

Magnetic Field Modulation of Recombination Processes in Organic Photovoltaics

Edward P. Booker, Sam L. Bayliss, Alex Jen*, Akshay Rao, Neil C. Greenham

Cavendish Laboratory, J. J. Thomson Avenue, Cambridge, United Kingdom CB3 0HE, * University of Washington, Department of Physics, Seattle, WA, USA

Abstract — Polymer:fullerene photovoltaics have potential in small-scale power production but low open-circuit voltages limit their efficiency. Understanding the processes affecting the charge recombination rate is key to increasing device efficiency through optimizing open-circuit voltage. Most polymer-fullerene systems have an intramolecular triplet exciton state lower in energy than the interfacial charge-transfer state, and its formation can provide a terminal recombination pathway that may limit device performance. We used magnetic fields to modulate intersystem crossing in a prototypical system, and monitored the effect on the open-circuit voltage to infer changes in the steady-state carrier density and hence in the net recombination rate constant. We analyzed these effects using density-matrix modeling, and quantified the various recombination rate constants for a working device.

Index Terms – Organic PV, Organic Semiconductors, Organic Magnetoresistance

I. INTRODUCTION

Organic photovoltaics show promise in small-scale power generation applications.[1] Over the previous two decades power conversion efficiencies (PCEs) have increased to the point where they may be commercially viable, as much as 13.1 % in small-area cells.[2] However even the best devices suffer from sub-optimal open-circuit voltages.[3]

The mechanisms through which free charges are generated and recombine are dependent on device architecture;[4] for example the ratio of polymer to fullerene in the active layer of a device can change the recombination mechanism.[5]

When organic semiconducting devices are subjected to applied magnetic fields their behavior changes. These changes are termed magnetic field effects (MFEs) and are seen in the performance of organic electronic devices, including light-emitting diodes (LEDs),[6] and photovoltaic (PV) cells [7]. The reported effects include changes in current and light output in LEDs, [8], [9], and photocurrent in PVs. By providing a way of externally tuning recombination MFEs allow charge dissociation and recombination to be studied in organic semiconductors, which could guide improvement in organic photovoltaic device performance.

Here magnetic fields are found to modulate the photovoltage and photocurrent of bulk heterojunction devices (PIDT-PhanQ (poly(indacenodithiophene-co-phenanthro[9,10-b]quinoxaline)) with PC(70)BM ([6,6]-phenyl-C70 -butyric acid methyl ester)) (Figure 1 a, b). The fractional modulation

is found to be independent of the intensity of incident light. Density matrix calculations are used to relate experimental results to the mechanisms driving charge generation and recombination. We conclude that applied magnetic field modulates the recombination of charge-transfer excitons to

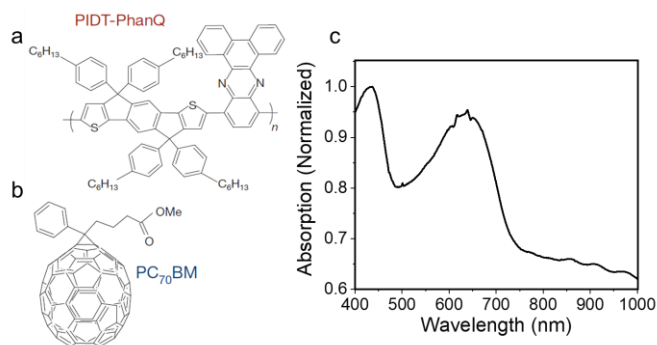


Figure 1: Chemical structures of a) PIDT-PhanQ and b) PC70BM. c) absorption spectrum for PIDT-PhanQ.

long-lived triplet excitons. This shows that magnetic field effects on photovoltage can directly investigate recombination in organic devices.

II. THEORETICAL BACKGROUND

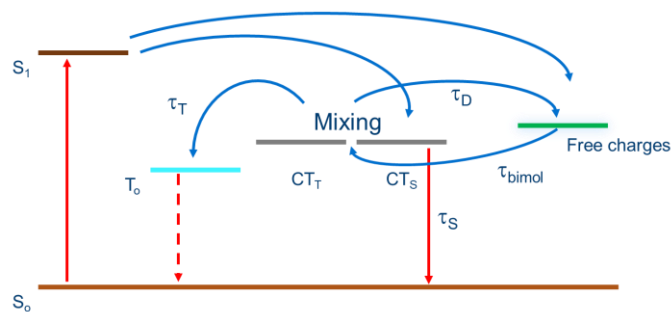


Figure 2: Schematic state diagram of the PIDT-PhanQ:PC(70)BM system as indicated by Rao et al.[10] Photoexcited excitons can dissociate to free charges or CT states. Free charges may recombine to CT states. CT states undergo spin mixing and spin-dependent CT state recombination.

