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Transport and Recombination Dynamics Studies of Polymer/Fullerene Based Solar Cells

S. A. Choulis, J. Nelson, S. M. Tuladhar, S. Cook, Y. Kim, J. R. Durrant,*
D. D. C. Bradley

Centre for Electronic Materials and Devices, Departments of Physics and Chemistry,
Imperial College, London SW7 2AY, UK
E-mail: s.choulis@imperial.ac.uk

Summary: We have studied the electron/hole transport and recombination dynamics in blends of poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene], (MDMO-PPV) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) at room temperature, as a function of laser excitation density and PCBM concentration. The experimental results of these studies indicate the important role played by hole-trap states in MDMO-PPV. Electron and hole transport are not balanced within the blend. PCBM is a less disordered material than MDMO-PPV and electron transport dominates the response of the solar cell device.

Keywords: blends; MDMO-PPV; PCBM; recombination dynamics; solar cells; transport; trap-states

Introduction

Solar cell devices based on conjugated polymer/ fullerene blends show power conversion efficiency ≥3 % [1,2] and are of considerable interest for further study [3]. In order to better understand the device physics of polymer/fullerene based solar cells we have made combined time of flight (ToF) photocurrent transient measurements of transport and transient absorption spectroscopy (TAS) measurements of polaron recombination dynamics in blends of poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene], (MDMO-PPV) and a soluble fullerene C_{60} derivative, namely PCBM, at room temperature (RT) and as a function of laser excitation density and PCBM concentration [4].

Experimental Results

Although the individual transport properties of both conjugated polymers and fullerenes have been studied separately [5], the carrier transport behavior of these materials in composite devices, has not been sufficiently well characterized. In order to investigate the transport of the carriers in

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these structures and the subsequent implications for device operation [4,6] we have performed room temperature (RT) photocurrent measurements of mobility in the same material system as a function of laser excitation density and PCBM concentration [4].

ToF mobilities were measured on MDMO-PPV:PCBM blend films with different composition and on films of the pristine polymer [4]. Films of thickness, $d \approx 1$ μm were deposited on ITO coated conducting glass electrodes. Al top contacts were evaporated through a shadow mask. A DC bias, $+50V \geq V \geq -50V$, was applied to the sample before excitation with a frequency tripled (355 nm) Nd:YAG laser. The transit time (t_{tr}) was deduced from the point of inflection (intersection point of the asymptotes) in a log-log plot of current versus time. The mobility (μ) can then be calculated from:

$$\mu = d^2/(Vt_{tr}) \qquad (1)$$

where V is the applied bias and d the thickness of the polymer film.

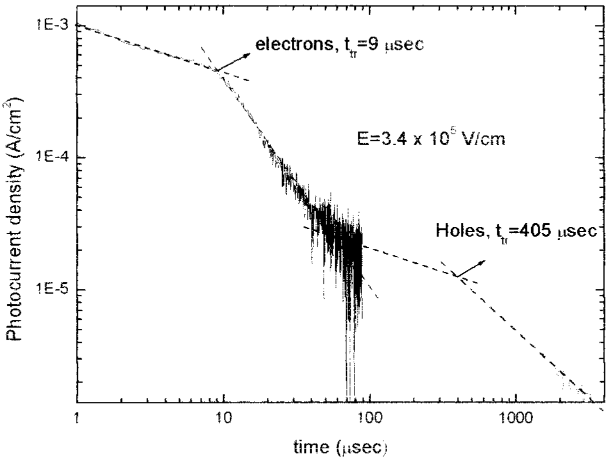

Figure 1: Typical RT electron and hole ToF transients at $E = 3.4 \times 10^5$ V/cm for the MDMO-PPV: PCBM blend with a 1:2 w:w composition.

Figure 1 shows representative RT photocurrent transients for electrons and holes in MDMO-PPV:PCBM blend films with a 1:2 weight (w:w) fraction. The t_{tr} times for electrons are much shorter than for holes in the same blend (see figure 1), indicating a much higher electron mobility of 2.9×10^{-5} cm²/Vs compared to a hole mobility of 6.5×10^{-7} at the same electric field

(E= V/d) of 3.4 x 10^5 V/cm. The electron photocurrent transients are also less dispersive than those for holes, indicating that within the blend, the electron transport states in PCBM are subjected to less disorder than the hole transport states in MDMO-PPV.

