Using Lateral Bulk Heterojunctions to Study the Effects of Additives on PTB7:PC₆₁BM Space Charge Regions

*Marlene Gutierrez, Oleksiy Slobodyan, Ananth Dodabalapur, David Vanden Bout**

The University of Texas at Austin
1 University Station, A5300, Austin, TX 78712

E-mail: dvandenbout@cm.utexas.

Abstract

Lateral bulk heterojunctions (LBHJ) provide a tool to directly probe the active area of photovoltaic devices using microscopy techniques. Here we use scanning photocurrent microscopy (SPCM) to probe an organic photovoltaic (OPV) device with Poly [{4,8-bis [(2-ethylhexyl) oxy] benzo [1,2-b: 4,5-b'] dithiophene-2, 6-diyl} {[3-fluoro-2- [(2-ethylhexyl) carbonyl] thieno [3,4-b] thiophenediyl)}] (PTB7): [6,6] Phenyl-C₆₁-butyric acid methel ester (PC₆₁BM). The effects of the additive 1,8-diiodooctane (DIO) on the recombination dynamics and morphology are probed in real space in a LBHJ structure. By using SPCM we can see a larger increase in the space charge region for samples with DIO when compared to those without DIO. This indicates that the additive improves film morphology leading to increased charge extraction efficiency and decreased recombination.

Keywords: bulk heterojunction, charge transport, space charge region, organic, photovoltaic devices

1. Introduction

Photovoltaics have been at the forefront of alternative energy research for some time, promising to become an efficient, clean, and economical option. Increasingly, the importance of economical and environmental factors in device implementation has driven research towards the development of organic photovoltaics (OPVs). OPVs have the potential to be very affordable due to low-cost starting materials and processing conditions. They also have the additional advantage of being printable on flexible substrates, which would provide an opportunity for integration into consumer electronics, among other uses.[1,2] Though OPVs have the potential to be less expensive than their inorganic counterparts; poor device efficiencies are a significant issue. Thus far, OPV efficiencies of up to 10% have been achieved through a combination of improvements in processing techniques that yield better control of nanoscale morphology, and molecular engineering developments, which have led to development of push-pull polymers with tunable band gaps. [1,3,4] Despite these advances, a gap in the fundamental understanding of charge separation and transport in these devices hinders OPV research from attaining higher efficiencies. Charge separation and transport theories for common silicon solar cells have assisted researchers in making advances in traditional photovoltaic efficiencies. It stands to

reason that a similar fundamental understanding of these processes in OPVs would likewise accelerate the development of truly competitive organic alternatives to silicon solar cells.

A promising OPV device active layer structure is a bulk heterojunction (BHJ), made from a mixture of an electron donating polymer and an electron accepting material. This structure leads to nanoscale phase separation and interconnected networks of its components enabling separation and transport of photogenerated carriers. Two types of recombination primarily interrupt charge transport. Due to the low dielectric constant of BHJ materials, absorption of a photon leads to the formation of an exciton (a bound electron-hole pair) rather than free carriers. The separation of an exciton into free carriers is a crucial step in OPV transport and current generations. As most organic materials are unable to easily separate excitons into free carries, geminate recombination (recombination of the coulombically bound electron and hole) significantly limits the photocurrent.[5] The phase separation and interconnected networks in the active layer of a BHJ structure limit germinate recombination and allow for the separation and transport of these carriers. Once an exciton is successfully separated into free carriers, the internal electric field drives the carriers to be collected at electrodes. This leaves bimolecular recombination (recombination of a free electron and free hole) as the main loss of photocurrent in these devices.[6]

