Ternary Porphyrinoid:Polymer:Fullerene Bulk
Heterojunction Organic Solar Cells

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A thesis submitted for the degree of
Doctor of Philosophy
Department of Chemistry
University of Newcastle
February 2013
Declaration

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N. A. Cooling ________________________________
Acknowledgements

This thesis would not have been possible without the guidance and help of many people. First and foremost, I would like to express my unconditional gratitude to both of my supervisors, Dr. Warwick Belcher and Professor Paul Dastoor, both of whom have encouraged and inspired me throughout my PhD project and who were instrumental in directing my work and guiding my development as a scientist, for which I am immeasurably grateful.

The conclusions of this thesis would have not been as compelling without the colleagues who have provided advice and assistance over the past few years. In particular, I would like to thank Dr Tim Jones for his assistance with the voltammetry measurements, Dr Kerry Burke for collecting the STXM images, Dr Sam Lind and Professor Keith Gordon for the molecular modelling calculations, Dr Glenn Bryant for his frequent assistance with laboratory equipment, and my summer students Tim Sales, Samantha Sauer, Tom Murphy and Chris Miekle for their assistance and enthusiasm.

To my fellow students with whom I have shared an office or laboratory over the years, I thank you for all the discussion, advice, laughter and friendship we have shared. In particular I would like to thank Glen Shennan, Ben Vaughan, Daniel Elkington, Natalie Holmes, Mitchell Wilson, Garth Berryman, Nicolas Nicolaidas, Andrew Stapleton, Kelly Young and Deborah Wakeham. I consider it an honour to have shared this journey with you.

To the two most important people in my life, my wife Sarah and daughter Rachael, you have both endured my crankiness, unavailability and endless bouts of panic. I would not have survived this PhD without your ongoing support, and I thank you from the bottom of my heart for the patience and understanding you have shown me.

And finally, I owe my deepest gratitude to my parents, Mum and John, for your belief in the value of education and for always providing me with every opportunity to succeed in life.
have been incredibly fortunate to have you both as parents, and I am eternally grateful for all that you do. It is the love and support which you have provided that has enabled me to achieve everything that I have. I love you both dearly, and it is with a feeling of immense accomplishment that I dedicate this thesis to you.
List of Publications


Abstract

This thesis will investigate how porphyrinic materials may be successfully incorporated into polymer/fullerene organic solar cells to broaden light absorption, enhance power conversion efficiency, and to further probe and broaden the understanding of the chemistry and physics of both binary and ternary blended organic solar cells.

This thesis will begin with a discussion of bulk heterojunction organic solar cells, and how porphyrinic materials can be incorporated into these devices to form ternary blends, including a review of the ternary polymer:porphyrinoid:fullerene literature published to date.

The performance of standard MEH-PPV:PCBM organic solar cells manufactured at the University of Newcastle during the course of this PhD will be examined to show how device efficiency has steadily improved over the course of the project (2007-2011). Furthermore, it will show that the incremental improvements made to the standard binary devices over time are directly transferable to ternary blend devices.

The effect of systematically changing the steric bulk of a porphyrin on the performance of ternary blend devices is then investigated, as is the effect of changing the electronic states of the core while maintaining a constant steric profile. The effect on device performance of varying the \textit{para}-phenyl substituents of a series of tetraphenylporphyrin derivatives is also examined. Finally, the effect of altering the central metal cation in a series of metalloporphyrins with octaethylporphyrins and tetraphenylporphyrins ligands is investigated.

This thesis as a whole provides an insight into the chemistry and physics of ternary blend organic solar cells, detailing not only the interaction of porphyrin with polymer and fullerene, but also the effects of porphyrin-porphyrin interactions and how these may be controlled. Steric, electronic, and morphological effects are investigated, to provide a comprehensive study of ternary blend organic solar cells.
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<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>AM1.5</td>
<td>reference solar spectrum for photovoltaic performance evaluation</td>
</tr>
<tr>
<td>b</td>
<td>broad singlet</td>
</tr>
<tr>
<td>BHJ</td>
<td>bulk heterojunction</td>
</tr>
<tr>
<td>d</td>
<td>doublet</td>
</tr>
<tr>
<td>device</td>
<td>an organic solar cell</td>
</tr>
<tr>
<td>DDQ</td>
<td>2,3-dichloro-5,6-dicyano-1,4-benzoquinone</td>
</tr>
<tr>
<td>DMF</td>
<td>dimethylformamide</td>
</tr>
<tr>
<td>efficiency</td>
<td>power conversion efficiency</td>
</tr>
<tr>
<td>EQE</td>
<td>external quantum efficiency</td>
</tr>
<tr>
<td>exciton</td>
<td>a coulombically bound electron-hole pair</td>
</tr>
<tr>
<td>FF</td>
<td>fill factor</td>
</tr>
<tr>
<td>$^1$H NMR</td>
<td>proton nuclear magnetic resonance spectroscopy</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecule orbital</td>
</tr>
<tr>
<td>$I_{SC}$</td>
<td>short-circuit current</td>
</tr>
<tr>
<td>ITO</td>
<td>indium-tin oxide</td>
</tr>
<tr>
<td>$J_{SC}$</td>
<td>short-circuit current density</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>m.p.</td>
<td>melting point</td>
</tr>
<tr>
<td>MEH-PPV</td>
<td>poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene)</td>
</tr>
</tbody>
</table>
MSA  | methanesulfonic acid  
NEXAFS  | near edge X-ray absorption fine structure spectroscopy  
OPV  | organic photovoltaic  
P3HT  | poly(3-hexylthiophene)  
PCBM  | [6,6]-phenyl C61-butyric acid methyl ester  
PEDOT:PSS  | A polymeric salt of doped poly(3,4-ethylenedioxythiophene) and its polymeric counterion poly(styrene sulfonate)  
POR  | porphyrin  
PPV  | polyphenylene vinylene  
Q-bands  | characteristic porphyrin absorption peaks in the red region of the spectrum  
R_f  | retention factor  
R_s  | series resistance  
R_{sh}  | shunt resistance  
s  | singlet  
Soret  | a very intense porphyrin peak, in the blue region of the spectrum  
STXM  | scanning transmission X-ray microscopy  
TEA  | triethylamine  
TFA  | trifluoroacetic acid  
TLC  | thin layer chromatography  
TMS  | tetramethylsilane  
UV-vis  | UV-visible spectrophotometry  
V_{oc}  | open-circuit voltage
## Porphyrinoid abbreviations

<table>
<thead>
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<th>Description</th>
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<td>2N-Me NCTBuPP</td>
<td>N-confused 2-methyl 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin</td>
</tr>
<tr>
<td>Ag-TPP</td>
<td>[5,10,15,20-tetraphenylporphyrinato] silver(II)</td>
</tr>
<tr>
<td>Co-OEP</td>
<td>[2,3,7,8,12,13,17,18-octaethylporphyrinato] cobalt(II)</td>
</tr>
<tr>
<td>Co-TPP</td>
<td>[5,10,15,20-tetraphenylporphyrinato] cobalt(II)</td>
</tr>
<tr>
<td>Cu-OEP</td>
<td>[2,3,7,8,12,13,17,18-octaethylporphyrinato] copper(II)</td>
</tr>
<tr>
<td>Cu-TPP</td>
<td>[5,10,15,20-tetraphenylporphyrinato] copper(II)</td>
</tr>
<tr>
<td>Cu-TBuPP</td>
<td>[5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrinato] copper(II)</td>
</tr>
<tr>
<td>Fe-OEP.Cl</td>
<td>[2,3,7,8,12,13,17,18-octaethylporphyrinato] iron(III) chloride</td>
</tr>
<tr>
<td>M-OEP</td>
<td>[2,3,7,8,12,13,17,18-octaethylporphyrinato] metal complex</td>
</tr>
<tr>
<td>M-TPP</td>
<td>[5,10,15,20-tetraphenylporphyrinato] metal complex</td>
</tr>
<tr>
<td>Mg-TPP</td>
<td>[5,10,15,20-tetraphenylporphyrinato] manganese(II)</td>
</tr>
<tr>
<td>Mn-OEP.Cl</td>
<td>[2,3,7,8,12,13,17,18-octaethylporphyrinato] manganese(III) chloride</td>
</tr>
<tr>
<td>NCTTP</td>
<td>N-confused 5,10,15,20-tetrakis(4-methylphenyl)porphyrin</td>
</tr>
<tr>
<td>NCTBuPP</td>
<td>N-confused 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin</td>
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<tr>
<td>NCTXP</td>
<td>N-confused 5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrin</td>
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<tr>
<td>Ni-NCTXBuPP</td>
<td>N-confused [5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrinato] nickel(II)</td>
</tr>
<tr>
<td>Ni-OEP</td>
<td>[2,3,7,8,12,13,17,18-octaethylporphyrinato] nickel(II)</td>
</tr>
</tbody>
</table>
Ni-TPP \(\text{[5,10,15,20-tetraphenylporphyrinato] nickel(II)}\)

Ni-T\(^{1}\)BuPP \(\text{[5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrinato] nickel(II)}\)

OEP \(2,3,7,8,12,13,17,18\text{-octaethyl-21H,23H-porphyrin}\)

Pd-OEP \(\text{[2,3,7,8,12,13,17,18-octaethylporphyrinato] palladium(II)}\)

Pd-TPP \(\text{[5,10,15,20-tetraphenylporphyrinato] palladium(II)}\)

Pt-OEP \(\text{[2,3,7,8,12,13,17,18-octaethylporphyrinato] platinum (II)}\)

Pt-TPP \(\text{[5,10,15,20-tetraphenylporphyrinato] platinum (II)}\)

Ru-OEP.C=O \(\text{[2,3,7,8,12,13,17,18-octaethylporphyrinato] ruthenium(II) carbonyl}\)

TpBrPP \(5,10,15,20\text{-tetrakis(4-bromophenyl)porphyrin}\)

TpClPP \(5,10,15,20\text{-tetrakis(4-chlorophenyl)porphyrin}\)

TpCOOCH\(_3\)PP \(5,10,15,20\text{-tetrakis(4-(methoxycarbonyl)phenyl)porphyrin}\)

TpNH\(_2\)PP \(5,10,15,20\text{-tetrakis(4-aminophenyl)porphyrin}\)

TpOCH\(_3\)PP \(5,10,15,20\text{-tetrakis(4-methoxyphenyl)porphyrin}\)

TpOHPP \(5,10,15,20\text{-tetrakis(4-hydroxyphenyl)porphyrin}\)

TPP \(5,10,15,20\text{-tetraphenylporphyrin}\)

TTP \(5,10,15,20\text{-tetrakis(4-methylphenyl)porphyrin}\)

TXP \(5,10,15,20\text{-tetrakis(3,5-dimethylphenyl)porphyrin}\)

T\(^{1}\)BuPP \(5,10,15,20\text{-tetrakis(3,5-di-tert-butylphenyl)porphyrin}\)

V=O-OEP \(\text{[2,3,7,8,12,13,17,18-octaethylporphyrinato] vanadium(IV) oxide}\)

Zn-OEP \(\text{[2,3,7,8,12,13,17,18-octaethylporphyrinato] zinc(II)}\)

Zn-TPP \(\text{[5,10,15,20-tetraphenylporphyrinato] zinc(II)}\)
Chapter 1 - Introduction

1.1 Overview

This chapter will discuss what is currently known about bulk heterojunction (BHJ) organic solar cells, and how porphyrinic materials can be incorporated into these devices to form ternary blends, with an aim toward broadening the spectral response and therefore increasing the efficiency of BHJ solar cells. It will also discuss some of the recent advances in ternary polymer:porphyrin:fullerene solar cell research.

1.2 Background

Anthropogenic climate change and growing concerns about limited fossil fuel resources are key motivators for the development of renewable energy technologies [1]. Clean, reliable energy at low cost is considered an essential part of providing a long-term solution to the world’s energy requirements [2]. Solar energy is one of the cleanest energy resources, however it is still viewed as one of the most expensive types of renewable energy [3]. However, in the past 15 years organic-based photovoltaic devices have emerged which offer the possibility of efficient yet low-cost solar power [4].

Conventional, silicon-based solar cells are now routinely reaching efficiencies exceeding 20 % [5], with the current world record efficiency for this technology recently set at 40.8 % [6]. While these efficiencies are respectable, the expense of high-purity crystalline silicon and the complex manufacturing procedure involved with inorganic photovoltaic devices have so far prohibited the technology from having a significant impact on global energy production [7].

Organic solar cells offer a much cheaper alternative for light harvesting. Aside from a reduction in cost, a number of other advantages exist. A light-harvesting material composed of a polymer allows considerable processing advantages, such as the ability to “print” devices onto flexible, light weight plastic substrates, which could be integrated into fabrics or roofing materials.
Polymer production techniques are already well established, which is a huge advantage in terms of processing and production costs [8]. In addition, the potential for further development by tuning the electronic properties of semiconducting polymers via organic synthesis is enormous. However, to date the highest independently certified efficiency for an organic thin-film solar cell is only 10 % [9]. There is still a great need for more research if organic photovoltaic cells are to become economically viable for large scale production.

1.3 Photovoltaic technology

Solar cells convert sunlight into electrical energy using the photoelectric effect. When photons are absorbed by a photoactive material, the electrons in that material become mobilised, and the resulting electrical charges can be extracted through the electrodes and used to energise an external circuit [8].

A variety of solar technologies exist, including inorganic devices based on various systems (e.g. amorphous [10], crystalline [11], thin film [12]) of silicon [13], gallium arsenide, cadmium telluride, and other semiconducting inorganic compounds [14]; while organic devices can be broadly classified into either bulk heterojunction [15] or dye sensitised [16] solar cells. We will first consider inorganic solar cells.

Inorganic solar cells are manufactured from an inorganic semiconductor such as silicon, which is doped to form a p-n junction, with an excess of positive charges (holes) on the p-side, and an excess of negative charges (electrons) on the n-side. One way this dopant distribution can be achieved is by diffusing a p-type dopant into one side of an n-type semiconductor wafer. Electrons migrate into the p-side leaving a positive donor ion behind in the n-side, and holes migrate into the n-side leaving a negative acceptor on the p-side. As a result of charge transfer across the polarised junction, an electric field is formed. When light is absorbed by the region near the junction (called the depletion region because mobile charge carriers have moved away), electrons and holes are generated and become accelerated by the electric field towards
their respective electrodes, and leave the device to power an external circuit [8]. A simple silicon solar cell is illustrated in Figure 1.1 below.

![Simple silicon solar cell](image)

**Figure 1.1: A simple silicon solar cell [5]**

In organic solar cells, the light absorbing material is either a small (<1000 Da) organic molecule or a conjugated polymer. These differ from inorganic semiconductor solar cells primarily in the way in which charge carriers are formed. When a photon of sunlight is absorbed by an inorganic material such as silicon, free electrons and holes are generated immediately, because the electron wavefunction (approximated by the Bohr radius \(r_B\) of the electron-hole pair) extends further than the radius of the Coulomb potential well \(r_C\) at \(k_BT\). In organic semiconductors such as polymers, the photogenerated electron-hole pair is electrostatically bound, because the electron wavefunction \(r_B\) lies within the radius of the potential well \(r_C\) [17]. The effect of binding energy on charge carrier separation is illustrated in Figure 1.2 below, where it can be seen that the electron wavefunction (black ellipse) is not of sufficient radius to overcome the Coulombic potential which binds the electron-hole pair together.
Figure 1.2: Charge carrier separation vs. binding energy for organic and inorganic semiconductors. The Coulomb potential of an electron-hole pair for an organic (excitonic) semiconductor (black line), and for an inorganic (conventional) semiconductor such as silicon (red line). The Bohr radius $r_B$ (which can be taken as the approximate size of the electron wavefunction) is compared to the radius of the Coulomb potential well $r_C$ [17].

Organic semiconductors are therefore also known as excitonic semiconductors. The formation of excitons (rather than free charge carriers) in organic solar cells has significant implications for device physics. Excitons are tightly bound, and will rarely dissociate into a free electron and hole without assistance. In polymer solar cells, for example, it has been estimated that only 10% of photoexcitations will lead directly to free charge carriers at room temperature [18]. Dissociation will usually only occur in the presence of strong electric fields, at defect sites within the material, or at the interface between two materials which have a large enough offset in energy levels [8]. If the photogenerated excitons are not separated rapidly, the electron and hole will recombine and the energy imparted by the photon will be lost as heat or, if a radiative transition is allowed, re-emission of light [19]. For power generation it is therefore essential to dissociate the exciton into free charges, which can travel to the electrodes and be extracted as electrical energy.
The most convenient method to dissociate excitons is the creation of an interface between materials. The earliest organic solar cells consisted of a thin film of a single organic compound sandwiched between two metal electrodes: one electrode of low work function such as aluminium or indium (deposited in a thin enough layer to still allow substantial light transmission), and the other of high work function such as gold or silver. The difference in work functions creates a built-in potential, making photovoltaic performance strongly dependent on the selection of appropriate electrodes. The organic component in these early solar cells was typically porphyrinic in structure, such as phthalocyanines and metallated porphyrins, chosen due to their strong visible light absorption and their resemblance to chlorophyll, the green photosynthetic pigment in plants. These devices, however, suffered from very low efficiencies (much less than 1%), as the need for interfacial exciton dissociation was not fully understood [20].

In 1986, Tang [21] was the first to realise the benefit of adding a second organic component to a solar cell. He constructed a bilayer device of copper phthalocyanine as the $p$-type and the perylene derivative bisbenzimidazo[2,1-$a$:2',1'-$a'$]antra[2,1,9-$d$:6,5,10-$d'e'f'$]diisoquinoline-10,21-dione as the $n$-type semiconductors. The structure of these compounds is shown in Figure 1.3 below.

![Figure 1.3: The organic compounds used in Tang’s [21] two-layer solar cell. Copper phthalocyanine (left) as the $p$-type material, and a perylene derivative (right) as the $n$-type material](image-url)
Tang’s devices reached an efficiency of 1 %, a significant improvement on previous single layer designs and the turning point in early organic photovoltaic research. He recognised that the interfacial region between the layers of organic compounds was the primary source of photocurrent, and showed that the fill-factor and open-circuit voltage were more dependent on the nature of the organic-organic interface than of the interface between the electrode and organic layer [21]. The bilayer design was successful because excitons generated in the bulk of the film could be separated into free electrons and holes at the interface, as the electrons could be transferred to the $n$-type electron accepting perylene, while the holes could be transferred to the $p$-type phthalocyanine. A basic organic solar cell is illustrated in Figure 1.4 below.

Figure 1.4: A simple organic solar cell [5]

The efficiency of these bilayer devices was limited not so much by the properties of the compounds Tang selected, but by the low interfacial area inherent in the bilayer design. The next major improvement to the design of organic solar cells occurred more than a decade later, with the introduction of the BHJ concept. Rather than a bilayer arrangement, BHJ devices are formed by mixing the electron donating and accepting materials together and spin coating
them as a single film from a common solution. As the film dries, phase separation within the mixture results in the formation of many interfaces, with a much larger interfacial area than bilayer devices, which greatly increases the dissociation of electrons into free charge carriers (electrons and holes). A schematic representation of the active layer morphology in BHJ solar cells is illustrated in Figure 1.5 below.

![Figure 1.5: Schematic representation of a bulk heterojunction solar cell, showing the donor (red) and acceptor (blue) materials [15]](image)

The \( n \)-type material used is typically a fullerene derivative (which is known to have excellent electron accepting and conducting properties), and a conjugated polymer as the electron donating hole conducting \( p \)-type material. The move toward polymers as the electron donor was also beneficial because many conducting polymers have absorption profiles which match the solar spectrum better than small molecules such as phthalocyanines.

Now that the basic difference between inorganic and organic solar cells has been addressed, further consideration and expansion of organic solar cell theory, and the materials used in their production, will follow.
1.4 Bulk-heterojunction organic photovoltaic devices

1.4.1 Device structure

Bulk-heterojunction organic solar cells are constructed in layers, with a typical arrangement shown below:

Figure 1.6: General structure of a bulk-heterojunction organic solar cell [5]

The device is usually built onto a glass substrate, although other transparent materials such as polymer sheets may also be employed. The substrate is coated with an optically transparent cathode, usually indium tin oxide (ITO), by vacuum deposition. It is important that the transparent electrode absorbs as little visible light as possible, as the solar cell is illuminated through this face. A thin film consisting of a polymeric salt of doped poly(3,4-ethylenedioxythiophene) and its polymeric counterion poly(styrene sulfonate) (PEDOT:PSS) is then applied to the ITO layer by spin-coating. The PEDOT:PSS assists charge transport and minimises short-circuits within the device. The next layer is the active layer, which is a blend of the electron-donating semiconducting polymer and electron-accepting fullerene. The active layer absorbs light and generates photocurrent. Finally, a metal anode, typically aluminium, is vacuum deposited to complete the cell. A schematic of the band structure of a typical
polymer(donor)/fullerene(acceptor) BHJ organic solar cell is shown in Figure 1.7, illustrating the relative placement of energy levels of the materials within the device.

Figure 1.7: Schematic of the band structure of a typical bulk heterojunction organic solar cell [5]

1.4.2 Materials

The photophysics of BHJ organic photovoltaic devices are based on the concept of photoinduced electron transfer from donor-type conjugated polymers onto acceptor molecules such as $C_{60}$ fullerene [22]. The choice of semiconducting polymers, fullerene acceptors, and supporting materials such as electrodes, all play a crucial role in the construction of an organic solar cell. In this section, these materials will be briefly considered, with a more in depth discussion of device physics and fabrication to follow.

1.4.2.1 Photoactive semiconducting polymers

The most studied electron donating conjugated polymers used in the manufacture of BHJ solar cells are derivatives of polythiophene and poly($p$-phenylenevinylene). These materials have been successful due to a combination of conductivity and stability (which are both due to $\pi$-orbital overlap in the conjugated backbone) [23], favourable absorption profiles that lie with
the solar spectrum, and the efficiency with which they transfer charge to electron accepting fullerenes. Polymers are in many ways an ideal material for research into electronic devices as the flexibility of organic synthesis allows for modification of many of their properties, such as absorption profiles and solubility.

**P3HT**

Bulk-heterjunction organic solar cells containing the alkylthiophene-based polymer poly(3-hexylthiophene) (P3HT) are the most studied organic solar cell devices to date [24], with a confirmed efficiency of 5.4 % for devices made with regioregular polymer [25]. The structure of P3HT is presented in Figure 1.8 below.

![Figure 1.8: The chemical structure of P3HT](image)

Polythiophenes were first investigated as photovoltaic materials in 1986 [26]. Unsubstituted polythiophene can be formed by metal-catalysed polycondensation polymerisation [27], electropolymerisation [28], or chemical oxidative polymerisation [29]. The low solubility of polythiophene limits its molecular weight, as the product tends to precipitate as the chain lengthens during polymerisation [23]. To address the solubility issues, poly(3-alkylthiophenes) were developed, and it was found that alkyl substituents at least 4 carbons long were necessary to enable solubility in a wide variety of organic solvents and thus produce high
quality thin films [23]. Poly(3-hexylthiophene) (P3HT) is the most widely used derivative, due to its low cost and ease of synthesis.

The dissymmetry of the 3-alkylthiophene monomer allows for the formation of a variety of regiomers during polymerisation [30]. The most suitable regiomer for organic solar cells is a head-to-tail coupled P3HT (HT-P3HT), also known as regioregular or RR-P3HT. Regioregularity allows for less contortion in the polymer backbone and therefore better π-orbital overlap which results in increased conductivity. In addition to head-to-tail (HT) coupling, head-to-head (HH) and tail-to-tail (TT) coupling is also possible [30], leading to four structurally non-equivalent triads, shown in Figure 1.9 below.

![Figure 1.9: Four possible non-equivalent structural couplings of poly(3-hexylthiophene) [30]](image)

A study of P3HT film morphology by Hugger et al. [31] found that a layered, crystalline structure occurs in annealed RR-P3HT, but in the regiorandom form the material is disordered. Not only does regioregularity increase charge carrier (hole) mobility, the enhanced intrachain conjugation and stronger interchain coupling also result in a red-shift of the absorption profile, which provides a better match with the solar spectrum [32].
MEH-PPV

Another type of semiconducting polymers commonly used are based on poly(p-phenylenevinylene) (PPV). Like all unsubstituted conjugated polymers, PPV suffers from poor solubility [33]. An alkoxy derivative, poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) has been synthesised which, due to its alkoxy side chain, is soluble in a variety of organic solvents. The polymers electronic energy gap is decreased resulting in a red-shift of the π-π* absorption in relation to unsubstituted PPV [34], so it has better overlap with the solar spectrum. The maximum efficiency for PPV based solar cells is approximately 2.5% [35].

Figure 1.10: The structure of MEH-PPV

MDMO-PPV

A more recently developed soluble PPV derivative is poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene (MDMO-PPV). MDMO-PPV has been shown to have almost identical electronic properties to MEH-PPV, with the advantage of superior processibility and film-forming properties [33].
1.4.2.2 Electron accepting fullerenes

Fullerenes are a group of carbon allotropes that form large geometrical structures such as spheres and ellipsoids. The most common member of this family is the Buckminsterfullerene or “buckyball”, a spherical macromolecular compound composed of 60 carbon atoms whose structure resembles a soccer ball. Fullerenes are fairly transparent to visible light and have good conductivity [36], which has led to their use as electron acceptors in organic solar cells.

$\text{C}_{60}$

$\text{C}_{60}$ has a high electron affinity and is able to gain up to 6 electrons [37]. It was first proposed as an electron acceptor for polymer solar cells in 1993 [19]. When polymer:fullerene devices are illuminated, a large photoresponse is observed, which is attributed to photoinduced electron transfer between the conducting polymer and $\text{C}_{60}$ fullerene [38].
$\text{C}_{60}$-PCBM

The solubility of $\text{C}_{60}$ in organic solvents is quite low [39], which limits its use in forming thin films for solar cells. In 1993, Wudl [40] synthesised the first soluble derivatives of $\text{C}_{60}$. These included a molecule called [6,6]-phenyl-$\text{C}_{61}$-butyric acid methyl ester (PCBM or $\text{C}_{60}$-PCBM). The substituted fullerenes such as PCBM were found to have almost identical UV-visible absorption spectra and cyclic voltammograms as $\text{C}_{60}$ [40], confirming their continued suitability as electron acceptors in organic solar cells, but with the enormous advantage of greatly increased solubility.
The UV-Vis absorption spectra of $C_{60}$-PCBM (and related fullerenes, to be discussed next) and the electron-donating polymer MEH-PPV in chloroform is shown in Figure 1.14.

![UV-Vis absorption spectra](image)

**Figure 1.14:** Solution UV-vis absorption spectra of the fullerenes: $C_{60}$-PCBM, $C_{70}$-PCBM, bis[$C_{60}$]-PCBM, and ICBA, in chloroform. Also shown for comparison is a solution UV-vis absorption spectrum of the electron-donating polymer MEH-PPV

**C$_{70}$-PCBM**

While $C_{60}$-PCBM is an excellent acceptor for photoinduced electron transfer, it has very little visible light absorption. However, it has been shown to contribute significantly to photocurrent generation, particularly in systems using high concentrations of fullerene such as MEH-PPV:PCBM [41]. The symmetry of $C_{60}$ means that a number of the low-energy transitions which give rise to visible light absorption are formally dipole forbidden. By exchanging the fullerene from spherical $C_{60}$ to ellipsoidal $C_{70}$, symmetry is reduced and more of these transitions become allowed, so more visible light is absorbed [42], as shown in Figure 1.14. Thus more light can be harvested and a significant increase in photocurrent (up to 50 % higher) is achieved in polymer:$C_{70}$-PCBM devices [43].
Efficient electron transfer from a donor polymer to acceptor fullerene requires that the lowest unoccupied molecular orbital (LUMO) of the donor is 0.3-0.5 eV higher than the LUMO of the acceptor molecule [44, 45]. However, for electron donors such as P3HT the energy difference is excessively higher (~1.1 eV) resulting in a loss of open-circuit voltage [46]. A recently discovered fullerene, bis[C₆₀]-PCBM, is a difunctionalised C₆₀ fullerene which was isolated as a by-product of PCBM synthesis. Its LUMO is of a higher energy than the monofunctionalised PCBM, which results in a greater offset between the HOMO of the donor polymer and the LUMO of the acceptor fullerene. This greater offset increases the efficiency of P3HT:bis[C₆₀]-PCBM solar cells by approximately 20 %, due entirely to the increased open circuit voltage arising from the ~100 meV higher LUMO [46].
A recently reported soluble C$_{60}$ derivative, indene-C$_{60}$ bisadduct (ICBA), has a higher LUMO energy level again, that enables the $V_{OC}$ of P3HT:fullerene solar cells to reach 0.84 V, compared with a typical $V_{OC}$ of 0.60 V for P3HT:PCBM devices, which improves power conversion efficiency by 30%. ICBA has excellent solubility in common organic solvents, and is more soluble than PCBM in chloroform. A further advantage is the ease of which ICBA can be synthesised, requiring a simple one-pot reaction [47].

1.4.2.3 Transparent anode

The most common anode material for organic solar cells is a thin film of indium-tin oxide (ITO) on a glass or flexible plastic substrate. Other materials such as a very thin layer of metal (e.g.
Al) or aluminium-doped zinc oxide (AZO) [48] have also been used. ITO is a superior material because it is highly conductive and has an optical transparency in the visible region of the spectrum of more than 90 % [49]. It also has a high workfunction of 4.7 eV [50] which facilitates hole injection from the active layer and is therefore particularly suited for use as an anode. The quality and conductivity of commercial ITO-coated glass substrates varies enormously, therefore some type of mechanical cleaning or ozone treatment is usually necessary to smoothen and abrade the features protruding from the surface of the film, that may cause a device to short-circuit if they are allowed to remain [36].

1.4.2.4 PEDOT:PSS

The ITO anode is usually coated with a thin film of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), an ionic compound made up of two polyelectrolytes which is very conductive to holes due to its highly $p$-doped nature [51]. It smooths the surface of the ITO to reduce short-circuiting, protects the active layer from oxidative degradation from ITO, and prevents indium from the anode from diffusing into the active layer and causing detrimental charge trapping defect sites [5]. PEDOT:PSS has a slightly higher workfunction than the ITO [51], so it also assists hole injection from the active layer into the electrode.

Figure 1.18: Structure of PEDOT (bottom) and PSS (top) [52]
1.4.2.5 Cathode

The cathode, thermally deposited on top of the active layer to complete the circuit, is typically a low-workfunction metal such as aluminium (due to its low cost, low boiling point, and high conductivity), but may also be calcium, silver or gold. [5]. Unfortunately, the conjugated polymer in the active layer may react with the electrode material to some extent. For example, in PPV devices with an Al cathode, it has been observed that Al atoms can diffuse into the active layer and react with vinyl groups on the polymer, disrupting conjugation. As this occurs a barrier layer forms at the interface, which prevents electron injection from the active layer into the Al electrode [36].

Depositing a thin layer of LiF between the active layer and the Al electrode has been found to be beneficial in preserving and even increasing device performance. A layer of LiF approximately 5-10 Å thick serves as a protective layer between the organic layer and the hot metal vapour during thermal deposition of the electrode [5], minimising diffusion of Al atoms into the active layer. Brabec et al. [53] showed that a layer of LiF up to 15 Å thick actually improved device performance by up to 20 % by increasing both fill factor and open-circuit voltage. The suggested mechanism for this enhancement was that the strong dipole moment of LiF lowers the workfunction of the Al and thus assists electron injection into the electrode.

1.4.2.6 Substrate

Typically the substrate upon which organic solar cells are built is glass, as it is cheap, readily available and optically clear. Ultimately, the goal is to move towards flexible plastic substrates which are stronger, cheaper, and easier to work with than brittle glass. Flexible plastic substrates also offer the potential to manufacture solar modules using a reel-to-reel process [8], where solutions of the active layer materials can be printed directly onto the substrate using a variety of printing technologies. Indeed, investigation has already begun into ITO coated polyester substrates [54]. Plastic substrates could also offer massive savings in
production time; for example, it has been calculated that a typical printing machine could produce in one hour the same surface area of organic photovoltaic material that a silicon wafer production plant would produce in a year [7].

1.4.3 Device fabrication and device performance

Recent improvements in organic solar cell performance have now seen devices approaching 10% efficiency [9]. Much of this success is due to specific fabrication and optimisation procedures which have been developed, such as annealing and the selection of correct material ratios, which enhance the favourable morphology necessary for free charge carrier generation and transport to the electrodes. In this section, some attention will be given to the fabrication procedures that have been proven to increase device performance, with an emphasis on the chemical and physical processes underlying organic photovoltaic theory.

When a photon of light is absorbed by a polymer, a short-lived exciton is produced. To extract free charge carriers (electrons and holes), the photogenerated exciton must reach an interface in the film so that charge separation can occur. Photoinduced charge transfer occurs on a much faster timescale (approximately 45 fs [55]) than the competing exciton recombination processes (which take up to 10 ms [56]). Therefore charge transfer at the polymer/fullerene (donor/acceptor) interface is a very effective method for extracting charge from excitons, as evident by a measured quantum efficiency for this process of nearly 100 % [57]. However, as the exciton diffusion length is only ~10 nm [58], and charge separation only occurs at interfaces in the film, photoexcitation must occur within close proximity (<10 nm) to the interface or the exciton will recombine and the energy imparted by the photon will be lost.

A bulk donor-acceptor heterojunction can be created by blending fullerene and polymer and spin-coating from a common solution. In this model, close interpenetration is achieved between the polymer and fullerene phases, creating a much larger interfacial surface area. Moreover, any point within the active layer of a bulk-heterojunction film is now within a short
distance of an interface, so photogenerated charge separation is more frequent [5]. Once separated, the electrons and holes need a continuous pathway of fullerene and polymer, respectively, to allow transport of these charges to the appropriate electrodes.

1.4.3.1 Materials ratio

In a polymer/fullerene solar cell, photon absorption is due mainly to the polymer component, as the typically used fullerene, PCBM, absorbs very little light above 350 nm. PCBM, in addition to allowing effective charge separation, forms the electron transport percolation network, which facilitates excellent electron conductivity. The ratio of polymer:PCBM is therefore crucial in determining the performance of the device. If there is too little polymer, then light absorption will not be maximised. On the other hand, if there is too little PCBM, then the electron transport networks to the electrode will not be continuous and charge collection will be inefficient. The OPV materials ratio is typically reported as the donor:acceptor ratio by weight.

The first published paper on MEH-PPV:PCBM solar cells found the optimal blend ratio (by mass) to be 1 part polymer to 4 parts PCBM, which resulted in approximately 1 PCBM acceptor for each polymer repeat unit [57]. As little as 5 % PCBM is necessary for effective charge separation, however 80% PCBM by mass is necessary to form an efficient charge transport network [59]. Early morphological studies showed that by increasing the concentration of fullerene, greater interconnection between fullerene domains could be observed [60]. Other studies support these findings, describing how increasing the concentration of fullerene also increases the short circuit current and power conversion efficiency (up to an optimal concentration of PCBM), which has been attributed to improved transport and collection of charges [61]. Fill factor has also been shown to increase with higher concentrations of fullerene [62].
In a study [63] of MDMO-PPV:PCBM, it was found that the films were fairly homogenous for blends with 50 % (by weight) PCBM or less. The onset of nanoscale phase separation only occurred when the concentration of PCBM reached 67 %, resulting in rather pure domains of PCBM. The optimal PCBM concentration for this polymer system was also found to be 80 %, which corresponds to maximum photocurrent that occurs due to an effective nanoscale network of PCBM domains, which are continuous through the entire film. Above 80 % PCBM, the current density begins to fall due to a decrease of the optical density of the film caused by a lack of polymer, which is the major light-absorbing species. Not only is light absorption reduced, but it appears that at PCBM concentrations above 86 %, the continuous pathways of the hole transporting network of polymer start to become separated, reducing hole transport and therefore lowering device efficiency [64].

Organic solar cells based on polythiophene require different weight ratios of polymer:fullerene than devices based on poly(phenylenevinylene). It has been found that in P3HT:PCBM based systems, a ratio of 1:1 by weight is the optimum concentration of components, which corresponds to approximately 1 PCBM molecule for every 5 polymer repeat units. In a P3HT:PCBM matrix, continuous electron transporting domains occur when the concentration of PCBM exceeds 47 % (much lower than the 67 % needed in PPV systems), and there is no further transport benefit to be gained if the concentration of PCBM is pushed past 50 %. Indeed, PCBM concentrations of 60 % and above were found to damage the active layer/metal electrode interface during thermal annealing, due to the formation of large aggregates of PCBM causing mechanical stress to the electrode [65]. Therefore a 1:1 ratio is generally considered optimal.

1.4.3.2 Solvent

Choice of solvent has a large influence on the performance of an organic solar cell. Not only must the solvent fully dissolve the polymer:fullerene mixture to enable thin (~100 nm) films to
be spin-cast, it must also promote phase-segregation of the components so as to achieve the optimal morphology for high performance devices.

Early MDMO-PPV:PCBM devices were typically spin-cast from toluene. It was found that by a simple change in solvent from toluene to chlorobenzene, the efficiency of the solar cell would almost triple. Atomic force microscopy (AFM) images of device films showed distinctly different surface morphology depending on the solvent used [35].

![AFM images of MDMO-PPV:PCBM 1:4 films.](image)

**Figure 1.19:** AFM and surface height images of MDMO-PPV:PCBM 1:4 films. The images on the left (a) are of a film spin coated from toluene, while the images on the right (b) are of a film spin coated from chlorobenzene. From [35]

Films spun from chlorobenzene have much smaller surface features and are much smoother than films spun from toluene, indicating better mixing of the polymer and fullerene (at least near the surface). The massive increase in device performance when chlorobenzene is used as the solvent has been attributed to better mixing of polymer and fullerene (due to the increased solubility of PCBM in chlorobenzene compared to toluene), which likely increases the interfacial area for charge separation. Also, chlorobenzene may have allowed more
favourable polymer chain interaction (observed as a red-shift in absorption spectra), which increases hole mobility along the domains. Finally, the smoother surface of the films allows better interfacial contact with the electrodes, enhancing charge collection [35].

A larger scale of phase separation is commonly observed in MDMO-PPV:PCBM films cast from toluene compared to films cast from chlorobenzene. The low photocurrent of toluene-cast films can therefore be explained as a result of low charge carrier generation due to the low exciton diffusion lengths (~10 nm [58]). For excitons to dissociate into free charge carriers an interface between donor and acceptor materials is necessary, but the large clusters of PCBM (up to 500 nm) observed in films cast from toluene make it difficult for photogenerated excitons to reach an interface, resulting in lower exciton dissociation and therefore lower device efficiency [59].

Using near-field scanning photocurrent microscopy (NSPM), McNeill et al. [66] found that the large clusters of PCBM observed in toluene-spun films of MDMO-PPV:PCBM devices were also associated with low photocurrent generation within the film. They proposed that the phase-segregation may result in the formation of a polymer rich shell around the large PCBM clusters, creating an insulating layer and preventing electron transport out of the PCBM island. This phase segregation behaviour is shown schematically in Figure 1.20 below, where in (a) the bicontinuous charge transport network in the chlorobenzene-spun film allows charge transport to the electrodes, but in (b) the large polymer encapsulated PCBM cluster does not allow electrons to escape, resulting in recombination and a lowering of photocurrent [67].
1.4.3.3 Annealing

In 2003, Padinger et al. [68] were the first to report how a thermal annealing treatment of P3HT:PCBM organic solar cell increased device efficiency. They attributed the improvement to an increase in hole mobility within the polymer, which resulted from enhanced crystallisation of the polymer that occurred upon annealing the film above its glass transition temperature.