The energy levels and the kinetics for the polymer system we used have been studied previously by Rao *et al.*[10] and are presented schematically in Figure 2. The relevant conclusion in this work was that in 1:1 weight ratio blends of PIDTPhanQ to PCBM both triplet and singlet charge-transfer states (CT_T and CT_S) are observed. This study also demonstrated that the CT_T lifetime was greater than the CT_S lifetime, as would be expected.

Magnetic fields modulate the recombination as an applied magnetic field changes the Zeeman splitting of the $m_s = -1, 0, +1$ CT_T states. This lifts the degeneracy between the $m_s = \pm 1$ CT_T states and the CT_S state, which changes the relative populations of the $CT_{T,S}$ states as interconversion between the two is hindered. When $CT_{T,S}$ have different decay kinetics this can alter the yield of free charges. This is measurable in the open-circuit voltage or short-circuit current which are logarithmically or directly proportional to the density of charges in the active layer of the solar cell respectively.[11]

There are other magnetic field effects that might modulate the current produced in photovoltaic devices under illumination. These include effects associated with bipolaron formation.[12][13] Distinguishing these effects from magnetic field effects on charge recombination motivates the current work.

III. EXPERIMENTAL RESULTS

We fabricated bulk heterojunction devices using indium-tin oxide coated with PEDOT:PSS (poly(3,4-ethylenedioxythiophene):polystyrene sulfonate) as bottom electrode. The active layer of a blend of PIDT-PhanQ (Figure 1a) and PC(70)BM (Figure 1b) in a 1:1 weight ratio was spin-coated at 800 rpm for 120 s then 2000 rpm for 5 s from 20 mg/ml solution in chlorobenzene. 20 nm of calcium followed by 100 nm of aluminum was evaporated on top of the

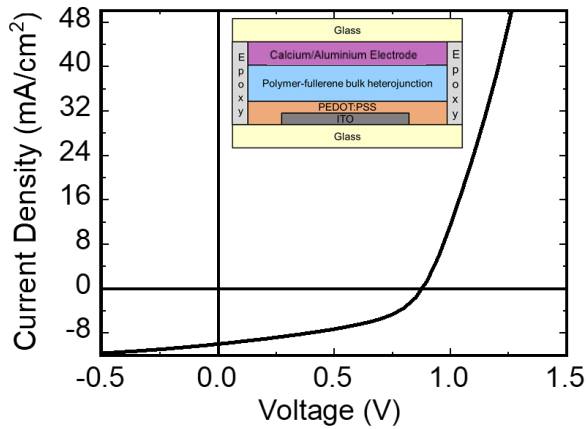


Figure 3: Typical current-voltage characteristic under 1 sun AM1.5G illumination. Inset shows a schematic of the cell architecture.

active layer prior to encapsulation to give a device area of 4.5 mm². As can be seen in Figure 1c PIDT-PhanQ has absorption maxima at 400 nm and 600 nm.

Current-voltage characteristics were measured under standard AM1.5G conditions in a solar simulator (Figure 3). The open-circuit voltage was 0.87 V, the short-circuit current density 9.8 mA/cm² and the power conversion efficiency was 3.9 %.

The effect of an applied magnetic field on the photovoltage and photocurrent (i.e. open-circuit voltage and short-circuit current respectively) was measured under illumination by white LED light of various intensities while the devices were held between the poles of an electromagnet and the applied magnetic field varied. Table I gives the details of device performance at tested intensities.

