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FAST TRACK COMMUNICATION

The effect of applied magnetic field on photocurrent generation in poly-3-hexylthiophene:[6,6]-phenyl C61-butyric acid methyl ester photovoltaic devices

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Abstract
The effect of a magnetic field on the photocurrent generated by a bulk heterojunction solar cell made from poly-3-hexylthiophene (P3HT) and [6,6]-phenyl C61-butyric acid methyl ester (PCBM) is investigated. At the operating voltage, increases in photocurrent of ∼9% can be obtained at magnetic fields of less than 100 mT. This increase in photocurrent is attributed to an increase in the rate of intersystem crossing, between the singlet and triplet states, leading to a higher net efficiency of exciton dissociation. Close to the open-circuit voltage, an increase of more than two orders of magnitude in the photocurrent could be obtained under applied magnetic field.

The effect of magnetic fields on the efficiency and current in organic light emitting diode (OLED) structures has been receiving increasing interest in recent years. Since the first observation of a change in the current through an OLED due to the action of a magnetic field (magnetoresistance) in 2003 [1], the effect has been observed in a number of conjugated small molecule [1–4] and polymer systems [5]. The fractional increase in the current through a device under applied magnetic field has been dubbed organic magnetoresistance (OMR) and OMRs of up to 15% have been observed at room temperature. We have recently investigated the OMR of tris(8-hydroxyquinoline) aluminium (Alq_3) based devices under illumination and found that, at applied voltages below the turn-on voltage, the device photocurrent increased under applied magnetic field. This was attributed to an increase in the triplet concentration due to an increase in the rate of intersystem crossing (k_{ISC} or ISC) from the photogenerated singlet to the triplet state [6]. Because of the longer lifetime of triplet states compared to singlet states, and the resulting higher probability that triplets will diffuse to an interface before decaying, the higher triplet concentration leads to a higher probability of interfacial exciton dissociation and charge separation. The view that applied magnetic field increases k_{ISC} was supported by a study of electrically pumped OLEDs based on gallium and indium quinolates where a clear increase in luminous efficiency was observed under low applied magnetic fields whilst device current remained unchanged [7]. This was attributed to an increase in k_{ISC} leading to an increase in the rate at which the singlet population is replenished from the triplet population and hence to an increase in the net emission rate, without perturbing the device current.

These results led us to propose that it may be possible to improve the efficiency of organic photovoltaic (OPV) devices by the application of a weak magnetic field. In this letter we

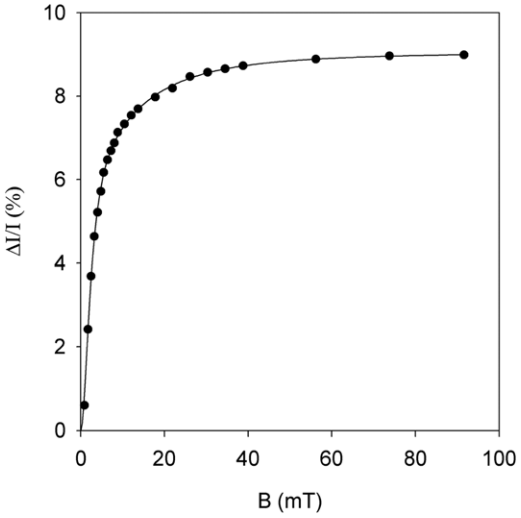

Figure 1. The percentage change in the photocurrent of a P3HT:PCBM PV cell at the maximum power voltage of 0.35 V. The solid line is a guide to the eye.

