ON THE CORRECTED PHOTOCURRENT OF ORGANIC BULK HETEROJUNCTION SOLAR CELLS

- A dissertation submitted for the degree of Doctor of Philosophy -

by

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For Ma, Pa, Wei, Yang, Jiamin and my cats Maui and Marble.
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Except where specific reference is made, the material contained in this thesis is the result of my own work. This dissertation has not been submitted in whole or in part for the reward of a degree at this or any other university.

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The measured photocurrent of a solar cell may be considered the sum of a photogenerated current due solely to the influx of photons, and a photovoltage-induced current due to carrier injection at the electrodes. Correcting the measured photocurrent for the injected current yields the voltage dependence of the photogenerated current alone. This corrected photocurrent can provide valuable insight into the processes governing the behaviour of a solar cell, yet is seldom measured or discussed within the community. In this dissertation, an original experimental technique designed specifically for the reliable measurement of the corrected photocurrent is described, with the intent of applying it to organic bulk-heterojunction solar cells.

Solar cells based on a number of donor-acceptor combinations were investigated. Using the experimental technique developed here, corrected photocurrent-voltage characteristics exhibiting remarkably anti-symmetric profiles were obtained and subsequently rationalised with a simple physical model. From the perspective of this model, the nature of charge extraction at the electrodes – and how this is affected by processes such as thermal annealing – was examined. Finally, a new low band-gap, small-molecule acceptor material was used in bulk-heterojunction solar cells, and shown to promising photovoltaic performance. Interestingly, these devices exhibited anomalous current-voltage characteristics, which, on closer examination, could be explained by an electric field dependence in the photogeneration rate. Throughout this work, particular attention was given to how these findings may be used to improve device efficiencies.
# TABLE OF CONTENTS

**ACKNOWLEDGEMENTS**  

2

**ABSTRACT**  

4

**TABLE OF CONTENTS**  

5

**LIST OF FIGURES**  

7

**PUBLICATIONS**  

17

**CHAPTER 1  SOLAR CELLS FROM ORGANIC SEMICONDUCTORS**  

19  

1.1  THE NEED FOR ORGANIC SOLAR CELLS  

19  

1.2  CONJUGATED MOLECULES AS SEMICONDUCTORS  

21  

1.2.1  Photoexcited states  

23  

1.2.2  Charge transport  

25  

1.3  GENERAL DEVICE STRUCTURE AND CHARACTERISTICS  

30  

1.3.1  Current-voltage response  

32  

1.3.2  Photovoltaic performance  

37  

1.3.3  Spectral response  

41  

1.3.4  Charge injection  

43  

1.3.5  Photogeneration at a donor/acceptor interface  

45  

1.3.6  Loss mechanisms  

49  

1.4  THE CORRECTED PHOTOCURRENT  

50  

1.5  EXPERIMENTAL METHODS  

54  

1.5.1  Device fabrication  

54  

1.5.2  Current-voltage response  

56  

1.5.3  Spectral response  

58  

1.5.4  Electroabsorption  

59

**CHAPTER 2  DEVELOPMENT OF THE PULSED MEASUREMENT TECHNIQUE**  

62  

2.1  STANDARD DC MEASUREMENT OF CORRECTED PHOTOCURRENT  

62  

2.1.1  Apparent gain effect under forward bias  

62  

2.1.2  Device heating due to illumination  

65  

2.2  EQUIPMENT FOR THE PULSED MEASUREMENT TECHNIQUE  

67  

2.3  THE PULSED MEASUREMENT TECHNIQUE — RADIATIVE HEATING  

71  

2.4  THE EFFECT OF RESISTIVE HEATING  

76  

2.5  REPEATING VOLTAGE SWEEPS AND PULSED LIGHT  

81  

2.6  CONCLUSIONS  

85
CHAPTER 3  THE ANTI-SYMMETRIC CORRECTED PHOTOCURRENT-VOLTAGE RESPONSE  

3.1  INTRODUCTION 88
3.2  THE ANTI-SYMMETRIC PROFILE OF THE CORRECTED PHOTOCURRENT 89
3.3  ANALYSIS OF THE ANTI-SYMMETRIC PROFILE 93
3.4  CHARGE CARRIER SELECTIVITY AT THE ELECTRODES 97
   3.4.1  Inverse-selectivity 105
   3.4.2  The offset current 108
3.5  CARRIER SELECTIVITY AND THE OPEN-CIRCUIT VOLTAGE 111
3.6  CONCLUSIONS 114

CHAPTER 4  THE PHOTOCONDUCTIVITY  

4.1  INTRODUCTION 118
4.2  INTENSITY DEPENDENT MEASUREMENTS ON A P3HT:PCBM-BASED SOLAR CELL 118
4.3  THE PHOTOCONDUCTIVITY OF A P3HT:PCBM-BASED SOLAR CELL 120
4.4  THE PHOTOCONDUCTIVITY OF AN MDMO-PPV:PCBM-BASED SOLAR CELL 128
4.5  THERMAL ANNEALING EFFECTS 132
4.6  OPTIMISATION OF SOLAR CELLS 137
4.7  CONCLUSIONS 139

CHAPTER 5  FIELD-DEPENDENT CARRIER PHOTOGENERATION  

5.1  INTRODUCTION 142
5.2  BHJ SOLAR CELLS BASED ON A LOW BAND-GAP SMALL-MOLECULE ACCEPTOR 142
5.3  INFLECTIONS IN THE CORRECTED PHOTOCURRENT 150
5.4  FIELD-DEPENDENT PHOTOGENERATION 154
   5.4.1  Effect on an imaginary model device 160
   5.4.2  Implications for device efficiency 162
5.5  MISLEADING INFLECTIONS IN THE (UN-CORRECTED) PHOTOCURRENT 165
5.6  CONCLUSIONS 166

CHAPTER 6  CONCLUSIONS AND FURTHER WORK  

6.1  Conclusions 169
6.2  FURTHER WORK
   6.2.1  Intentionally introducing self-selectivity 172
   6.2.2  The field dependence of the offset current 173
   6.2.3  Wavelength-dependent measurements 173

REFERENCES  

APPENDIX  

Theoretical photoconductivity (exponential generation profile) 179
LIST OF FIGURES

Figure 1-1 ..............................................................................................................................................22
A schematic energy level diagram that shows the energy levels of bonding and anti-bonding orbitals. As the conjugation length increases, the number of levels increases so that in a sufficiently large system, a pseudo-continuum of states develops (a ‘band’). The energy gap between the bonding and anti-bonding orbitals also decreases as a consequence.

Figure 1-2 ..............................................................................................................................................25
A schematic energy level diagram showing the formation of photoexcited states. An electron is promoted from the HOMO to the LUMO level upon absorption of a photon of sufficient energy. The molecule relaxes into a distorted form due to the presence of the exciton. If the exciton dissociates by overcoming the binding energy, the electron and hole are free to move to different neighbouring molecules as unbound negative and positive polarons, respectively.

Figure 1-3 ..............................................................................................................................................27
A schematic illustration of a thin slice of semiconductor of width \( \delta x \) and cross-sectional area \( A \). The electron population in this volume increases with the incoming electron current \( j_e(x) \) and photogeneration rate \( G(x) \), and decreases with the outgoing electron current \( j_e(x+\delta x) \) and recombination rate \( R(x) \).

Figure 1-4 ..............................................................................................................................................29
A collection of localised electron transport states in the presence of an electric field. In the Gaussian disorder model, the states are distributed according to a Gaussian envelope about a mean energy level. An electron has to hop from one state to another, corresponding to hopping from one molecule to a neighbouring one.

Figure 1-5 ..............................................................................................................................................32
A simple model of a single-layered organic solar cell. The organic layer is sandwiched between electrodes of differing work functions. At equilibrium, the Fermi levels of the electrodes equalise, thus developing a built-in electric field. Due to low intrinsic carrier density, the built-in field is constant throughout the device thickness \( d \).

Figure 1-6 ..............................................................................................................................................33
A schematic diagram illustrating the direction of current flow at various applied voltages.

Figure 1-7 ..............................................................................................................................................36
Simulated data for the injected current \( j_{\text{dark}} \) and the photogenerated current \( j_{\text{ph}} \). Under illumination the total measured photocurrent \( j_{\text{light}} \) is a sum of the injected and photogenerated currents.

Figure 1-8 ..............................................................................................................................................37
The fourth (or power-producing) quadrant of the current-voltage plot showing simulated photocurrent-voltage data. The secondary axis shows the power output, which is equal to the product of the photocurrent and the voltage. In use, the solar cell exhibits maximum power output when the load resistance equals \( V^*/j_{\text{ph}}(V^*) \).
Figure 1-9 ..............................................................................................................................................40
The spectral irradiance of the standard Air Mass 1.5 Global spectrum (total radiant power density 100 mW/cm²). Inset: A comparison of the spectral irradiance of the solar simulator used in this work against the AM1.5G spectrum, magnified to the wavelength range over which organic solar cells are typically responsive.

Figure 1-10 ............................................................................................................................................44
A schematic of energy barrier lowering due to the image charge effect. At zero-field, the barrier is 0.2 eV, but becomes significantly reduced in the presence of an electric field.

Figure 1-11 ............................................................................................................................................46
An energy diagram for a CuPC:PTCBI bi-layer solar cell illustrating the formation of an exciton in the CuPC layer close to the heterojunction. At the heterojunction, the electron is transferred to the PTCBI layer, releasing ~0.6 eV of energy in the process due to the LUMO-LUMO offset. This energy release overcomes the attraction between the electron and hole, which are driven to their respective electrodes by the built-in field.

Figure 1-12 ............................................................................................................................................48
An energy diagram for an MDMO-PPV:PCBM bulk heterojunction solar cell. The presence of heterojunctions dispersed throughout the blend layer allows a large proportion of excitons to reach a heterojunction where they subsequently dissociate. The separated electron and hole are driven to their respective electrodes by the built-in field, provided there is a continuous pathway for carrier transport.

Figure 1-13 ............................................................................................................................................56
A schematic diagram of the solar cells fabricated in IMRE.

Figure 1-14 ............................................................................................................................................57
A schematic diagram of the experimental set up used to measure the current-voltage response of solar cells.

Figure 1-15 ............................................................................................................................................60
A schematic representation of the experimental set up for an electroabsorption experiment.

Figure 2-1 ..............................................................................................................................................64
The current-voltage response of an ITO / PEDOT:PSS / P3HT:PCBM / Al solar cell in the dark and under illumination by a solar simulator, measured using a Keithley 2400 sourcemeter. The corrected photocurrent was calculated by subtracting the dark current from the photocurrent. The secondary y-axis shows the quantum efficiency of the device for photons in the 300 – 700 nm spectral range. The quantum efficiency apparently exceeds unity at biases greater than 1.5 V.

Figure 2-2 ..............................................................................................................................................66
The current-voltage response of a P3HT:PCBM solar cell measured by the standard DC method of sequential current-voltage scans under white LED light and in the dark. Although the quantum efficiency (secondary y-axis) of the device did not exceed unity, a temperature rise of ~2 °C was still recorded when the device was illuminated.
Figure 2-3 ..............................................................................................................................................68
Top: A circuit diagram of the voltage-to-current amplifier used to drive the LED at a current that could be controlled by an output voltage from the DAQ card. **Bottom:** The spectral power distribution of the white LED (normalised) and the spectral transmittance of the liquid light guide. The good overlap with the spectral response of P3HT:PCBM devices (denoted by the dotted line) makes the LED a suitable source for photo-exciting such devices.

Figure 2-4 ..............................................................................................................................................70
A circuit diagram depicting the unity gain voltage follower and transimpedance amplifier connected to an organic solar cell. The desired bias from the DAQ card was supplied as an input to the voltage follower, which in turn supplied the necessary current to the solar cell. The current was then converted to a proportional voltage signal via the transimpedance amplifier, which was then fed as an input to the DAQ card. Note that the input impedance of the transimpedance amplifier is negligible.

Figure 2-5 ..............................................................................................................................................72
A schematic diagram of the excitation scheme used to investigate radiative heating. (A): A DC voltage is applied on the device, while (B): the light is pulsed at 50% duty cycle and a fixed frequency. (C): The current response of the device was expected to alternate between the dark current and the photocurrent.

Figure 2-6 ..............................................................................................................................................73
The time-varying response of the solar cell over a single LED on-off cycle. Here, the LED pulse frequency is 5 kHz, and the sampling rate is 1 MHz. A signal overshoot occurs when the applied voltage is stepped, but rapidly decays within a few microseconds. The slow response of the solar cell is also evident for the initial 20-30 μs after switching the LED on or off. To avoid recording both of these effects, only the last 10 μs of data were recorded.

Figure 2-7 ..............................................................................................................................................74
The corrected photocurrent-voltage response as measured by the standard DC method (blue) and by the scheme illustrated in Figure 2-5, where the LED is pulsed (red and green). The red and green curves were obtained when the LED was pulsed at 97 Hz (red) and 997 Hz (green), and are virtually identical.

Figure 2-8 ..............................................................................................................................................75
$J_{\text{dark}}$-V curves as measured by the standard DC method and during the LED off-cycle of the pulsed scheme. The magnified inset shows the offset more clearly, which is on the order of a few mA/cm$^2$. Note that the pulsed measurement gives a slightly higher value due to radiative heating from the LED when the $J_{\text{dark}}$ signal is not being recorded.

Figure 2-9 ..............................................................................................................................................77
A schematic diagram of an excitation scheme used to investigate the effects of resistive heating. (A): The applied voltage is pulsed at 1 kHz with a 10% duty cycle, while (B): the LED is switched off. (C): The current response is expected to be in the form of dark current pulses synchronised with the voltage pulses.

Figure 2-10 ..............................................................................................................................................78
Dark current-voltage curves as measured with a DC voltage and with a voltage pulsed at 10% duty cycle (see Figure 2-9).
Figure 2-11 ............................................................................................................................................79
Schematic of an excitation scheme designed to investigate the effect of resistive heating.  
**Pulsed Voltage:** (A): The applied voltage is pulsed at ~1 kHz and (B): the light source pulsed at exactly half that frequency. Both voltage and light pulses have widths of 100 μs, and are synchronised so that the device is illuminated on every alternate voltage pulse.  
(C): The expected device response has alternating 100 μs light and dark pulses.  
**DC Voltage:**  
(A): This excitation scheme uses a DC voltage and (B): 100 μs light pulses.  
(C): The current response is expected to be dark throughout except when the light is pulsed on, during which time the device responds with light for 100 μs.

Figure 2-12 ............................................................................................................................................80
A comparison between corrected photocurrent-voltage curves obtained using the schemes shown in Figure 2-11. The two schemes use: 1) a DC voltage with pulsed light, and 2) a pulsed voltage with pulsed light. The curves correspond closely with each other throughout the measurement range, although a slight discrepancy is seen at high forward biases (> 1 V).

Figure 2-13 ............................................................................................................................................83
A schematic diagram of the final pulsed excitation scheme and the expected device current-voltage response.  
(A): Each voltage step has a time width of 200 μs and the full sweep is repeated several hundred times.  
(B): The light pulses, with a time width of 100 μs each, were programmed to illuminate the device for the second half of each voltage step.  
(C): The expected current response of the device.

Figure 2-14 ............................................................................................................................................84
(Lower): A staircase plot showing the variation of the applied voltage with time for the pulsed scheme.  
The voltage is incremented in steps of height 20 mV and duration 200 μs.  
The LED was programmed to illuminate the solar cell for the second half of each voltage step.  
(Upper Main): The time-dependence of the measured device response.  
(Upper inset): Expanded view of the time-dependence of the measured response, showing alternating dark current and photocurrent responses.

Figure 2-15 ............................................................................................................................................85
Corrected photocurrent-voltage curves obtained using: 1) the standard DC method, 2) pulsed voltage and pulsed light, and 3) repeating voltage sweeps and pulsed light.

Figure 3-1 ..............................................................................................................................................88
The chemical structures of the donor polymer poly[2-methoxy-5-(3',7''-dimethyloctyloxy)-p-phenylenevinylene] [MDMO-PPV] and the acceptor molecule (6,6)-phenyl-C₆₁-butyric acid methyl ester [PCBM].

Figure 3-2 ............................................................................................................................................90
Current-voltage characteristics for an ITO / PEDOT:PSS / MDMO-PPV:PCBM / Ag device as measured by the pulsed technique.  
The $j_{\text{light}}$-$V$ and $j_{\text{ph}}$-$V$ curves were obtained under an instantaneous light intensity of 90.2 mW/cm².  
Inset: Spectral response of the device under low intensity illumination and short-circuit conditions.
Figure 3-3 ..............................................................................................................................................91
(A): The $J_{ph}$-$V$ curve for the ITO / PEDOT:PSS / MDMO-PPV:PCBM / Ag device from Figure 3-2. The data has been divided into two parts to the left (L) and right (R) of the point of optimal symmetry (POS) at $V = 0.80 \pm 0.01$ V. The left side has been rotated by 180° about the POS to create a new curve (L rot) that overlaps closely with R, implying a high degree of anti-symmetry in the $J_{ph}$-$V$ characteristics. (B): The slope of the $J_{ph}$-$V$ curve as a function of applied voltage. The slope peaks at $V_{POS}$ and decreases monotonically at higher and lower voltages.

Figure 3-4 ..............................................................................................................................................92
Magnified plots of the R and L rot curves from Figure 3-3, each corresponding to a slightly different choice of rotational point: (A): $V_{rot} = 0.78$ V, (B): $V_{rot} = 0.79$ V, (C): $V_{rot} = 0.80$ V, (D): $V_{rot} = 0.81$ V, (E): $V_{rot} = 0.82$ V. The quality of overlap, as determined both visually and by the figure of merit D, is clearly optimised when $V_{rot} = 0.80$ V.

Figure 3-5 ..............................................................................................................................................93
(A): Energy level diagrams of an ITO / PEDOT:PSS / MDMO-PPV:PCBM / Ag device, showing donor and acceptor HOMO and LUMO levels and electrode Fermi levels. The blend layer was treated as a composite semiconductor, in which the HOMO and LUMO levels were derived from the donor HOMO level and the acceptor LUMO level, respectively. (B): There are no energy barriers to the extraction of electrons or holes at either electrode.

Figure 3-6 ..............................................................................................................................................97
The chemical structure of regioregular poly(3-hexylthiophene-2,5-diyl) [P3HT], which is used as an electron donor.

Figure 3-7 ..............................................................................................................................................98
The corrected photocurrent-voltage curve of an ITO / PEDOT:PSS / P3HT:PCBM / Al device as measured by the pulsed technique. The data has been divided into two zones to the left (L) and right (R) of the point of optimal symmetry (POS) at $V = 0.60 \pm 0.01$ V. The left side has been rotated by 180° about the POS to create a new curve (L rot) that overlaps closely with R, implying a high degree of anti-symmetry in the $J_{ph}$-$V$ characteristics.

Figure 3-8 ..............................................................................................................................................99
An energy level diagram showing the relative positions of the HOMO and LUMO levels of P3HT and PCBM, and the Fermi levels of the ITO anode and Al cathode. The Fermi levels of the anode and cathode are pinned to the P3HT HOMO level and the PCBM LUMO level, respectively.

Figure 3-9 ............................................................................................................................................101
(A) Main: The reverse-bias 1 st-harmonic electromodulation (EM) spectrum of the ITO / PEDOT:PSS / P3HT:PCBM / Al device, obtained with a 6 kHz 0.3 V AC bias, at a DC offset of -2 V. Inset: The actual forward-bias EM spectrum of the device, obtained with a 6 kHz 0.3 V AC bias at a DC offset of +1 V (black), and the spectrum that would be expected on the basis of the reverse-bias spectrum if the signal were purely due to electroabsorption (red). (B): The DC bias dependence of the 1 st-harmonic EM response at 644 nm. The signal varies linearly with DC bias in accordance with Equation (1.35) until a bias of 0 V and then deviates strongly due to charge-induced modulation. The built-in potential was determined by using the initial twelve reverse-bias data points – which are uncontaminated by charge-induced features – and then extrapolating to zero, yielding a value $V_{BI} = 0.59 \pm 0.02$ V.
Figure 3-10 ..........................................................................................................................................104
An energy level diagram showing vertical phase separation as a possible explanation for self-selectivity in ITO / PEDOT:PSS / P3HT:PCBM / Al solar cells. A P3HT-enriched layer near the anode would prevent electron leakage to the anode, while a PCBM-enriched layer near the cathode would prevent hole leakage to the cathode. This would result in a net negative photocurrent even in the absence of an electric field.

Figure 3-11 ..........................................................................................................................................105
The chemical structures of the donor polymer poly(3,3”-didodecyl quarterthiophene) [PQT-12] and the small-molecule acceptor 4,7-bis(2-(1-hexyl-4,5-dicyanoimidazol-2-yl)vinyl)benzo[c]1,2,5-thiadiazole [HV-BT].

Figure 3-12 ..........................................................................................................................................106
The $J_{ph}$-$V$ curve of an ITO / PEDOT:PSS / PQT-12:HV-BT / Ag device. The data has been divided into two zones to the left (L) and right (R) of the point of optimal symmetry (POS) at $V_{POS} = 1.22$ V and $J_{POS} = 1.10$ mA/cm$^2$. The left side has been rotated by 180° about the POS to create a new curve (L$^{rot}$) that overlaps closely with R, implying a high degree of anti-symmetry in the $J_{ph}$-$V$ characteristics.

Figure 3-13 ..........................................................................................................................................109
A schematic representation of vertical phase separation in the blend layer that can result in carrier-selectivity at the electrodes. (A): A donor-rich region at the cathode blocks electrons from reaching the cathode, while an acceptor-rich region at the anode blocks holes from reaching the anode, resulting in a positive offset current. (B): The absence of phase-rich regions allow both carriers to be rapidly depleted at either electrode, so to a good approximation, $n_{eh}(0) = n_{eh}(d) = n_{eh}(0) = n_{eh}(d) = 0$, and the offset current is zero. (C): A donor-rich region at the anode blocks electrons from reaching the anode, while an acceptor-rich region at the cathode blocks holes from reaching the cathode, resulting in a negative offset current.

Figure 3-14 ..........................................................................................................................................112
Simulated $J_{dark}$-$V$ and $J_{ph}$-$V$ curves. In Device #2, in which the offset current is positive, the open-circuit voltage has been reduced significantly. The zero-crossing of the $J_{ph}$-$V$ curve, which signifies the maximum possible open-circuit voltage, has also been shifted to the left due to the positive offset current.

Figure 3-15 ..........................................................................................................................................113
Simulated $J_{dark}$-$V$ and $J_{ph}$-$V$ curves. In Device #3, in which the offset current is negative, the open-circuit voltage has been increased significantly. The zero-crossing of the $J_{ph}$-$V$ curve, which signifies the maximum possible open-circuit voltage, has also been shifted to the right due to the negative offset current.

Figure 3-16 ..........................................................................................................................................114
Current-voltage response of an ITO / PEDOT:PSS / P3HT:PCBM / Al solar cell. The $J_{light}$-$V$ and $J_{ph}$-$V$ characteristics were obtained under an incident intensity of 98 mW/cm$^2$. The built-in potential, as implied by the point of optimal symmetry of the $J_{ph}$-$V$ curve, is 0.58 ± 0.01 V. The open-circuit voltage, determined from the zero-crossing of the $J_{light}$-$V$ curve, is 0.63 ± 0.002 V, some 50 ± 12 mV above the built-in potential. The zero-crossing of the $J_{ph}$-$V$ curve at 0.93 ± 0.002 V suggests that the upper limit for $V_{OC}$ under intense illumination may be as high as 0.93 V, some 350 mV above $V_{BI}$. 
Figure 4-1: The \( J_{ph}-V \) characteristics of an ITO / PEDOT:PSS / P3HT:PCBM / Al device at multiple light levels. The curves have similar values of \( V_{POS} \) and similar zero-crossings in the ranges of 0.6 ± 0.02 V and 0.9 ± 0.05 V, respectively. (B): The intensity dependence of \( J_{ph} \) at 0, 0.6 and 1.5 V, where 0.6 V corresponds to the point of optimal symmetry.

Figure 4-2: (A): The field-dependence of \( (J_{ph} - J_{off}) \) for an ITO / PEDOT:PSS / P3HT:PCBM / Al device measured by the pulsed technique under an instantaneous light intensity of 98 mW/cm². (B): The field-dependence of the estimated photoconductivity \( \hat{\sigma} \), as calculated from Equation (4.7) using data from (A).

Figure 4-3: (A): The experimentally and theoretically determined \( \sigma-E \) curves for a P3HT:PCBM device, obtained using a single fitting parameter \( G = 3.65 \times 10^{27} \text{ m}^{-3} \text{ s}^{-1} \). (B): The experimentally and theoretically determined \( J_{ph}-V \) curves agree well in the voltage range \( V = V_{BI} \pm 0.2 \text{ V} \), but diverge outside this range.

Figure 4-4: (A): The field dependence of \( (J_{ph} - J_{offs}) \) for an ITO / PEDOT:PSS / MDMO-PPV:PCBM / Ag solar cell. (B): The field dependence of \( \hat{\sigma} \), obtained by dividing the curve in (A) by the electric field \( E \).

Figure 4-5: (A): The analytically and experimentally determined \( \sigma-E \) curves for the MDMO-PPV:PCBM device, as calculated from Equations (4.7) and (4.22). The analytically-derived photoconductivity was obtained using the values \( G = 2.75 \times 10^{27} \text{ m}^{-3} \text{ s}^{-1} \) (optimised fitting parameter), \( d = 80 \text{ nm} \) (experimentally determined) and \( T = 300 \text{ K} \). (B): The analytically and experimentally determined \( J_{ph}-V \) curves for the MDMO-PPV:PCBM device.

Figure 4-6: (A): The \( J_{ph}-V \) characteristics of an ITO / PEDOT:PSS / MDMO-PPV:PCBM / Ag device at multiple light levels. The curves have similar points of optimal symmetry in the range of 0.81 ± 0.01 V. (B): The intensity dependence of \( J_{ph} \) at 0.78 V and 0.86 V, which correspond to voltages near the POS. The sub-linear \( J_{ph}-I \) curves indicate that bimolecular recombination is significant near the built-in potential. The red lines correspond to a power law fit of the form shown in Equation (4.3).

Figure 4-7: (A): \( J_{ph}-V \) curves for an ITO / PEDOT:PSS / P3HT:PCBM / Al device before and after annealing for twenty minutes at 140 °C. (B): Comparison of the \( R \) and \( L^{rot} \) curves (see Section 3.2) before and after annealing. The points of optimal symmetry have been shifted to a common origin for ease of comparison.

Figure 4-8: (A): \( J_{ph}-V \) curves for an ITO / PEDOT:PSS / MDMO-PPV:PCBM / Al device before and after annealing for twenty minutes at 140 °C. (B): Comparison of the \( R \) and \( L^{rot} \) curves before and after annealing. The points of optimal symmetry have been shifted to a common origin for ease of comparison.
Figure 4-9

(A): Annotated schematic of a typical \( j_{ph}-V \) curve, illustrating five key parameters for optimisation. \( A \) and \( B \) are the value and slope of the corrected photocurrent at short-circuit; \( C \) is the bias at the point of optimal symmetry (POS); \( D \) and \( E \) are the value and slope of the corrected photocurrent at the POS. To optimise device performance, fabrication conditions should be sought that maximise \( A \), \( C \), \( D \) and \( E \), whilst yielding a value of \( B \) close to zero, subject to the additional condition that \( D \) should be negative. (B): Schematic illustrating the appearance of the \( j_{ph}-V \) curve after optimisation.

Figure 5-1

The chemical structures of 4,7-bis(2-(1-(2-ethylhexyl)-4,5-dicyano-imidazol-2-yl)vinyl) benzo[c][1,2,5]thiadiazole [EV-BT] and poly[N-(2′-decyltetradecyl) carbazole]-2,7-diyl [PCz], and the energy level diagram for the ITO / PEDOT:PSS / PCz:EV-BT / Ca / Ag device investigated here.

Figure 5-2

(A): Absorption and photoluminescence (PL) spectra for a pristine EV-BT film. When blended with PCz in equal weight ratio and excited at 444 nm, the EV-BT PL is quenched. (B): Absorption and PL spectra for a pristine PCz film. When blended with EV-BT in equal weight ratio and excited at 395 nm, the PCz PL is quenched. The absorption spectrum of EV-BT shows a better correspondence with the AM1.5G spectrum than PCz.

Figure 5-3

(A): The effect of annealing temperature on \( J_{SC} \), \( V_{OC} \), fill factor and power conversion efficiency for three blend compositions consisting of 50, 70 and 90% EV-BT content (by mass). (B): The effect of the annealing temperature on spectral quantum efficiency (under short-circuit conditions) for the three blend compositions.

Figure 5-4

Current-voltage characteristics of the PCz:EV-BT with highest PCE (Device #6). \( J_{SC} = 1.14 \) mA/cm\(^2\), \( V_{OC} = 1.36 \) V, \( FF = 0.49 \) and \( PCE = 0.75\% \). Note the unusual “kinks” in the \( J_{light}-V \) curve.

Figure 5-5

\( J_{light}-V \), \( J_{dark}-V \) and \( J_{ph}-V \) characteristics of the ITO / PEDOT:PSS / PCz:EV-BT / Ca / Ag device with the highest PCE (Device #6), as measured by the pulsed technique at an instantaneous light intensity of 90 mW/cm\(^2\). The \( J_{light}-V \) curve show two points of inflection, while the \( J_{ph}-V \) curve shows three. Inset: The spectral quantum efficiency at short-circuit and under low intensity illumination.

Figure 5-6

(A): The \( J_{ph}-V \) curve for the PCz:EV-BT device from Figure 5-5. The data has been divided into two parts to the left (L) and right (R) of the point of optimal symmetry (POS) at \( V_{POS} = 1.62 \) V. The L curve has been rotated by 180° about the POS to obtain a new curve L\(^{rot}\) that overlaps closely with R, implying a high degree of anti-symmetry in the current-voltage characteristics. (B): The slope of the \( J_{ph}-V \) curve as a function of applied voltage. The slope has a minimum at the POS and two maxima at 1.29 V and 2.07 V.
Figure 5-7

(A): The slope of the $J_{ph}$-V curves as a function of applied voltage for the devices used in the previous chapters: ITO / PEDOT:PSS / P3HT:PCBM / Al, ITO / PEDOT:PSS / MDMO-PPV:PCBM / Ag and ITO / PEDOT:PSS / PQT-12:HV-BT / Ag. In all three devices, the slope has a single maximum and decreases monotonically either side. (B): The estimated photoconductivity of the three devices as a function of electric field, all of which peak at $E = 0$ and decreases monotonically with increasing field strength.

Figure 5-8

The estimated photoconductivity of the PCz:EV-BT device as a function of electric field, obtained using Equation (5.4) and the values of $V_{in} = V_{pcs}$ and $J_{off} = J_{pcs}$ from Figure 5-6.

Figure 5-9

A schematic illustrating the exciton dissociation process at a donor/acceptor heterojunction. (A): An exciton in the acceptor phase is split at a heterojunction, where the hole is transferred from the acceptor HOMO level to the donor HOMO level. (B): If the energy level offset between the HOMO energies is sufficiently large, the partitioning results in a free electron and hole, otherwise (C): a charge-transfer (CT) exciton is formed, consisting of a spatially-separated, but Coulombically-bound electron-hole pair that will eventually recombine.