Figures 2 and 3 shows the logarithm of the drift mobility of holes and electrons respectively, within the MDMO-PPV:PCBM blend with a 1:2 w:w composition. The electron and hole mobilities of the blend both appear to follow the Poole-Frenkel dependence on electric field (E):

$$\mu(E) = \mu_0 . \exp(\alpha E^{1/2}) \qquad (2)$$

where μ_0 is the zero field mobility and α is a constant for any given sample and temperature, the value of which increases with increasing energetic disorder. This Poole-Frenkel dependence on field is found for many different types of disordered materials [7,8]. Figures 2 and 3 show that α has a larger value for hole transport within the blend. This is another indication that disorder effects will be more important for the hole transporting states. As a result, the zero field mobility (μ_0) for the electrons is 7.4 x 10^{-6} cm^2 $V^{-1}s^{-1}$, some two orders of the magnitude larger than for holes within the same blend (μ_0 = 4.2 x 10^{-8}). This indicates that hole, rather than electron transport will most likely limit device performance.

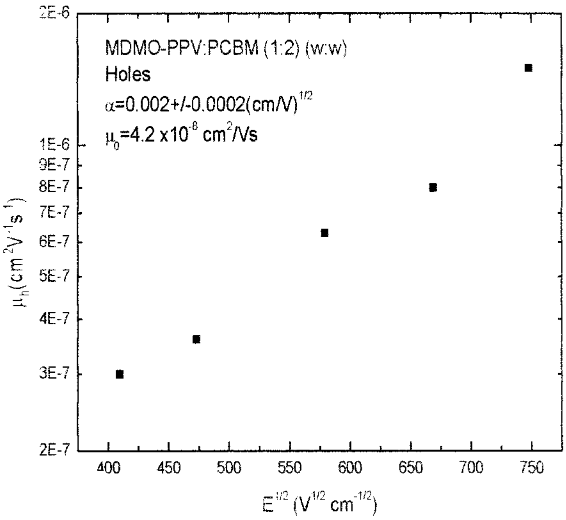

Figure 2: Logarithm of the hole drift mobility in the blend versus square root of the electric field. The squares are the experimental points and the lines are fits to equation 2.

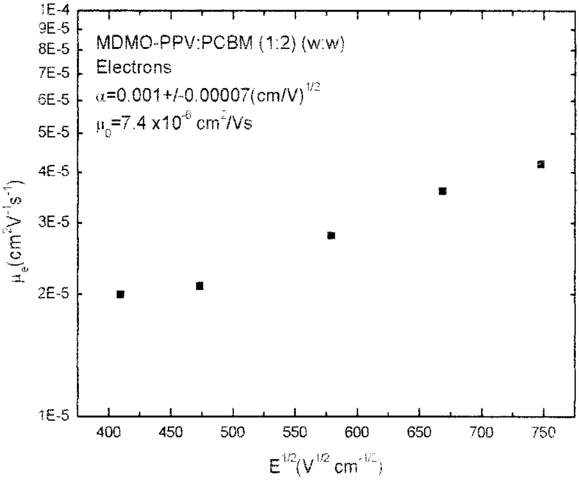

Figure 3: Logarithm of the electron drift mobility in the blend versus square root of the electric field. The squares are the experimental points and the lines are fits to equation 2.

Earlier we have reported TAS studies as a function of laser intensity that revealed the influence of localised and mobile MDMO-PPV$^+$ polarons in the recombination dynamics properties of the blends [9-11]. These results were explained by assuming a density of around 10^{17} cm^{-3} of deep traps in the MDMO-PPV polymer. They suggest that hole transport should become easier with increasing excitation density on account of trap filling.

Figure 4 shows representative photocurrent transients as a function of laser intensity for the holes in pristine MDMO-PPV. No change in the t_{tr} or in the shape of the photocurrent transients is observed as a function of laser intensity in the pristine polymer. However the quantum efficiency (QE), for polaron formation in the pristine polymer is only about 1% [12] which means that even at the highest laser power the photogenerated polarons are present in insufficient numbers capable of filling the traps.