The effect of thermal annealing on the optical properties of P3HT:PCBM solar cells has also been investigated. Chirvase et al. [65] showed that thermal annealing of a blend of polymer and fullerene changed the absorption profile considerably, enhancing and red-shifting visible light absorption. The changes in absorption were found to increase solar cell efficiency, partly from increased photon collection and better overlap with the solar spectrum, due to stronger interchain interaction and better ordering in the P3HT domains caused by annealing.
Figure 1.21: UV-visible absorption spectrum of a P3HT:PCBM film, showing the increase in absorption and shift to longer wavelengths that occurred after annealing [65]

The ideal annealing parameters for a P3HT:PCBM 1:1 blended solar cell have been reported as 140 °C for 4 minutes [69]. Annealing above the glass transition temperature of the P3HT mobilises PCBM within the film, allowing self-assembly into more ordered nanoscale domains which enhance charge transport. Upon cooling, crystallisation of P3HT leads to macroscopic phase separation by enriching the amorphous polymer phase with PCBM beyond its miscibility limit, effectively ejecting PCBM from the miscible phase [70].

Transmission electron microscopy (TEM) studies of P3HT:PCBM solar cells have found that thermal annealing creates a crystalline nanoscale interpenetrating network of both polymer and fullerene components. P3HT was found to form long fibrillar crystals which weave throughout a microcrystalline phase of PCBM. This interpenetrating network increased device efficiency, due to enhancement of charge carrier mobility in both the electron transporting PCBM phase and the hole transporting P3HT phase [32].

Another technique for molecular reorganisation is solvent annealing, where the organic layers are exposed to solvent vapour post-deposition. Solvent annealing can also be achieved
through the addition of less-volatile chemical additives such as 1-chloronaphthalene [71], 1,8-diiodooctane [72] and 1,8-octanedithiol [73], that leave the spun film much more slowly, thus allowing a greater span of time for optimal organization of the blend. Power conversion efficiency of P3HT:PCBM devices have been observed to increase threefold after solvent annealing, an improvement of similar magnitude to that of thermal annealing. Solvent vapour annealing temporarily softens the P3HT:PCBM film and allows demixing of the components, leading to a more ordered structure that enhances charge transport through ordering of P3HT chains [74].

It is important to note that PPV-derivatives such as MEH-PPV and MDMO-PPV are amorphous polymers and therefore do not form a crystallised phase upon annealing. However, the low glass transition temperature of MDMO-PPV ($T_g = 80 ^\circ C$) allows significant mobility of PCBM when annealed, promoting the growth of micron-size PCBM-rich domains which are not conducive to exciton dissociation [75]. As such, the highest performing devices based on the PPV system are not annealed [76], and in fact thermal annealing of PPV:PCBM devices decreases photovoltaic performance [77].

### 1.5 Device characterisation

A variety of methods exist for the characterisation of organic solar cells. These methods allow the determination of current and voltage characteristics which are used to calculate device efficiency, optical techniques to determine the light absorption of the active layer materials, and spectral response techniques to investigate photon to photocurrent conversion at specific wavelengths.

#### 1.5.1 Current-voltage (I-V) characteristics

A graph of current (I) versus voltage (V) is commonly used to investigate the properties of a solar cell, and provides the necessary information needed to calculate the power conversion
efficiency of the device. In an I-V plot, potential (voltage) is applied to the cell and a current response is measured. Generally, the dark I-V characteristics are ohmic. When illuminated, however, additional photocurrent is generated in addition to the ohmic response, resulting in the shift in the plot.

![I-V curve showing current versus voltage for a solar cell](image)

**Figure 1.22:** An I-V curve showing current versus voltage for a solar cell [5]

I-V curves are usually collected under Air Mass 1.5 (AM 1.5) illumination. Air mass is a standardised spectrum of light that informs us as to how much atmosphere sunlight must travel through before it reaches the surface of the earth. The numerical value (e.g. 1.5) is the inverse of the cosine of the zenith angle of the sun. A variety of values (e.g. 1, 1.5, 2) can be used, but a value of 1.5 is most common, and corresponds to the sun at an angle of 48° [5]. It is important to specify this value, because the spectrum of sunlight changes as it passes through the atmosphere, due to photon absorption by molecules in the air such as water. Standardised testing procedures are necessary for accurate comparison and authentication of results by different research groups. As air mass only describes the spectrum of light; solar cells are commonly measured at a fixed intensity of 100 mW/cm² [5].
IV curves are collected by applying a voltage to the device and measuring the photocurrent that is produced under illumination by a light source that is appropriately filtered so that it simulates sunlight.

**Open-circuit voltage**

The open-circuit voltage ($V_{OC}$) is the maximum voltage across the illuminated device when no current is flowing (i.e. open-circuit conditions). The maximum possible $V_{OC}$ is set by the energetic distance between the HOMO of the donor polymer and the LUMO of the acceptor fullerene [51], and is rather insensitive to variation in the work function of the negative electrode [78]. Theoretical $V_{OC}$ is never achieved however, as some voltage losses always occur. The primary loss mechanism limiting the voltage in organic solar cells is thought to be bimolecular recombination of charge carriers [79].

**Short-circuit current**

The short circuit current ($I_{SC}$) is the current produced by the illuminated device when there is no voltage (i.e. the cell is short-circuited so that there are no external resistances). $I_{SC}$ is the maximum current that a cell can produce since there is no external load on the circuit [5], and is a function of the amount of light absorbed by the photovoltaic materials (polymer and fullerene) and the efficiency with which the photons are converted into charges [51]. Provided that favourable morphology exists to transport charges to the electrodes, the main current limiting factor in organic solar cells is the mismatch between the absorption profile of the material and the solar spectrum, which restricts the wavelengths of light that are absorbed. Increasing the thickness of the active layer (to increase light absorption) only works up to a point – eventually the limited charge mobilities of the polymer and fullerene will negate further increases in active layer thickness. Short circuit current is typically reported as short-circuit current density ($J_{SC}$ in mA cm$^{-2}$), to take into account the area of the device.
Fill factor

The fill factor (FF) is the ratio of a solar cell’s actual maximum power output to its theoretical maximum output if the current and voltage were held at their maximum values [5]. In Figure 1.22 above, the fill factor is equivalent to the area of the shaded rectangle (within the confines of the IV curve) divided by the area of the larger rectangle (whose edges intersect the $V_{OC}$ and $I_{SC}$). If the fill factor is 1, it indicates that the cell is performing to its maximum potential. A low fill factor is indicative of high series resistance and/or low shunt resistance within the device [51]. With reference to Figure 1.22, the fill factor (FF) can be calculated by:

$$\text{FF} = \frac{I_{mpp} \times V_{mpp}}{V_{OC} \times I_{SC}}$$  \hspace{1cm} (1)

where $I_{mpp}$ is the current at the maximum power point, $V_{mpp}$ is the voltage at the maximum power point, $V_{OC}$ is the open circuit voltage, and $I_{SC}$ is the short circuit current.

Power conversion efficiency

The power conversion efficiency (PCE or $\eta_e$) is the ratio of photogenerated power output to incident light input, and describes how efficient a solar cell is in generating electricity from available sunlight [5]. PCE can be calculated from an IV curve by:

$$\text{PCE} = \frac{I_{mpp} \times V_{mpp}}{P_{in}} = \frac{I_{SC} \times V_{OC} \times \text{FF}}{P_{in}}$$ \hspace{1cm} (2)

where $I_{mpp}$ is the current at the maximum power point, $V_{mpp}$ is the voltage at the maximum power point, $I_{SC}$ is the short circuit current, $V_{OC}$ is the open circuit voltage, FF is the fill factor (as calculated from equation (1)), and $P_{in}$ is power of the solar radiation incident on the cell [5].
1.5.2  UV-visible absorption spectra

A UV-visible spectrophotometer can be used to measure the light absorbed by solar cell materials (e.g. polymer, fullerene, porphyrin) over a variety of wavelengths of light. The absorption spectrum provides the absorption profile of a solar cell, and can be compared to the solar spectrum profile to determine the compatibility of a material for photovoltaic applications. Ideally, the light absorption of a material would perfectly match the light radiated in the solar spectrum, and thus absorb all available sunlight. However, so far no materials have been discovered which fully meet these criteria, and the common polymers: MEH-PPV, MDMO-PPV and P3HT, all absorb only a small portion of available sunlight, which severely limits their theoretical efficiency. Ultimately, new materials need to be developed which better absorb sunlight [80].

1.5.3  Spectral response

The spectral response of a solar cell is a measurement of the amount of current produced by a solar cell at each wavelength of incident light. It can be used to determine the photoactivity of solar cell materials. By comparing a plot of spectral response to the UV-visible absorption spectrum of a solar cell, the wavelengths of absorbed light that are converted into photocurrent can be determined. This is an important characterisation method, but can be somewhat deceptive as it does not take into account the strength of the incident light.

1.5.4  External quantum efficiency

A much more useful and accurate indication of spectral response is to measure the external quantum efficiency (EQE) of a device over the entire absorption spectrum of the materials. EQE is the ratio of the number of collected electrons to incident photons. It describes how many electrons are produced for each photon of light absorbed by the photovoltaic materials. By collecting EQE measurements across a range of wavelengths, we can determine which
components are producing photocurrent, and for a polymer:fullerene blend, how much each component contributes.

1.6 Ternary polymer:porphyrin:PCBM solar cells

Over the past few years, there have been a number of papers published which investigate the use of porphyrin and phthalocyanines in thin-film polymer/fullerene organic solar cells, to enhance the efficiency of these devices primarily through improved light harvesting. This section will address the key findings of each study.

Device data for each paper has been listed in Table 1.1 below. Some information is absent as it was not provided in the publications.

One of the earliest reported porphyrin-based thin-film solar cells utilised a layer of electrodeposited chlorophyll-\(\alpha\) sandwiched between two electrodes as the active layer, achieving a power conversion efficiency of approximately 0.01 %, which was among the highest reported efficiencies at that time (1975) [81]. The first heterojunction bilayer device was reported in 1986, composed of copper phthalocyanine (CuPc) donor and a perylene derivative acceptor, reaching a power conversion efficiency of 1 % [21]. Thin-film devices based on a metal phthalocyanine and \(C_{60}\) fullerene have appeared in many guises, such as co-deposited single layer [82], bilayer [83], multilayer [84], and gradient deposition [85] devices. All require high temperature vacuum deposition of materials, which limits their cost effectiveness. The development of conducting polymers and soluble fullerenes led to solution-deposited thin-film organic solar cells, and it is the incorporation of soluble porphyrinic materials into that architecture which is the main focus of this literature survey.
Table 1.1: Device data for porphyrinoid containing thin-film solar cells, with porphyrinoid species highlighted in bold

<table>
<thead>
<tr>
<th>Year</th>
<th>Donor</th>
<th>Acceptor</th>
<th>Thickness (nm)</th>
<th>(J_{SC}) (mA/cm(^2))</th>
<th>(V_{OC}) (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2006</td>
<td>MEH-PPV</td>
<td>PcH(<em>2) + C(</em>{60})</td>
<td>150</td>
<td>0.00027</td>
<td>1.40</td>
<td>0.69</td>
<td>-</td>
</tr>
<tr>
<td>2007</td>
<td>P3HT + Cu(CN)(_4)PP</td>
<td>PCBM</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2007</td>
<td>MEH-PPV + Cu(CN)(_4)PP</td>
<td>PCBM</td>
<td>110</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2007</td>
<td>P3HT + GaOHPc</td>
<td>C(_{61})(CO(_2)Et)(_2)</td>
<td>200</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2007</td>
<td>MEH-PPV + PdTCP</td>
<td>CuPc</td>
<td>-</td>
<td>-</td>
<td>0.55</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2008</td>
<td>LCP</td>
<td>PCBM</td>
<td>-</td>
<td>3.99</td>
<td>0.51</td>
<td>-</td>
<td>0.712</td>
</tr>
<tr>
<td>2009</td>
<td>ZnTPP</td>
<td>C(_{60})</td>
<td>150</td>
<td>0.62</td>
<td>0.33</td>
<td>0.38</td>
<td>0.078</td>
</tr>
<tr>
<td>2009</td>
<td>P3HT + OBuOPc</td>
<td>PCBM</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2009</td>
<td>P3HT + ZnOOOPc</td>
<td>PCBM</td>
<td>100</td>
<td>6.2</td>
<td>0.48</td>
<td>0.37</td>
<td>1.1</td>
</tr>
<tr>
<td>2009</td>
<td>P3HT + SiPc</td>
<td>PCBM</td>
<td>100</td>
<td>7.9</td>
<td>0.58</td>
<td>0.59</td>
<td>2.7</td>
</tr>
<tr>
<td>2009</td>
<td>MDMO-PPV + PtOEP</td>
<td>PCBM</td>
<td>130</td>
<td>3.4</td>
<td>-</td>
<td>-</td>
<td>1.6</td>
</tr>
<tr>
<td>2010</td>
<td>MEH-PPV + CuPc</td>
<td>PCBM</td>
<td>-</td>
<td>5.04</td>
<td>0.75</td>
<td>0.37</td>
<td>1.41</td>
</tr>
<tr>
<td>2010</td>
<td>ZnPcFSR</td>
<td>Py-C(_{60})</td>
<td>70</td>
<td>1.24</td>
<td>0.41</td>
<td>0.29</td>
<td>0.12</td>
</tr>
<tr>
<td>2011</td>
<td>PQT-12 + TiOPc</td>
<td>PCBM</td>
<td>66</td>
<td>3.80</td>
<td>0.52</td>
<td>0.40</td>
<td>0.79</td>
</tr>
</tbody>
</table>

Abbreviations: C\(_{60}\) = C\(_{60}\) fullerene; C\(_{61}\)(CO\(_2\)Et)\(_2\) = di(ethoxycarbonylmethano)fullerene carboxylate; Cu(CN)\(_4\)PP = [2,3,12,13-tetracyano-5,10,15,20-tetraakis(3,5-di-tert-butylphenyl)porphyrinato]copper(II); CuPc = copper(II) phthalocyanine; GaOHPc = hydroxygallium phthalocyanine; LCP = liquid-crystalline porphyrin; MEH-PPV = poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene]; OBuOPc = 1,4,8,11,15,18,22,25-octabutoxy-29H,31H-phthalocyanine; PCh\(_2\) = phthalocyanine; PCBM = phenyl-C\(_{61}\)-butyric acid methyl ester; PdTCP = palladium(II) mesotetra[benzo-15-crown-5]porphyrinate; SiPc = silicon phthalocyanine bi(trihexyloxiloxide); ZnOOOPc = zinc(II) phthalocyanine.
2,3,9,10,16,17,23,24-octakis(octyloxy)-29H,31H-phthalocyanine; ZnTPP = zinc(II) 5,10,15,20-tetraphenylporphyrin; PtOEP = platinum(II) octaethylporphyrin; CuPc = copper(II) phthalocyanine; ZnPcFSR = a blend of thioalkane substituted hexadecafluorophthalocyaninatozinc(II) compounds; PQT-12 = poly(3,3′′′-didodecyl-2,2′:5′,2″:5″,2‴-quaterthiophene); TiOPc = phthalocyanine titanium(IV) oxide; Py-C₆₀ = pyridine-substituted pyrroloidinofullerene

Ltaief et al. (2006) were the first to incorporate a porphyrinoid into a MEH-PPV/C₆₀ heterojunction device with the aim of photosensitisation through broadening of the active layer absorption profile [86]. The addition of freebase phthalocyanine (PcH₂) to the device (ratios not stated) was found to increase the $V_{OC}$, $J_{SC}$ and FF, and expand the spectral response, although the relevance of this is questionable considering the very low device efficiency ($J_{SC} = 0.00027 \text{ mA/cm}^2$) and poor quality IV curves. They also incorporated the dye coumarin 343 into some devices to achieve a similar outcome.

![Molecular structures and J-V characteristics](image)

Figure 1.23: The molecular structure of phthalocyanine (top left), coumarin 343 (top right), and the J-V characteristics of MEH-PPV:C₆₀ devices with added organic dyes (bottom) [86]
They hypothesised that addition of \( \text{PcH}_2 \) improved the device properties by extending the spectral response and enhancing the concentration of photogenerated pairs as observed from photoluminescence measurements. They also suggested that the addition of the dyes increases the hole conductivity of the active layer, and although no direct conductivity measurements were made, the increase in device performance in what is a fundamentally hole mobility limited device would appear to support this claim.

Belcher et al. (2007) introduced a copper porphyrin into P3HT:PCBM bulk heterojunction devices also with the aim of broadening the spectral response [87]. The porphyrin \([2,3,12,13	ext{-tetracyano-5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrinato}]\text{copper(II)}\) \((\text{Cu(CN)}_4\text{PP})\) was selected to complement the absorption profile of the other components, and this widening of light absorption was found to translate well into a broadening of the spectral response of the device, due to the addition of photocurrent contribution from both the Soret and Q-bands of the porphyrin. Figure 1.24 shows the absorption peaks of the materials (bottom left) and the resulting spectral response of the solar cells (bottom right). Note in particular the Soret band at 445nm and Q-band at 635nm in both graphs.

Interestingly, when the devices were annealed (as is common practice with P3HT:PCBM devices), the porphyrin contribution disappeared, indicating that the changes in morphology from the annealing step were in fact detrimental in this case. Porphyrins are well known to aggregate strongly both in solution and in the solid state [98-100], which can be observed spectroscopically as a shifting of absorption peaks. It was suggested that the ternary heterojunction devices lost their porphyrin photocurrent contribution upon annealing due to an increase in aggregation. The formation of large aggregates may have resulted in reduced free charge carrier production as excitons formed in the porphyrin islands could not diffuse to the distant interface before recombination occurred. However, while the spectral response was enhanced, overall device efficiency was reduced as a result of porphyrin inclusion [87].
Ternary blends composed of MEH-PPV:Cu(CN)$_4$PP:PCBM have also been investigated by Dastoor et al. (2007) [41]. Porphyrin inclusion also broadened the spectral response of the PPV device, and allowed the construction of efficient solar cells containing less than 10 % polymer. This observation was attributed to a good compatibility of the porphyrin within the polymer/fullerene blend, as a favourable morphology was maintained (despite the addition of the porphyrin) that allowed a similar peak external quantum efficiency of ~35 % for both the binary and ternary blends. Light absorbed by the porphyrin produced 15-20 % of the total photocurrent, with both the porphyrin Soret and Q-bands contributing equally.

In the same study, three other porphyrins were also incorporated into MEH-PPV based devices. These were the freebase, diprotonated salt, and zinc-metalated tetraxylylporphyrin. It
was found that all three of these porphyrins contributed photocurrent, as evident from the porphyrin Q-band photogenerated current between 600-700 nm, seen in Figure 1.25, below. However, the overall efficiency of these devices was quite low.

Figure 1.25: Chemical structures of (A) diprotonated tetraxylylporphyrin acid salt, (B) freebase tetraxylylporphyrin, and (C) zinc-metalated tetraxylylporphyrin; and (D) the internal quantum efficiency spectra of ternary blend devices composed of MEH-PPV:porphyrin:PCBM [41]
Kaulachs et al. (2007) attempted to extend the spectral response of a P3HT:fullerene solar cell into the near infrared region by adding the electron donating porphyrinoid hydroxygallium phthalocyanine (GaOHPc) [88].

\[
\text{Ga} = \text{O} - \text{H} \quad \text{N} \\
\text{N} \quad \text{N} \quad \text{N} \\
\text{N} \quad \text{Ga} = \text{OH} \quad \text{N} \\
\text{N} \quad \text{N} \\
\text{N} \quad \text{N} \\
\text{N}
\]

**Figure 1.26: Chemical structure of hydroxygallium phthalocyanine (GaOHPc)**

This particular phthalocyanine was selected as it complements the absorption spectrum of the polymer/fullerene blend well, allowing almost uniform light absorption in the 350-1000 nm region. External quantum efficiency (EQE) measurements performed at low incident light levels showed a large charge transfer band at 875 nm, coinciding with the absorption band of the GaOHPc, which suggests that the GaOHPc and fullerene are closely associated within the film to form a charge-transfer complex. EQE measurements at higher light intensities were attempted but resulted in lower device efficiencies, which the authors attribute to the formation of an insulating Al$_2$O$_3$ layer beneath the aluminium electrode, the result of electrode deposition at insufficiently low pressure [88]. The highest reported EQE of any device was less than 3 % (and the other reported EQEs considerably less again), and a direct comparison with a standard P3HT:fullerene device was not undertaken. While broadening of device spectral response was observed due to the addition of the phthalocyanine, there appears to be little benefit in doing so when the performance of the resulting device is so poor.
Kolesnikov et al. (2007) produced bilayer devices consisting of a blend of MEH-PPV and palladium(II) meso-tetra(benzo-15-crown-5)porphyrinate (PdTCP) as an electron conduction layer, and copper(II) phthalocyanine (CuPc) as a hole transport layer [89]. While the two layers have absorption spectra that adequately cover the region from 350-750 nm, device performance was poor (<0.1 %), attributed to the formation of electron traps due to oxygen adsorbed onto the substrate and the interfaces between layers.

Figure 1.27: The chemical structure of palladium(II) meso-tetra(benzo-15-crown-5)porphyrinate

Li et al. (2008) synthesised a series of porphyrins exhibiting liquid crystalline properties, which were found to form homeotropically aligned domains (nanostructured columns of porphyrins formed by intermolecular π-π stacking) when heated films were cooled under controlled conditions [90].
They hypothesised that this morphology might be favourable for solar cells because not only is higher light absorption achieved, but the stacked domains should also allow for greater electron and hole mobility within the active layer of the device by providing a favourable molecular arrangement for efficient flow of charge. Organic solar cells of pure porphyrin films had low efficiencies, as expected in the absence of a doping electron acceptor since the diffusion length of excitons is significantly less than the film thickness. Bulk heterojunction solar cells were prepared from a 1:1 w/w blend of the porphyrin (electron donor) and PCBM (acceptor), and after annealing at 140 °C and cooling slowly to room temperature, device performance tripled to a PCE of 0.712 % under AM1.5G illumination, primarily due to an increase in short circuit current density. The improvement was attributed to improved alignment of the porphyrin stacks [90].

Oku et al. (2009) fabricated bulk heterojunction solar cells from zinc(II) tetraphenylporphyrin and C\textsubscript{60} fullerene. Device efficiencies were low (<0.1 %), but improved slightly with the addition
of an exciton-diffusion blocking layer (EBL) of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) between the active layer and the aluminium electrode [91]. The EBL was found to suppress the migration of holes to the Al interface, resulting in increased device efficiency. X-ray diffraction data was presented which suggested the formation of ZnTPP:C₆₀ cocrytallites within the film, and the authors hypothesised that device efficiency might be further improved by the formation of a more continuous cocrytallite microstructure which may allow for improved exciton dissociation and less recombination.

Figure 1.29: Chemical structures of zinc(II) tetraphenylporphyrin (left) and 3,4,9,10-perylenetetracarboxylic dianhydride (right)

Burke et al. (2009) [98] published a study on the effect of solvent trapping by porphyrin aggregates on the structure and morphology of ternary blend organic devices, which followed from previous work using P3HT:Cu(CN)ₓPP:PCBM blends [87], discussed above. Scanning transmission X-ray microscopy (STXM) measurements revealed depressions in the active layer film of annealed ternary devices that were consistent with the evolution of solvent trapped within porphyrin clathrates during film formation and released as gas upon annealing [98].
As the concentration of porphyrin was increased, so did the density of the depressions in the film due to bubble formation from trapped gases during annealing. The disorder of the polymer chains also increased with increasing bubble formation, which hindered charge transport along P3HT chains and accounted for the lowering of device performance upon annealing [98]. Porphyrins are well known for their aggregation properties, and this study highlights the need for a more thorough understanding of the sometimes unexpected consequences of their addition as ternary blend materials.

Johansson et al. (2009) [92] extended the spectral response of a P3HT:PCBM solar cell by utilising the dye 1,4,8,11,15,18,22,25-octabutoxy-29H,31H-phthalocyanine (OBuOPc), which has light absorption at longer wavelengths than the P3HT (above 650 nm). The efficiency of the device was found to be dependent on the concentration of the porphyrinoid dye, with only the lowest concentration of 5 % OBUOPc displaying an increase in device EQE. Higher concentrations of up to 33 % dye, which preserved the extended spectral response >650 nm due to dye absorption, had a polymer response which decreased with increasing dye concentration.
Figure 1.31: Chemical structure of the dye 1,4,8,11,15,18,22,25-octabutoxy-29H,31H-phthalocyanine (top), and absorbance (bottom left) and external quantum efficiency (bottom right) of device components and films in various weights ratios [92].

The authors reasoned that higher concentrations of dye do not improve device efficiency because the dye itself is unable to efficiently transfer charge directly to the electrodes. Instead, photogenerated electrons and holes originating from light absorption by the dye are transported to the electrodes by PCBM and P3HT and not regions of dye, thus higher concentrations of dye do not improve device function but rather hinder the transport of charge within the device. Transient absorption spectroscopy indicated that upon excitation of
the dye molecule an electron is transferred from the dye to the PCBM, followed by hole transfer to the P3HT (Figure 1.32), forming a long-lived P3HT+/dye/PCBM− charge separated state. Transient spectroscopy measurements also indicated that in blends of higher dye concentration, the efficiency of hole transfer from the dye to the P3HT is reduced, which lowers the EQE. However, as the magnitude of the reduction in EQE cannot be explained by reduced transfer efficiency alone, the charge transport must also be affected by the dye molecule disrupting polymer and fullerene domains [92]. While the HOMO and LUMO energy levels of the blend materials were not stated, transient absorption spectroscopy measurements highlight the need for consideration of the energetics of materials and how they are placed with respect to one another, so that efficient charge transport occurs and detrimental charge trapping can be avoided.

Honda et al. (2009) [93] identified that a major efficiency limiting factor with using a dye to extend the spectral response in polymer/fullerene solar cells was the propensity of the dye to form aggregates in the film, which can reduce charge mobility and also light absorption of the active layer. Two near-infrared absorbing phthalocyanine dye molecules, zinc

Figure 1.32: Proposed model of charge transfer within the device. Upon light absorption, an electron is transferred to the PCBM and on to the aluminium electrode. The hole is transferred from dye to P3HT, and then to the PEDOT:PSS layer and transparent conducting oxide electrode [92]
2,3,9,10,16,17,23,24-octakis(octyloxy)-29H,31H-phthalocyanine (ZnPc) and silicon phthalocyanine bis(trihexylsilyloxide) (SiPc) were introduced into P3HT/PCBM cells in order to study the relationship between device performance and the formation of dye aggregates.

Figure 1.33: The molecular structures of the phthalocyanine dyes zinc 2,3,9,10,16,17,23,24-octakis(octyloxy)-29H,31H-phthalocyanine (left) and silicon phthalocyanine bis(trihexylsilyloxide) (right) [93]

Absorption peaks could clearly be observed in both solution and thin-film UV-vis spectra of the SiPc active layer blends, but interestingly, while the ZnPc absorption peak was clearly visible in the UV-vis spectrum of solution dissolved active layer blends, the absorption was greatly reduced in the spectrum of active layer thin-films, and remained weak even after annealing. This observation was seen as an indication that significant aggregation of ZnPc was occurring, which reduced the effective absorption coefficient of the material. Also, upon annealing the ternary blend films, the usual increase in absorption at the lower energy shoulder of the P3HT peak at around 600 nm, which reflects the post-annealing increase in crystalline structure of the P3HT [99, 100], was diminished for the ZnPc ternary blend relative to the SiPc blend, again indicating that the ZnPc was disrupting the morphology of the blend film [93]. Annealed ternary blend devices containing the SiPc showed an improvement in power conversion efficiency from 2.2 % (control P3HT:PCBM solar cell) to 2.7 %, primarily driven by an increase in
while the equivalent blend using ZnPc suffered a decrease in performance to 1.1 %. EQE spectra of the SiPc ternary blend showed not only a strong peak (20 %) corresponding to the SiPc absorption band indicating direct photoexcitation of the SiPc, but also an increase from 50% to 60% of the peak EQE corresponding to P3HT absorption. This observation suggested that the SiPc also serves to improve charge generation from P3HT excitons [93].

The authors concluded that the bulky axial ligands on the SiPc suppress the formation of aggregates within the ternary blend film, which allows a greater amount of SiPc to be located at the interface between P3HT and PCBM domains where SiPc excitons can successfully inject an electron into PCBM and a hole into P3HT, and contribute to device photocurrent. The interfacial placement of SiPc, enhanced by thermal annealing, was driven by the crystalline nature of both P3HT and PCBM, which expel SiPc from each domain. Thus direct photocurrent generation from the SiPc molecules increases, as well as the exciton harvesting efficiency through energy transfer to the dye molecule, which enhances the P3HT contribution to photocurrent generation [93]. This observation is in contrast to other studies of annealed P3HT-based ternary blend devices which observed device degradation upon thermal annealing [87] and again illustrates the importance of control of active layer morphology, and in particular porphyrin and phthalocyanine aggregation, when working with these materials.

Rand et al. (2009) [94] found that the exciton diffusion length in porphyrin-containing ternary blend devices could be increased by converting singlet excitons into long-lived triplet excitons using the phosphorescent dopant platinum(II) octaethylporphyrin (PtOEP). PtOEP was chosen as it satisfies the energetic criteria for triplet exciton generation, namely having its lowest excited singlet state ($S_1$) lower than that of MDMO-PPV to facilitate energy transfer to the PtOEP, followed by rapid intersystem crossing to the triplet state ($T_1$) of the PtOEP. Population of the MDMO-PPV $T_1$ level is also efficient, as the $T_1$ of the PtOEP is ~0.3 eV larger than in the MDMO-PPV. Hole trapping on the PtOEP is also prevented as the HOMO of both the PtOEP and the MDMO-PPV are equal [94].
The addition of 5% PtOEP enhanced photocurrent by 20%, while preserving the open-circuit voltage and fill factor of the device. EQE spectra show not only the presence of a new peak due to light absorption by the PtOEP, but also an increase in the EQE due to the MDMO-PPV, which the authors state shows that a larger percentage of excitons were able to reach a donor-acceptor interface as a result of increased exciton diffusion length [94]. This publication is a well thought out study where the porphyrinic species was selected to fulfil specific energetic criteria, and demonstrates the improvements to device efficiency that can be gained through this approach, whereby all blend materials work harmoniously to achieve enhanced charge transport.

Chen et al. (2010) [95] recognised that MEH-PPV:PCBM solar cells do not absorb light at wavelengths longer than 550 nm, so they incorporated 15% (by weight) of the near infrared absorbing dye copper(II) phthalocyanine (CuPc) to broaden light absorption. Despite a small reduction in $V_{OC}$, this increased the efficiency of the device by 12%, which they attributed primarily to an increase in short-circuit current density through enhanced light absorption. Increasing the concentration of CuPc beyond 15% resulted in a decrease in device efficiency from reduced $V_{OC}$ and $J_{SC}$. SEM images identified large (> 600 nm) aggregates of CuPc in ternary blended films containing 30% CuPc. Mobility measurements extracted from OTFTs fabricated
from device films showed significant lowering of hole mobility in the same blends, suggesting that the large CuPc aggregates were hindering charge transport and mobility by forming interfacial potential barriers between the polymer [95]. Thus improvements to device efficiency from the use of spectral dopants can be a valid strategy so long as a favourable film morphology is maintained.

![Chemical structure of copper(II) phthalocyanine](image)

**Figure 1.35: The chemical structure of copper(II) phthalocyanine**

Varotto (2010) [96] synthesised a series of optically tuned phthalocyanines by the substitution of peripheral fluoro groups on hexadecafluorophthalocyaninatozinc(II) (ZnPcF₁₆) by thioalkanes [CH₃(CH₂)₁₁SH]. Delocalisation of the HOMO and LUMO orbitals on the ring periphery of ZnPcF₁₆ allows a decrease in optical bandgap as electron-donating thioalkanes are substituted onto the phthalocyanine. The effect is additive, which enabled the optical absorbance of the molecules to be tuned depending on the degree of thioalkane substitution (Figure 1.36).

Organic solar cells were fabricated with a layer of either pure or blended phthalocyanines as donor molecules, and an evaporated layer of pyridine-substituted pyroridinofullerene (Py-C₆₀) as the acceptor material. The most efficient devices had a layer of blended phthalocyanine which produced more than 3 times the photocurrent compared with single-phthalocyanine devices, attributed to the Pc components contributing to absorption at different photon energies [96]. Device power conversion efficiency was very low at just 0.12 %, however this
approach demonstrates how porphyrinic materials can be tuned to absorb specific spectral regions via simple modification of substituents.

\[
\text{ZnPcF}_{16} : \quad R_{1,4-8,11-15,18-22,25} = \text{F} \\
\text{HS(CH}_2\text{)}_{11}\text{CH}_3
\]

Figure 1.36: Chemical structures of thioalkane-substituted hexadecafluorophthalocyaninatozinc(II) (top left) and pyridine-substituted pyrroridinofullerene (top right), UV-vis absorption spectra for thioalkane-substituted ZnPcF\textsubscript{16} (bottom left), and change in optical band gap with the number of peripheral thioalkane substituents (bottom right) [96]
Bamsey (2011) [97] reported bulk heterojunction devices consisting of a blended active layer of poly(3,3′′′-didodecyl-2,2′,5′,2″,5″,2″′-quaterthiophene) (PQT-12) and PCBM, with an additional interlayer of metalated phthalocyanine (M-Pc) between PEDOT:PSS and the active layer. The highest performing M-Pc was phthalocyanine titanium (IV) oxide (TiOPc), which improved power conversion efficiency to 0.79 % from the 0.37 % efficiency of the standard polymer:fullerene device. Despite low overall device efficiency, the TiOPc interlayer cause significant improvement in current generation, with EQE values of up to 16 % observed between 600-900 nm, where the polymer:fullerene contribution is negligible [97].

Figure 1.37: Chemical structures of poly(3,3′′′-didodecyl-2,2′,5′,2″,5″,2″′-quaterthiophene) (top left) and metalated phthalocyanine (top right), and EQEs of the control polymer:fullerene device, and of the device with TiOPc interlayer, along with UV-Vis absorption spectra of the blend materials (bottom) [97]
All devices with the M-Pc interlayer also showed an increase in $V_{OC}$, although the exact mechanism for this is unclear as there was no apparent correlation between the HOMO level of the M-Pc and the LUMO level of the PCBM [97].

An increasing number of research groups have adopted porphyrinic materials as ternary components of thin-film organic solar cells. While many have reported improvements in ternary blend device efficiency compared with non-porphyrin binary devices, the performance of the standard devices with which they have been compared is often very poor, being far less efficient than those considered state of the art for a given donor:acceptor system. Thus the effectiveness of the addition of a porphyrinic material is in many cases questionable, even when an improvement has been reported. Furthermore, few publications give any indication of the error of their measurements, whether within their testing apparatus or even simply the number of replicate devices contributing to a data set. Key information that would be required should anyone wish to repeat or compare to the experiments is often absent (e.g. film thickness, external quantum efficiency, even overall device efficiency in some cases) and for those few papers where a genuine improvement appears to have occurred, the rationale behind the choice of porphyrin/phthalocyanine and the blend ratio used is not always apparent. The effect of porphyrin/phthalocyanine aggregation is often alluded to but rarely investigated, and optimisation of blend ratios is only rarely reported. Finally, further consideration of the energy levels of the porphyrinic compound needs to occur so that they may be appropriately positioned with respect to other blend components, to provide favourable conditions not only for light absorption, but also charge separation and charge transport within the device. This thesis seeks to address these issues and provide a systematic study of porphyrin-containing ternary blend OPV devices which might be used to better understand this complex field of study, and push toward efficient devices and consistent, reproducible, ternary blend systems.
1.7 The chemistry of porphyrinic compounds

Much research has been conducted on the synthesis and characterisation of porphyrins and related molecules. The interest is owed to their important roles in nature as two of the central molecules of life: haem (or heme), the red coloured iron-containing porphyrin found in the blood, which selectively binds and transports molecular oxygen around the human body; and chlorophyll, the green coloured pigment responsible for the light-harvesting reactions of photosynthesis, upon which all life on earth depends.

![Figure 1.38: Haem B (left) and chlorophyll-α (right), with the porphyrinic core highlighted in red](image)

1.7.1 Porphyrin synthesis

Porphyrin synthesis was first reported by Rothemund in 1935 [101]. He prepared the compound 5,10,15,20-tetraphenylporphyrin (TPP) by the direct condensation of pyrrole and benzaldehyde in pyridine. Even with forcing conditions (sealed vessel at 150 °C for 24 hours) yields of less than 5 % were achieved. The severe reaction conditions also meant that very few substituted benzaldehydes could be used successfully [102]. It was over 30 years before improvements to the methodology allowed greater yields and greater flexibility in the choice of aldehyde. Adler and Longo published their modification of Rothemund’s procedure in 1967
They used an acidic solvent to catalyse the condensation reaction, and performed the reaction in air to ensure complete oxidation into the conjugated porphyrin structure. This simple modification allowed yields of up to 20%, and reduced reaction time to just 30 minutes. In addition, the milder conditions allowed a greater variety of substituted benzaldehydes to be used.

**Figure 1.39: Adler and Longo’s synthesis of tetraphenylporphyrin**

While there are now a huge variety of synthetic methods to prepare porphyrins, the Adler and Longo synthesis is still often used for simple porphyrins, due to its ease of workup and reasonable yields. By changing the identity of the benzaldehyde, a variety of substituents can be introduced at the meso- (i.e. 5,10,15,20-) positions [104].

Lindsey et al. (1987) [102] presented a new synthetic strategy for preparing tetraarylporphyrins that has been widely adopted. They recognised that moderate dilutions ($10^{-2}$ M) are thermodynamically preferred for the formation of intermediate cyclic porphyrinogens from pyrrole and substituted benzaldehydes at room temperature. The reaction is catalysed by a trace amount of acid, and once the porphyrinogen is formed it is irreversibly converted to the corresponding porphyrin with the addition of an oxidant such as p-chloranil or 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), allowing small amounts of porphyrin to be synthesised in high yield without difficult purification procedures. This methodology is applicable to a wide variety of meso-tetraalkyl- and aryl- porphyrins, and is
suitable for sensitive aldehydes which would otherwise fail under the harsher Adler-Longo conditions.

Figure 1.40: Lindsey’s synthesis of tetraphenylporphyrin

MacDonald et al. (1960) [105] pioneered the early work of unsymmetrical porphyrin synthesis from dipyrromethanes, commonly called 2 + 2 syntheses, referring to the two different dipyrromethanes that give rise to an unsymmetrical porphyrin once joined. One dipyrromethane unit bears two formyl groups, and the other has no α-substitution [106]. This method can be used to synthesise a wide variety of unsymmetrical porphyrins and has also led to a number of similar syntheses based on the basic 2 + 2 method [107-111].