Figure 5-10

(A): $J_{ph}$-V curves for the ITO / PEDOT:PSS / PCz:EV-BT / Ca / Ag device obtained at multiple light intensites ranging from 15 to 90 mW/cm$^2$. The curves share similar values of $V_{pcs}$, lying in a tight band between 1.62 and 1.64 V. (B): The linear intensity dependence of $J_{ph}$ at applied voltages of 0 V and 3 V.

Figure 5-11

Schematic diagram explaining the effect of field-dependent carrier generation on the current-voltage characteristics, assuming an offset current of zero. (A): The “ideal” situation in which the free carrier yield $g_0(E)$ is 100 % at all field strengths. (B): The (arbitrary unit) photoconductivity $\sigma(E)$ corresponding to case (A); $\sigma(E)$ is an even monotonically decreasing function of the electric field. (C): The corrected photocurrent $J_{ph}(E) = \sigma(E)E$ corresponding to case (A). (D): The free carrier yield $g_1(E)$ for an “intermediate” situation in which the carrier yield increases monotonically from 50 % at $E = 0$ to 100 % as $E \rightarrow \pm \infty$; (E): The photoconductivity $\sigma(E) = \sigma(E)g_1(E)$ corresponding to case (D); (F): The corrected photocurrent $J_{ph}(E) = \sigma(E)g_1(E)E$, corresponding to case (D). (G): The free carrier yield $g_2(E)$ for an “extreme” case in which the yield increases monotonically from zero at $E = 0$ to 100 % as $E \rightarrow \pm \infty$; (H) and (I) show the photoconductivity and corrected photocurrent corresponding to case (G).

Figure 5-12

Schematic diagram showing the overlaid $J_{ph}$-V curves for the three cases considered in Figure 5-11. The three curves intersect at the built-in potential where the current falls to zero due to the assumed zero offset current. The curves bend inwards towards the origin as the spontaneous yield of free carriers diminishes. The inset shows the voltage-dependence of the power curve for the three situations. There is a progressive reduction in the peak power as the yield diminishes.
Figure 5-13  ..........................................................................................................................................164
(A): A simulated $J_{ph}$-$V$ curve with field-independent carrier generation. The curve is almost a straight line through $J_{SC}$ and $V_{BI}$, resulting in a fill factor ~0.25. (B): A simulated $J_{ph}$-$V$ curve with field-dependent carrier generation, showing the characteristic “kinks” near the built-in potential. The inward bending of the curve towards the origin results in the fill factor being reduced below 0.25.

Figure 5-14  ..........................................................................................................................................165
Simulated $J_{dark}$-$V$ and $J_{ph}$-$V$ curves showing how “kinks” may be apparent in the $J_{light}$-$V$ curve even though the $J_{ph}$-$V$ curve is not “kinked”.

Figure 7-1  ............................................................................................................................................182
Main: The photoconductivity-field curves for a flat generation profile and for exponential generation profiles with $\alpha = d$, $\alpha = 0.5d$ and $\alpha = 0.2d$, where $d = 100$ nm. The values of $G_0$ were chosen to normalise the curves to a common peak. Inset: The (normalised) generation profiles corresponding to the flat profile and to the exponential profiles for $\alpha = d$, $\alpha = 0.5d$ and $\alpha = 0.2d$. 


**PUBLICATIONS**

“On the pseudo-symmetric current-voltage response of bulk heterojunction solar cells”,
Z. E. Ooi, R. Jin, J. Huang, Y. F. Loo, A. Sellinger and J. C. deMello,

“Field-dependent carrier photogeneration in bulk heterojunction solar cells”,
Z. E. Ooi, T. L. Tam, A. Sellinger and J. C. deMello,

“Solution processable bulk-heterojunction solar cells using a small-molecule acceptor”,
M. Baumgarten, K. Mullen and J. C. deMello,
SOLAR CELLS FROM ORGANIC SEMICONDUCTORS

Why do we need solar cells and why organic ones? An overview of the working principles driving organic solar cells follows.
There is currently a heavy dependence on fossil fuels to meet our civilization’s ever-growing demand for energy which is currently estimated to be in excess of 10 Gtoe (gigatonne oil equivalent, 1 Gtoe = 4.19 × 10^19 J) per year[^1] with an annual growth rate of 3 – 4%. While total fossil fuel reserves have been estimated to be relatively abundant at 5000 Gtoe and should last us through the century, oil and gas production is predicted to peak by year 2015, beyond which decline in readily-accessible supply will cause their prices to inflate drastically.[^2] From an environmental perspective, a departure from fossil fuel dependence would help tackle the urgent issue of global warming by reducing emission rates of carbon dioxide into the atmosphere. Economically, the expected rise in the cost of energy from fossil fuels presents a growth opportunity for renewable sources of energy presently regarded as expensive.

‘Renewable’ energy sources can be broadly classified into three main categories. Gravitational energy derives from the gravitational effects of the moon (and to a much lesser extent, the sun), and manifests itself as tidal energy. Geothermal energy stems from the radioactivity present in the Earth’s core, and is released as heat nearer to the crust. Solar energy derives from the radiation incident on the Earth, and is several orders of magnitude more abundant than both gravitational and geothermal sources combined. Solar energy may be tapped as wind or hydroelectric power, or more directly through water heating or photovoltaic conversion of light into electricity.
Given an average of 1750 kWh/(m$^2$yr) of annual sunlight on the Earth’s surface at the equator, covering an area equivalent to $\sim 7 \times 10^5$ square kilometres (or $\sim 8\%$ of the area of the Sahara desert) with 10%-efficient solar cells would more than satisfy the world’s energy demand.

Solar cells are semiconductor devices that directly convert light into electrical power, and those based on inorganic semiconductors such as silicon have been around for decades. These inorganic solar cells have remarkably high power efficiencies approaching the Shockley-Quiesser limit of 31%\cite{3} (for single-junction devices under 100 mW/cm$^2$ of sunlight). For example, gallium arsenide and monocrystalline silicon single-junction solar cells have been made to attain power conversion efficiencies of $\sim 25\%$.\cite{4} More common are lower-cost commercially available polycrystalline silicon cells that are $\sim 15\%$ efficient. The production of all such cells, however, is encumbered by high materials cost and energy consuming processes.\cite{5}

The challenge in harnessing sunlight as a major source of energy is to make large area devices at low cost. A critical aspect of this is enhancing power efficiency to reduce device area and hence production costs, which in turn will lead to smaller and more deployable devices. Solar cells based on organic materials, such as conjugated polymers and small molecules, have the potential to address both the economic and environmental concerns of world energy production. Many of these materials are soluble in common organic solvents such as toluene and acetone and can be solution-processed at room temperature, minimising energy costs and carbon impact. In addition, they have high absorption coefficients, which reduce material usage and allow them to be deployed as thin, mechanically flexible films. These properties
allow large-area devices to be made using low-cost processes like inkjet printing and roll-to-roll coating.

1.2 **Conjugated Molecules as Semiconductors**

Organic (*i.e.* carbon-based) molecular semiconductors share a common trait: the bonding in the molecule, or along the polymer chain, consists of alternating single and double carbon-carbon bonds, a structural feature known as conjugation. Double bonds result from the bonding between $sp^2$ hybrid orbitals in carbon atoms. The combination of the $s$ orbital and two of the three $p$ orbitals gives a trigonal planar arrangement of three hybrid orbitals, of which two are usually $\sigma$-bonded to adjacent carbon atoms on the conjugated chain/segment (thus propagating it), and the third to a side-group/atom off the main conjugation chain. These strong $\sigma$ bonds define the shape and structure of the molecule. This leaves a single non-hybridized $p_z$ orbital perpendicular to the plane of $\sigma$-bonds per carbon atom. Overlap of $p_z$ orbitals on adjacent carbon atoms lead to the formation of $\pi$ bonds, which are delocalized over the conjugation chain. In the ground state, the lower-energy bonding $\pi$ orbitals are filled while the higher-energy anti-bonding $\pi^*$ orbitals are empty, constituting valence and conduction states, respectively. The delocalization of these states along the conjugated backbone allows charge to be transported over the conjugation chain and is largely responsible for the electronic and optical properties of the conjugated systems.
Figure 1-1
A schematic energy level diagram that shows the energy levels of bonding and anti-bonding orbitals. As the conjugation length increases, the number of levels increases so that in a sufficiently large system, a pseudo-continuum of states develops (a ‘band’). The energy gap between the bonding and anti-bonding orbitals also decreases as a consequence.

As the conjugation length increases, the $\pi$ molecular orbital system grows to form two nearly-continuous bands of filled, and empty, states. The top level of the filled (valence) band is known as the highest occupied molecular orbital (HOMO), while the bottom level of the empty (conduction) band is the lowest unoccupied molecular orbital (LUMO). The energy gap (band gap) between the HOMO and LUMO levels decreases as the $\pi$ system grows, meaning longer conjugated molecules typically have smaller band gaps. In the event that an electron in the valence band is supplied with sufficient energy, it may be excited to the conduction band. On the conjugation chain, this causes a rearrangement of the electronic charge distribution along the delocalized $\pi$ system. In this excited state, the electronic charge distributes to create a region of concentrated negative charge and a corresponding region of positive
charge (since the system remains neutral overall). In the context of the band picture, excitation promotes an electron from the valence band to the conduction band, and the minimal energy required for this process is the band gap energy. The positive charge left in the wake of excitation is represented by a hole in the valence band. Organic semiconductors have low dielectric constants of ~3, thus there is strong Coulombic attraction between an excited electron and a hole, resulting in a tightly bound state known as an exciton. The binding energy is estimated to range roughly from 0.2 to 1.4 eV\[^{[6]}\] in organic materials and so is much larger than the thermal energy $k_B T \sim 25$ meV at room temperature. This means that spontaneous thermal dissociation of excitons does not occur at an appreciable rate and the vast majority of excitons decay radiatively or non-radiatively to the ground state.

1.2.1 Photoexcited states

In the context of studying organic solar cells, we are primarily interested in excitation through the absorption of a photon. The minimum photon energy required for photoexcitation corresponds to the promotion of an electron from the HOMO to the LUMO, and as stated above, results in the formation of an exciton. Absorption of a photon with energy higher than the minimum results in the electron being promoted to a higher anti-bonding orbital. The electron then decays to the LUMO by internal conversion, with the surplus energy converted to heat (vibration of the molecules). $\sigma$ bonds in conjugated systems play a secondary, but not insignificant, role in determining the optical and electronic properties of conjugated systems. These bonds are strong enough to hold the conjugated chain together even in the presence of excited states in the $\pi$ system. However, the conjugated chain, including both $\sigma$ and $\pi$ bonds, can be locally distorted by an excited state and relax into a lower-
energy deformation. Because the relaxation time of this distortion is instantaneous compared to the transfer time of the excited state to a neighbouring chain, the distortion follows the excited state and the two may be regarded as a single entity in the material. Thus, upon formation, an exciton loses some of its energy to that deformation and relaxes “into” the band gap. If the excited state is an unbound electron (hole), distortion also results in relaxation into the band gap, and the combined entity of charge and its associated distortion is known as a negative (positive) polaron. Because real organic semiconductors consist of more than just a single conjugated chain, there can also be significant overlap between $\pi$ orbitals from separate conjugation chains. These weak inter-molecular interactions not only influence the inter-molecular structure of the material, but can also affect its optical and electronic properties, due to the increased delocalization of the $\pi$ systems in the bulk material. The distortion associated with excited states can therefore extend beyond a single molecule to its immediate neighbours and, for this reason, the actual energy levels which the electrons and holes occupy (bound as an exciton or not) in an organic semiconductor depends on the arrangement of the molecules in the vicinity of the excited state. Unless the material is highly crystalline, the molecules arrange themselves such that there is a distribution of orientations relative to one another; and in polymers, the situation is further complicated by the fact that the chain lengths are not sharply defined. The result is a distribution of excitonic/polaronic states that has been widely modelled as a Gaussian distribution.$^{[7]}$
Figure 1-2
A schematic energy level diagram showing the formation of photoexcited states. An electron is promoted from the HOMO to the LUMO level upon absorption of a photon of sufficient energy. The molecule relaxes into a distorted form due to the presence of the exciton. If the exciton dissociates by overcoming the binding energy, the electron and hole are free to move to different neighbouring molecules as unbound negative and positive polarons, respectively.

If the excitonic electron and hole do not dissociate into free carriers, the electron eventually falls back into the valence band and recombination is then said to have occurred. Excitons may recombine non-radiatively (by internal conversion) with the energy released as heat, or more likely in a highly fluorescent material, radiatively by emitting a photon.

1.2.2 Charge transport

In the presence of an electric field \( E \), charges in a solid develop a mean drift speed \( v_{\text{drift}} \) given by \( v_{\text{drift}} = \mu E \), where \( \mu \) is the charge carrier mobility. In a semiconductor, a current results from the drift of electrons and holes, so that the total drift current density \( j^{\text{drift}} \) is given by the sum of the electron drift current
and the hole drift current

\[ J_h^{\text{drift}} = e \mu_h n_h E. \]  

(1.2)

where \( n_e \) and \( n_h \) are the free electron and hole densities, respectively, and \( e \) is the electronic charge. Electrons and holes in filled states are immobile, and thus cannot contribute to a current flow.

In addition to being driven by an electric field, carriers diffuse from regions of higher carrier concentration to those of lower concentration at a rate that is proportional to the concentration gradient, and the resultant currents are referred to as diffusion currents. In one dimension, the electron and hole diffusion currents are:

\[ J_e^{\text{diffusion}} = e D_e \frac{d n_e}{d x}, \]  

(1.3)

\[ J_h^{\text{diffusion}} = -e D_h \frac{d n_h}{d x}, \]  

(1.4)

where \( x \) is the spatial coordinate, and \( D_e \) and \( D_h \) are the electron and hole diffusivities. For ideal non-interacting particles, the mobilities and diffusivities are related by the Einstein relation\(^\text{[8]}\):

\[ D_e = \frac{\mu_e k_B T}{e} \quad \text{and} \quad D_h = \frac{\mu_h k_B T}{e}, \]  

(1.5)

where \( k_B \) is Boltzmann’s constant and \( T \) is the absolute temperature.
In one dimension, the rate of change in the number of electrons \( N_e \) in a thin slice of semiconductor of width \( \delta x \) is:

\[
\frac{dN_e}{dt} = A \delta x \frac{dn_e}{dt} = - \frac{A}{e} \left[ J_e(x) - J_e(x + \delta x) \right] + G(x) A \delta x - R(x) A \delta x,
\]  

(1.6)

where \( A \) is the cross-sectional area of the slice, \( n_e \) is the free electron density, \( J_e(x) \) is the electron current at \( x \), \( G(x) \) is the rate of free electron generation per unit volume and \( R(x) \) is the rate of loss of free electrons per unit volume due to recombination. Charge trapping has been neglected here. In the limit as \( \delta x \to 0 \), Equation (1.6) becomes:

\[
\frac{dn_e}{dt} = \frac{1}{e} \frac{dJ_e}{dx} + G - R.
\]  

(1.7)

An analogous derivation for holes leads to:
where $J_h$ is the hole current. Equations (1.7) and (1.8) are known as continuity equations, and under steady-state conditions reduce to:

$$\frac{1}{e} \frac{dJ_e}{dx} = R - G,$$

and

$$\frac{1}{e} \frac{dJ_h}{dx} = G - R.$$  \hspace{1cm} (1.10)

The addition of Equations (1.9) and (1.10) gives:

$$\frac{dJ_e}{dx} + \frac{dJ_h}{dx} = \frac{dJ_{tot}}{dx} = 0,$$  \hspace{1cm} (1.11)

where the total current $J_{tot}$ is the sum of the electron and hole currents. The integration of Equation (1.11) yields a constant. It follows that, under steady-state conditions, the total current is a constant.

Unlike their inorganic counterparts, organic semiconductors typically have very low intrinsic free charge carrier densities, due to a relatively large bandgap (~1 to 3 eV) – in consequence, there are practically no thermally-excited free carriers. However, free carriers can be introduced into the semiconductor by direct injection from an electrode under an applied bias, chemical doping or photoexcitation.

In disordered films of organic semiconductors, holes and electrons are transported through the bulk by hopping from one molecule to a neighbouring molecule. The localized transport (polaronic) states of the molecules are distributed non-homogeneously with respect to their energies.
and their spatial location. Thus, there is a distribution of energy differences – and hence hopping probabilities – when carriers hop from molecule to molecule.

![Diagram](Image)

**Figure 1-4**
A collection of localised electron transport states in the presence of an electric field. In the Gaussian disorder model, the states are distributed according to a Gaussian envelope about a mean energy level.[7] An electron has to hop from one state to another, corresponding to hopping from one molecule to a neighbouring one.

In the Gaussian disorder model for hopping transport, the density of localized states is assumed to follow a Gaussian distribution function \( S_{\text{Gaussian}} \) where the mean \( \bar{E} \) is the bulk transport energy level, and the deviation \( \delta \) arises from the variation of individual transport states.[7]

\[
S_{\text{Gaussian}}(\bar{E}, \delta) = \frac{\exp\left(-\frac{\bar{E}^2}{2\delta^2}\right)}{\sqrt{2\pi\delta^2}}
\]  

(1.12)

Hopping processes from an energetically-higher site to a lower one occur spontaneously; whereas those involving moves to a higher energy state require an activation energy equal to the difference in the energy levels. The
activation energy is thermally activated, with the resulting charge carrier mobility given by\[^7\]:

\[
\mu(T) = \mu_0 \exp \left[ -\left( \frac{T_0}{T} \right)^2 \right].
\] (1.13)

where \( T_0 = 2\delta/3k_B \), and \( \mu_0 \) is the hypothetical mobility if the semiconductor were perfectly ordered and \( T \to \infty \). Hence, there is a sharp increase in mobility with increasing temperature. The mobility is also dependent on the electric field strength and, in many materials, is observed to have the following empirical form:\[^9-11\]

\[
\ln[\mu(E)] \propto \sqrt{E}.
\] (1.14)

### 1.3 General Device Structure and Characteristics

Organic semiconductor diodes include devices such as organic light-emitting diodes (OLEDs) and organic solar cells (OSCs), and they are most commonly fabricated as sandwich-geometry cells. One or more thin films (~100-200 nm) of the organic semiconducting material are sandwiched between two planar electrodes, of which at least one must be transparent in order for light to pass in or out. This transparent electrode usually consists of glass coated with indium tin oxide (ITO), which is a durable, electrically-conducting layer (~200 nm thick) with a high transmittance in the visible spectrum, composed of ~90% In\(_2\)O\(_3\) and ~10% SnO\(_2\). Alternatively, a thin (< 20 nm) semi-transparent layer of metal deposited on glass may also be used, or even a conducting polymer. The other electrode is usually a layer of moderately low work function metal, commonly aluminium, calcium, silver etc.
The difference in the work functions between the two electrodes sets up an electric field in the organic layer which, in an OSC, is responsible for driving free charge carriers to their respective electrodes (for extraction into an external circuit). ITO has a work function of ~ 4.5 eV\(^ {12}\), and a metal of lower work function (Al ~ 4.2 eV, Ca ~ 2.9 eV, Ag ~ 4.4 eV\(^ {13}\)) is usually chosen as the other electrode. Under illumination and in the absence of an external voltage, the built-in field drives free electrons to the low work function (metal) electrode, while holes are driven to the high work function (ITO) electrode. Hence the ITO is referred to as the anode, and the metal electrode as the cathode.

Due to the low intrinsic carrier density, the built-in field may be regarded as constant throughout the organic layer.\(^ {14}\) The built-in field is calculated from

\[
E_{\text{BI}} = -\frac{V_{\text{BI}}}{d}
\]

where \(d\) is the thickness of the organic semiconducting layer, and \(V_{\text{BI}}\) is the built-in potential, which (to a first approximation) is the potential difference of the electrode work functions\(^ {14}\).

\[
V_{\text{BI}} = \frac{\Phi_\text{A} - \Phi_\text{C}}{e}
\]

The schematic in Figure 1-5 shows the equilibrium state of a typical sandwich-geometry organic diode, with the presence of the built-in internal field.
A simple model of a single-layered organic solar cell. The organic layer is sandwiched between electrodes of differing work functions. At equilibrium, the Fermi levels of the electrodes equalise, thus developing a built-in electric field. Due to low intrinsic carrier density, the built-in field is constant throughout the device thickness $d$.\cite{14}

1.3.1 Current-voltage response

We consider now the behaviour of the device when an external bias $V$ is applied between the anode and cathode, modifying the internal field to a value

$$E = \frac{V - V_{BI}}{d}. \quad (1.17)$$

In the series of schematic diagrams in Figure 1-6, the low work function cathode is grounded at 0 V, while the anode potential is increased from a negative ($V < V_{BI}$) to a positive ($V > V_{BI}$) voltage. Using these conditions, the flow of injected ($J_{dark}$) and photogenerated ($J_{ph}$) charge carriers are separately analysed in a qualitative manner.

Figure 1-5

Before contact

After contact

Vacuum level

LUMO

HOMO

Fermi levels aligned

$\Phi_A$

$\Phi_C$

Energy

Before contact

After contact
**Figure 1-6**
A schematic diagram illustrating the direction of current flow at various applied voltages.

(A) \( V < 0 \)
- Poor electron injection
- \( J_{\text{dark}} \) small and negative
- \( J_{\text{ph}} < 0 \)

(B) \( V = 0 \)
- \( J_{\text{dark}} = 0 \)

(C) \( 0 < V < V_{\text{BI}} \)
- \( J_{\text{dark}} \) small and positive

(D) \( V = V_{\text{BI}} \)
- \( J_{\text{dark}} > 0 \)
- \( J_{\text{ph}} = 0 \)
- Recombination

(E) \( V > V_{\text{BI}} \)
- \( J_{\text{dark}} > 0 \)
- Possible recombination
- Strong electron injection
- Strong hole injection
- \( J_{\text{ph}} > 0 \)
In The Dark

(B): We start by considering the situation at equilibrium, depicted by Figure 1-6B. Electrons are injected into the semiconductor at both electrodes, but because of the smaller energy difference between the cathode Fermi level and the semiconductor LUMO level, electron injection occurs much more readily at the cathode than at the anode. As a result, the electron density in the semiconductor is higher at the cathode than at the anode, so electrons diffuse from cathode to anode. Under short-circuit conditions \( (V = 0) \), the built-in electric field causes an electron drift current that exactly opposes the diffusion current, resulting in the net current flow being zero. (A): Under reverse bias \((V < 0)\), the electric field [determined by Equation (1.17)] results in a drift current that over-compensates the diffusion current, so that the net electron current is small and negative. The analogous argument applies for the hole current, so that the total current obtained is zero under short-circuit conditions, but small and negative under reverse bias. (C): When the external voltage is increased above \( 0 \) \( V \), the reduced field strength leads to a reduction in the negative drift current, thus allowing the positive diffusion current to grow, resulting in a positive current overall. (D): With the externally applied voltage effectively cancelling \( V_{B1} \), the internal electric field (and thus the drift current) is zero. The dark current is completely driven by the diffusion of carriers from their respective dominant injection electrodes. (E): With the external voltage exceeding \( V_{III} \), the electric field provides a driving force that acts in the same direction as the already-present concentration gradient. Also, an alternative route for injection, in the form of tunnelling through the triangular energy barrier, becomes possible due to the switch in the electric field direction. These factors can lead to a sharp positive increase in the dark injection current. It is possible that an injected electron, instead of completing
its journey from cathode to anode, is intercepted midway by a hole. Their mutual Coulombic attraction leads to the formation of an exciton, which readily recombines with the possible emission of a photon – this is the basic operating principle behind an OLED.

*Under Illumination*

**(A) and (B):** For simplicity, the situation considered here is one where photogenerated excitons spontaneously dissociate into free carriers. At steady-state, it can be shown that the photogenerated carriers diffuse to both electrodes equally, so the net diffusion current for each photogenerated carrier is effectively zero – this result applies for all external voltages so the role of diffusion in determining the magnitude of the total photogenerated current may be neglected in the ensuing discussion. The electric field causes photogenerated electrons and holes to drift to the cathode and anode, respectively, resulting in a negative drift photocurrent that grows with increasing field strength. **(C):** The external voltage now opposes the built-in potential, further reducing the electric field strength and in consequence, the negative photogenerated current decreases in magnitude. **(D):** With the built-in field nullified by the external voltage, photogenerated carriers do not drift to either electrode, but diffuse equally to both electrodes, so the total photogenerated current is zero. **(E):** Due to the reversal of the electric field direction, photogenerated free carriers now drift in the opposite direction i.e. electrons drift to the anode, and holes to the cathode, resulting in a positive current. If the electric field strength is sufficiently high, the carrier flux ceases to be a function of the driving electric field, but instead becomes limited by the rate of photogeneration (for a given illumination level). In such a situation, the photogenerated current saturates.
Since (for any given voltage) the injection current is present regardless of the illumination conditions, the current response of a solar cell is a superposition of the dark injection current and the photogenerated current. If the influx of photons does not affect the injection process, the injection current at a given voltage will equal the current when the same device is measured in the dark, so the total measured light current ($I_{\text{light}}$) may be considered a sum of the dark ($I_{\text{dark}}$) and the photogenerated current ($I_{\text{ph}}$). The current-voltage response of a solar cell in the dark and in the light is graphically summarized in Figure 1-7. It should be noted that the photogenerated current $I_{\text{ph}}$ cannot be measured directly (except at $V = 0$ V where $I_{\text{ph}} = I_{\text{light}}$) and a major objective of the work described in this thesis was to develop a reliable means of determining $I_{\text{ph}}$.

![Figure 1-7](image)

**Figure 1-7**
Simulated data for the injected current $I_{\text{dark}}$ and the photogenerated current $I_{\text{ph}}$. Under illumination the total measured photocurrent $I_{\text{light}}$ is a sum of the injected and photogenerated currents.
1.3.2 Photovoltaic performance

The measured photocurrent \( J_{\text{light}} \) is the primary means by which the current-generating properties of solar cells are assessed. Several performance indicators can be obtained directly from the \( J_{\text{light}} - V \) characteristics, including: the short-circuit current \( J_{\text{SC}} \), the open-circuit voltage \( V_{\text{OC}} \), the fill factor \( \text{FF} \) and the power conversion efficiency \( \text{PCE} \). These parameters provide important but crude information about photovoltaic behaviour.

![Figure 1-8](image)

The fourth (or power-producing) quadrant of the current-voltage plot showing simulated photocurrent-voltage data. The secondary axis shows the power output, which is equal to the product of the photocurrent and the voltage. In use, the solar cell exhibits maximum power output when the load resistance equals \( V^*/J_{\text{light}}(V^*) \).

Figure 1-8 shows a simulated current-voltage curve, accompanied by the output power curve given by \( P_{\text{out}} = -J_{\text{light}} \times V \). In normal operation, we do not directly apply a voltage to the solar cell, but instead use it to provide useful...
power to an external load. The short-circuit current $J_{sc}$ is the maximum photocurrent that can be produced by the solar cell (at a given light intensity). However, this maximum current is only attainable if the load resistance is zero, in which case the solar cell does not produce any useful power. At the other extreme, if the load resistance is infinite, photogenerated electrons (holes) accumulate at the cathode (anode), hence raising (lowering) the potential of that electrode. This results in a photo-voltage developing across the electrodes which stabilises at a value that is dependent on the light intensity. This voltage represents the largest voltage possible from the solar cell at that illumination level, and is referred to as the open-circuit voltage $V_{oc}$. Operating the solar cell at this point also yields zero power (since the current flow is zero due to infinite resistance). A load of finite resistance $r$ allows a current to flow through it, and in response a voltage develops across the load and the solar cell such that:

$$V_{load} = V = J_{light}(V)Ar$$

(1.18)

where $A$ is the active area of the solar cell. The voltage at which a solar cell will operate when driving a load resistance $r$ can then be found from plotting

$$r(V) = \frac{V}{A J_{light}(V)}$$

(1.19)

and finding the voltage that matches $r$.

The power curve in Figure 1-8 shows a maximum at a certain operating voltage. For a given load resistance, we can choose a matching active area so that the solar cell operates at this maximum power point, which is where the solar cell is most efficient at converting incident light into electrical power. The power conversion efficiency is calculated from
\[ PCE = \frac{P_{\text{out}}(\text{max})}{I}, \]  

(1.20)

where \( I \) is the intensity of the incident light.

Two messages may be drawn from the discussion above:

1) The injection current may be viewed as a loss process as it opposes the photogenerated current (see Figure 1-6C). Consequently, if the injection current can be reduced in magnitude, the solar cell will become more efficient.

2) If the photogenerated carriers could be readily transported to the electrodes (before they have an opportunity to recombine) even in the presence of a very small electric field, then the photogenerated current would attain saturation in the close vicinity to \( V_{\text{bi}} \). This will lead to a situation where the photogenerated current increases from 0 at \( V_{\text{bi}} \) to its saturation value at \( V = V_{\text{bi}} - \Delta V \), where \( \Delta V \) is a small voltage difference.

Achieving these two aims simultaneously would lead to a theoretically perfect solar cell, where the operating point with maximum output power approaches the point \((V_{\text{oc}}, J_{\text{sc}})\). The fill factor FF is a crude measure of how closely a real solar cell approaches this ideal situation.

\[ \text{FF} = \frac{P_{\text{out}}(\text{max})}{V_{\text{oc}} J_{\text{sc}}} \]  

(1.21)

In this picture, the perfect solar cell has a FF of 1, while a solar cell with a \( J_{\text{light}} - V \) response resembling a straight line through \( J_{\text{sc}} \) and \( V_{\text{oc}} \) has a FF of 0.25. The most efficient fully-organic solar cells have fill factors of \( \sim 0.6 \) to 0.7 and power conversion efficiencies of \( \sim 4 \) to 5 \(^\circ\)\(^{\circ}\).\(^{[15, 16]}\)
Clearly, these performance indicators are dependent on the nature of the light incident on the solar cell. Illumination with a standardized light intensity and spectrum during $J_{light}-V$ measurement is necessary for meaningful comparisons between solar cells. This standard light is a representation of the natural sunlight arriving on the Earth’s surface after passing through the Earth’s atmosphere at an angle of 48.2° from the zenith, and taking into account global diffuse reflection off terrestrial objects. It is known as Air Mass 1.5 Global (AM1.5G), because the angle ensures that the sunlight passes through 1.5 times the thickness of the atmosphere. The atmospheric conditions specified for the reference was chosen as an averaged representation for the 48 contiguous United States. This reference spectrum has an intensity of ~100 mW/cm² with a spectral irradiance shown in Figure 1-9.

![Figure 1-9](image)

The spectral irradiance of the standard Air Mass 1.5 Global spectrum (total radiant power density 100 mW/cm²). Inset: A comparison of the spectral irradiance of the solar simulator used in this work against the AM1.5G spectrum, magnified to the wavelength range over which organic solar cells are typically responsive.
The reference AM1.5G spectrum is difficult to access naturally, so a white light source is required to simulate it in a controlled and reproducible manner in the laboratory. The inset of Figure 1-9 is a magnified view of the spectral range 300-700 nm, comparing the spectral irradiance of our metal halide K. H. S. solar simulator (at a total intensity ~100 mW/cm²) against the AM1.5G spectrum. Although there is a fair correspondence between the two spectra, some discrepancies are present, particularly in the regions 300 nm < \(\lambda\) < 420 nm and 550 nm < \(\lambda\) < 600 nm. No solar simulator is perfect, and values of \(J_{SC}\), \(V_{OC}\), FF and PCE obtained under such simulation do not reflect the ‘true’ values obtained under standard AM1.5G. However, certain correction factors and procedures are available that allow the measurements obtained under a solar simulator to approach the true AM1.5G values. One such correction is Osterwald’s spectral mismatch factor, which takes into account the relative spectral responses of the device under test and a calibrated photodiode and their respective responses when under the solar simulator and when under AM1.5G illumination.\(^{[17]}\)

### 1.3.3 Spectral response

The spectral efficiency of a solar cell can be characterised as a ratio of short-circuit current to incident power in units of mA/W. Because the electronic structure – and hence the absorption characteristics – of each organic semiconductor are different, the spectral response of solar cells made from different materials vary widely. This wavelength dependence of \(J_{SC}\), known as the spectral response, provides information on how effectively the solar cell utilizes photons from AM1.5G sunlight (or, for that matter, any given illumination source). The active layer in many OSCs is composed of more than a single organic semiconductor material, and spectral response
measurements are often used to discern the photogenerative contribution of each component.