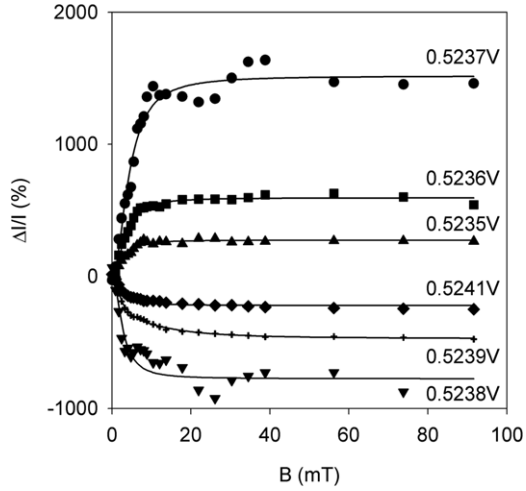

Figure 2. The percentage change in the photocurrent of a P3HT:PCBM PV cell as a function of applied field for various voltages around V_{OC}. The solid lines are a guide to the eye.

report the results of preliminary measurements of the effect of a magnetic field on the photocurrent generated in a poly(3-hexylthiophene) (P3HT): phenyl-C_{61}-butyric acid methyl ester (PCBM) bulk heterojunction solar cell structure. We have found that the effect of a field as low as 15 mT is sufficient to increase the photocurrent in the device at the maximum power voltage, V_{MP}, by ∼8% while the increase at high fields saturates at ∼9%. Around the open-circuit voltage, V_{OC}, we observe an increase in the current of ∼4 μA cm^{-2} which corresponds to an increase of more than two orders of magnitude relative to the field free case. This dramatic response may be useful, for example for magnetic field sensing.

Photovoltaic devices were fabricated on indium tin oxide (ITO) coated glass substrates of sheet resistivity ∼13 Ω/□. Substrates were lithographically etched and then cleaned prior to use. A 50 nm film of polystyrene sulfonate doped poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) was spin coated onto the substrates then annealed at 200 °C for 5 min. A 170 nm blend film of P3HT:PCBM (1:1 by weight) was prepared and coated onto the PEDOT:PSS layer as described in [8]. Aluminium was then evaporated onto the surface to a thickness of 100 nm to define several devices of area 4.1 mm^2. Following evaporation devices were annealed at 150 °C for an hour. Current density–voltage measurements were made using a Keithley 236 Source-Measure Unit. Devices were isolated from all external sources of light and illuminated using a 28 mW light emitting diode (LED) with emission maximum at 520 nm, close to the absorption maximum of P3HT. Under these conditions the device produced a short-circuit current density of ∼2 mA cm^{-2} and a V_{OC} of ∼0.5 V and a monochromatic power conversion efficiency of ∼1.2%. The samples were stored under vacuum. To measure the effect of magnetic fields the sample was placed between the poles of an electromagnet in a vacuum chamber, along with the LED. Before and after each measurement under applied field the sample was measured under null field conditions and these two null field measurements were averaged to give a baseline measurement with which to compare the effect of the magnetic field. This procedure was adopted to remove any effects due to drift in the sample. The reproducibility of the null field trace indicated good device stability.

Figure 1 shows the percentage increase in photocurrent through a P3HT:PCBM device operating at 0.35 V, which is close to the V_{MP} for this device under the ∼28 mW, 520 nm illumination used in these experiments. As applied magnetic field strength increases the photocurrent first rises rapidly and then saturates at ∼9% with increasing field. At short-circuit conditions a similar but smaller effect was seen, with the maximum increase in photocurrent of 0.12%. The same behaviour was observed for Alq_3 based LEDS operating below the turn-on voltage, where application of a B field produced a clear increase in photocurrent under illumination, whilst producing no effect on device current in the dark [6]. This lack of OMR in the dark shows that it cannot be simply carrier mobility that is being modified by the magnetic field. For the OPV devices studied here, as in the case of the Alq_3 diodes, the behaviour can be explained in terms of a B field induced increase in k_{ISC}, as discussed below.