Researchers have found that the morphology of the active layer is crucial to device efficiency. A complication that typically arises in the BHJ active layer is the presence of a large amount of phase segregation, which leads to isolated fullerene and polymer domains with little intermixing. In order to separate into free carriers the exciton must reach a donor/acceptor interface, which provides the driving force to separate electron-hole pair, before recombination occurs.[7,8] Films with sufficient mixing of the fullerene and polymer have been shown to create

free carriers almost instantaneously, and it provides a good pathway to nanoscale pure domains, which are necessary for efficient collection.[9,10] Large domains of pure polymer or fullerene lead to an enhancement of geminate recombination, since an exciton will decay back to the ground state before being separated into free carriers or free carriers may be trapped in a isolated domain. Furthermore polymers have numerous degrees of freedom that lead to a complex energetic landscape that may limit the transport of carriers due to trap assisted recombination.[4, 5]

In order to further study these systems there is a need to understand the transport dynamics within the device active layer. Unfortunately few methods allow for directly probing the active layer of a working device. Instead inferences must be made from techniques that employ vertical cells such as transient photocurrent measurements, time-resolved microwave conductivity, and photo-generated charge extraction in a linearly increasing voltage (photo-CELIV).[12–14] While extremely valuable, these transient measurements rely on complex data interpretation and are generally not performed under a steady state condition. In addition, unlike other scanning photocurrent techniques, implementing a lateral device structure with the scanning confocal microscope allows for decoupling of the transit length from device thickness and also allows for uniform charge generation. A similar technique used to look at the local photocurrent is photoconductive atomic force microscopy (pcAFM). This technique use the AFM tip as the back contact of the device. Images must be collected in contact mode and samples are limited to very smooth surfaces. [15,16] In contrast, scanning photocurrent microscopy (SPCM) is a complementary tool that can be used to examine a wide array of samples.

In this article we directly measure the steady state photocurrent generated within the active layer of a lateral bulk heterojunction (LBHJ) device using SPCM. In a LBHJ device the two electrodes are defined on the same plane and the active material is deposited on top of these electrodes. This allows us to interrogate the active material in-between two electrodes of different work function by illuminating with a focused laser beam from below. LBHJ devices allow the electrode distance to be varied from 2-100 μm , permitting scanning along the charge transport direction as a function of position from the electrode. Previous experiments have shown that lateral devices are a useful platform for interrogating BHJ materials and can provide valuable information about the size of the space-charge region, mobility, and lifetime of carriers.[17,18] Although transport in a vertical cell is dominated by charges moving vertically through the film, it is also useful to study these parameters in the lateral direction. Experimentally derived quantities such as carrier densities and recombination coefficient depend on charge flow during the experiment, it is therefore important to measure such parameters along multiple directions. Multiple studies implementing a LBHJ have been able to compare their results to vertical cells. [19,20]

There has been wide interest in the low band gap polymer [(2-ethylhexyl) oxy] benzo [1,2-b: 4,5-b'] dithiophene-2, 6-diyl} {[3-fluoro-2- [(2-ethylhexyl) carbonyl] thieno [3,4-b] thiophenediyl}] (PTB7), which has reached device efficiencies up to 9% by implementing an inverted structure while also using the additive 1,8-diiodooctane (DIO).[21] It has been previously shown when the additive, DIO, is added to a chlorobenzene solution, the solubility of the fullerene increases and yields smaller domains of PC₆₁BM when films are made.[22] Transmission electron images of films without DIO show that there are round aggregates, which are attributed to PC₆₁M domains. This study by Foster et al found that adding DIO leads to

better intercalation of the PCB₆₁M and PTB7.[23] An explanation for the enhanced solubility of PCB₆₁M when DIO is added to the solutions is the interaction between the iodine atom with a partial negative charge and electron deficient PCB₆₁M.[24] Poly (3-hexylthiophene-2, 5-diyl) (P3HT) is considered the standard polymer for OPV research, though its recombination dynamics may differ from most other polymers. Therefore PTB7 may give a broader insight into recombination in OPV systems. In the present study we examine the effects of DIO on the space charge region (SCR) of PTB7: PC61BM and demonstrate that measurable changes of the SCR can be seen experimentally.

2. Materials and Methods

Lateral devices were fabricated using photolithography onto a glass substrate with a thickness of 150 μm . 50 nm of aluminum (Al) and gold (Au) electrodes were deposited via thermal (Denton thermal deposition chamber) and E-beam deposition (Cooke E-beam/sputter deposition). These metals were chosen as the electrodes to suppress reverse bias carrier injection.