The spectral response of a solar cell in units of (mA W⁻¹ nm) is defined as

\[ S(\lambda) = \frac{J_{SC}(\lambda)}{I(\lambda)}, \tag{1.22} \]

where \( I(\lambda) \) is the spectral irradiance in (W/nm). A separate calibrated photodetector, with a known spectral response \( S^\text{cal}(\lambda) \), is used to calculate the incident spectral irradiance \( I(\lambda) \) by the reverse process:

\[ I(\lambda) = \frac{J_{SC}^\text{cal}(\lambda)}{S^\text{cal}(\lambda)} \tag{1.23} \]

Therefore, the spectral response of the test device at a desired wavelength is

\[ S(\lambda) = \frac{J_{SC}(\lambda)}{J_{SC}^\text{cal}(\lambda)} S^\text{cal}(\lambda). \tag{1.24} \]

Closely related to the spectral response is the spectral quantum efficiency (under short-circuit conditions) \( \eta_{SC}(\lambda) \) of a solar cell. The quantum efficiency is the probability that an incident photon will be converted into an electron that contributes to the short-circuit photocurrent, and it is also widely known as the incident photon-to-electron conversion efficiency (IPCE). Since the energy of a photon is \( hc/\lambda \), the photon flux \( \Imath \) can be calculated from the incident power using

\[ \Imath = \frac{I(\lambda) \lambda}{hc}, \tag{1.25} \]
where \( h \) is Planck’s constant and \( c \) is the speed of light. The quantum efficiency may be expressed as a ratio of the electron flux to the photon flux, which can then be expanded into measurable quantities:

\[
\eta_{\text{sc}}(\lambda) = \frac{j_{\text{sc}}(\lambda)}{e \lambda S(\lambda)} = \frac{hc}{e \lambda} \frac{j_{\text{sc}}(\lambda)}{I(\lambda)}.
\]

Note that we can substitute the spectral response \( S(\lambda) \) into the expression, which yields

\[
\eta_{\text{sc}}(\lambda) = \frac{hc}{e \lambda} S(\lambda).
\]

This implies that the spectral response and quantum efficiency are related to one another through a wavelength-dependent factor \( hc/e \lambda \) and can thus be measured in a similar fashion. Some of the most efficient fully-organic solar cells have peak quantum efficiencies of 60% to 70\%\(^{18, 19} \) at the material’s peak absorption wavelength.

### 1.3.4 Charge injection

As mentioned in the qualitative discussion of the current-voltage response, the energy difference \( \Phi_\text{B} \) between the electrode Fermi energy and the semiconductor LUMO energy (HOMO for holes) plays an important role in the injection of electrons into the semiconductor. For the sake of argument, electron injection will be discussed, but analogous principles apply to hole injection as well. For electron injection to occur, the electron must possess sufficient thermal energy to overcome the potential barrier, or it must tunnel through it. An electron in the semiconductor, at some spatial distance \( x \) away from the electrode-semiconductor interface, creates a positive image charge in the electrode through Coulombic influence. This image charge lowers the
electric potential in the semiconductor by an amount known as an image potential:[20]

\[ \Phi_{\text{image}} = -\frac{e^2}{16\pi\varepsilon_0 x} \]  

(1.28)

In the presence of an electric field \( E \), which arises from a combination of the built-in potential and the externally applied voltage, the original potential barrier height \( \Phi_B \) is reduced to \( \Phi_{\text{B,eff}} \) (see Figure 1-10).

\[ \Phi_{\text{B,eff}} = \Phi_B - \sqrt{\frac{e^3 E}{4\pi\varepsilon_0}} \]  

(1.29)

**Figure 1-10**

A schematic of energy barrier lowering due to the image charge effect. At zero-field, the barrier is 0.2 eV, but becomes significantly reduced in the presence of an electric field.

Figure 1-10 depicts the situation when \( V > V_{\text{Bt}} \), with the relevant potentials calculated using the values \( \varepsilon = 3 \), and \( E = 1.5 \times 10^7 \) V/m, which are typical for
organic solar cells. Under these conditions, the effective energy barrier is approximately halved from 0.2 eV to 0.12 eV. Clearly, any increase in the applied bias $V$ leads to a lowering of the effective barrier height $\Phi_{B,\text{eff}}$ and a reduction in the tunnelling distance, thus enhancing tunnel injection. The lowered barrier makes injection a much more effective process, resulting in strong voltage and temperature dependences of the dark current in the $V > V_{\text{bi}}$ regime.

1.3.5 Photogeneration at a donor/acceptor interface

The rate of spontaneous exciton dissociation in solar cells based on pure organic semiconductors is low due to the strong Coulomb attraction between the excitonic electron and hole pair ($\sim 0.5 \text{ eV}$), which is much larger than the thermal energy at room temperature ($\sim 25 \text{ meV}$). Coulomb attraction is much stronger in organic semiconductors because of the low dielectric constant. Even the presence of a large built-in electric field ($\sim 10^7 \text{ V/m}$) is not likely to dissociate excitons since the potential drop across the small spatial extent ($< 1 \text{ nm radius}$) of an exciton is insufficient to overcome the exciton binding energy. By far the most important means of dissociating excitons is the use of an interface between dissimilar semiconductors, also known as a heterojunction.

The first use of a heterojunction in a solar cell is usually attributed to C. W. Tang$^{[23]}$. Tang’s solar cell, which utilized a bilayer prepared by the sequential thermal evaporation of copper phthalocyanine (CuPC) and 3,4,9,10-perylenetetracarboxyl-bis-benzimidazole (PTCBI), attained a power conversion efficiency of 1% – a significant breakthrough at the time. To understand the basic mechanism of exciton dissociation at a heterojunction
using Tang’s bilayer solar cell as an example, we consider the HOMO and LUMO levels of CuPC and PTCBI.\[^{[24]}\]

![Energy Diagram](image)

**Figure 1-11**
An energy diagram for a CuPC:PTCBI bi-layer solar cell illustrating the formation of an exciton in the CuPC layer close to the heterojunction. At the heterojunction, the electron is transferred to the PTCBI layer, releasing ~0.6 eV of energy in the process due to the LUMO-LUMO offset. This energy release overcomes the attraction between the electron and hole, which are driven to their respective electrodes by the built-in field.

For the CuPC/PTCBI system, Peumans and co-workers estimated the exciton binding energy as ~0.2 eV.\[^{[25]}\] The ~0.6 eV energy difference between the LUMO levels of CuPC and PTCBI is more than sufficient to overcome the exciton binding energy, hence energetically favouring the transfer of an electron across the interface from CuPC to PTCBI. Once the electron and hole are spatially and energetically separated, they are free to drift towards their respective electrodes. PTCBI is also a strong absorber of light, and excitons created in PTCBI dissociate through an analogous process of HOMO-HOMO...
hole transfer to the CuPC layer, where the energy offset is $\sim 1$ eV. The ability to form well-defined/abrupt junctions between donor and acceptor materials is possible in organic semiconductors due to the absence of dangling bonds. A distinct advantage of using a heterojunction is the fact that the electric field and carrier concentration gradient both act to drive the carriers toward the electrodes, making the photo-response of the device less reliant on the internal electric field as well as lowering the probability of the free carriers from recombining. The operation of such heterojunction-based solar cells relies on the energy level offset such that one semiconductor donates electrons to another semiconductor, where the offset needs to exceed the exciton binding energy (typically $\sim 0.5$ eV$^{[21]}$). The electron-donating (or hole-accepting) phase is known as the donor material, while the electron-accepting (or hole-donating) phase is the acceptor material. For good photovoltaic performance, the donor (acceptor) should preferably possess reasonable hole (electron) mobility in order to transport holes (electrons) effectively to the anode (cathode).

Peumans and co-workers estimated that an exciton created in CuPC typically diffuses $\sim 10$ nm away from the absorption/generation site before it recombines.$^{[25]}$ In other words, on average only those excitons created within a $\sim 10$ nm vicinity of the heterojunction have a good chance of dissociating to yield free carriers – photons absorbed away from this region are wasted. In PTCBI, the exciton diffusion length is even smaller, at $\sim 3$ nm.$^{[25]}$

The absorption coefficient of most conjugated molecules and polymers are such that a film of at least $\sim 100$ nm thickness is necessary to absorb a large proportion of the incident light.$^{[26]}$ By mixing donor and acceptor materials in a single blended film, it is possible to disperse heterojunctions throughout the
blended film thickness. Solar cells based on such blends are referred to as bulk heterojunction (BHJ) solar cells. With the use of an appropriate solvent, Shaheen and co-workers produced a BHJ solar cell in 2001 that attained 2.5% power efficiency, which was considered a breakthrough efficiency.\cite{27} Their BHJ system, which is still widely studied (including work in this thesis), was based on a mixture of poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-p-phenylenevinylene] (MDMO-PPV, donor) and (6,6)-phenyl-C_{61}-butyric acid methyl ester (PCBM, acceptor). To fabricate a BHJ solar cell, the donor and acceptor are dissolved together in a solvent, and a blend film deposited on the anode by spin-coating. Controlled thermal co-evaporation of small-molecule donors and acceptors is also a well-known method of obtaining BHJ blend films\cite{28}, but was not used in this work. Using the MDMO-PPV:PCBM system as an example, BHJ energy levels\cite{29} can be represented as in Figure 1-12.

![Energy diagram for an MDMO-PPV:PCBM bulk heterojunction solar cell.](image)

**Figure 1-12**
An energy diagram for an MDMO-PPV:PCBM bulk heterojunction solar cell. The presence of heterojunctions dispersed throughout the blend layer allows a large proportion of excitons to reach a heterojunction where they subsequently dissociate. The separated electron and hole are driven to their respective electrodes by the built-in field, provided there is a continuous pathway for carrier transport.

Because donor-acceptor heterojunctions are present throughout the blended film, photogeneration of free carriers can occur over a much larger volume
than a comparable bilayer device, allowing more free carriers to be generated. Provided the carriers have a continuous pathway to drift to their respective electrodes, relatively high efficiencies can be achieved, and the present record for the most efficient (5.5%) all-organic solar cell is held by Peet and co-workers, whose solar cell is based on a blend of poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b’]-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) and the C70 version of PCBM.[16]

However, the phase separation of donor and acceptor materials in a blended film is neither easily-controlled nor well-understood. If the phase separation produces phase domains that are too fine, the percolation of one material in the other tends to be broken, so the probability of a free carrier finding a continuous pathway to its destination electrode is low. The carrier is thus liable to become trapped at a dead-end where it will eventually recombine with an oppositely charged carrier.[30] On the other hand, excitons created in phase domains that are too large cannot reach an interface before recombination takes place, thus facing the same limitation as in a bilayer device. The degree of phase separation is highly sensitive not only to the donor and acceptor materials used, but also to the fabrication conditions, such as the choice of solvent[27, 31], blend composition[32, 33] and heat treatment[34]. The fabrication conditions for the optimum degree of phase segregation are therefore not easily found, and inevitably require “brute force” experimentation to find.

1.3.6 Loss mechanisms

As discussed in the previous section, the $I_{\text{light}} - V$ profile of an ideal solar cell with a fill factor approaching unity should resemble a rectangle with
opposing corners defined by $J_{SC}$ and $V_{OC}$ (see Figure 1-8). Any internal process that causes a departure from this ideal may be thought of as a loss mechanism. The injected current results directly from the photovoltage and opposes the flow of the photogenerated current. Consequently if one could suppress the dark current, the fill factor and power efficiency would improve. The voltage dependence of the photogenerated current represents in part the inability of the electric field to extract free charge carriers to their appropriate electrodes before they have an opportunity to recombine. The shape of the $J_{light}$-$V$ curve is determined by a combination of these two loss mechanisms.

Recombination of electrons and holes clearly reduces device efficiency. Geminate recombination generally refers to the annihilation of the electron-hole pair before complete dissociation has taken place. Non-geminate recombination occurs when a free carrier recombines with an oppositely charged free carrier that originated from a different exciton. Geminate recombination is largely overcome by the use of bulk heterojunctions*, as is clear from the very high peak quantum efficiencies observed in these devices.[19] Increased carrier mobilities reduce the dwell time of free carriers in the semiconductor layer, thus decreasing the rate of non-geminate recombination.

1.4 **The Corrected Photocurrent**

The total measured photocurrent of a solar cell may be treated as the sum of a bias-induced current $J_{V_{photo}}$ due to the light-induced voltage $V_{photo}$ across the

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* However, as we will show in Section 5.4, care must be taken to select donor and acceptor materials with sufficiently offset HOMO and LUMO levels.
electrodes, and a photogenerated current $I_{ph}$ due solely to the influx of photons.

$$J_{light} = J_{v\text{photo}} + I_{ph}$$  \hfill (1.30)

Assuming that the rate of carrier injection is unaffected by the presence of photogenerated carriers, $J_{v\text{photo}}$ will equal the current measured when the same device in the dark is subjected to an applied voltage $V = V_{\text{photo}}$. $J_{v\text{photo}}$ therefore equals the dark current $I_{\text{dark}}$ and we may write:

$$J_{light}(V) = J_{\text{dark}}(V) + I_{ph}(V)$$  \hfill (1.31)

Since $I_{ph}(V)$ cannot be measured directly, it is obtained by subtracting the dark current from the measured photocurrent, and is hence referred to here as the corrected photocurrent.

$$I_{ph}(V) = J_{light}(V) - J_{\text{dark}}(V)$$  \hfill (1.32)

The corrected photocurrent reflects the current-producing potential of a solar cell, since it is isolated from the loss process of charge injection. Much can be learnt about the photogeneration, recombination and carrier extraction processes in a solar cell from studying its corrected photocurrent, as we shall see in the subsequent chapters.

The blend layer in bulk heterojunction solar cells is often treated as a single layer of a composite semiconductor in which the HOMO level is derived from the donor and the LUMO level from the acceptor (Figure 1-12). The internal electric field strength plays a central role in understanding the corrected photocurrent of such devices as it directly influences the rate at which photogenerated carriers are driven to the electrodes and then extracted into the external circuit. The electric field may also assist charge dissociation at
donor-acceptor interfaces in BHJ solar cells. The field strength is determined by the difference between the measured photovoltage and the built-in potential. In previous studies, Malliaras and co-workers sought the voltage at which \( J_{\text{light}} = J_{\text{dark}} \) (i.e. \( J_{\text{ph}} = 0 \)), which they referred to as the compensation voltage \( V_0 \).\(^{[14]} \) By comparing \( V_0 \) with values of \( V_{\text{BI}} \) as determined by electroabsorption measurements, they found that \( V_0 = V_{\text{BI}} \) under low-temperature conditions.

Electroabsorption is a technique used to directly measure \( V_{\text{BI}} \), and relies on the fact that the absorption coefficient of the polymer layer varies in proportion to the square of the electric field (see Section 1.5.4).\(^{[35]} \) \( V_{\text{BI}} \) corresponds to the applied voltage \( V \) at which the electroabsorption response vanishes. The technique has been applied successfully to BHJ\(^{[29, 36]} \) as well as bilayer solar cells\(^{[37, 38]} \). The difficulty of the measurement lies in the need to apply a fairly large alternating voltage (\( V_{\mathrm{AC}} \sim 1 \text{ V} \)) to the device in order to obtain reasonable signal-to-noise ratios\(^{[14]} \), which can lead to device degradation. Other effects – such as charge injection – can dominate the signal and in such situations, determination of \( V_{\text{BI}} \) may be problematic.\(^{[39]} \)

Owing to such difficulties, obtaining the compensation voltage appears to be the more common method of estimating \( V_{\text{BI}} \) in the literature.\(^{[14, 40, 41]} \)

A theoretical/numerical study by Sokel and Hughes on a photoconductor sandwiched between similar non-blocking metal contacts yielded an analytical solution for the drift-diffusion and the continuity equations under the assumptions of zero recombination and a flat generation profile:\(^{[8]} \)

\[
J_{\text{ph}} = eGd \left[ \exp\left(\frac{eV}{k_B T}\right) + 1 \right] \frac{1}{\exp\left(\frac{eV}{k_B T}\right) - 1 - \frac{2 k_B T}{eV}}.
\]  

(1.33)
Here, $V$ accounts for the total field strength since the contacts are of similar metals but, in the context of a sandwich-geometry solar cell, could be modified to $(V - V_{in})$. $G$ is the carrier photogeneration rate, which was assumed uniform throughout the photoconductor layer and independent of the electric field and temperature. Other assumptions made to reach this analytical solution were the absence of traps, a constant electric field and perfect carrier extraction at the photoconductor-metal interfaces.

Mihailetschi, Koster and co-workers compared Sokel and Hughes’ analytical solution to corrected photocurrents experimentally obtained from a BHJ solar cell. They observed that as the field strength was increased, the experimental corrected photocurrent surpassed the saturation value of the analytical corrected photocurrent.$^{[40]}$ They suggested that this discrepancy arose from the field dependence of photogeneration, and subsequently modified the model by introducing a field and temperature dependent photogeneration $G(E,T)$, in accordance with Braun’s geminate recombination theory$^{[42]}$.

Despite the importance of the corrected photocurrent in OSC research, we will show that the conventional methods used to determine it are experimentally flawed. Although conceptually simple, the prevalent method of subtracting the dark current from the measured photocurrent is based on the assumption that the two separate measurements are performed under comparable conditions. As described under the section on charge injection, the dark current can vary very strongly with temperature and voltage, which can easily amplify errors at the subtraction stage, particularly if the dark current is much larger than the corrected photocurrent. It is perhaps for this reason that the vast majority of the work on corrected photocurrents has been limited to measurements in the voltage range $V \leq V_0$.$^{[40, 41]}$, which severely limits the
The scope of what can be analysed and learnt. Researchers who model the full current-voltage response of OSCs over a broad voltage range often assume that when $V > V_{\text{Bi}}$, the corrected photocurrent will behave in a manner that mirrors what has thus far been found for $V < V_{\text{Bi}}$.\textsuperscript{[43, 44]} The remaining chapters of this thesis will challenge these assumptions and provide fresh insight into the operating principles of BHJ solar cells.

1.5 **Experimental Methods**

We review below the routine methods and procedures used to fabricate and characterise the devices reported in this thesis.

1.5.1 **Device fabrication**

Almost all the solar cell samples studied in this work were fabricated using similar equipment and fabrication protocols in our laboratory in IMRE. The commercially-obtained (Merck Display Technologies) substrates consisted of square glass slides that were 25 mm wide and 0.7 mm thick, and pre-coated on one side with indium tin oxide (ITO). The sheet resistance of the ITO-coated glass was not measured, but was specified as 15 $\Omega/\square$ by the manufacturer. Patterning of the ITO involved etching the undesired ITO in an aqueous solution of hydrochloric acid.

Once patterned, the glass/ITO slides were cleaned in ultrasonic baths of acetone, propan-2-ol (IPA), detergent and de-ionized water, with the slides immersed in each solvent for 10 mins. The slides were then treated in an ultraviolet (UV)-ozone chamber at 100 $^\circ$C for 10 mins and then allowed to cool to ambient temperature. Poly(3,4-ethylene-dioxythiophene) [PEDOT] in the
oxidized state is a conjugated polymer exhibiting high electrical conductivity, excellent thermal stability and good film-forming properties. When doped with poly(styrenesulphonate) [PSS] the PEDOT attains a positive charge, while the PSS forms a polyanion. The resulting mixture [PEDOT:PSS] forms a dispersion in water, and yields a highly conducting transparent pale blue film upon drying. PEDOT:PSS, purchased from H. C. Stark under the trade name Baytron P VP Al 4083, was spin-coated onto the clean glass-ITO slides at 1500 rpm and then heated to 140 °C for 20 mins in air to drive off excess water, giving ~60 nm films. The samples were then allowed to cool and transferred to a dry nitrogen glovebox, where all subsequent fabrication steps and testing were performed.

Having deposited the PEDOT:PSS film, the general procedure was to spincoat the donor-acceptor blend solution onto the samples, but the exact conditions varied according to the choice of donor and acceptor materials. After deposition, the samples were left on a hotplate at 60 °C for one hour to drive off excess solvent, or – if required – were thermally annealed at higher temperatures. Details of the specific fabrication conditions used will be reported with experimental findings. To complete the devices, they were loaded into a thermal evaporation chamber, where the desired top electrode metal was thermally evaporated through a shadow mask under a vacuum better than $10^{-5}$ mbar. Thermal annealing may also be performed after metal deposition. The devices are represented by the schematic Figure 1-13, with the region in green representing the location where the organic layers were mechanically scratched away to expose the ITO electrode for the purpose of electrical contacting. Each sample contained 10 separate devices with dimensions determined by the spatial overlap of the ITO and metal electrodes, measuring 3 mm by 5 mm.
Silver paste was applied on the ITO and metal contact areas to provide mechanical protection and improved electrical contact. Electrical contact was made via spring-loaded gold-plated probe pins, which were mounted in a plastic housing that was designed to provide a secure, immovable mount for the sample.

1.5.2 Current-voltage response

The current-voltage response of devices was measured using a Keithley 2400 source-measure unit, with the electrical connections schematically shown in Figure 1-14.
The voltage source was programmed to sweep through a user-defined voltage range in typical fixed steps of 20 or 50 mV. Upon advancing to a new voltage, 20 successive current readings were made after a programmed delay of 1 second to allow stabilisation of the signal, following which the average was calculated. Measurements were performed under dry nitrogen, with the devices exposed to simulated sunlight (100 mW/cm\(^2\) intensity) to obtain the photocurrent. They were subsequently wrapped in aluminium foil to exclude light, and the sweep repeated for the dark current.

Simulated sunlight was provided by a K. H. S. metal-halide solar simulator, which was positioned under the nitrogen glovebox where device characterization took place. Light reached the device by means of a quartz window built into the floor of the glovebox, and its intensity was adjusted to 100 mW/cm\(^2\). The intensity was monitored by an Ophir power meter, which uses a thermopile head with a flat spectral response. The device characteristics were not corrected for the spectral mismatch (versus AM1.5G) because an AM1.5G-calibrated photodiode was unavailable for the duration of this project.
1.5.3 Spectral response

The light source used for the quantum efficiency measurements was a Newport-Oriel 150 W xenon lamp, whose white light output was focused into a Cornerstone 130 1/8m monochromator, where the width of both entry and exit slits were set to 760 μm, providing a wavelength resolution of ~5 nm (at 500 nm) as specified by its manufacturer.\textsuperscript{[46]} The monochromatic light was channelled into the glovebox and onto the solar cell through a broadband telecommunication-grade optical fibre of core diameter 0.9 mm.

While a simple current meter (such as a Keithley 2400 sourcemeter) would in principle suffice to detect the current output from the solar cell, such a method requires all stray light to be excluded from the experiment. A more elegant (and practical) approach is to use a lock-in amplifier to differentiate the current output in the frequency domain. A mechanical chopper was introduced in the light path between the xenon lamp and monochromator to modulate the light in square pulses at 237 Hz. Typical organic BHJ devices at room temperature respond within microseconds so transient effects due to the modulation at this frequency are negligible.\textsuperscript{[47]} This results in a square-modulated current output from the solar cell at the same frequency, which was converted into a proportional voltage signal via a 50 Ω resistor. A Stanford Research 830 lock-in amplifier was programmed to lock onto that frequency and detect only the voltage signal due to the monochromatic light while excluding signals resulting from stray light at other frequencies, such as steady sunlight and room illumination (connected to the 50 Hz grid power supply).

It is noted that the resistor introduces a slight inaccuracy to the quantum efficiency measurements because the presence of a load leads to a
photovoltage across the solar cell, and the solar cell is consequently no longer under short-circuit condition. However, the voltage across the resistor (and the solar cell) was on the order of a few mV, based on photocurrents of ~100 μA, and hence did not present a significant biasing effect.

The solar cell quantum efficiency $\eta_{SC}(\lambda)$ was determined from the quantum efficiency of a calibrated Hamamatsu S1337 crystalline Si photodiode $\eta_{SC,\text{cal}}(\lambda)$:

$$\eta_{SC}(\lambda) = \frac{J_{SC}(\lambda)}{J_{SC,\text{cal}}(\lambda)} \eta_{SC,\text{cal}}(\lambda).$$  \hspace{1cm} (1.34)

### 1.5.4 Electroabsorption

In electroabsorption, a combined AC and DC bias $V = V_{DC} + V_{AC} \sin \omega t$ is applied to a device and changes in the transmission $\tau$ of a probe beam are monitored by lock-in detection. If the origin of the electromodulation signal is electroabsorption (i.e. the Stark effect), the fractional change in the transmission is proportional to the third-order DC Kerr nonlinear susceptibility and the square of the electric field.\textsuperscript{[35]} The differential transmission is therefore modulated at the 1st- and 2nd-harmonic frequencies in accordance with:

\begin{align*}
\frac{\Delta \tau}{\tau}_{\omega} & \propto 2 \text{Im} \chi^{(3)}(\lambda) E_{DC} E_{AC} \sin \omega t, \hspace{1cm} (1.35) \\
\frac{\Delta \tau}{\tau}_{2\omega} & \propto \frac{1}{2} \text{Im} \chi^{(3)}(\lambda) E_{AC}^2 \cos 2\omega t. \hspace{1cm} (1.36)
\end{align*}

Under conditions of low carrier densities, the bulk electric field $E_{DC}$ is related to the DC component of the applied bias $V_{DC}$ by:

$$E_{DC} = \frac{(V_{DC} - V_{BL})}{d}. \hspace{1cm} (1.37)$$
Therefore \( (\Delta \tau/\tau)_{\omega} \) varies linearly with \( V_{\text{DC}} \), passing through zero at \( V_{\text{DC}} = V_{\text{BI}} \), and \( (\Delta \tau/\tau)_{2\omega} \) is independent of \( V_{\text{DC}} \).\[35\]

![Schematic diagram](image)

**Figure 1-15**

A schematic representation of the experimental set up for an electroabsorption experiment.

The electroabsorption measurements in this work were performed by Rui Jin in the Chemistry Department, Imperial College. The internal reference signal \( (V_{\text{AC}} \sin \omega t) \) from a SR830 lock-in amplifier and a DC voltage \( (V_{\text{DC}}) \) from one of its auxiliary outputs were supplied as the inputs to a unity-gain summing amplifier. The output of the amplifier \( V = V_{\text{DC}} + V_{\text{AC}} \sin \omega t \) was applied as a modulation voltage to the solar cell. The monochromated output of a 50 W xenon lamp was focused onto the aluminium cathode of the solar cell (via the glass substrate), and the reflected light refocused onto a Si photodetector with an integrated gain-\(10^6\) \( \Omega \) trans-impedance amplifier. The amplified output of the photodetector was supplied as an input to the SR830 lock-in amplifier. The first-harmonic electroabsorption response was obtained by locking into the \( \omega \) frequency component of the detected signal and the second harmonic response by locking into the \( 2\omega \) component.
This chapter identifies a flaw in the standard procedure of determining corrected photocurrents, and describes the progressive development of a new technique that allows for the reliable determination of corrected photocurrents.
2.1 **STANDARD DC MEASUREMENT OF CORRECTED PHOTOCURRENT**

As stated previously, the standard (and simplest) method of measuring the bias-dependence of the corrected photocurrent, or the $J_{\text{ph}}$-$V$ curve, is to perform sequential current-voltage sweeps under dark and illuminated conditions, and then calculate the difference between the two curves thus obtained.\textsuperscript{[14, 40, 41, 44]} Before describing our new improved technique, results from this standard procedure will be presented, and the deficiencies of the method will be highlighted and discussed.

2.1.1 **Apparent gain effect under forward bias**

In this experiment, the test device was an ITO / PEDOT:PSS / P3HT:PCBM / Al bulk heterojunction solar cell. $J$-$V$ sweeps of the device were obtained using a Keithley 2400 Sourcemeter, with the device first strongly illuminated under a K. H. S. solar simulator, and then completely wrapped in aluminium foil to exclude light. The dark current $J_{\text{dark}}$ was subsequently subtracted from the photocurrent $J_{\text{light}}$ to obtain the corrected photocurrent $J_{\text{ph}}$.

Using this so-determined $J_{\text{ph}}$-$V$ curve, we can calculate the corrected quantum efficiency $\eta_{\text{ph}}$ at any given bias, which is the ratio between the photogenerated electron flux and the incident photon flux. The incident photon flux has a spectral distribution $f(\lambda)$, so the total photon flux over the spectral range $\lambda_1 < \lambda < \lambda_2$ of the solar cell is:
The electron flux $F_e$, at short-circuit, due to this photon flux is
\[ F_e = \int_{\lambda_1}^{\lambda_2} f(\lambda) \eta_{SC}(\lambda) d\lambda, \]  

where $\eta_{SC}(\lambda)$ is the spectral quantum efficiency of the device at short-circuit. We can thus obtain an integrated short-circuit quantum efficiency for the spectral range $\lambda_1 < \lambda < \lambda_2$ by dividing Equation (2.2) by Equation (2.1):
\[ \eta_{ph}(0V) = \frac{F_e}{F} = \frac{\int_{\lambda_1}^{\lambda_2} f(\lambda) \eta_{SC}(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} f(\lambda) d\lambda}, \]  

The integrated quantum efficiency at a general photovoltage $V$ is obtained by multiplying the integrated short-circuit quantum efficiency by the normalised $J_{ph}-V$ curve.
\[ \eta_{ph}(V) = \eta_{ph}(0V) \frac{J_{ph}(V)}{J_{SC}} = \frac{\int_{\lambda_1}^{\lambda_2} f(\lambda) \eta_{SC}(\lambda) d\lambda}{J_{SC} \int_{\lambda_1}^{\lambda_2} f(\lambda) d\lambda} \]  

Current-voltage sweeps using the standard DC method are shown in Figure 2-1, with the $J_{ph}-V$ curve calculated by subtracting the $J_{dark}-V$ curve from the $J_{light}-V$ curve. The quantum efficiency of the device [as determined from Equation (2.4) over the 300-700 nm operating range of the solar cell] is shown on the secondary $y$-axis.
The current-voltage response of an ITO / PEDOT:PSS / P3HT:PCBM / Al solar cell in the dark and under illumination by a solar simulator, measured using a Keithley 2400 sourcemeter. The corrected photocurrent was calculated by subtracting the dark current from the photocurrent. The secondary y-axis shows the quantum efficiency of the device for photons in the 300 – 700 nm spectral range. The quantum efficiency apparently exceeds unity at biases greater than 1.5 V.

The $\eta_{ph}-V$ curve appears quite flat at biases less than ~0.4 V, indicating near-saturation of the device quantum efficiency. Above ~0.4 V, the quantum efficiency diminishes, and crosses the $V$-axis at 0.65 V. Beyond 0.65 V, the $\eta_{ph}-V$ curve increases steadily, and surprisingly surpasses unity at ~1.5 V, which would seem to imply that, on average, each incident photon generates more than one electron-hole pair.