Figure 1.41: MacDonald’s 2 + 2 porphyrin synthesis [106]

Metal complexes of porphyrins can be easily formed by a variety of methods. Usually the porphyrin is dissolved in chloroform and refluxed with a solution of metal acetate (or sometimes metal chloride) which has been dissolved in glacial acetic acid [112]. As an example, the preparation of Ni(II)-TPP is shown below. For common metals such as nickel, copper and zinc, this procedure will give the metalloporphyrin in near quantitative yield.
In 1994 two groups led by Furuta [113] in Japan and Latos-Grazynski [114] in Poland independently reported an isomer of porphyrin called 2-aza-21-carba-5,10,15,20-tetraphenylporphyrin (NC-TPP), or “N-confused porphyrin”. N-confused porphyrin has a very similar framework to regular porphyrin, but with one of the pyrrole rings connected to its adjacent meso-carbon through an α-β’ linkage, rather than the usual α-α’ linkage. The result of this modification is that one of the pyrrole rings appears “confused”, and has its nitrogen oriented towards the outside of the porphyrin macrocycle, rather than inward towards the core as do the other pyrrole rings. The synthesis of N-confused porphyrin is a modification of the Rothemund procedure, involving acid-catalysed condensation of pyrrole and an aldehyde, followed by chemical oxidation with chloranil. Both groups reported yields of around 5 % [113, 114]. Despite the similarities of synthetic method to regular porphyrin synthesis, during condensation N-confused porphyrin is produced in preference to regular porphyrin primarily through the selection of the acid catalyst and the gentle, room temperature reaction conditions which are performed at very low dilutions.

A few years later, in 1999, a greatly improved synthesis was reported by Lindsey’s group [115, 116]. Their modified procedure gave yields approaching 40 %, using methanesulfonic acid.
(MSA) as the catalyst, followed by oxidation with DDQ to convert the intermediate porphyrinogen to the aromatic N-confused porphyrin.

Figure 1.43: Lindsey’s synthesis of N-confused porphyrin

This procedure allows a variety of electron-donating aryl groups (e.g. para-anisyl) to be incorporated into the structure. For electron-withdrawing groups (e.g. 4-cyanophenyl), BF$_3$·OEt$_2$ was found to be the superior acid catalyst [117]. Again, as with regular porphyrins, the meso-substituents can be varied by the selection of aldehyde [104].

Metalated N-confused porphyrins can be prepared similarly to regular porphyrins. The metal acetate or chloride is usually dissolved in an alcohol and stirred or heated at reflux for around 60 minutes with a chloroform solution of the N-confused porphyrin [114]. An example is the preparation of N-confused Ni(II)-TPP, shown below.

Figure 1.44: Preparation of N-confused Ni(II) TPP
The external nitrogen of the inverted pyrrole ring is also able to be modified by the addition of a variety of substituents. The simplest is the N-methyl derivative, which is synthesised by the addition of methyl iodide to a solution of N-confused porphyrin dissolved in dichloromethane [118].

![Figure 1.45: Synthesis of 2N-methyl N-confused porphyrin](image)

In addition, the inner nitrogen can also be alkylated to give the dimethylated N-confused porphyrin. The HI generated from the first alkylation was found to protonate the internal nitrogen and prevent dimethylation from occurring. To overcome this issue, Xiao and Dolphin used the addition of the base Na₂CO₃ to neutralise the protonated intermediate and make the inner nitrogens more nucleophilic, thus allowing the dimethylated species to form [119].

![Figure 1.46: Synthesis of N,N'-dimethyl N-confused porphyrin](image)
1.7.3 Phthalocyanine synthesis

Phthalocyanines are molecules that share common structural aspects with porphyrins, and have been used extensively in small molecule organic solar cells. Generally phthalocyanine is prepared from the cyclotetramerisation of 1,2-dicyanobenzene (phthalonitrile) [120]. High purity metal-free phthalocyanine was synthesised by Thompson et al. [121] by the direct cyclisation of a melt consisting of phthalonitrile and the oxidant hydroquinone in a weight ratio of 4:1.

![Figure 1.47: Synthesis of phthalocyanine](image)

Metallated phthalocyanines can be prepared by refluxing phthalocyanine with the desired metal salt, or direct tetramerisation of phthalonitrile using the metal as a template, while substituted phthalocyanines are usually prepared by starting with the appropriately substituted phthalonitrile [120].

Whilst phthalocyanines have very strong visible light absorption, their utilisation as a material for solution-processed thin-film solar cells is limited due to their poor solubility and strong aggregation properties. Additionally, they are more difficult to derivatise than the closely related porphyrins. As such, the focus of this thesis will be polymer:fullerene blend devices using porphyrin and N-confused porphyrin derivatives as ternary components to probe device function and performance.
1.8 Summary

This introduction has summarised the current knowledge regarding polymer:fullerene bulk heterojunction organic solar cells in terms of materials, device physics, processing procedures and characterisation techniques. The synthesis of simple porphyrinic compounds, and the current state of ternary polymer:porphyrin:fullerene solar cell research, has been considered.

Porphyrins can be synthesised with a range of substituents, and can be successfully introduced into organic photovoltaic devices and contribute to photocurrent generation. However, a fundamental understanding of how this might be utilised to improve device performance is still lacking.

A thorough, systematic study of ternary blend devices is absent from the literature. For reports of improved devices, full characterisation data is lacking and there is often little to suggest how or why a particular porphyrin was chosen for a particular study. Only infrequently is there consideration of the placement of the porphyrin frontier orbitals in relation to other blend components, and while the aggregation properties of porphyrinic materials is often mentioned, the implications for device morphology, and methods to better control this phenomenon, are rarely examined in detail.

This thesis aims to address these issues and to provide the foundations for further research whereby the fundamental interactions between porphyrins and other blend components are better understood, so that more directed research into the key processes of light absorption, charge separation, and charge transport within these complex ternary blend systems can be used not only to enhance device efficiency, but to probe the chemistry and physics of device operation at a fundamental level, ultimately leading to our shared goal of achieving economically feasible renewable energy.
1.9 References


Chapter 2 – Experimental

2.1 Materials and reagents

All solvents were either A.R. or A.C.S grade and purchased from Sigma-Aldrich or Merck. All reagents were purchased from Sigma-Aldrich and used as supplied.

Poly[2-methoxy-5-(2’-ethylhexyloxy)-p-phenylenevinylene] (MEH-PPV) was purchased from American Dye Source Inc., Canada ($M_w = 290K, 374K, 600K g mol^{-1}$); Sigma-Aldrich Inc., Australia ($M_w = 40-70K, 150-250K g mol^{-1}$); and Jenpolymer Materials Ltd., Germany ($M_w = 10K$ and $16K g mol^{-1}$) and stored under nitrogen.

Poly(3-hexylthiophene) (P3HT) was purchased from Rieke Metals Inc, Nebraska USA ($M_w = 60K g mol^{-1}$, PDI = 2.1, RR = 91-95 %); and Luminescence Technology Corp., Taiwan ($M_w = 58-63K g mol^{-1}$, PDI = 3.6, RR = 93-95 %), and stored under nitrogen.

[6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) was purchased from Nano-C Inc., Massachusetts USA (99.0 % purity); Luminescence Technology Corp., Taiwan (99.5 % purity); and Solenne BV, the Netherlands (99.5 % purity), and stored under nitrogen.

Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) was purchased from H.C. Starck as Clevios P VP Al 4083, with a solid content of 1.3 – 1.7 % by weight, and a PEDOT:PSS ratio of 1:6 by weight, and stored in a refrigerator at 5 °C until it was used as supplied.

ITO coated slides ($R_s = 8-12 \Omega$) were purchased from Delta Technologies Limited. Pre-patterned ITO slides ($R_s = 15 \Omega$) were purchased from Kintec Company, Hong Kong.

5,10,15,20-Tetrakis(4-aminophenyl)porphyrin (TpNH$_2$PP), 5,10,15,20-tetrakis(4-hydroxyphenyl)-porphyrin (TpOHPP), 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin (TpOCH$_3$PP), 5,10,15,20-tetrakis(4-chlorophenyl)porphyrin (TpClPP), 5,10,15,20-tetrakis(4-bromophenyl)-
porphyrin (TpBrPP) and 5,10,15,20-tetrakis(4-(methoxycarbonyl)phenyl)porphyrin (TpCOOCH₃PP) were purchased from Frontier Scientific, Utah USA.


2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphyrin (OEP), [2,3,7,8,12,13,17,18-octaethylporphyrinato] vanadium(IV) oxide (V=O-OEP), [2,3,7,8,12,13,17,18-octaethylporphyrinato] manganese(III) chloride (Mn-OEP.Cl), [2,3,7,8,12,13,17,18-octaethylporphyrinato] iron(III) chloride (Fe-OEP.Cl), [2,3,7,8,12,13,17,18-octaethylporphyrinato] cobalt(II) (Co-OEP), [2,3,7,8,12,13,17,18-octaethylporphyrinato] nickel(II) (Ni-OEP), [2,3,7,8,12,13,17,18-octaethylporphyrinato] copper(II) (Cu-OEP), [2,3,7,8,12,13,17,18-octaethylporphyrinato] zinc(II) (Zn-OEP), [2,3,7,8,12,13,17,18-octaethylporphyrinato] ruthenium(II) carbonyl (Ru-OEP.C=O), [2,3,7,8,12,13,17,18-octaethylporphyrinato] palladium(II) (Pd-OEP) and [2,3,7,8,12,13,17,18-octaethylporphyrinato] platinum(II) (Pt-OEP) were purchased from Sigma-Aldrich Inc., Australia.

All porphyrinoid compounds were used as received without further purification.

All further porphyrins were synthesised as described in section 2.3.

2.2 General techniques and instrumentation

Thin layer chromatography (TLC) was performed on Sigma-Aldrich aluminium backed sheets pre-coated with silica gel and UV indicator.

Melting points were determined with a Stuart SMP11 melting point apparatus.
Column chromatography was performed using a 40 mm diameter column packed with either activity III basic alumina ~150 mesh, which was prepared by mixing 300 g of activity I basic alumina with 19 g of reagent water, or silica gel grade 60, 70-230 mesh.

UV-visible spectra were recorded on a Varian Cary 6000i UV-vis-NIR spectrophotometer. All slides and cuvettes were made of quartz. The scanning range used was 300-1100 nm unless otherwise noted. UV-vis spectra of device films were recorded as-spun. UV-vis of pure porphyrins were recorded from either spin-cast thin films on quartz slides (e.g. for bandgap measurement) or from solution (e.g. for comparison of absorption peaks). In the case of spectra recorded from solution, the porphyrin solution was typically diluted with chloroform or chlorobenzene such that the maximum Soret peak absorbance was between 0.5 and 0.9. Solutions typically had a concentration of between $1 \times 10^{-6}$ and $5 \times 10^{-5}$ M.

$^1$H NMR spectra were recorded at 300 MHz using a Bruker Avance-300DPX NMR spectrometer with deuterated chloroform (CDCl$_3$) as the solvent. All spectra were calibrated against the residual $^1$H solvent signal at $\delta_H$ 7.24 ppm.

2.3 Synthetic methods

Porphyrinoids used in this study were prepared by the following methods. Where preparing porphyrin that were previously published/prepared, spectra was compared with existing literature spectra to confirm identity.

2.3.1 Synthesis of 5,10,15,20-tetraphenylporphyrin

Method follows the procedure of Alder et al. (1967) [1].
Figure 2.1: Synthesis of 5,10,15,20-tetraphenylporphyrin

Pyrrole (1.12 mL, 0.016 mol) and benzaldehyde (1.60 mL, 0.016 mol) were added to 60 mL of refluxing propionic acid. After refluxing for 30 min, the solution was cooled to room temperature and filtered through Whatman grade 4 filter paper. The filter cake was washed thoroughly with methanol, followed by a brief hot water wash, and the resulting purple crystals were air dried on a Buchner funnel under vacuum for 1 hour. TLC of the purified compound showed only one visible spot, indicating that the compound was of high purity.

Yield  = 427 mg (17 %)

m.p.  = >250 °C

$R_t$ (silica, CH$_2$Cl$_2$/1 % MeOH): 0.93

$\lambda_{\text{max}}$/nm (CH$_2$Cl$_2$): 418 (Soret), 447, 517, 552, 592, 649 (Q-bands).

$^1$H NMR (300 MHz, CDCl$_3$, 21 °C): δ 8.82 (d, 8H, pyrrolic $\beta$-H); 8.20 (m, 8H, ortho-Ar-H); 7.73 (m, 12H, meta- and para-Ar-H); -2.76 (s, 2H, inner N-H).

2.3.2 Synthesis of 5,10,15,20-tetrakis(4-methylphenyl)porphyrin

Method follows the procedure of Alder et al. (1967) [1].
Figure 2.2: Synthesis of 5,10,15,20-tetrakis(4-methylphenyl)porphyrin

Pyrrole (2.24 mL, 0.033 mol) and para-tolualdehyde (3.38 mL, 0.029 mol) were added to refluxing propionic acid (120 mL). After refluxing for 30 min, the solution was cooled to room temperature and filtered through Whatman grade 4 filter paper. The filter cake was washed thoroughly with methanol, followed by a brief hot water wash, and the resulting purple crystals were air dried on a Buchner funnel under vacuum for 2 hours. TLC indicated that the compound was of high purity.

Yield = 1020 mg (21 %)

m.p. = >250 °C

\( R_f \) (silica, CH\(_2\)Cl\(_2\)/1 % MeOH): 0.95

\( \lambda_{max}/\text{nm} \) (CH\(_2\)Cl\(_2\)): 418 (Soret), 484, 515, 551, 591, 647 (Q-bands).

\(^1\text{H NMR (300 MHz, CDCl}_3, 21 \, ^\circ\text{C}): \delta 8.84 \, (d, 8H, pyrrolic \beta-H); \ 8.08 \, (d, 8H, ortho-Ar-H); \ 7.54 \, (meta-Ar-H); \ 2.70 \, (s, 12H, CH}_3\); -2.74 \, (bs, 2H, inner N-H).\)

2.3.3 Synthesis of 5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrin

Method follows the procedure of Alder et al. (1967) [1].
Pyrrrole (1.12 mL, 0.016 mol) and 3,5-dimethylbenzaldehyde (2.15 mL, 0.016 mol) were added refluxing propionic acid (60 mL). After refluxing for 30 min, the solution was cooled to room temperature and filtered through Whatman grade 4 filter paper. The filter cake was washed thoroughly with methanol, followed by a brief hot water wash, and the resulting purple powder was air dried on a Buchner funnel under vacuum for 90 mins. TLC indicated that the compound was of high purity.

Yield = 435 mg (15 %)

m.p. = >250 °C

$R_f$ (silica, CH$_2$Cl$_2$/1 % MeOH): 0.94

$\lambda_{max}$/nm (CH$_2$Cl$_2$): 419 (Soret), 516, 551, 591, 647 (Q-bands).

$^1$H NMR (300 MHz, CDCl$_3$, 21 °C): δ 8.85 (d, 8H, pyrrolic $\beta$-H); 7.82 (d, 8H, ortho-Ar-H); 7.39 (s, 4H, para-Ar-H); 2.59 (s, 24H, meta-Ar-CH$_3$); -2.76 (s, 2H, inner N-H).

2.3.4 Synthesis of 3,5-di-tert-butylbenzaldehyde

Method follows the procedure of Karame et al. (2004) [2].
To a solution of 3,5-di-tert-butyltoluene (5.0 g, 24.46 mmol) and N-bromosuccinimide (9.0 g, 50.56 mmol) in 80 mL of CCl₄ was added benzoyl peroxide (41 mg, 1.69 x 10⁻⁴ mol) to initiate the reaction. The solution was heated at reflux for 18 h, and then the warm reaction mixture was filtered, by gravity, through Whatman grade 4 filter paper to remove any insoluble material. Solvent was removed from the filtrate under vacuum to give an oily mixture of 3,5-di-tert-butylbenzylbromide and 3,5-di-tert-butylbenzyldibromide. This mixture was added to a solution of 9.45 g of hexamethylenetetramine in 7 mL of water and 7 mL of ethanol, and refluxed for 4 h. The product was extracted with 3 x 30 mL of Et₂O/toluene mixture (50/50), rinsed with 3 x 20 mL of brine, and the organic layer dried with MgSO₄. The solvents were evaporated to give the product 3,5-di-tert-butylbenzaldehyde as a white solid.

Yield  = 3.75 g (66 %)
m.p.  = 79-80 °C

¹H NMR (300 MHz, CDCl₃, 21 °C): δ 9.992 (s, 1H, CHO); 7.705 (m, 3H, Ar-H); 1.347 (s, 18H, C(CH₃)₃).

2.3.5  Synthesis of 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin

Figure 2.5: Synthesis of 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin

A solution of 3,5-di-tert-butylbenzaldehyde (1.273 g, 5.82 mmol) in dry toluene 9.1 mL was heated in a reflux apparatus. Just before reflux, para-toluenesulfonic acid (p-TsOH.H$_2$O) (18.2 mg, 0.09 mmol) and pyrrole (0.436 mL, 6.36 mmol) were added. The mixture was heated at reflux for 16 h. The crude mixture was filtered through a column containing 30 g of silica, and the silica washed with additional toluene (300 mL) until no further porphyrin was eluted. Fractions of 30 mL were collected and analysed by TLC (silica, toluene). Pooled fractions were reduced to dryness and recrystallised with CH$_2$Cl$_2$/MeOH to give the product as a purple/red solid.

Yield = 265 mg (17 %)

m.p. = >250 °C

$R_t$ (silica, CH$_2$Cl$_2$/1 % MeOH): 0.98

$\lambda_{\text{max}}$/nm (CH$_2$Cl$_2$): 420 (Soret), 451, 517, 553, 592, 649 (Q-bands)

$^1$H NMR (300 MHz, CDCl$_3$, 21 °C): $\delta$ 8.86 (s, 8H, pyrrolic $\beta$-H); 8.06 (s, 8H, ortho-Ar-H); 7.77 (s, 4H, para-Ar-H); 1.50 (m, 72H, C(CH$_3$)$_3$); -2.67 (pyrrolic N-H).
2.3.6 Synthesis of 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin nickel(II) complex

The following synthesis is a modification of the Rothemund and Menotti (1948) procedure [4]:

![Figure 2.6: Synthesis of 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin nickel(II) complex](image)

A solution of 295 mg of T^BuPP (2.77 x 10^{-4} mol), 17 mL chloroform, 17 mL glacial acetic acid, and 120 mg nickel(II) acetate tetrahydrate (4.82 x 10^{-4} mol) were refluxed for 1 hour. The crude mixture was then reduced to dryness and chromatographed on a silica column and the product eluted with hexanes:CH_2Cl_2 3:1 v/v. The solvent was removed under reduced pressure to give the product as red crystals.

Yield = 291 mg (94 %)
m.p. = >250 °C

R_f (silica, hexanes:CH_2Cl_2 5:1 v/v): 0.64

λ_{max}/nm (CH_2Cl_2): 409 (Soret), 518 (β-band)

^1H NMR (300 MHz, CDCl_3, 21 °C): δ 8.78 (s, 8H, pyrrolic β-H); 7.85 (s, 8H, ortho-Ar-H); 7.69 (s, 4H, para-Ar-H); 1.45 (s, 72H, Ar-C(CH_3)_3).

2.3.7 Synthesis of 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin copper(II) complex

The following synthesis is a modification of the Rothemund and Menotti (1948) procedure [4]:
Figure 2.7: Synthesis of 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin copper(II) complex

A solution of 288 mg (2.708 x 10^{-4} mol) of T^BuPP, 17 mL chloroform, 17 mL glacial acetic acid, and 75 mg copper(II) acetate hydrate (4.13 x 10^{-4} mol) were heated at reflux for 1 hour. After reflux the solution was reduced to dryness. The crude mixture was chromatographed on a silica column and the product eluted with hexanes:CH$_2$Cl$_2$ 3:1 v/v. The first red band to elute was collected and the solvent removed under vacuum.

Yield = 269 mg (88 %)

m.p. = >250 °C

$R_t$ (silica, hexanes:CH$_2$Cl$_2$5:1 v/v): 0.65

$\lambda_{max}$/nm (CH$_2$Cl$_2$): 409 (Soret), 531 (β-band)

$^1$H NMR (300 MHz, CDCl$_3$, 21 °C): δ 7.63 broad (s, pyrrolic β-H and ortho/para-Ar-H); 1.40 (s, 72H, Ar-C(CH$_3$)$_3$).

2.3.8 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin zinc(II) complex synthesis

The following synthesis is a modification of the Rothemund and Menotti (1948) procedure [4]:
A solution of 288 mg (2.708 x 10^{-4} mol) of T^BuPP, 17 mL of chloroform, 100 mg (4.556 x 10^{-4} mol) of zinc acetate dehydrate, and 83 mL of glacial acetic acid were refluxed for 1 hour at ~120 °C. The solvent was then removed under reduced pressure. The crude mixture was chromatographed on silica and the product eluted with hexanes:CH_2Cl_2 3:1 (v/v), and the solvent removed under reduced pressure.

Yield = quantitative
m.p. = >250 °C

R_f (silica, hexanes:CH_2Cl_2 4:1 v/v): 0.30

λ_max/nm (CH_2Cl_2): 414 (Soret), 541 (β-band), 580 (α-band)

^1H NMR (300 MHz, CDCl_3, 21 °C): δ 8.99 (s, 8H, pyrrolic β-H); 8.07 (s, 8H, ortho-Ar-H); 7.77 (s, 4H, para-Ar-H); 1.50 (m, 72H, Ar-C(CH_3)_3).

**2.3.9 Synthesis of N-confused 5,10,15,20-tetrakis(4-methylphenyl)porphyrin**

Method follows the procedure of Lindsey, Geier and Haynes (1999) [5].
To a solution of pyrrole (1.04 mL, 0.015 mol) and para-tolualdehyde (1.78 mL, 0.015 mol) in dichloromethane (1.5 L) was added methanesulfonic acid (MSA) (0.681 mL, 0.010 mol) to initiate the reaction. The reaction mixture was stirred for 30 min, then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (3.00 g, 0.013 mol) was added and the mixture stirred for a further 1 min. The acid was then quenched by addition of triethylamine (TEA) (5.80 mL, 0.042 mol). Without reduction of solvent volume, the crude reaction mixture was gravity fed through a column containing 300 g (~4.0 x 20 cm) of activity III basic alumina. After the 1.5 L of reaction solvent had eluted, the alumina was rinsed with 1 L of CH$_2$Cl$_2$ containing 1 % TEA. All eluent was collected as a single fraction, which was evaporated to near dryness and then adsorbed onto 15 g of activity III basic alumina. The adsorbed sample was added to the top of a column containing 300 g of activity III basic alumina in 3:1 hexanes/CH$_2$Cl$_2$. The polarity of the eluent was increased from 3:1 to 1:1 to 1:2 hexanes/CH$_2$Cl$_2$ to 100 % CH$_2$Cl$_2$ with 500 mL of each eluent being used. Nitrogen was used to force eluent through the column. Fractions of approximately 50 mL were collected. Tetrakis(4-methylphenyl)porphyrin was eluted first by 3:1 hexanes/CH$_2$Cl$_2$. The N-confused porphyrin then began to slowly elute at 1:2 hexanes/CH$_2$Cl$_2$ and was completely removed by 100 % CH$_2$Cl$_2$. The fractions were analysed by TLC (silica, CH$_2$Cl$_2$ with 1 % MeOH) and pooled. The combined fractions were evaporated to dryness under reduced pressure, resulting in a dark purple powder of NCTTP.
Yield = 882 mg (39 %)

m.p. = >250 °C

$R_f$ (silica, CH$_2$Cl$_2$/1 % MeOH): 0.17

$\lambda_{max}$/nm (CH$_2$Cl$_2$): 439 (Soret), 506, 543, 585, 668, 729 (Q-bands)

$^1$H NMR (300 MHz, CDCl$_3$, 21 °C): $\delta$ 8.95 (d, 1H), 8.90 (d, 1H, pyrrolic $\beta$-H’s closest to confused ring); 8.74 (s, 1H, pyrrolic $\alpha$-H on the confused ring); 8.57 (m, 4H, pyrrolic $\beta$-H’s furthest from the confused ring); 8.12 (d, 8H, ortho-Ar-H); 7.57 (d, 8H, meta-Ar-H); 2.68 (s, 12H, CH$_3$); -2.40 (bs, 2H, inner pyrrolic N-H); -4.96 (s, 1H, inner pyrrolic C-H).

2.3.10 Synthesis of N-confused 5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrin


Figure 2.10: Synthesis of N-confused 5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrin

To a solution of pyrrole (1.04 mL, 0.015 mol) and 3,5-dimethylbenzaldehyde (2.02 mL, 0.015 mol) in dichloromethane (1.5 L) was added methanesulfonic acid (MSA) (0.681 mL, 0.010 mol) to initiate the reaction. The reaction mixture was stirred for 30 min at room temperature, then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (3.00 g, 0.013 mol) was added and the mixture stirred for a further 1 min. The reaction was quenched by the addition of triethylamine (TEA) (5.80 mL, 0.042 mol). Without reduction of solvent volume, the crude reaction mixture
was gravity fed through a column containing 250 g (~4.0 x 17 cm) of activity III basic alumina. After the 1.5 L of reaction solvent had eluted, the alumina was rinsed with 500 mL of CH₂Cl₂. All eluent was collected as a single fraction, which was evaporated to near dryness and then adsorbed onto 15 g of activity III basic alumina. The adsorbed sample was added to the top of a column containing 300 g of activity III basic alumina in 3:1 hexanes/CH₂Cl₂. The polarity of the eluent was increased from 3:1 to 1:1 to 1:2 hexanes/CH₂Cl₂ to 100 % CH₂Cl₂ with 500 mL of each eluent being used. Nitrogen was used to force eluent through the column. Fractions of approximately 50 mL were collected. The regular tetrakis(3,5-dimethylphenyl)porphyrin was eluted first by 3:1 hexanes/CH₂Cl₂. The N-confused porphyrin then began to elute at 1:2 hexanes/CH₂Cl₂ and was completely removed by 100 % CH₂Cl₂. The fractions were analysed by TLC (silica, CH₂Cl₂ with 1% MeOH) and pooled. The combined fractions were evaporated to dryness under reduced pressure, resulting in a very dark green powder of NCTXP.

Yield = 796 mg (29 %)
m.p. = >250 °C

Rⁱ (silica, CH₂Cl₂/1 % MeOH): 0.09

λmax/nm (CH₂Cl₂): 441 (Soret), 507, 541, 583, 728 (Q-bands).

¹H NMR (300 MHz, CDCl₃, 21 °C): δ 8.95 (d, 1H), 8.85 (d, 1H, pyrrolic β-H’s closest to confused ring); 8.75 (s, 1H, pyrrolic α-H on the confused ring); 8.56 (m, 4H, pyrrolic β-H’s furthest from the confused ring); 7.92 (s, 4H, ortho-Ar-H’s adjacent to confused ring);7.75 (s, 4H, ortho-Ar-H’s opposite the confused ring); 7.37 (s, 4H, para-Ar-H); 2.61 (s, 24H, Ar-CH₃); -2.50 (bs, 2H, inner pyrrolic N-H); -5.02 (s, 1H, inner pyrrolic C-H).

2.3.11 Synthesis of N-confused 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin

Method follows the procedure of Shaw et al. (2004) [6].
Figure 2.11: Synthesis of N-confused 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin

To a solution of pyrrole (0.69 mL, 10.0 mmol) and 3,5-di-tert-butylbenzaldehyde (2.183 g, 10.0 mmol) in CH$_2$Cl$_2$ (1 L) was added MSA (0.453 mL, 7.0 mmol) and the reaction was stirred for 30 min at room temperature. DDQ (2.0 g, 8.8 mmol) was added, and the reaction stirred for another 10 min before TEA (4.0 mL) was added to quench the reaction. The crude reaction mixture was passed through a 300 g column of activity III basic alumina to remove DDQ and polypyrrole impurities, and the column flushed with 500 mL of CH$_2$Cl$_2$ containing 1 % TEA. All eluent was collected as a single fraction, which was evaporated to near dryness and then adsorbed onto 15 g of activity III basic alumina. The adsorbed sample was added to the top of a column containing 300 g of activity III basic alumina in 3:1 hexanes/CH$_2$Cl$_2$. The N-confused porphyrin was eluted with a total of 1300 mL of 3:1 hexanes/CH$_2$Cl$_2$. Fractions of ~50 mL were collected and analysed by TLC (silica, CH$_2$Cl$_2$/1 % MeOH). The solvents were removed from the pooled fractions under reduced pressure to give the product as a dark purple solid.

Yield = 637 mg (24 %)

m.p. = >250 °C

$R_f$ (silica, CH$_2$Cl$_2$/1 % MeOH): 0.09

$\lambda_{max}$/nm (CH$_2$Cl$_2$): 441 (Soret), 542, 584, 665, 728 (Q-bands)
**2.3.12 Synthesis of N-confused 2-methyl-5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)-porphyrin**

Method is a modification of Chmielewski and Latos-Grażyński (1995) [7].

![Synthesis of N-confused 2-methyl-5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)-porphyrin](image)

Figure 2.12: Synthesis of N-confused 2-methyl-5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)-porphyrin

The reagents NCTBuPP (1.92 x 10^-4 mol, 204 mg) and CH₃I (7.89 x 10^-2 mol, 4.91 mL) were dissolved in CH₂Cl₂ (100 mL) and the reaction mixture was stirred for 24 hrs at 20 °C in darkness. The solution was taken to dryness to remove solvent and residual CH₃I, then redissolved in a few mL of CH₂Cl₂ and chromatographed on a column packed with alumina with CH₂Cl₂ as the eluent. The first green band to elute was collected, and the product was precipitated by the addition of methanol and reduction of the solvent volume. The precipitate was collected on a porosity 5 sintered glass disk and air dried to give the product as a green powder.
Yield = 153 mg (74 %)

m.p. = >250 °C

$R_f$ (alumina, CH$_2$Cl$_2$): 0.28

$\lambda_{\text{max}}$/nm (CH$_2$Cl$_2$): 449 (Soret), 662, 719 (Q-bands)

$^1$H NMR (300 MHz, CDCl$_3$, 21 °C): $\delta$ 7.38 (d, 1H, pyrrolic $\alpha$-H on the confused ring); 7.79-7.86 (m, 8H, ortho-Ph-H); 7.57 (m, 4H, para-Ph-H); 3.40 (s, 3H, 2N-CH$_3$); 1.45 (m, 72H, C(CH$_3$)$_3$); 3.40 (interior pyrrolic N-H, hidden under 2N-CH$_3$ resonance [7]) and 0.86 (s br, 1H, internal pyrrolic C-H)

2.3.13 Synthesis of N-confused 2-methyl-5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)-porphyrin nickel(II) complex

Method is a modification of Chmielewski and Latos-Grażyński (1995) [7].

The reagent 2-MeNCT$^t$BuPP (125 mg, 1.16 x 10$^{-4}$ mol) was dissolved in 200 mL of CH$_2$Cl$_2$, to which was added 500 mg (2.00 x 10$^{-3}$ mol) of nickel(II) acetate tetrahydrate in 25 mL of MeOH. The reaction mixture was stirred for 1 hr, and the solvent was removed under reduced pressure. The crude mixture was chromatographed on a column packed with alumina in

\[ \text{Ni(OOCCH$_3$)$_2$·4H$_2$O} \]}

Figure 2.13: Synthesis of N-confused 2-methyl-5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)-porphyrin nickel(II) complex

The reagent 2-MeNCT$^t$BuPP (125 mg, 1.16 x 10$^{-4}$ mol) was dissolved in 200 mL of CH$_2$Cl$_2$, to which was added 500 mg (2.00 x 10$^{-3}$ mol) of nickel(II) acetate tetrahydrate in 25 mL of MeOH. The reaction mixture was stirred for 1 hr, and the solvent was removed under reduced pressure. The crude mixture was chromatographed on a column packed with alumina in
CH$_2$Cl$_2$. The first brown band was collected. MeOH (30 mL) was added to the collected fraction, and the product was precipitated by evaporation of the CH$_2$Cl$_2$. The dark purple crystals were collected on a porosity 5 sintered glass disk and dried under suction in air.

Yield = 80 mg (61 %)

m.p. = >250 °C

$R_f$ (alumina, CH$_2$Cl$_2$): 0.95

$\lambda_{\text{max}}$/nm (CH$_2$Cl$_2$): 366, 430 (Soret), 462 (sh), 715, 783 (Q-bands)

$^1$H NMR (300 MHz, CDCl$_3$, 21 °C): $\delta$ 8.07 (d, 1H, pyrrolic $\alpha$-H on the confused ring); 7.65-7.72 (m, 8H, ortho-Ph-H); 7.56-7.61 (m, 4H, para-Ph-H); 3.51 (s, 3H, 2N-CH$_3$); 1.41 (m, 72H, C(CH$_3$)$_3$); absence of interior pyrrolic N-H and C-H resonance indicates successful metalation.

2.3.14 Synthesis of N-confused 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin nickel(II) complex

Method is a modification of Latos-Grazynski et al. (1994) [8]:

![Diagram](image_url)

Figure 2.14: Synthesis of N-confused 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin nickel(II) complex

An amount of 500 mg (4.70 x 10$^{-4}$ mol) of NCT$^t$BuPP was dissolved in 50 mL of chloroform. 1.1184 g (4.70 x 10$^{-3}$ mol) of NiCl$_2$.6H$_2$O was dissolved in 50 mL ethanol. The two solutions
were combined and heated at reflux for 30 mins. The solvent was removed, and the crude product was redissolved in CH$_2$Cl$_2$ and filtered through a porosity 5 sintered glass disc to remove residual NiCl$_2$.6H$_2$O. The crude mixture was then chromatographed on silica and developed with CH$_2$Cl$_2$. The first green band to elute was the desired product, Ni-NCT' BuPP. The solvent was removed under reduced pressure to yield the product as a dark green powder.

Yield = 259 mg (53 %)

m.p. = >250 °C

$R_f$ (silica, hexanes:CH$_2$Cl$_2$ 2:1 v/v): 0.60

$\lambda_{max}$/nm (CH$_2$Cl$_2$): 353, 418 (Soret), 508, 548, 588 (β-band), 707 (α-band)

$^1$H NMR (300 MHz, CDCl$_3$, 21 °C): δ 8.56 (d, 1H, outer C-H on confused pyrrole), 8.09, 8.03, 7.85, 7.80 (d, 1H, pyrrolic β-H’s on pyrrole closest to confused ring); 7.90, 7.93 (d, 1H, pyrrolic β-H’s on pyrrole opposite to confused ring); 7.70 (m, 4H, ortho-Ph-H); 7.64 (m, 4H, ortho-Ph-H); 7.56(m, 4H, para-Ph-H);1.48 (s, 72H, Ar-C(CH$_3$)$_3$)

2.3.15 Synthesis of N-confused 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin$^{2+}$ acid salt

![Synthesis of N-confused 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin$^{2+}$ acid salt](image)

Figure 2.15: Synthesis of N-confused 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin$^{2+}$ acid salt
An amount of 100 mg (9.40 x 10^{-5} mol) of NCTtBuPP was dissolved in 20 mL of CH$_2$Cl$_2$. To this solution was added 20 equivalents of trifluoroacetic acid (TFA, 140 μL, 1.88 x 10^{-3} mol). The solution was stirred for 10 minutes in air, covered in foil to exclude light. The solution was then evaporated to dryness under reduced pressure to remove the solvent and excess TFA. The product was washed with a large volume of distilled water, filtered and air dried to yield the product as a dark green powder.

Yield = quantitative

m.p. = >250 °C

λ$_{max}$/nm (CH$_2$Cl$_2$): 474 (Soret), 669, 835 (Q-bands)

2.3.16 Synthesis of 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin$^{2+}$ acid salt

100 mg (9.40 x 10^{-5} mol) of TtBuPP was dissolved in 20 mL of CH$_2$Cl$_2$. To this solution was added 20 equivalents of trifluoroacetic acid (TFA, 140 μL, 1.88 x 10^{-3} mol). The solution was stirred for 10 minutes in air, covered in foil to exclude light. The solution was then evaporated to dryness under reduced pressure to remove the solvent and excess TFA. The product was washed with a large volume of distilled water, filtered and air dried to yield the product as a bright green powder.
Yield = quantitative
m.p. = >250 °C

\( \lambda_{\text{max}}/\text{nm (CH}_2\text{Cl}_2): 447 \) (Soret), 668 (Q-band)

2.4 Device fabrication

2.4.1 General device architecture

A typical organic solar cell consists of a thin film (100 nm) of photoactive material sandwiched between two electrodes of differing workfunction. The devices investigated in this project are built onto a glass substrate in layers. The glass slides were purchased pre-coated with a ~140 nm thick film of ITO, a conducting yet transparent material that forms the anode of the device (Figure 2.17a). The ITO slides were then etched to form the pattern of finger/electrodes shown below (Figure 2.17b). Patterning allows six separate devices to be made on each slide. PEDOT-PSS was then deposited by spin-coating from solution to form a thin film (~50 nm) on top of the ITO. PEDOT-PSS smooths the surface of the ITO, functions as a hole transporter and exciton and electron blocker and helps prevent short circuits in the device. The active layer, consisting of polymer, PCBM and porphyrin was then deposited by spin-coating from solution (Figure 2.17c). A small area of active layer was then removed from the lower edge of the slide, exposing the bottom electrode (Figure 2.17d). Calcium (20 nm) and aluminium (100 nm), which formed the cathode, was then evaporated onto the central region of the slide (Figure 2.17e). The calcium/aluminium contacted the bottom electrode, completing the circuit. The resulting device architecture has six electrically insulated ITO fingers acting as six separate anodes, and therefore six separate solar cells on each slide, with a common calcium/aluminium cathode. Spin-coating of the active layer and all subsequent fabrication steps were performed in a glove box in a nitrogen atmosphere, to prevent device degradation by water and oxygen.
Figure 2.17: Fabrication of an organic solar cell

Each device was then tested by measuring its current-voltage (IV) characteristic and spectral response, as described below.

2.4.2 Etching ITO

In-house patterning of ITO slides were undertaken as follows. The ITO slides ($R_s = 8-12 \, \Omega$, purchased from Delta Technologies Limited) were first cleaned thoroughly with acetone, dried with lint-free tissue, and blown with nitrogen to remove any dust. A uniform layer of photoresist was then sprayed onto the ITO surface, and the slides baked in darkness on a hotplate at 50 °C for 20 minutes to dry the photoresist. Once dry, a mask was aligned with each slide, and the photoresist was exposed to UV light for 18 minutes. The pattern was clearly visible at this point, with exposed regions of photoresist changing colour from green to brown. Slides were then developed in a 0.3 M solution of NaOH to remove the exposed areas of photoresist. After rinsing with water, the slides were etched by soaking in a 9 M HCl solution until the exposed ITO was removed. The remaining photoresist mask was removed with acetone to uncover the ITO pattern below. Slides were tested with a multimeter to ensure each finger/electrode was electrically isolated, before being scored with a glasscutter and snapped into individual substrates.
Commercial pre-patterned ITO slides were also utilised.

2.4.3 Cleaning substrates

Each substrate was thoroughly cleaned before use. Only analytical grade solvents were used. After cutting to size, slides were sonicated for 10 minutes with acetone in a Unisonsics FXP10M ultrasonic bath to remove residual cutting oil. Slides were then dried with lint-free tissues, and sonicated in a water-detergent solution for 10 minutes at 40 °C in the ultrasonic bath. Next, the slides were rinsed repeatedly, first with boiling water, followed by distilled water, until all detergent was removed. The final steps were 10 minute sonication with hexanes, acetone and then isopropyl alcohol in the ultrasonic bath. The substrates were stored in the IPA solution until required.