Figure 1. (a) Schematic of experimental microscope, (b) structure of lateral BHJ illuminated from below.

Figure 2. Example of photocurrent image (a), example of reflectance image (b), and example of fluorescence image (c).

Prior to deposition of the BHJ active material, the glass substrate was cleaned with phosphoric acid to remove any oxide that maybe present on the Al electrode. A solution of PTB7 and PC₆₀BM (1:1.5) in dichlorobenzene was heated for at least 6 hours at 120°C. The same process was followed for blends with 3-v/v% 1,8-diiodooctane (DIO). The solution was then spun-cast on to cleaned substrates at 1000 rpm for 60 s. The sample was then annealed at 120°C for 10min followed by encapsulation in nitrogen atmosphere.

SPCM measurements were acquired using 20 μm active area LBHJ devices; biases of -100 V, -150 V, and -200 V, which correspond to respective electric field strengths of $-5 \times 10^4 \text{ V cm}^{-1}$, $-7.5 \times 10^4 \text{ V cm}^{-1}$, $-10 \times 10^4 \text{ V cm}^{-1}$, were applied during photocurrent collection. These field strengths are consistent with fields for a working 100nm device. [18,25] The negative bias was applied to the Au electrode, and the Al was grounded. A negative base was applied via a Keithley sourcemeter and the photocurrent was collected via a Lock-in amplifier. The incident light was chopped at 141 Hz. The active area was excited using a 633.8 nm laser beam (Melles Griot) focused though an oil immersion objective (Ziss) with a 1.25 numerical aperture and 100x magnification. The focused laser spot is 350 nm diameter for the wavelength used in the experiment. Laser power did not exceed 75 nW, which resulted in an incident power density of 78 W/cm^2 . Even at these high power densities the sample was stable and showed no signs of degradation during scanning. There is a potential for phase segregation issues that could lead to a substantially different entrenchment in PC₆₁M aggregation at the air-surface interface.[26,27]

However the current experiment will only minimally probe these regions, as we illuminate from the bottom. Since the electrodes are 50 nm thick and the film is 100 nm thick, the photocurrent will originate in the first 50 nm. The sample was raster scanned across the objective using a piezoelectric stage (Queensgate), and photocurrent, reflectance and fluorescence were collected simultaneously. A white light bias of 80 W/cm^2 was applied. This experimental setup in this work is similar to previously described set-ups.[28,29] AFM measurements we made using an Asylum AFM (MFP-3D) in tapping mode.

3. Results and Discussion

SPCM measurement allow for the simultaneous collection of induced photocurrent, fluorescence, and reflectance images. **Figure 1a** shows a schematic of the experimental microscope set-up. **Figure 1b** shows a diagram of the device scanned; here the electrodes are in same plane as the active material. A focused laser beam illuminates the device from below, and the sample is scanned across the objective. Photocurrent, fluorescence, and reflectance images are collected pixel-by-pixel. Induced photocurrent is collected via a lock-in amplifier (**Figure 2a**) while the reflectance is measured (**Figure 2b**) via an avalanche photodiode. Although fluorescence (**Figure 2c**) was collected there were no apparent features that could be distinguished, or they were beyond our resolution. There was a constant fluorescence signal across the entirety of the channel. This is not surprising since it is a common radiative recombination pathway in OPV systems. Using the reflectance image we distinguish between the electrodes and determine orientation of the device. SPCM measurements were taken on $20 \mu\text{m}$ devices with applied bias of -100 V, -150 V, and -200 V, which correspond to a potential per unit length of $-5 \times 10^4 \text{ V cm}^{-1}$, $-7.5 \times 10^4 \text{ V cm}^{-1}$, $-10 \times 10^4 \text{ V cm}^{-1}$. For simplicity the potential per unit

Figure 3. Averaged line scans for sample without DIO under dark (a) and white light bias (b) conditions. All samples were scanned with -100 V, -150 V, and -200 V bias. The dash line represents the

length will be referred to as the electric field, but it is important to realize that the true electric field within lateral devices is not uniform. These fields are similar to those found in vertical cells due to the vast difference in device length when compared to that of a typical vertical cell where the active layer is usually around 100 nm.