Gain-inducing effects, such as impact ionization, are well-known in inorganic semiconductors[48] and find applications in photomultiplier tubes and other highly sensitive optical detectors[49], but are unlikely explanations for these results as they require carrier velocities higher than those typical in organic materials.[50] Hence, there is good reason to believe that the standard DC method for determining the corrected photocurrent is flawed in some way.
2.1.2 Device heating due to illumination

A more prosaic explanation for the anomalously high inferred corrected quantum efficiencies is a mismatch in the conditions under which $J_{\text{light}}$ and $J_{\text{dark}}$ were measured. The most likely difference between the two measurements is a temperature mismatch. To investigate this possibility, a small platinum (Pt100) temperature sensor with a footprint of 2 mm × 2.3 mm was attached directly onto the aluminium cathode backing of a device, using conductive silver paste as an adhesive to ensure good thermal contact. The resistance of the Pt100 sensor was then measured with a Keithley 2400 Sourcemeter, subject to a constant current of 0.100 mA. The resistance of the Pt100 sensor rose from 112.4 ± 0.1 Ω in the dark to 117.3 ± 0.1 Ω when illuminated by the solar simulator after 3 minutes. These values were linearly interpolated from a standard Pt100 resistance table, and imply a temperature increase of 12.7 ± 0.4 °C due to radiative heating from the solar simulator.

If the temperature of the device is $T_d$ in the dark and $T_l$ in the light (where $T_d < T_l$), then the “true” value of the corrected photocurrent is

$$J_{\text{ph}}(V) = J_{\text{light}}(V, T_l) - J_{\text{dark}}(V, T_l),$$

(2.5)

whereas what is in fact measured using the standard DC method is

$$J_{\text{ph}}^{\text{DC}}(V) = J_{\text{light}}(V, T_l) - J_{\text{dark}}(V, T_d).$$

(2.6)

Hence, the standard DC approach overestimates $J_{\text{ph}}$ by an amount

$$\Delta J = J_{\text{ph}}^{\text{DC}}(V) - J_{\text{ph}}(V) = J_{\text{dark}}(V, T_l) - J_{\text{dark}}(V, T_d)$$

(2.7)

where $J_{\text{dark}}(V, T_l) > J_{\text{dark}}(V, T_d)$. Due to the rapid growth of the dark current with increasing applied voltage, $\Delta J$ increases rapidly, thus explaining the anomalously large $J_{\text{ph}}^{\text{DC}}$ values when $V > 0.65$ V in Figure 2-1.
It was recognized that the solar simulator output contains a large proportion of infrared radiation, which contributes heavily to heating the device. To reduce the effect of radiative heating, light from a high brightness white LED (more detail in the following section, see Figure 2-3) was directed onto the same P3HT:PCBM device, and current-voltage sweeps were again obtained using a Keithley 2400 (Figure 2-2). Under these conditions, $\eta_{\text{ph}}$ did not exceed unity in the measurement range from -0.4 to 1.7 V. However, despite reduced infrared heating from the LED, a steady state temperature rise of $2.3 \pm 0.4$ °C was recorded, which would still introduce a significant error $\Delta J$. This is because $J_{\text{ph}}$ is much smaller than $J_{\text{dark}}$, leading to a large value of $\Delta J / J_{\text{ph}}$ even when $\Delta J / J_{\text{dark}}$ is small.

![Figure 2-2](image)

**Figure 2-2**
The current-voltage response of a P3HT:PCBM solar cell measured by the standard DC method of sequential current-voltage scans under white LED light and in the dark. Although the quantum efficiency (secondary y-axis) of the device did not exceed unity, a temperature rise of ~2 °C was still recorded when the device was illuminated.
2.2 Equipment for the Pulsed Measurement Technique

In the previous section, we demonstrated a temperature mismatch between dark and illuminated conditions in the standard DC method when obtaining the $J_{\text{dark}}$-$V$ and $J_{\text{light}}$-$V$ characteristics of a device, even with a relatively cool LED light source. The reliability of the resultant $J_{\text{ph}}$-$V$ data was hence questionable, and highlighted the need for a new method of obtaining these current-voltage characteristics. Since the temperature mismatch was caused by the radiative heating from the light source, one plausible solution to the problem was to implement a pulsed light source, in accordance with the following argument: if the pulse frequency was made sufficiently high so that the device had inadequate time to heat and cool between the light pulses, the device temperature would stabilise at an intermediate temperature between $T_d$ and $T_l$. Hence, the $J_{\text{light}}$-$V$ and $J_{\text{dark}}$-$V$ characteristics would be obtained under comparable conditions, and a reliable $J_{\text{ph}}$-$V$ curve could thus be calculated. The following sections describe the development of this new method of obtaining current-voltage characteristics, and will be referred to in the ensuing discussion as the pulsed technique.

The platform on which the pulsed technique was developed consists of the graphical programming language Labview and a PCI-6251 M Series data acquisition (DAQ) card, both products of National Instruments. The PCI-6251 has a single 16-bit analog-to-digital converter (ADC) with a sampling rate of up to 1.25 MHz for input voltage signals. In addition, there are two analog voltage output channels, which sample at a rate up to 2.86 MHz via a 16-bit digital-to-analog converter (DAC), and source voltages of up to ±10 V with a current output of up to 5 mA. The DAQ card is installed as a PCI board within a desktop computer, and externally connected to a block of BNC connectors that accompanies the DAQ card.
Mechanically-chopped light from a solar simulator was originally considered as a possible source of modulated illumination. However, the solar simulator output warms the device and its surroundings considerably; thus, to alleviate any temperature mismatch over the $J_{\text{light}}-J_{\text{dark}}$ cycle, we opted for an electrically-chopped Philips Luxeon III high-brightness white light-emitting diode (LED) as a relatively cool light source. Electrical chopping suffers from less “jitter” than mechanical chopping and enables higher modulation.
frequencies to be employed. To modulate the LED, a gain $5 \Omega^{-1}$ voltage-to-current amplifier was built to source a current to the LED that is proportional to the voltage input to the amplifier, allowing the LED intensity to be controlled via a voltage signal from the DAQ card. The modulated light from the white LED was first made to pass through a ground glass diffuser, and the homogenized output was then channelled through a liquid light guide to the device, which was placed a considerable distance away from the LED so that dissipated heat emanating from the LED heat sink would not affect the device.

A second voltage output from the DAQ card was used to bias the device for current-voltage sweeps, with a unity gain voltage follower supplying the necessary current [the maximum current output of the DAQ card is 5 mA, whereas the operational amplifier (op amp) can output up to 45 mA]. The time-varying current response of the device was amplified to a proportional voltage signal using a $100 \Omega$ gain transimpedance amplifier with negligible input impedance, and this amplified signal was supplied as an input to the DAQ card.

It is worth mentioning in a little detail the design of the transimpedance amplifier, which was the product of considerable experimentation. The key issue we faced in designing the transimpedance amplifier was the high capacitance of organic photovoltaic cells. A large input capacitance to an op amp often results in unstable operation, which manifests itself as a large oscillatory signal that contaminates the desired output signal. A capacitor was introduced into the feedback loop of the op amp circuit to suppress oscillatory signals. However, the feedback capacitance also had the effect of lowering the effective transimpedance bandwidth, and a high-bandwidth (gain-bandwidth product 90 MHz) op amp was required to counteract this
Maintaining a reasonably high transimpedance bandwidth was important because the pulsed signal was also time-varying, and the effective transimpedance amplifier bandwidth had to be above the pulse frequency in order to avoid unintentionally damping the desired pulsed signal. The eventual design for the transimpedance amplifier circuit and the unity gain voltage follower is shown in Figure 2-4 with a test device (labelled OSC) to show the relevant electrical connections.

![Circuit Diagram](image_url)

**Figure 2-4**
A circuit diagram depicting the unity gain voltage follower and transimpedance amplifier connected to an organic solar cell. The desired bias from the DAQ card was supplied as an input to the voltage follower, which in turn supplied the necessary current to the solar cell. The current was then converted to a proportional voltage signal via the transimpedance amplifier, which was then fed as an input to the DAQ card. Note that the input impedance of the transimpedance amplifier is negligible.

The Labview program controlling the experimental set up was developed on an iterative basis over several stages, with each stage revealing information about the heating effect of electrical and/or light excitation on the device, and leading to improvements implemented in the following stage of development. These different excitation schemes are discussed in more detail in the coming sections of this chapter.
2.3 **The Pulsed Measurement Technique – Radiative Heating**

As mentioned earlier, the temperature mismatch associated between dark and illuminated conditions must be removed in order to obtain reliable measurements of the $J_{ph}$-$V$ characteristics. The method developed in this work to alleviate the temperature mismatch involved the use of a pulsed light source. $J_{light}$ would be recorded during the “on” cycle of the light pulse, and $J_{dark}$ would be recorded during the “off” cycle. If the pulse frequency was made sufficiently high, the device would have inadequate time to heat and cool, hence settling at an intermediate temperature $T_i$ between $T_d$ and $T_l$. The $J_{light}$-$V$ and $J_{dark}$-$V$ characteristics would thus be obtained at the same temperature, allowing a reliable determination of the $J_{ph}$-$V$ characteristics.

The first obvious question was: at what frequency should the LED be pulsed? To answer this question, the experimental set up was programmed to perform the following tasks (schematic illustration in Figure 2-5 below):

(A) Apply a non-pulsing DC voltage to the device and increment the voltage by 50 mV every 10 s.

(B) Pulse the LED at a user-defined frequency. In this case, 97 Hz and 997 Hz were investigated, corresponding to pulse widths of ~10 and ~1 ms respectively.

(C) Record the current-to-voltage signal and average over the multiple dark-light cycles at each voltage. To avoid recording transient device response and any amplifier signal overshoots\[^{52}\] (see Figure 2-6), only the last 10 μs of data (corresponding to 10 data points at a 1 MHz sampling rate) were collected and averaged during the “on” and “off” cycle of each pulse.
A schematic diagram of the excitation scheme used to investigate radiative heating. (A): A DC voltage is applied on the device, while (B): the light is pulsed at 50% duty cycle and a fixed frequency. (C): The current response of the device was expected to alternate between the dark current and the photocurrent.

The test device was a bulk heterojunction solar cell based on a blend of regioregular poly(3-hexylthiophene-2,5-diyl) [P3HT] as the donor and (6,6)-phenyl-C$_{61}$-butyric acid methyl ester [PCBM] as the acceptor with the structure ITO / PEDOT:PSS / P3HT:PCBM / Al. P3HT:PCBM-based solar cells have been extensively studied in the literature$^{33, 54}$, and devices with power efficiencies as high as 5% have been successfully fabricated.$^{15}$ They were therefore considered an appropriate test system for evaluating the pulsed measurement technique.
The time-varying response of the solar cell over a single LED on-off cycle. Here, the LED pulse frequency is 5 kHz, and the sampling rate is 1 MHz. A signal overshoot occurs when the applied voltage is stepped, but rapidly decays within a few microseconds. The slow response of the solar cell is also evident for the initial 20-30 μs after switching the LED on or off. To avoid recording both of these effects, only the last 10 μs of data were recorded.

The current-voltage characteristics of the same device were measured using the excitation scheme in Figure 2-5, at two very different light modulation frequencies, namely 97 Hz and 997 Hz.† In addition, a third current-voltage measurement was performed on the device with a Keithley 2400 using the standard DC method, i.e. sequential measurements of $J_{\text{light}}$ and $J_{\text{dark}}$ as described in Section 1.5.2. Subsequently, the $J_{\text{ph}}$-$V$ curves corresponding to each of the three measurement methods were calculated by subtracting $J_{\text{dark}}(V)$ from $J_{\text{light}}(V)$. The results are shown in Figure 2-7.

† Care was taken to avoid “nice” frequency values such as 100 or 1000 Hz to avoid interference from the harmonics of the 50 Hz grid.
All three curves correspond very closely with one another when $V < 0.6$ V, showing that the experimental set-up used for the pulsed measurement was behaving sensibly with no obvious deficiencies in its implementation. In addition, the data also shows that the test device was unaltered by the act of repeated measurement.

The two $J_{ph}$-$V$ curves from the pulsed measurement are virtually identical, suggesting that a pulse frequency of 97 Hz is sufficient to eliminate any temperature difference between the light and dark phases. Hence, the heating/cooling time of the device must be much larger than ~0.01 s (corresponding to ~100 Hz). The $J_{ph}$-$V$ curve measured by the standard DC method significantly exceeds the other two curves when $V$ increases beyond 0.6 V, due to the rapid growth of $J_{dark}$ (see Section 2.1.2). Hence, we conclude...
that the standard DC measurement is unreliable when the solar cell is subjected to an appreciable forward bias.

Figure 2-8 shows the dark current-voltage response of a similar test device as obtained during the LED “off” cycle of the pulsed measurement \[ J_{\text{dark}}^{\text{pulsed}}(V) \], and compared with the dark current measured by the standard DC method \[ J_{\text{dark}}^{\text{DC}}(V) \]. There is a small offset between the two curves, with the \[ J_{\text{dark}}^{\text{pulsed}} - V \] curve being slightly larger than the \[ J_{\text{dark}}^{\text{DC}} - V \] curve. This is consistent with the device temperature settling at an intermediate temperature \( T_i \) that is larger than \( T_d \) during the pulsed measurement, since \[ J_{\text{dark}}^{\text{pulsed}}(V, T_i) > J_{\text{dark}}^{\text{DC}}(V, T_d) \].

![Figure 2-8](image)

\( J_{\text{dark}} - V \) curves as measured by the standard DC method and during the LED off-cycle of the pulsed scheme. The magnified inset shows the offset more clearly, which is on the order of a few mA/cm\(^2\). Note that the pulsed measurement gives a slightly higher value due to radiative heating from the LED when the \( J_{\text{dark}} \) signal is not being recorded.
2.4 **The Effect of Resistive Heating**

In addition to the effects of radiative heating – which could be circumvented by modulating the light source at a frequency of ≥ 100 Hz as shown in the previous section – it was proposed that heating of the solar cell may also occur electrically due to the device’s inherent resistance to current flow. The diode characteristic of a solar cell suppresses current when reverse biased, but allows a large current under forward bias, therefore it is plausible that the solar cell being tested will be hotter at e.g. 2 V than at -1 V. This resistive heating – if present – would lead to a temperature mismatch across the voltage sweep. In order to test this hypothesis, we applied a pulsed voltage to the device and varied its duty cycle\(^\text{1}\), so that we could adjust the amount of resistive heating of the test device. The dark current-voltage curves thus obtained were then compared and used to “diagnose” any internal temperature changes in the solar cell. For these measurements, the experimental set up was programmed to perform the following tasks:

(A) Apply a voltage pulsed at ~1 kHz with a duty cycle of 10%. (At 10% duty cycle, each pulse has a duration of ~100 μs.)

(B) Keep the LED light source switched off completely.

(C) Record the current-to-voltage signal and calculate the average over the multiple voltage pulses. (Again, only the last 10 μs from each ‘on’ pulse was used for averaging.)

Figure 2-9 schematically illustrates the voltage pulses used to excite the device as described above.

\(^{1}\) The duty cycle is defined as the ratio of the “on” duration of the pulse to the period of a single full cycle.
A schematic diagram of an excitation scheme used to investigate the effects of resistive heating. (A): The applied voltage is pulsed at 1 kHz with a 10% duty cycle, while (B): the LED is switched off. (C): The current response is expected to be in the form of dark current pulses synchronised with the voltage pulses.

The pulsed voltage scheme was applied to an ITO / PEDOT:PSS / P3HT:PCBM / Al test device to obtain the $J_{\text{dark}}^{\text{pulsed}}$ - $V$ curve in Figure 2-10. The $J_{\text{dark}}^{\text{DC}}$ - $V$ curve, obtained through a standard DC current-voltage sweep of the same device, is also shown for comparison. At high forward biases, the DC measurement gives an appreciably higher current, indicating that the device is warmer when subject to a DC voltage, and cooler under the pulsed voltage. This result is consistent with the hypothesis of resistive heating, since the average resistive heating experienced by a device under a pulsed voltage is much less than when under a DC bias.
Having demonstrated that some device heating due to current flow is clearly present, the next question was: how would this affect the measurement of corrected photocurrent-voltage characteristics? At any one particular applied voltage, we can modulate the light source to obtain $J_{\text{light}}$ and $J_{\text{dark}}$ at effectively the same temperature, and hence obtain a “true” $J_{\text{ph}}$ value for that applied voltage at an intermediate temperature $T_i$ between $T_l$ and $T_d$. However, due to resistive heating, $T_i$ will be larger at, for example, 2 V than at -1 V. Hence, the $J_{\text{ph}}$-$V$ curve would reflect an increasing temperature as the applied voltage increases, with the incurred temperature-induced error dependent on the actual temperature dependence of the corrected photocurrent. To see the magnitude of this error in the $J_{\text{ph}}$-$V$ characteristics, we re-introduced pulsed light into the measurement scheme and compared $J_{\text{ph}}$-$V$ curves as measured with 1) a DC applied voltage, and 2) a pulsed voltage. To this end, the experimental set up was programmed to perform the following tasks:
(A) Apply either: 1) a DC voltage, or 2) a ~1 kHz, 10% duty cycle pulsed voltage to the device, corresponding to a pulse width of 100 μs.

(B) For both applied voltage schemes, pulse the LED at ~0.5 kHz (exactly half the frequency of the voltage pulses) with a duty cycle of 5%, corresponding to a pulse width of 100 μs. The light pulses are synchronised with the voltage pulses so that the device is illuminated on every alternate voltage pulse.

(C) Record and average the signal using only the last 10 μs of data of each signal pulse.

**Figure 2-11**

Schematic of an excitation scheme designed to investigate the effect of resistive heating. **Pulsed Voltage:** (A): The applied voltage is pulsed at ~1 kHz and (B): the light source pulsed at exactly half that frequency. Both voltage and light pulses have widths of 100 μs, and are synchronised so that the device is illuminated on every alternate voltage pulse. **(C):** The expected device response has alternating 100 μs $J_{\text{light}}$ and $J_{\text{dark}}$ pulses. **DC Voltage:** (A): This excitation scheme uses a DC voltage and (B): 100 μs light pulses. **(C):** The current response is expected to be $J_{\text{dark}}$ throughout except when the light is pulsed on, during which time the device responds with $J_{\text{light}}$ for 100 μs.
The schematic of the pulsed measurement scheme involving pulsed light and voltage is shown in Figure 2-11(Left), while the scheme with DC voltage and pulsed light is shown in Figure 2-11(Right). The only difference between the two schemes is the voltage duty cycle.

The $J_{ph}-V$ characteristics were obtained for the same test device with the excitation schemes shown in Figure 2-11, and are shown in Figure 2-12.

![Figure 2-12](image)

**Figure 2-12**
A comparison between corrected photocurrent-voltage curves obtained using the schemes shown in Figure 2-11. The two schemes use: 1) a DC voltage with pulsed light, and 2) a pulsed voltage with pulsed light. The curves correspond closely with each other throughout the measurement range, although a slight discrepancy is seen at high forward biases (> 1 V).

The two $J_{ph}-V$ curves correspond closely with each other throughout the measurement voltage range, indicating that the $J_{ph}-V$ measurement was relatively insensitive to the temperature difference across the voltage sweep arising from resistive heating. This is likely due to the corrected photocurrent being only weakly dependent on temperature for the small range of temperatures across the voltage sweep arising from resistive heating.
Combining this result with the findings from the previous section on circumventing radiative heating effects, we conclude that fairly reliable $J_{ph}$-$V$ characteristics may be obtained as long as the light source is modulated at frequencies of $\sim$100 Hz or more. Nonetheless, for the purposes of good practice, we decided to make one final change to the measurement procedure that would in principle eliminate even the progressive heating of the device across the voltage sweep, whilst also speeding up the measurement procedure. This is described in the next section.

### 2.5 Repeating Voltage Sweeps and Pulsed Light

From the results presented in the previous two sections, it was learnt that reliable measurements of $J_{ph}$ may be obtained as long as the light is modulated at a frequency of $\sim$100 Hz or more to avoid a temperature mismatch when the device is under dark and illuminated conditions. The differential heating effect during a voltage sweep – due to current flow – is a much smaller effect and could even be considered insignificant. Therefore, an excitation scheme with a DC voltage and modulated LED illumination would suffice to obtain fairly reliable measurements of $J_{ph}$. Two viable measurement schemes were described in the previous section – one involving a DC applied voltage and the other a pulsed voltage. Both have their drawbacks, however, as the DC voltage scheme stresses the device over a prolonged period without actually recording data, while the pulsed voltage scheme leaves the device unprobed for a large proportion of the measurement time. These schemes either degrade the device (for the DC voltage scheme) or slow down the measurement unnecessarily (for the pulsed voltage scheme).
To circumvent these drawbacks, a new excitation scheme was programmed to perform the following tasks (schematic illustration in Figure 2-13):

(A) Apply voltage steps of width ~200 μs and step height 20 mV to complete a full voltage sweep. Repeat the voltage sweep several hundred times to obtain multiple $J_{\text{light}} - J_{\text{dark}}$ data for averaging.

(B) Synchronise the LED to switch on during the second half of each voltage step, corresponding to a pulse width of ~100 μs and a frequency of ~5 kHz.

(C) As before, record and average data from the last 10 μs of each half-step.

The key advantages of this scheme over those in Section 2.4 are:

- Since the device is not subject to any “dead time”, the measurement time is much shorter.

- The modulation of the full voltage sweep in principle minimises the progressive heating across the sweep (due to resistive heating), since the device changes rapidly between low- and high-bias states.
A schematic diagram of the final pulsed excitation scheme and the expected device current-voltage response. (A): Each voltage step has a time width of 200 μs and the full sweep is repeated several hundred times. (B): The light pulses, with a time width of 100 μs each, were programmed to illuminate the device for the second half of each voltage step. (C): The expected current response of the device.

The 5 kHz LED modulation frequency was sufficient to prevent any appreciable temperature difference between the dark and illuminated conditions. Figure 2-14 shows the time-varying current response of an ITO / PEDOT:PSS / P3HT:PCBM / Al device under this pulsed excitation scheme, after averaging over 200 complete cycles. Here, the voltage was swept from -1 V to 1.8 V in steps of 20 mV of 200 μs each, with one complete cycle requiring 28 ms (corresponding to a sweep frequency of ~36 Hz), as shown in
the staircase plot at the bottom of the figure. The magnified inset in the upper portion of the figure shows that some signal overshooting occurs when there is a step change in applied voltage. As mentioned previously, the source of the overshoot was likely from the transimpedance amplifier\[52\], but did not pose a serious problem because it decayed within a few microseconds, and only the last 10 μs of data from each half-step was used.

![Staircase plot and time-dependence of measured device response](image)

**Figure 2-14**

*Lower*: A staircase plot showing the variation of the applied voltage with time for the pulsed scheme. The voltage is incremented in steps of height 20 mV and duration 200 μs. The LED was programmed to illuminate the solar cell for the second half of each voltage step. *Upper Main*: The time-dependence of the measured device response. *Upper inset*: Expanded view of the time-dependence of the measured response, showing alternating dark current and photocurrent responses.

Finally, a comparison was made between the $J_{ph}$-$V$ curves as measured by:

1) the standard DC method,

2) the measurement scheme with pulsed voltage (1 kHz, 10% duty cycle) and pulsed light (0.5 kHz, 5% duty cycle) (see Figure 2-11A), and
3) the measurement scheme with repeating voltage sweeps and pulsed light (Figure 2-13).

The results of the three approaches are shown in Figure 2-15.

![Corrected photocurrent-voltage curves](image)

**Figure 2-15**  
Corrected photocurrent-voltage curves obtained using: 1) the standard DC method, 2) pulsed voltage and pulsed light, and 3) repeating voltage sweeps and pulsed light.

Below ~0.6 V, all three methods are equivalent, but (2) and (3) diverge from (1) when $V > ~0.6$ V. (2) and (3) overlap almost perfectly, with the exception being a slight difference for $V > 0.9$ V, likely due to a slight temperature difference attributable to electrical resistive heating. The technique of Figure 2-13 is considered more reliable for the reasons outlined above.

### 2.6 Conclusions

The standard literature method of obtaining the corrected photocurrent by measuring successive current-voltage sweeps in the dark and under
illumination is applicable only when the solar cell is under relatively low bias. At higher applied voltages, it results in serious errors due to a temperature mismatch between the illuminated and un-illuminated device. A new technique, based on the use of modulated light to excite the solar cell, was devised to overcome this problem. Our technique underwent a number of iterations to improve acquisition times and reduce secondary errors associated with electrically-induced heating. The final method that we settled on involves modulating the light source and performing rapid voltage sweeps repeatedly. The technique agrees well with the standard method under low applied biases, but removes the temperature mismatch so that a reliable estimate of the corrected photocurrent can also be obtained under high forward bias. We cannot directly validate the corrected photocurrents we obtain with the pulsed technique, because – to the best of our knowledge – there have not been any reliable reports in the literature of corrected photocurrent measurements under high applied voltages. However, as we will show in the subsequent chapters, the results we obtain are completely consistent with standard drift-diffusion models of device operation.
Using the pulsed measurement technique, the corrected photocurrent-voltage characteristics of various bulk heterojunction solar cells are measured. The highly anti-symmetric curves thus obtained are rationalised using a simple physical model.
CHAPTER 3

THE ANTI-SYMMETRIC CORRECTED PHOTOCURRENT-VOLTAGE RESPONSE

3.1 INTRODUCTION

Organic bulk heterojunction solar cells based on blends of poly[2-methoxy-5-(3',7”-dimethyloctyloxy)-p-phenylenevinylene] (MDMO-PPV, donor) and (6,6)-phenyl-C_{61}-butyric acid methyl ester (PCBM, acceptor) have been extensively studied in the literature\cite{27, 29, 55}, and devices with power efficiencies as high as 2.5\%\cite{27} have been successfully fabricated. Although chronologically, the first devices that we studied were based on P3HT:PCBM blends, we begin our discussion here with MDMO-PPV:PCBM-based devices since their current-voltage characteristics are more easily understood.

![Chemical structures of MDMO-PPV and PCBM](image)

**Figure 3-1**

The chemical structures of the donor polymer poly[2-methoxy-5-(3',7”-dimethyloctyloxy)-p-phenylenevinylene] [MDMO-PPV] and the acceptor molecule (6,6)-phenyl-C_{61}-butyric acid methyl ester [PCBM].

The MDMO-PPV:PCBM devices had the following structure: ITO / PEDOT:PSS / MDMO-PPV:PCBM / Ag. Standard procedures for cleaning the ITO substrate and spin-coating the PEDOT:PSS, as described in Chapter 1,
were followed. The blend layer (of approximate thickness 80 nm) was spin-coated directly on the PEDOT:PSS layer at 1500 rpm for 30 s, from a chlorobenzene solution containing 3.5 mg/ml of MDMO-PPV (Sigma-Aldrich) and 14 mg/ml of PCBM (American Dye Source). The sample was dried on a hotplate at 60 °C for one hour, before being loaded into a vacuum chamber, where 140 nm of Ag metal was deposited by thermal evaporation through a shadow mask to complete the device. No thermal annealing of the device was undertaken since protocols reported in the literature tend not to involve thermal annealing\[56, 57\] (we rationalise this in the following chapter). All measurements were performed under dry nitrogen.

3.2 **The anti-symmetric profile of the corrected photocurrent**

The $J_{\text{dark}}$-$V$, $J_{\text{light}}$-$V$ and $J_{\text{ph}}$-$V$ curves were determined with the pulsed measurement scheme using voltage steps of 20 mV and an instantaneous LED light intensity of 90.2 mW/cm$^2$.

The results are shown in Figure 3-2, together with an inset showing the spectral response of the device under low intensity illumination. Under the quoted illumination level, the device had an overall quantum efficiency of 11.4% (determined over the approximate spectral range of the solar cell, 300-700 nm) and an open-circuit voltage of 0.71 V. The $J_{\text{dark}}$-$V$ and $J_{\text{light}}$-$V$ curves are fairly standard in appearance and are similar to those reported elsewhere in the literature.\[57\] The $J_{\text{ph}}$-$V$ curve, however, is more interesting since it has a highly anti-symmetric appearance.
Figure 3-2
Current-voltage characteristics for an ITO / PEDOT:PSS / MDMO-PPV:PCBM / Ag device as measured by the pulsed technique. The $J_{\text{light}}-V$ and $J_{\text{ph}}-V$ curves were obtained under an instantaneous light intensity of 90.2 mW/cm². Inset: Spectral response of the device under low intensity illumination and short-circuit conditions.

The curve is reproduced in Figure 3-3A, where it has been divided into two zones to the left (L) and right (R) of a selected voltage that we refer to as the point of optimal symmetry (POS). To aid visualization, the left side of the data has been rotated 180° about the POS to generate a new curve (L$^{\text{rot}}$) that overlaps closely with the right-side data. The POS is simply the voltage that yields the optimal overlap between L$^{\text{rot}}$ and R. The POS occurs at a voltage of $V_{\text{POS}} = 0.80$ V and a current of $J_{\text{POS}} = 0.25$ mA/cm². The slope of the $J_{\text{ph}}-V$ curve as a function of the applied voltage is plotted in Figure 3-3B and is seen to decrease monotonically either side of the POS, a point that we will return to later.
Figure 3-3

(A): The $J_{ph}$-$V$ curve for the ITO / PEDOT:PSS / MDMO-PPV:PCBM / Ag device from Figure 3-2. The data has been divided into two parts to the left (L) and right (R) of the point of optimal symmetry (POS) at $V = 0.80 \pm 0.01$ V. The left side has been rotated by 180° about the POS to create a new curve (L$^{rot}$) that overlaps closely with R, implying a high degree of anti-symmetry in the $J_{ph}$-$V$ characteristics. (B): The slope of the $J_{ph}$-$V$ curve as a function of applied voltage. The slope peaks at $V_{POS}$ and decreases monotonically at higher and lower voltages.

The quality of overlap between L$^{rot}$ and R is highly sensitive to the choice of the point about which the curve L is rotated. Figure 3-4 compares the overlap of these two curves as the rotational point $V_{rot}$ (marked by an asterisk) is varied over a small range from 0.78 V to 0.82 V in steps of 0.01 V. To quantify the quality of the overlap, we define a “discrepancy value” $D$ between L$^{rot}$ and R for a voltage range $V_{rot} \pm \Delta V$:

$$D = \sum_{V=V_{rot}}^{V_{rot}+\Delta V} \left( J_{ph}^R - J_{ph}^{L^{rot}} \right)^2 V_{int}$$  \hspace{1cm} (3.1)$$

where $J_{ph}^R$ and $J_{ph}^{L^{rot}}$ are the $J_{ph}$ values along the curves R and L$^{rot}$ respectively, and $V_{int}$ is the uniform voltage interval of the data. The discrepancy was
calculated for each $V_{\text{rot}}$ over the same range $\Delta V = 0.5$ V and is printed with each plot in Figure 3-4.