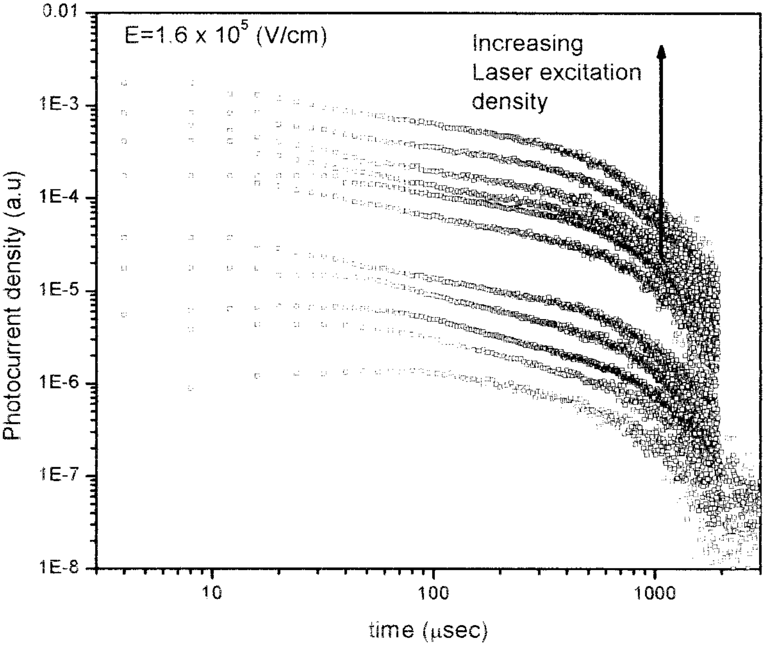

Figure 4: Typical RT hole ToF photocurrent transient decays as a function of laser excitation intensity at E = 1.6×10^5 V/cm for a pristine MDMO-PPV film. The highest laser power corresponds to a polaron density of around 10^{16} cm^{-3}

Figure 5 shows the hole mobility as a function of excitation laser intensity for the 6.5:1 w:w blend at E = 1.1×10^6 V/cm. It has previously been reported that by adding over 5 % of PCBM the QE of polaron formation increases to around unity [11,12]. In this case we were able, by increasing the laser intensity, to fill the trap states and consequently observed a dependence on laser intensity for the hole mobility within the blend. This mobility slightly increases when all the localised states are filled. We note here that the collected charges at high laser power were less than 10 % of the sample capacitor charge so that we are confident that we were working in a regime where the electric field across the sample can still be assumed more or less constant (as required for equation 1). The same behaviour was observed for higher PCBM concentrations [4]. In contrast, no clear change in the t_{tr} or in the shape of the photocurrent transients is observed as a function of laser intensity for the electrons in any of the MDMO-PPV:PCBM blends [4]. We interpret this observation as another indication that the electron transport states in PCBM are subjected to less trapping compared to holes in MDMO-PPV.

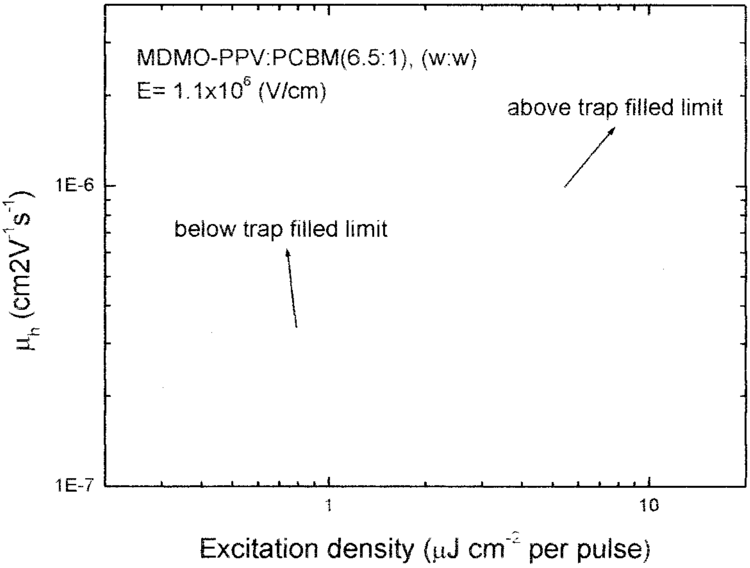

Figure 5. Room temperature hole mobilities deduced from ToF measurements for an MDMO-PPV:PCBM blend film of composition 6.5:1 w:w at an applied electric field of 1.1 x 10^6 V/cm. The data are displayed as a function of laser excitation density and illustrate the step change that occurs above a specified energy density.

Conclusions

The experimental results (ToF and TAS measurements) are consistent with the existence of hole-trap states in the MDMO-PPV polymer. The hole mobility within the blend slightly increased with increasing laser excitation density on account of trap filling. PCBM appears to be less disordered than MDMO-PPV in the blend, with electron mobilities exceeding hole mobilities by some two orders of magnitude. Hole transport is most likely to limit device performance.

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