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Insights into the photo-physics of single luminescent conjugated polymers of PPV derivatives using single molecule techniques

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The time dependent photo-luminescent behavior of PPV derivatives is studied. Insights gained from short-chain analogues are used to aid in interpretation. Emission is characterized by periods of constant intensity emission punctuated by abrupt intensity changes. A model in which exciton migration is dominated by three-dimensional effects is shown to adequately explain experimental results.

Keywords: Photoluminescence; luminescent conjugated polymers, single molecule spectroscopy

Introduction

Organic thin-film electro-luminescence based on conjugated polymers is the focus of extensive research due to their potential application in next generation thin film displays [1]. Considerable questions remain to be answered, however, regarding the fundamental photo-physics and exciton migration within these polymers. In this paper we report on a series of experiments dealing with the photo-physics of two closely related, and extensively studied, PPV derivatives MEH-PPV [2,3] and DOO-PPV[4] conducted at the millisecond time scale. Such experiments are expected to shed light on exciton migration within the polymer.

Published works have reported vastly different behavior for the fluorescent time trace. Exponential decay [2], emission at 1 or 2 discrete intermediate levels [3], and emission at 4 or 5 equally spaced intensities [4] have all been observed. A direct comparison, however, is difficult due to differences in sample preparation. In this work, we have repeated these experiments varying only one parameter – chain length.

Experimental Procedure

Two samples were observed. High molecular weight MEH-PPV was extracted from pristine MEH-PPV. MEH-PPV was chosen rather than DOO-PPV for the high molecular weight investigation due to its comparatively better solubility. Low molecular weight DOO-PPV was extracted from pristine MEH-PPV by taking advantage of the limited solubility of this symmetrically substituted structure. The first polymer is thus a few thousand monomers long, would be expected to support a few hundred excitons if there was no interaction between different chain segments, and take a defect coiled structure when spin coated [5]. The second polymer contains ~24 monomers, would be expected to support 4 or 5 excitons, and take a linear rod-shape structure when spin coated [4].

Each powder, after dilution into a polystyrene matrix was spun-cast onto UV grade silica cover slips to obtain a ~100nm thick conjugated polymer / polystyrene film. After placing the sample in vacuum, a 200nm layer of aluminum was evaporated directly on top of the film to provide protection from oxygen. The samples were excited by an linearly polarized cw-Argon laser (TEMoo, 488nm) and the fluorescent time trace recorded (with 10 ms time resolution) using a sample scanning confocal microscope operating in epi-fluorescence mode [6].

Results

In all cases, the polymers remained active for up to an hour. Figs 1 and 2 present results typical for the short and long chain polymers. Common to both samples is the fact that emission occurs at a number of discrete intensities punctuated by sudden intensity

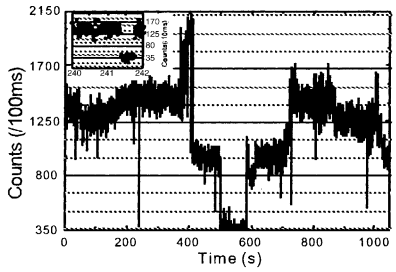

Fig. 1 Typical segment of the fluorescence time trace of a single short chain of DOO-PPV. The polymer remained active for over 1 hour. The data was taken with an excitation irradiance of 1100 W/cm2 and is displayed with an integration time of 100ms. The inset illustrates that the recoverable drop to background occurring at the 240 s point is in fact a real drop and not just noise.

drops. After a drop the intensity may or may not recover. There are however a number of key

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differences between the two transients. Firstly, in short chain DOO-PPV emission occurs at a few (~9) discrete intensity levels (each an integral multiple of a fundamental intensity) while in the long chain polymer emission occurs at a large number of discrete intensities. Secondly, the initial count rate for the long chain polymer is a factor of 10 greater then that of the short chain analogue. Thirdly, in the long chain case, the emission can be divided into two phases: an initial high intensity phase (1 minute) in which the count rate quickly drops, in large steps, by a factor of 10, and a long, lower intensity phase characterized by smaller, recoverable and non-recoverable intensity drops. No such division is possible in the short chain case. Fourthly, while in the short chain case, similar fluorescent time traces are seen for most single polymers, long chain polymers exhibit a much greater variety of behavior – most likely due to their more complicated three dimensional structure. Fifthly, the half-life of the shorter chain derivative is an order of magnitude longer than the long-chain derivative.

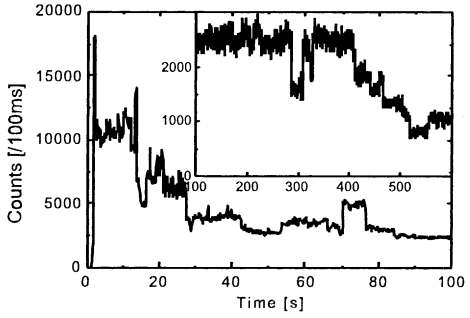

Fig. 2. Typical segment of the fluorescence time trace of a single long chain of MEH-PPV. This polymer remained active for 20 minutes. The data was taken with an excitation irradiance of 1100 W/cm2 and is displayed with an integration time of 100ms. While the main figure shows the large intensity fluctuations occurring during first 100 s. the inset allows the small discrete intensity jumps in the next 500s to be clearly observed.

Discussion

The above results are compatible with a model in which the migration of thermalized excitons is dominated by three-dimensional conformation effects rather than by transmission along the polymer background. In other words, folding induced interactions between nearby chain segments provide the channel for exciton migration.

Considering first the short-chain case in which the polymer resembles a rigid rod in which there are no paths for three-dimensional exciton migration. In the above model one would expect that since migration is relatively slow, the segment that absorbs a 488nm photon will also emit a longer wavelength photon. Emission will thus occur at a limited number of discrete intensities, each representing the total emission of a combination of excitons. Limited migration ensures that quenching is limited to only a single exciton. In the case of the polymer in Fig. 1, only 5 segments and one tetrahedral defect is required to explain the experimental results.

Three dimensional effects complicate the picture in the longer chain case. Hu et al [5] have suggested that the defect-coil structure prodominates in this type of polymer. Thus the polymer contains both sections in which neighbouring chains lie close together and other sections in which the chain is relatively far away from any neighbours. In those tightly bound sections, exciton migration will be efficient (as will be quenching) while in the relatively isolated segments, exciton migration and hence quenching will be relatively inefficient. During the first 40 s of Fig. 2 emission is relatively high, involving most of the segments. At early time intervals, large intensity drops are observed. This can be seen to be the result of quenching in those tightly bound sections in which efficient exciton migration allows for efficient quenching. As time evolves, these tightly bound segments become quenched, resulting in a factor of ten intensity drop in the first 40 seconds. For the following 20 minutes, intensity drops are smaller. Emission during this time frame is most likely coming from the extended segments where a quench site can at most affect a single exciton resulting in a slow quenching of the remaining sites.

Conclusion

Three-dimensional effects dominate the migration of thermalized excitons in polymers of the PPV family. Elimination of these three dimensional channels results in a much longer half-life for the luminescent conjugated polymer.

In Jesus' Name,

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