**Figure 3-4**

Magnified plots of the $R$ and $L_{\text{rot}}$ curves from Figure 3-3, each corresponding to a slightly different choice of rotational point: (A): $V_{\text{rot}} = 0.78$ V, (B): $V_{\text{rot}} = 0.79$ V, (C): $V_{\text{rot}} = 0.80$ V, (D): $V_{\text{rot}} = 0.81$ V, (E): $V_{\text{rot}} = 0.82$ V. The quality of overlap, as determined both visually and by the figure of merit $D$, is clearly optimised when $V_{\text{rot}} = 0.80$ V.
Clearly, the optimum overlap between the two curves is obtained when $V_{\text{rot}} = 0.80 \text{ V}$, and this is the value that determines the point of optimal symmetry in Figure 3-3. A shift of just 0.01 V either side from the POS increases the discrepancy by more than an order of magnitude and results in a clear visual worsening of the overlap. Hence, the errors associated with determining $V_{\text{POS}}$ are quite small.

### 3.3 Analysis of the Anti-Symmetric Profile

It is worth stressing again that symmetric plots of the kind shown in Figure 3-3 have not (as far as we are aware) been reported previously in the literature due to the deficiencies of the prevalent method of determining the $J_{\text{ph}}-V$ characteristics (see Section 2.1.2).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3-5.png}
\caption{(A): Energy level diagrams of an ITO / PEDOT:PSS / MDMO-PPV:PCBM / Ag device, showing donor and acceptor HOMO and LUMO levels and electrode Fermi levels. The blend layer was treated as a composite semiconductor, in which the HOMO and LUMO levels were derived from the donor HOMO level and the acceptor LUMO level, respectively. (B): There are no energy barriers to the extraction of electrons or holes at either electrode.}
\end{figure}

The remarkable anti-symmetry in the $J_{\text{ph}}-V$ characteristics of the MDMO-PPV:PCBM device may be rationalised by treating the active blend layer as a...
single layer of composite semiconductor, in which the HOMO level is derived from the donor (~ -5.2 eV\textsuperscript{29}), and the LUMO level is derived from the acceptor (~ -4.3 eV\textsuperscript{58}). This single layer is sandwiched between a PEDOT:PSS anode and a Ag cathode, which have work functions of ~5.2 eV\textsuperscript{59} and ~4.4 eV\textsuperscript{13} respectively.

As illustrated in Figure 3-5B, the Fermi levels of the two electrodes lie within the effective HOMO-LUMO gap, so there are no energy barriers to the extraction of electrons or holes at either electrode. The corrected photocurrent $J_{ph}$ may be decomposed into separate drift and diffusive contributions:

$$J_{ph} = [J_{ph}^{\text{diff}}] + [J_{ph}^{\text{drift}}]$$

$$= e \left[-D_h \frac{\partial n_{h}^{\text{ph}}(x)}{\partial x} + D_e \frac{\partial n_{e}^{\text{ph}}(x)}{\partial x}\right] + e \left[\mu_h n_{h}^{\text{ph}}(x)E(x) + \mu_e n_{e}^{\text{ph}}(x)E(x)\right]$$  \hspace{1cm} (3.2)

where $D$ is the diffusivity, $\mu$ is the carrier mobility, $e$ is the electronic charge, $E$ is the internal electric field strength, the subscripts $e$ and $h$ denote electrons and holes respectively, $x$ is the distance from the anode, and $n_{e}^{\text{ph}}$ and $n_{h}^{\text{ph}}$ represent the steady-state distributions of photogenerated electrons and holes respectively. At steady-state, the current $J_{ph}$ is constant throughout the entire device so, taking spatial averages (<…>) of each term across the entire device thickness, we obtain without loss of generality:

$$J_{ph} = e \left[-D_h <\frac{\partial n_{h}^{\text{ph}}(x)}{\partial x}> + D_e <\frac{\partial n_{e}^{\text{ph}}(x)}{\partial x}>\right] + e \left[\mu_h <n_{h}^{\text{ph}}(x)E(x)> + \mu_e <n_{e}^{\text{ph}}(x)E(x)>\right].$$  \hspace{1cm} (3.3)

The diffusive term can be further simplified with the application of the identity

$$<\frac{df(x)}{dx}> = \frac{1}{x_2 - x_1} \int_{x_1}^{x_2} \frac{df(x)}{dx} dx = \frac{f(x_2) - f(x_1)}{x_2 - x_1},$$  \hspace{1cm} (3.4)
where \( f(x) \) is an arbitrary function of \( x \), and \( x_1, x_2 \) represent the lower and upper spatial limits over which the average is calculated. Hence we can rewrite Equation (3.3) as:

\[
J_{ph} = e \left[ -D_h \frac{n_{ph}^h(d) - n_{ph}^h(0)}{d} + D_e \frac{n_{ph}^e(d) - n_{ph}^e(0)}{d} \right] \\
+ e \left[ \mu_h < n_{ph}^h(x)E(x) > + \mu_e < n_{ph}^e(x)E(x) > \right] \\
(3.5)
\]

where \( d \) is the thickness of the device and \( x = 0 \) and \( x = d \) represent the locations of the anode and cathode, respectively. Under ordinary light levels, the internal field may be considered uniform throughout the device\(^{[14]}\), so Equation (3.5) further simplifies to:

\[
J_{ph} = e \left[ -D_h \frac{n_{ph}^h(d) - n_{ph}^h(0)}{d} + D_e \frac{n_{ph}^e(d) - n_{ph}^e(0)}{d} \right] \\
+ e \left[ \mu_h < n_{ph}^h(x) > + \mu_e < n_{ph}^e(x) > \right] E. \\
(3.6)
\]

The rapid barrier-free extraction of photogenerated carriers at the electrodes depletes their concentration at the electrodes, so to a good approximation, we may write:

\[
n_{ph}^h(0) = n_{ph}^h(d) = n_{ph}^e(0) = n_{ph}^e(d) = 0. \tag{3.7}
\]

This effectively reduces the spatially averaged diffusive current to zero, so Equation (3.6) simplifies to:

\[
J_{ph} = e \left[ \mu_h < n_{ph}^h(x) > + \mu_e < n_{ph}^e(x) > \right] E \\
(3.8)
\]

Since the internal field is

\[
E = \frac{V - V_{bi}}{d}, \tag{3.9}
\]
it follows directly from Equation (3.8) that $J_{ph}$ should reduce to zero at the built-in potential, where $E = 0$. The average carrier densities $\langle n_e^{ph} \rangle$ and $\langle n_h^{ph} \rangle$ are determined by the average dwell-times of the electrons and holes inside the device, which vary inversely with the drift-speed and hence inversely with $|E|$, and (for a reasonably flat generation profile) should therefore be even functions of the internal field strength. The electron and hole mobilities may also exhibit field dependences, but these too are even functions of the internal field strength. The term in square brackets in Equation (3.8) is therefore an even function of the electric field. It follows that $J_{ph}$ is an odd function of the internal electric field and an anti-symmetric function of the applied voltage with a symmetry point at $(V_{BI}, 0)$.

This result implies that the voltage at the point of optimal symmetry $V_{POS}$ from Figure 3-3 corresponds to the built-in potential $V_{BI}$. Close examination of the experimental $J_{ph}$-$V$ data indicates a slight non-zero photocurrent at the POS ($J_{POS} \sim 4\%$ of the short-circuit current), which does not agree fully with the theoretical analysis. We overlook this slight discrepancy for now but will return to it shortly.\(^5\)

For the ITO / PEDOT:PSS / MDMO-PPV:PCBM / Ag device, the built-in potential implied by the point of optimal symmetry is 0.80 V. This value is consistent with the work functions of the PEDOT:PSS anode and the Ag cathode which, based on the difference between the electrode work functions, would be expected to yield a built-in potential of $5.2 - 4.4 = 0.8$ V (Figure 3-5). The pulsed technique therefore offers a novel means of determining the built-

\(^5\) In devices based on donor-acceptor blends other than MDMO-PPV:PCBM, much larger photocurrents have been observed at the POS; we defer a detailed discussion on the physical significance of $J_{POS}$ to a subsequent section.
in potential without resorting to more complex measurements such as electroabsorption\textsuperscript{35, 60}.

### 3.4 Charge Carrier Selectivity at the Electrodes

Having rationalised the remarkable anti-symmetry exhibited by the corrected-photocurrent-voltage characteristics of the MDMO-PPV:PCBM-based device with a simple physical model, we return to the results obtained using the P3HT:PCBM-based device which we touched on briefly in Chapter 2. BHJ solar cells based on blends of P3HT and PCBM have been widely-studied in the literature, and have yielded some of the highest reported efficiencies to date (~5\%).\textsuperscript{15, 54, 61}

![Figure 3-6](image)

The chemical structure of regioregular poly(3-hexylthiophene-2,5-diyl) [P3HT], which is used as an electron donor.

BHJ solar cells with the structure ITO / PEDOT:PSS / P3HT:PCBM / Al were investigated. Samples of ITO / PEDOT:PSS were prepared according to the procedures described in Chapter 1. Blend films of approximate thickness 100 nm were spin-coated from a solution containing 15 mg/ml each of P3HT (Sigma-Aldrich) and PCBM (American Dye Source) in chlorobenzene, and subsequently heated to 60 °C for one hour to drive away excess solvent. A 100 nm layer of Al was deposited by thermal evaporation under a pressure of < 10\textsuperscript{-5} mbar. Post-fabrication annealing of the devices was carried out at
140 °C for 20 mins, in accordance with published protocols.\cite{15, 62} (This widely-practiced procedure, which differs from the procedure for MDMO-PPV:PCBM devices, will be rationalised in the next chapter.)

The pulsed technique was used to obtain the current-voltage characteristics of the P3HT:PCBM device under an instantaneous light intensity of 27.6 mW/cm$^2$ using voltage steps of 20 mV. As with the MDMO-PPV:PCBM device, the resultant $J_{ph}$-$V$ curve is highly anti-symmetric in shape (Figure 3-7). The curve has again been divided into two zones to the left (L) and right (R) of the point of optimal symmetry, defined by the coordinates ($V_{POS}$, $J_{POS}$), and to aid visualisation, the data in the left zone has been rotated about the POS to form a new curve $L_{rot}$ that overlaps closely with R. (Again, the POS is the voltage that yields the optimum overlap between $L_{rot}$ and R.)

![Figure 3-7](image)

The corrected photocurrent-voltage curve of an ITO / PEDOT:PSS / P3HT:PCBM / Al device as measured by the pulsed technique. The data has been divided into two zones to the left (L) and right (R) of the point of optimal symmetry (POS) at $V = 0.60 \pm 0.01$ V. The left side has been rotated by 180° about the POS to create a new curve ($L_{rot}$) that overlaps closely with R, implying a high degree of anti-symmetry in the $J_{ph}$-$V$ characteristics.
Here, the POS occurs at $V_{\text{POS}} = 0.60 \pm 0.01$ V, with the resultant $L^\text{rot}$ and $R$ curves showing a very close correspondence in the vicinity of the POS, implying near-perfect anti-symmetry in this voltage range ($V \sim V_{\text{POS}}\pm 0.2$ V). At higher voltages, the two curves diverge slightly with $R$ being somewhat larger in magnitude. Based on the discussion in the previous section, the built-in potential of the P3HT:PCBM device, as implied by the value of $V_{\text{POS}}$, is found to be $0.60 \pm 0.01$ V. In contrast to the MDMO-PPV:PCBM device, the corrected photocurrent $J_{\text{POS}}$ at the point of optimal symmetry is relatively large at $-1.50$ mA/cm$^2$, which is roughly 50% of the short-circuit current – an important observation that we will return to shortly.

In the P3HT:PCBM devices investigated here, treating the blend layer as a single composite semiconductor yielded a HOMO level of -5.1 eV and LUMO level of -4.3 eV$^{[58]}$, as derived from the donor HOMO and acceptor LUMO levels, respectively. As shown in Figure 3-8, the Fermi level of the PEDOT:PSS anode (-5.2 eV$^{[59]}$) is lower than the donor HOMO level and the Fermi level of the Al cathode (-4.2 eV$^{[13]}$) is higher than the acceptor LUMO level. Due to energy level pinning, the electrode Fermi levels are constrained

\[
\begin{align*}
\Phi_{\text{Anode}} & \sim 5.2 \text{ eV} \\
\Phi_{\text{Cathode}} & \sim 4.2 \text{ eV} \\
\text{HOMO(D)} & \sim -5.1 \text{ eV} \\
\text{LUMO(D)} & \sim -3.2 \text{ eV} \\
\text{HOMO(A)} & \sim -5.6 \text{ eV} \\
\text{LUMO(A)} & \sim -4.3 \text{ eV}
\end{align*}
\]
to lie within the derived LUMO-HOMO energy gap of the composite semiconductor.\textsuperscript{[60, 63]} The anode and cathode Fermi levels would therefore be expected to pin to the donor HOMO and acceptor LUMO levels respectively, giving an estimated built-in potential of $5.1 - 4.3 = 0.8$ V.

This simple 0.8 V estimate of $V_{\text{BI}}$ is, however, quite far from the value of 0.60 V inferred from the POS of the anti-symmetric $J_{\text{ph}}-V$ characteristics. Electromodulation (EM) spectroscopy (performed by Rui Jin in Imperial College) was therefore used to directly measure the built-in potential to validate the value implied by the POS. If the origin of the EM signal is electroabsorption (\textit{i.e.} the Stark effect), the first-harmonic signal of the differential transmission ($\Delta \tau/\tau$) will vary linearly with the DC offset bias $V_{\text{DC}}$ [see Equation (1.35), Section 1.5.4], and vanish when $V_{\text{DC}} = V_{\text{BI}}$.\textsuperscript{[35]}

Figure 3-9A shows the first-harmonic electromodulation spectrum obtained with a 6 kHz, 0.3 V AC voltage and under a DC reverse bias of -2 V. The spectrum shows a number of oscillatory features with peaks at 538, 578 and 624 nm and nodes at 558 and 596 nm (and additional less well-resolved features below 538 nm), typical of electroabsorption (EA). Under forward bias, however, the EA signal is obscured by strong charge-induced absorption features that mask the weaker EA signal.\textsuperscript{[39]} The inset shows the EM signal measured under a forward bias of 1 V, together with the EA signal that would be expected on the basis of the reverse-bias spectrum and Equation (1.35). They are quite different, showing that charge-related features dominate the signal in forward bias. In consequence, reliable estimates of the built-in potential must be obtained using reverse-bias data only.
Figure 3-9

(A) Main: The reverse-bias 1st-harmonic electromodulation (EM) spectrum of the ITO / PEDOT: PSS / P3HT:PCBM / Al device, obtained with a 6 kHz 0.3 V AC bias, at a DC offset of -2 V. Inset: The actual forward-bias EM spectrum of the device, obtained with a 6 kHz 0.3 V AC bias at a DC offset of +1 V (black), and the spectrum that would be expected on the basis of the reverse-bias spectrum if the signal were purely due to electroabsorption (red). (B): The DC bias dependence of the 1st-harmonic EM response at 644 nm. The signal varies linearly with DC bias in accordance with Equation (1.35) until a bias of 0 V and then deviates strongly due to charge-induced modulation. The built-in potential was determined by using the initial twelve reverse-bias data points – which are uncontaminated by charge-induced features – and then extrapolating to zero, yielding a value $V_{bi} = 0.59 \pm 0.02$ V.

The DC-bias dependence of the 1st-harmonic EM response at 644 nm is shown in Figure 3-9B using a 6 kHz, 0.3 V AC bias. The EM signal varies linearly with DC bias in accordance with Equation (1.35) from -2 up to 0 V, and then deviates strongly, exhibiting features due to charge-induced modulation. The built-in potential was determined by using the twelve initial reverse-bias data points – which are not contaminated by charge-induced features – and then extrapolating to zero. This yields a value $V_{bi} = 0.59 \pm 0.02$ V, which coincides with the point of optimal symmetry extracted from the anti-symmetric $J_{ph}$-V characteristics.
In the previous section, it was shown from standard drift-diffusion equations that:

\[ J_{ph} = e \left[ \mu_h < n_{h}^{ph}(x) > + \mu_e < n_{e}^{ph}(x) > \right] E, \]  

(3.10)

which successfully explained the anti-symmetric shape of the \( J_{ph}-V \) curve for the ITO / PEDOT:PSS / MDMO-PPV:PCBM / Ag device. However, as observed earlier for the ITO / PEDOT:PSS / P3HT:PCBM / Al device (Figure 3-7), the \( J_{ph}-V \) curve is anti-symmetric about a point \( (V_{POS}, J_{POS}) \), where \( V_{POS} \) corresponds to the built-in potential \( V_{BI} \) and \( J_{POS} \) is a large negative photocurrent -1.50 mA/cm\(^2\), or roughly 50% of the short-circuit current. Equation (3.10) explains why the anti-symmetry point occurs at \( V_{BI} \), but fails to account for the observed negative current \( J_{POS} \) at this voltage. This suggests that the representation of an ITO / PEDOT:PSS / P3HT:PCBM / Al solar cell as a single layer device with non-selective electrodes is flawed. The negative current \( J_{POS} \) can be rationalised by assuming that at least one of the two electrodes is self-selective, i.e. preferentially selective towards its own carrier type; the anode to holes and/or the cathode to electrons. For the sake of argument, we will consider the case where the anode (at \( x = 0 \)) is self-selective and the cathode is non-selective. This gives rise to a situation in which \( n_{h}^{ph}(0) = n_{e}^{ph}(d) = n_{e}^{ph}(d) = 0 \) as before (due to rapid extraction), but \( n_{e}^{ph}(0) > 0 \).

In this case, we obtain for the spatially-averaged diffusive photocurrent:

\[ J_{ph}^{diff} = e \left[ -D_h \frac{n_{h}^{ph}(d) - n_{h}^{ph}(0)}{d} + D_e \frac{n_{e}^{ph}(d) - n_{e}^{ph}(0)}{d} \right] \]

(3.11)

Hence, \( J_{ph} \) can be written as:
\[ J_{ph} = \left[ -\frac{eD_en_e^{ph}(0)}{d} \right] + e\left[ \frac{\mu_h < n_h^{ph}(x) > + \mu_e < n_e^{ph}(x) >}{E} \right] \]

(3.12)

In the event that \( n_e^{ph}(0) \) is independent of (or only weakly dependent on) the electric field \( E \), the anti-symmetric appearance of the \( J_{ph}-V \) curve will be retained, except the symmetry point will be offset in the direction of negative current by an amount \( eD_en_e^{ph}(0)/d \). The symmetry point would be similarly offset in the negative direction by an amount \( eD_en_e^{ph}(d)/d \) if the cathode were self-selective. Since the \( J_{ph}-V \) curve in Figure 3-7 is nearly perfectly anti-symmetric in the central portion (\( V \sim V_{bi} \pm 0.2 \text{ V} \)) of the curve, we conclude that the carrier densities at the electrodes are indeed independent of (or only weakly dependent on) the electric field in the vicinity of the built-in potential.

Self-selectivity of the electrodes – as the data implies is the case for the P3HT:PCBM device – leads to a beneficial increase in device efficiency since it yields a larger (more negative) photocurrent \( J_{light} \) than would otherwise be obtained in the operating range of the solar cell (\( 0 < V < V_{oc} \)). A previous study in the literature showed that devices with the structure ITO / CuPC / CuPC:C_{60} / C_{60} / Al had a higher short-circuit current and power efficiency than a device with structure ITO / CuPC:C_{60} / Al.\textsuperscript{[64]} Although the study was not specifically carried out with self-selectivity in mind, the results are consistent with the findings in this work. In devices with non-selective electrodes, the undesired extraction of electrons at the anode and holes at the cathode constitutes a loss mechanism since it generates a positive current that partially opposes the negative photocurrent arising from the extraction of carriers at the correct electrodes.

One possible explanation for the observed self-selectivity is the use of PEDOT:PSS, which has previously been found to block electrons in

\[ \text{CHAPTER 3} \]

\[ \text{THE ANTI-SYMMETRIC CORRECTED PHOTOCURRENT-VOLTAGE RESPONSE} \]
polyfluorene-based devices\textsuperscript{[65, 66]} due to the formation during annealing of a thin layer of insoluble polyfluorene at the surface of the PEDOT:PSS\textsuperscript{[67]}. However, we found no evidence of a similar insoluble layer when P3HT:PCBM was annealed on top of PEDOT:PSS; brief immersion in chlorobenzene removed all traces of the P3HT and PCBM absorption spectra. Hence, it seems unlikely that PEDOT:PSS is the cause of the self-selectivity in P3HT:PCBM solar cells.

A more likely explanation is vertical phase separation of the P3HT:PCBM composite, which has previously been observed to yield thin regions of enhanced P3HT and PCBM concentration close to the anode and cathode, respectively.\textsuperscript{[68]} The presence of these layers would in effect give rise to self-selectivity by preventing electron leakage to the anode and hole leakage to the cathode. This explanation is lent additional weight by changes in the composite film characteristics under annealing: Kim \textit{et al.} reported a large increase in the P3HT emission intensity and a substantial enhancement in a

---

\textbf{Figure 3-10}

An energy level diagram showing vertical phase separation as a possible explanation for self-selectivity in ITO / PEDOT:PSS / P3HT:PCBM / Al solar cells. A P3HT-enriched layer near the anode would prevent electron leakage to the anode, while a PCBM-enriched layer near the cathode would prevent hole leakage to the cathode. This would result in a net negative photocurrent even in the absence of an electric field.
thiophene-related X-ray diffraction peak after annealing, indicating increased phase separation.[69] TEM studies by Yang et al. revealed a favourable enlargement of the P3HT and PCBM domains in the central mixed region, leading to superior bulk transport properties.[70]

### 3.4.1 Inverse-selectivity

Highly anti-symmetric $J_{ph}$-$V$ characteristics of BHJ devices based on well-known materials systems (P3HT:PCBM and MDMO-PPV:PCBM) have so far been presented in this chapter. In this section, we report similar measurements on a new donor/acceptor combination that also yields anti-symmetric $J_{ph}$-$V$ characteristics, but one that has a positive photocurrent at the point of optimal symmetry.

![Figure 3-11](image)

The chemical structures of the donor polymer poly(3,3’’-didodecyl quarterthiophene) [PQT-12] and the small-molecule acceptor 4,7-bis(2-(1-hexyl-4,5-dicyanoimidazol-2-yl)vinyl)benzo[c]1,2,5-thiadiazole [HV-BT].

Poly(3,3’’-didodecyl quarterthiophene) [PQT-12] is a relatively new donor polymer that has recently become commercially available (American Dye Source), and studies have shown it to be an air-stable material that exhibits good hole mobilities between 0.1 and 0.2 cm$^2$(Vs)$^{-1}$ in thin-film transistors.[71, 72] The HOMO and LUMO levels of PQT-12 are reported as -5.2 eV and -3.0 eV respectively by the supplier.[73] 4,7-bis(2-(1-hexyl-4,5-dicyanoimidazol-2-yl)vinyl)benzo[c] 1,2,5-thiadiazole [HV-BT] is a recently-reported low-
bandgap, solution processable small-molecule acceptor that was synthesized at IMRE by Teck Lip Tam under the direction of Dr. Alan Sellinger, with HOMO and LUMO levels of -5.9 eV and -3.5 eV respectively.\textsuperscript{[74]} In a recent study, BHJ solar cells based on PQT-12:HV-BT showed promising preliminary device performance, with power conversion efficiencies of 0.7% under 100 mW/cm\textsuperscript{2} of white light.\textsuperscript{[75]}

BHJ solar cells with the structure ITO / PEDOT:PSS / PQT-12:HV-BT / Ag were fabricated by spin-coating a solution containing 3.5 mg/ml each of PQT-12 and HV-BT in chloroform onto ITO / PEDOT:PSS substrates. The resulting ~120 nm films were annealed at 80 °C for 10 mins, followed by deposition of the Ag cathode by thermal evaporation in a vacuum chamber.

**Figure 3-12**
The $J_{ph}$-$V$ curve of an ITO / PEDOT:PSS / PQT-12:HV-BT / Ag device. The data has been divided into two zones to the left (L) and right (R) of the point of optimal symmetry (POS) at $V_{POS} = 1.22$ V and $J_{POS} = 1.10$ mA/cm\textsuperscript{2}. The left side has been rotated by 180° about the POS to create a new curve (L\textsuperscript{rot}) that overlaps closely with R, implying a high degree of anti-symmetry in the $J_{ph}$-$V$ characteristics.
The $J_{ph} - V$ characteristics of the PQT-12:HV-BT device were obtained with the pulsed technique under an instantaneous intensity of 28 mW/cm$^2$ and are shown in Figure 3-12. As before, rotating the left-side data (L) about the point of optimal symmetry at 1.22 V by 180° yields a new curve L$^{\text{rot}}$ that overlaps closely with the right-side data (R), indicative of the $J_{ph} - V$ curve being highly anti-symmetric about the POS. In this case, there is a significant positive current $I_{POS}$ of 1.10 mA/cm$^2$ at the point of optimal symmetry, which can be rationalised by assuming that one or both of the electrodes in the PQT-12:HV-BT device are inverse-selective, i.e. preferentially selective towards their opposite carrier type; the anode towards electrons and/or the cathode towards holes.

For the sake of argument, we consider the situation in which the cathode is inverse-selective and the anode is non-selective, which gives rise to $n_{e}^{ph}(d) = n_{h}^{ph}(0) = n_{e}^{ph}(0) = 0$ due to rapid extraction, but $n_{e}^{ph}(d) > 0$. In this case, we obtain for the spatially averaged diffusive photocurrent:

$$J_{ph}^{\text{diff}} = e \left[ -D_{h} \frac{n_{h}^{ph}(d) - n_{h}^{ph}(0)}{d} + D_{e} \frac{n_{e}^{ph}(d) - n_{e}^{ph}(0)}{d} \right]$$

(3.13)

Hence, $J_{ph}$ can be written as:

$$J_{ph} = \frac{eD_{e}n_{e}^{ph}(d)}{d} + e \left[ \mu_{h} < n_{h}^{ph}(x) > + \mu_{e} < n_{e}^{ph}(x) > \right] E$$

(3.14)

If the carrier densities at the electrodes are independent of (or only weakly dependent on) the electric field, the $J_{ph} - V$ curve will retain its anti-symmetric profile, but the spatially averaged diffusive photocurrent will displace the curve in the positive current direction by an amount $eD_{e}n_{e}^{ph}(d)/d$. (The curve would be similarly displaced in the positive direction by an amount $eD_{h}n_{h}^{ph}(0)/d$ if the anode were inverse-selective.)
Inverse-selectivity reduces device efficiency because the electrodes block extraction of their own carrier type, yielding a photocurrent that is smaller (less negative) than would otherwise be obtained if the electrodes were non-selective or self-selective. (In the event that one electrode were inverse-selective and the other self-selective, the offset could occur in either direction, depending on whichever electrode were more strongly selective.)

### 3.4.2 The offset current

For all three BHJ solar cell systems discussed so far, the high degree of anti-symmetry in the $J_{ph}-V$ curves indicates that, in the vicinity of $V_{Bi}$ (which corresponds to the $V_{POS}$), the carrier densities at the electrodes may be regarded as independent of the applied voltage (or approximately so). Therefore, in this voltage range the spatially averaged diffusive current is approximately constant and has the effect of vertically displacing (or “offsetting”) the $J_{ph}-V$ curve without substantially changing its shape. Hence from here on, we refer to the spatially averaged diffusive photocurrent as the *offset current (density)* $J_{off}$ and assume it has an approximately constant value $J_{off}(V) = J_{POS}$ across the entire measurement range.” Hence, Equations (3.12) and (3.14) become:

$$J_{ph} = J_{off} + e \left[ \mu_h < n_h^{ph} (x) > + \mu_e < n_e^{ph} (x) > \right] E.$$ (3.15)

$J_{off}$ is negative when the electrodes are self-selective, positive when they are inverse-selective, and zero when they are non-selective.

---

*The loss of anti-symmetry outside this range is attributable to $J_{off}$ having a non-constant value which, from Equation (3.15), causes the $J_{ph}-V$ curve to deviate in shape from the anti-symmetric curve described by Equation (3.10).*
The vertical phase separation that we used to rationalise self-selectivity in P3HT:PCBM devices may also explain inverse-selectivity. In this case, there may be a thin layer enriched with (hole-transporting) PQT-12 at the cathode, and/or a similar layer enriched with (electron-transporting) HV-BT at the anode. Figure 3-13 summarises the possible scenarios leading to positive, zero and negative diffusive photocurrents, based on donor-rich and/or acceptor-rich layers/islands at the electrodes.

![Figure 3-13](image)

A schematic representation of vertical phase separation in the blend layer that can result in carrier-selectivity at the electrodes. (A): A donor-rich region at the cathode blocks electrons from reaching the cathode, while an acceptor-rich region at the anode blocks holes from reaching the anode, resulting in a positive offset current. (B): The absence of phase-rich regions allow both carriers to be rapidly depleted at either electrode, so to a good approximation, \[ J_{\text{diff}}^{\text{ph}}(0) = J_{\text{diff}}^{\text{ph}}(d) = J_{\text{diff}}^{\text{ph}} = 0, \] and the offset current is zero. (C): A donor-rich region at the anode blocks electrons from reaching the anode, while an acceptor-rich region at the cathode blocks holes from reaching the cathode, resulting in a negative offset current.
Figure 3-13A represents a BHJ device with an acceptor-rich layer close to the anode and a donor-rich layer close to the cathode, with a homogeneously distributed donor/acceptor bulk-heterojunction sandwiched in-between. Free electrons generated in the BHJ layer are blocked from reaching the cathode due to poor electron mobility in the donor-rich layer close to the cathode. The same blocking effect occurs for holes attempting to reach the anode, resulting in the cathode becoming in effect preferentially selective towards hole extraction, and the anode similarly preferential towards electron extraction. The effect of this inverse-selectivity, as illustrated schematically in the energy level diagram, is the undesirable net migration of carriers to their opposite electrodes at zero field, giving rise to a positive offset current.

Figure 3-13B represents a device with non-selective electrodes, which give rise to rapid barrier-less extraction of electrons and holes at both electrodes. The resultant zero offset current results in a point of anti-symmetry at \((V_{BI}, 0)\). Figure 3-13C represents a BHJ device with an acceptor-rich layer close to the cathode and a donor-rich layer close to the anode. In contrast to the inverse-selectivity depicted in Figure 3-13A, these enriched layers block the accidental extraction of electrons and holes at the anode and cathode respectively. This gives rise to an offset current that beneficially displaces the photocurrent in the negative direction (hence increasing its magnitude).

Previous reports in the literature have assumed that the voltage at which \(J_{ph} = 0\) is the built-in potential \(V_{BI}\).\textsuperscript{40, 41, 43} The results presented here clearly show that this assumption holds only in devices in which the electrodes are non-selective (so the offset current is zero).
3.5 CARRIER SELECTIVITY AND THE OPEN-CIRCUIT VOLTAGE

For a device with self-selective electrodes, the resulting negative offset current contributes constructively to the photocurrent, increasing the power conversion efficiency; but for a device with inverse-selective electrodes, the resulting positive offset current adds destructively to the photocurrent, thereby reducing device efficiency. This vertical displacement of the $J_{\text{ph}}$-$V$ curve is the most evident effect of the offset current.

We now turn to the more subtle effect that the offset current has on the open-circuit voltage $V_{\text{OC}}$. We consider hypothetical BHJ solar cells in which the anode is non-selective, but the cathode is either (#1) non-selective, (#2) inverse-selective or (#3) self-selective. We assume the cathode work function is the same in all cases. In addition, we approximate the offset current $J_{\text{off}}$ (where present) as a field-independent quantity in the operating voltage range of the devices. The $J_{\text{dark}}$-$V$ characteristics and shape of the $J_{\text{ph}}$-$V$ curves of these devices are assumed to be identical, and the $J_{\text{ph}}$-$V$ characteristics differ only in the offset direction caused by $J_{\text{off}}$.