TABLE I

Summary of device performance with white LED excitation

Intensity (equivalent suns)	Voc (V)	Jsc (mA cm ⁻²)
0.050	0.84	0.58
0.10	0.86	1.2
0.15	0.87	1.7
0.20	0.88	2.1

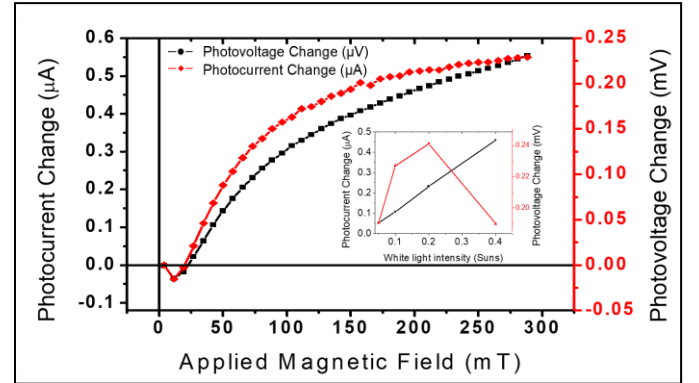


Figure 4: Magnitude of the change in short-circuit photocurrent (black) and photovoltage (red) with applied magnetic field at 0.4 suns white light LED illumination. Lineshape was consistent at different levels of incident radiation. Inset shows the variation of photovoltage and photocurrent change with white light intensity at 205 mT.

The magneto-photocurrent has a similar lineshape to the magneto-photovoltage (Figure 4), which suggests that at both short circuit and open circuit the dominating recombination mechanism is the same. For both photovoltage and photocurrent, the MFE is negative at low magnetic fields (<25 mT) and becomes positive at higher fields. This trend was seen at all intensities used.

IV. NUMERIC MODELING

To quantitatively assess the experimental results, we created a model based on the work by Rao *et al.* The model considers the CT state population as a function of applied magnetic field. To investigate the quantum mechanical behaviour of the system CT state density matrix equations (Equations 1 & 2) were solved in the steady state. This allowed us to model the effect of applied magnetic field on the interaction of the CT states with terminal loss states and free charges.

$$\begin{aligned} \partial_t \rho &= \frac{-i}{\hbar} [\hat{H}, \rho] - \frac{1}{\tau_D} \rho - \frac{1}{2\tau_S} \{\hat{P}_S, \rho\} - \frac{1}{2\tau_T} \{\hat{P}_T, \rho\} + G \\ &= -L\hat{\rho} + G \end{aligned} \quad (1)$$

$$H = g_1 \mu_B (B + b_{hf,1}) \cdot s_1 + g_2 \mu_B (B + b_{hf,2}) \cdot s_2 \quad (2)$$

Here \hat{H} (Equation 2) is the Hamiltonian governing the system which includes Zeeman splitting, exchange interactions, and hyperfine interactions. τ_D , τ_S and τ_T are the decay lifetimes of the CT state for spin-independent dissociation, singlet decay to the ground state, and triplet decay to terminal intramolecular triplet excitons respectively. $\hat{P}_{T,S}$ is the $CT_{T,S}$ projection operator.

The diagonal elements of the density matrix, ρ , gives the relative proportions of $|\downarrow\downarrow\rangle$, $|\downarrow\uparrow\rangle$, $|\uparrow\downarrow\rangle$, & $|\uparrow\uparrow\rangle$ electron and hole pairs, which measure the proportions of CT_T and CT_S . The trace of the density matrix is the population of CT states. How this population changes with magnetic field gives a measure of the overall change in change in charge density of the system, assuming that the dissociation to free charges is spin-independent

The G term is the generation term and is a 4×4 matrix giving the charges entering the model. In the case of bimolecular recombination, it is proportional to the identity matrix as all electron and hole spin pairs are produced with equal probability. For singlet CT state generation, (i.e. directly following photon absorption) the generation matrix only populates states with singlet character.

The parameters $g_{1,2}$ are the relevant Landé g-factor for the electron/hole on the fullerene/polymer molecule respectively, and $s_{1,2}$ represents the electron/hole spin vector. The hyperfine field in the different environments is $b_{hf,1,2}$, and the applied magnetic field is B .

Equation 1 can be simplified by identifying the terms which In the steady state $\partial_t \rho = 0$, so this problem reduces to solving $\rho = \hat{L}^{-1}G$. This gives the steady state density matrix as the product of the inverted operator matrix, \hat{L}^{-1} , with the generation term. The trace of the density matrix then gives a measure of the CT state population.

The open-circuit voltage depends logarithmically on the free carrier concentration.[11] For small perturbations the fractional change in the photovoltage is proportional to the fractional change in carrier concentration. The fractional change in

density matrix population with magnetic field therefore approximates the results obtained for fractional photovoltage change with applied magnetic field. This is referred to as the normalized magnetic response.