2.4.4 Solution preparation

The materials forming the active layer of the device were spin-coated from solution using a Laurell WS-400A-6NPP/LITE spin coater. Each solution was prepared in a 1 mL vial, to a concentration of 40 g L\(^{-1}\) material/solvent for MEH-PPV-based devices, or 24 g L\(^{-1}\) for P3HT-based devices. The solvents chosen were chlorobenzene for MEH-PPV-based solutions or chloroform for P3HT-based solutions. MEH-PPV/PCBM devices were prepared with a weight ratio of 1:4 (i.e. 8 mg of MEH-PPV and 32 mg of PCBM dissolved in 1 mL of chlorobenzene) unless otherwise stated. MEH-PPV/porphyrin/PCBM solutions were normally prepared with a weight ratio of 1:1:8, unless otherwise stated. P3HT/PCBM devices were prepared with a weight ratio of 1:1, and ternary P3HT blends in various ratios as stated in the text. Each solution was placed into an ultrasonic bath for between 30 mins and 90 mins to completely dissolve each component and to obtain a homogeneous solution. Where variations to the usual procedures have been made (due to solubility limitations, for example), these are clearly stated in the appropriate sections of this thesis.
2.4.5 Spin coating

Uniform thin films were deposited onto the glass/ITO substrate by spin-coating with a Laurell WS-400A-6NPP/LITE spin coater (Figure 2.18). Spin-coating involved securing the substrate onto the chuck of the spin-coater, using a vacuum system to hold it in place. A few drops of solution were then placed onto the slide, and then spun at a fixed velocity for 60 seconds to obtain a thin film. The final thickness of the film was varied as required by altering the viscosity of solution (i.e. increasing concentration), changing the rate of acceleration, or altering the velocity (spin-speed) of the instrument. The latter was found to be the most convenient method, and therefore most commonly employed.

Figure 2.18: Laurell WS-400A-6NPP/LITE spin coater

PEDOT:PSS was spun at 3000 rpm for 60 seconds, resulting in a film thickness of approximately 50 nm. Substrates were then heated on a hotplate under nitrogen at 120 °C for 10 mins to drive off residual water. The substrates were cooled, and the active layer solution was spun usually at 1500 rpm for 60 seconds under nitrogen, although spin-speeds as low as 1000 rpm and as high as 5000 rpm were also used, to achieve an active layer thickness of 100 ± 10 nm.
2.4.6  Film thickness measurement

The thickness of the spin-coated films was determined using a KLA Tencor Alpha-step 500 surface profilometer (Figure 2.19). After spin-coating a test film onto glass, a scratch was made across the slide, and the profilometer used to determine the depth profile of the scratch by passing the profilometer tip across the surface of the film. The thickness of the film could be calculated by measuring the distance between the surface of the film and the glass exposed by the scratch.

![Figure 2.19: KLA Tencor Alpha-step 500 surface profilometer](image)

2.4.7  Ca/Al evaporation

After deposition, the film of active layer covering the common bottom ITO electrode was exposed (see Figure 2.17d above), so that the calcium/aluminium layer would contact the ITO beneath it. The slides were then mounted into a sample holder, and aligned so that only the central area of each slide could be seen through the mask. The sample holder was then
introduced into a vacuum chamber (Figure 2.20), and the chamber evacuated to a pressure of $10^{-7}$ mbar. Calcium and aluminium slugs sat in separate crucibles within the chamber. The crucibles were wrapped with tungsten wire, so that when a large current (~10 A) was passed through the wire, the crucible heated the metal slugs to boiling point. When the slug started to vapourise, the sample holder was moved into the line of sight of the crucible, and a thin layer of calcium, followed by aluminium, was deposited onto the non-masked areas of the slide, as indicated in Figure 2.17e above. The rate of deposition was monitored by a quartz crystal microbalance. Evaporation was continued until a calcium thickness of 20 nm was achieved, followed by an aluminium thickness of 100 nm. This formed the cathode of the device.

![Figure 2.20: Inside the vacuum chamber, showing crucibles used for the evaporation of metal slugs. Samples to be coated are positioned on the inside ceiling of the chamber (not visible in photograph) during the plating procedure](image)

### 2.4.8 Cleanroom Facility

Construction of a cleanroom facility within the Centre for Organic Electronics at the University of Newcastle was completed in April 2008, and the air quality certified to Class 1000 Standard (<1000 particles per cubic foot of air). The clean room facility enabled for the first time at Newcastle University the fabrication of devices under controlled atmospheric conditions,
minimising the damage that can occur to cells due to dust and other debris present during device fabrication.

2.5 Device testing and characterisation

There are two main techniques used to characterise an organic solar cell. The first is the current-voltage (I-V) characteristic, which provides data that can be used to calculate the power conversion efficiency of the device, and other key parameters. The second is the spectral response, which provides details of the amount of photocurrent generated for each wavelength of light incident on the device.

2.5.1 I-V characteristic

The current-voltage characteristic can be measured by applying a voltage to the device, and measuring the current that is produced under illumination by a light source simulating the solar spectrum. The main parameters measured from the I-V characteristic are the short circuit current \(I_{SC}\) and open circuit voltage \(V_{OC}\), which can be used to calculate the fill factor \(FF\) and power conversion efficiency (PCE) of the device. With reference to Figure 2.21 they are defined as follows:

![Figure 2.21: Typical IV curve of an organic solar cell](image)

**Figure 2.21: Typical IV curve of an organic solar cell**
Open-circuit voltage ($V_{oc}$) is the voltage across the device when under open circuit conditions (i.e. when no current is flowing).

Short-circuit current ($I_{sc}$) is the current produced by the device when it is short circuited (when there is no voltage across the device).

Fill-factor ($FF$) is the ratio of the maximum power output of the device ($I\cdot V_{max}$) to the product of $V_{oc}$ and $I_{sc}$, and is defined as:

$$FF = \frac{(I\cdot V)_{\text{MAX}}}{V_{oc} \cdot I_{sc}}$$

Power conversion efficiency (PCE) is the ratio of the output electrical power to the incident optical power, and is defined as:

$$PCE = \frac{FF \cdot V_{oc} \cdot I_{sc}}{L}$$

where $V_{oc}$ is in volts, $I_{sc}$ is in mA/cm$^2$ and $L$ is the incident optical power density in mW/cm$^2$.

The IV characteristics of all devices were measured under AM1.5 conditions using a Newport Solar Simulator, and recorded using a Keithley 2400 source meter unit controlled by National Instruments LabVIEW software. The light intensity was measured with a calibrated silicon photodiode, and was typically equivalent to 1.00 ± 0.05 sun.

All device efficiency data (efficiency, open-circuit voltage, short circuit current, current density and fill factor) was reported as the average of at least 6 individual devices, with the error reported as the value ± standard deviation. Averaging of results is important to account for any slight changes in device area due to the Ca/Al mask alignment during the electrode evaporation step, which may otherwise lead to an over- or underrepresentation of device efficiency and also variations arising from the fabrication process. A control device (standard MEH-PPV:PCBM 1:4) was also fabricated with every batch to ensure that fabrication conditions were consistent and to avoid confounding variables.
The spectral response provides an accurate measurement of the amount of current generated by the device for each wavelength of incident light. It provides important information about the photovoltaic properties of the active materials used to manufacture the device. We also calculate the external quantum efficiency, or EQE, of the device. The EQE is the ratio of the number of electrons collected at the solar cell electrodes to the number of incident photons reaching the device. It is calculated by determining the number of electrons collected through measurement of the photocurrent generated by the device, and determining the number of incident photons at each wavelength by measuring the incident irradiance on the device. By comparing the spectral response and EQE graph to a UV-visible spectrum, one can determine how much of the light absorbed by the device material is actually converted into photocurrent.

External quantum efficiency measurements were recorded by exposing the devices to light from a tungsten halogen lamp passed through an Oriel Cornerstone 130 monochromator, using an Ithaco Dynatrac 395 analogue lock-in amplifier and Thorlabs PDA55 silicon diode to
collect the reference signal (irradiance), and a Stanford Research Systems SR830 DSP digitising
lock-in amplifier to measure device current.

![Equipment for measuring the external quantum efficiency of organic solar cells](image)

**Figure 2.23: Equipment for measuring the external quantum efficiency of organic solar cells**

### 2.6 Computational modelling

Geometry optimisations were performed on all compounds using density functional theory
(DFT) with the Becke-3-Lee-Yang-Parr (B3LYP) functional and 6-31G(d) basis set on all atoms.
No symmetry constraints were imposed on any of the structures. Vibrational energies of the
calculated structures were evaluated to ensure an energy minimised geometry. Ionisation
potentials and electron affinities were determined by taking the absolute energy difference
between calculations of the neutral state geometry and the same structure with a +1 and -1
charge respectively. Single point energies were determined with the ‘very tight’ convergence
criteria. All calculations were carried out using the Gaussian 03W computational package [9].

M-T'BuPP calculations were undertaken on porphyrinoids with the computationally less
demanding phenyl group at the meso position, rather than the T'Bu substituted derivatives,
since we have shown that these groups are electronically identical [10]. M-OEP calculations were undertaken on porphyrins with the computationally less demanding methyl group at the beta position, rather than the ethyl substituted derivatives. All computational modelling was performed by Samuel Lind at the University of Otago, New Zealand, under the direction of Professor Keith Gordon. All data analysis was performed by Nathan Cooling at the University of Newcastle.

2.7 Optical microscopy

Optical microscopy of device films was recorded with a Zeiss Axioplan2 microscope, illuminated by a tungsten lamp. Images were captured with an Olympus DP70 CCD camera and converted to jpeg format using Olympus DP Controller version 2.1.1.183 software. Films were spin coated onto glass from the chlorobenzene solutions prepared as above, to achieve a film thickness of approximately 125 nm.

Figure 2.24: Zeiss Axioplan2 microscope
2.8 Atomic force microscopy

AFM images were captured with an Asylum Research Cypher scanning probe microscope (Figure 2.25), operating in AC mode in air, using an AC160TS AFM probe with a tip radius of <10 nm.

![Asylum Research Cypher scanning probe microscope](image)

*Figure 2.25: Asylum Research Cypher scanning probe microscope*

2.9 Scanning transmission X-ray microscopy

Films were prepared by spin-coating onto a thin (~20 nm) film of PEDOT:PSS on glass. The films were then floated off the substrate into deionised water by dissolving the underlying PEDOT:PSS layer, then picked up onto copper TEM grids for analysis. STXM measurements were performed at the Advanced Light Source on Beamline 5.3.2. The STXM has a demonstrated ability to resolve 30 nm features [11]. The sample is mounted with the X-ray beam at normal incidence and the sample is rastered with respect to the beam to form an image at any specific beam energy. The sample chamber is backfilled with 0.33 atm of helium gas and is isolated from the synchrotron ring and beamline optics via a silicon nitride window. The transmitted X-ray beam is detected by a scintillator and a photomultiplier tube. The energy of the X-ray beam was varied between 270 and 340 eV which covered the carbon K-
shell to molecular orbital transitions. Compositional maps were derived from images collected at energies that maximized the X-ray intensity contrast between the two components. Singular value decomposition was then used to fit a linear combination of the normalized blend component spectra to the spectrum of the blend films at each pixel. The resulting coefficients are the masses of the blend components present at each pixel. The STXM experimental procedure and data analysis using the Axis2000 package was performed as previously described [12, 13]. The STXM images were collected by Kerry Burke from the University of Newcastle, from samples prepared by Nathan Cooling.

2.10 Experimental determination of bandgap and HOMO-LUMO energies

The bandgap and highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the materials were determined experimentally via cyclic voltammetry of porphyrin solutions and UV-vis spectroscopy of porphyrin films [14]. The HOMO was determined from the first oxidation onset potential. The bandgap was determined optically from the onset of absorption of the porphyrin Soret band, and these values in combination were used to determine the absolute value of the LUMO energy.

![Graphs showing first oxidation onset potential and absorption onset for porphyrin](image)

Figure 2.26: Example of first oxidation onset potential of a porphyrin (left), and the onset of optical absorption of the porphyrin Soret band (right), used for the experimental determination of bandgap and HOMO-LUMO energies
2.11 Cyclic voltammetry

The HOMO levels of the porphyrins were determined experimentally via cyclic voltammetry, using the approach outlined in previous publications [14, 15] as a starting point for experimentation. All experiments employed a Pt disk working electrode (A = 0.0314 cm²), Pt-coil counter electrode, and a home-made Ag/Ag⁺ reference electrode. The electrolyte contained the porphyrinoid chromophore (1 mM) and tetrabutylammonium hexafluorophosphate (TBAPF₆; 0.1 M) in dichloromethane solvent dried over molecular sieves and purged with nitrogen gas. The Pt disk was polished with a 0.05 μm alumina slurry on a polishing pad, washed thoroughly with de-ionised water, and dried with lint-free paper between each experiment. The Ag/Ag⁺ RE was constructed as follows: a ~7 cm length of Ag wire (Sigma-Aldrich, 99.999 %, Φ = 1 mm) was polished with a fine-grade garnet paper, before being inserted into Luggin capillary tube, which housed the RE and the internal electrolyte. Electrolyte (0.01 M AgNO₃ + 0.1 M TBAPF₆ in dry CH₂CN) was filled to a 3-4 cm depth, and the open end sealed with Teflon tape. The 1-2 cm of external Ag wire acted as the RE contact. Experiments were performed using an Autolab PGSTAT12 potentiostat at 50 mV s⁻¹ between 1.0 and -1.8 V vs. Ag/Ag⁺, starting from the solution open-circuit potential with the initial sweep in the anodic direction. After the voltammetry regime was complete, a mass of ferrocene corresponding to the amount required to make the electrolyte around 1 mM, was added to the porphyrin solution and stirred to dissolve the solid. The cyclic voltammetry regime was then repeated for one more cycle, and the voltages corrected using the experimentally-determined standard reduction potential of the reversible Fc/Fc⁺ couple, defined as the average potential of the cathodic (E_{pc}) and anodic (E_{pa}) peaks. All voltages are reported against this internal standard, following published methods [15]. Uncompensated resistance was corrected for using a typical value for a 0.1 M TBAPF₆ solution in CH₂Cl₂ of 2.5 kΩ[16]. Due to the low currents observed as a result of both small WE area and low concentration of electroactive species, this correction was typically in the order of ~4 mV. The
determined onset voltage vs. the Fc/Fc+ couple was converted to a normal hydrogen electrode (NHE) scale by adding 630 mV [15], from which the energy can be converted from the electrochemical potential scale to an absolute energy vs. vacuum with:

\[ E_{\text{HOMO}} = -(V_{\text{on}} + 4.5) \]

where \( E_{\text{HOMO}} \) is energy of the HOMO in the absolute energy level scale, \( V_{\text{on}} \) is the voltage (vs. NHE) at which the faradaic current onsets, and 4.5 is a conversion constant between electrochemical potential vs. NHE and vacuum scales. Figure 2.27 provides a visual summary of these calculations.

![Diagram of energy levels and bandgap calculation](image)

**Figure 2.27: Calculation of porphyrinoid energy levels and bandgap using CV and UV-vis**

Cyclic voltammetry was collected at the University of Newcastle and the CSIRO Energy Centre, Mayfield NSW, with the assistance of Dr Tim Jones of the CSIRO.

### 2.12 Statistics

Basic statistical analysis was performed on recorded data to determine whether observed trends were statistically significant. Statistical analysis of scatter plots was performed by applying the multiple correlation coefficient \( (R^2) \) to linear trend lines fitted to the data point.
The multiple correlation coefficient generalises the standard coefficient of correlation, and assesses the quality of the prediction of the independent variable [17]. It provides a measure of the proportion of the variability of the dependent variable (y) by its relationship with the independent variable (x). The maximum $R^2$ value of 1 indicates a perfect correlation, while the minimum value of 0 indicates no correlation [18].

Error analysis of device parameters was performed by calculating the standard deviation (σ) of the sample population of at least 6 devices. Standard deviation is a measure of how much variation exists from the average value, with low standard deviation indicating values close to the mean, and a large standard deviation indicating values spread out over a large range. Results are typically presented as the mean value ± σ.

### 2.13 References


16. Bond, A. M., Oldham, K. B., and Snook, G. A., Use of the ferrocene oxidation process to provide both reference electrode potential calibration and a simple measurement (via


3.1 Introduction

Over the four years of this project, there has been a series of improvements to both the manufacturing techniques and fabrication facilities at the University of Newcastle Centre for Organic Electronics, which resulted in systematic improvements in the efficiency of the organic photovoltaic devices. While many experiments were repeated towards the end of the project in order to show the maximum attainable efficiency of the devices under optimal conditions, some older device data is included in this thesis. Although the reported efficiency of the standard device (MEH-PPV:PCBM 1:4 by weight) and ternary blends may appear to be inconsistent between different experiments, the results within a reported experiment have in all cases been performed under exactly the same conditions, and should not necessarily be compared to device efficiency data obtained at a different time. In most cases, an increase in the efficiency of a standard (binary) device resulted in a near linear increase in the efficiency of the ternary device as well. This improvement is shown to be most directly due to enhancement of the current density of the device, achieved through gradual improvements to the device fabrication procedure, and the purchase of higher quality polymer as it became available over the course of the study.

3.2 Improvements to device efficiency

A table of the standard MEH-PPV:PCBM 1:4 device efficiency data and corresponding date/event is shown below. All 2008-2010 device data is presented as the average of at least 6 devices. The error measurements are the standard deviation of each set of devices. Data from 2007 is presented as the highest attained value to date rather than an average, because of the
high rate of device failure. Typically only 1 in 6 cells was a functioning device, due to limitations of the manufacturing and testing facilities (for example, the lack of an inert atmosphere for device fabrication) during that time, as will be discussed below.

Table 3.1: Standard MEH-PPV:PCBM 1:4 device efficiency data and corresponding date/event. 2008-2010 data is presented as an average of at least 6 devices. 2007 data is presented as the highest observed value. Error measurements are the standard deviation of averaged devices

<table>
<thead>
<tr>
<th>Date</th>
<th>Efficiency / %</th>
<th>$V_{oc}$ / mV</th>
<th>$J_{sc}$ / mA cm$^{-2}$</th>
<th>FF</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>06/02/2007</td>
<td>0.299</td>
<td>800</td>
<td>1.025</td>
<td>0.292</td>
<td>first devices</td>
</tr>
<tr>
<td>25/07/2007</td>
<td>0.410</td>
<td>740</td>
<td>1.271</td>
<td>0.347</td>
<td>best device by end of honours project</td>
</tr>
<tr>
<td>17/04/2008</td>
<td>0.464 ±0.091</td>
<td>780 ±0</td>
<td>0.382 ±0.233</td>
<td>0.343 ±0.011</td>
<td>new glove box in clean room, inert fabrication atmosphere</td>
</tr>
<tr>
<td>17/07/2008</td>
<td>0.534 ±0.063</td>
<td>680 ±41</td>
<td>2.320 ±0.090</td>
<td>0.337 ±0.013</td>
<td>new batch of PEDOT, re-optimised PEDOT thickness</td>
</tr>
<tr>
<td>24/07/2008</td>
<td>0.783 ±0.070</td>
<td>735 ±10</td>
<td>3.066 ±0.202</td>
<td>0.347 ±0.011</td>
<td>changed from ADS to Sigma-Aldrich polymer</td>
</tr>
<tr>
<td>09/12/2009</td>
<td>1.015 ±0.086</td>
<td>703 ±10</td>
<td>3.857 ±0.260</td>
<td>0.374 ±0.011</td>
<td>changed to Jenpolymer MEH-PPV, much better quality</td>
</tr>
<tr>
<td>06/05/2010</td>
<td>1.290 ±0.110</td>
<td>779 ±13</td>
<td>5.352 ±0.490</td>
<td>0.310 ±0.010</td>
<td>new evaporator allows both Ca and Al to be deposited</td>
</tr>
<tr>
<td>07/06/2010</td>
<td>1.772 ±0.053</td>
<td>831 ±6</td>
<td>5.340 ±0.303</td>
<td>0.400 ±0.014</td>
<td>New Jenpolymer batch 2</td>
</tr>
</tbody>
</table>

The first devices were made in February 2007 and reached an efficiency of 0.30 %. Spin-coating of the PEDOT:PSS and active layer (MEH-PPV:PCBM 1:4) occurred in air, and the aluminium evaporation was performed in a vacuum chamber that vented to air. As a result of moisture in the air being drawn into the evaporator as it was opened, the chamber typically took a number
of hours to reach a low enough pressure for Al evaporation. During this process the device was in contact with both water and oxygen, which is known to degrade the solar cell significantly [1-6]. Degradation mechanisms include the absorption of water from the air into the hygroscopic PEDOT:PSS layer, which results in increased resistance at the PEDOT:PSS/active layer interface [1], and the formation of a charge-blocking layer at the organic/metal electrode interface when the device is exposed to both oxygen and water in the air [2]. After evaporation, device parameters such as efficiency and spectral response were also measured in air, and therefore devices typically lasted less than 12 hours before they were no longer responsive due to degradation. However, through careful device preparation such as thorough cleaning of the substrate, optimisation of the thickness of the PEDOT:PSS and active layers, and rapid testing upon completion of device fabrication, by July 2007 the efficiency of a standard device had risen to 0.41 %. Figure 3.1 illustrates the increase in device efficiency for the period 2007-2010.

![Figure 3.1: Standard device efficiency for the period 2007-2010](image)
In early 2008, construction of the Newcastle University and Australian Research Council (ARC) funded Nanostructure Deposition Facility at the Centre for Organic Electronics at the University of Newcastle was completed and the cleanroom was certified to Class 1000 standard (<1000 particles per cubic foot). Spin-coating of the active layer was then performed within a glovebox in the cleanroom, under a dry and inert nitrogen atmosphere that typically achieved a dew point of -45 °C, corresponding to a relative humidity of <1 %, and with an oxygen content of <2 ppm. Device fabrication in a glovebox resulted in an improvement in device efficiency to just over 0.46 %. With both the fabrication and testing of the devices now performed in an inert atmosphere, the devices lasted much longer before significant degradation occurred (>24 hours), and so a larger number of devices could be made in each batch, leading to more consistent and reproducible results, and a greater number of repeat devices for the purpose of statistical averaging of results.

In mid-2008, a fresh batch of Baytron PEDOT:PSS suspension was purchased to replace the old batch which was by this stage over 12 months old and showing visible signs of particle aggregation/degradation. Fresh PEDOT:PSS resulted in an improvement of device efficiency to 0.53 %. However, the largest increases in device performance occurred through the sourcing and purchase of higher quality polymer.

By the end of July 2008, a new batch of Sigma-Aldrich MEH-PPV was being used that enabled the efficiency of the standard device to rise to 0.78 %. This new polymer dissolved more rapidly into the solvent (chlorobenzene) and also produced smoother films with fewer defects than the American Dye Source (ADS) MEH-PPV that had been used until this point. The increase in solubility was most likely due to a reduction in the weight average molecular weight of the polymer, down from 374000 g mol$^{-1}$ (Product ADS100RE, Lot No. 06E042M) for the ADS material to 150000-250000 g mol$^{-1}$ (Product 536512, Lot No. 05208LI) for the Sigma-Aldrich material. The polydispersity index PDI of the ADS polymer was very high at 10.4,
indicating that a large proportion of the material would actually be significantly higher in molecular weight than the stated average of 374000 g mol\(^{-1}\). The PDI of the Sigma-Aldrich polymer was not provided in the certificate of analysis.

At the end of 2009, the MEH-PPV supplier was again changed to Jenpolymer Materials in Germany (JP). Jenpolymer produces high quality MEH-PPV for organic photovoltaic devices, and the efficiency of devices made using this material rose above 1.0 % for the first time. The weight average molecular weight for this material (JP1) was 10500 g mol\(^{-1}\) (Product JPM 018-04, Lot No. 07082008). While studies of the effect of MEH-PPV molecular weight on device efficiency have not been published, it will be shown in Section 3.4 that this is close to the optimal molecular weight for MEH-PPV:PCBM 1:4 devices. The polydispersity index was also low at 2.8, indicating that the distribution of molecular weight within the polymer sample was much more uniform than the polymer sourced from ADS, which appeared to result in higher quality films with less visible surface defects.

In early 2010, a new glovebox and metal electrode deposition chamber (evaporator) was commissioned, which enabled the deposition of a thin layer of calcium (20 nm) immediately prior to the aluminium deposition. The Ca/Al electrode system has been shown to improve the fill factor and open-circuit voltage with respect to an aluminium cathode [7]. The improvement is achieved through enhanced carrier collection by lowering the work function of the electrode, and reduced electrode degradation when compared with an Al electrode [8]. With fresh catalyst in the glovebox recirculator, an oxygen level of 2 ppm and atmospheric moisture content of 1 ppm was achieved inside the glovebox and evaporator, providing favourable conditions for solar cell fabrication and electrode evaporation. It was also decided to anneal the PEDOT:PSS coated substrates in this dry atmosphere for 10 minutes at 120 °C to drive off excess water, which has been shown to improve devices by increasing conductivity of the film [9]. It is important to perform this step in a dry atmosphere because air-annealed films begin
to re-absorb moisture from the atmosphere as the substrate cools to below 50 °C [9], which subsequently decreases conductivity [10]. The combination of these improvements enabled a 30 % increase in device efficiency to almost 1.3 %.

Finally, in July 2010, the latest batch of Jenpolymer MEH-PPV became available (JP2), with a weight average molecular weight of 16000 g mol\(^{-1}\) and a PDI of 1.88. This batch produced the highest quality devices that, along with the improvements stated above, reached an efficiency of 1.7 %.

The improvements observed during the period 2007-2010 do not appear to correlate directly with improvements in either the open-circuit voltage (\(V_{OC}\)) or fill factor (FF), which can be seen from Table 3.1 to display no apparent trend with increasing device efficiency, although it may be noted that the most efficient device has the highest \(V_{OC}\) and FF.

Figure 3.2: IV plots of standard MEH-PPV:PCBM 1:4 devices over the period 2007-2010
While $V_{OC}$ in all instances is within the range of 0.70-0.83 V, the current increases almost 7 fold over the 3 ½ year period (Figure 3.2). The current density correlates well with the efficiency of the devices, with a coefficient of determination $R^2$ value of 0.92 (Figure 3.3).

![Figure 3.3: Plot of device efficiency vs. current density of standard MEH-PPV:PCBM 1:4 devices over the period 2007-2010](image)

The increase in current density observed over time suggests that the primary mechanism of device improvement is improved active layer morphology, as opposed to say an interface or recombination effect [11-13], which may otherwise have been concluded had the $V_{OC}$ varied significantly. Such behaviour is consistent with the improved polymer quality obtained from suppliers during the thesis period. Enhanced current density is also likely to be the result of improved fabrication conditions due to device preparation and testing under dry and inert conditions, as discussed below.
3.3 Improvements to device characterisation consistency and reproducibility

As mentioned above, there have been a series of procedural and equipment developments that have led to much improved device efficiency over the four years of this project. The consistency and reproducibility of the device characterisation data has also improved, as observed by a clear trend toward lower relative error over time (Figure 3.4). These improvements will now be explored in greater detail.

![Graph](image)

**Figure 3.4**: Standard deviation as a percentage of device efficiency for standard MEH-PPV:PCBM 1:4 devices over the period 2008-2010.

3.3.1 Fabrication atmosphere

Over the course of the project, device manufacture has progressed from fabrication in air, to fabrication in a glovebox with a nitrogen atmosphere and moisture content of <1 %, and further to the complete fabrication and metal electrode deposition within a glovebox under nitrogen and with a moisture and oxygen content of <1 ppm and <2 ppm, respectively. Also, device testing moved from air into a glovebox under dry nitrogen with an oxygen content of
approximately <2 ppm. Not only did the commissioning of these inert atmosphere gloveboxes lead to enhanced device efficiency as discussed above, the reproducibility of device testing improved considerably, because the devices were no longer subjected to the large variation in atmospheric moisture content experienced in a regular laboratory environment.

![Device fabrication glovebox](image)

**Figure 3.5: Device fabrication glovebox**

### 3.3.2 Baking PEDOT:PSS layer under nitrogen

Initially the PEDOT:PSS hole blocking layer was spin-coated and then heated in air for 10 minutes at 120 °C, to dry the film. However, due to the hydroscopic nature of PEDOT:PSS, the film reabsorbs moisture from the air [9]. This results in a decrease in conductivity [10] which reduces the amount of charge reaching the electrodes and lowers device efficiency. (The moisture content of the film is therefore dictated by the relative humidity in the laboratory at the time of spin-coating.) When fabrication of the PEDOT:PSS layer is performed under the dry nitrogen atmosphere of the glovebox, reabsorption of water is minimal, and since the rest of the fabrication and testing procedure occurred under an inert atmosphere the devices remained water free, leading to higher efficiency devices and more reproducible results.
3.3.3 Certified Cleanroom

Commissioning of a certified Class 1000 standard cleanroom facility in April 2008 enabled for the first time at Newcastle University the fabrication of devices under controlled atmospheric conditions. Dust particles and other unwanted debris present during fabrication introduce defect sites into device thin films, which we have observed to lower device efficiency due to short circuits and loss of photoactive surface area. It is also important to avoid dust and particles when handling the devices during fabrication and testing, as debris can abrade the device leading to irreversible damage. As part of the cleanroom procedure, users are required to wear a cleanroom suit consisting of coveralls, boots, gloves and a hood. There is also a positive pressure differential between the cleanroom, the dressing room, and the outside laboratory, so that dust adhered to the suit or equipment entering the room is continually blown away from the work area by the positive pressure in the cleanroom.

Figure 3.6 Cleanroom fabrication and testing facility
3.3.4 AM1.5 solar simulator device testing

Shortly after the cleanroom was completed in 2008, an AM1.5 solar simulator was acquired to characterise our devices. A solar simulator is a standardised light source that allows devices to be tested under identical conditions to all other research groups adhering to this standard. The xenon lamp is fitted to a AM1.5G filter that complies with ASTM E 927-05 as a Class A product, and provides confidence that our light source has a similar spectrum as sunlight at AM1.5 conditions, and is directly comparable to the results published by other research groups using a solar simulator with the same certification. We also ensured that the light intensity was equivalent to 1 sun by measuring the light output of the filtered xenon lamp using a calibrated standard silicon solar cell before each set of solar cells was tested. Prior to this we had been using unfiltered light which, while of a similar intensity to 1 sun, had a mismatched solar spectrum which had to be corrected for. Unless otherwise stated, all solar cell results in this thesis have been performed using a certified AM1.5 solar simulator to ensure consistency and reproducibility of results.

3.3.5 Evaporator masking

Initially, substrates for aluminium deposition were loaded into a cell holder and the masks that patterned the electrode during deposition were manually aligned. Aligning the mask perfectly with the ITO substrate beneath was problematic as it was often (especially with thinner films) quite difficult to see exactly where the almost transparent ITO fingers were positioned beneath the mask. The result was often misaligned electrodes where in the most extreme circumstance the device area might vary by up to 50 %. This problem was overcome by the commissioning of a new cell holder with fine tolerance CNC machined recesses for the substrates to be secured into, and a mask which could be identically positioned each time and fixed into place by screws. In combination with the purchase of commercially cut and etched pre-patterned ITO substrates of uniform dimensions, it was possible to ensure that the Ca/Al
electrode was thermally deposited into the correct position each time, and therefore the solar cells in each batch were of consistent cell area, making device efficiency calculation more accurate and reproducible between batches of devices.

![Device mask used to set the position of the Al electrode onto the solar cells](image)

**Figure 3.8: Device mask used to set the position of the Al electrode onto the solar cells**

### 3.3.6 Cleaning/exposing the solar cell ITO electrodes

The final development which led to better consistency and reproducibility was the method by which the electrodes were cleaned prior to device testing. Cleaning is an important step, because unless the outer 2-3 mm of the spin-coated PEDOT:PSS and active layer film is physically removed from the edge of the electrodes before testing, the contacts between the electrodes and the testing rig will be poor and little or no current will be able to be measured from the device. Initially, we had a cell holder with a built-in knife edge, which scraped clean the electrodes as the device was loaded into the testing holder. The knife edge was unreliable, and did not always clean the electrode thoroughly. The next method was to scrape clean the edge of the electrodes using a scalpel. Scraping was much more effective, but it was difficult to
handle the blade precisely and safely through the bulky glovebox gauntlets. Finally, it was decided to clean the electrodes using a cotton bud and appropriate solvent. This procedure works well, resulting in good electrical contacts.

3.4 The effect of polymer molecular weight on the performance of MEH-PPV:PCBM organic photovoltaic devices

There does not exist in the literature any studies on the effect of MEH-PPV molecular weight on the performance of MEH-PPV:PCBM solar cells. There are however studies using a similar polymer:fullerene system, poly(3-hexylthiophene) (P3HT):PCBM.

The molecular weight distribution of a polymer sample is typically stated as either number average molecular weight ($M_n$) or weight average molecular weight ($M_w$), referring to the arithmetic means of the number or weight distributions of all of the polymer chains in a sample [14]. In a sample of polymer, the polymer distribution is such that there will be an equal number of polymer chains either side of $M_n$, and an equal weight of polymer chains either side of $M_w$.

Schilinsky [15] found that P3HT with an $M_n$ of >10000 g mol$^{-1}$ was necessary to produce high efficiency P3HT:PCBM devices. Lower $M_n$ P3HT samples had distinctly reduced charge carrier (hole) mobility due to reduced intermolecular ordering of the P3HT phase, resulting in poorly performing devices. Ballantyne [16] also noted a molecular weight dependence, and suggested that the optimum $M_n$ of P3HT was between 13000 – 34000 g mol$^{-1}$. Both electron and hole mobilities were observed to decrease with increasing $M_n$, with a corresponding decrease in solar cell performance. They hypothesised that the observed change in surface morphology with increasing $M_n$ was due to tangling of polymer chains and associated twisting of the polymer backbone, decreasing intra-chain transport and inter-chain charge hopping.
We examined the effect of polymer molecular weight on device performance by fabricating a series of MEH-PPV:PCBM 1:4 (by weight) solar cells, using a variety of MEH-PPV polymer batches varying in $M_w$ between 10000 and 600000 g mol$^{-1}$. Device efficiency data for this series is presented in Table 3.2.

**Table 3.2:** Device efficiency data for standard MEH-PPV:PCBM 1:4 solar cells where polymer batches vary in molecular weight. Data is presented as an average of at least 6 devices, with error measurements calculated from the standard deviation of averaged devices.

<table>
<thead>
<tr>
<th>$M_w$ of polymer</th>
<th>Efficiency / %</th>
<th>$V_{oc}$ / mV</th>
<th>$J_{sc}$ / mA cm$^{-2}$</th>
<th>FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>10K</td>
<td>1.211 ±0.050</td>
<td>826 ±5</td>
<td>3.754 ±0.100</td>
<td>0.391 ±0.005</td>
</tr>
<tr>
<td>16K</td>
<td>1.796 ±0.085</td>
<td>838 ±5</td>
<td>5.058 ±0.261</td>
<td>0.424 ±0.002</td>
</tr>
<tr>
<td>40-70K</td>
<td>1.316 ±0.041</td>
<td>834 ±7</td>
<td>3.882 ±0.089</td>
<td>0.406 ±0.002</td>
</tr>
<tr>
<td>150-250K</td>
<td>1.142 ±0.055</td>
<td>799 ±7</td>
<td>3.900 ±0.114</td>
<td>0.366 ±0.005</td>
</tr>
<tr>
<td>374K</td>
<td>1.070 ±0.086</td>
<td>844 ±3</td>
<td>3.365 ±0.270</td>
<td>0.377 ±0.003</td>
</tr>
<tr>
<td>600K</td>
<td>0.720 ±0.040</td>
<td>818 ±14</td>
<td>2.870 ±0.094</td>
<td>0.306 ±0.007</td>
</tr>
</tbody>
</table>

A strong correlation between the molecular weight of the MEH-PPV polymer and the efficiency of our devices was observed, as seen in Figure 3.9 below. The highest efficiency of an MEH-PPV:PCBM 1:4 by weight device was produced using MEH-PPV with a weight average molecular weight of 160000 g mol$^{-1}$. Efficiency then decreased as the polymer weight was increased or decreased from this value. Improved efficiency at this molecular weight is likely due to a combination of film quality, conductivity/mobility, and solubility of polymer.
Figure 3.9: The effect of molecular weight on the efficiency of MEH-PPV:PCBM organic solar cells.

The molecular weight of the polymer has little effect on the open-circuit voltage of the devices (Table 3.2). This observation was to be expected, as the maximum \( V_{OC} \) is determined by the energy gap between the lowest unoccupied molecular orbital (LUMO) of the acceptor material (in this case PCBM) and the highest occupied molecular orbital (HOMO) of the donor material (MEH-PPV polymer) [17]. The monomer structure does not change as molecular weight is varied, nor does the \( \pi \)-orbital overlap and effective conjugation length vary once a chain length of between eleven [18] and twenty [19, 20] monomers is reached, so energy levels should remain effectively constant as molecular weight of the polymer is varied over a wide range.

The parameter that most influences device efficiency is clearly the short-circuit current of the solar cell (Figure 3.10). The current generation ability in organic bulk-heterojunction photovoltaic devices is affected by a number of factors, all of which can be influenced by the molecular weight of the polymer. Film morphology can be significantly influenced by polymer
weight [21]. The size of domains within the heterojunction structure is well known to be influenced by molecular weight [22, 23], which then has an effect on charge transport within the device. From the results stated in this chapter we can conclude (within the limitations of the range of MEH-PPV available to us) that the combination of optimised device morphology, domain size, interfacial area available for exciton dissociation, and charge transport to the electrodes, all occurs optimally with polymer with a molecular weight of around 16000 g mol$^{-1}$. External quantum efficiency (EQE) measurements (discussed later) also support this conclusion.

![Graph](image)

Figure 3.10: Plot of device efficiency vs. current density of MEH-PPV:PCBM 1:4 devices where the polymer varies in molecular weight

Fill factor (Table 3.2) also roughly follows device efficiency but the effect is less pronounced. This is perhaps unsurprising considering that improved fill factor should be expected in higher efficiency devices due to increased series resistance and decreased shunt resistance, which enables the device to reach a fuller potential given the ultimate electrical limitations dictated by the $V_{OC}$ and $J_{SC}$ of a particular device.
There is some variation in the UV-vis absorption spectra of device active layer films (Figure 3.11) of similar thickness. The MEH-PPV absorption band centred around 500 nm is generally enhanced relative to the PCBM shoulder at 350 nm in the lower molecular weight polymer films. This observation may reflect greater structure or purity within the MEH-PPV domains, as can be seen for example in high efficiency P3HT:PCBM devices after annealing [24-26], suggesting polymer chain alignment which has been known to improve charge transport within polymer/fullerene solar cells [27]. The lower intensity MEH-PPV absorption peaks will also be a reflection of the lower solubility of higher molecular weight polymers. If the MEH-PPV:PCBM 1:4 blend is not properly dissolved before spin-coating, aggregates of undissolved material deposit on and within the film, disrupting the morphology considerably through the formation of short-circuits or areas of reduced photocurrent activity. The ideal polymer:fullerene ratio of 1:4 by weight [28] would also be shifted to a greater percentage of PCBM within the bulk of
the film if such polymer aggregates were excluded from the blend. Indeed, the disruption of film morphology can be seen at optical resolution as shown in Figure 3.12 below.