We start by comparing the inverse-selective (#2) and non-selective (#1) cases. To indicate the open-circuit voltage $V_{\text{OC}}$ at which $J_{\text{dark}} = -J_{\text{ph}}$, a vertical line has been drawn connecting $J_{\text{dark}}$ to each of the $J_{\text{ph}}$ curves corresponding to Devices #1 and #2 in Figure 3-14. The symmetry point $(V_{\text{Bi}}, J_{\text{off}})$ for each $J_{\text{ph}}$-$V$ curve is marked by a ‘*’. Under this illumination level, the $V_{\text{OC}}$ in Device #2 is clearly reduced as a result of the positive offset current.
Figure 3-14
Simulated $I_{\text{dark}}$-$V$ and $I_{\text{ph}}$-$V$ curves. In Device #2, in which the offset current is positive, the open-circuit voltage has been reduced significantly. The zero-crossing of the $I_{\text{ph}}$-$V$ curve, which signifies the maximum possible open-circuit voltage, has also been shifted to the left due to the positive offset current.

The voltage at which $I_{\text{ph}} = 0$, which we refer to here as the zero-crossing voltage, signifies the maximum attainable $V_{\text{OC}}$ of a device. In the case of Device #1, the zero-crossing voltage – and hence the maximum attainable $V_{\text{OC}}$ – is at the built-in potential. However, for Device #2, the positive offset current has lowered the zero-crossing voltage by a significant margin below the built-in potential. Importantly, this implies that the positive offset current has the effect of reducing the maximum $V_{\text{OC}}$ that is attainable by Device #2.

We now turn to a comparison of the self-selective (#3) and non-selective (#1) cases (Figure 3-15). In the case of Device #3, the negative offset current has increased the maximum attainable $V_{\text{OC}}$ – as implied by the zero-crossing voltage – such that it exceeds the built-in potential. This suggests that, under sufficiently high illumination levels, the $V_{\text{OC}}$ can exceed $V_{\text{BI}}$, as illustrated by Figure 3-15.
Figure 3-15
Simulated \( J_{\text{dark}} - V \) and \( J_{\text{ph}} - V \) curves. In Device \#3, in which the offset current is negative, the open-circuit voltage has been increased significantly. The zero-crossing of the \( J_{\text{ph}} - V \) curve, which signifies the maximum possible open-circuit voltage, has also been shifted to the right due to the negative offset current.

The \( J_{\text{ph}} - V \) characteristics of Device \#3 in Figure 3-15 are similar to those of the ITO / PEDOT:PSS / P3HT:PCBM / Al device that were shown earlier in Figure 3-7. Figure 3-16 shows the \( J_{\text{light}} - V \), \( J_{\text{dark}} - V \) and \( J_{\text{ph}} - V \) characteristics of the P3HT:PCBM device as measured by the pulsed technique under a white light intensity of 98 mW/cm\(^2\).

The open-circuit voltage, defined by the zero-crossing of the \( J_{\text{light}} - V \) curve, is 0.63 ± 0.002 V, compared to the built-in potential of 0.58 ± 0.01 V. The difference between the two voltages 50 ± 12 mV, although relatively small, provides direct evidence that \( V_{\text{OC}} \) can, in fact, exceed \( V_{\text{BI}} \). This is important because it has conventionally been assumed that the built-in potential places an upper limit on the open-circuit voltage of BHJ solar cells.[57, 58] Moreover, the position of the zero-crossing suggests that the open-circuit voltage of the P3HT:PCBM solar cell might reach a value as high as 0.93 V at high
illumination levels, although changes in the shape of the $I_{ph}-V$ curve – due e.g. to increased bimolecular recombination at higher intensities – might prevent this value from being reached in practice.

![Current-voltage response of an ITO / PEDOT:PSS / P3HT:PCBM / Al solar cell.](image)

**Figure 3-16**

Current-voltage response of an ITO / PEDOT:PSS / P3HT:PCBM / Al solar cell. The $I_{light}-V$ and $I_{ph}-V$ characteristics were obtained under an incident intensity of 98 mW/cm$^2$. The built-in potential, as implied by the point of optimal symmetry of the $I_{ph}-V$ curve, is $0.58 \pm 0.01$ V. The open-circuit voltage, determined from the zero-crossing of the $I_{light}-V$ curve, is $0.63 \pm 0.002$ V, some $50 \pm 12$ mV above the built-in potential. The zero-crossing of the $I_{ph}-V$ curve at $0.93 \pm 0.002$ V suggests that the upper limit for $V_{OC}$ under intense illumination may be as high as $0.93$ V, some $350$ mV above $V_{BI}$.

### 3.6 Conclusions

Using the pulsed technique described in Chapter 2, we have measured the corrected photocurrent-voltage characteristics of BHJ solar cells based on the blends P3HT:PCBM, MDMO-PPV:PCBM and PQT-12:HV-BT. The $I_{ph}-V$ curves in all three systems are remarkably anti-symmetric in shape, which can be rationalised in terms of a simple physical model based on standard drift-diffusion equations. According to this model, the voltage at the symmetry
point of the $J_{ph}$-$V$ curve corresponds to the built-in potential of the device, thus providing a new method of obtaining the built-in potential of BHJ solar cells.

In the case of P3HT:PCBM and PQT-12:HV-BT devices, non-zero corrected photocurrents were observed at the point of optimal symmetry, consistent with carrier selectivity at one or both electrodes which gives rise to a non-zero spatially averaged diffusive photocurrent. This photocurrent may be approximated by a constant offset current in the region where the $J_{ph}$-$V$ curve is highly anti-symmetric. Three types of selectivities exist:

1) **Self-selectivity**, in which one or both electrodes are preferentially selective towards their own carrier type, resulting in a negative offset current. The offset current contributes constructively to the overall photocurrent in the operating range of the solar cell, and is therefore beneficial to device efficiency. This behaviour was exemplified by the P3HT:PCBM-based device.

2) **Inverse-selectivity**, in which one or both electrodes are preferentially selective towards their *opposite* carrier type, resulting in a positive offset current. In this case, the offset current diminishes the overall photocurrent in the operating range of the solar cell, and is therefore detrimental to device efficiency. This behaviour was exemplified by the PQT-12:HV-BT device.

3) **Non-selectivity**, in which neither of the electrodes is preferentially selective to either carrier type, resulting in zero offset current. This behaviour was exemplified by the MDMO-PPV:PCBM device.

Closer examination of the $J$-$V$ characteristics of the P3HT:PCBM device showed that another effect of self-selectivity is to increase the open-circuit
voltage above the built-in potential by a substantial margin – in this case by a margin of $50 \pm 12$ mV.
In this chapter, the factors that determine the detailed shape of the corrected photocurrent-voltage curve are explored in greater detail. The results of the analysis provide further insight into how device efficiencies may be improved.
CHAPTER 4  THE PHOTOCONDUCTIVITY

4.1 INTRODUCTION

In the previous chapter, a simple expression for the corrected photocurrent \( J_{ph} \) was developed from the drift-diffusion equations. The corrected photocurrent was written as the sum of an (approximately) voltage-independent spatially averaged diffusive photocurrent \( J_{\text{ph}}^{\text{diff}} \) and a drift-based photocurrent:

\[
J_{\text{ph}} = J_{\text{ph}}^{\text{diff}} + e \left[ \mu_n < n_n^{\text{ph}}(x) > + \mu_e < n_e^{\text{ph}}(x) > \right] E. \quad (4.1)
\]

In this chapter, we examine more closely the role of the carrier mobilities and carrier distributions on the magnitude and shape of the corrected photocurrent.

4.2 INTENSITY DEPENDENT MEASUREMENTS ON A P3HT:PCBM-BASED SOLAR CELL

The pulsed technique was used to obtain \( J_{\text{ph}}-V \) curves from an ITO / PEDOT:PSS / P3HT:PCBM / Al device under multiple light intensities, as shown in Figure 4-1A. The points of optimal symmetry lie in a tight band between 0.58 to 0.61 V, shifting slightly to the left with increasing light intensity, from 0.61 ± 0.01 V at 1.73 mW/cm\(^2\) to 0.58 ± 0.01 V at 97.9 mW/cm\(^2\), due presumably to an increase in the temperature of the device. The \( J_{\text{ph}}-V \) curves cross the voltage axis at approximately the same voltage 0.90 ± 0.05 V, which is a natural consequence of the curves varying approximately linearly in magnitude with the incident light intensity \( I \). The linear dependence of \( J_{\text{ph}} \)
on $I$ is shown in Figure 4-1B for three illustrative voltages 0, 0.6 and 1.5 V, where 0.6 V corresponds to the approximate built-in potential $V_{\text{BI}}$ of the device.

\[J_{\text{ph}}(V) = J_{\text{dark}}(V) + J_{\text{ph}}(V)\]  

(4.2)

Figure 4-1 provides direct experimental validation for Equation (4.2) since the shape of the calculated $J_{\text{ph}}-V$ curves would change with light intensity if the photovoltage-induced injection current were dependent on the concentration of photogenerated carriers (only the magnitude changes with light intensity).
The invariance in shape further implies that the observed discrepancy between the $L^{\text{rot}}$ and $R$ curves in Figure 3-7 is a real observation, rather than an experimental artefact arising from incomplete elimination of the temperature mismatch when measuring $I_{\text{light}}$ and $I_{\text{dark}}$ by the pulsed technique.

Under steady-state conditions, the photogeneration of free charge carriers inside the device is balanced by a combination of carrier extraction at the electrodes (leading to an external current $J_{\text{ph}}$) and bulk recombination. In the event that recombination is a negligible process, then $J_{\text{ph}}$ will vary linearly with the photogeneration rate, and hence with the light intensity.$^{[76]}$ However, in situations where bimolecular recombination dominates, $J_{\text{ph}}$ will vary with $\sqrt{I}$ instead.$^{[77]}$ In reality, the intensity dependence of $J_{\text{ph}}$ normally falls somewhere in between these two extremes, such that (at high intensities):

$$J_{\text{ph}} \propto I^p,$$

(4.3)

where $p$ is an empirical exponent between 0.5 and 1, depending on the degree of bimolecular recombination.$^{[32]}$ Returning to Figure 4-1, the approximately linear variation of the corrected photocurrent with intensity implies that bimolecular recombination is a negligible process in the P3HT:PCBM device at light levels up to ~100 mW/cm$^2$ – a fact we will return to shortly.

### 4.3 The Photoconductivity of a P3HT:PCBM-Based Solar Cell

Equation (4.1) can be re-written in the abbreviated form:

$$J_{\text{ph}} = J_{\text{ph}}^{\text{diff}} + \sigma E,$$

(4.4)

where $\sigma$ is referred to here as the photoconductivity, and is given by:

$$\sigma = e \left[ \mu_h < n_{h}^{\text{ph}}(x) > + \mu_e < n_{e}^{\text{ph}}(x) > \right].$$

(4.5)
As argued in the previous chapter, the average carrier densities \( \langle n_e^{ph} \rangle \) and \( \langle n_h^{ph} \rangle \) are determined by the average dwell-times of the electrons and holes inside the device, which vary inversely with the drift-speed and hence inversely with field strength, and (for a reasonably flat generation profile) should therefore be even functions of the internal field strength. The electron and hole mobilities may also exhibit field dependencies, but these too are even functions of the internal field strength. Therefore, \( \sigma \) should also be an even function of the electric field with a maximum at \( E = 0 \) (and monotonically decreasing on either side).

To experimentally determine the photoconductivity \( \sigma \) of the P3HT:PCBM BHJ layer, we can re-arrange Equation (4.4) to obtain:

\[
\sigma = \frac{J_{ph} - J_{ph}^{diff}}{E}.
\] (4.6)

In reality, the spatially averaged diffusive photocurrent \( J_{ph}^{diff} \) is (weakly) field-dependent but, following the arguments outlined in Section 3.4.2, we can approximate it as a field-independent offset current \( J_{off} \) with a value equal to the corrected photocurrent at the point of optimal symmetry \( J_{POS} \). In the case of the P3HT:PCBM device, this approximation is most accurate in the vicinity of the built-in potential \( (V = V_{bi} \pm 0.2 \, V) \) where the \( J_{ph}V \) curve has “exact” anti-symmetry, and is less valid outside of this range where the \( L^{rot} \) and \( R \) curves diverge slightly. In view of this approximation, Equation (4.6) is re-written as:

\[
\hat{\sigma} = \frac{J_{ph} - J_{off}}{E},
\] (4.7)

where the notation \( \hat{\sigma} \) emphasizes the approximate nature of the photoconductivity thus obtained. Using \( E = (V - V_{bi})/d \), the field dependence
of the corrected photocurrent for the P3HT:PCBM device, at 98 mW/cm² illumination, is shown in Figure 4-2A.

![Figure 4-2](image_url)

**Figure 4-2**

(A): The field-dependence of \( (J_{\text{ph}} - J_{\text{off}}) \) for an ITO / PEDOT:PSS / P3HT:PCBM / Al device measured by the pulsed technique under an instantaneous light intensity of 98 mW/cm². (B): The field-dependence of the estimated photoconductivity \( \hat{\sigma} \), as calculated from Equation (4.7) using data from (A).

As expected from the above argument, the (estimated) photoconductivity in Figure 4-2B is an even function of the electric field that has a maximum at \( E = 0 \), and decreases monotonically either side. To rationalise the shape of the \( \hat{\sigma} - E \) curve in further detail, we examine the photoconductivity from the following analytical viewpoint. Under steady-state conditions and neglecting charge traps, the one-dimensional continuity equations for electrons and holes at a distance \( x \) from the anode are (see Section 1.2.2):

\[
-\frac{1}{e} \frac{dJ_{\text{ph}}^e}{dx} = G(x) - R(x)
\]

(4.8)

and
\[
\frac{1}{e} \frac{dJ_{ph}^e}{dx} = G(x) - R(x) . \tag{4.9}
\]

Here, \( J_{ph}^e \) and \( J_{ph}^h \) are the local electron and hole currents due to photogenerated free carriers, \( G(x) \) is the free carrier photogeneration rate and \( R(x) \) is the rate of bimolecular recombination. The linear intensity dependence of \( J_{ph} \) seen in Figure 4-1 implies that bimolecular recombination is a negligible process in the P3HT:PCBM device. Hence, assigning \( R(x) = 0 \), the continuity equations simplify to:

\[
\frac{dJ_{ph}^e}{dx} = -eG(x) \tag{4.10}
\]

and

\[
\frac{dJ_{ph}^h}{dx} = eG(x) . \tag{4.11}
\]

Integrating Equations (4.10) and (4.11) yields:

\[
J_{ph}^e = -e \int G(x) dx \tag{4.12}
\]

and

\[
J_{ph}^h = e \int G(x) dx . \tag{4.13}
\]

From the drift-diffusion equations (Section 1.2.2), the electron and hole currents due to the photogenerated carriers are:

\[
J_{ph}^e = e \mu_e n_{ph}^e E + \mu_e k_B T \frac{dn_{ph}^e}{dx} \tag{4.14}
\]

and

\[
J_{ph}^h = e \mu_h n_{ph}^h E - \mu_h k_B T \frac{dn_{ph}^h}{dx} . \tag{4.15}
\]
Equating Equations (4.12) and (4.13) to Equations (4.14) and (4.15) respectively, we obtain a differential equation for each charge carrier.

\[
\frac{d n_{p}^{\text{ph}}}{d x} + \frac{e E}{k_{B} T} n_{p}^{\text{ph}} = -\frac{e}{\mu_{e} k_{B} T} \int G(x) dx \quad (4.16)
\]

and

\[
\frac{d n_{h}^{\text{ph}}}{d x} - \frac{e E}{k_{B} T} n_{h}^{\text{ph}} = -\frac{e}{\mu_{h} k_{B} T} \int G(x) dx \quad (4.17)
\]

Since charge carrier densities in organic semiconductors are relatively low, the electric field strength may be considered constant throughout the device. Equations (4.16) and (4.17) above are consequently linear and can be solved analytically. Assuming the photogeneration rate is flat, we can obtain the following expressions for the carrier densities in Equations (4.16) and (4.17):

\[
n_{e}^{\text{ph}}(x) = -\frac{G d}{\mu_{e} E} \left[ x \frac{\exp\left(-e E x / k_{B} T\right) - 1}{\exp\left(-e E d / k_{B} T\right) - 1}\right] \quad (4.18)
\]

and

\[
n_{h}^{\text{ph}}(x) = \frac{G d}{\mu_{h} E} \left[ x \frac{\exp\left(e E x / k_{B} T\right) - 1}{\exp\left(e E d / k_{B} T\right) - 1}\right], \quad (4.19)
\]

where we have also applied the boundary conditions \( n_{h}^{\text{ph}}(0) = n_{h}^{\text{ph}}(d) = n_{e}^{\text{ph}}(0) = n_{e}^{\text{ph}}(d) = 0 \) for non-blocking electrodes.\(^{††}\) Taking the spatial average of the carrier densities, we obtain:

\[
< n_{e}^{\text{ph}}(x) >= -\frac{G d}{\mu_{e} E} \left[ \frac{1}{2} + \frac{k_{B} T}{e E d} + \frac{1}{\exp\left(-e E d / k_{B} T\right) - 1}\right] \quad (4.20)
\]

\(^{††}\) The P3HT:PCBM device has self-selective electrodes (i.e. \( n_{e}^{\text{ph}}(0) > 0 \) and/or \( n_{h}^{\text{ph}}(d) > 0 \)), so, strictly speaking, the boundary conditions used here are inappropriate. We will account for self-selectivity as a separate effect shortly.
and

\[< n^\text{ph}_h(x) > = \frac{Gd}{\mu_b E} \left[ \frac{1}{2} - \frac{k_b T}{eEd} + \frac{1}{\exp(eEd/k_b T) - 1} \right]. \quad (4.21)\]

The theoretical photoconductivity \( \sigma_t \) is obtained by substituting Equations (4.20) and (4.21) into Equation (4.5).

\[\sigma_t = \frac{eGd}{E} \left[ \frac{\exp(eEd/k_b T) + 1}{\exp(eEd/k_b T) - 1} - \frac{2k_b T}{eEd} \right]. \quad (4.22)\]

One surprising revelation from Equation (4.22) is that (under the approximations made) the corrected photocurrent is \textit{independent} of carrier mobilities. This implies that the photoconductivity depends only on the average density of carriers in the device, and \textit{not} on their mobilities.

An analytical expression for the photoconductivity was also derived for an exponential free carrier generation profile \( G(x) = G_0 \exp(-x/\alpha) \), where \( G_0 \) is the generation rate at \( x = 0 \) and \( \alpha \) is the absorption length. This generation profile more accurately reflects the Beer-Lambert absorption profile that is likely to apply inside the device (although it ignores potential optical interference effects\(^{[26]}\)). In practice, it was found that, for absorption lengths \( \alpha > 0.5d \) (\( d \) is the device width of \( \sim 100 \) nm), the \( \sigma-E \) curves for the two situations are virtually identical. The interested reader is referred to the Appendix for further details.

The analytical corrected photocurrent \( J_{\text{ph,t}}^{\text{drift}} \) (we will explain the “drift” superscript shortly) can be calculated by multiplying \( \sigma_t \) by \( E \).

\[J_{\text{ph,t}}^{\text{drift}} = \sigma_t E = eGd \left[ \frac{\exp(eEd/k_b T) + 1}{\exp(eEd/k_b T) - 1} - \frac{2k_b T}{eEd} \right]. \quad (4.23)\]
The absence of carrier mobility terms in Equation (4.23) is particularly interesting, because one would intuitively expect increased carrier mobilities to increase the corrected photocurrent, since carriers would develop higher drift velocities in a given field strength, and hence may be extracted at a faster rate. This apparent contradiction may be resolved by looking back at Equations (4.18) and (4.19), which indicate that carrier densities are inversely proportional to mobilities – a logical relation, since in a situation where carriers are rapidly transported to the electrodes, the density of carriers should diminish.

In Figure 4-3A, the experimental photoconductivity $\hat{\sigma}$ obtained from the P3HT:PCBM device is reproduced, where it shows very good correspondence with the analytical photoconductivity $\sigma$. Here, $\sigma$ was calculated using the values $d = 100$ nm (as experimentally determined for the device) and $T = 300$ K. The only fitting parameter used was the generation rate $G$, which was chosen to minimise the discrepancy $D_\sigma$ between the experimental and analytical curves, defined as:

$$D_\sigma = \sum_{E=E_{\text{min}}}^{E_{\text{max}}} \left| \hat{\sigma} - \sigma \right|,$$

where $E_{\text{min}}$ and $E_{\text{max}}$ are the lower and upper electric field limits of the measurement range, respectively. In this case, the optimum value of $G$ is $3.65 \times 10^{27}$ m$^{-3}$ s^{-1}. The degree of overlap between the experimental and analytical photoconductivity-field curves is quite astonishing, despite the simplicity of the analytical model. An estimate of $G$ may be calculated based on the rate of extracted carriers at short-circuit $J_{\text{SC}}/ed \sim 7 \times 10^{27}$ m$^{-3}$ s$^{-1}$, which is in the same order of magnitude as the fitted value for $G$. The fact that a real P3HT:PCBM device exhibits behaviour approaching a theoretical ideal is
highly encouraging, since it suggests that we will be able to learn a great deal about the operating mechanisms of BHJ solar cells using more sophisticated models.

![Graph](image)

**Figure 4-3**

(A): The experimentally and theoretically determined $\sigma$-$E$ curves for a P3HT:PCBM device, obtained using a single fitting parameter $G = 3.65 \times 10^{27} \text{ m}^3 \text{ s}^{-1}$. (B): The experimentally and theoretically determined $J_{ph}$-$V$ curves agree well in the voltage range $V = V_{bi} \pm 0.2 \text{ V}$, but diverge outside this range.

The analytical model presented above does not account for carrier selectivity at the electrode(s), resulting in zero diffusive contribution to the corrected photocurrent $J_{ph,t}^{drift}$. [The superscript “drift” is used to denote the drift-only nature of Equation (4.23)]. To simulate the effect of carrier selectivity, we add the (approximately) constant offset current $J_{off}$ (as found experimentally) to Equation (4.23):

$$J_{ph,t} = J_{ph,t}^{drift} + J_{off} = eGd \left[ \frac{\exp \left(\frac{eEd}{k_B T} + 1\right) + 2k_B T}{\exp \left(\frac{eEd}{k_B T} - 1\right) - \frac{2k_B T}{eEd}} \right] + J_{off} \quad (4.25)$$
Figure 4-3B shows the experimental $J_{ph}$-$V$ curve and the analytical $J_{ph,t}$-$V$ curve as calculated from Equation (4.25). The curves overlap in the voltage range $V = V_{bi} \pm 0.2$ V, but diverge outside of this range, with the magnitude of the experimental $J_{ph}$ being slightly larger than the analytical $J_{ph,t}$. As reasoned earlier, the constant offset current $J_{off}$ is an approximation of the actual field dependent $J_{ph}^{diff}$, and is most accurate in the range $V = V_{bi} \pm 0.2$ V, where anti-symmetry is “exact”. Beyond this range, the accuracy of the approximation becomes weaker as the field dependence of $J_{ph}^{diff}$ becomes more significant. This is presumably the reason for the divergence between the experimentally and theoretically determined $J_{ph}$-$V$ curves when $V > 0.8$ V.

Returning to the absence of carrier mobility terms in Equation (4.23), one conclusion we can draw from the remarkable correspondence between the experimentally- and analytically-determined curves in Figure 4-3 is: the shape of the $J_{ph}$-$V$ curves for P3HT:PCBM devices are probably independent of carrier mobilities. Contrary to claims in the literature[15, 78, 79], increasing carrier mobilities in the P3HT:PCBM system is therefore unlikely to improve device efficiencies (in particular fill factors), and this is because losses from recombination are negligibly low regardless of the operating voltage.

4.4 **The Photoconductivity of an MDMO-PPV:PCBM-based Solar Cell**

After successfully rationalising the shape of the photoconductivity-field characteristics of the ITO / PEDOT:PSS / P3HT:PCBM / Al solar cell, we sought to apply the same principles to the ITO / PEDOT:PSS / MDMO-PPV:PCBM / Ag solar cell.
Using the $J_{ph}-V$ data in Figure 3-3, the photoconductivity of the MDMO-PPV:PCBM solar cell was estimated using Equation (4.7). In this case, the $J_{ph}-V$ curve exhibits highly anti-symmetric behaviour over a wide voltage range $V = V_B \pm 0.8 \text{ V}$, implying that approximating $J_{ph}^{\text{diff}}(E)$ with the constant $J_{\text{sat}}$ (corresponding to $J_{\text{POS}} = 0.25 \text{ mA/cm}^2$, see Figure 3-3) is likely to be accurate in this data range. The field dependence of $(J_{ph} - J_{\text{sat}})$ is shown in Figure 4-4A. Dividing the $(J_{ph} - J_{\text{sat}})-E$ curve by $E$ gives the field dependence of the estimated photoconductivity $\hat{\sigma}(E)$, as shown in Figure 4-4B.

![Figure 4-4](image)

(A): The field dependence of $(J_{ph} - J_{\text{POS}})$ for an ITO / PEDOT:PSS / MDMO-PPV:PCBM / Ag solar cell. (B): The field dependence of $\hat{\sigma}$, obtained by dividing the curve in (A) by the electric field $E$.

The resulting $\hat{\sigma}-E$ curve is a positive, monotonically decreasing function of the field strength with a maximum at $E = 0$, and agrees qualitatively with the field-dependent curves shown earlier (Figure 4-3A) for the P3HT:PCBM device.
The $\hat{\sigma} - E$ curve of the MDMO-PPV:PCBM device is reproduced in Figure 4-5A, and is compared directly with the analytical photoconductivity $\sigma_t$. Here, the values $d = 80$ nm (experimentally determined), and $T = 300$ K are used in the calculation of $\sigma_t$. An optimum value of $G = 2.75 \times 10^{27}$ m$^3$ s$^{-1}$, which minimises the discrepancy $D_\sigma$ [Equation (4.24)] between the $\hat{\sigma} - E$ and $\sigma_t - E$ curves, is used as the only fitting parameter in the calculation.

![Figure 4-5](image)

(A): The analytically and experimentally determined $\sigma-E$ curves for the MDMO-PPV:PCBM device, as calculated from Equations (4.7) and (4.22). The analytically-derived photoconductivity was obtained using the values $G = 2.75 \times 10^{27}$ m$^3$ s$^{-1}$ (optimised fitting parameter), $d = 80$ nm (experimentally determined) and $T = 300$ K. (B): The analytically and experimentally determined $J_{ph} - V$ curves for the MDMO-PPV:PCBM device.

In this case, the analytical and experimental $\sigma-E$ curves show an obvious mismatch, with the peak analytical photoconductivity exhibiting a much larger value than the experimental peak value. In Figure 4-5B, the analytically-determined $J_{ph} - V$ curve, as calculated from Equation (4.25), is compared with the experimental one. The experimental $J_{ph} - V$ curve greatly
exceeds the theoretical one at high electric fields, which is very odd, considering the derivation in Section 4.3 assumes zero recombination.

The mismatch between the experimental and analytical curves in Figure 4-5 suggests that the analytical model is flawed in some way. In particular, bimolecular recombination – which was neglected in the derivation – may be a significant process in the case of the MDMO-PPV:PCBM device. To experimentally assess the importance of bimolecular recombination in the device, we look again to intensity dependent $J_{ph}$-$V$ measurements.

![Figure 4-6](image)

**Figure 4-6**

(A): The $J_{ph}$-$V$ characteristics of an ITO / PEDOT:PSS / MDMO-PPV:PCBM / Ag device at multiple light levels. The curves have similar points of optimal symmetry in the range of 0.81 ± 0.01 V. (B): The intensity dependence of $J_{ph}$ at 0.78 V and 0.86 V, which correspond to voltages near the POS. The sub-linear $J_{ph}$-$I$ curves indicate that bimolecular recombination is significant near the built-in potential. The red lines correspond to a power law fit of the form shown in Equation (4.3).

In Figure 4-6A, $J_{ph}$-$V$ curves from the MDMO-PPV:PCBM device as measured under multiple light intensities from 3.16 to 90.2 mW/cm$^2$ are shown. The points of optimal symmetry fall within a narrow band between 0.80 and 0.82 V. Since the greatest discrepancy between the photoconductivity curves
in Figure 4-5A occurs at zero field, we focus here on the $J_{ph}$ values close to the built-in potential at 0.8 V. The $J_{ph}$ values at $V = 0.78$ and 0.86 V are plotted against the incident light intensity $I$ in Figure 4-6B, and exhibit a sub-linear dependence on $I$, with exponents of $0.906 \pm 0.043$ and $0.922 \pm 0.042$, respectively. Hence, it is clear that bimolecular recombination is a significant loss process in these devices, and the recombination-free model outlined in Section 4.3 is therefore inappropriate in this case.

4.5 **THERMAL ANNEALING EFFECTS**

In the previous chapter, we demonstrated that electrodes can exhibit carrier selectivity, and examined the role of selectivity on device efficiency. In an ITO / PEDOT:PSS / P3HT:PCBM / Al solar cell, self-selective electrodes lead to a larger short-circuit current and a higher open-circuit voltage than would be obtained with non-selective electrodes. In Section 4.3, we rationalised the field dependence of the photoconductivity $\sigma$ for a P3HT:PCBM solar cell in terms of an analytical model derived from continuity and drift-diffusion equations. The analytical expression obtained for the $\sigma$-$E$ curve was found to be independent of carrier mobilities, implying that, in this system, the experimentally estimated photoconductivity can provide direct information about the average carrier densities inside the device. In this section, we apply these findings to better understand the reasons why thermal annealing improves the efficiencies of P3HT:PCBM-based solar cells.

In accordance with published protocols, the P3HT:PCBM device was annealed at 140 °C for 20 mins after deposition of the Al cathode during the fabrication process.\[15, 62\] Figure 4-7A shows the $J_{ph}$-$V$ characteristics, before and after thermal annealing, at an illumination level of 97.9 mW/cm².
Annealing appears to have four main effects. Firstly, it leads to a marginal reduction in the built-in potential ($\Delta V_{\text{BI}} = 30 \text{ mV}$). Secondly, it increases the symmetry of the $J_{\text{ph}}-V$ characteristics, as evident from the substantially reduced divergence between the $R$ and $L^{\text{rot}}$ curves in Figure 4-7B. (Here the points of optimal symmetry have been shifted to a common origin for ease of comparison.) Thirdly, it displaces the $J_{\text{ph}}-V$ curve further in the negative current direction so that the corrected photocurrent at $V_{\text{BI}}$ increases in magnitude by 2.36 mA/cm$^2$, which is beneficial to device efficiency. Fourthly, it increases the slope of the $J_{\text{ph}}-V$ curve at the built-in potential from 211 to 359 $\Omega^{-1}$ m$^{-2}$.