The photocurrent at operating voltages close to V_{OC} are displayed in figure 2 as a function of applied magnetic field. It can be seen that as the applied voltage (V_{App}) approaches V_{OC} (∼0.5237 V) and the field free current density approaches zero the magnitude of OMR increases dramatically to ∼50% at 0.522 V and ∼1500% at 0.5237 V. At $V_{App} > V_{OC}$ the OMR changes sign to large negative values and then falls sharply towards zero for increasing V_{App}. At all applied voltages the current plots show similar features, namely a sharp rise in OMR at fields up to ∼10 mT, followed by a saturation regime for increasing magnetic field. Figure 3 shows the individual current versus applied field curves for two voltages immediately surrounding V_{OC}. From these plots it can be seen that at both voltages, the effect of the field is to increase the photocurrent. The switch to negative OMR at 0.5328 V can easily be understood from the observation that the device

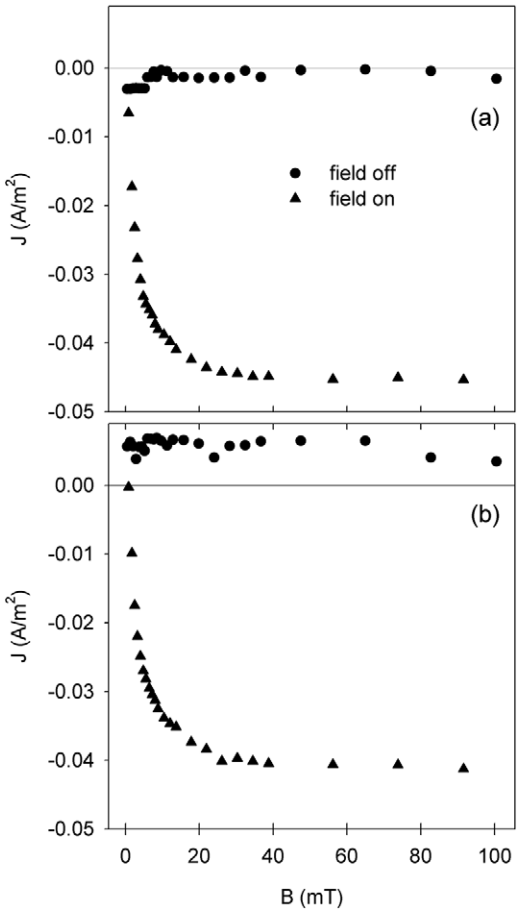

Figure 3. Device current density versus applied field for (a) 0.5237 V and (b) 0.5238 V. *B* field scale refers to field on values, as denoted by the legend.

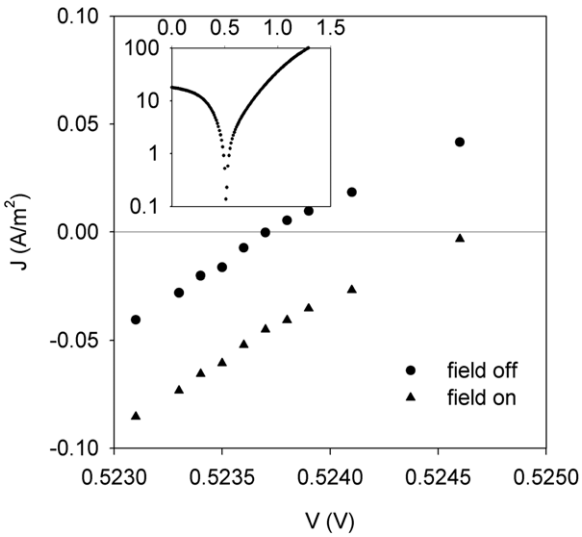

Figure 4. Current density versus voltage plot for both null and applied magnetic field (75 mT).

current at null field is positive, while the applied magnetic field drives it negative. For voltages lower than 0.5237 V the OMR is positive because the currents, both with and without field, are negative. For fields of >20 mT, an absolute change of up to 5 μA cm^{-2} can be observed with the null field currents at V_{OC} being ∼20 nA cm^{-2}. This should be compared with the much smaller photocurrent increases of ∼25 nA cm^{-2} seen in our earlier work on Alq_3 based devices [6]. In figure 4 we have reconstructed the effect of a ∼75 mT field on the current density–voltage curve near V_{OC} from the current field scans at different voltages. Again the effect of the field on increasing the current in the device is clear. What this figure also shows is that the effect of the magnetic field is actually to increase V_{OC} slightly. This is exactly what is observed with an increase in light intensity and is further evidence that it is photogeneration rather than carrier mobility that is being affected by the magnetic field.