![Figure 3.12](image)

**Figure 3.12: Optical microscopy of MEH-PPV:PCBM 1:4 device films where the molecular weight of the polymer is: (a) 40-70K, (b) 290K, and (c) 374K g mol$^{-1}$. Materials were dissolved in chlorobenzene with the assistance of an ultrasonic bath for 30 minutes before deposition. Note the increased presence of aggregates in the films of devices made with polymer of higher weight average molecular weight. The white scale bar represents 0.5 mm**

Figure 3.13 shows that devices fabricated with higher molecular weight MEH-PPV display EQE plots that have reduced polymer contribution (centred around 500 nm) to the current generated by the device. Fullerene contribution also appears to diminish to a lesser extent. This observation suggests that excitons generated within MEH-PPV domains are more successfully dissociated into free charge carriers, and that these charge carriers have appropriate percolation pathways to the electrode materials, in devices utilising lower molecular weight polymer. Unfavourable blend morphology due to aggregation of poorly dissolved polymer creates regions of low polymer concentration in the bulk of the film leading to poor charge transport, as holes can only be transported through polymer-only pathways [29]. The absorption coefficient for PCBM in the visible region is almost negligible [30], so loss of polymer concentration in the bulk of the film also leads directly to a loss of polymer photocurrent generation through lower light absorption. Finally, since the photo-generated current is governed not only by the number of photo-generated charge carriers but also the carrier mobility [29], any loss of polymer concentration, considering that the hole mobility of
donor-type PPV derivatives is already much lower than electron mobility of PCBM [31], may enhance detrimental space-charge effects that are inherent in the bulk-heterojunction structure due to imbalanced electron and hole mobility [32].

Figure 3.13: The effect of molecular weight on the external quantum efficiency spectra of MEH-PPV:PCBM organic solar cells

3.5 Ternary device efficiencies scale linearly with improved standard device efficiency

The factors leading to improved device function in binary MEH-PPV:PCBM 1:4 devices have been discussed above. However, much of this thesis looks at ternary devices, which have the addition of a third component (a porphyrinoid species) to the blend. The addition of a third component can significantly complicate the device structure and photovoltaic performance, and it is therefore important to determine that any observed change in device function from binary compared with ternary blends occurs as a result of the added porphyrinoid itself, and is not confused with other factors, such as an improvement in polymer performance or fabrication conditions, as discussed above. The following graphs are a small selection of
control ternary devices that were repeated at intervals over the period 2007-2010, and show that ternary devices, as with binary devices, also scale linearly with improved fabrication and materials over time.

This observation reinforces the fact that whilst some more recent device data presented in this thesis may appear to be in conflict with older data, trends within device data are relevant and can be compared. While reported device parameters such as power conversion efficiency, open-circuit voltage and short-circuit current density should not be quantitatively compared to other experiments, the general trends observed may be compared, as will be demonstrated below. Table 3.3 details the fabrication conditions for each set of data.


<table>
<thead>
<tr>
<th>Date</th>
<th>Efficiency / %</th>
<th>Polymer Supplier</th>
<th>M.W.</th>
<th>Fabrication Atmosphere</th>
<th>Anode</th>
</tr>
</thead>
<tbody>
<tr>
<td>2007</td>
<td>0.471</td>
<td>American Dye Source</td>
<td>374K</td>
<td>air</td>
<td>Al</td>
</tr>
<tr>
<td>2008</td>
<td>0.783</td>
<td>Sigma-Aldrich</td>
<td>150-250K</td>
<td>inert nitrogen</td>
<td>Al</td>
</tr>
<tr>
<td>2010</td>
<td>1.796</td>
<td>Jenpolymer</td>
<td>16K</td>
<td>inert nitrogen</td>
<td>Ca + Al</td>
</tr>
</tbody>
</table>

Figure 3.14 illustrates the efficiency of a standard MEH-PPV:PCBM 1:4 device and a selection of MEH-PPV:porphyrin:PCBM 1:1:8 devices that have been studied during the course of this project. It clearly shows that despite the significant changes to polymer quality, molecular weight, electrode material, and fabrication and testing conditions, ternary devices continue to display the same trend in efficiency and other parameters relative to each other. An explanation of the difference in performance for each porphyrin is the core subject of this thesis, and will be discussed in detail in the following chapters.
Figure 3.14: Power conversion efficiency of standard MEH-PPV:PCBM 1:4 by weight and ternary blended MEH-PPV:porphyrin:PCBM 1:1:8 by weight devices over the period 2007-2010. Data from 2008 and 2010 is presented as an average of at least 6 devices. 2007 data is presented as the highest observed value. Error bars are calculated from the standard deviation of averaged devices. Cu-T^1BuPP = tetrakis(3,5-di-tert-butylphenyl)porphyrin copper(II) complex; T^1BuPP = tetrakis(3,5-di-tert-butylphenyl)porphyrin; TTP = tetratolylporphyrin; NCT^1BuPP = N-confused tetrakis(3,5-di-tert-butylphenyl)porphyrin; and NCTTP = N-confused tetratolylporphyrin

Similar trends are observed for other device parameters such as open-circuit voltage and short-circuit current density (Figures 3.15 and 3.16).
Figure 3.19: Open-circuit voltage of ternary blended MEH-PPV:Porphyrin:PCBM 1:1:8 by weight devices over the period 2007-2010. Data from 2008 and 2010 is presented as an average of at least 6 devices. 2007 data is presented as the highest observed value. Error bars are calculated from the standard deviation of averaged devices.

Figure 3.20: Short-circuit current density of ternary blended MEH-PPV:Porphyrin:PCBM 1:1:8 by weight devices over the period 2007-2010. Data from 2008 and 2010 is presented as an average of at least 6 devices. 2007 data is presented as the highest observed value. Error bars are calculated from the standard deviation of averaged devices.
3.6 Conclusions

Multiple factors affect the performance of organic thin-film solar cells. During the course of this PhD, incremental improvements have been made which ultimately have resulted in significant overall improvements in device performance. Device manufacturing conditions and device testing results have been well documented and have illustrated a steady improvement of the standard MEH-PPV:PCBM 1:4 bulk heterojunction organic solar cells over the course of the project (4 years). Furthermore, the factors leading to the improvements have been identified, and a thorough error analysis performed. We show that a similar trend is observed in the device parameter results for ternary MEH-PPV:porphyrin:PCBM devices as with a standard polymer/fullerene binary device. Therefore, while multiple efficiencies of the standard binary device are reported throughout this thesis, the comparison to the ternary devices in each set of reported data remains valid, and we can be confident that the trends in ternary blend data are due to the inclusion of the porphyrin and its interaction with the other materials, rather than other factors related to polymer quality or variations in experimental procedure.

3.7 References


9. Huang, J., Miller, P. F., Wilson, J. S., de Mello, A. J., de Mello, J. C., and Bradley, D. D. C., *Investigation of the effects of doping and post-deposition treatments on the conductivity, morphology, and work function of poly(3,4-


Chapter 4 - The effect of porphyrin steric bulk on the performance of ternary MEH-PPV:porphyrin:PCBM organic solar cells

The content of this chapter was published in March 2011:


4.1 Introduction

During this study a series of freebase tetraphenylporphyrins were synthesised and introduced into the active layer of MEH-PPV:PCBM photovoltaic devices in an effort to understand how the structure of the porphyrin, in particular the steric bulk, might affect device performance. Previous work by our group [1] has shown that the porphyrin [2,3,12,13-tetracyano-5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrinato] copper(II) can be successfully incorporated into MEH-PPV:PCBM organic solar cells to achieve an enhancement of the spectral response of the device, without substantially affecting overall device performance. However, other work has shown that varying the device components can result in a significant reduction in device efficiency [2], which has been attributed to aggregation of the porphyrin component within the blend [3]. It was hypothesised that this aggregation resulted in the disruption of the favourable bulk heterojunction morphology of the device, thus decreasing overall device efficiency. Porphyrin self-aggregation is commonly observed in both solution and in the solid-state [4-6] due to the planarity and polarisability of the porphyrin molecules [5]. This effect has been shown to decrease the efficiency of organic dye-sensitised solar cells [7] and it has been suggested that porphyrin aggregation may result in a shortening of
photoexcited-state lifetimes due to chromophore self-quenching [5]. It has also been reported that both freebase and metallloporphyrins can strongly interact and aggregate with fullerenes, due to the attraction of the curved π surface of a fullerene to the centre of the flat π surface of a porphyrin [8, 9]. It is clear that all of these interactions may lead to disruption of the optimum bulk heterojunction morphology required for efficient device performance.

The study presented here was therefore predicated by the hypothesis that control of porphyrin aggregation within the ternary blend could be achieved by the attachment of bulky functional groups to the periphery of the porphyrin macrocycle, preserving favourable active layer morphology and therefore allowing charge separation and charge transport within the device to be maintained, whilst extending the spectral response of the device.

4.2 Porphyrins used in this study

It has been previously shown that porphyrin aggregation can to some degree be controlled by the placement of sterically hindered peripheral groups on the porphyrin [5, 6, 10]. To this end a series of substituted tetra-aryl porphyrins:

(a) 5,10,15,20-tetrakis(4-methylphenyl)porphyrin (TTP, tetratolylporphyrin)

(b) 5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrin (TXP, tetraxylylporphyrin), and

(c) 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin (TtBuPP)

were prepared where the meta substituent on the aryl functionality was sequentially:

(a) hydrogen

(b) methyl, and

(c) tert-butyl

The structures of the porphyrins used in this study are illustrated in Figure 4.1. These porphyrins were then incorporated into MEH-PPV:PCBM based organic solar cells.
Figure 4.1: Chemical structures of (A) TTP, (B) TXP and (C) TtBuPP

These porphyrins vary most significantly in the steric bulk of substituents present at the meta position on the meso-phenyl groups of the porphyrin ring. Increasing the steric bulk of groups in these positions has been shown to result in a decrease of the aggregation of these porphyrins in both solution and the solid state [10]. Optical microscopy images as presented in Figure 4.2 (a-c) show that this reduced aggregation is clearly evident for thin films spin-coated from chlorobenzene for the three pure porphyrins TTP, TXP and TtBuPP, and follows the increasing steric bulk of the peripheral groups.

For the 1:1:8 by weight MEH-PPV:porphyrin:PCBM ternary blend films (Figure 4.2 (d-f)), where the porphyrin constitutes only 10 wt % of the total film, each film appears to be uniformly blended at the resolution of the optical microscopy images, and lack any visible signs of a change in the degree of aggregation between porphyrins. This observation suggests that while pure porphyrin films can display significant aggregation effects, the smoother ternary blended films should be well-suited as active layers in organic photovoltaic devices as disruption of the film morphology, at least at this scale, appears to be minimal.
Figure 4.2: Optical microscopy images of pure porphyrin and 1:1:8 by weight MEH-PPV:Porphyrin:PCBM ternary blend films, spin-coated from chlorobenzene: (A) TTP, (B) TXP, (C) T^BuPP, (D) MEH-PPV:TTP:PCBM, (E) MEH-PPV:TXP:PCBM and (F) MEH-PPV:T^BuPP:PCBM. The white scale bars indicate 1 mm on the sample. The visible scratch marks have been used to determine film thickness via profilometry.

4.3 Quantification of porphyrin steric bulk

The relative magnitude of steric bulk can be quantified by either the Taft steric parameters, $E_s$ [11, 12], or by the Charton van der Waals radii, $r_v$ [13-16], for each of the substituents present at the meta position on the meso phenyl groups of the porphyrin ring. Quantification is necessary because it allows us to develop a quantitative structure-activity relationship between the steric bulk of the porphyrin and photovoltaic device performance.

The Taft equation [17], published in 1952 as a modification of the Hammett equation [18], is a linear free energy relationship relating reaction rates and equilibrium constants for the reactivity of ortho-monosubstituted benzoate and aliphatic esters toward esterification and hydrolysis.
The Taft equation can be written as:

$$\log \frac{k_s}{k_{CH3}} = \rho^* \sigma^* + \delta E_s$$  \hspace{1cm} (4.2)

where $\log(k_s/k_{CH3})$ is the ratio of the rate of the substituted reaction compared to the reference reaction (where $R = CH_3$), $\sigma^*$ is the polar substituent constant that describes the polar (i.e. field and induction) effects of the substituent, $E_s$ is the steric substituent constant that reflects the steric influence of substituents on various reactions, $\rho^*$ is the sensitivity factor for the reaction to polar effects, and $\delta$ is the sensitivity factor for the reaction to steric effects [19]. The Taft equation expands on the Hammett equation in that it also describes the steric effects of a substituent, by use of the steric substituent constants, $E_s$:

$$E_s = \frac{1}{\delta} log \left( \frac{k_s}{k_{CH3}} \right)$$  \hspace{1cm} (4.3)

where $k_s$ is the rate of the studied reaction, $k_{CH3}$ is the rate of the reference reaction (where $R = methyl$), and $\delta$ is a proportionality constant that gives a measure of the susceptibility of a reaction series to substituent effects [20]. In general, $E_s$ decreases as steric bulk increases. These parameters are given in Table 4.1.

Charton [13] later defined a steric parameter that was independent of kinetic data, based upon the van der Waals radii of the substituent group. He used a modified Taft equation to correlate the Charton van der Waals radii to the rate constants of various esterification reactions, and the close correlation led to the proposal that the rates of acid-catalysed esterification reactions are solely a function of steric effects. These parameters are also provided in Table 4.1.
Table 4.1: Taft parameters [11] and Charton van der Waals radii [13] for the substituents at the *meta* positions on the *meso*-phenyl groups of the porphyrins.

<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>Substituent</th>
<th>$E_s$ – Steric Taft parameter</th>
<th>$r_v$ - Charton van der Waals radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTP</td>
<td>– H</td>
<td>0</td>
<td>1.20</td>
</tr>
<tr>
<td>TXP</td>
<td>– CH$_3$</td>
<td>-1.24</td>
<td>1.72</td>
</tr>
<tr>
<td>T$^3$BuPP</td>
<td>– C(CH$_3$)$_3$</td>
<td>-2.78</td>
<td>2.44</td>
</tr>
</tbody>
</table>

As can be seen from both of these sets of values, the steric bulk at the *meta* position on the *meso*-phenyl groups for these porphyrins increases in the order H < Me < \textsuperscript{t}Bu. While both the Taft steric substituent constant and the Charton van der Waals radii are useful in describing these free-energy relationships, the Charton van der Waals radii are likely more relevant in describing the quantitative structure-activity relationship between porphyrin steric bulk and OPV device performance as they are independent of kinetic data and focus solely on functional group spatial volume. They will therefore be the parameter chosen for the discussion below.

4.4 MEH-PPV:porphyrin:PCBM 1:1:8 devices

The porphyrins were introduced into the active layer of these devices to give a blend materials ratio of MEH-PPV:porphyrin:PCBM 1:1:8 by weight, a composition consistent with previous work by our group with porphyrin containing ternary blend devices which effectively equates to the replacement of one half of the polymer component within the device by porphyrin [1].

Figure 4.3(a) shows the UV-vis absorbance spectrum for the three porphyrins in dichloromethane solution. The UV-vis spectrum exhibits the characteristic strong optical absorbances from the Soret band at 420 nm and the Q bands at 520, 555, 595, and 650 nm. It is clear that the absorption spectra of each compound is almost identical, which is unsurprising since the modification of the *meta*-substituents on the *meso*-phenyl peripheral rings with alkyl
groups does not disrupt the electronic nature of the aromatic 18-π electron core of the porphyrin, which is the chromophore primarily responsible for light absorption.

Figure 4.3: (a) UV-vis absorbance spectrum for porphyrins in dichloromethane solution. The inset shows an enlarged view of the 475 – 675 nm wavelength region highlighting peaks in the absorbance spectra arising from photon absorption of the porphyrin Q bands. (b) External quantum efficiency (EQE) as a function of wavelength for MEH-PPV:PCBM 1:4 by weight standard device and MEH-PPV:porphyrin:PCBM 1:1:8 by weight ternary blend devices. The inset shows an enlarged view of the 550 – 700 nm wavelength region highlighting peaks in the EQE spectra arising from photon absorption of the porphyrin Q bands.
Figure 4.3(b) shows external quantum efficiency as a function of wavelength for each of the MEH-PPV:Porphyrin:PCBM 1:1:8 ternary blend devices, compared with a standard MEH-PPV:PCBM 1:4 binary device. It is clear from this graph that while the absorption spectra for each porphyrin are essentially identical, they have a distinct effect on the amount of current generated within the device at each wavelength. There is some loss of polymer contribution at lower wavelengths as indicated by a reduction in the total EQE in the region 375-550 nm, but each porphyrin clearly contributes to the device photocurrent generation as can be seen by the similarity between the UV-vis and EQE spectra in both graphs of Figure 4.3.

A comparison of the UV-vis absorption spectra and EQE for MEH-PPV:TtBuPP:PCBM ternary blend is shown in Figure 4.4.

Figure 4.4: UV-vis absorbance (solid line) and external quantum efficiency (dotted line) as a function of wavelength for the MEH-PPV:TtBuPP:PCBM ternary blend device. The inset shows an enlarged view of the 600 – 750 nm wavelength region highlighting peaks in the EQE spectra arising from photon absorption of the porphyrin Q bands.

The UV-vis spectrum clearly shows contributions from the Soret and Q bands of the porphyrin superimposed on the absorption due to the polymer (which is characterised by the broad absorption band up to approximately 550 – 600 nm) and that due to the PCBM (which is
characterised by an increasing absorption background at low wavelength). However, compared with the UV-vis absorption spectra for the porphyrin in solution, the ternary blend spectrum reveals that the Soret and Q bands are shifted to longer wavelengths (the Soret band, for example, has shifted from 420 nm in solution to 440 nm in the blend film) and broadened consistent with enhanced porphyrin-porphyrin interactions such as aggregation or interaction of the porphyrins with the blend medium [21]. Figure 4.4 also shows the external quantum efficiency (EQE) of the ternary blend device as a function of wavelength. The photocurrent output peaks in the EQE spectrum clearly match the positions of the Soret and Q band absorptions of the porphyrin molecule. The inset of Figure 4.4 highlights the fact that even at high wavelengths the Q-band UV-vis absorption and EQE of the ternary blend are closely correlated to one another. This data clearly demonstrates that the T' BuPP porphyrin is actively involved in photocurrent generation and, although the relative contributions are different, is consistent with previous published observations for other porphyrins [1]. Other ternary blends containing TTP and TXP exhibit similarly correlated behaviour, as shown in Figure 4.3(b).

The typical current density-voltage (I-V) characteristics for a MEH-PPV:PCBM 1:4 by weight binary device and MEH-PPV:porphyrin:PCBM 1:1:8 by weight ternary devices are shown Figure 4.5. It can be seen that while the short-circuit current density ($J_{SC}$) and open-circuit voltage ($V_{OC}$) of the ternary blend devices are lower than that of the standard MEH-PPV:PCBM device, the $V_{OC}$ and $J_{SC}$ increase systematically as the steric bulk of the porphyrin is increased. The dark current I-V characteristics are also shown, and indicate that there is negligible leakage current present in the ternary blend devices.
Figure 4.5: Current density-voltage (I-V) characteristics for a MEH-PPV:PCBM 1:4 binary device and MEH-PPV:Porphyrin:PCBM 1:1:8 by weight devices (equimass porphyrin) with varying steric bulk of the substituent in the *meta* positions (solid lines). Also shown are the dark current J-V characteristics for each binary/ternary blend (dashed lines).

It is conventional within the OPV research community to report blended materials as donor:acceptor ratio by mass. However, this can lead to misinterpretation in systems with multiple light-absorbing materials as it does not provide any direct indication of the relative number of chromophore sites within the active layer. In the case of the three porphyrins presented in this study, the mass of the porphyrin varies by up to 40 %, which translates into a significant variation in the relative number of chromophores in each blended film. This variation can appear to exaggerate the magnitude of the effect of lower mass porphyrins on the device, through increased chromophore density. Using the MEH-PPV:TtBuPP:PCBM device as a reference, a series of ternary devices were fabricated in which the number of moles of porphyrin was kept constant in each blend, so as to eliminate the effect of changing the percentage of chromophores within each device. The result was a set of devices in which the total number of moles of polymer, porphyrin and fullerene were kept constant, leading to weight ratios in the series MEH-PPV:TTP:PCBM, MEH-PPV:TXP:PCBM and MEH-
PPV:TtBuPP:PCBM of approximately 1:0.6:8, 1:0.7:8 and 1:1:8, respectively, which corresponds to a molar ratio (MEH-PPV monomer:porphyrin:PCBM) of approximately 4:1:9.

Figure 4.6: Current density-voltage (I-V) characteristics for a MEH-PPV:PCBM 1:4 binary device and MEH-PPV:TTP:PCBM, MEH-PPV:TXP:PCBM, MEH-PPV:TtBuPP:PCBM devices with corresponding (equimolar porphyrin) weight ratios of approximately 1:0.6:8, 1:0.7:8 and 1:1:8 (solid lines). Also shown are the dark current I-V characteristics for each binary/ternary blend (dashed lines).

The equimolar current density-voltage (I-V) characteristics of these devices are shown in Figure 4.6. This graph reveals that while the systematic change in $J_{SC}$ observed in the equimass devices in Figure 4.5 is almost completely removed, the $V_{OC}$ of the equimolar and equimass devices remain almost unchanged. As such, while the $J_{SC}$ of these ternary blend devices is heavily dependent on the number of porphyrin chromophores in each blend, the $V_{OC}$ is determined by the structure of the porphyrin as it remains relatively unchanged as porphyrin density within the active layer is altered.
Table 4.2: Device characteristics for a MEH-PPV:PCBM 1:4 binary device and MEH-PPV:porphyrin:PCBM 1:1:8 by weight devices (equimass) and MEH-PPV:TTP:PCBM, MEH-PPV:TXP:PCBM, MEH-PPV:T^BuPP:PCBM devices with corresponding weight ratios of approximately 1:0.6:8, 1:0.7:8 and 1:1:8 (equimolar). The errors have been calculated from the standard deviation across eight independent OPV devices. The zero error values simply indicate an absolute error of less than 0.01.

<table>
<thead>
<tr>
<th>Equimass Device</th>
<th>$V_{oc}$/V</th>
<th>$J_{sc}$/mA/cm$^2$</th>
<th>FF</th>
<th>$R_{sh}$/kΩ</th>
<th>$\eta$/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEH-PPV:PCBM</td>
<td>0.83 ±0.01</td>
<td>5.34 ±0.28</td>
<td>0.40 ±0.01</td>
<td>6.84</td>
<td>1.77 ±0.05</td>
</tr>
<tr>
<td>MEH-PPV:TTP:PCBM</td>
<td>0.45 ±0.02</td>
<td>1.97 ±0.10</td>
<td>0.31 ±0.00</td>
<td>7.11</td>
<td>0.27 ±0.00</td>
</tr>
<tr>
<td>MEH-PPV:TXP:PCBM</td>
<td>0.58 ±0.02</td>
<td>2.64 ±0.13</td>
<td>0.32 ±0.00</td>
<td>6.36</td>
<td>0.48 ±0.00</td>
</tr>
<tr>
<td>MEH-PPV:T^BuPP:PCBM</td>
<td>0.64 ±0.01</td>
<td>3.90 ±0.30</td>
<td>0.33 ±0.01</td>
<td>6.10</td>
<td>0.83 ±0.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Equimolar Device</th>
<th>$V_{oc}$/V</th>
<th>$J_{sc}$/mA/cm$^2$</th>
<th>FF</th>
<th>$R_{sh}$/kΩ</th>
<th>$\eta$/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEH-PPV:PCBM</td>
<td>0.83 ±0.01</td>
<td>5.34 ±0.28</td>
<td>0.40 ±0.01</td>
<td>6.84</td>
<td>1.77 ±0.05</td>
</tr>
<tr>
<td>MEH-PPV:TTP:PCBM</td>
<td>0.50 ±0.01</td>
<td>3.22 ±0.21</td>
<td>0.31 ±0.00</td>
<td>4.83</td>
<td>0.51 ±0.00</td>
</tr>
<tr>
<td>MEH-PPV:TXP:PCBM</td>
<td>0.59 ±0.01</td>
<td>3.68 ±0.18</td>
<td>0.33 ±0.00</td>
<td>5.79</td>
<td>0.70 ±0.00</td>
</tr>
<tr>
<td>MEH-PPV:T^BuPP:PCBM</td>
<td>0.64 ±0.01</td>
<td>3.90 ±0.30</td>
<td>0.33 ±0.01</td>
<td>6.10</td>
<td>0.83 ±0.00</td>
</tr>
</tbody>
</table>

Table 2 and Figure 4.7 illustrate that while the efficiency of all the ternary MEH-PPV:porphyrin:PCBM devices are lower than that of the standard MEH-PPV:PCBM device, the efficiency of the ternary blends systematically increases with increasing steric bulk of the porphyrin species. The reduced efficiency of the blends cannot be explained by the reduction in polymer alone, as earlier work on ternary blend devices has shown that even with half of the polymer component removed from MEH-PPV:PCBM 1:4 devices, performance and efficiency can be similar to that of a standard device, and furthermore, the porphyrin can contribute significantly to primary charge separation [1]. As the $J_{sc}$ and fill factor of the equimolar devices
are essentially invariant within the error of measurement (Table 4.2), it is hypothesised that the increase in device efficiency is due to an increase in the $V_{OC}$ with increased steric bulk of the porphyrin species (Figure 4.8).

**Figure 4.7: Power conversion efficiency of a MEH-PPV:PCBM 1:4 binary device and MEH-PPV:porphyrin:PCBM 1:1:8 by weight devices (equimass = blue) and MEH-PPV:TTP:PCBM, MEH-PPV:TXP:PCBM, MEH-PPV:TtBuPP:PCBM devices with corresponding weight ratios of approximately 1:0.6:8, 1:0.7:8 and 1:1:8 (equimolar = red).**

**Figure 4.8: Open-circuit voltage of a MEH-PPV:PCBM 1:4 binary device and MEH-PPV:porphyrin:PCBM 1:1:8 by weight devices (equimass = blue) and MEH-PPV:TTP:PCBM, MEH-PPV:TXP:PCBM, MEH-PPV:TtBuPP:PCBM devices with corresponding weight ratios of approximately 1:0.6:8, 1:0.7:8 and 1:1:8 (equimolar = red).**
There are a number of possible explanations which may account for the observed behaviour in these devices. Firstly, variations in the electronic nature of the porphyrin could account for the observed differences in $V_{OC}$. Secondly, morphological differences such as pinholes or aggregates could cause short-circuit pathways in the device, or addition of porphyrin could cause changes in domain size that could affect charge transport through the device. These will now be explored in more detail.

If the porphyrin was the dominant charge generating species, and each different porphyrin had significantly different electronic structure, then the change in $V_{OC}$ might be explained by the difference in the energy offset between the porphyrin donors HOMO and the fullerene acceptors LUMO. However, the porphyrin is clearly not the dominant contributor to charge generation in these devices, as is clear from a visual comparison of the contribution of the relative peaks of the polymer, porphyrin, and fullerene in the EQE (Figure 4.3(b)), which is consistent with earlier work [1]. The striking similarity of the TTP, TXP and T$^5$BuPP UV-vis absorption spectra presented in Figure 4.3(a) would also suggest that there is practically no difference in electronic structure between the porphyrins. To confirm this, the bandgap of each porphyrin was determined experimentally by analysis of the UV-vis absorption spectra of solid-state films and, combining this measurement with cyclic voltammetry, the HOMO and LUMO energies were calculated. Density functional theory (DFT) calculations were also performed for each structure, and it was found that both theoretically and experimentally derived values were in good agreement with reported values [22] and that the HOMO and LUMO energies of the porphyrins (Table 4.3) differ by less than ±0.02 eV by each method. This finding confirms that variation of the alkyl functionality at the meta-position of the meso-phenyl groups does not significantly change the electronic structure of the porphyrin core.
Table 4.3: Calculated ionisation potentials (IP), electron affinities (EA), highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and bandgap for TTP, TXP and T\(^\text{BuPP}\). The percentage differences are given relative to TTP and a zero value signifies a difference of less than 0.1%. The model values were calculated using the B3LYP/6-31G(d) DFT method. Also shown are the experimental values derived from cyclic voltammetry and UV-vis measurements.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>TTP</th>
<th>% Difference</th>
<th>TXP</th>
<th>% Difference</th>
<th>T(^\text{BuPP})</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy (cm(^{-1}))</td>
<td>47104</td>
<td>0.0</td>
<td>47252</td>
<td>0.3</td>
<td>46706</td>
<td>0.8</td>
</tr>
<tr>
<td>Energy (cm(^{-1}))</td>
<td>8159</td>
<td>0.0</td>
<td>7880</td>
<td>3.4</td>
<td>7773</td>
<td>4.7</td>
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</tbody>
</table>

**Calculated Values**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>TTP</th>
<th>% Difference</th>
<th>TXP</th>
<th>% Difference</th>
<th>T(^\text{BuPP})</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LUMO (eV)</td>
<td>-2.11</td>
<td>0.0</td>
<td>-2.07</td>
<td>1.4</td>
<td>-2.06</td>
<td>1.9</td>
</tr>
<tr>
<td>HOMO (eV)</td>
<td>-4.80</td>
<td>0.0</td>
<td>-4.77</td>
<td>0.6</td>
<td>-4.76</td>
<td>0.8</td>
</tr>
<tr>
<td>Bandgap (eV)</td>
<td>2.69</td>
<td>0.0</td>
<td>2.70</td>
<td>0.0</td>
<td>2.70</td>
<td>0.0</td>
</tr>
</tbody>
</table>

**Experimental Values**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>TTP</th>
<th>% Difference</th>
<th>TXP</th>
<th>% Difference</th>
<th>T(^\text{BuPP})</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LUMO (eV)</td>
<td>-1.81</td>
<td>0.0</td>
<td>-1.84</td>
<td>1.7</td>
<td>-1.82</td>
<td>0.6</td>
</tr>
<tr>
<td>HOMO (eV)</td>
<td>-4.69</td>
<td>0.0</td>
<td>-4.72</td>
<td>0.6</td>
<td>-4.71</td>
<td>0.4</td>
</tr>
<tr>
<td>Bandgap (eV)</td>
<td>2.88</td>
<td>0.0</td>
<td>2.88</td>
<td>0.0</td>
<td>2.89</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Morphological anomalies caused by the inclusion of porphyrins to the device could also have an effect on the observed $V_{\text{oc}}$ reduction by the introduction of short-circuit pathways due to the presence of aggregates, pinholes, or other defects, as some porphyrinic species have been known to influence heterojunction morphology [3] and co-crystallise with PCBM [8, 9]. However, atomic force microscopy of the binary and ternary film surface (Figure 4.8) do not reveal any significant change to the surface roughness or continuity of the ternary blend films.
Figure 4.8: Representative 2.5 micron x 2.5 micron square atomic force micrographs of (A) MEH-PPV:PCBM binary blend film (z range = 25 nm) and (B) MEH-PPV:TtBuPP:PCBM ternary blend film (z range = 10 nm).

It is also possible that introduction of porphyrins with different structures as a third component to standard MEH-PPV:PCBM devices might induce phase segregation resulting in low resistance pathways through the device that are not detectable using either optical of scanning probe microscopy. Scanning transmission X-ray microscopy (STXM) is a technique that can be used for the analysis of bulk-heterojunction solar cell active layer films, by quantitatively mapping the chemical composition of the component materials down to a resolution of less than 50 nm [23]. Figure 4.9 shows the STXM compositional images for the active layer film of an MEH-PPV:TTP:PCBM ternary blend.

Figure 4.9: Representative 10 micron x 10 micron square scanning transmission X-ray compositional micrographs of a 100nm thick MEH-PPV:TTP:PCBM ternary blend film. (A) MEH-PPV compositional map, (B) TTP compositional map and (C) PCBM compositional map.
There is no evidence of phase segregation in the ternary blend film containing TTP upon this length scale, which from the optical microscopy images in Figure 4.2 was shown to be the porphyrin with the greatest tendency to aggregate. We can be confident then that the materials are uniformly blended even down to the nanometre length scale.

Finally, the dark I-V curves in Figure 4.6 show that there is no discernible leakage current in the ternary blend devices. Considering all these points, it is unlikely that the variation observed in $V_{oc}$ for the ternary blend films is due to morphological defects caused by the porphyrins within the active layer of each device.

There are two main types of charge recombination that may occur in organic solar cells. Geminate (or monomolecular) recombination is the recombination of an initially generated electron-hole pair, and bimolecular recombination occurs when independently generated charge carriers (electrons and holes) recombine [24]. It has been shown that the open-circuit voltage in bulk heterojunction solar cells is a function of the rate of bimolecular recombination of separated charges [25], and that bimolecular recombination is the dominant mechanism in polymer:fullerene solar cells by which charge carriers recombine to the ground state with a corresponding loss of absorbed light energy [26]. It can be seen from Table 2 that the equimolar ternary devices show a small but systematic increase in shunt resistance as the steric bulk of the porphyrin in increased. As it has already been shown from the dark J-V characteristics that this change in $R_{sh}$ is not due to low resistance pathways, it must therefore be due to a decrease in recombination as the steric bulk of the porphyrin is increased.

Mandoc et al. has shown that the addition of a third material to PPV:PCBM devices can produce recombination sites which act to lower the $V_{oc}$ of the device [27]. It is therefore hypothesised that the porphyrin in these ternary blend devices act as a site for bimolecular recombination, and that the amount of recombination can be reduced by increasing the steric bulk of the porphyrin species. Figure 4.10 is a plot of the variation of $V_{oc}$ with increasing
porphyrin steric bulk, and shows that the $V_{\text{OC}}$ increases (and therefore recombination decreases) almost linearly as the Charton van der Waals radius of the substituents in the *meta* position of the porphyrins phenyl groups is increased. As such, we hypothesise that an increase in the spacial separation of charges within the device (brought upon by the increased bulk of the porphyrin) is responsible for the decrease in recombination observed.

![Graph showing variation of open circuit voltage with Charton van der Waals radius of the substituents in the *meta* positions of the porphyrin for equimolar ternary blend devices.](image)

**Figure 4.10:** Variation of open circuit voltage with Charton van der Waals radius of the substituents in the *meta* positions of the porphyrin for equimolar ternary blend devices.

Figure 4.11 is a schematic diagram of the well established model for exciton dissociation and charge recombination at interfaces within the bulk heterojunction active layers of organic solar cells.

Unlike silicon solar cells, light absorption by the active layer materials (polymer, fullerene, and porphyrin) in organic solar cells does not produce free charge carriers (electrons and holes) but rather a photogenerated exciton, which must be separated at a donor-acceptor interface (with a rate constant $k_s$). Dissociation does not initially produce free charge carriers, but instead a bound electron-hole pair [28] (also known as a charge transfer state [29], bound radical pair (BRP) state [30] or bound polaron pair [31]), due to the Coulombic attraction across the interface between charge carriers. Energy is required for a further dissociation step (with rate constant $k_o$) to separate the bound electron-hole pair into free charge carriers, which is
dependent upon the electric field across the interface and the temperature, before the bound pair decays to the ground state (with rate constant $k_F$). Recombination (either geminate or bimolecular) of free charge carriers can also regenerate the bound state (with rate constant $k_R$) [29]. Excitons can also be regenerated at donor-acceptor interfaces (with rate constant $k_{ex}$) and can be transferred back into the bulk [31, 32].

Figure 4.11: Schematic of free carrier generation in organic photovoltaic cells. The wavy line denotes an interface and the dotted ellipse denotes a coulombic binding between an interface separated electron-hole pair.

The ratio of the dissociation, $k_D$, and recombination, $k_R$, rate constants can be expressed in terms of the charge separation, $a$, the temperature, $T$, and the binding energy, $E_B$, such that [29]:

$$\frac{k_B}{k_R} = \frac{3}{4\pi a^3} e^{-E_B/kT} \left[ 1 + \frac{b^2}{3} + \frac{b^3}{18} + \frac{b^4}{180} + \ldots \right]$$  \hspace{1cm} (4.4)

where, for a given electric field, $E$, relative permittivity, $\epsilon$, and temperature, $T$, then $b$ is a constant defined by:

$$b = \frac{e^3 E}{8\pi(\epsilon)\epsilon_0 k^2 T^2}$$  \hspace{1cm} (4.5)
where $e$ is the electronic charge, $k$ is the Boltzmann constant and $\varepsilon_0$ is the permittivity of free space, and:

$$E_B = \frac{e^2}{4\pi(\varepsilon_0)e_0 a}$$  \hspace{1cm} (4.6)

Substituting Equation (4.6) into Equation (4.4) and rearranging:

$$\frac{k_D}{k_R} = A \left( \frac{1}{\alpha^2} \right) \exp \left\{ - \frac{B}{\alpha} \left( \frac{1}{kT} \right) \right\}$$  \hspace{1cm} (4.7)

where

$$A = \frac{3}{4\pi} \left[ 1 + b + \frac{b^2}{3} + \frac{b^3}{18} + \frac{b^4}{180} + \cdots \right]$$  \hspace{1cm} (4.8)

and

$$B = \frac{e^2}{4\pi(\varepsilon_0)e_0}$$  \hspace{1cm} (4.9)

Thus, from Equation (4.7) we see that the ratio of the dissociation and recombination rates is a function of both the separation of the bound electron-hole pair ($a$) and the effective thermal energy of the bound state ($kT$). The overall probability that a bound electron-hole pair dissociates into free charge carriers is also a function of $k_T$ [29], which is likely to have a similar dependence upon charge separation and effective thermal energy since a strong coupling between the bound electron and hole is also expected to increase $k_T$ [31]. Therefore, the overall dissociation probability is a function of both initial charge separation ($a$) and effective thermal energy of the bound state ($kT$).

The dependence of recombination upon initial charge separation ($a$) and effective thermal energy of the bound state ($kT$) has been investigated separately by other authors. Mandoc et al. [33] showed that increasing polymer domain size can lead to an increase in charge separation efficiency (and therefore a reduction in recombination) because enhanced domain size results in greater special separation of the initially generated electron-hole. Others have
also shown that thermal energy can have a significant effect on the dissociation efficiency of the bound electron-hole [30].

It can therefore be concluded that the porphyrins used in this ternary device study act as centres for the recombination of bound electron-hole pairs, and that by increasing the steric bulk of the porphyrins through modification of the substituents at the meta position on the porphyrin meso-phenyl ring, the rate of recombination can be decreased by increasing initial charge separation distance. While the exact mechanism is still unclear, we hypothesise that the electron-hole pair formed at the interface between porphyrin and PCBM is more likely to separate than to recombine for porphyrins with greater steric bulk.

This study has shown that the addition of porphyrin as a third component introduced into MEH-PPV:PCBM solar cells can cause a decrease in device performance through the porphyrin acting as a site for recombination. However, chemical modification of the peripheral substituents of the porphyrin molecule can mitigate losses and enhance performance through increasing spatial separation between the porphyrin dopant and the other blend components. As such, this work demonstrates an important pathway to the further development and refinement of multi-component organic solar cells. The knowledge gained could also potentially be applied to the redesign of the chemical components of binary blends, as recombination in bulk heterojunction devices is a recognised problem that affects $V_{OC}$ and efficiency, to significantly increase device function [30]. As such, we have developed a new synthetic strategy to achieve efficient charge separation, reduce the rate of recombination, and enhance device characteristics.