From Equation (4.4) (and explained in Section 3.4.2), the $J_{\text{ph}}^\text{diff}$ term is the cause of non-symmetry in $J_{\text{ph}}-V$ curves and so the improved symmetry after annealing is attributable to a reduction in the field dependence of $J_{\text{ph}}^\text{diff}$ and, by the extension, a reduction in the field dependence of the carrier densities at
the electrodes $n_{ph}^0(d)$ and $n_{ph}^0(0)$. From Equation (3.14), the displacement of the $J_{ph}-V$ curve in the negative direction can be attributed to an enhancement of the self-selective characteristics at the electrodes, and/or an increase in carrier mobilities associated with annealing P3HT:PCBM films\cite{80}. To rationalise the increase in slope at the built-in potential, we differentiate Equation (4.4) with respect to the applied voltage:

$$\frac{dJ_{ph}}{dV} = \frac{dJ_{ph}^{diff}}{dV} + E \frac{d\sigma}{dV} + \sigma \frac{dE}{dV}.$$ \hspace{1cm} (4.26)

We argued earlier that the carrier densities at the electrodes must depend only weakly on the electric field in order to achieve approximate antisymmetry in the $J_{ph}-V$ characteristics. This leads to the approximation made previously that $J_{ph}^{diff}$ can be treated as a constant offset current $J_{off}$ at and near the $V_{BI}$, so that:

$$\frac{dJ_{ph}^{diff}}{dV} = \frac{dJ_{off}}{dV} = 0.$$ \hspace{1cm} (4.27)

The electric field is zero at the built-in potential, so when Equation (4.27) is substituted into Equation (4.26), we obtain:

$$\frac{dJ_{ph}}{dV} \bigg|_{V_{BI}} = \sigma \frac{dE}{dV} = \sigma \frac{d}{d}.$$ \hspace{1cm} (4.28)

It follows that the apparent increase in the slope at the built-in potential after annealing is related to an increase in photoconductivity. Referring to Equation (4.5), this increase in photoconductivity could be due to enhancements in carrier mobilities and/or higher average carrier densities inside the device after annealing. The first of these explanations is unlikely, however, since the analytical expression we derived for the photoconductivity [Equation (4.22), which was found to fit the P3HT:PCBM device remarkably
well] is independent of carrier mobilities. Therefore, the steeper slope of the $J_{ph}$-$V$ curve (at $V_{bi}$) after annealing is almost certainly due to higher average carrier densities, which implies an increased rate of free carrier photogeneration.

The $J_{ph}$-$V$ characteristics of an ITO / PEDOT:PSS / MDMO-PPV:PCBM / Al device were obtained before and after thermal annealing at 140 °C for 20 mins under the same light level (38 mW/cm$^2$), as shown in Figure 4-8A. In Figure 4-8B, the corresponding R and $L^\text{rot}$ curves of both sets of $J_{ph}$-$V$ data have been shifted to a common origin for ease of comparison.

In this case, annealing appears to have three observable effects: firstly, it increases the symmetry of the $J_{ph}$-$V$ characteristics, as evident from the quality of overlap between the R and $L^\text{rot}$ curves derived from the pre- and post-annealed device. Secondly, $V_{POS}$ increases from 0.74 V to 0.80 V after

Figure 4-8

(A): $J_{ph}$-$V$ curves for an ITO / PEDOT:PSS / MDMO-PPV:PCBM / Al device before and after annealing for twenty minutes at 140 °C. (B): Comparison of the R and $L^\text{rot}$ curves before and after annealing. The points of optimal symmetry have been shifted to a common origin for ease of comparison.
annealing; thirdly – and of particular interest here – $J_{\text{POS}}$ is shifted in the \textit{upwards} direction by 1.21 mA/cm$^2$, with the offset current direction switching from negative to positive. In spite of the change in offset direction and magnitude, the slope of the $J_{\text{ph}}$-$V$ curve at $V_{\text{bi}}$ remained roughly constant after annealing, as seen from Figure 4-8B in the range $V_{\text{bi}} \pm 0.15$ V.

Device performance is clearly reduced as a result of thermal annealing, since the photocurrent is smaller (less negative) than before. The invariance in the slope at and near the built-in potential implies that the photoconductivity was unaffected by the annealing process [Equation (4.28)], suggesting that neither carrier mobilities nor average carrier densities were changed by annealing. Hence, the apparent reduction in photocurrent may be largely attributed to changes in the nature of the electrodes’ selectivity – which turn from self-selective to inverse-selective.

This observed switch from self-selectivity to inverse-selectivity is consistent with ellipsometric studies by Campoy-Quiles and co-workers, who have shown that vertical concentration profiles of donor and acceptor are sensitive to thermal annealing and electrode/substrate material.$^{[68]}$

In concluding this section, we note that annealing is a standard processing step for P3HT:PCBM devices in the literature$^{[15, 62]}$, but not for MDMO-PPV:PCBM devices$^{[56, 57]}$. Annealing beneficially increases the diffusive contribution toward the photocurrent in the operating range of P3HT:PCBM devices and enhances the rate of free carrier photogeneration. However, in the case of MDMO-PPV:PCBM devices, annealing switches the electrodes’ selectivities from self-selective to inverse-selective, which has the effect of diminishing the photocurrent.
4.6 **Optimisation of Solar Cells**

We turn now to the important issue of how the $J_{ph}$-$V$ characteristics can be used to screen new photovoltaic materials and to identify optimal blend compositions\*\* and processing protocols. The schematic in Figure 4-9A shows a typical $J_{ph}$-$V$ curve on which five important optimisation parameters are marked, denoted A to E: A and B are the value and slope of the corrected photocurrent at $V = 0$; C is the voltage at the point of optimal symmetry; and D and E are the value and slope of the corrected photocurrent at the point of optimal symmetry. A and B correspond to the photocurrent and shunt conductance under illumination; C corresponds to the built-in potential; and D is the spatially averaged diffusive photocurrent at the built-in potential. E corresponds to the photoconductivity at the built-in potential and, from Equation (4.5), is closely related to the carrier densities at the built-in potential.

To optimise device performance, processing conditions should be sought that maximise A, C, D and E whilst simultaneously yielding a value of B close to zero, subject to the additional condition that D should be negative. The conditions on A and B are satisfied when the electric field thresholds for efficient carrier generation and extraction are low (such that complete saturation of the photocurrent can occur at field strengths less than or equal to the built-in electric field $E_{\text{bi}}$). The condition on C is satisfied when $E_{\text{bi}}$ attains its largest possible value and the internal field strength is therefore maximised in the range $0 < V < V_{\text{bi}}$. The conditions on D are satisfied when the spatially averaged diffusive photocurrent is large and negative and so adds constructively to the overall photocurrent. Finally, the condition on E is

\*\* The phrase ‘blend composition’ is used here to refer to any donor/acceptor combination of fixed ratio in solution. Any changes to the active materials, their ratio or even solvent composition are considered to constitute a material change in the blend composition, requiring a fresh optimisation to be undertaken.
satisfied when the photogeneration properties of the active layer are optimised.

\[
\begin{align*}
&J_{\text{ph}} = J_{\text{ph}}^{\text{cor}} |_{V=0} \\
&B = dJ_{\text{ph}} / dV |_{V=0} \\
&\text{(A)} \\
&C = V_{\text{POS}} \\
&D = J_{\text{ph}}^{\text{cor}} |_{\text{POS}} \\
&E = dJ_{\text{ph}} / dV |_{\text{POS}} \\
\end{align*}
\]

Figure 4-9

(A): Annotated schematic of a typical $J_{\text{ph}}$-$V$ curve, illustrating five key parameters for optimisation. $A$ and $B$ are the value and slope of the corrected photocurrent at short-circuit; $C$ is the bias at the point of optimal symmetry (POS); $D$ and $E$ are the value and slope of the corrected photocurrent at the POS. To optimise device performance, fabrication conditions should be sought that maximise $A$, $C$, $D$, and $E$, whilst yielding a value of $B$ close to zero, subject to the additional condition that $D$ should be negative. (B): Schematic illustrating the appearance of the $J_{\text{ph}}$-$V$ curve after optimisation.

In the event that all the above conditions are simultaneously satisfied, a $J_{\text{ph}}$-$V$ response similar to the one shown in Figure 4-9B would be obtained, representing the best performance one could expect from the selected blend composition. On the other hand, if the processing conditions do not yield such an idealised response, analysis of parameters $A$ to $E$ can provide considerable insight into the reasons why. It may, for instance, prove impossible to optimise one parameter without worsening others, or alternatively, the threshold for efficient charge generation and extraction may significantly exceed the built-in field. In which case, one can then use this information to decide if further time and effort should be invested in continuing the search for optimal processing conditions, or whether it would
instead be better to move on to an alternative materials system or blend composition.

4.7 CONCLUSIONS

The photoconductivity \( \sigma \) of a BHJ solar cell is an even function of the electric field, and, when multiplied by the odd function \( E \), yields an odd function \( J_{ph}(E) \) that is anti-symmetric about \( E = 0 \). This argument explains the anti-symmetry of the \( J_{ph}-V \) curve, but the detailed shape of the \( J_{ph}-V \) curve – such as how its slope changes with the field and the threshold field beyond which it saturates – is determined by the functional form of \( \sigma(E) \).

An analytical expression for \( \sigma(E) \) was derived from continuity and drift-diffusion equations, assuming negligible bimolecular recombination – as was the case in the ITO / PEDOT:PSS / P3HT:PCBM / Al device. Using the \( J_{ph}-V \) response of the P3HT:PCBM-based device, the field dependence of its photoconductivity was estimated, and found to correspond very closely to the analytically-determined curve. Of particular interest is the absence of carrier mobility terms in the analytical expression for photoconductivity. This information, combined with the good agreement between theory and experiment, implies that the shape of the \( J_{ph}-V \) curve (excluding the offset current) was independent of carrier mobilities. On the other hand, the experimental and analytical \( \sigma-E \) curves did not agree well for the MDMO-PPV:PCBM device. Intensity dependent \( J_{ph}-V \) measurements revealed significant bimolecular recombination in the device to be the cause of the mismatch.
Fundamental understanding of widely-used fabrication procedures for P3HT:PCBM and MDMO-PPV:PCBM devices was obtained from the examination of their $J_{ph}$-$V$ characteristics before and after thermal annealing. Improvement in P3HT:PCBM device efficiencies after annealing was found to be due to enhanced free carrier photogeneration in the device, and a beneficial increase in the diffusive contribution to the photocurrent, therefore rationalising the widespread inclusion of an annealing step as part of the fabrication process. Annealing of MDMO-PPV:PCBM devices, however, affects neither the carrier mobilities nor the rate of free carrier photogeneration, but switches the electrodes from being self-selective to inverse-selective, which explains why these devices are not normally annealed during fabrication.

Finally, we have identified a number of parameters that characterise the shape of the $J_{ph}$-$V$ curves for BHJ solar cells. For these parameters, a set of conditions were outlined that, if fulfilled through suitable fabrication conditions, would yield the optimum device performance that can be expected from the device. This analysis can provide a potentially powerful means of screening new photovoltaic materials and identifying optimal blend compositions and processing protocols.
Devices fabricated from a new donor/acceptor blend combination show promising photovoltaic performance and unusual current-voltage behaviour. Their behaviour, which we attribute to a field-dependent photogeneration rate, is analysed using their corrected photocurrent-voltage characteristics.
5.1 INTRODUCTION

In this chapter, we introduce a promising new bulk heterojunction blend system based on the donor polymer poly(2,7-carbazole) and a new low band gap acceptor, which is a small-molecule derivative of the Vinazene molecule. The effects on device efficiency of varying the blend composition and annealing temperature during device fabrication were investigated. Interestingly, the current-voltage characteristics of these devices exhibited unusual features that are not observed with MDMO-PPV:PCBM or P3HT:PCBM devices. These features were subsequently studied in greater depth using the pulsed technique. A further modification to the model for corrected photocurrents – developed over the course of the previous two chapters – was made to account for the anomalous behaviour. In short, the behaviour was attributed to the exciton dissociation probability being dependent on the electric field strength.

5.2 BHJ SOLAR CELLS BASED ON A LOW BAND-GAP SMALL-MOLECULE ACCEPTOR

The electron acceptor material found in the most efficient BHJ solar cells is PCBM, which is a derivative of the C_{60} fullerene molecule that is highly soluble in standard organic solvents. The fullerene core of PCBM readily accepts electrons from a wide range of organic donor materials and exhibits high electron mobilities even in composite form. Nonetheless, it is a non-ideal material for photovoltaic applications due to its weak absorption in the
solar spectrum\textsuperscript{[33]} and its excessively deep-lying LUMO level\textsuperscript{[58]}, which results in needless energy loss during electron transfer and so limits the efficiencies of the final devices.

There is a clear need for alternative acceptor materials that – like PCBM – exhibit favourable electron-transporting and processing properties, but which also absorb strongly in the solar spectrum. Of particular interest in this regard is a new class of small-molecule acceptor materials based on 2-vinyl-4,5-dicyanoimidazole (Vinazene\textsuperscript{TM}) as recently reported by Shin and co-workers.\textsuperscript{[74]} Vinazene\textsuperscript{TM} derivatives are soluble in standard organic solvents, have good film-forming properties, and exhibit high optical densities. An added advantage is the simple high-yield chemistry involved in their synthesis which, coupled with their inherent chemical flexibility, offers considerable scope for tuning the HOMO and LUMO levels and thereby optimising photovoltaic performance.

Here, we investigate the photovoltaic response of BHJ solar cells based on blends of:

- the Vinazene\textsuperscript{TM}-based small-molecule acceptor 4,7-bis(2-(1-(2-ethylhexyl)-4,5-dicyano-imidazol-2-yl)vinyl) benzo[c][1,2,5]thiadiazole [EV-BT], and

- the donor polymer poly[N-(2'-decyltetradecyl) carbazole]-2,7-diyl [PCz].

The chemical structures of these two materials are shown in Figure 5-1. In the initial report by Shin and co-workers, a hexyl- version [HV-BT] of the acceptor was reported that showed good photovoltaic response when blended with regioregular poly(3-hexylthiophene) P3HT, reaching a power conversion
efficiency of 0.45% under simulated solar irradiation.\textsuperscript{[74]} EV-BT improves on HV-BT by offering superior solubility in common solvents due to the 2-ethylhexyl side chain in place of the hexyl one. PCz has previously been shown to perform well as a donor material when blended with the small molecule electron transporter perylene tetracarboxydiimide [PDI]\textsuperscript{[81]} and was chosen for use here because its absorption spectrum beneficially plugs a gap in the absorption spectrum of EV-BT, thus ensuring good light harvesting properties from 300 nm to 520 nm (Figure 5-2). Importantly, chloroform-based solutions of EV-BT and PCz have excellent film-forming properties, yielding smooth uniform films when spin-coated and remaining visually homogenous even after extended annealing. Another important factor in the choice of PCz as the donor material is the relatively large energy difference of 2 eV between the donor HOMO and the acceptor LUMO, which in principle should allow photovoltages of up to 2 V to be realised.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure_5-1.png}
\caption{The chemical structures of 4,7-bis(2-(1-(2-ethylhexyl))-4,5-dicyano-imidazol-2-yl)vinyl benzo[c][1,2,5]thiadiazole [EV-BT] and poly[N-(2’-decyltetradecyl) carbazole]-2,7-diyl [PCz], and the energy level diagram for the ITO / PEDOT:PSS / PCz:EV-BT / Ca / Ag device investigated here.}
\end{figure}
In the work described here, PCz was provided by Prof. Klaus Mullen and Dr. Martin Baumgarten of the Max Plank Institute for Polymer Research, Mainz, Germany, and EV-BT was synthesised by Teck Lip Tam in IMRE, Singapore, under the direction of Dr. Alan Sellinger.

Figure 5-2
(A): Absorption and photoluminescence (PL) spectra for a pristine EV-BT film. When blended with PCz in equal weight ratio and excited at 444 nm, the EV-BT PL is quenched. (B): Absorption and PL spectra for a pristine PCz film. When blended with EV-BT in equal weight ratio and excited at 395 nm, the PCz PL is quenched. The absorption spectrum of EV-BT shows a better correspondence with the AM1.5G spectrum than PCz.

The HOMO and LUMO levels for PCz were taken from the literature (-5.6 and -2.6 eV respectively\cite{81}), while the LUMO level of EV-BT was estimated as -3.6 eV using cyclic voltammetry (as performed by Teck Lip Tam). The onset of optical absorption occurs at ~520 nm (see Figure 5-2), giving an
estimated band-gap of 2.4 eV and an inferred HOMO level of approximately -6.0 eV. For the purposes of preliminary characterisation, equal weight ratios of the two materials were dissolved in chloroform and spin coated to produce a thin composite film. The film was separately excited by monochromatic light of 395 and 444 nm, which correspond to the respective absorption peaks of PCz and EV-BT. In both cases, the photoluminescence was substantially weaker than similarly excited films of neat EV-BT and PCz, indicating efficient exciton dissociation in the blend (see Figure 5-2).

BHJ solar cells of the form ITO / PEDOT:PSS / PCz:EV-BT / Ca / Ag were fabricated by spin-coating PCz:EV-BT films of varying composition from 10 mg/ml solution in chloroform onto ITO / PEDOT:PSS substrates. Devices were thermally annealed for 10 mins prior to the sequential deposition of the Ca cathode and Ag protective layer via a shadow mask. The influence of blend composition and annealing temperature was investigated using

- three different weight ratios (PCz:EV-BT = 50:50, 30:70 and 10:90) and
- three different annealing temperatures (un-annealed, 60 °C and 80 °C),

which correspond to nine different fabrication conditions in total. The current-voltage characteristics were measured under the 100 mW/cm² output of a K. H. S. metal halide solar simulator, but were uncorrected for spectral mismatch (since we did not have access to an AM1.5G-calibrated photodiode). The short-circuit current $J_{SC}$, the open-circuit voltage $V_{OC}$, the fill factor FF and the power conversion efficiency PCE thus obtained are listed in Table 5a and shown in Figure 5-3A. The quantum efficiency curves under low-intensity monochromatic light are shown in Figure 5-3B.
Figure 5-3

(A): The effect of annealing temperature on $J_{SC}$, $V_{OC}$, fill factor and power conversion efficiency for three blend compositions consisting of 50, 70 and 90% EV-BT content (by mass).  (B): The effect of the annealing temperature on spectral quantum efficiency (under short-circuit conditions) for the three blend compositions.

Table 5a

<table>
<thead>
<tr>
<th>Device No.</th>
<th>EV-BT wt%</th>
<th>Anneal Temp</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>Fill Factor</th>
<th>PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>50 %</td>
<td>N/A</td>
<td>0.78</td>
<td>1.21</td>
<td>0.27</td>
<td>0.25 %</td>
</tr>
<tr>
<td>#2</td>
<td>50 %</td>
<td>60 °C</td>
<td>1.40</td>
<td>1.30</td>
<td>0.32</td>
<td>0.59 %</td>
</tr>
<tr>
<td>#3</td>
<td>50 %</td>
<td>80 °C</td>
<td>1.08</td>
<td>1.36</td>
<td>0.38</td>
<td>0.56 %</td>
</tr>
<tr>
<td>#4</td>
<td>70 %</td>
<td>N/A</td>
<td>1.24</td>
<td>1.33</td>
<td>0.30</td>
<td>0.50 %</td>
</tr>
<tr>
<td>#5</td>
<td>70 %</td>
<td>60 °C</td>
<td>1.44</td>
<td>1.39</td>
<td>0.34</td>
<td>0.69 %</td>
</tr>
<tr>
<td>#6</td>
<td>70 %</td>
<td>80 °C</td>
<td>1.14</td>
<td>1.36</td>
<td>0.49</td>
<td>0.75 %</td>
</tr>
<tr>
<td>#7</td>
<td>90 %</td>
<td>N/A</td>
<td>0.32</td>
<td>1.35</td>
<td>0.30</td>
<td>0.13 %</td>
</tr>
<tr>
<td>#8</td>
<td>90 %</td>
<td>60 °C</td>
<td>0.38</td>
<td>1.10</td>
<td>0.31</td>
<td>0.13 %</td>
</tr>
<tr>
<td>#9</td>
<td>90 %</td>
<td>80 °C</td>
<td>0.44</td>
<td>0.96</td>
<td>0.34</td>
<td>0.14 %</td>
</tr>
</tbody>
</table>

It is clear from Figure 5-3A that the device characteristics depend on the processing conditions in a fairly complex manner, and trends that apply for one blend composition do not necessarily hold for others. For instance, whilst the short-circuit photocurrent increases steadily with annealing temperature
for 90% EV-BT content, at lower EV-BT content it appears to peak at some intermediate temperature between 25 and 80 °C. Nonetheless, some general conclusions may be drawn from the data. All devices with 90% EV-BT content had relatively poor performance, presumably due to the low donor-acceptor interfacial area and insufficient PCz pathways for continuous hole transport. Of the devices studied, those containing 70% EV-BT content displayed the best overall characteristics, yielding the best performance at all three annealing temperatures in terms of $J_{SC}$, $V_{OC}$, fill factor and PCE. Reducing the EV-BT content from 70% to 50% resulted in a slight loss of $J_{SC}$ and a substantial decrease in fill factor at an annealing temperature of 80 °C. The most efficient device was obtained using 70% EV-BT followed by annealing at 80°C. This yielded a PCE of 0.75%, a $J_{SC}$ of 1.14 mA/cm$^2$, a $V_{OC}$ of 1.36 V and a fill factor of 49%.

The current-voltage characteristics of the most efficient device (Device #6) under simulated sunlight (100 mW/cm$^2$) and in the dark are shown in Figure 5-4. The open-circuit voltages of the devices were all 1 V or above, compared to typical values of 0.5 to 1 V for PCBM-based BHJ devices$^{[83, 84]}$ – a consequence of the favourably located -3.6 eV LUMO level of EV-BT compared to the -4.3 eV level of PCBM$^{[58]}$. High quantum efficiencies (and therefore $J_{SC}$’s) were obtained for all devices with 50% or 70% EV-BT content, and Device #6 had a good fill factor approaching 50%, indicating relatively low losses.
This study was preliminary and the fabrication conditions used here were not fully optimised. From numerous studies on other materials systems, the film morphology is known to have a significant influence on the final photovoltaic performance of the device.\cite{69,70} Apart from blend composition and annealing temperature, other factors such as solvent choice\cite{27,31} and concentration\cite{85} can drastically alter the way donor and acceptor materials phase separate in the film and so greatly influence exciton dissociation and charge transport.\cite{30} In the case of P3HT:PCBM devices, substantial year-on-year improvements in device efficiencies have been achieved as materials quality and processing know-how have improved, and we would envisage similar improvements over time for EV-BT:PCz. Even so, these preliminary results are encouraging and compare very favourably with the small number of solution-processable small molecule acceptor materials reported elsewhere in the literature, which...
have yielded efficiencies in the range 0.07% to 0.45% with open-circuit voltages of less than 1 V at solar illumination levels.\[74, 81, 86, 87\]

We also note that the PCz:EV-BT combination has considerable potential for improvement through the chemical modification of the PCz donor material to widen the absorption range (see recent work by Blouin and co-workers\[88, 89\]). Studies by colleagues at IMRE have also used EV-BT in conjunction with other well-known donor polymers such as PQT-12 and P3HT.\[75\]

5.3 **INFLECTIONS IN THE CORRECTED PHOTOCURRENT**

![Diagram](image-url)

**Figure 5-5**

$J_{\text{light}}$-$V$, $J_{\text{dark}}$-$V$ and $J_{\text{ph}}$-$V$ characteristics of the ITO / PEDOT:PSS / PCz:EV-BT / Ca / Ag device with the highest PCE (Device #6), as measured by the pulsed technique at an instantaneous light intensity of 90 mW/cm$^2$. The $J_{\text{light}}$-$V$ curve show two points of inflection, while the $J_{\text{ph}}$-$V$ curve shows three. Inset: The spectral quantum efficiency at short-circuit and under low intensity illumination.
We draw attention to a number of unusual “kinks” (inflections) in the current-voltage curves in Figure 5-4 close to the open-circuit voltage. Figure 5-5 shows the $I_{\text{dark}}$-$V$, $I_{\text{light}}$-$V$ and $I_{\text{ph}}$-$V$ characteristics of Device #6 (70% EV-BT, 80 °C anneal) determined using the pulsed measurement technique under an instantaneous white LED light intensity of 90 mW/cm$^2$. The inset shows the spectral quantum efficiency under low-intensity monochromatic illumination.

The device had an overall short-circuit quantum efficiency of 5.7% (300 < $\lambda$ < 700 nm) and an open-circuit voltage of 1.30 V under the quoted illumination. The “kinks” seen in the $I_{\text{light}}$-$V$ characteristics are also evident in the $I_{\text{ph}}$-$V$ curve, implying they are related in some way to the charge generation or extraction properties of the active layer.

The $I_{\text{ph}}$-$V$ curve, which is replicated in Figure 5-6A, has a roughly anti-symmetric profile with a point of optimal symmetry at 1.62 ± 0.01 V. To aid visualisation the data has, as before, been divided into two parts L and R, and the left-side data has been rotated by 180° to generate a new curve $L^{\text{rot}}$. $L^{\text{rot}}$ and $R$ show a very close correspondence from $V_{\text{POS}}$ to 2.1 V, implying excellent anti-symmetry in this range, but diverge somewhat at higher biases with $R$ being substantially larger in magnitude. The current $J_{\text{POS}}$ at the point of optimal symmetry has a small positive value of 0.12 ± 0.01 mA/cm$^2$, consistent with at least one of the electrodes being (slightly) inverse-selective in nature.

§§ The pulsed measurement subjected the device to applied voltages of up to 3.5 V, leading to a slight change in the electrical characteristics. This is evident in the larger $I_{\text{dark}}$ in Figure 5-5 compared to Figure 5-4, and explains the higher vertical position of the “kinks” in $I_{\text{light}}$ in Figure 5-5.
In Chapter 3, it was shown that by treating a BHJ solar cell as a simple device with a single layer of composite semiconductor, the anti-symmetric $J_{ph}$-$V$ response of a solar cell may be rationalised using the expression:

$$J_{ph} = J_{ph}^{diff} + \sigma E,$$  \hspace{1cm} (5.1)

where $\sigma$ is the photoconductivity of the active layer,

$$\sigma = e \left[ \mu_h < n_h^{ph}(x) > + \mu_e < n_e^{ph}(x) > \right],$$  \hspace{1cm} (5.2)

and $J_{ph}^{diff}$ is the spatially averaged diffusive photocurrent:

$$J_{ph}^{diff} = e \left[ -D_h \frac{n_h^{ph}(d) - n_h^{ph}(0)}{d} + D_e \frac{n_e^{ph}(d) - n_e^{ph}(0)}{d} \right].$$  \hspace{1cm} (5.3)
The term $\sigma E$ represents the drift photocurrent, which is responsible for the anti-symmetric shape of the $J_{\text{ph}}$-$V$ curve centred about a symmetry point at the built-in potential. The Fermi level of the Ca cathode is expected to pin to the -3.6 eV LUMO level of the acceptor.$^{[63]}$ Hence, the built-in potential of 1.62 V (as inferred from the point of optimal symmetry) is consistent with the 1.6 eV energy difference between the -5.2 eV work function of PEDOT:PSS and the pinned -3.6 eV Fermi level of Ca. Following the arguments and results presented in Section 4.3, we would expect $\sigma$ to be a monotonically decreasing function of the field strength $|E|$ with a maximum at $E = 0$.

In the event that the carrier densities at the electrodes are independent – or only weakly dependent – on the electric field, $J_{\text{ph}}^{\text{diff}}(E)$ may be considered a constant offset current $J_{\text{off}}$ and therefore has the effect of vertically displacing the $J_{\text{ph}}$-$V$ curve without significantly changing its shape. This approximation is most valid for the region of the $J_{\text{ph}}$-$V$ curve between 1.1 and 2.1 V, where the anti-symmetry is nearly “exact”. In any case, the vertical displacement is fairly close to zero with $J_{\text{off}}$ being roughly 4% of the short-circuit current.

Of particular interest in the current context are the three points of inflection in the $J_{\text{ph}}$-$V$ curve: one is located at the 1.62 V symmetry point where the slope has a local minimum; the other two are located at 1.29 V and 2.07 V where the slope has local maxima (Figure 5-6B). These inflection points are hard to rationalise in terms of the simple model set out above as can be seen from the following argument. Ignoring for a moment the small offset current $J_{\text{off}}$, $J_{\text{ph}}$ is the product of a supposedly monotonically decreasing even function $\sigma(E)$ and the linear function $E$. Hence, $J_{\text{ph}}$ should exhibit a sub-linear dependence on $E$. In other words, the slope of the $J_{\text{ph}}$-$V$ curve should be largest at the built-in potential $V_{\text{bi}}$ (where $E = 0$) and decrease steadily towards zero with increasing
field strength. This behaviour was observed in the devices presented in the previous chapters – the slope of the $J_{ph}$-$V$ curve as a function of $V$ is shown in Figure 5-7A for the P3HT:PCBM, MDMO-PPV:PCBM and PQT-12:HV-BT devices – but it is most certainly not the case for the PCz:EV-BT device, whose $J_{ph}$-$V$ curve exhibits a minimum in the slope at $V_\text{bi}$ (Figure 5-6B).

![Figure 5-7](image)

(A): The slope of the $J_{ph}$-$V$ curves as a function of applied voltage for the devices used in the previous chapters: ITO / PEDOT:PSS / P3HT:PCBM / Al, ITO / PEDOT:PSS / MDMO-PPV:PCBM / Ag and ITO / PEDOT:PSS / PQT-12:HV-BT / Ag. In all three devices, the slope has a single maximum and decreases monotonically either side. (B): The estimated photoconductivity of the three devices as a function of electric field, all of which peak at $E = 0$ and decreases monotonically with increasing field strength.

### 5.4 Field-dependent Photogeneration

Evidently the model presented above, which could rationalise the $J_{ph}$-$V$ characteristics of the devices studied in the previous chapters, cannot account for the inflections in the $J_{ph}$-$V$ curve of the PCz:EV-BT device. If the PCz:EV-BT device can still be treated as a simple single-layer device, we conclude that $\sigma(E)$ is not in fact a monotonically decreasing function of the field strength (as
expected from the field-sweeping argument proposed in Section 4.3), and must therefore have a more complex functional form. By approximating \( J_{\text{ph}}^{\text{diff}} = J_{\text{off}} \) we can obtain an approximation \( \hat{\sigma}(E) \) for the field-dependence of the photoconductivity from Equation (5.1):

\[
\hat{\sigma} = \frac{J_{\text{ph}} - J_{\text{off}}}{E}
\]  

(5.4)

The result, shown in Figure 5-8, is a roughly even double-humped function of the electric field which decreases towards zero in the limit of high absolute field strength.

![Figure 5-8](image)

The estimated photoconductivity of the PCz:EV-BT device as a function of electric field, obtained using Equation (5.4) and the values of \( V_{\text{BI}} = V_{\text{POS}} \) and \( J_{\text{off}} = J_{\text{POS}} \) from Figure 5-6.

In the central region of the curve, where the anti-symmetry is “exact”, \( \hat{\sigma} \) approximates \( \sigma \) most closely. In this region, it is observed to increase sharply with increasing field strength. For the reasons outlined in Section 4.3, this
implies an increase in the density of photogenerated charge carriers with increasing field strength.\textsuperscript{[54, 90]}

\textbf{Figure 5-9}

A schematic illustrating the exciton dissociation process at a donor/acceptor heterojunction. (A): An exciton in the acceptor phase is split at a heterojunction, where the hole is transferred from the acceptor HOMO level to the donor HOMO level. (B): If the energy level offset between the HOMO energies is sufficiently large, the partitioning results in a free electron and hole, otherwise (C): a charge-transfer (CT) exciton is formed, consisting of a spatially-separated, but Coulombically-bound electron-hole pair that will eventually recombine.

