Unfortunately, little is actually known about the nature of triplet excitons in organic lasers.<sup>5-8</sup> Triplets are rather elusive in organic solids and are generally only detectable at low temperatures using photoinduced absorption,<sup>3,9-15</sup> delayed luminescence,<sup>16</sup> or magnetic resonance techniques.<sup>9,17</sup> A particularly powerful and versatile window to triplet excitons is opened through the nominally forbidden radiative decay channel in the form of phosphorescence.<sup>1,2</sup> While most organic semiconductors, in particular, conjugated polymers, only exhibit extremely weak phosphorescence at low temperatures, if any, we recently developed a technique to visualize triplets by accelerating the radiative decay rate.<sup>2,18</sup> Integrating heavy metal atoms into the polymer backbone at minuscule concentrations of ~100 ppm enables the radiative decay of triplets without significantly perturbing the decay path of singlets or the generation path of triplets.<sup>18</sup> The reason for this is that the triplet diffusion length is much greater than the singlet diffusion length, so that triplets on average reach the heavy metal sites, whereas singlets do not.

Here, we show how this technique can be applied to monitor the dynamics of triplet generation in a conjugated polymer laser. Stimulated emission (SE) acts as a competing

channel to triplet formation by intersystem crossing (ISC) and therefore reduces the triplet population. Interestingly, this depletion is not complete, which may be a signature of not all of the excitation energy being converted into laser action above threshold. Alternatively, some triplets may be generated quasi-instantaneously prior to ISC and SE.<sup>3,9,11-14,19,20</sup> Wavelength dependent excitation shows pump photon energy independent depletion behavior, suggesting that higher-lying states or exciton fission processes are not dominant in triplet formation.

Figure 1 illustrates the prompt and delayed emission of a distributed feedback (DFB) laser based on the phosphorescent ladder-type diphenyl-substituted para-phenylene polymer<sup>2</sup> (PhLPPP) at 4 and 300 K. The laser was fabricated by spin coating the polymer on a two-dimensional plastic DFB substrate (300 nm grating period) in a layer approximately 300 nm thick as described previously<sup>6</sup> and mounted in a cold finger He cryostat. The prompt emission under excitation by a 1 kHz regeneratively pumped Ti:sapphire amplifier running at 400 nm (~3 nJ pulse energy, 130 fs

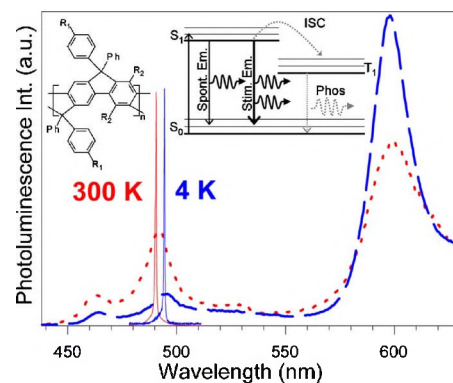


FIG. 1. (Color online) Prompt (solid lines) and delayed (300 K, dotted; 4 K, dashed lines) emission spectra of a PhLPPP DFB laser at 4 K (blue) and 300 K (red). The delayed emission displays both fluorescence (spontaneous emission) around 480 nm and phosphorescence around 600 nm. The structure of PhLPPP is also given ( $R_1$ , decyl;  $R_2$ , hexyl). The inset shows the competing relaxation channels of the optically excited  $S_1$  state, namely, spontaneous emission, SE, and ISC, which leads to phosphorescence.

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pulse length, spot diameter  $\sim 100 \mu\text{m}$ ) is dominated by a narrow laser line around 490 nm. The laser emission shifts slightly to the red upon cooling. This may be either due to the characteristic thermochromic shift of the gain spectrum or because of a slight change in the period of the plastic DFB grating, which most likely expands upon cooling. The delayed luminescence from the laser recorded using an image intensifier in front of a charge coupled device (CCD) camera at a delay of 50 ns after excitation in a gate window of 100  $\mu\text{s}$  (integration time of 30 s) reveals two distinct features: delayed fluorescence from the singlet exciton (spontaneous emission) peaking at 460 nm (the 0-0 transition) and 490 nm (the 0-1 transition) and phosphorescence from the triplet exciton at 600 nm. Note that the fluorescence spectrum is somewhat distorted and weighted towards the 0-1 peak due to Bragg scattering from the grating.