The result of combining the lateral geometry of the device and the operational mode is the manifestation of space-charge-limited (SCL) photocurrent. SCL photocurrent device physics has

been reported both in vertical and lateral structures.[17,18,30] Photocurrent images were used to create averaged line scans for PTB7: PC61BM samples (**Figure 3**). **Figure 3a** shows the averaged line scans for induced photocurrent under dark conditions (no white light bias) exhibiting two current peaks near the electrodes that decay as the beam moves away from the electrode. Peaks are located near the edge of the electrode representing where most of the photocurrent is being collected. In the center of the device there is a large recombination zone, an area of little to no photocurrent since the free carriers must travel farther to reach the electrodes, hence the chances of recombination before being collected are much higher. The left electrode corresponds to the electron-collecting cathode, and the right electrode corresponds to the hole-

collecting anode; thus, the current near each electrode is due to the accumulation of carriers which it is collecting.[30] In order to fit the SCR regions an exponential decay function convoluted with a Gaussian beam in order to account for instrument broadening of the data that occurs near the edge of the device (See Supporting Information). The length of the SCR is

Figure 4. AFM height (a, b) and phase (c, d) images show the morphology differences for samples without (a, c) and with (b, d) DIO.

taken to be the length associated with the exponential decay in the fit. Fitting the PTB7:PC61BM data using this method resulted in the following space charge lengths near the cathode: 625 nm, 875 nm, and 1050 nm for -100V, -150V, and -200 V respectively. The length of the SCR near the anode were found to be; 750 nm, 925 nm, and 1000 nm for -100V, -150V, and -200V respectively. The increase in bias causes an increase in the intensity of the photocurrent peaks as well as a small increase in the size of the SCR (**Table 1**), which is consistent with previous results.[18] Under dark conditions there is a feature that is not accounted for in the fitting scheme used. It is important to note that it is not in the scans with a white light bias.

In order to study the effects of light on a working device the sample was exposed to a constant white light bias. Exposing a device to a white light bias will increase the carrier concentration, filling energetic traps. The carriers that are created using the white light bias are not represented in the current scans because measurements were taken via lock-in detection to only measure the AC current induced by the laser probe. Due to the increase in carrier concentration there are less carriers to be excited by our laser probe, therefore there is a decrease

in the photocurrent when under a white light bias. **Figure 3b** shows averaged line scans for the device under white light bias conditions. When the PTB7: PC60BM is illuminated with a white light bias there is an increase in the SCR length for both the cathode (675 nm, 900 nm, 1150 nm) and anode (700 nm, 1150 nm, and 1200 nm) for applied biases of -100V, -150V, and -200V, respectively. These increases are expected and can be attributed to trap filling which allows collection of free carriers farther from the electrodes by allowing more trap free pathways to the electrodes.

The effects of morphology on the SCR were studied by using the additive DIO, which selectively dissolves PC₆₁BM in the solution before spin casting. **Figure 4** shows AFM height (a and b) and phase (c and d) images of films without (a and c) and with (b and d) DIO. The sample without DIO has round isolated PC₆₁BM domains, which have been circled in white in **Figure 4a**. The height images that these aggregates are protruding above the rest of the film, which range between 500nm and 10nmn in size. In the phase image we see a slightly different composition for the aggregates then that of the rest of the film. The top of these aggregates have similar composition to that around the aggregates due to the polymer that if formed on top of these aggregates at the surface/air interface.[27] **Figure 4b** and d shows that with the addition of the DIO the round features in the height and phase are no longer apparent. We theorize that the absence of these large round features indicates a larger amount of intermixing between the PC₆₁BM and the PTB7. Pervious reports have also shown round PCB₆₁M domains in transmission electron images of PTB7: PC₆₁BM of similar size in devices made without DIO.[31] Large isolated domains of PC₆₁BM have the potential to trap many free carriers and leads to trap limited recombination, this effect has been seen in PTB7 devices without the use of an

additive.[32–34] Using SPCM we can detect the effects that morphology has on the space charge region in PTB7 devices.