In BHJ solar cells, the key step in generating a photocurrent is exciton splitting at the phase boundaries of the donor/acceptor blend, which has the effect of partitioning the holes and electrons into the donor and acceptor phases, respectively.\textsuperscript{[91]} This step, however, does not in itself guarantee exciton dissociation since the electron-hole pairs may remain Coulombically-bound in the form of intermolecular charge-transfer (CT) excitons\textsuperscript{[92]} even after partitioning has occurred, leaving them susceptible to eventual geminate recombination. To achieve complete dissociation, the electrons and holes

\textsuperscript{**} Even if the analytical model is inapplicable to these devices, time-of-flight measurements on other photovoltaic blend systems indicate that carrier mobilities typically show only a weak dependence on the electric field, and in some cases can even decline with increasing field strength.
must gain sufficient kinetic energy in the charge transfer process to overcome their residual attraction, which is thought to require an offset of at least \(-0.5\) eV in the energies of the relevant frontier orbitals.\[23\]

For devices such as the P3HT:PCBM, MDMO-PPV:PCBM devices, charge separation occurs mainly via an electron transfer from the LUMO levels of the donor phase to the LUMO level of PCBM. In both cases, the energy offset exceeds 1 eV\[29, 58\], a value considerably larger than the \(-0.5\) eV requirement. In the PQT-12:HV-BT blend system, excitons are generated in both phases, and the energy offset for the respective frontier orbitals for electron and hole transfer also exceed the \(-0.5\) eV requirement\[†††\]. However, in materials systems where this energy offset requirement is not met, the yield of free carriers is expected to be low, resulting in significantly reduced device efficiencies.

For the PCz:EV-BT devices investigated, EV-BT was the dominant light harvester in the blend system, so charge separation occurs mainly via the transfer of holes from the -6.0 eV HOMO level of EV-BT to the -5.6 eV HOMO level of PCz. The 0.4 eV offset in the PCz:EV-BT blend system is lower than the above-mentioned \(-0.5\) eV requirement for complete dissociation. This suggests that the photogenerated carrier yield may depend sensitively on the electric field strength, since a sufficiently strong electric field will polarize a CT exciton and hence increase the probability of dissociation.\[42, 93\]

\[†††\] [PQT-12: HOMO \(-5.2\) eV, LUMO \(-3.0\) eV], [HV-BT: HOMO \(-6.0\) eV, LUMO \(-3.6\) eV]. Hence, the energy offset for electron transfer is \(-0.6\) eV, and the energy offset for hole transfer is \(-0.8\) eV.
The $J_{ph}$-$V$ response of the PCz:EV-BT device under multiple light intensities ranging from 15 to 90 mW/cm$^2$ is shown in Figure 5-10A. The points of optimal symmetry lie in a tight band between 1.62 and 1.64 V. However, the main point of interest in the current context is the linear dependence of $J_{ph}$ on the incident light intensity $I$. This is shown for two illustrative voltages at 0 V and 3 V in Figure 5-10B, and implies that $J_{ph}(E)$, $J_{ph}^{diff}(E)$ [and hence $J_{off}(E)$] and $\sigma(E)$ are all proportional to the exciton photogeneration rate, an important fact that we will make use of in the ensuing discussion.

To allow for the dependence of the photogenerated carrier yield on the electric field, we introduce a new function $g(E)$ – defined as the fraction of photogenerated excitons that dissociate into free electron-hole pairs under an electric field $E$. As shown above, the entire $J_{ph}(E)$ curve is proportional to the exciton generation rate, and therefore must be proportional to $g(E)$ as well.
As we now show, $g(E)$ allows us to reconcile the monotonically decreasing form of the photoconductivity in Figure 5-7B with the double-humped form in Figure 5-8. Inserting $g(E)$, Equation (5.1) then becomes:

$$J_{ph} = [J_{off} + \sigma_0 (E)E] g(E),$$

(5.5)

where $J_{off}$ and $\sigma_0$ are the offset current and photoconductivity that would be obtained in the event of complete exciton dissociation. From Equation (5.2), $\sigma_0(E)$ is equal to:

$$\sigma_0(E) = e^{\left[\mu_h < n_{h0}^{ph} (x,E) > + \mu_e < n_{e0}^{ph} (x,E) > \right]},$$

(5.6)

where $n_{h0}^{ph} (x,E)$ and $n_{e0}^{ph} (x,E)$ are the densities of the photogenerated holes and electrons that would be obtained in the event of complete exciton dissociation. For the reasons outlined in Chapter 3, $< n_{h0}^{ph} (x,E)>$ and $< n_{e0}^{ph} (x,E)>$ are expected to decrease monotonically with increasing field strength. Hence, $\sigma_0(E)$ should be a monotonically decreasing function of the electric field, resembling the curves in Figure 5-7B. The fractional free carrier yield $g(E)$ by contrast should be a monotonically increasing function of the electric field, saturating at unity (or less) at high field strengths. The actual photoconductivity $\sigma(E)$ is obtained by multiplying together $\sigma_0(E)$ and $g(E)$, and is expected to be an even double-humped function similar in appearance to the $\hat{\sigma}(E)$ curve in Figure 5-8.

Finally, in anticipation of the discussion in the next section, we differentiate Equation (5.5) to give the following expression for the slope of the $J_{ph}-E$ curve.

$$\frac{dJ_{ph}}{dE} = [J_{off} + \sigma_0 (E)E] \frac{dg(E)}{dE} + g(E) \left( \frac{dJ_{off}}{dE} + \sigma_0 (E) + E \frac{d\sigma_0 (E)}{dE} \right)$$

(5.7)
which, if the offset current is zero, reduces to the following form at the built-in potential:

$$\left. \frac{dJ_{ph}}{dE} \right|_{E=0, J_{off}=0} = \sigma_0(E)g(E)$$  \hspace{1cm} (5.8)

### 5.4.1 Effect on an imaginary model device

Considerable insight into the consequences of field-dependent carrier generation can be obtained by applying the arguments outlined above to an imaginary “model” device in which we are able to control the fractional free carrier yield $g(E)$. We start by considering the ideal situation in which all photogenerated excitons dissociate spontaneously into free electrons and holes even when the electric field strength is zero, *i.e.* the yield $g(E) = g_0(E)$ is unity at all field strengths (Figure 5-11A). As stated above, $\sigma_0(E)$ is the photoconductivity in the event of complete exciton dissociation. In Figure 5-11B, we have modelled $\sigma_0(E)$ using the analytically-derived photoconductivity $\sigma_i(E)$ (Section 4.3), which is a monotonically decreasing function of the electric field $E$. For simplicity, the offset current $J_{off}$ is taken to be zero.††‡‡ The $j_{ph}-E$ curve is given by Equation (5.5) and is self-evidently anti-symmetric due to the even symmetries of $\sigma_0(E)$ and $g_0(E)$, and the odd symmetry of $E$ (Figure 5-11C).

††‡‡ A non-zero $J_{off}$ will disrupt the anti-symmetry of the $j_{ph}-V$ curve because, from Equation (5.3), it introduces an additional even-symmetry term $J_{off}q(E)$. However, if $J_{off}$ is small, as is the case for the PCz:EV-BT device investigated here, this effect will be small and the anti-symmetry will be retained to a good approximation.
Schematic diagram explaining the effect of field-dependent carrier generation on the current-voltage characteristics, assuming an offset current of zero. (A): The “ideal” situation in which the free carrier yield $g_0(E)$ is 100% at all field strengths. (B): The (arbitrary unit) photoconductivity $\sigma(E)$ corresponding to case (A); $\sigma(E)$ is an even monotonically decreasing function of the electric field. (C): The corrected photocurrent $J_{ph}(E) = \sigma(E)E$ corresponding to case (A). (D): The free carrier yield $g_1(E)$ for an “intermediate” situation in which the carrier yield increases monotonically from 50% at $E=0$ to 100% as $E \to \pm \infty$; (E): The photocconductivity $\sigma(E) = \alpha(E)g_1(E)$ corresponding to case (D); (F): The corrected photocurrent $J_{ph}(E) = \sigma(E)g_1(E)E$, corresponding to case (D). (G): The free carrier yield $g_3(E)$ for an “extreme” case in which the yield increases monotonically from zero at $E = 0$ to 100% as $E \to \pm \infty$; (H) and (I) show the photoconductivity and corrected photocurrent corresponding to case (G).

We now consider the effect of introducing a simple field-dependence into the carrier yield, assuming no other changes to the device. In Figure 5-11D, we consider an “intermediate” situation in which the yield $g_1(E)$ is 50% at zero-field, rising monotonically to 100% at high field strengths. Following Equation (5.5), the photoconductivity $\sigma_1(E)$ is obtained by multiplying $\sigma_0(E)$ by $g_1(E)$, which yields a curve with a double-humped functional form (Figure 5-11E). Multiplying $\sigma_1(E)$ by $E$ gives $J_{ph}(E)$, which retains an anti-symmetric appearance, but develops three points of inflection (Figure 5-11F). In accordance with Equation (5.8), the slope of the $J_{ph}-E$ curve at the central point.
of inflection \((E = 0)\) is reduced by a factor of two relative to Figure 5-11C due to the two-fold reduction in \(g(0)\).

The same general behaviour is observed when the yield \(g_x(E)\) is 0\% at zero-field rising monotonically to 100\% at high field strengths (Figure 5-11G). \(\sigma_x(E)\) again has a double-humped appearance, although it now obviously equals zero when \(E = 0\) (Figure 5-11H). The anti-symmetric \(J_{ph}E\) curve again has the expected three points of inflection, and its slope at the central inflection is now zero in agreement with Equation (5.8) (Figure 5-11I).

### 5.4.2 Implications for device efficiency

In Figure 5-12, we overlay the three \(J_{ph}V\) curves corresponding to the illustrative data in Figure 5-11. The curves all pass through zero at \(V = V_{bi}\) (due to the assumption \(J_{off} = 0\)) albeit with diminishing slopes as \(g(0)\) tends towards zero. The inflections caused by the field-dependent free carrier yield are (unsurprisingly) detrimental to device performance since, geometrically speaking, they cause the \(J_{ph}V\) curve [and hence the \(J_{light}V\) curve] to bend inwards to the origin, lowering the fill factor. The effect is most pronounced when the free carrier yield is zero at the built-in potential, since this causes a complete flattening of the \(J_{ph}V\) curve.

The “intermediate” case in Figure 5-12 is similar to the situation observed experimentally in Figure 5-6A, where the slope has a non-zero local minimum at the point of optimal symmetry. One possible explanation for the non-zero slope is a contribution to the photocurrent from excitons generated in the less-strongly absorbing PCz phase. These excitons dissociate via an electron transfer process, for which the \(\sim 1\) eV LUMO-LUMO offset is large enough to
ensure efficient spontaneous free carrier generation even in the absence of an electric field.

![Figure 5-12](image)

**Figure 5-12**
Schematic diagram showing the overlaid $J_{ph}$-$V$ curves for the three cases considered in Figure 5-11. The three curves intersect at the built-in potential where the current falls to zero due to the assumed zero offset current. The curves bend inwards towards the origin as the spontaneous yield of free carriers diminishes. The inset shows the voltage-dependence of the power curve for the three situations. There is a progressive reduction in the peak power as the yield diminishes.

Returning to the excitons harvested in the EV-BT layer, the locations of the outer points of inflection provide some indication of the field needed to initiate significant free carrier generation – in this case $\sim 8 \times 10^6$ Vm$^{-1}$. Importantly, it should be possible to lower this value by functionalising PCz in such a way as to raise its HOMO level (to a less negative value) by a few tenths of an electron-Volt (thereby ensuring that the electron and hole gain sufficient kinetic energy to overcome their residual attraction after partitioning has occurred, see Figure 5-9). In principle, it should be possible to raise the HOMO level of PCz to -5.2 eV (which is the work function of PEDOT:PSS) without risking any reduction in the built-in field.
The bending of the $J_{\text{ph}}$-$V$ curve towards the origin, as a result of field-dependent free carrier generation, provides one possible explanation for the occurrence of very low fill factors $< 0.25$ occasionally reported in the literature\cite{94}. For a device in which free carrier losses are high (due, perhaps, to bimolecular recombination), a large electric field would be required to extract carriers to the external circuit. In such a case, saturation of the $J_{\text{ph}}$-$V$ and $J_{\text{light}}$-$V$ curves does not occur near/within the fourth (power-producing) quadrant, meaning the curves appear almost as a straight line through $J_{SC}$ and $V_{OC}$ in that quadrant. The fill factor calculated from such a $J_{\text{light}}$-$V$ curve would approach a value of 0.25. However, if this same device were to also exhibit field-dependent carrier photogeneration, the $J_{\text{ph}}$-$V$ and $J_{\text{light}}$-$V$ curves would bend inwards towards the origin, reducing the fill factor below 0.25.

**Figure 5-13**

(A): A simulated $J_{\text{ph}}$-$V$ curve with field-independent carrier generation. The curve is almost a straight line through $J_{SC}$ and $V_{BI}$, resulting in a fill factor $\approx 0.25$. (B): A simulated $J_{\text{ph}}$-$V$ curve with field-dependent carrier generation, showing the characteristic “kinks” near the built-in potential. The inward bending of the curve towards the origin results in the fill factor being reduced below 0.25.
5.5 **Misleading inflections in the (un-corrected) photocurrent**

The occurrence of three points of inflection in the $J_{ph}-V$ characteristics of a BHJ solar cell is indicative of field-dependent carrier generation and is manifested in the (un-corrected) photocurrent as two points of inflection (Figure 5-5). However, it does not necessarily follow that the appearance of points of inflection in the $J_{light}-V$ response of a solar cell implies field-dependent generation. In Figure 5-14, we consider a model device which exhibits field-independent carrier generation, *i.e.* there are no “kinks” in the $J_{ph}-V$ curve. In situations in which the dark current is small and/or the incident light intensity is sufficiently high, the $J_{light}-V$ curve also develops two points of inflection (see Figure 5-14), resembling the $J_{light}-V$ curve for PCz:EV-BT in Figure 5-5.

![Figure 5-14](image)

**Figure 5-14**
Simulated $J_{dark}-V$ and $J_{ph}-V$ curves showing how “kinks” may be apparent in the $J_{light}-V$ curve even though the $J_{ph}-V$ curve is not “kinked”.

The curves in Figure 5-14 in fact show favourable device performance since efficiency loss due to the injected current is suppressed, as opposed to the unfavourable situation of field-dependent carrier generation. The main
difference between the $J_{\text{light}}$-$V$ curve from the PCz:EV-BT device and the $J_{\text{light}}$-$V$ curve in Figure 5-14 is the voltage position of the first (left-most) inflection. In the case of field-independent generation, the first inflection occurs at or near the built-in potential, corresponding to the maximum slope of the $J_{\text{ph}}$-$V$ curve. In contrast for the PCz:EV-BT device, it is the second (right-most) inflection that occurs at or near the built-in potential, corresponding to the local minimum slope in the $J_{\text{ph}}$-$V$ curve, while the first inflection occurs at a voltage $V < V_{\text{bi}}$.

Hence, identifying the occurrence of field-dependence in free carrier generation requires either knowledge of the built-in potential, or a measurement of the corrected photocurrent-voltage characteristics. Knowledge of only the (uncorrected) photocurrent-voltage characteristics can be misleading, and any inflections thus observed should not be immediately attributed to field-dependent carrier generation. Thus it is clear that studying the $J_{\text{ph}}$-$V$ characteristics provides powerful insight into deciphering the “inner workings” of solar cells.

## 5.6 Conclusions

Bulk heterojunction solar cells based on a new blend system PCz:EV-BT have been reported. A basic investigation into the effect of fabrication conditions on device efficiency was performed and, even though the fabrication conditions were far from optimal, devices made from this new materials system showed promising performance. The most efficient PCz:EV-BT device exhibited a good short-circuit current of 1.14 mA/cm$^2$, a power conversion efficiency of 0.75% and an open-circuit voltage 1.36 V under 100 mW/cm$^2$ of white light.
In the course of studying these devices, unusual “kinks” were observed in both their un-corrected and corrected photocurrent-voltage characteristics, which were not seen in the materials systems studied earlier. The behaviour of the earlier devices was consistent with a model in which all – or at least a fixed field-independent fraction of – photogenerated excitons dissociate spontaneously into free electron-hole pairs. The anti-symmetric $J_{ph}-V$ characteristics of the PCz:EV-BT device by contrast are consistent with a model in which the fraction $g(E)$ of photogenerated excitons that dissociate into free electron-hole pairs is a monotonically increasing function of the electric field strength. In this case, three points of inflection appear in the $J_{ph}-V$ curve, with the central inflection coinciding with the built-in potential and corresponding to a minimum in the slope of the curve. The two outer points of inflection – which are distributed roughly symmetrically about the built-in potential – correspond to local maxima in the slope.

The occurrence of field-dependent carrier generation in PCz:EV-BT is consistent with the relatively small -0.4 eV energy offset between the HOMO levels of PCz and EV-BT. The spatially-separated electron and hole are unlikely to gain sufficient kinetic energy in the charge transfer process to overcome the binding energy of the charge-transfer exciton so-formed, and consequently they have a high probability of recombining. In the presence of a sufficiently strong electric field, the electron and hole are pulled in opposite directions, lowering their recombination probability and hence improving carrier yields.
CONCLUSIONS AND FURTHER WORK
CHAPTER 6 CONCLUSIONS AND FURTHER WORK

6.1 CONCLUSIONS

The work presented in this thesis has focussed on providing insight into the mechanisms governing the operation of organic bulk heterojunction solar cells. In particular, the corrected photocurrent of devices based on blends of a variety of donor and acceptor materials were examined. The standard method of obtaining the corrected photocurrent – which involves measuring the dark current and the total photocurrent characteristics in sequence and subsequently calculating the difference – was found to over-estimate the corrected photocurrent at high forward biases. This error was attributed to a temperature mismatch in the two measurements caused by radiative heating from the light source. A new technique was developed to circumvent radiative heating through the use of high-frequency pulsed light, thereby allowing reliable corrected photocurrent-voltage characteristics to be obtained under both reverse and forward bias conditions.

With the new measurement technique, the corrected photocurrent-voltage characteristics of solar cells based on a variety of blend materials were measured, and found to share a common characteristic: all the curves had highly anti-symmetric “S”-shaped profiles. Using a simple physical model, the built-in potential of BHJ solar cells was shown to coincide with the symmetry point of the curves, providing a simple experimental means of determining the built-in potential.
The corrected photocurrent-voltage curves for the different materials systems were observed to be vertically displaced by varying amounts and in differing directions. This behaviour was attributed to *charge carrier selectivity* at the electrodes. Three types of selectivity exist, which correspond to three different directions of vertical displacement. Zero vertical displacement in the corrected photocurrent-voltage curve implies non-selective electrodes, which show no preference to either charge carrier so both electrons and holes are extracted rapidly. An inverse-selective electrode preferentially extracts its *opposite* carrier type, and results in a positive vertical displacement of the corrected photocurrent-voltage curve. In devices with non-selective and inverse-selective electrodes, the unintended extraction of holes at the cathode or electrons at the anode constitutes a loss process, since the consequent positive current reduces the magnitude of the observed photocurrent.

On the other hand, a self-selective electrode preferentially extracts its own carrier type, preventing the extraction of electrons at the anode and of holes at the cathode. This gives rise to a negative net diffusive photocurrent that increases the magnitude of the observed photocurrent. Self-selectivity also increases the photo-voltage such that, under ordinary light levels, it can exceed the built-in potential by a considerable margin. These findings on carrier selectivity provide an added dimension to how device efficiencies can be enhanced in BHJ solar cells (see Section 6.2.1).

Neglecting the vertical displacement arising from electrode selectivity, an analytical expression was obtained for the field-dependent photoconductivity, thus explaining in detail the “S”-shape of the corrected photocurrent-voltage curve. This was found to be independent of carrier mobilities (at least in the absence of bimolecular recombination). A device based on a blend of P3HT
and PCBM was shown, by intensity-dependent measurements, to have negligible bimolecular recombinative losses. The analytically-derived expression was found to correspond exceptionally well with the experimentally-obtained photoconductivity-field curve for the P3HT:PCBM device, thus proving to be a rare example of a real device exhibiting ideal theoretical behaviour.

Blends of two new materials, PCz (Li et al., MPI)\cite{81} and EV-BT (Shin et al., IMRE), were investigated for application in BHJ solar cells, with the electron acceptor EV-BT being a potential substitute for PCBM. Devices cast from blends of these materials showed promising photovoltaic performance for a fully-organic, non-PCBM device, attaining power conversion efficiencies of 0.75\% and open-circuit voltages exceeding 1.3 V under 100 mW/cm$^2$ of simulated sunlight. The performance shown by the PCz:EV-BT devices exceed those reported in the literature\cite{74, 81, 86, 87} for solar cells based on other non-PCBM small-molecule acceptors.

The corrected photocurrent-voltage characteristics of the PCz:EV-BT solar cells had inflections around the symmetry point of the curve, and further analysis suggested that, in this system, average photogenerated carrier densities depend strongly on the electric field strength. Although this behaviour differed from the other blend systems, it was possible to account for it through a simple modification of the analytical model. The field-enhanced carrier generation was attributed to the small energy offset between the relevant frontier orbitals during charge transfer. In consequence, charge-transfer excitons are likely formed at the heterojunctions, which require an electric field to dissociate into free electrons and holes.
Finally, having drawn a number of valuable conclusions about the photogeneration, recombination and charge extraction processes in BHJ solar cells by inspecting corrected photocurrents, we advocate the corrected photocurrent measurement as a very powerful tool for understanding device operation.

6.2 Further Work

6.2.1 Intentionally introducing self-selectivity

Self-selectivity at the electrodes in a BHJ solar cell gives rise to a negative offset current that adds constructively to the total photocurrent of the device, and improves its efficiency. Therefore, one potentially powerful way of improving efficiencies in BHJ solar cells would be to intentionally induce self-selectivity in devices that have been identified to have non-selective or inverse-selective electrodes. As an example, the devices based on the new blend system PCz:EV-BT exhibit very promising performance, but were shown to have slightly inverse-selective electrodes. To help induce self-selectivity at the cathode (preferential extraction of electrons) a thin film of the EV-BT electron acceptor could be deposited by thermal evaporation\footnote{Thermal evaporation of EV-BT is an alternative deposition route, possible because the molecule is relatively small and stable at elevated temperatures. This deposition route has been used successfully in work by others in IMRE, and will be reported in the near future.} onto the spin-coated PCz:EV-BT blend film prior to cathode deposition. The device structure would then be ITO / PEDOT:PSS / PCz:EV-BT / EV-BT / Ca / Ag. (Ideally, one would introduce self-selectivity at both electrodes, but due to solvent compatibility issues during the fabrication, this may not be possible.)
6.2.2 The field dependence of the offset current

In our estimation of the photoconductivity in the various BHJ devices investigated here, we approximated the spatially averaged diffusive photocurrent as a constant offset current. In order to better understand the corrected photocurrent-voltage characteristics, we need to examine the actual field dependence of this diffusive contribution. This is a potentially difficult task, considering the spatially averaged diffusive photocurrent cannot be measured directly without the interference of the drift contribution. One candidate BHJ system for such a study would be a P3HT:PCBM device, since it was shown to behave closely to a theoretical ideal. Recent preliminary work in Imperial involving device modelling has also provided some valuable insight into the field dependence of the diffusive contribution.

6.2.3 Wavelength-dependent measurements

BHJ devices based on blends of PCz:EV-BT were found to exhibit behaviour that was explained by field-dependent carrier generation. Specifically, excitons created in the EV-BT phase were unlikely to dissociate even after the HOMO-HOMO hole transfer, due to the relatively small energy offset between the PCz and EV-BT HOMO levels. The charge-transfer excitons thus formed required an electric field to dissociate into free electron-hole pairs, resulting in points of inflection in the corrected photocurrent-voltage curve. However, excitons created in the PCz phase could dissociate normally since the LUMO-LUMO energy offset was much larger. An interesting experiment would be to measure the corrected photocurrent-voltage characteristics separately under monochromatic illumination at wavelengths 395 and 444 nm, corresponding to the absorption peaks of PCz and EV-BT respectively. One
would then expect the corrected photocurrent-voltage curve to exhibit inflections when measured at 444 nm, but not when measured at 395 nm.
REFERENCES


[51] [www.thermocouple.co.uk/TD_TV_PT1A.pdf](http://www.thermocouple.co.uk/TD_TV_PT1A.pdf).


In Section 4.3, the photoconductivity was derived analytically for the case where the carrier generation term \( G(x) \) was flat i.e. \( G(x) \) was a constant \( G \). Here we derive the photoconductivity for an exponential generation profile following the Beer-Lambert absorption profile:

\[
G(x) = G_0 \exp\left(-\frac{x}{\alpha}\right), \tag{7.1}
\]

where \( G_0 \) is the generation rate per unit volume at \( x = 0 \) (anode) and \( \alpha \) is the absorption length of the blend layer for a particular wavelength of light. Under steady-state conditions and neglecting charge traps, the one dimensional continuity equations for photogenerated electrons and holes at a distance \( x \) from the anode are

\[
-\frac{1}{e} \frac{dJ_e^{\text{ph}}}{dx} = G(x) - R(x) \tag{7.2}
\]

and

\[
\frac{1}{e} \frac{dJ_h^{\text{ph}}}{dx} = G(x) - R(x), \tag{7.3}
\]

where \( J_e^{\text{ph}} \) and \( J_h^{\text{ph}} \) are the photogenerated electron and hole currents, respectively. If bimolecular recombination is a negligible process, then \( R(x) = 0 \). Substituting \( R(x) = 0 \) and Equation (7.1) into Equations (7.2) and (7.3) gives:

\[
\frac{dJ_e^{\text{ph}}}{dx} = -eG_0 \exp\left(-\frac{x}{\alpha}\right) \tag{7.4}
\]
and

\[
\frac{dJ_{e}^{ph}}{dx} = eG_0 \exp\left(-\frac{x}{\alpha}\right). \quad (7.5)
\]

From the drift-diffusion equations, the electron and hole currents are:

\[
J_e^{ph} = e\mu_e n_e^{ph} E + \mu_e k_B T \frac{dn_e^{ph}}{dx} \quad (7.6)
\]

and

\[
J_h^{ph} = e\mu_h n_h^{ph} E - \mu_h k_B T \frac{dn_h^{ph}}{dx} \quad (7.7)
\]

Treating the electric field as a constant throughout the device, differentiating Equations (7.6) and (7.7) gives:

\[
\frac{dJ_{e}^{ph}}{dx} = e\mu_e E \frac{dn_e^{ph}}{dx} + \mu_e k_B T \frac{d^2 n_e^{ph}}{dx^2} \quad (7.8)
\]

and

\[
\frac{dJ_{h}^{ph}}{dx} = e\mu_h E \frac{dn_h^{ph}}{dx} - \mu_h k_B T \frac{d^2 n_h^{ph}}{dx^2} \quad (7.9)
\]

Equating Equations (7.4) and (7.5) to Equations (7.8) and (7.9), respectively, yields:

\[
\frac{d^2 n_e^{ph}}{dx^2} + \frac{eE}{k_B T} \frac{dn_e^{ph}}{dx} = - \frac{eG_0}{\mu_e k_B T} \exp\left(-\frac{x}{\alpha}\right) \quad (7.10)
\]

and

\[
\frac{d^2 n_h^{ph}}{dx^2} - \frac{eE}{k_B T} \frac{dn_h^{ph}}{dx} = - \frac{eG_0}{\mu_h k_B T} \exp\left(-\frac{x}{\alpha}\right) \quad (7.11)
\]
Solving the differential equations (7.10) and (7.11) with the boundary conditions \( n_{\text{e}}(0) = n_{\text{e}}(d) = n_{\text{h}}(0) = n_{\text{h}}(d) = 0 \) (for non-selective electrodes) gives the carrier densities as functions of \( x \).

\[
n_{\text{e}}(x) = \frac{1 - \exp \left( -\frac{x}{\alpha} \right) + \frac{\exp(-d/\alpha) - 1}{\exp(-eE/k_{\text{B}} T) - 1} \left[ \exp \left( -eE/\alpha k_{\text{B}} T \right) - 1 \right]}{\mu_{\text{e}} K_{\text{e}}} \tag{7.12}
\]

and

\[
n_{\text{h}}(x) = \frac{1 - \exp \left( -\frac{x}{\alpha} \right) + \frac{\exp(-d/\alpha) - 1}{\exp(eE/k_{\text{B}} T) - 1} \left[ \exp \left( eE/\alpha k_{\text{B}} T \right) - 1 \right]}{\mu_{\text{h}} K_{\text{h}}} \tag{7.13}
\]

where

\[
K_{\text{e}} = \frac{k_{\text{B}} T - e\alpha E}{e\alpha^2 G_0} \quad \text{and} \quad K_{\text{h}} = \frac{k_{\text{B}} T + e\alpha E}{e\alpha^2 G_0} \tag{7.14}
\]

Taking the spatial average of the carrier densities, we obtain:

\[
<n_{\text{e}}(x)> = \frac{1 + \exp \left( -\frac{d}{\alpha} \right) - 1 \left[ \frac{\alpha}{d} - \frac{k_{\text{B}} T}{eE} - \frac{1}{\exp(-eE/k_{\text{B}} T) - 1} \right]}{\mu_{\text{e}} K_{\text{e}}} \tag{7.15}
\]

and

\[
<n_{\text{h}}(x)> = \frac{1 + \exp \left( -\frac{d}{\alpha} \right) - 1 \left[ \frac{\alpha}{d} + \frac{k_{\text{B}} T}{eE} - \frac{1}{\exp(eE/k_{\text{B}} T) - 1} \right]}{\mu_{\text{h}} K_{\text{h}}} \tag{7.16}
\]

The photoconductivity can then be calculated by multiplying Equations (7.15) and (7.16) by \( e\mu_{\text{e}} \) and \( e\mu_{\text{h}} \) respectively [see Equation (4.5)], and subsequently adding the two resultant expressions together.
\[ \sigma_{\text{t,exp}} = \frac{e}{K_e} + \frac{e}{K_h} \exp\left(-\frac{d}{\alpha}\right) - 1 \left[ \frac{eK_e - eK_h \exp(eEd/k_BT)}{K_eK_h \exp(eEd/k_BT) - 1} \right] \]  

(7.17)

The \( \sigma_t-E \) curve for a flat generation profile from Figure 4-2B is reproduced in Figure 7-1. \( \sigma_{\text{t,exp}} \)-E curves are calculated from Equation (7.17) for \( \alpha = 100, 50 \) and 20 nm, using values of \( d = 100 \) nm and \( T = 300 \) K (similar to the curve for a flat generation profile), as shown in Figure 7-1. Values of \( G_0 \) were chosen to normalise the curves at \( E = 0 \) for ease of comparison.

![Figure 7-1](image)

**Figure 7-1**

**Main:** The photoconductivity-field curves for a flat generation profile and for exponential generation profiles with \( \alpha = d, \alpha = 0.5d \) and \( \alpha = 0.2d \), where \( d = 100 \) nm. The values of \( G_0 \) were chosen to normalise the curves to a common peak.

**Inset:** The (normalised) generation profiles corresponding to the flat profile and to the exponential profiles for \( \alpha = d, \alpha = 0.5d \) and \( \alpha = 0.2d \).

An exponential generation profile has the effect of broadening the \( \sigma_t-E \) curve as the absorption strength of the organic layer increases. \( \alpha = 50 \) nm is an upper limit for typical absorption lengths in organic semiconductors, but from Figure 7-1, the \( \sigma_{\text{t,exp}}-E \) curve for \( \alpha = 50 \) nm is nearly identical to the \( \sigma_t-E \) curve (flat generation profile).