We now discuss the origin of the OMR effect in the P3HT:PCBM photovoltaic devices. Photocurrent generation in a bulk heterojunction solar cell results from four sequential processes, (i) the absorption of a photon to generate a singlet exciton in either material (for the 520 nm irradiation used here, singlet generation occurs predominantly in the P3HT); (ii) the diffusion of the exciton to the interface between the donor and acceptor materials where the offset in energy levels of the two components provides a driving force for charge separation; (iii) the dissociation of the exciton to form, first, a bound radical pair and then, if the pair does not recombine, a separated charge pair; and (iv) the transport of each of the charges through the donor or acceptor phase to reach the appropriate electrode before bimolecular recombination with an opposite charge occurs. The efficiency of the second stage depends upon the lifetime of the singlet exciton and the size of the domains of the light absorbing phase. In P3HT the singlet lifetime is approximately 300 ps [9] and the resulting singlet exciton diffusion length is reported in the range 3–6 nm [10]. This is comparable to or shorter than the size of the domains of P3HT and PCBM observed in annealed blend films [11], with the result that singlet exciton quenching is expected to be incomplete. Indeed, photoluminescence quenching measurements confirm that only some 90% [12] of the photoluminescence from P3HT is quenched upon blending with 50% PCBM by weight, after thermal annealing. (PL quenching is more efficient before thermal annealing on account of more intimate mixing of the phases [13].) In contrast, the P3HT triplet lifetime is on the order of 10 μs [14] implying a triplet exciton diffusion length of the order of 100 nm, such that all triplet states can be expected to reach an interface. Dissociation of a triplet state to generate a radical bound pair and then separate charges is possible when the energy of the triplet is significantly greater than the energy of the separated charge pair. Charge separation from the triplet state is known in other molecular photovoltaic systems [15]. This is the case in P3HT:PCBM, where the ^{3}P3HT energy is estimated as 1.6 eV compared to 1.1 eV for the charge separated state [16]. Thus, an increase in k_{ISC} would result in an increase in the population of triplet states relative to singlets and thereby would increase the efficiency of charge separation. The most likely mechanism for the increase in photocurrent under applied magnetic field is thus an increase in triplet population via an increase in k_{ISC}. In

the present case, the saturation may result from a saturation in k_{ISC} with applied field, or it may result from the depletion of undissociated singlets, (noting that in P3HT non-radiative decay pathways are already an efficient means of exciton quenching) [16]. Studies of the effect of domain size and B field on photoluminescence quenching are needed to resolve this issue.

We now consider the voltage dependence of the photocurrent increase. k_{ISC} is expected to be independent of electric field. The larger absolute increase in photocurrent at V_{MP} than at short circuit may, however, be attributed to an increasing fraction of undissociated singlets with reducing electric field (increasing V_{App}), and this in turn could result from a electric field dependence of the charge pair generation process [17, 18]. The effect of the applied B field would then be to increase the fill factor of the photovoltaic response and reduce the negative dependence of photocurrent generation on V_{App}. In the present case, the power conversion efficiency and fill factor are increased by ∼9% of their initial values. In other materials systems where singlet exciton dissociation is incomplete and dissociation of triplet states is energetically favoured, the application of magnetic field has the potential to improve the photovoltaic response significantly.

In conclusion, we have observed that a modest magnetic field of ∼15 mT can produce an increase in the photocurrent of P3HT:PCBM bulk heterojunctions of up to 9%. This is consistent with previous studies of Alq_3 based devices which indicated that applied magnetic field increases the intersystem crossing rate leading to an increase in the triplet population which in turn increases the efficiency of photocurrent generation. The largest increases in photocurrent were observed at voltages close to V_{OC}, leading to OMR values of up to 1500%.

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