Figure 5 shows averaged line scans for a device with 3% v/v DIO under dark (**Figure 5a**) and illuminated (**Figure 5b**) conditions. All SCR lengths are reported in **Table 1**. The magnitude of the photocurrent for devices with DIO is smaller than that for devices without DIO. The magnitude of the photocurrent is dependent on multiple processes including the generation rate and mobility as shown by Ooi et al. in addition, it also depends on the extraction at the contacts.[35] The lower photocurrent in the sample with DIO is most likely due to less efficient collection at the electrodes. It is

Figure 5. Averaged line scans for sample with DIO under dark (a) and white light bias (b) conditions. All samples were scanned with -100 V, -150 V, and -200 V bias. The dash line represents the electrode

important to not that the main concern for these experiments is the special dependence of the SCR region. The devices with DIO have larger space charge regions under both the dark and light conditions than a device without DIO, indicating that we are able to collect charges generated farther from the electrodes with to the addition of DIO. The average increase of the SCR for the sample without DIO when comparing the dark conditions and the white light biased conditions was 6% and 9% for the cathode and anode, respectively. The sample with DIO showed a SCR growth of 21% for near the cathode and 16% near the anode. We can conclude

that there is a stronger dependence on carrier concentration; evidently filling traps will increase the efficiency of collection for a sample with DIO

Table 1. Extracted space charge region lengths for samples with and without DIO.

Applied Bias [V]	Dark				Light			
	W/O DIO		W/ DIO		W/O DIO		W/ DIO	
	Left [nm]	Right [nm]	Left [nm]	Right [nm]	Left [nm]	Right [nm]	Left [nm]	Right [nm]
-100	625	750	1000	1000	675	700	1200	1150
-150	875	925	1050	1050	900	1150	1250	1250
-200	1050	1000	1125	1025	1150	1200	1625	1450

while having a smaller effect on a sample without. When you compare the SCR size under illumination for a sample without and with DIO reveals a significant increase in the SCR for the sample with DIO, with an average increase of 52% and 31% for the cathode and anode, respectively. As DIO incorporation changed the cathode SCR length more, its effect is greater on collection of electrons rather than holes. This can be confirmed by analyzing the ratio of the size of the SCR since it is proportional to the mobility ratio by,

$$\frac{L_C}{L_A} = \frac{\mu_p}{\mu_n} \quad (1)$$

where L_C and L_A are the lengths of the SCR at the cathode and the anode respectively, and μ_p and μ_n are the mobilities for the hole and electron respectively.[36] The mobility ratio for the line scans without DIO are averaged for all voltages and are greater than one for both dark (1.1) and light (1.09) conditions. Indicating that the hole is the faster mobility carrier. When DIO is added the mobility ratio is slightly less than one for dark (0.97) and light (0.95) conditions. Therefore, from the changes in SCR length we conclude that the addition of DIO increases the mobility of the electron due to the decrease of PC₆₁M electron traps.

DIO has previously been shown to dramatically increase the efficiency of PTB7 solar cells by increasing the solubility of PC₆₁BM into solution, therefore promoting strong intermixing of

the acceptor and donor materials.[37,38] The nanoscale morphology of the acceptor and donor provides a bicontinuous pathway to the electrodes, which leads to better transport and collection of the free carriers. Hedley et al found that by using DIO in BHJ films results in fiber-like fullerene- and polymer- rich domains lead to extremely fast dissociation of excitons and high extraction efficiency when compared to that with out DIO.[34] The current profiles show that there is a dramatic increase in the SCR length of samples with DIO compared to those without, as samples that contain DIO allow collection of carriers farther from the electrodes due to fewer isolated domains, which could trap carriers. In addition, based on the current profiles this morphology has a larger effect on the collection of electrons than holes, which has a larger growth in the cathode SCR under a white light bias. Since the PC₆₁BM is the electron acceptor, isolated domains leave the electrons no pathway to the electrode, leading them to recombine with free carriers near the polymer/fullerene interface. The large growth in the SCR with DIO implies that we are able to collect carriers farther from that electrode, confirming the consequences of trapping and a lack of pathways to the electrode due to morphology.