4.5 Conclusions

The addition of porphyrins into MEH-PPV:PCBM solar cells as additional light-harvesting components has resulted in enhancement of the spectral response at the absorption peaks of the porphyrin, but at the cost of an overall reduction in device efficiency. We have shown that
despite the propensity for porphyrinic materials to aggregate, at the blend ratios used in this study the morphology of the active layer ternary blended films remain uniform. The reduced efficiency of the ternary devices is instead dominated by changes to the electronic structure of the active layer. The porphyrin was found to act as a site for enhanced recombination of electron-hole pairs, and by altering the steric bulk of the peripheral porphyrin substituents, the charge separation distance could be increased which led to an enhancement of $V_{OC}$ and device efficiency through reduced recombination. This approach demonstrates that it is possible to design organic solar cell materials which minimise charge recombination and therefore offers a general pathway to significant efficiency improvements.

4.6 References


in polythiophene/fullerene blend films studied by transient absorption spectroscopy.


Chapter 5 - Electronic effects in porphyrinoid ternary blend bulk heterojunction MEH-PPV:porphyrin:PCBM organic solar cells

The content of this chapter was published in March 2012:


5.1 Introduction

There has been an increasing number of reports in the literature detailing the addition of porphyrinoid photosensitising materials to bulk-heterojunction solar cells, in an attempt to increase device performance [1-7]. This approach has been met with limited success, with a few papers reporting modest improvements in device performance from the addition of small (<5 % by weight) amounts of porphyrin [7, 8], while the majority of reports of the addition of larger amounts of porphyrin have been shown to either not adversely affect device performance or to significantly reduce device efficiency [2-4].

In the previous chapter, for OPV devices with a MEH-PPV:porphyrin:PCBM blend active layer, it was shown that altering the steric bulk on the periphery of the porphyrin had a significant effect on device performance. Increasing steric bulk resulted in increased charge separation distance between the porphyrin and polymer or fullerene components, which improved device performance through reduced charge recombination. In that study, the electronic nature of the porphyrins was identical with only steric bulk of porphyrin altered. Here we now probe the electronic effects of porphyrinoid addition to OPV devices by analysing a series of ternary
blend OPV devices in which the effect on device morphology is held constant whilst the electronic nature of the porphyrinoid is changed.

5.2 Porphyrinoids used in this study

To this end, a series of substituted tetra-aryl porphyrins and N-confused porphyrins:

(a) 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin (TtBuPP)

(b) N-confused 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin (NCTtBuPP)

(c) N-confused 2-methyl 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin (2N-Me NCTtBuPP)

(d) N-confused [5,10,15,20-tetrakis (3,5-di-tert-butylphenyl)porphyrinato] nickel(II) (Ni-NCTtBuPP), and

(e) N-confused 2-methyl [5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrinato] nickel(II) (Ni-2N-Me NCTtBuPP)

have been prepared. Importantly, the meta substituent on the aryl functionality of the porphyrinoid (a tert-butyl group) is kept constant. This series of compounds was incorporated into MEH-PPV:PCBM based OPV devices.

The base compound in this series of porphyrinoids is 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin (TtBuPP). The steric bulk of the tert-butyl groups at the meta position on the meso phenyl groups of the porphyrin ring are known to decrease the natural tendency for the porphyrins to aggregate and have been shown in the previous chapter to allow the formation of MEH-PPV:TtBuPP:PCBM active layers which are then fully blended on the tens of nanometre scale [3]. In order to probe the electronic effect of porphyrinoids we have here prepared a series of N-confused porphyrins which retain the peripheral tert-butyl group motif to minimise changes in the aggregation and phase separation in the device active layers. N-confused porphyrins are structural isomers of the parent porphyrin macrocycle, which differ
only in the orientation of one of the pyrrole rings. While the framework of N-confused porphyrin is almost identical to normal porphyrin, it differs because one of the pyrrole rings is connected to the adjacent meso-carbon through its $\alpha$-$\beta'$ axis rather than the usual $\alpha$-$\alpha'$ linkage. The result is that one of the pyrrole rings appears inverted, with its nitrogen atom oriented to the outside of the macrocycle [9, 10]. The external nitrogen allows derivatisation beyond that of an ordinary porphyrin. In a manner analogous to a conventional porphyrin the internal cavity may be metallated by a wide variety of metal ions [11], however coordination is also possible to the external pyrrolic nitrogen [12]. In this work we altered the electronic state of the porphyrinoid by both metallating the internal cavity with nickel(II) ions and alkylating the external nitrogen with methyl groups to give the four N-confused porphyrins shown below.

Figure 5.1: Chemical structures of: (A): T' BuPP, (B): N CT'T BuPP, (C): 2N-Me N CT'T BuPP, (D): Ni-N CT'T BuPP and (E): Ni-2N-Me N CT'T BuPP

The UV-visible absorbance spectra for the five compounds studied are shown in Figure 5.2. While the porphyrins are structurally similar, their UV-visible spectra differ considerably [13]. In particular, inversion of the pyrrole ring destroys molecular symmetry resulting in broadening and splitting of the porphyrinoid B and Q bands, even within the metallated species. Both the
Q and B bands are red-shifted in the N-confused species as a result of a reduced HOMO-LUMO band gap [13], and consequently, the low energy absorption onset moves from approximately 660 nm in TtBuPP to 760 nm for NCTtBuPP and out beyond 800 nm for the metallated and methylated species.

![Absorbance spectra](image)

Figure 5.2: Normalised UV-vis absorbance spectra for porphyrinoids studied in dichloromethane solution

### 5.3 MEH-PPV:porphyrin:PCBM 1:1:8 devices

The porphyrins were introduced into the active layer of these devices to give a blend materials ratio of MEH-PPV:porphyrinoid:PCBM 1:1:8 by weight. This composition is consistent with previous work by our group with porphyrin containing ternary blend devices, which equates to the replacement of one half of the polymer component within the device by the porphyrinoid species [3, 4].
Figure 5.3: Optical microscopy images (1 x 1 mm) of pure (A): TtBuPP and (B): NCTtBuPP films and (C): MEH-PPV:TtBuPP:PCBM and (D): MEH-PPV:NCTtBuPP:PCBM ternary blend films. AFM (2.5 x 2.5 μm) and STXM porphyrin composition images (10 x 10 μm) for MEH-PPV:TtBuPP:PCBM ((E) and (G)) and MEH-PPV:NCTtBuPP:PCBM ((F) and (H)) ternary blend films, respectively.

Figure 5.3 shows optical microscopy of spin cast films of TtBuPP and NCTtBuPP, as well as optical microscopy, atomic force microscopy (AFM) and scanning transmission X-ray microscopy (STXM) porphyrin composition images of the corresponding spin cast ternary blend films (1:1:8 MEH-PPV:TtBuPP:PCBM and 1:1:8 MEH-PPV:NCTtBuPP:PCBM respectively). The combination of these three microscopy techniques clearly demonstrates that these films remain fully blended at all the length scales probed (millimetre, micrometre and nanometre). The AFM images indicate that the TtBuPP and NCTtBuPP blend films have surface RMS roughness values of 3.7 and 3.6 nm respectively. Therefore, the ternary butyl groups prevent porphyrin aggregation and there is no lateral phase segregation within these films down to the ~30 nm scale, which means that we can exclude changes in active layer morphology as a cause for any observed changes in device performance.
Table 5.1 presents the device characteristics and Figure 5.4 the current density-voltage (I-V) curves for 1:1:8 MEH-PPV:porphyrinoid:PCBM OPV devices with each of the porphyrinoids included.

Table 5.1: Device characteristics for all MEH-PPV:porphyrinoid:PCBM devices. The errors have been calculated from the standard deviation across a minimum of eight independent devices.

<table>
<thead>
<tr>
<th>Device</th>
<th>$V_{oc}$/ mV</th>
<th>$J_{sc}$/ mA/cm$^2$</th>
<th>FF</th>
<th>$R_{series}$/ Ω</th>
<th>$R_{shunt}$/ kΩ</th>
<th>PCE / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEH-PPV:T$t$BuPP:PCBM</td>
<td>644 ±12</td>
<td>3.904 ±0.300</td>
<td>0.332 ±0.005</td>
<td>295</td>
<td>5.52</td>
<td>0.833 ±0.028</td>
</tr>
<tr>
<td>MEH-PPV:NCT$t$BuPP:PCBM</td>
<td>243 ±12</td>
<td>0.546 ±0.032</td>
<td>0.282 ±0.004</td>
<td>186</td>
<td>12.31</td>
<td>0.038 ±0.005</td>
</tr>
<tr>
<td>MEH-PPV: 2N-Me NCT$t$BuPP:PCBM</td>
<td>169 ±7</td>
<td>0.644 ±0.048</td>
<td>0.283 ±0.002</td>
<td>120</td>
<td>7.56</td>
<td>0.031 ±0.003</td>
</tr>
<tr>
<td>MEH-PPV: Ni-NCT$t$BuPP:PCBM</td>
<td>633 ±10</td>
<td>1.229 ±0.037</td>
<td>0.275 ±0.001</td>
<td>557</td>
<td>10.50</td>
<td>0.214 ±0.007</td>
</tr>
<tr>
<td>MEH-PPV: Ni-2N-Me NCT$t$BuPP:PCBM</td>
<td>681 ±19</td>
<td>2.200 ±0.151</td>
<td>0.298 ±0.005</td>
<td>111</td>
<td>7.08</td>
<td>0.448 ±0.046</td>
</tr>
</tbody>
</table>

Figure 5.4: Current density-voltage (I-V) characteristics for all MEH-PPV:porphyrinoid:PCBM devices.
A number of trends can be observed in the data presented. The power conversion efficiencies of all of the N-confused porphyrin devices are significantly lower than the corresponding porphyrin device, due most obviously to a reduction in $J_{sc}$. The two non-metallated N-confused porphyrins also have a much lower $V_{oc}$, and the fill factors of all the N-confused porphyrins are ~20 % lower than the porphyrin device. Metallation of the N-confused porphyrin core results in a recovery of the $V_{oc}$, which rises equal to or slightly above the value for the corresponding porphyrin device, along with a smaller increase in $J_{sc}$. The net result is almost an order of magnitude increase in the PCE for the devices upon porphyrinoid metallation. By contrast, methylation of the external pyrrolic nitrogen results in only a small change in the corresponding device $V_{oc}$, but does lead to an increase in $J_{sc}$ resulting in a more modest increase in the overall PCE.

Figure 5.5 shows the blend film UV-vis absorption spectra and the device external quantum efficiency (EQE) as a function of wavelength for the MEH-PPV:T'BuPP:PCBM and the MEH-PPV:NCT'BuPP:PCBM blends. A comparison of the two spectra and the solution UV-vis absorption spectra for the pure porphyrinoids, shown in Figure 5.3, clearly shows photocurrent contributions from the porphyrinoid Q and B bands superimposed upon polymer and fullerene contributions in the device. This behaviour is consistent with observations in the previous chapter [3] and earlier work by our group [4] that porphyrins contribute significantly to the photocurrent in ternary blend devices.

The reduction in performance that we observe cannot simply be attributed to the removal of some MEH-PPV as a photoactive material, as it has been shown that ternary MEH-PPV:porphyrin:PCBM devices in the ratio used here can have similar performance to binary blends [4]. We have also shown that there are not any significant changes in active layer morphology and phase segregation so the reduction in performance is not a morphological effect. The observed results must therefore arise from changes in the charge generation
contribution of the porphyrinoids themselves or the detrimental effect of the porphyrinoids on charge transport and recombination within the devices.

Figure 5.5: (A): UV-vis absorbance and (B): external quantum efficiency (EQE) as a function of wavelength for the MEH-PPV:TtBuPP:PCBM ternary blend device (blue line) and MEH-PPV:NCTtBuPP:PCBM ternary blend device (red line). The insets show an enlarged view of the 600 – 800 nm wavelength region highlighting peaks arising from photon absorption of the porphyrinoid Q bands

The previous chapter has established that porphyrins act as recombination sites in MEH-PPV:porphyrin:PCBM OPV devices, which reduces the V_{oc} of these devices and disrupts the charge transport within them [3]. In that case it was changes in the steric bulk of the porphyrin, and the consequential change in charge separation distance within the device, that resulted in changes in device performance. In the current study the steric bulk of the porphyrinoids is held constant through the placement of identical di-tert-butylphenyl peripheral substituents in all compounds, so the observed changes in device performance must therefore arise from changes in the electronic nature of the porphyrinoids.

To evaluate the energetics of the materials, the HOMO and LUMO energies and bandgap of all five porphyrinoids were determined both experimentally via UV-Vis spectroscopy of solid films and cyclic voltammetry of solutions, and theoretically via density functional theory (DFT) calculations. The results obtained by both methods are in good agreement with reported values [13]. Because the environment of the porphyrin is very different in each case, it is not
possible to directly compare the *absolute* values obtained by experimentally derived energy levels to theoretically calculated values, as the absolute values of each are always offset by some amount. We can however compare the *relative* HOMO and LUMO energy level value for our series, to identify trends in the data. Calculated and experimentally derived energy level data for the porphyrinoids in this study are presented in Table 5.2 below.

**Table 5.2: Calculated ionisation potentials (IP), electron affinities (EA), HOMOs, LUMOs and bandgaps, and experimentally determined HOMOs, LUMOs and bandgaps, for all five porphyrinoids.** The model values were calculated using the B3LYP/6-31G(d) DFT method. An error of ± 0.1 eV is applied to the experimental HOMO and LUMO values based upon the accuracy of determining the oxidation onset of the porphyrinoids.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>T^1BuPP</th>
<th>NCT^1BuPP</th>
<th>2N-Me NCT^1BuPP</th>
<th>Ni-NCT^1BuPP</th>
<th>Ni-2N-Me NCT^1BuPP</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Calculated Values</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IP (cm^{-1})</td>
<td>47991</td>
<td>44402</td>
<td>44442</td>
<td>45256</td>
<td>44825</td>
</tr>
<tr>
<td>EA (cm^{-1})</td>
<td>8976</td>
<td>10550</td>
<td>10422</td>
<td>9364</td>
<td>8902</td>
</tr>
<tr>
<td>LUMO (eV)</td>
<td>-2.20</td>
<td>-2.37</td>
<td>-2.34</td>
<td>-2.29</td>
<td>-2.23</td>
</tr>
<tr>
<td>HOMO (eV)</td>
<td>-4.91</td>
<td>-4.46</td>
<td>-4.42</td>
<td>-4.53</td>
<td>-4.48</td>
</tr>
<tr>
<td>Bandgap (eV)</td>
<td>2.71</td>
<td>2.09</td>
<td>2.08</td>
<td>2.24</td>
<td>2.25</td>
</tr>
<tr>
<td><strong>Experimental Values</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LUMO (eV)</td>
<td>-2.54</td>
<td>-2.55</td>
<td>-2.64</td>
<td>-2.56</td>
<td>-2.57</td>
</tr>
<tr>
<td><em>Error</em></td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>HOMO (eV)</td>
<td>-5.48</td>
<td>-5.16</td>
<td>-5.18</td>
<td>-5.20</td>
<td>-5.24</td>
</tr>
<tr>
<td><em>Error</em></td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Bandgap (eV)</td>
<td>2.91</td>
<td>2.61</td>
<td>2.54</td>
<td>2.64</td>
<td>2.67</td>
</tr>
<tr>
<td><em>Error</em></td>
<td>0.14</td>
<td>0.14</td>
<td>0.14</td>
<td>0.14</td>
<td>0.14</td>
</tr>
</tbody>
</table>
Figure 5.6 illustrates the relationships between the ionization potential and HOMO and LUMO energies of the porphyrinoids and the power conversion efficiency of the corresponding ternary blend devices. A strong linear correlation is observed between the efficiency of the devices and the energy levels of the porphyrinoid HOMO and LUMO, for both calculated and experimentally derived values, showing that we can successfully model the electronic states of these molecules.

Figure 5.6: Plots of (A): the ionisation potential, where diamond = 2N-Me NCT^BuPP, square = NCT^BuPP, cross = Ni-NCT^BuPP, plus = Ni-2N-Me NCT^BuPP and circle = T^BuPP, and (B): the HOMO and LUMO energies (modelled data, solid markers and solid line; experimental data, open markers and dashed line), of the five porphyrinoids versus the PCE of the corresponding MEH-PPV:porphyrinoid:PCBM ternary blend OPV devices

Ionisation potential and electron affinity have been shown to be crucial to the photophysics of components in blend OPV devices. For example, thiophene copolymers with higher IPs than poly(3-hexylthiophene) (P3HT) have been observed to lead to significant recombination pathways in blend devices through efficient formation of triplet excitons [14]. In addition, the optimal orbital energy offset (i.e. HOMO and LUMO energies) for efficient polymer:PCBM cells is the subject of much current debate [15-20]. Our observation of a direct correlation between these parameters confirms that the porphyrinoids are not merely spectator species in the
blend device but are, as demonstrated by the EQE plots (Figure 5.5), intimately involved in charge generation and transport. The overall energy diagram of our devices is shown systematically in Figure 5.7.

![Energy Diagram](image)

**Figure 5.7**: Schematic energy diagram for the MEH-PPV:porphyrinoid:PCBM organic photovoltaic cells. The overall range of the modelled HOMO and LUMO energies of the five porphyrinoids is defined by the grey-scale boxes.

It is apparent that the LUMOs of all porphyrinoids are well positioned for the transfer of an electron to either the polymer or fullerene species. The HOMOs of some porphyrin species however, are poorly placed with respect to other device components. The energy level of all N-confused porphyrin HOMOs sit above that of the polymer hole transport network, the PEDOT:PSS interfacial layer, and the ITO electrode. The N-confused porphyrins therefore function as recombination sites within these devices, effectively disrupting charge transport by acting as hole traps. The relative energy of this orbital determines the ‘depth’ of this trap and explains the correlation between the HOMO energy in the porphyrinoid and the device efficiency. Figure 5.8 is a plot of the $V_{oc}$ of the ternary blend devices verses the corresponding porphyrinoid HOMO energy.
Figure 5.8: A plot of the $V_{oc}$ of a MEH-PPV:porphyrinoid:PCBM ternary blend device versus the HOMO energy of the component porphyrinoid. Purple = 2N-Me NCT'BuPP, red = NCT'BuPP, orange = Ni-2N-Me NCT'BuPP, green = Ni-NCT'BuPP, blue = NCT'BuPP. The vertical dashed line indicates the “threshold energy” at which the device becomes functional.

A distinct threshold energy between -4.46 and -4.48 eV is observed. For HOMO levels above this threshold the energy mismatch is such that the porphyrin acts primarily as a hole trapping material and the device is “switched off”, limiting $V_{oc}$ to approximately 200 mV. As the HOMO energies drop below this threshold the energy difference gradually improves hole transport from the porphyrinoid and the device becomes functional, restoring the $V_{oc}$ to ~650 mV. It is also likely that poor mobility of charges in porphyrins and porphyrinoids assists the observed charge recombination. Hole mobilities in porphyrin materials are highly dependent on the degree of crystallinity of the porphyrin. Hole diffusivities as low as $7 \times 10^{-11}$ cm² s⁻¹ are observed for porphyrins in amorphous films [21], whilst mobilities as high as $5 \times 10^{-5}$ cm² V⁻¹ s⁻¹ have been observed in porphyrin columnar stacks [22]. By comparison MEH-PPV films have hole mobilities of approximately $10^{-5}$ cm² V⁻¹ s⁻¹ [23]. Since the device films studied in this work have been shown to be fully blended on the 10s of nm scale, we can conclude that the
porphyrin is unlikely to exist in a crystalline state, but rather an amorphous distribution within the other blend components, therefore porphyrinoid hole mobility is very low and the likely limiting factor in these devices. Even in the case of T<sup>8</sup>BuPP (which has the minimum energy mismatch of the porphyrinoids in this study), the limited hole mobility of the porphyrin results in enhanced recombination and means that device performance is still reduced to ~650 mV relative to a MEH-PPV:PCBM binary device which typically has a $V_{OC}$ approaching 850 mV.

In summary, we have shown here that a combination of poor charge mobility of these porphyrinoids and HOMO energy mismatch with other device materials results in the porphyrinoids serving as hole trapping sites which promote charge recombination within ternary blend MEH-PPV:porphyrinoid:PCBM devices. The observed linear correlation between the ionization potential of the porphyrin and the power conversion efficiencies of the corresponding ternary blend OPV device provides a pathway to engineer future porphyrinoid materials such that they minimise the disruption to charge transport and maximise its photocurrent contribution to OPV devices, which may lead to improvements in overall device performance above that of a standard polymer:fullerene binary device.

5.4 Conclusions

By preparing a series of porphyrins and N-confused porphyrins in which the peripheral groups are unchanged we have created a series of porphyrinoids which differ only in the nature of their electronic states. By choosing sterically bulky peripheral groups we have shown that the inclusion of these compounds in binary MEH-PPV:PCBM OPV devices does not significantly alter the morphology of the device active layers through phase segregation. Porphyrinoids contribute to the photocurrent of these ternary devices through a broadening of the spectral response of the cells in accordance with the absorption spectra of the porphyrinoid, but at the same time overall device performance is reduced. Consideration of the device parameters and an observed linear correlation between the ionisation potential and thus highest occupied
molecular orbital energy of the porphyrinoids, and the power conversion efficiency of the ternary blend devices, indicates that the porphyrinoids act as hole trapping sites within these devices, increasing bimolecular recombination and lowering device efficiency through a reduction in both the devices’ charge densities and open circuit voltages. By modifying the porphyrinoid added, either by metallation or N-alkylation of the N-confused porphyrin, we systematically change the ionisation potential of the species and therefore directly affect the power conversion efficiency of the resultant device. This approach demonstrates a method by which we may directly design materials that minimise recombination within bulk heterojunction devices and thus offers a general pathway to significant efficiency improvements in ternary blend devices.

5.5 References


6.1 Introduction

In the previous chapter, the electronic nature of porphyrin and N-confused porphyrin ternary polymer:porphyrin:fullerene photovoltaic devices was explored, and it was found that by altering the ionisation potential of the porphyrinoid species, the HOMO level could be shifted into energetic alignment with the other components of the device. It was also discovered that N-confused porphyrins are generally poor materials for integration into organic photovoltaic devices due to poor hole transport properties [1]. In the current chapter, the concept of “fine-tuning” the porphyrins’ energy levels will be approached in a different manner, by varying the electron-donating and withdrawing ability of the porphyrins \textit{para}-phenyl substituents. A series of freebase tetraphenylporphyrins differing only in the identity of the \textit{para}-substituent of the \textit{meso}-phenyl groups were incorporated into ternary MEH-PPV:porphyrin:PCBM organic solar cells in the ratio of either 4:4:32 or 8:1:32 by weight, and the effect on device performance investigated. The aim was to show that by changing the identity of the \textit{para}-phenyl substituents, the HOMO and LUMO could again be altered to a more suitable energy level compared with the polymer and fullerene. As such, the goal was to expand on the methodology for directing charge-separation events by rational design of donor molecules for organic photovoltaic devices. Porphyrinoids are very strong chromophores which can be tuned for HOMO, LUMO, and band gap by either disrupting the symmetry of the molecule [2], or by changing the electron density distribution in the conjugated system by modification of substituents [3, 4]. In this study, we have chosen the latter approach.
6.2 Porphyrins used in this study

Figure 6.1 illustrates the various tetraphenylporphyrin derivatives that were used in this study. Freebase tetraphenylporphyrins were selected due to their ease of synthesis, the ability to alter their optical properties through choice of substituents, and their generally improved solubility compared with other porphyrinoid species such as octaethylporphyrins [5] and phthalocyanines [6]. The core tetraphenylporphyrin structure remains constant, with only the substituents at the \( \text{para} \)-phenyl position altered. A range of substituents were selected, ranging from: electron-donating (amino, hydroxyl, methoxy, and methyl), neither electron-donating nor withdrawing (hydrogen), and electron-withdrawing (chloro, bromo, and acetate methyl ester) substituents (Figure 6.1).

![Molecular structures of tetraphenylporphyrins with the para-phenyl substituents](image)

**Figure 6.1:** Molecular structures of tetraphenylporphyrins with the \( \text{para} \)-phenyl substituents: (a) \( \text{NH}_2 \), (b) \( \text{OH} \), (c) \( \text{OCH}_3 \), (d) \( \text{CH}_3 \), (e) \( \text{H} \), (f) \( \text{Cl} \), (g) \( \text{Br} \), (h) \( \text{COOCH}_3 \) used in this study

The compounds and their assigned abbreviations are therefore:

a) \( 5,10,15,20\)-tetrakis(4-aminophenyl)porphyrin (\( \text{TpNH}_2\text{PP} \))

b) \( 5,10,15,20\)-tetrakis(4-hydroxyphenyl)porphyrin (\( \text{TpOHPP} \))

c) \( 5,10,15,20\)-tetrakis(4-methoxyphenyl)porphyrin (\( \text{TpOCH}_3\text{PP} \))

d) \( 5,10,15,20\)-tetrakis(4-methylphenyl)porphyrin (\( \text{TTP} \))

e) \( 5,10,15,20\)-tetraphenylporphyrin (\( \text{TPP} \))
f) 5,10,15,20-tetrakis(4-chlorophenyl)porphyrin (TpClPP)

g) 5,10,15,20-tetrakis(4-bromophenyl)porphyrin (TpBrPP)

h) 5,10,15,20-tetrakis(4-(methoxycarbonyl)phenyl)porphyrin (TpCOOCH₃PP)

Perturbing the conjugated π system with \textit{meso}-phenyl substituent groups is an effective way to vary the optical properties of tetraphenylporphyrins [7]. Although the porphine and phenyl planes are generally considered not to be coplanar, rotation of the porphyrins \textit{meso}-phenyl rings allows them to be in direct conjugation with the porphyrin core at least some of the time [8]. By attaching various electron-donating or electron-withdrawing substituents onto the peripheral phenyl groups the electron density of the porphyrin core is altered, which changes the optical properties of the porphyrin such as the position and magnitude of the UV-visible absorption peaks [9].

The electron-donating and electron-withdrawing properties of tetraphenylporphyrin substituents can be compared quantitatively by using the Hammett sigma parameter [10]. This value is determined by considering both the resonance and field effects of a substituent attached to a benzene ring, and how these affect the ionization rate of benzoic acid in water (Figure 6.2).

\[
R\text{-}\text{C}_6\text{H}_4\text{O}^+ + \text{H}_2\text{O} \xleftrightarrow{25^\circ \text{C}} R\text{-}\text{C}_6\text{H}_4\text{O}^- + \text{H}_3\text{O}^+ 
\]

\textit{Figure 6.2: The chemical equilibrium for the ionisation of benzoic acid derivatives}

The Hammett equation is as follows:

\[
\sigma_x = \log K_X - \log K_H
\]

where \( K_H \) is the ionisation constant for benzoic acid in water at 25 °C and \( K_X \) is the ionisation constant for the substituted benzoic acid. Hammett parameters are typically calculated for
substituents at both the meta- and para-phenyl positions, however in the present study we will only be concerned with substituents at the para-phenyl position on the porphyrin molecules. Table 6.1 lists the Hammett parameters for these substituents (with values quoted from [10] and [11]), which will be used as a quantitative measure of the electron-donating and withdrawing ability in this study. A positive $\sigma_{\text{para}}$ value indicates that a substituent group is electron withdrawing, a negative $\sigma_{\text{para}}$ indicates that it is electron donating, and the size of $\sigma_{\text{para}}$ is dependent on the magnitude of the effect.

Table 6.1 Hammett parameters for the substituents in the para-phenyl position of the porphyrins used in this study. From [10] and [11]

<table>
<thead>
<tr>
<th>para-phenyl substituent</th>
<th>Hammett $\sigma_{\text{para}}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_2$</td>
<td>-0.66</td>
<td>[11]</td>
</tr>
<tr>
<td>OH</td>
<td>-0.37</td>
<td>[11]</td>
</tr>
<tr>
<td>OCH$_3$</td>
<td>-0.27</td>
<td>[11]</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>-0.17</td>
<td>[11]</td>
</tr>
<tr>
<td>H</td>
<td>0</td>
<td>[11]</td>
</tr>
<tr>
<td>Cl</td>
<td>0.227</td>
<td>[10]</td>
</tr>
<tr>
<td>Br</td>
<td>0.232</td>
<td>[10]</td>
</tr>
<tr>
<td>COOCH$_3$</td>
<td>0.45</td>
<td>[11]</td>
</tr>
</tbody>
</table>

6.3 MEH-PPV:porphyrin:PCBM 4:4:32 devices

Ternary MEH-PPV:porphyrin:PCBM devices were initially fabricated in the ratio of 4:4:32 by weight, which corresponds to the replacement of one half of the polymer content (by weight) of a standard MEH-PPV:PCBM 1:4 device with porphyrin. Optical microscopy images of the active layer film of each blend are shown in Figure 6.3.
Figure 6.3: Optical microscopy of MEH-PPV:porphyrin:PCBM 4:4:32 ternary blended device films, where the \textit{para}-phenyl substituents are: (A) CH$_3$, (B) H, (C) Cl, (D) Br, (E) NH$_2$, (F) OH, (G) OCH$_3$, (H) COOCH$_3$. The white scale bar represents 50 μm

It is important to ensure that the incorporation of a photosensitising compound into a bulk-heterojunction organic photovoltaic device does not disrupt active layer morphology or adversely affect device performance. It is clear from Figure 6.3 that the addition of some of the porphyrinic compounds has resulted in the formation of aggregates within the film. Specifically, the porphyrins TpNH$_2$PP, TpOHPP, TpOCH$_3$PP, and TpCOOCH$_3$PP were observed to disrupt film morphology, reflecting their limited solubility in chlorobenzene at these concentrations.

To illustrate the effect of poorly dissolved active layer constituents on device performance, we will compare the UV-vis absorption spectra and external quantum efficiency (EQE) of two ternary blend MEH-PPV:porphyrin:PCBM 4:4:32 solar cells with active layers of identical thickness (Figure 6.4). In one blend, the porphyrin has –NH$_2$ substituents, which from Figure 6.3 are observed to have poor solubility at the specified concentration. In the second ternary blend the substituent is –Cl, which was observed to have excellent solubility and uniform film morphology.
Despite having active layers of identical thickness, the absorption of the active layer containing TpNH$_2$PP appears to be significantly larger than the active layer blend containing the TpCIPP, across the entire visible spectrum. However, this apparently increased visible light absorption is actually the result of light scattering from TpNH$_2$PP aggregates away from the detector of the spectrometer, most clearly detected by the non-baseline absorbance above 750 nm, a region where the neither the polymer, porphyrin or fullerene absorb any light. Disruption of the active layer morphology by TpNH$_2$PP aggregates likely contributes to the poor maximum EQE of approximately 12 %, indicating that not only is light absorption affected by the poorly dissolved aggregates, but that the ability of the active layer to extract charge from the device is also impacted by the morphological disruption. In contrast, the uniformly-blended TpCIPP ternary blend shows a relatively high EQE, with strong current output by both the polymer and the porphyrin components of the active layer film. There are of course other factors
contributing to the observed performance, which will be discussed later in this chapter, but this example highlights the importance of uniform blending of device components in the active layer film.

Compounds that were observed to have poor solubility at the 4:4:32 ratio were excluded from the present device study. Device characteristics for the remaining compounds, where the ternary active layer blends were observed to have uniform film morphology, are shown in Table 6.2. Note that the Hammett $\sigma_{para}$ value for the para-phenyl substituent of each tetraphenylporphyrin derivative is also shown in Table 6.2, and that the data in this table and in subsequent graphs derived from this data, is arranged in order of increasing $\sigma_{para}$ and therefore increasing electron-withdrawing character of each porphyrin substituent.

Table 6.2: Device characteristics for MEH-PPV:porphyrin:PCBM 4:4:32 ternary blend OPV devices. Errors are calculated from the standard deviation across a minimum of 8 devices. The Hammett $\sigma_{para}$ for the para-phenyl substituent of each TPP is also shown.

<table>
<thead>
<tr>
<th>Porphyrin $p$-phenyl substituent</th>
<th>Efficiency</th>
<th>$V_{oc}$</th>
<th>$J_{sc}$</th>
<th>Fill Factor</th>
<th>$R_s$</th>
<th>$R_{sh}$</th>
<th>Hammett $\sigma_{para}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$</td>
<td>0.489 ±0.026</td>
<td>467 ±10.0</td>
<td>2.949 ±0.089</td>
<td>0.354 ±0.002</td>
<td>967</td>
<td>6194</td>
<td>-0.17</td>
</tr>
<tr>
<td>H</td>
<td>0.547 ±0.015</td>
<td>531 ±9.4</td>
<td>2.898 ±0.033</td>
<td>0.355 ±0.004</td>
<td>1279</td>
<td>5999</td>
<td>0</td>
</tr>
<tr>
<td>Cl</td>
<td>0.980 ±0.033</td>
<td>628 ±7.4</td>
<td>3.929 ±0.101</td>
<td>0.397 ±0.005</td>
<td>812</td>
<td>7385</td>
<td>0.227</td>
</tr>
<tr>
<td>Br</td>
<td>1.508 ±0.021</td>
<td>694 ±8.4</td>
<td>4.685 ±0.070</td>
<td>0.464 ±0.004</td>
<td>448</td>
<td>8919</td>
<td>0.232</td>
</tr>
</tbody>
</table>

Figure 6.5 focuses on the power conversion efficiency of the series of MEH-PPV:porphyrin:PCBM 4:4:32 devices varying only in the para-phenyl substituent of the porphyrin.
We observe a significant improvement in device efficiency with increasing Hammett $\sigma_{\text{para}}$ of the porphyrin para-substituent, increasing three-fold from the lowest to the highest Hammett $\sigma_{\text{para}}$ value. This trend indicates that the electron-withdrawing characteristic of the porphyrin $\text{para}$-phenyl substituents has a significant effect on the device efficiency, likely due to the spectral and electronic properties of each porphyrin.

We see from a plot of the open-circuit voltage ($V_{\text{OC}}$) of the devices (Figure 6.6) that a similar trend is observed, with $V_{\text{OC}}$ increasing as the electron-withdrawing character of the $\text{para}$-phenyl substituent becomes stronger. The $V_{\text{OC}}$ of a bulk heterojunction OPV device is related to the difference in energy between the highest occupied molecular orbital of the donor material ($\text{HOMO}_{\text{donor}}$) and the lowest unoccupied molecular orbital of the acceptor material ($\text{LUMO}_{\text{acceptor}}$), and changing either one of these energy levels has an effect on the $V_{\text{OC}}$ of a device [12]. In the present study, the porphyrinic materials act as a donor material, therefore changes in the HOMO of the porphyrin, attributed to the electron donating or withdrawing
character of the *para*-phenyl substituent on the porphyrin, may drive the observed improvement in efficiency through an increase in open-circuit voltage. The relationship between the HOMO of the porphyrin and device $V_{OC}$ will be explored in more detail later.

![Figure 6.6: Open-circuit voltage of MEH-PPV:porphyrin:PCBM 4:4:32 ternary blend OPV devices](image)

From Figure 6.7 we observe that the short-circuit current density ($J_{SC}$) also generally improves with increasing electron-withdrawing character of the porphyrin substituent. The $J_{SC}$ is a function of the amount of light absorbed by the active layer materials, and the efficiency with which the photons are converted to charges and able to exit the device via the electrodes [13]. It is therefore dependent not only on the absorption coefficients of the solar cell materials, but also on the morphological structure of the heterojunction which affects both the rate of dissociation and the charge transport pathways to the electrodes of the device [14]. It has been demonstrated that disruption of favourable active layer morphology due to aggregation of porphyrinoid additives can lead to diminished device performance [15-17]. We see from
Figure 6.3 that each of the active layer films in this study are uniformly blended at the optical length scale, with no visible aggregates observed in the film. Furthermore, we have previously shown that similar ternary blended porphyrinic materials are uniformly blended down to the nanometre scale [1, 18]. Indeed, the molecules in the present study vary only by the nature of the substituent at the porphyrin para-phenyl position, and therefore differ little in structure from our previously studied materials. We can therefore conclude that the observed changes in $J_{SC}$ are unlikely to be due to disruption of the active layer morphology due to addition of the porphyrin.

![Graph showing short-circuit current density](image)

**Figure 6.7: Short-circuit current density of MEH-PPV:porphyrin:PCBM 4:4:32 ternary blend OPV devices**

The trends in device $J_{SC}$ may be due to differences in the amount of light absorbed, the efficiency in which photons are converted to charge carriers, or a change in charge mobility, due to the presence of the porphyrin molecules.
We see from Figure 6.8 that device fill factor also increases with increasing electron withdrawing character of the porphyrin \textit{para}-phenyl substituents. The fill factor of a solar cell is a measure of the quality of the diode, and is essentially determined by the series ($R_s$) and shunt ($R_{sh}$) resistances of the device, which can be approximated by the inverse of the slope of the I-V curve at open-circuit voltage and short-circuit current, respectively. The series resistance is related to the intrinsic resistance, thickness and morphology of the active layer, whereas the shunt resistance is correlated with the level of impurities or defect sites in the active layer which cause leakage current and increase charge recombination [19]. As we have already determined that the active layer morphology and thickness do not vary significantly between blends, the observed improvements in fill factor may be due to increased shunt resistance in the devices. From the I-V curve (Figure 6.9) we can calculate the shunt resistances, which are listed in Table 6.2 above.
We do indeed observe an increase in shunt resistance with increasing device efficiency, suggesting that there is some mechanism by which porphyrins with \( para \)-phenyl substituents having a large \( \sigma_{para} \) (i.e. more electron withdrawing character) are correlated with improved device performance.

The UV-visible absorption spectra of the four ternary active layer blends are shown in Figure 6.10. Note that all films are of the same thickness (120 nm). The porphyrin Soret band absorption is clearly visible as a distinct peak at approximately 440 nm. We generally observe a decrease in the magnitude of absorption, and an increase in the wavelength position of the absorption peak by the porphyrin compound at the Soret band as the electron withdrawing character of the \( para \)-phenyl substituents is increased. These observations are consistent with published studies [7]. This decrease in absorption means that generally porphyrins in the ternary porphyrin devices displaying higher efficiency actually absorb less light than porphyrins in lower efficiency devices. The observed trends in efficiency must therefore be related to the
efficiency with which photons are converted to charge, or the amount of charge recombination, present within the active layer of the device.

