

## Singlet exciton diffusion in MEH-PPV films studied by exciton–exciton annihilation

A.J. Lewis<sup>a</sup>, A. Ruseckas<sup>a</sup>, O.P.M. Gaudin<sup>a</sup>, G.R. Webster<sup>b</sup>,  
P.L. Burn<sup>b</sup>, I.D.W. Samuel<sup>a,\*</sup>

<sup>a</sup> *Organic Semiconductor Centre and Ultrafast Photonics Collaboration, School of Physics and Astronomy, University of St. Andrews, North Haugh, St. Andrews, Fife KY16 9SS, United Kingdom*

<sup>b</sup> *Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Mansfield Road, Oxford, Oxfordshire, OX1 3TA, United Kingdom*

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### Abstract

We report time-resolved photoluminescence studies in MEH-PPV films for a wide range of excitation intensities. The results fit well to a diffusion-limited exciton–exciton annihilation model with an annihilation constant  $\gamma = (2.8 \pm 0.5) \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ . This enables us to estimate the exciton diffusion coefficient to be  $D = (3 \pm 1) \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ . This corresponds to a diffusion length between 5 and 8 nm for one-dimensional diffusion.

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### 1. Introduction

Conjugated polymers show great potential for applications in photovoltaics because of a high absorption coefficient ( $\sim 10^5 \text{ cm}^{-1}$ ) in thin films and ability to transport charge [1–3] combined with simple processing and hence the scope for low cost manufacture. Primary photoexcitations in conjugated polymers are singlet excitons with the Coulombic binding energy generally accepted to lie between 0.3 and 1 eV [4–6], although lower values have been reported [7]. Because of this, charge sep-

aration generally occurs at an interface with another material at a planar or bulk heterojunction [8–12]. For photovoltaic devices it is essential to convert excitons into charge carriers, so the transport (by diffusion) of excitons to the heterojunction is a very important step in the operation of an organic solar cell. A widely used method to study exciton diffusion is based on interface quenching in which the reduction of fluorescence lifetime is studied by a quenching layer [13–17]. In this method the interface with a quencher should be sharp (no inter-diffusion), and short capture distance as well as high capture rate at the interface are desirable. It is not always possible to satisfy all these three conditions.

In this paper we explore an alternative way to measure exciton diffusion by studying exciton–

\* Corresponding author. Tel.: +44 133 446 3114; fax: +44 133 446 3104.

E-mail address: [ids@st-and.ac.uk](mailto:ids@st-and.ac.uk) (I.D.W. Samuel).

exciton annihilation (or exciton fusion). It occurs when two excitons in close proximity (within an annihilation or reaction radius) combine, forming a higher excited state, which relaxes quickly to the lowest excited state. As a result, one exciton is lost into heat. This process occurs when the density of excitons reaches a sufficient level, usually greater than  $10^{17} \text{ cm}^{-3}$  [18–21], although this does vary between materials. We have previously used it to determine the exciton diffusion coefficient in light emitting dendrimers [22]. The dynamics of exciton density is described as a bimolecular process, and the exciton diffusion coefficient can be calculated from the annihilation rate provided the annihilation (or reaction) radius is known.

The use of MEH-PPV in devices is quite extensive, including solar cells [3], light-emitting diodes (LEDs) [23], and optically pumped polymer lasers [24]. Consequently, it is extremely beneficial to understand the processes involved in this polymer in order to enhance devices fabricated with it. Previously reported studies have shown a one-dimensional diffusion length of the exciton in MEH-PPV films in the range of 6–14 nm [9,16,17] using interface quenching methods. This variation can be explained to some extent by different morphologies of the bulk films and interfaces used in these studies as well as by different lifetimes of the mobile intrachain excitons. Excitation intensity dependent exciton lifetime has been reported in MEH-PPV films [25], but quantitative estimates of annihilation parameters were not given.

We report here quantitative studies of exciton–exciton annihilation in MEH-PPV films using time-resolved photoluminescence (PL). PL kinetics can be described with a time independent annihilation rate, which provides information on exciton diffusion in the bulk MEH-PPV films without the complexity of surface effects.

## 2. Experimental

Fused silica substrates were cleaned by ultrasonication in acetone for 6 min then in propan-2-ol for 6 min. MEH-PPV films were deposited by spin-coating from solution in chlorobenzene. The weight average molecular weight of the MEH-PPV was 320,000 and the polydispersity was 12. Film thickness was calculated from the measured absorbance (see Fig. 1) using an absorption coefficient determined by spectroscopic ellipsometry. A thin film of 35 nm was used to ensure no amplified spontaneous

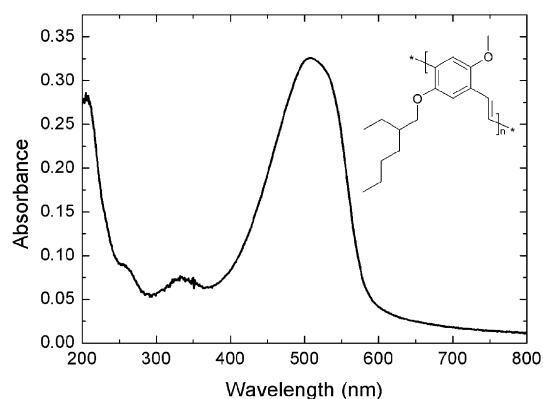


Fig. 1. Molecular structure and absorbance spectrum of MEH-PPV.

emission (ASE) was present, which could add a further decay channel for excitons [26]. Excitation was by 100 fs pulses at 400 nm with a repetition rate of 50 kHz. For comparison some experiments were performed using a 5 kHz pulse repetition rate. Time-resolved PL integrated over the spectral range of 550–680 nm was measured using a synchroscan streak camera. The instrumental response function was  $\sim 5$  ps (FWHM). PL decays were measured under a vacuum of  $2 \times 10^{-5}$  mbar. The excitation spot size was measured to have a diameter of 0.5 mm at  $1/e^2$  of the maximum intensity and the excitation pulse energy was varied using neutral density filters. The excitation density was calculated assuming one absorbed photon produces one exciton, which is justified because the chromophore density is more than two orders of magnitude higher than the highest excitation density of  $1.5 \times 10^{18} \text{ cm}^{-3}$ , so that sequential photon absorption is negligible. The excitation density is essentially uniform through the film as the absorbance of the 35 nm thick film at 400 nm is only 0.08.

## 3. Results and discussion

The results of time-resolved luminescence measurements as a function of excitation density are shown in Fig. 2. The initial PL decay at low excitation density ( $< 10^{17} \text{ cm}^{-3}$ ) is close to mono-exponential with a time constant of 140 ps. This is consistent with previous literature work [27]. As the excitation density is increased, the decays become progressively faster due to exciton–exciton annihilation. At high repetition rates, accumulated long-lived excitations, such as triplets and photogenerated charges (polarons) can potentially quench singlet excitons and

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