

## Charge recombination dynamics in a polymer/fullerene bulk heterojunction studied by transient absorption spectroscopy

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### Abstract

The recombination kinetics of long-lived photogenerated charge carriers are investigated by transient absorption spectroscopy on nano- to millisecond time scales in a composite of poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1-4-phenylene vinylene], (MDMO-PPV) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C<sub>61</sub> (PCBM) at room temperature. The decay dynamics of the positive polarons, attributed to recombination with PCBM anions, were found to be either monophasic or biphasic, dependent upon the laser excitation density. The slower decay phase is assigned to recombination dynamics of localized polarons while the fast component (<20 ns) is assigned to the recombination of mobile polarons when the density of photogenerated polarons is higher than the available density of localized states (~10<sup>17</sup>cm<sup>-3</sup>).

*Keywords:* conducting polymer, fullerene, solar cells, photoinduced absorption spectroscopy, charge recombination, power dependence

### 1. Introduction

Organic bulk heterojunctions are currently attracting attention for low cost plastic photovoltaic cells. Devices fabricated from conjugated polymer / methanofullerenes blends have been reported with energy conversion efficiencies of 3 % [1-2]. A key issue in the development of such devices is the blending of the electron and hole transporting materials on the nanometer scale. This blending is essential to ensure efficient charge separation, with exciton diffusion lengths in such molecular materials being of the order of 10 nm. A downside of this blending is that photogenerated electrons and holes may not spatially be well separated, resulting in recombination losses being a factor limiting device performance.

In this paper we employ nanosecond to millisecond transient absorption spectroscopy (TAS) to study the recombination dynamics in a blend of poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1-4-phenylene vinylene], (MDMO-PPV) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C<sub>61</sub> (PCBM) at room temperature and the dependence on light intensity.

### 2. Experimental

The active layer consisting of MDMO-PPV/PCBM (1:2 or 1:4 by weight) was spin-coated on a glass substrate to a thickness of ~ 100 nm from chlorobenzene solution. Nano to millisecond time TAS was carried out using a nitrogen

laser pumped - dye laser as a pump and a tungsten lamp/monochromator (typically set to 940 nm) or a laser diode ( $\lambda=830$  nm) as a probe. The samples were excited at 500 nm, corresponding to the maximum of MDMO-PPV absorption. The change in optical density ( $\Delta OD$ ) at a selected wavelength as a function of time is the outcome of the experiment. Transient absorption spectra at fixed delay times from the excitation laser pulse were constructed by measuring kinetics at different wavelengths. Experiments as a function of the excitation power employed neutral density filters to vary the laser intensity from 20 nJ to 80  $\mu\text{J}\cdot\text{cm}^{-2}$  per pulse.

### 3. Results and discussion

We consider first the assignment of the transient optical signal observed in our studies. Pulsed laser excitation of the MDMO-PPV/PCBM film resulted in a broad, long-lived photoinduced absorption increase in the red/near-infrared. The transient spectrum of this transient signal measured at 296 K at a time delay of 125  $\mu\text{s}$  is displayed in fig. 1. For comparison the PIA spectrum for the same blend obtained from frequency domain studies (132 Hz modulation) at 100K is also shown.

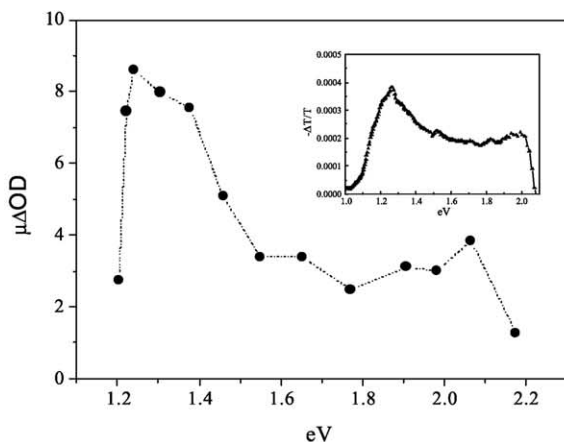


Fig. 1. Transient absorption spectra of a MDMO-PPV/PCBM blend at 125  $\mu\text{s}$ ,  $T = 300$  K. The inset shows the frequency domain PIA spectra of the blend employing excitation at 488 nm with 40 mW and 132 Hz modulation,  $T = 100$  K.