Figure 6.10: UV-Vis absorption spectroscopy of MEH-PPV:porphyrin:PCBM 4:4:32 ternary blend OPV device films on quartz

Figure 6.11: EQE of MEH-PPV:porphyrin:PCBM 4:4:32 ternary blend OPV devices
Figure 6.11 shows the external quantum efficiency of each of the ternary blend devices. Current contribution from the porphyrin Soret transition (440 nm) and Q-bands (580 – 750 nm) is clearly observed. While the relative magnitude of the Soret contribution essentially mirrors the absorption profile of the device active layer UV-vis absorption spectra, the EQE of the polymer (440 – 500 nm) and fullerene (375 nm) components vary significantly between blends. Total current generation is highest for the porphyrin with the largest Hammett $\sigma_{para}$ (TpBrPP), followed by TpClPP, and the porphyrins with the two lowest Hammett $\sigma_{para}$ (TTP and TPP) both have poor EQEs. The observation that the performance of the polymer and fullerene components varies greatly between blends supports the hypothesis that the porphyrins are having an effect on the degree of charge recombination within the active layer films. It also suggests that there may be an energetic mismatch between the HOMO or LUMO energies of the porphyrin and the polymer or fullerene, which diminishes exciton separation or prevents charge generated at the polymer or fullerene interfaces from being extracted from the active layer. To further explore the observed trends, a further series of devices were fabricated incorporating a smaller weight percentage of porphyrin, to allow the inclusion of additional, less soluble porphyrin species, to the series. The additional compounds expand the series of Hammett $\sigma_{para}$ values to both higher and lower values than previously investigated above.

6.4 MEH-PPV:porphyrin:PCBM 8:1:32 devices

A series of ternary devices were fabricated with a small amount of porphyrin added (in the amount of 2.5 %) into a standard MEH-PPV:PCBM 1:4 by weight device. This lowered porphyrin concentration has the advantage of better solubility of the porphyrin species in the non-polar chlorobenzene solvent, and allows the series of ternary devices to be expanded. The series now includes a total of six porphyrins, with an MEH-PPV:porphyrin:PCBM ratio of 8:1:32 by weight. Each porphyrin compound is a freebase tetraphenylporphyrin differing only by the
The functional group present at the 4- or para-phenyl position. The porphyrins, arranged in order of increasing Hammett $\sigma_{para}$ of the para-phenyl substituent, are:

a) $5,10,15,20$-tetrakis(4-aminophenyl)porphyrin (TpNH$_2$PP)
b) $5,10,15,20$-tetrakis(4-methylphenyl)porphyrin (TTP)
c) $5,10,15,20$-tetraphenylporphyrin (TPP)
d) $5,10,15,20$-tetrakis(4-chlorophenyl)porphyrin (TpClPP)
e) $5,10,15,20$-tetrakis(4-bromophenyl)porphyrin (TpBrPP)
f) $5,10,15,20$-tetrakis(4-(methoxycarbonyl)phenyl)porphyrin (TpCOOCH$_3$PP)

Figure 6.12 shows optical microscopy images of the six ternary blend device films used in this study.

![Optical microscopy images](image)

Figure 6.12: Optical microscopy of MEH-PPV:porphyrin:PCBM 8:1:32 ternary blended device films, where the para-phenyl substituents are: (A) NH$_2$, (B) CH$_3$, (C) H, (D) Cl, (E) Br, (F) COOCH$_3$. The white scale bar represents 50 μm.

Each ternary mixture is well blended at optical microscopy resolution, and the series now contains the additional compounds tetrakis(4-aminophenyl)porphyrin (TpNH$_2$PP) and tetrakis(4-(methoxycarbonyl)phenyl)porphyrin (TpCOOCH$_3$PP). The performance
characteristics of the 8:1:32 ratio ternary blend devices are shown in Table 6.3. Note that they are once again listed in order of increasing Hammett $\sigma_{\text{para}}$, in Table 6.3 and in all subsequent graphs. A standard binary device is also shown for comparison.

Table 6.3: Device characteristics for MEH-PPV:porphyrin:PCBM 8:1:32 ternary blend OPV devices

<table>
<thead>
<tr>
<th>Porphyrin para-phenyl substituent</th>
<th>Efficiency %</th>
<th>$V_{oc}$ mV</th>
<th>$J_{sc}$ mA.cm$^{-2}$</th>
<th>Fill Factor</th>
<th>$R_s$</th>
<th>$R_{sh}$</th>
<th>Hammett $\sigma_{\text{para}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_2$</td>
<td>0.398 ±0.020</td>
<td>376 ±11.7</td>
<td>2.809 ±0.097</td>
<td>0.376 ±0.005</td>
<td>899</td>
<td>4661</td>
<td>-0.66</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>0.718 ±0.074</td>
<td>553 ±13.7</td>
<td>3.362 ±0.255</td>
<td>0.385 ±0.002</td>
<td>938</td>
<td>5001</td>
<td>-0.17</td>
</tr>
<tr>
<td>H</td>
<td>0.794 ±0.041</td>
<td>597 ±10.5</td>
<td>3.439 ±0.136</td>
<td>0.386 ±0.005</td>
<td>1037</td>
<td>6214</td>
<td>0</td>
</tr>
<tr>
<td>Cl</td>
<td>1.008 ±0.024</td>
<td>707 ±8.4</td>
<td>3.744 ±0.087</td>
<td>0.380 ±0.004</td>
<td>1097</td>
<td>8144</td>
<td>0.227</td>
</tr>
<tr>
<td>Br</td>
<td>1.131 ±0.035</td>
<td>712 ±8.9</td>
<td>3.964 ±0.077</td>
<td>0.401 ±0.007</td>
<td>755</td>
<td>7591</td>
<td>0.232</td>
</tr>
<tr>
<td>COOCH$_3$</td>
<td>1.173 ±0.090</td>
<td>720 ±9.3</td>
<td>3.989 ±0.266</td>
<td>0.408 ±0.003</td>
<td>561</td>
<td>6682</td>
<td>0.45</td>
</tr>
<tr>
<td>MEH-PPV:PCBM 8:32</td>
<td>1.464 ±0.141</td>
<td>842 ±6.5</td>
<td>4.488 ±0.319</td>
<td>0.387 ±0.013</td>
<td>574</td>
<td>9465</td>
<td>-</td>
</tr>
</tbody>
</table>

From Figure 6.13 below we once again observe that the power conversion efficiency of the MEH-PPV:porphyrin:PCBM ternary blend devices improves as the porphyrin para-phenyl substituents become more electron withdrawing (Hammett $\sigma_{\text{para}}$ increases). TpNH$_2$PP, with the lowest Hammett $\sigma_{\text{para}}$ of just -0.66, has the lowest efficiency in the series at 0.40 %. TpCOOCH$_3$PP, with the highest Hammett $\sigma_{\text{para}}$ of 0.45, has the highest average efficiency of the series at 1.17 %, however this only slightly improves on TpBrPP at 1.13 %.
Figure 6.13: Efficiency of MEH-PPV:porphyrin:PCBM 8:1:32 ternary blend OPV devices

![Efficiency Chart]

Figure 6.14: Open-circuit voltage of MEH-PPV:porphyrin:PCBM 8:1:32 ternary blend OPV devices

![Voltage Chart]

Figure 6.14 shows a steady increase in $V_{OC}$ as Hammett $\sigma_{para}$ increases to TpCIPP, where TpCIPP, TpBrPP and TpCOOCH$_3$PP have approximately the same voltage of slightly over 700
mV. If the electron donating or withdrawing character of the para-phenyl substituents on the porphyrins are having an effect on the HOMO and LUMO energy levels of the porphyrins, this result suggests that substituents with a Hammett $\sigma_{para}$ equivalent to 0.227 or higher (i.e. TpClPP, TpBrPP and TpCOOCH$_3$PP) are well set up energetically for exciton generation and charge separation between the porphyrin and other components of the blend, which allows an open-circuit voltage close to that of the binary blend to be achieved. Below a Hammett $\sigma_{para}$ of 0.227, the voltage decreases.

The fill factors of all of the ternary blend devices are similar and while the general trend of increasing shunt resistance with increasing porphyrin Hammett $\sigma_{para}$ is present (Table 6.3), the correlation is unsurprisingly weaker given that the porphyrin is now present at a much lower concentration of only 2.5%.

![Figure 6.15: Short-circuit current density of MEH-PPV:porphyrin:PCBM 8:1:32 ternary blend OPV devices](image)

Figure 6.15 shows an increase in short-circuit current density with increasing Hammett $\sigma_{para}$ of the porphyrins para-phenyl substituent, however again the effect is of lesser magnitude than it
was for the MEH-PPV:porphyrin:PCBM 4:4:32 ratio devices, which is due to the much smaller concentration of porphyrin in the active layer of the MEH-PPV:porphyrin:PCBM 8:1:32 ratio devices. We have earlier shown that blends containing porphyrins with more electron-withdrawing character display higher current output despite absorbing less light. The observed differences in current output between blends could be due to differences in the rates of porphyrin hole mobility. However, Meot-Ner and Adler [9] have shown that the basicity of the internal pyrrolic nitrogens (i.e. the molecular site at which hole may be trapped) actually decreases with increasing electron-withdrawing character of the porphyrin substituents, therefore we discount changes in hole mobility as a contributing factor. While the exact mechanism is unknown, we hypothesise that the observed increase in short-circuit current density is due to either a decrease in charge recombination or to differences in the scale of donor/acceptor phase separation (which is below the scale at which we are able to resolve). Either of these possibilities would lead to the observed reduction in both polymer and fullerene contribution to total external quantum efficiency with increasing electron-donating character of the porphyrin substituents (Figure 6.16).

It is clear from Figure 6.14 that the $V_{OC}$ is the dominant parameter contributing to the observed efficiencies, and that the $V_{OC}$ of the ternary blends is closely correlated with the Hammett $\sigma_{para}$ constants of the $para$-phenyl substituents of the porphyrins. A plot of device $V_{OC}$ against Hammett $\sigma_{para}$ constants for the MEH-PPV:porphyrin:PCBM 8:1:32 ternary blend OPV devices (Figure 6.17) gives an excellent linear correlation, with an $R^2$ of 0.97.
Figure 6.16: External quantum efficiency spectrum of MEH-PPV:porphyrin:PCBM 8:1:32 ternary blend OPV devices

Figure 6.17: Open-circuit voltage and Hammett $\sigma_{para}$ constants for MEH-PPV:porphyrin:PCBM 8:1:32 ternary blend OPV devices
The strong dependence of the efficiency of the ternary blend devices on $V_{OC}$ indicates that the variations in the electron withdrawing character of the porphyrin substituents affects the molecular orbital energy of the porphyrin, since the $V_{OC}$ is related to the HOMO$_{donor} -$ LUMO$_{acceptor}$ energy difference.

Kadish and Morrison [20] were the first to quantify the effect of electron-donating and electron-withdrawing substituents of free base porphyrins on the redox potentials of the porphyrins. Ransdell and Wamer [21] showed that Hammett constants can be used to predict redox potentials of freebase para-substituted tetraphenylporphyrins, observing a linear correlation between the oxidation potential of the porphyrin and the Hammett $\sigma$ constant, with deviations from linearity noted only for highly electron-donating substituents such as NH$_2$.

In order to probe the porphyrin energy levels, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of each porphyrin were determined both experimentally via cyclic voltammetry and UV-visible absorption spectroscopy, and theoretically via density functional theory (DFT) calculations. As shown in Table 6.4, the results obtained from both methods agree well with reported values [22, 23].

As the electron-withdrawing character of the porphyrin substituents increases, we observe a simultaneous decrease in the energies of both the HOMO and LUMO of the porphyrins. Moreover, while the DFT derived values for the energy levels are slightly higher than those which were experimentally derived (as discussed in previous chapters), the relative trend toward higher device efficiency with lower HOMO and LUMO energies is consistent, as seen in Figure 6.18. It is also interesting to note that both HOMO and LUMO decrease with increasing device efficiency at a similar rate, an observation consistent with the absorption spectra (Figure 6.10) which shows that the Soret bands of each porphyrin are of similar wavelength.
Table 6.4: Calculated and experimentally determined HOMOs and LUMOs for the para-substituted tetraphenylporphyrin used in this study. The model values were calculated using the B3LYP/6-31G(d) DFT method.

<table>
<thead>
<tr>
<th>Porphyrin para-phenyl substituent</th>
<th>Hammett $\sigma_{para}$</th>
<th>Calculated HOMO / eV</th>
<th>Calculated LUMO / eV</th>
<th>Experimental HOMO / eV</th>
<th>Experimental LUMO / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_2$</td>
<td>-0.66</td>
<td>-4.47</td>
<td>-1.87</td>
<td>-5.15</td>
<td>-2.36</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>-0.17</td>
<td>-4.80</td>
<td>-2.11</td>
<td>-5.42</td>
<td>-2.54</td>
</tr>
<tr>
<td>H</td>
<td>0</td>
<td>-4.91</td>
<td>-2.20</td>
<td>-5.44</td>
<td>-2.56</td>
</tr>
<tr>
<td>Cl</td>
<td>0.227</td>
<td>-5.28</td>
<td>-2.56</td>
<td>-5.55</td>
<td>-2.66</td>
</tr>
<tr>
<td>Br</td>
<td>0.232</td>
<td>-5.27</td>
<td>-2.56</td>
<td>-5.52</td>
<td>-2.64</td>
</tr>
<tr>
<td>COOCH$_3$</td>
<td>0.45</td>
<td>-5.22</td>
<td>-2.52</td>
<td>-5.61</td>
<td>-2.74</td>
</tr>
</tbody>
</table>

Figure 6.18: HOMO and LUMO energies (modelled and experimental) of para-phenyl substituted tetraphenylporphyrins and the efficiency of the corresponding MEH-PPV:porphyrin:PCBM 8:1:32 ternary blend OPV devices.
A plot of $V_{OC}$ against modelled HOMO shows that the two parameters are closely aligned, with device $V_{OC}$ increasing almost linearly as the HOMO of the porphyrin decreases (Figure 6.19), despite the porphyrin being present at only 2.5 % concentration in the active layer blend. Clearly the porphyrin component has significant influence on the performance of the device.

![Figure 6.19: Open-circuit voltage of MEH-PPV:porphyrin:PCBM 8:1:32 ternary blend OPV devices and the modelled HOMO of the corresponding porphyrins](image)

Oxidation of *para*-phenyl substituted freebase tetraphenylporphyrins usually occurs as a single electron transfer from the porphyrin π system, except when the substituent is highly electron-donating (e.g. alkoxy and amino substituents) in which case the initial oxidation is believed to occur at the phenyl rings rather than at the porphyrin ring [21]. The addition of substituents of increasing electron-withdrawing ability in the porphyrin *para*-phenyl position decreases electron-density in the porphyrin core which then results in a decrease in the energy of the HOMO of the porphyrin [9]. Since the porphyrin is the electron donor molecule in this system, the porphyrin HOMO energy is altered such that the $HOMO_{donor} - LUMO_{acceptor}$ energy gap is
widened. This increase in energy gap is responsible for the improved device $V_{OC}$, which is the dominant parameter driving the observed enhancements in device efficiency.

In addition to the HOMO$_{donor} - $LUMO$_{acceptor}$ energy gap, we must also consider the placement of the orbitals in relation to the other components of the active layer such as the polymer and fullerene. The overall energy diagram of the devices (Figure 6.20) shows that the LUMO levels of all of the porphyrins sit above that of the polymer, therefore they are well placed to transfer electrons to either the polymer or the fullerene species. The HOMO energies, however, are not all placed ideally with respect to the other device components. The TpNH$_2$PP HOMO, which is positioned at -4.47 eV, is above the energy of the ITO electrode and therefore too high to allow successful hole transfer to the electrode, which causes the TpNH$_2$PP to trap holes and act as a recombination site in the device. The other porphyrins (particularly those with the lowest three HOMOs: TpClPP, TpBrPP and TpCOOCH$_3$PP) have orbital energies that are well placed for charge transfer to the polymer, the PEDOT:PSS interfacial layer and electrode, and therefore in those ternary blends, trapping sites within the active layer are minimised, allowing a higher open-circuit voltage from the materials to be achieved.

It might appear that the data presented in this chapter showing a linear increase in device $V_{OC}$ with decreasing HOMO energy of the porphyrin is in conflict with that of the previous chapter, where we showed a distinct threshold HOMO level between -4.46 and -4.48 eV below which the energy levels were no longer mismatched and the device “switched on”, improving $V_{OC}$ dramatically. At first, such a defined threshold does not appear to exist for the current study.

In order to investigate this point more fully, we will now compare the device data from Chapters 5 and 6.
Clearly the molecules studied in both chapters are quite different in terms of size, functionality, porphine core structure, and whether or not they are in a metallated or freebase form. However, if we assume that it is primarily the HOMO energy of the porphyrins that drives the efficiency of the devices through improvements in $V_{OC}$, we can compare both sets of data by plotting HOMO against $V_{OC}$ for both.

Obviously we see a change in $V_{OC}$ if the materials ratio of the components is altered, as we are affecting the relative contribution of each material to the whole. However, we do observe that the trends in device performance remain the same, regardless of blend ratios. For example, Figure 6.21 shows that in the current chapter, while the materials ratio of components in the blend was altered from 1:1:8 to 8:1:32 due to solubility limitations of some of the porphyrins,
the trend of improving $V_{oc}$ with increasing electron-withdrawing character of the para-phenyl substituent of the porphyrin remained constant.

Figure 6.21: Modelled HOMO of the porphyrins used in this study and the corresponding $V_{oc}$ of the ternary blend solar cells containing each porphyrin, at both the 1:1:8 and 8:1:32 blend ratios

For a valid comparison to be made, the materials ratio should be constant between studies, therefore in both case we will compare the MEH-PPV:porphyrin:PCBM data presented at the 1:1:8 (i.e. 4:4:32) blend ratio. As stated earlier, the TpCOOCH$_3$PP and TpNH$_2$PP were unable to be included in the 1:1:8 blend ratio series due to solubility limitations. However, as this chapter has clearly established (as have others in the literature, see [20] and [21]), there is a strong linear correlation between the Hammett $\sigma$$_{para}$ and the oxidation potential of the porphyrin. Therefore, had the TpCOOCH$_3$PP and TpNH$_2$PP had high enough solubility at the 1:1:8 blend ratio, it seems reasonable to hypothesise that they would follow the same trends as previously observed. We can therefore interpolate their positions onto Figure 6.22 by
plotting a line of best fit (using a least-squares algorithm) and inserting the interpolated points alone the trend line at the position of their HOMO energy. Figure 6.22 plots the positions of the HOMO of all of the porphyrinoids studied in Chapters 5 and 6 against the corresponding $V_{OC}$ of the ternary blend devices containing each porphyrinoid species.

![Figure 6.22: Modelled HOMO and $V_{OC}$ for the porphyrinoids studied in Chapter 5 and 6 of this thesis. Red diamonds represent Chapter 5 data points, and the red dashed line is a linear fit trend line of above-threshold data points. Blue circles represent Chapter 6 data points, and the blue dashed line is the linear fit trend line. The purple squares are the interpolated data points representing the position of TpNH$_2$PP and TpCOOCH$_3$PP at the 1:1:8 blend ratio. The green solid line represents the position of the threshold energy level between -4.46 and -4.48 eV](image)

We see that in fact TpNH$_2$PP is positioned directly on the threshold voltage, defined as between -4.46 and -4.48 in Chapter 5. The remaining porphyrins from the present study, which all have HOMOs below -4.48 eV, exceed this threshold level and therefore display much higher open-circuit voltages. We therefore observe three distinct types of porphyrin:
1) Porphyrsins with a HOMO energy below the threshold level (the solid green line in Figure 6.22) where the HOMO is too high in energy to pass transfer holes to the ITO electrode, thus the porphyrin acts as a hole trapping species leading to charge recombination. There is a very sharp transition at the threshold level between -4.46 and -4.48 eV, and ternary devices with porphyrins near to the threshold display large variations in $V_{OC}$ depending on which side of the threshold they fall.

2) Porphyrsins that appear to “switch on” and achieve high $V_{OC}$’s provided that the threshold energy level of the HOMO has been exceeded.

3) Porphyrsins above the threshold energy level that, whilst having high $V_{OC}$’s, can be further improved upon by lowering the donor’s HOMO and thus expanding the $\text{HOMO}_{\text{donor}}-\text{LUMO}_{\text{acceptor}}$ gap, leading to improved power conversion efficiency through enhanced $V_{OC}$’s.

We attribute the differences between points (2) and (3) above to a combination of structural and electronic changes in the porphyrins. For example, the porphyridoids in Chapter 5 with HOMOs exceeding the threshold energy level likely display the observed dramatic improvements through a combination of both peripheral steric bulk effects which lead to increased charge separation distances, and metallation and methylation of the porphyrin which “shields” holes diffusing through the bulk of the active layer film from the basic pyrrolic nitrogens. Porphyrin studied in the current chapter lack both of these features, therefore the improvements upon crossing the threshold energy are not of as great a magnitude; however, improvements can clearly be achieved through electronic adjustments.

### 6.5 Conclusions

We have shown that modification of the electron-donating or electron-withdrawing character of the substituents in the para-phenyl position of tetraphenylporphyrin has a significant and
controllable effect on the performance of ternary MEH-PPV:porphyrin:PCBM bulk heterojunction organic solar cells. Increasing the electron-withdrawing ability of the substituents, as quantified by the Hammett $\sigma_{\text{para}}$ constant, leads to an improvement in device efficiency which is driven primarily through enhancements to the open-circuit voltage of the cell. Substituents with a larger Hammett $\sigma_{\text{para}}$ constant were found to increase the oxidation potential of the porphyrin, leading to a decrease in the highest occupied molecular orbital energy, which improves device $V_{\text{OC}}$ through widening of the $\text{HOMO}_{\text{donor}}$-$\text{LUMO}_{\text{acceptor}}$ energy gap. Comparison with data from the previous chapter suggested that further improvements to device efficiency might be achieved through a combination of both electronic and structural modifications, so that the porphyrin is not only well-placed energetically within the ternary blend system, but that molecular centres for charge recombination are both spatially separated from other device components and chemically shielded from diffusing charges.

In summary, we have shown the application of Hammett parameters to design porphyrins that are energetically compatible with polymer:fullerene solar cells, and the ability to fine-tune the porphyrin HOMO energy to achieve significant gains in ternary blend device efficiency.

6.6 References


Chapter 7 – The effect of transition metal octaethylporphyrin and tetrphenylporphyrin dopants on the performance of MEH-PPV:PCBM organic solar cells

7.1 Introduction

A number of recent publications have reported limited success utilising metallated porphyrins and phthalocyanines as photosensitisers in organic solar cells [1-7]. However, to date there has been no systematic study investigating the variation in device performance from a series of d-block transition metal porphyrins as ternary blend dopant molecules. In this chapter, we will probe the effect of the addition of a series of metallo-tetraphenylporphyrins (M-TPP) and metallo-octaethylporphyrins (M-OEP) on the performance of organic photovoltaic devices with an MEH-PPV:porphyrin:PCBM blend active layer. Additionally, the effect on device performance of altering the structure of the porphyrin ligand itself will be discussed by comparing device performance of both M-TPP and M-OEP ternary blends bearing identical central metal ions.

7.2 Porphyrinoids used in this study

A broad range of metallo-tetraphenylporphyrins and metallo-octaethylporphyrins were initially selected for this study, and are listed in Table 7.1, with the corresponding chemical structures presented in Figure 7.1. The initial goal was to screen a selection of compounds varying primarily in the identity of the central transition metal ion, and from this survey select the most appropriate compounds for further study, excluding any compounds not suitable due to factors such as poor solubility or energetic mismatch with other components of the blend.
Table 7.1: Porphyrinoids used in this study

<table>
<thead>
<tr>
<th>Metallo-octaethylporphyrin</th>
<th>Metallo-tetraphenylporphyrin</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Central atom</strong></td>
<td><strong>Oxidation state</strong></td>
</tr>
<tr>
<td>H₂</td>
<td>-</td>
</tr>
<tr>
<td>V</td>
<td>4</td>
</tr>
<tr>
<td>Mn</td>
<td>3</td>
</tr>
<tr>
<td>Fe</td>
<td>3</td>
</tr>
<tr>
<td>Co</td>
<td>2</td>
</tr>
<tr>
<td>Ni</td>
<td>2</td>
</tr>
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<td>2</td>
</tr>
<tr>
<td>Ru</td>
<td>2</td>
</tr>
<tr>
<td>Pd</td>
<td>2</td>
</tr>
<tr>
<td>Pt</td>
<td>2</td>
</tr>
</tbody>
</table>

Figure 7.1: The chemical structure of metallated OEP (left) where M = H₂, V⁴⁺, Mn³⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Ru²⁺, Pd²⁺ or Pt²⁺; and the chemical structure for metallated TPP (right) where M = H₂, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Pd²⁺, Ag²⁺ or Pt²⁺. Axial ligands present for some compounds (V, Mn, Fe and Ru porphyrins) have been omitted from the diagram for simplicity.
Beginning with the metallo-octaethylporphyrins, ternary blend device films were spin-coated from a blend of MEH-PPV:M-OEP:PCBM with a weight ratio of 4:4:32 dissolved in chlorobenzene, a blend ratio consistent with our previous publications [8, 9]. Optical microscopy of the films appears in Figure 7.2.

![Figure 7.2: Optical microscopy of MEH-PPV:PCBM 8:32 device film (A) and metalated octaethylporphyrin:MEH-PPV:PCBM 4:4:32 ternary blended device films, where the central metal species is: (B) vanadium (IV) oxide, (C) manganese (III) chloride, (D) iron (III) chloride, (E) nickel (II), (F) ruthenium (II) carbonyl, (G) palladium (II), (H) platinum (II). The white scale bar represents 100 μm.](image)

There are clearly significant solubility issues with some of the ternary blends, most notably those containing the [2,3,7,8,12,13,17,18-octaethylporphyrinato] manganese(III) chloride (Mn-OEP.Cl), [2,3,7,8,12,13,17,18-octaethylporphyrinato] iron(III) chloride (Fe-OEP.Cl), and [2,3,7,8,12,13,17,18-octaethylporphyrinato] ruthenium(II) carbonyl (Ru-OEP.C=O).

In an effort to improve the morphology of the ternary blend films, the MEH-PPV:porphyrin:PCBM weight ratio was changed to 8:1:32 mg/mL in chlorobenzene. This represents a standard MEH-PPV:PCBM 8:32 blend ratio with the incorporation of approximately 2.5 % porphyrin dopant by weight, consistent with the blend ratio in Chapter 6. This component ratio was shown to be a low enough porphyrin concentration for favourable
film active layer morphology to be maintained, whilst still containing enough porphyrin content to have a significant effect on ternary device performance and thus probe the effect of porphyrin inclusion on device function. Publications of ternary blends containing similar small amounts of dopant (<5 % porphyrin/phthalocyanine) have appeared recently [3, 4] and have shown that the use of a small amount of dopant molecule is a successful strategy to achieve improved efficiency over a standard binary device. Moreover, increasing the concentration of the porphyrinoid beyond 5 % has generally been shown to reduce charge transport by disrupting polymer and fullerene domains, which lead to a decrease in overall device performance [10]. The molecular weight of transition metal porphyrins can vary significantly depending on the identity of the central metal, so the mass of each porphyrin added to the blend was made equimolar based on 1 mg of tetraphenylporphyrin (TPP). Consistent molarity ensures that the number of light-absorbing porphyrin chromophore in the active layer film remains constant. Thus the actual MEH-PPV:porphyrin:PCBM weight ratio of all blends in this study varied from 8:0.9:32 to 8:1.2:32, representing a constant [MEH-PPV monomer]:[porphyrin molecule]:[PCBM molecule] ratio of approximately 19:1:22. Hereafter, the blend ratio of 8:1:32 shall be stated to mean equimolar porphyrin content of approximately 2.5 % based on TPP, although it should be understood that the actual ratio differs slightly based on the molecular weight of the porphyrin, as explained above.

Optical microscopy of the films of the MEH-PPV:OEP:PCBM 8:1:32 blended active layer OPVs can be seen in Figure 7.3. The improvement in morphology after moving to the 8:1:32 ratio is clear, with only the ternary blend films containing metalloporphyrins bearing chloride axial ligands still suffering from poor porphyrin solubility and visible surface aggregates. The power conversion efficiency of the devices (Figure 7.4) shows large variations, considering that the majority of the blend components are unchanged (note that only 2.5% of the blend by weight is porphyrin, the remaining material in each blend is a constant 1:4 ratio of MEH-PPV:PCBM).
Figure 7.3: Optical microscopy of MEH-PPV:PCBM 8:32 device film (A) and M-OEP:MEH-PPV:PCBM 1:8:32 ternary blended device films, where the central metal species is: (B) vanadium (IV) oxide, (C) manganese (III) chloride, (D) iron (III) chloride, (E) cobalt (II), (F) nickel (II), (G) copper (II), (H) zinc (II), (I) ruthenium (II) carbonyl, (J) palladium (II), (K) platinum (II), (L) H$_2$OEP. The white scale bar represents 100 μm.

Figure 7.4: Power conversion efficiency of a MEH-PPV:PCBM 1:4 binary device and MEH-PPV:M-OEP:PCBM ternary devices containing approximately 2.5 % M-OEP by weight. Note that all M-OEPs are present in equimolar amounts.
The large variation in performance is unsurprising, as transition metals vary enormously in their chemical properties, most notably in their mass, size, electron configuration, and in the large number of oxidation states in which transition metals can exist. The chemistry and structure of transition metal porphyrinoids is correspondingly diverse, thus transition metal porphyrinoids have found application in areas such as catalysis [11-16], photodynamic therapy [17-20], dye-sensitised solar cells [21-26], as artificial heme analogues [27-32] and in redox chemistry [33-36].

In order to discover and understand trends present in the data, the focus was narrowed to a smaller series of compounds, whose central metal ions are adjacent in the periodic table. As the oxidation state of transition metal compounds can vary widely (e.g. oxidation states can be as low as -2 for some iron compounds [37], and as high as +8 for some osmium compounds [38]), we decided to focus only on metallo-octaethylporphyrins and metallo-tetraphenylporphyrins with central metal cations in the +2 oxidation state. The geometry around the metal ion in metalloporphyrins also varies considerably depending on the presence or absence of axial ligands (e.g. both Fe(II) and Fe(III) porphyrins can exist as four, five-, and six-coordinate derivatives [39]) and while the geometry around the metal is typically square-planar (or slightly out-of-plane), square pyramidal, or octahedral [39], some unusual geometries such as slipped and skewed [40] or mono-, di-, and triatom bridged dimers [41] have also been reported. Axial ligands are common in transition metal porphyrins, and changing the ligand is known to alter both the spectral [42] and electrochemical [43] properties of the compound. Thus for the present study, only d-block transition metal porphyrins in the +2 oxidation state which do not have any axial ligands, were studied. These exclusions avoid complications such as large variations in the extent of porphyrin-porphyrin aggregation or in the solubility of the transition metal complex which can be affected by changes in oxidation state and ligand identity and therefore will allow trends in the data to be more readily understood.
We therefore focused only on the following transition metal octaethylporphyrins and tetraphenylporphyrins (Figure 7.5):

- **Period 4** transition metal octaethylporphyrins and tetraphenylporphyrins occurring across a row of the periodic table
  - Co-OEP and Co-TPP
  - Ni-OEP and Ni-TPP
  - Cu-OEP and Cu-TPP

- **Group 10** transition metal octaethylporphyrins and tetraphenylporphyrins occurring down a column of the periodic table
  - Ni-OEP and Ni-TPP
  - Pd-OEP and Pd-TPP
  - Pt-OEP and Pt-TPP

---

<table>
<thead>
<tr>
<th>Group</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
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<tr>
<td><strong>Period 4</strong></td>
<td>Sc</td>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
<td>Fe</td>
<td>Co</td>
<td>Ni</td>
<td>Cu</td>
<td>Zn</td>
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<td><strong>Period 5</strong></td>
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<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
<td>Rh</td>
<td>Pd</td>
<td>Ag</td>
<td>Cd</td>
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<tr>
<td><strong>Period 6</strong></td>
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<td>Re</td>
<td>Os</td>
<td>Ir</td>
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<td>Hs</td>
<td>Mt</td>
<td>Ds</td>
<td>Rg</td>
<td>Cn</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 7.5:** Transition metals used as the central divalent cations of metallo-octaethylporphyrins and metallo-tetraphenylporphyrins used in this study (highlighted in yellow). Compounds excluded from the study are shaded grey.

The device characteristics for MEH-PPV:PCBM organic solar cells doped with approximately 2.5% metalloporphyrin (all porphyrins are present in equimolar amounts) are presented in Table 7.2, with a plot of the power conversion efficiency of these devices in Figure 7.6. Note that a standard (control) MEH-PPV:PCBM device is shown in Table 7.2 for comparison, but omitted from the graph.

<table>
<thead>
<tr>
<th>Device</th>
<th>$V_{oc}$/ mV</th>
<th>$J_{sc}$/ mA/cm$^2$</th>
<th>FF</th>
<th>PCE / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEH-PPV:PCBM (8:32)</td>
<td>854 ±8</td>
<td>4.189 ±0.112</td>
<td>0.386 ±0.007</td>
<td>1.381 ±0.101</td>
</tr>
<tr>
<td>MEH-PPV:Co-OEP:PCBM (8:1:32)</td>
<td>789 ±23</td>
<td>3.590 ±0.074</td>
<td>0.356 ±0.012</td>
<td>1.009 ±0.074</td>
</tr>
<tr>
<td>MEH-PPV:Ni-OEP:PCBM (8:1:32)</td>
<td>841 ±3</td>
<td>3.647 ±0.097</td>
<td>0.385 ±0.002</td>
<td>1.183 ±0.024</td>
</tr>
<tr>
<td>MEH-PPV: Cu-OEP:PCBM (8:1:32)</td>
<td>814 ±4</td>
<td>4.482 ±0.048</td>
<td>0.395 ±0.004</td>
<td>1.440 ±0.033</td>
</tr>
<tr>
<td>MEH-PPV:Co-TPP:PCBM (8:1:1:32)</td>
<td>731 ±16</td>
<td>1.552 ±0.040</td>
<td>0.354 ±0.013</td>
<td>0.402 ±0.027</td>
</tr>
<tr>
<td>MEH-PPV:Ni-TPP:PCBM (8:1:1:32)</td>
<td>700 ±17</td>
<td>2.752 ±0.099</td>
<td>0.422 ±0.010</td>
<td>0.813 ±0.041</td>
</tr>
<tr>
<td>MEH-PPV: Cu-TPP:PCBM (8:1:1:32)</td>
<td>705 ±7</td>
<td>3.371 ±0.115</td>
<td>0.439 ±0.019</td>
<td>1.040 ±0.022</td>
</tr>
</tbody>
</table>
Figure 7.6: Power conversion efficiency of MEH-PPV:M-OEP:PCBM 8:1:32 and MEH-PPV:M-TPP:PCBM 8:1:32 ternary devices containing approximately 2.5 % porphyrin by weight. Note that all porphyrins are present in equimolar amounts.

Clearly there is significant variation in the performance of each device. The porphyrins in Figure 7.6 are arranged in the same order that their central metal atoms appear in period 4 of the periodic table. We observe a systematic increase in device efficiency as we progress across the periodic table, with Co-OEP < Ni-OEP < Zn-OEP, and with the same trend repeated for the M-TPPs. Note that whilst all porphyrins are present in equimolar amounts, the power conversion efficiency is considerably higher for those ternary devices containing metalloporphyrins based upon the octaethylporphyrin ligand than those based on the tetraphenylporphyrin ligand. This difference in performance when changing ligand will be addressed later in this chapter.

There are a number of possible factors to explain the trends in efficiency observed in Figure 7.6. Firstly, favourable active layer device morphology, known to be crucial to the performance of organic photovoltaic cells [44], may be disrupted by porphyrin addition, as porphyrins are
well known for their aggregation properties [45-47]. However, it can be seen from the optical microscopy in Figure 7.7 (M-OEP) and Figure 7.8 (M-TPP) that each ternary film appears uniformly blended, at least at the optical scale shown, lacking the gross aggregation present for some of the materials shown previously in Figure 7.2. Whilst we have not had the opportunity to perform nano-scale microscopy (STXM) of these films, we have previously demonstrated that similar ternary MEH-PPV:porphyrin:PCBM OPV films can indeed blend uniformly down to the nano-scale, with no observable change in active layer morphology [8, 9]. It is therefore believed that large-scale disruption of active layer morphology is not responsible for the observed trends.

Figure 7.7: Optical microscopy of MEH-PPV:PCBM 8:32 device film (A) and MEH-PPV:porphyrin:PCBM 8:1:32 ternary blended device films, where the porphyrin species is: (B) Co-OEP (C) Ni-OEP and (D) Cu-OEP. The white scale bar represents 100 μm
Figure 7.8: Optical microscopy of MEH-PPV:PCBM 8:32 device film (A) and MEH-PPV:porphyrin:PCBM 8:1:32 ternary blended device films, where the porphyrin species is: (B) Co-TPP (C) Ni-TPP and (D) Cu-TPP. The white scale bar represents 100 μm.

Each ternary blend contained the same molecular ratio of blend constituents, with the only difference in composition being the identity of the porphyrin. All of the device blends were of similar thickness (120 ±10 nm) so a variation in the number of porphyrin or polymer chromophores can be excluded as a factor affecting device performance.

Energetic alignment of the valence orbitals of OPV active layer materials is crucial for optimised device performance [48], and we have previously shown that poor energetic positioning of porphyrin HOMOs relative to other active layer components significantly lowers device efficiency [9]. Table 7.4 shows the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and bandgap of each M-OEP and M-TPP. Note that these are calculated values using the B3LYP/6-31G(d) density functional theory (DFT) method. We have previously shown through comparison to experimentally derived values and to literature values that they provide a good indication of the relative HOMO and LUMO values of our materials [9]. From Table 7.3 and the energy level diagram shown in Figure 7.9 we see that the...
energy levels of the compounds in each set (M-OEP or M-TPP) are essentially constant, with little difference in either the HOMO or LUMO energy of the porphyrins. Consequently we observed very little variation in the open-circuit voltage within each set of porphyrins (Table 7.2). Furthermore, from Figure 7.9 we see that each compound has a LUMO energy well positioned for transfer of an electron to the polymer or PCBM, and a HOMO well placed to accept holes from the PCBM for transfer to the ITO electrode. Therefore variations in the energy levels of the porphyrins are unlikely to be responsible for the observed trend in device efficiency.

Table 7.3: Calculated highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and bandgap for Co-OEP, Ni-OEP, Cu-OEP, Co-TPP, Ni-TPP and Cu-TPP. The model values were calculated using the B3LYP/6-31G(d) DFT method.

<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>HOMO / eV</th>
<th>LUMO / eV</th>
<th>Bandgap / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-OEP</td>
<td>-4.84</td>
<td>-1.75</td>
<td>3.09</td>
</tr>
<tr>
<td>Ni-OEP</td>
<td>-4.80</td>
<td>-1.73</td>
<td>3.07</td>
</tr>
<tr>
<td>Cu-OEP</td>
<td>-4.81</td>
<td>-1.78</td>
<td>3.03</td>
</tr>
<tr>
<td>Co-TPP</td>
<td>-4.99</td>
<td>-2.25</td>
<td>2.74</td>
</tr>
<tr>
<td>Ni-TPP</td>
<td>-5.08</td>
<td>-2.03</td>
<td>3.05</td>
</tr>
<tr>
<td>Cu-TPP</td>
<td>-5.00</td>
<td>-2.09</td>
<td>2.91</td>
</tr>
</tbody>
</table>
From Table 7.2 we see that the open-circuit voltage ($V_{oc}$) within each set of porphyrins is essentially unchanged, as a result of the similar energy levels of the porphyrins within each series. There is a slight positive correlation between device efficiency and fill factor (FF), which certainly contributes to the enhanced performance observed as our series progresses across Period 4 of the periodic table. However, it is the short-circuit current density ($J_{sc}$) seen in Figure 7.10 which correlates most closely with device efficiency, and contributes most significantly to the observed trends in device performance within each set (M-OEP or M-TPP) of porphyrin materials.
Figure 7.10: Short-circuit current density of MEH-PPV:M-OEP:PCBM 8:1:32 and MEH-PPV:M-TPP:PCBM 8:1:32 ternary devices containing approximately 2.5 % porphyrin by weight. Note that all porphyrins are present in equimolar amounts.