The inset summarizes the elementary processes to be taken into consideration. The polymer is excited by absorption of a photon at 400 nm into a vibrationally hot singlet state, which rapidly cools via internal conversion. Three relaxation pathways from the excited  $S_1$  state are considered: spontaneous emission, SE, and ISC to the triplet state, from which phosphorescence then occurs. Clearly, the nonlinear process of SE, which has an intrinsic lifetime of  $\sim 36$  ps in LPPP (Ref. 6) but is typically accelerated to below 1 ps under feedback conditions in a laser geometry,<sup>21</sup> competes with ISC, which is a spin-forbidden process and therefore much slower. SE has previously been shown to efficiently deplete the  $S_1$  state so that fluorescence suppression occurs.<sup>22</sup> We therefore anticipate that SE will also lead to a reduced population of the  $T_1$  state, if this is fed through the (depleted)  $S_1$  state. SE depletion (STED) has also been used in high-contrast far-field fluorescence microscopy, but suffers some limitations due to the spectral overlap between the fluorescence and the SE band.<sup>22</sup> STED of the triplet, however, is beneficial due to the large spectral separation between singlet and triplet emission and can readily be detected without interference of the fluorescence or the SE band.

To be able to identify STED of the triplet we compared the  $S_1$  and  $T_1$  emission intensities as a function of pump pulse energy of films deposited either on a DFB laser substrate or on an indium tin oxide (ITO) covered glass substrate, which is known to suppress amplified spontaneous emission due to effective waveguiding in the ITO.<sup>23</sup> The two films were of comparable thickness ( $\sim 300$  nm) and thus had a similar absorption so that the *immediate* singlet excitation density was equivalent. The suppression of SE in the ITO configuration, however, results in a slower decay of the  $S_1$  population, thereby providing more opportunity for ISC. To maximize material stability and triplet emissivity, the measurements were carried out at 4 K. The pump fluence was not varied continuously but was arbitrarily set to higher and lower values so as to exclude the possibility of material degradation. The phosphorescence was detected in a 100  $\mu\text{s}$  gate 50 ns after excitation using an intensified gated CCD, whereas the fluorescence and laser emission were recorded both by the CCD and by a sensitive photodiode. Figure 2(a) shows the dependence of the singlet emission intensity as a function of pump fluence of the laser structure ( $\square$ ) and of the film on ITO ( $\blacksquare$ ) on a double logarithmic scale. Whereas the laser displays clear threshold behavior at a pump pulse energy of 2.4 nJ, which is identical to the threshold observed for the metal-free methyl-substituted LPPP,<sup>6</sup> the film on the

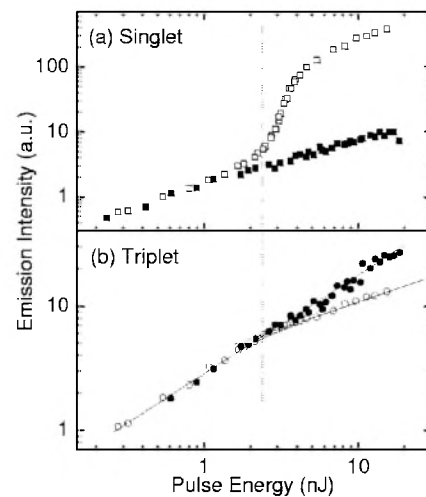


FIG. 2. Emission intensity of a PhLPPP polymer film on a corrugated plastic DFB laser substrate ( $\square$ ,  $\circ$ ) and on an ITO covered glass substrate ( $\blacksquare$ ,  $\bullet$ ) shown in the singlet (panel a) and triplet (panel b) channel. Note that the ITO attenuates SE. The vertical dotted line at an excitation pulse energy of 2.4 nJ marks the laser threshold observed on the corrugated substrate, which coincides with the leveling off in the triplet channel. The solid lines indicate power laws of exponents of 0.8 and 0.4, respectively.

ITO substrate does not exhibit any discrete threshold.<sup>23</sup> Both curves show the same gradient below threshold. The behavior in the singlet channel correlates directly with the triplet, given in panel (b). At the threshold, the gradient of the phosphorescence intensity versus pump intensity drops in the polymer laser due to STED, whereas no effect is observed for the planar ITO substrate. An increase in singlet emission due to SE in the laser structure clearly coincides with a relative reduction in triplet intensity due to STED. The triplet intensity depends sublinearly on excitation power, following a power law of  $I^{0.8}$  and dropping to  $I^{0.4}$  above laser threshold. Interestingly, the singlet emission intensity also appears to follow a slightly sublinear dependence below threshold, which may be a signature of higher order loss processes.

Possible mechanisms of triplet formation in  $\pi$ -conjugated materials under optical excitation have been debated intensively in the literature. Besides ISC, exciton fission,<sup>3,9,10,19,20</sup> fusion,<sup>13</sup> and dissociation<sup>12,14</sup> processes via intermediates have been put forward. Ultrafast spectroscopic studies of triplet formation are, however, complicated by the fact that different photoinduced absorptions may overlap in energy and therefore mask the true triplet dynamics.<sup>12,13</sup> This complication is circumvented by studying the distinct phosphorescence signature of the triplet. Beyond the laser threshold the rise in phosphorescence intensity with pump fluence is clearly impeded. This demonstrates directly that a significant proportion of triplets are formed on time scales *longer* than that of SE. However, the triplet density does not level off at a constant value above threshold, but rather continues to increase. This suggests either that there is a triplet formation channel which acts much faster than SE or that only a certain fraction of singlet excitons is actually affected by SE.