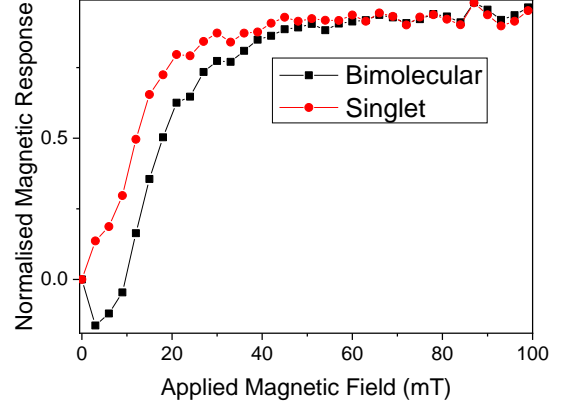


Figure 5: Comparison of singlet and bimolecular CT state generation. Trace of the steady state density matrix obtained as a solution to equations 1 & 2 at various magnetic fields plotted when the generation term produces both singlets and triplets, or singlets only.

To determine whether the generation of CT states is predominantly from singlet excitons or from bimolecular recombination we performed simulations of both cases with a range of parameters. Representative results are shown in Figure 5. The Landé g-factor was 2. The hyperfine field used was 10 mT in all simulations, τ_S , τ_T and τ_D were 200 ns, 800 ns and 1000 ns respectively. As can be seen in this case the bimolecular generation of CT states produces the negative magnetic field effect at low magnetic field and generation from singlet excitons does not, producing only a positive magnetic field effect. For this reason, and taking the result from Rao et

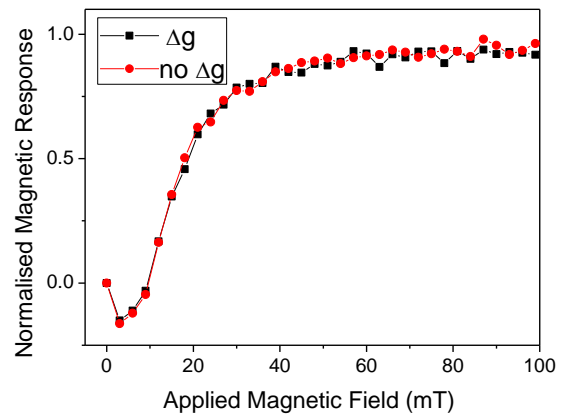


Figure 6: Comparison of solutions to equations 1 & 2 at various magnetic fields plotted when there is a Δg of 0.002, and when there is no Δg .

al. that photoexcited singlets in this system may directly dissociate to free charges, we used bimolecular generation of

singlet and triplet CT states at a 1:3 ratio in all further simulations.

We also looked at the effect of the Δg mechanism. Introducing a Δg between the electron and hole of 0.002 has a minimal effect on the MFE (Figure 6), confirming that Δg effects are not important at these fields. Here we used the same parameters as used in Figure 5. A Δg value of 0.002 is physically reasonable in this system when compared to similar polymer:fullerene blends.[14]

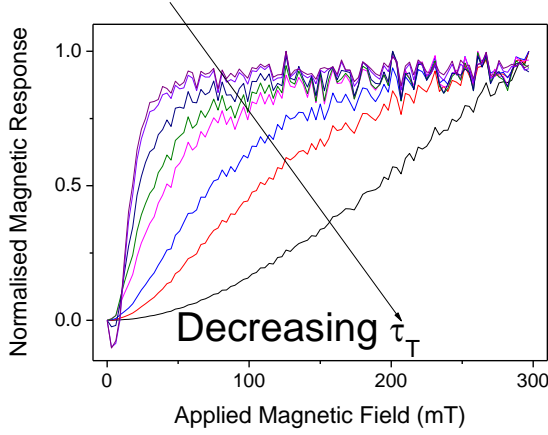


Figure 7: Variation in the solutions to equations 1 & 2 as the ratio $\tau_S:\tau_T:\tau_D$ was varied from 3:0.5:10 to 3:0.001:10 ($\tau_S = 300$ ns).

The effect of a changing τ_T was investigated in the simulation. The results are shown in Figure 7. We see that, at constant τ_S and τ_D , when τ_T is low compared to τ_S we do not produce the negative magnetic field effect; it is only when the triplet CT state is longer lived that we see the negative feature.