The similarity between both spectra is an indication that the photoinduced absorption at long time scale is due to the same species for both samples. The PIA spectrum shown in the insert to fig. 1 is characterised by a plateau between 1.5 and 1.9 eV and a maximum between 1.2 to 1.5 eV and another less intense maximum between 1.8 and 2.2 eV. These transient absorption features have been assigned to the absorption of photogenerated positive MDMO-PPV polarons [3-5]. The similarity between this PIA spectrum and the transient spectrum observed here (fig. 1,  $\cdots \bullet \cdots$ ) indicates the transient absorption signal should also be assigned to positive MDMO-PPV polarons generated by the pulsed laser excitation.

Fig. 2 shows the room temperature transient absorption kinetics for the MDMO-PPV/PCBM blend on ns to ms time scale using excitation densities ranging from 20 nJ to 80  $\mu\text{J}\cdot\text{cm}^{-2}$  per pulse. It is apparent that the decay dynamics are strongly dependent upon laser intensity. At early times, the data is observed to be strongly laser intensity dependent, with a fast ( $< 20$  ns) decay component observed for laser intensities  $> 2$   $\mu\text{J}\cdot\text{cm}^{-2}$ , referred to hereafter as the threshold intensity  $I_{\text{th}}$ . In contrast the long time decay dynamics are found to be remarkably insensitive to laser power in this range. However for intensities lower than 2  $\mu\text{J}\cdot\text{cm}^{-2}$  ( $I < I_{\text{th}}$ ) the long time decay amplitude becomes dependent upon excitation intensity (see inset fig. 2). Assuming a unity quantum yield for charge separation in the film, this threshold intensity corresponds to  $\sim 10^{17}$  photogenerated polarons. $\text{cm}^{-3}$ .

The dependence on excitation density can be viewed according to the model described in fig. 2a-c based upon a tail of localised states below the MDMO-PPV mobility edge. Recombination of polarons trapped in the tail states is limited by thermal activation and is responsible for the slow tail in the recombination dynamics. When the excitation intensity  $I_{\text{th}}$  is equal to excitation energy ( $\sim 2$   $\mu\text{J}\cdot\text{cm}^{-2}$  per pulse), the tail of localized states is fully occupied (fig. 2b) and the decay of polarons follows a power law. However, for excitation densities higher than  $I_{\text{th}}$ , as all the localised states are completely full, the additional polarons

occupy MDMO-PPV localised states above its mobility edge (fig. 1c), where they are relatively more mobile due to the manifold of closely spaced energy levels available. The implications of these observations for the function of MDMO-PPV/PCBM solar cells will be presented elsewhere [5].

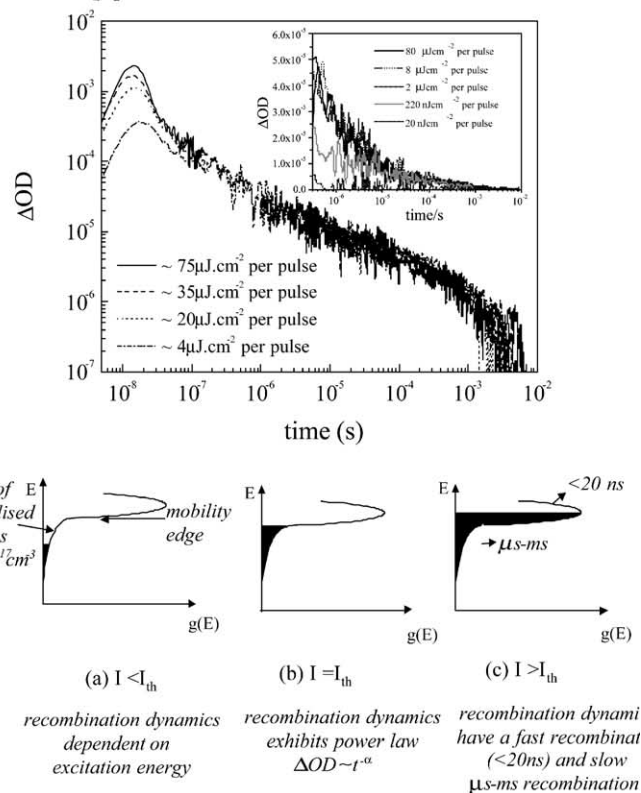


Fig. 2. Transient absorption kinetics for MDMO-PPV/PCBM blend on the ns to ms time scales. The excitation densities ranged between 4 to 80  $\mu\text{J}\cdot\text{cm}^{-2}$  per pulse. The inset shows the decay at millisecond time scale down to 20 nJ. $\text{cm}^{-2}$  per pulse. (a-c) Proposed model for laser dependence based on availability of the PPV polaron density of states,  $g(E)$ .

### 3. Acknowledgements

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