Any of the aforementioned alternative triplet formation channels should display a distinct dependence on excitation wavelength. We therefore studied the STED of the triplet at three different excitation energies, spanning a range of 0.26 eV. Figure 3 shows the dependence of phosphorescence intensity on pump fluence for three different excitation wavelengths. The curves are normalized to the laser threshold



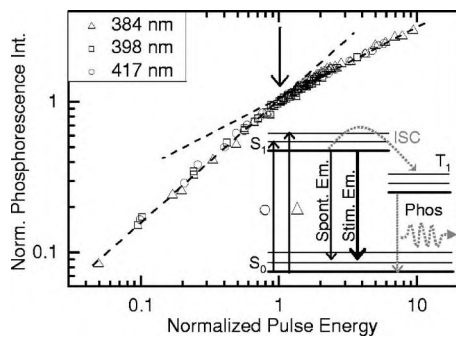


FIG. 3. Phosphorescence intensity of a polymer laser near threshold as a function of excitation pulse energy for three different excitation wavelengths. The curves are normalized to the pulse energy at laser threshold. The saturation behavior of the triplet emission is independent of pump photon energy.

energy on the  $x$  axis and to the emission intensity at laser threshold on the  $y$  axis. All three curves clearly lie on top of each other above and below threshold. If triplet formation occurred via higher-lying states, the flattening off of the curve above threshold should become more gradual for shorter excitation wavelengths, which is not observed. Interestingly, cw modulation spectroscopy on LPPP has previously identified a triplet formation mechanism which is strongly wavelength dependent in this spectral region and was attributed to singlet fission.<sup>3</sup> Since then, however, phosphorescence spectroscopy has placed a definite value of 2.07 eV on the triplet energy,<sup>1,2</sup> implying that singlet fission cannot occur at energies below 4.1 eV (300 nm). While we cannot make a statement about the overall triplet yield, our data do demonstrate the absence of a photon energy dependent branching between different triplet formation mechanisms. Note also that the highest photon energy chosen is 0.53 eV above the optical gap of the material, i.e., is expected to be able to compensate the exciton binding energy.

Singlet breaking into a charge transfer state or even nongeminate carriers has also previously been put forward as a route to anomalous triplet generation.<sup>12–14</sup> However, we note that electric-field-assisted fluorescence and phosphorescence modulation has clearly shown the absence of nongeminate recombination in these materials.<sup>18</sup> Additionally, charge transfer states maintain their overall spin over very long times.<sup>18</sup> It is therefore hard to conceive how carrier formation could also lead to triplet formation. On the other hand, unambiguous evidence exists for the presence of triplet polaron pairs following photoexcitation.<sup>17,18</sup> A possible mechanism of such pair generation could lie in an exchange-type rather than a dipolar interaction of optically generated singlet excitons with polarons or metastable charge separated states forming large dipoles on the polymer chain.<sup>24</sup> In this case the excitation photon wavelength would not necessarily control ultrafast singlet exciton conversion into triplets. We note, however, that the absence of complete saturation of the intensity dependence of phosphorescence may also simply arise from the fact that the organic laser structure is not perfect and leaks a constant fraction of excitation intensity into the spontaneous emission channel. Indeed, we find that the broad spontaneous emission background increases slightly with increasing excitation power, although this rise is harder to quantify than the rise in phosphorescence.

Exploiting the phosphorescence channel allows us to measure the triplet density directly in an organic laser. In a pump-probe configuration, for example, we anticipate to be able to directly time resolve ISC. The triplet STED process constitutes an implementation of an optical excitonic switch which, in contrast to pure singlet switches, does not suffer from interference effects due to the high degree of nondegeneracy arising from the exchange interaction. In summary, we have shown that ISC is the dominant route to triplet population in conjugated polymers by considering the phosphorescence channel of a laser structure. While STED of the triplet clearly occurs above the laser threshold, it is not complete. This is either due to ultrafast triplet formation channels or due to leakage of spontaneous emission in the laser structure. We find no evidence for singlet exciton fission or for a photon energy dependence in STED, suggesting that only one triplet formation mechanism is dominant.

The authors are grateful to W. Stadler and A. Helfrich for technical support and are indebted to S. Patil for the synthesis of PhLPPP and to K. Forberich, A. Gombert, and V. Wittwer for the kind provision of flexible DFB laser gratings. The authors thank the DFG for financial support through the Gottfried Wilhelm Leibniz award as well as the BMBF for support through the OLAS collaboration.

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