Studies have found that the use of additives suppresses trap-limited recombination. Li et al reported transient photocurrent measurements which demonstrated that there is less-trap assisted recombination in a PTB7 sample with DIO compared to those without, and directly connected device efficiency to charge trapping.[39] Lambardo et al demonstrated through transient photovoltage, voltage dependent charge extraction, and timed delayed collection field measurements that devices processed without DIO show photocurrent losses from both geminate and nongeminate recombination, while nongeminate recombination is more important in devices processed with DIO.[40] Additionally, a study on the thickness dependence of PTB7 devices showed that efficient charge collection in thick devices could be improved via increase of

PC₆₁BM phase connectivity, although this was done by increasing PC₆₁BM content. Our findings support that DIO does improve charge extraction as well.[41] Due to the lack of mixed phase in samples without DIO it is difficult to create free carriers in just the pure polymer or fullerene regions, which in turn leads to an increase in geminate recombination. In addition the mixed phase can provide a vital pathway to the pure phase, which serves as the pathway to the appropriate electrode.

The results herein demonstrate that SPCM is a valuable technique for quantifying and visualizing the effects that additives have on the SCR of LBHJs. Although this technique can only measure free carriers, it is evident that the small increase of the SCR length in samples without DIO (6% and 9% for cathode and anode, respectively) is due to the absence of an efficient pathway to the electrodes. Addition of DIO results in significant growth of the SCR when comparing between dark and illuminated conditions (21% and 16% for cathode and anode, respectively). We attribute this to an increase in mixed phase within the film morphology, allowing for more efficient separation of the free carriers, and more importantly better transport conditions.

4. Conclusion

We have demonstrated that SPCM is a useful tool for probing a device under working solar cell conditions. A LBHJ structure was used to probe the active layer of a PTB7: PC₆₁BM with and without DIO. Using SPCM we found that the space charge region increased when using the additive DIO. It has previously been seen that DIO increases the efficiency of devices containing PTB7 in the BHJ and by using techniques such as transient photovoltage, voltage dependent charge extraction, and timed delayed collection field measurements researchers have found that DIO reduces trap assisted recombination and geminate recombination. SPCM

measurements show that DIO has a larger effective SCR near the cathode, which is a measure of how far electrons may be collected from the electrode. This growth can be attributed to a better mixing of the acceptor and donor phases that allow for less charge trapping and, more importantly a better network for charge transport, leading to a better efficiency of collecting charges further from the electrodes.

The lack of growth in the SCR for samples without DIO demonstrates the crippling effect that poor morphology has on the collections efficiency. Hence we conclude that filling traps has little effect on the collection of free carriers for samples without DIO and the efficiency deteriorates because of poor pathways for charges traveling to the electrodes. The growth of the SCR in samples with DIO can be attributed to improved pathways to electrodes, therefore other recombination pathways become of greater importance for device charge extraction, leading to the larger change under white light bias.

SPCM is a relatively new technique that can distinguish small changes in the SCR for a device under working conditions. As these are direct rather than indirect measurements, there is no need to make inferences about the active layer since we can directly probe it using a lateral bulk heterojunction structure. This type of scanning microscopy could be useful not only for bulk heterojunctions but other photovoltaic materials as well. It is important to note that there are still differences between lateral and vertical cells, such as the direction of transport and the direction of phase separations. However, using SPCM would allow researchers to make direct correlations between morphology, processing techniques, and space charge current, providing answers to vital questions that previously could not be directly probed.

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