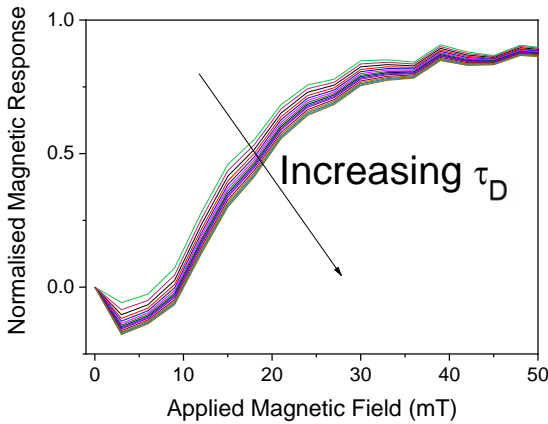


Figure 8: Variation in the solutions to equations 1 & 2 as the ratio $\tau_S:\tau_T:\tau_D$ was varied from 1:9:1 to 1:9:20.

Figure 8 shows the results of the simulation as the dissociation time is increased from $\tau_S:\tau_T:\tau_D = 1:9:1$ to $\tau_S:\tau_T:\tau_D = 1:9:20$ ($\tau_S = 100$ ns). The results show that in this regime,

where the singlet and triplet lifetimes are kept constant, as the dissociation lifetime increases there is always a negative MFE at low magnetic field, but the minimum of the MFE occurs at progressively higher magnetic field and has progressively higher magnitude.

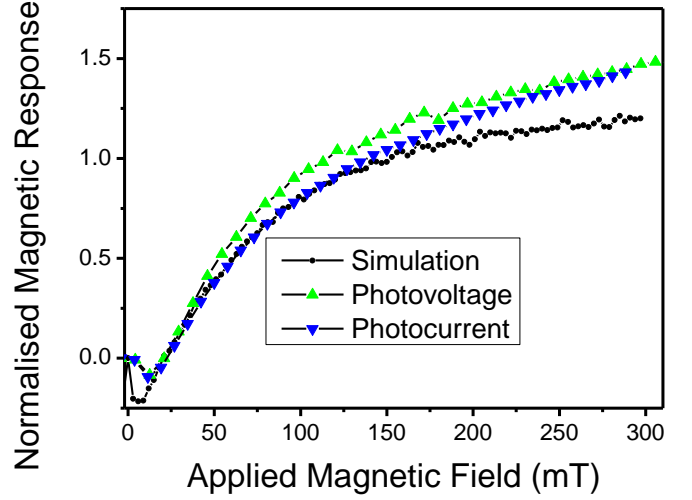


Figure 9: Normalized trace of the steady state density matrix obtained as a solution to equations 1 & 2 at various magnetic fields plotted with normalized photovoltage and photocurrent response at 0.1 suns. The simulation had the ratio $\tau_S:\tau_T:\tau_D$ at 2:2000:1000. The Δg was 0.002, the hyperfine field was 10 mT.

From these investigations of the different parameters of the simulation we could identify a regime which corresponds to the photovoltage and photocurrent measured from the devices. The singlet to triplet to spin-independent CT state lifetime ratio was 2:2000:1000. The hyperfine field was 10 mT. With these parameters the simulation produces a CT state population that initially decreases to a minimum at an external magnetic field of approximately 10 mT. The CT state population then increases, becomes positive at roughly 25 mT and saturates by 300 mT. This simulation approximately reproduces the experimental results, as can be seen in Figure 9.

V. DISCUSSION

We have seen that open-circuit voltage and short-circuit current may be modulated by magnetic fields applied to functioning devices. In the materials system studied, the generation of CT state excitons is shown to have a significant contribution from bimolecular recombination of free charges.

We have also seen singlet CT state lifetimes which are much smaller than the triplet CT state lifetimes. This might be expected if singlet CT state decay is radiative and triplet CT state decay is non-radiative via a triplet exciton, which is suggested by the work inspiring this paper.[10] The high ratio of the singlet to the triplet CT states is plausible given the large range of lifetimes of different components of the CT state decay.[15]

We propose that studying the effect of magnetic fields on photovoltage provides a potentially useful complementary measurement to magnetophotocurrent, since it is sensitive only to recombination effects, and not effects of the magnetic field on charge transport.

This study shows that magnetic fields influence the recombination of charge transfer excitons in organic photovoltaic devices. We see lineshapes in the magnetic field effect measurements indicative of bimolecular recombination which is confirmed by simulations which provide quantitative analysis of the recombination mechanisms in these materials. This study demonstrates the effectiveness of magnetophotovoltage and magnetophotocurrent measurements in studying recombination mechanisms in working devices.

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