As the ternary blend devices each contain a different porphyrin species, the observed increase in $J_{SC}$ could be due to an increase in the total light absorbed by the porphyrin chromophore. From the UV-visible spectroscopy of the ternary MEH-PPV:M-OEP:PCBM 8:1:32 active layer films shown in Figure 7.11, it appears that there is a greater contribution to the active layer light absorption at the porphyrin Soret peak (at around 410-420 nm) for those blends showing greater device efficiency, therefore it is possible that the more efficient devices may have improved performance due to an increase in light absorption and subsequent charge carrier generation by the porphyrin.
It is clear from the UV-vis absorption spectra of the pure porphyrins (Figure 7.12) that the majority of visible light absorbed by the porphyrins occurs at the Soret peak around 410 – 420 nm. To quantify the amount of light absorbed, the molar absorption coefficient at the Soret peak of each porphyrin in dichloromethane solution was determined (Figure 7.13). Although the molar extinction coefficient only specifies the maximum absorption at a single wavelength, in this case it is a good indication of the relative amount of light absorbed by each porphyrin as the Soret peak arises from the dominant absorption process, a transition from the ground state to the second excited state ($S_0 \rightarrow S_2$) which is much stronger than the transition to the first excited state ($S_0 \rightarrow S_1$) that produces the remaining weak Q-band absorption peaks [49]. Therefore the majority of light absorption occurs at the Soret absorption peak, and so we will use this as a measure of the relative light absorption by each compound.

Figure 7.11: UV-visible spectroscopy of the active layer films of an MEH-PPV:PCBM 1:4 binary device and MEH-PPV:M-OEP:PCBM ternary devices containing approximately 2.5% M-OEP by weight. Note that all porphyrins are present in equimolar amounts.
Figure 7.12: UV-visible absorption spectra of Co-OEP, Ni-OEP and Cu-OEP in dichloromethane solution

Figure 7.13: Soret molar absorption coefficients for the M-OEP and M-TPP series, measured at the Soret peak in dichloromethane
We observe that the molar extinction coefficient at the porphyrin Soret peak follows the same trend as do both the device efficiency (Figure 7.6) and $J_{SC}$ (Figure 7.10), increasing from Co-porphyrin < Ni-porphyrin < Cu-porphyrin in both the M-OEP and M-TPP series of ternary devices. We therefore hypothesise that the increased amount of light absorption by the porphyrin chromophores are contributing directly to the observed $J_{SC}$, thus improving the efficiency as we progress across period 4 of the periodic table from Co < Ni < Cu.

Figure 7.14 shows the external quantum efficiency (EQE) of an MEH-PPV:PCBM 1:4 binary device and MEH-PPV:M-OEP:PCBM ternary devices containing approximately 2.5% M-OEP by weight, normalised to the polymer absorption peak to highlight the relative porphyrin contribution to the overall EQE.

Figure 7.14: Normalised EQE of an MEH-PPV:PCBM 1:4 binary device and MEH-PPV:M-OEP:PCBM ternary devices containing approximately 2.5% M-OEP by weight. Note that all porphyrins are present in equimolar amounts.
Comparison with the UV-vis absorption spectra in Figure 7.11 clearly indicates that the porphyrin Soret peak is contributing to photocurrent, particularly for the highest performing device using the Cu-OEP dopant, where the peak at 415 nm shows that the porphyrin is contributing significantly, even though it is present at concentrations of only 2.5 % by mass. We also see that the magnitude of the contribution within this series follows the same trend as observed in the molar absorption coefficient of the porphyrin compounds, increasing from Co < Ni < Cu, thus each porphyrin contributes a progressively greater percentage of photocurrent to the devices, relative to the polymer absorption peak, by virtue of improved light absorption and subsequent exciton generation. Although not shown, the same trend is observed for the MEH-PPV:M-TPP:PCBM series of devices.

Despite the relative contribution of each porphyrin, we see from the raw EQE graph shown in Figure 7.15 that only the ternary blend device containing the Cu-OEP shows improved overall photocurrent generation compared with a standard MEH-PPV:PCBM 8:32 binary organic solar cell, whilst the ternary devices containing Co-OEP and Ni-OEP suffer a reduction in current of approximately 15% compared with the standard MEH-PPV:PCBM device.

Whilst the exact mechanism of the observed reduction in performance in some of the blends is unknown, we believe that the losses are at least partly due to increased recombination resulting in reduced shunt resistances in the Co-OEP and Ni-OEP ternary devices.
Figure 7.15: EQE of an MEH-PPV:PCBM 1:4 binary device and MEH-PPV:M-OEP:PCBM ternary devices containing approximately 2.5% M-OEP by weight. Note that all porphyrins are present in equimolar amounts.

Figure 7.16: Fill factors of MEH-PPV:M-OEP:PCBM 8:1:32 and MEH-PPV:M-TPP:PCBM 8:1:32 ternary devices containing approximately 2.5% porphyrin by weight. Note that all porphyrins are present in equimolar amounts.
From Figure 7.16 we observe that the fill factor of the devices decreases with decreased efficiency. The reduction in fill factor can be due to a reduction shunt resistance ($R_{sh}$), an increase in series resistance ($R_s$), or both. The series resistance of an organic solar cell is a function of the combined resistivity of the organic materials, the electrodes, and the interfaces between these layers, while the shunt resistance is a function of both geminate and bimolecular recombination, as well as sources of leakage current such as defect sites in the active layer [50]. These resistances can be approximated from the I-V curves under illumination, with $R_s$ equal to the inverse of the slope at $I = 0$, $R_{sh}$ equal to the inverse of the slope at $V = 0$, and in an ideal cell $R_s = 0$ and $R_{sh} \to \infty$ [51]. The series and shunt resistances for the MEH-PPV:M-OEP:PCBM series have been calculated and are shown in Table 7.4.

Table 7.4: Series and shunt resistances for standard MEH-PPV:PCBM 8:32 and ternary MEH-PPV:M-OEP:PCBM 8:1:32 devices containing approximately 2.5 % porphyrin by weight. Note that all porphyrins are present in equimolar amounts.

<table>
<thead>
<tr>
<th>Blend</th>
<th>$R_s$ (Ω)</th>
<th>$R_{sh}$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>with 2.5 % Co-OEP</td>
<td>925</td>
<td>7656</td>
</tr>
<tr>
<td>with 2.5 % Ni-OEP</td>
<td>540</td>
<td>8232</td>
</tr>
<tr>
<td>with 2.5 % Cu-OEP</td>
<td>677</td>
<td>12435</td>
</tr>
</tbody>
</table>

Although $R_s$ is highest for the lowest efficiency device (Co-OEP) suggesting some additional series resistance between materials in that particular blend, there is no clear trend in $R_s$ across the series. The $R_{sh}$ however does correlate well with device efficiency, with the best performing device Cu-OEP having significantly improved $R_{sh}$ compared with the other two ternary blends. The lower $R_{sh}$ in the Co-OEP and Ni-OEP devices suggest that they suffer from enhanced recombination losses compared with the Cu-OEP devices, and while there is no apparent reduction of open-circuit voltage between each blend, there is a general reduction in
current generation observed in the EQE plot (Figure 7.15) across the entire spectrum, including a reduction in current generation on the polymer absorption peak, observed for the lower performing devices.

Recombination losses are minimised for the Cu-OEP blend, such that the EQE of the polymer:fullerene matrix is unaffected by the addition of the Cu-OEP, therefore enhanced light absorption by the Cu-OEP Soret transition improves power conversion efficiency over that of the standard binary device. While only a modest improvement, we have shown an enhancement of approximately 5% to the efficiency of an MEH-PPV:PCBM solar cell by the addition of 2.5% by weight of the ternary dopant chromophore, Cu-OEP, through a combination of reduced charge recombination and enhanced light absorption by the porphyrin chromophore.


Trends in the effect of the addition of Group 10 transition metal octaethylporphyrins and tetraphenylporphyrins to MEH-PPV:PCBM organic solar cells will now be investigated. The six porphyrin compounds used in this study are:

- Ni-OEP and Ni-TPP
- Pd-OEP and Pd-TPP
- Pt-OEP and Pt-TPP

The device characteristics for MEH-PPV:PCBM organic solar cells doped with approximately 2.5% metalloporphyrin (all porphyrins are present in equimolar amounts) are presented in Table 7.5, with a plot of the power conversion efficiency of these devices in Figure 7.17. Note that a standard (control) MEH-PPV:PCBM device is shown in Table 7.5 for comparison, but omitted from the graph.
Table 7.5: Device characteristics for a standard MEH-PPV:PCBM 8:32 device and for MEH-PPV:M-OEP:PCBM 8:1:32 and MEH-PPV:M-TPP:PCBM 8:1:32 devices. All porphyrins are equimolar with 1 mg of TPP. The errors have been calculated from the standard deviation across a minimum of six independent OPV devices.

<table>
<thead>
<tr>
<th>Device</th>
<th>( V_{oc} ) / mV</th>
<th>( J_{sc} ) / mA/cm²</th>
<th>FF</th>
<th>PCE / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEH-PPV:PCBM (8:32)</td>
<td>851 ±6</td>
<td>3.495 ±0.060</td>
<td>0.425 ±0.017</td>
<td>1.265 ±0.044</td>
</tr>
<tr>
<td>MEH-PPV: Ni-OEP:PCBM (8:1:32)</td>
<td>833 ±15</td>
<td>2.897 ±0.053</td>
<td>0.432 ±0.036</td>
<td>1.043 ±0.092</td>
</tr>
<tr>
<td>MEH-PPV: Pd-OEP:PCBM (8:1:32)</td>
<td>843 ±17</td>
<td>3.363 ±0.130</td>
<td>0.462 ±0.030</td>
<td>1.308 ±0.070</td>
</tr>
<tr>
<td>MEH-PPV: Pt-OEP:PCBM (8:1:2:32)</td>
<td>845 ±12</td>
<td>3.478 ±0.129</td>
<td>0.478 ±0.017</td>
<td>1.403 ±0.038</td>
</tr>
<tr>
<td>MEH-PPV: Ni-TPP:PCBM (8:1:1:32)</td>
<td>700 ±17</td>
<td>2.752 ±0.099</td>
<td>0.422 ±0.010</td>
<td>0.813 ±0.041</td>
</tr>
<tr>
<td>MEH-PPV: Pd-TPP:PCBM (8:1:2:32)</td>
<td>846 ±8</td>
<td>3.209 ±0.204</td>
<td>0.437 ±0.034</td>
<td>1.183 ±0.059</td>
</tr>
<tr>
<td>MEH-PPV: Pt-TPP:PCBM (8:1:3:32)</td>
<td>846 ±2</td>
<td>3.316 ±0.072</td>
<td>0.480 ±0.013</td>
<td>1.345 ±0.025</td>
</tr>
</tbody>
</table>

The porphyrins in Figure 7.17 and all subsequent graphs are presented in the order they appear progressing down Group 10 of the periodic table, from Ni to Pd to Pt. We observe a systematic increase in device efficiency from Ni-OEP < Pd-OEP < Pt-OEP, and with the same trend repeated for the M-TPPs. As was the case in the previous study of Co/Ni/Cu-metalloporphyrins, the power conversion efficiency is considerably higher for those ternary devices containing metalloporphyrins based upon the octaethylporphyrin ligand than those based on the tetraphenylporphyrin ligand. This observation will be addressed later in Section 7.5.
Figure 7.17: Power conversion efficiency of MEH-PPV:M-OEP:PCBM 8:1:32 and MEH-PPV:M-TPP:PCBM 8:1:32 ternary devices containing approximately 2.5% porphyrin by weight. Note that all porphyrins are present in equimolar amounts.

It can be seen from the optical microscopy in Figure 7.18 (M-OEP) and Figure 7.19 (M-TPP) that each ternary film appears uniformly blended at the optical scale shown. Gross aggregation effects that were present in the microscopy images of ternary blend film containing higher concentrations of porphyrin (Figure 7.2) are not observed. It is therefore believed that large-scale disruption of active layer morphology is not contributing to the observed trends.
Figure 7.18: Optical microscopy of MEH-PPV:PCBM 8:32 device film (A) and MEH-PPV:porphyrin:PCBM 8:1:32 ternary blended device films, where the porphyrin species is: (B) Ni-OEP (C) Pd-OEP and (D) Pt-OEP. The white scale bar represents 100 μm.

Figure 7.19: Optical microscopy of MEH-PPV:PCBM 8:32 device film (A) and MEH-PPV:porphyrin:PCBM 8:1:32 ternary blended device films, where the porphyrin species is: (B) Ni-TPP (C) Pd-TPP and (D) Pt-TPP. The white scale bar represents 100 μm.
As with the previous study, all blend constituents are present in equimolar amounts, with the only difference in composition being the identity of the porphyrin. Likewise, all of the device blends were of similar thickness (120 ±10 nm) so a variation in the number of chromophores can be excluded as a factor affecting device performance.

Table 7.6 shows the HOMO, LUMO and bandgap of each M-OEP and M-TPP. These values were calculated using the B3LYP/6-31G(d) density functional theory (DFT) method. From Table 7.6 and the energy level diagram shown in Figure 7.20 we see that the energy levels of the compounds in each set (M-OEP or M-TPP) show little difference in either the HOMO or LUMO energy of the porphyrins. As a consequence we observed very little variation in the open-circuit voltage within each set of porphyrins (Table 7.5), with most devices having a $V_{OC}$ of approximately 840 mV, except for the Ni-TPP device which is slightly lower. We see from the schematic energy diagram (Figure 7.20) that each porphyrin has a LUMO energy well positioned for transfer of an electron to the polymer or PCBM, and a HOMO well placed to accept holes from the PCBM for transfer to the ITO electrode. Therefore variations in the HOMO and LUMO energy levels of the porphyrins are unlikely to be responsible for the observed trend in device efficiency.

We see from Table 7.5 that $J_{SC}$ correlates closely with device efficiency, increasing from Ni < Pd < Pt for both the M-OEP and M-TPP ternary blend devices (Figure 7.21). One of the reasons for the observed increases in device efficiency might be due to increased light absorption from the porphyrin chromophores.
Table 7.6: Calculated HOMO, LUMO and bandgap for Ni-OEP, Pd-OEP, Pt-OEP, Ni-TPP, Pd-TPP and Pt-TPP. The model values were calculated using the B3LYP/6-31G(d) DFT method.

<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>HOMO / eV</th>
<th>LUMO / eV</th>
<th>Bandgap / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-OEP</td>
<td>-4.80</td>
<td>-1.73</td>
<td>3.07</td>
</tr>
<tr>
<td>Pd-OEP</td>
<td>-4.92</td>
<td>-1.83</td>
<td>3.09</td>
</tr>
<tr>
<td>Pt-OEP</td>
<td>-4.96</td>
<td>-1.81</td>
<td>3.15</td>
</tr>
<tr>
<td>Ni-TPP</td>
<td>-5.08</td>
<td>-2.03</td>
<td>3.05</td>
</tr>
<tr>
<td>Pd-TPP</td>
<td>-5.04</td>
<td>-2.12</td>
<td>2.92</td>
</tr>
<tr>
<td>Pt-TPP</td>
<td>-5.18</td>
<td>-2.11</td>
<td>3.07</td>
</tr>
</tbody>
</table>

Figure 7.20: Schematic energy diagram for the MEH-PPV:PCBM organic photovoltaic cells doped with 2.5 % M-OEP or M-TPP. The overall range of the modelled HOMO and LUMO energies of the porphyrins is defined by the grey-scale boxes.
Figure 7.21: Short-circuit current density of MEH-PPV:M-OEP:PCBM 8:1:32 and MEH-PPV:M-TPP:PCBM 8:1:32 ternary devices containing approximately 2.5 % porphyrin by weight. Note that all porphyrins are present in equimolar amounts.

The UV-visible spectroscopy of the ternary MEH-PPV:M-TPP:PCBM 8:1:32 active layer films (Figure 7.22) clearly show contribution of the porphyrin Soret band absorption (between 400 – 450 nm) to the total absorption spectra of the device. As each porphyrin species is present in equimolar concentration, the relative contribution of each porphyrin to the total light absorption of the active layer can be quantified by determining the molar extinction coefficient of the porphyrin Soret-band, which is the transition responsible for the majority of light absorption by the porphyrin chromophore.
Figure 7.22: UV-visible spectroscopy of the active layer films of an MEH-PPV:PCBM 1:4 binary device and MEH-PPV:M-TPP:PCBM ternary devices containing approximately 2.5 % M-TPP by weight. Note that all porphyrins are present in equimolar amounts.

![UV-visible spectroscopy graph]

Figure 7.23: Soret molar absorption coefficients for the M-OEP and M-TPP series, measured at the Soret peak in dichloromethane.

![Soret molar absorption plot]
From Figure 7.23 we see that whilst the ternary blend device with the highest $J_{SC}$ and efficiency within each set also have the porphyrins with the highest molar absorptivity (Pt-OEP and Pt-TPP), there is no clear correlation between device efficiency and light absorption by the porphyrin, other than the fact that each M-TPP has a higher absorptivity than the M-OEP ligated to the same transition metal. Whilst the extra light absorption by the Pt-porphyrins certainly contributes to the high efficiency of the ternary blend device, it is not the dominating factor driving the improvements in efficiency. In fact, light absorption by the M-TPPs in particular varies little between compounds.

Figure 7.24 shows the external quantum efficiency (EQE) of an MEH-PPV:PCBM 1:4 binary device and MEH-PPV:M-TPP:PCBM ternary devices containing approximately 2.5% M-TPP by weight.

![EQE graph](image.png)

Figure 7.24: EQE of an MEH-PPV:PCBM 1:4 binary device and MEH-PPV:M-TPP:PCBM ternary devices containing approximately 2.5% M-OEP by weight. Note that all porphyrins are present in equimolar amounts.
The contribution of each porphyrin to total photocurrent is clearly seen in the porphyrin Soret region of the EQE plot at approximately 400 – 450 nm in Figure 7.24. Whilst all ternary blends show relatively high EQEs, current generation at the polymer (as indicated by the broad peak between 450 and 600 nm) is diminished slightly for all of the ternary blend devices. However, the maximum EQE for the Pt-TPP (and to a lesser extent, the Pd-TPP) exceeds the current output of the standard device in the Soret region of the plot. Although the $J_{SC}$ of the Pt-TPP (and Pt-OEP) ternary devices are lower than the $J_{SC}$ of the standard MEH-PPV:PCBM device, the efficiency of the ternary Pt-porphyrin devices is actually higher, due to a higher fill factor (Figure 7.25).

![Chart showing fill factors](image)

**Figure 7.25:** Fill factors of a MEH-PPV:PCBM 1:4 standard device, and MEH-PPV:M-OEP:PCBM 8:1:32 and MEH-PPV:M-TPP:PCBM 8:1:32 ternary devices containing approximately 2.5% porphyrin by weight. Note that all porphyrins are present in equimolar amounts.

We see from Figure 7.25 than the average fill factor (FF) of both Pt-OEP and Pt-TPP ternary blend devices is 0.48, compared with an average FF of 0.43 for the standard devices in this
study. This observed FF of 0.48 is very high for an OPV device based on MEH-PPV and PCBM as the main donor and acceptor species, and is actually the highest FF reported in this thesis. In fact, over the course of this PhD, most standard devices have had FF less than 0.40 (see Chapter 3, Table 3.1) and many ternary blend devices had a FF lower than 0.30 (see for example Chapter 5, Table 5.1).

As discussed previously, a high FF is due to an increase in shunt resistance ($R_{sh}$) or a decrease in series resistance ($R_s$), or both. Device resistances were calculated from the I-V curves under illumination, and are shown in Table 7.7 below.

Table 7.7: Series and shunt resistances for standard MEH-PPV:PCBM 8:32 and ternary MEH-PPV:M-TPP:PCBM 8:1:32 devices containing approximately 2.5 % porphyrin by weight. Note that all porphyrins are present in equimolar amounts

<table>
<thead>
<tr>
<th>Blend</th>
<th>$R_s$ (Ω)</th>
<th>$R_{sh}$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard device</td>
<td>511</td>
<td>12572</td>
</tr>
<tr>
<td>with 2.5 % Ni-TPP</td>
<td>1085</td>
<td>11512</td>
</tr>
<tr>
<td>with 2.5 % Pd-TPP</td>
<td>512</td>
<td>12751</td>
</tr>
<tr>
<td>with 2.5 % Pt-TPP</td>
<td>474</td>
<td>25648</td>
</tr>
</tbody>
</table>

We see that the shunt resistance of the ternary blend devices increases with device efficiency. Remarkably, the $R_{sh}$ of the Pt-TPP ternary device is almost twice that of the standard device. As $R_{sh}$ is a function of both geminate and bimolecular recombination [50], we hypothesise that the degree of charge recombination becomes less as we progress from Ni-TPP > Pd-TPP > Pt-TPP, with the presence of the Pt-TPP chromophore in the MEH-PPV:PCBM blend significantly lowering the degree of recombination within the device (as evident from a large increase in $R_{sh}$), resulting in enhanced efficiency compared with a standard device.
We also see that the series resistance for the ternary blend devices decreases as device efficiency increases, with $R_s$ of the Pt-TPP device lower even than the standard binary device. This decrease suggests that the addition of the Pt-TPP to the binary blend results in lowered resistivity in either the active layer materials or the interfaces between donor and acceptor phases [50].

From the EQE of the M-TPP ternary blends (Figure 7.24) we observe that the porphyrin peaks become increasingly larger as we go from Ni-TPP to Pd-TPP to Pt-TPP, despite the molar absorptivities (Figure 7.22 and 7.23) of each porphyrin being of similar magnitude. This increase in relative EQE contributions suggest that as we progress through the series to Pt-TPP, the degree of exciton generation by the porphyrin increases, contributing to the observed increase in current generation. We believe this increase in exciton generation is due to a decrease in the ionisation energy of the transition metal porphyrins, which makes removing an electron from the porphyrins HOMO easier, thus promoting efficient exciton generation.

The transition metal of each porphyrin is formally in the 2+ oxidation state. Absorption of a photon and subsequent generation of an exciton represents a change in metal oxidation state of $M^{II}$ to $M^{III}$. Therefore, a decrease in the energy required for ionisation energy as we progress down Column 10 from Ni to Pd to Pt would enhance exciton generation by the porphyrin component leading to a contribution to the observed increase in device efficiency. Table 7.8 lists the third ionisation energy, that is, the energy required to remove an electron from $M^{2+}$ to form $M^{3+}$. We do in fact observe that it becomes progressively easier to oxidise the transition metal as we move down the column from Ni(II) to Pd(II) to Pt(II). However, the formal oxidation state has little to do with the actual charge on the metal when part of a transition metal complex [52], and so it is difficult to directly ascribe any physical property to oxidation state alone. It has also been demonstrated that the oxidation of $M^{II}$ transition metal porphyrins does not always occur at the metal ion, and may instead occur preferentially at the porphyrin ring, dependant on activation or deactivation of the $\pi$ electron conjugated
system through the electrostatic action of the central ions [53]. These observations make it
difficult to support our hypothesis that exciton generation is dependent on the ionisation
energy of the transition metal alone. We have therefore theoretically determined the
ionisation potential of each porphyrin molecule via density functional theory (DFT) calculations
using the B3LYP/6-31G(d) DFT method.

Table 7.8: Third ionisation energy for the metals Ni, Pd and Pt (from [54]), and calculated
ionisation potentials for Ni-TPP, Pd-TPP and Pt-TPP. Porphyrin IP was calculated using the
B3LYP/6-31G(d) DFT method

<table>
<thead>
<tr>
<th>Transition metal</th>
<th>Third ionisation energy / eV [54]</th>
<th>Porphyrin</th>
<th>Ionisation potential / cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>35.16</td>
<td>Ni-TPP</td>
<td>50387</td>
</tr>
<tr>
<td>Pd</td>
<td>32.92</td>
<td>Pd-TPP</td>
<td>49286</td>
</tr>
<tr>
<td>Pt</td>
<td>29.02</td>
<td>Pt-TPP</td>
<td>47862</td>
</tr>
</tbody>
</table>

From Table 7.8 we observe that not only does the third ionisation energy of the transition
metal decrease as we progress through the series of porphyrins, but the ionisation potential of
the metalloporphyrin molecule itself also decreases with increasing device efficiency. We
believe this observation, combined with the relative increase in current contribution at the
porphyrin Soret peak in the EQE spectra, supports our hypothesis that exciton generation is
made more efficient by a reduction in ionisation energy of the porphyrin. Whilst we recognise
that this observation is not a dominant effect on device performance (because we do not
observe much variation in device \(V_{oc}\)) it nonetheless contributes to overall device efficiency.

Finally, we note that the addition of 2.5 % by weight of Pt-TPP and Pt-OEP to a standard MEH-
PPV:PCBM device results in an increase in device efficiency of 6 % and 11 %, respectively. This
increase is driven primarily by a reduction in the degree of charge recombination in the device,
which increases $R_{th}$, leading to a significantly improved FF of 0.48%. Lowering the ionisation potential of the porphyrin also contributes to improved current density through more efficient exciton generation by the Pt-porphyrin.

### 7.5 The difference in photovoltaic performance between transition metal compounds ligated with octaethylporphyrin and tetraphenylporphyrin

Throughout this chapter we have consistently observed higher photovoltaic performance of ternary blended organic solar cells using transition metal porphyrins bearing the OEP ligand compared with the TPP ligand. For the Co/Ni/Cu series, M-OEPs display improved power conversion efficiencies of at least 30% over the equivalent M-TPP complex, with the efficiency of Co-OEP more than doubling compared with the Co-TPP. The higher efficiencies are not only a result of improved open-circuit voltage, but also of significant improvements in short-circuit current density. The mechanisms behind this difference in photovoltaic performance will now be explored.

If we consider the data from the Co/Ni/Cu series for example, the observed higher efficiency of the ternary M-OEP solar cells may be due to a number of factors. Firstly, it may be due to differences in light absorption by the porphyrin (to generate an exciton). Secondly, it may be due to differences in exciton diffusion to an interface leading to exciton dissociation, and finally it may be due to charge transport through the semiconductor materials to the electrodes of the device.

Considering the relationship we have established between light absorption and device efficiency in the first part of this chapter, we might also reasonably expect that the device efficiency of the M-OEP devices is higher than that of the M-TPP devices due to improved light absorption. In fact, it is the M-TPPs that actually absorb more light than OEPs (Figure 7.13), as they have both higher molar absorptivity and broader absorption peaks. Despite this fact, the observed short-circuit current density is lower for the M-TPP devices than the M-OEP devices.
Therefore the improved power conversion efficiency of the M-OEP devices is not due to enhanced light absorption by the porphyrin, and must be influenced by other factors.

We have shown in the previous two chapters that differences in $\text{HOMO}_{\text{donor}} - \text{LUMO}_{\text{acceptor}}$ energy gap can have a large effect on device efficiency by altering device $V_{OC}$, so we might also expect that the HOMO energy of the donor M-OEPs are positioned more favourably compared with the LUMO of the PCBM acceptor species. However, we see from Figure 7.9 that whilst the HOMOs of the M-TPP (-4.99 and -5.08 eV) are positioned lower than the HOMOs of the M-OEP (-4.80 and -4.84 eV), the $V_{OC}$ of the M-TPP devices are actually lower, not higher, than the $V_{OC}$ of the M-OEP ternary blend devices. Therefore it is not differences in the energetic alignment of the materials which are dominating the observed trends in device efficiency.

We therefore believe that it is changes in the nanoscale morphology of the active layer, which is influenced by the structure of the metalloporphyrin ligand itself, which causes the M-OEP devices to have higher device efficiency than the equivalent M-TPP blends. By enhancing charge transport through improved active layer morphology we are able to extract more charges out of the device, which improves $J_{SC}$, while simultaneously lowering charge recombination leading to higher $V_{OC}$. While it is generally considered that OEP derivatives are more soluble in typical organic solvents than TPP derivatives [55], this has not been our experience in this study. At the blend ratio of 4:4:32 that was initially used, we observed the strong tendency of M-OEP to form large aggregates within the active layer films. In fact it was this aggregation that made it necessary to adopt a lower concentration of porphyrin, in order to avoid the detrimental effects of gross aggregation, such as reduced device efficiency, which have been previously reported [7]. If we compare optical microscopy images of active layer films (Figure 7.26) at the higher 4:4:32 concentration, the greater tendency of M-OEP to aggregate is clear. (Note that the porphyrins are actually present in equimolar amounts based on 4mg of TPP, thus are present at approximately 10 % porphyrin relative to the other blend components.) The ternary blend films containing the M-TPP show less gross aggregation.
effects at 10% concentration because the solubility of tetraphenylporphyrin (37.5 mmol L\(^{-1}\) in chloroform [56]) is much higher than the solubility of octaethylporphyrin (3.5 mmol L\(^{-1}\) chloroform [56]).

![Optical microscopy images of MEH-PPV:porphyrin:PCBM 4:4:32 mg/mL chlorobenzene (approximately) device films where the porphyrin ligand is tetraphenylporphyrin (top row) and octaethylporphyrin (bottom row). Note that all porphyrins are present in equimolar amounts, based on 4 mg of tetraphenylporphyrin, thus the actual mass of metalloporphyrin varies slightly between blends. The white scale bar represents 100 μm.

It is also possible that the enhanced aggregation observed in OEP blends may be the result of fullerene-porphyrin cocrystallate formation. It has been reported that the metal-carbon(fullerene) bond lengths in complexes of Co-TPP:C\(_{60}\) and Co-OEP:C\(_{60}\) range from 2.67-2.71 and 2.63-3.11 Å, respectively [57]. While the shortest bond length of 2.63 Å is observed for the Co-TPP:C\(_{60}\) complex, suggesting a stronger affinity of fullerene to M-TPP than to M-OEP, the range of values for bond length are generally lower for Co-OEP than for Co-TPP. However, it should be noted that it is difficult to rationalise the binding of fullerenes in metalloporphyrin hosts due to the relatively small magnitudes of the electrostatic and covalent components [58]. Suggested further testing for the presence of cocrystallates in the ternary blend films.
could include NMR studies, as it has been reported that mutual upfield ring current-induced shifts can be detected in the $^1$H NMR spectrum of the H$_2$TPP and the $^{13}$C NMR spectrum of C$_{60}$ of mixtures in toluene solution to as a method to confirm their presence [58].

When we lowered the blend ratio to MEH-PPV:porphyrin:PCBM 8:1:32, while few gross aggregates were visible in the optical microscopy images (Figure 7.7 and 7.8), it is likely that the greater tendency of the M-OEP to form aggregates results in the formation of small, nanostructured domains which improve charge transport in the device.

Self-association of molecules plays an important role in nature. For example, molecular aggregates of chlorophyll (which itself is a porphyrin) are responsible for the primary light harvesting and charge transfer processes in photosynthesising plants and bacteria [49]. Even some organic photovoltaic devices have been reported [59] where the self-aggregation of the light-absorbing porphyrin species led to the formation of nanostructured columns of porphyrins by intermolecular π-π stacking, which enhanced device efficiency by improving charge mobility within the porphyrin stacks. However, larger-scale aggregation due to excessive concentrations of porphyrin have also been observed to diminish device performance by hindering charge transport [2] and disrupting polymer and fullerene domains [10].

We therefore hypothesise that the enhanced efficiency of the M-OEP ternary blends is due to improved nanostructured active layer morphology, arising from a combination of both low concentration of porphyrin (which avoids gross aggregation effects that hinder charge transport), and selection of a porphyrin species that displays a strong tendency to self-assemble (thus creating nanostructured domains which have been shown to enhance device efficiency). The combination of these conditions leads to enhanced $V_{oc}$ and $J_{sc}$ through improved charge transport and reduced charge recombination in the active layer. Further investigation using a technique such as near edge X-ray absorption fine structure (NEXAFS)
spectroscopy would be necessary to confirm the presence, orientation and alignment of the M-OEP structures present in the active layer, and could provide a quantitative comparison to active layer films containing M-TPPs to validate this hypothesis.

7.6 Conclusions

We have performed a study of the performance of ternary organic photovoltaic devices made from MEH-PPV, PCBM and a series of transition metal porphyrins. The effect of the transition metal in each porphyrin was examined by systematically varying the identity of the metal both across Period 4 and down Column 10 of the periodic table. We have shown that improved short-circuit current density and power conversion efficiency is a result of reduced charge recombination and increasing light absorption by the porphyrin species as we progress across Period 4 of the periodic table from Co(II) to Ni(II) to Cu(II). These trends were consistent for transition metals with both octaethylporphyrins ligands and tetraphenylporphyrin ligands.

In addition, we have shown an enhancement of approximately 5% to the efficiency of an MEH-PPV:PCBM solar cell by the addition of 2.5% by weight of the ternary dopant chromophore, Cu-OEP.

We have also shown improvements in device efficiency as we progress down Column 10 of the periodic table. This increase is driven primarily by a reduction in the degree of charge recombination in the device, which increases $R_{sp}$, leading to a significantly improved fill factor of the devices, which for the ternary blend containing Pt-porphyrin reached 0.48. Lowering the ionisation potential of the porphyrin also contributes to improved current density through more efficient exciton generation by the porphyrin. The addition of 2.5% by weight of Pt-TPP or Pt-OEP to a standard MEH-PPV:PCBM device results in an increase in device efficiency of 6% and 11%, respectively.

Finally, we have hypothesised that the improved device performance observed for the OEP porphyrin structure over the TPP porphyrin structure is a result of the formation of
nanostructured porphyrin domains, leading to enhanced charge transport and reduced recombination within the ternary blend system. This morphology arises due to a combination of both low porphyrin concentration and the selection of a porphyrin species which has a strong tendency to self-associate due to low solubility properties.

7.7 References


Chapter 8 – Conclusions

The motivation for exploration of porphyrinoid compounds as organic photovoltaic materials comes from their ease of synthesis and modification, high molar absorptivities, and obvious structural resemblance with the light-harvesting pigment chlorophyll which is found in all photosynthetic plants and bacteria. Until this thesis there has not been, to the best of our knowledge, a thorough and systematic study of the incorporation of porphyrinic compounds into bulk heterojunction organic solar cells for the purpose of broadening spectral response and probing device function. There have been some publications looking at porphyrinoids, but only a small number demonstrated significant improvements in doing so and even in those that did, the physical and chemical processes affecting device function were poorly understood. This thesis sought to address those gaps in the scientific knowledge. It investigated how porphyrinic materials may be successfully incorporated into polymer/fullerene organic solar cells, to not only broaden the wavelengths of light that the devices absorb but more importantly, to further probe the chemistry and physics and enhance our understanding of both binary and ternary blended organic solar cells.

We have probed the effect of both structural and electronic changes in our light-absorbing dopant molecules and in doing so, have been able to control the way materials interact with other species in the solar cell active layer, as well as interactions between the porphyrins themselves. We have shown that they can be structurally altered such that their frontier orbital energies are more suitably aligned with respect to acceptor species, and as a consequence we can “tune” the open-circuit voltage of the device. We have also shown that by modifying the steric bulk of a porphyrin, the initial charge separation distance can be controlled, which reduces power-diminishing recombination events and consequently leads to improved open-circuit voltage and efficiency. In doing so we have shown that porphyrinoid
molecules are generally compatible with polymer:fullerene systems, and through simple structural modifications, can be tuned to achieve maximum device efficiency.

Chapter 3 investigated the performance of standard MEH-PPV devices that I have manufactured at the University of Newcastle, and how device efficiency has steadily improved over the course of the project. It showed that the incremental improvements made to the standard binary devices over time were directly transferable to ternary blend devices.

Chapter 4 investigated the addition of porphyrins into MEH-PPV:PCBM solar cells as additional light-harvesting components, which resulted in enhancement of the spectral response at the absorption peaks of the porphyrin, but at the cost of an overall reduction in device efficiency. We have shown that despite the propensity for porphyrinic materials to aggregate, at the blend ratios used in this study the morphology of the active layer ternary blended films remain uniform. The reduced efficiency of the ternary devices was instead dominated by changes to the electronic structure of the active layer. The porphyrin was found to act as a site for enhanced recombination of electron-hole pairs, and by altering the steric bulk of the peripheral porphyrin substituents, the charge separation distance could be increased which led to an enhancement of $V_{OC}$ and device efficiency through reduced recombination. This demonstrated that it is possible to design organic solar cell materials which minimise charge recombination and therefore offers a general pathway to significant efficiency improvements. Future work could include the synthesis of porphyrins of even greater steric bulk (for example, by the addition of trityl substituents) to determine and direct the optimum charge-separation distance between donor and acceptor species.

Chapter 5 discussed devices prepared using a series of porphyrins and N-confused porphyrins in which the peripheral groups were unchanged, to create a series of porphyrinoids which differ only in the nature of their electronic states. By choosing sterically bulky peripheral groups we have shown that the inclusion of these compounds in binary MEH-PPV:PCBM OPV
devices does not significantly alter the morphology of the device active layers through phase segregation. Porphyrinoids contribute to the photocurrent of these ternary devices through a broadening of the spectral response of the cells in accordance with the absorption spectra of the porphyrinoid, but at the same time overall device performance is reduced. Consideration of the device parameters and an observed linear correlation between the ionisation potential and thus highest occupied molecular orbital energy of the porphyrinoids, and the power conversion efficiency of the ternary blend devices, indicates that the porphyrinoids act as hole trapping sites within these devices, increasing bimolecular recombination and lowering device efficiency through a reduction in both the devices’ charge densities and open circuit voltages. By modifying the porphyrinoid added, either by metallation or N-alkylation of the N-confused porphyrin, we systematically changed the ionisation potential of the species and therefore directly affect the power conversion efficiency of the resultant device. This approach demonstrates a method by which we may directly design materials that minimise recombination within bulk heterojunction devices and thus offers a general pathway to significant efficiency improvements in ternary blend devices.

In Chapter 6 we have shown that modification of the electron-donating or electron-withdrawing character of the substituents in the para-phenyl position of tetraphenylporphyrin has a significant effect on the performance of ternary MEH-PPV:porphyrin:PCBM bulk heterojunction organic solar cells. Increasing the electron-withdrawing ability of the substituents, as quantified by the Hammett $\sigma_{para}$ constant, leads to an improvement in device efficiency which is driven primarily through enhancements to the open-circuit voltage of the cell. Substituents with a larger Hammett $\sigma_{para}$ constant were found to increase the oxidation potential of the porphyrin, leading to a decrease in the highest occupied molecular orbital energy, which improved device $V_{OC}$ through widening of the HOMO$_{donor}$--LUMO$_{acceptor}$ energy gap. Comparison with data from the previous chapter suggested that further improvements to device efficiency might be achieved through a combination of both electronic and structural
modifications, so that not only is the porphyrin well-placed energetically within the ternary blend system, but that structural characteristics exist such that molecular centres for charge recombination are both spatially separated from other device components and chemically shielded from diffusing charges. We have shown the application of Hammett parameters to design porphyrins that are energetically compatible with polymer:fullerene solar cells, and the ability to fine-tune the porphyrin HOMO energy to achieve significant gains in ternary blend device efficiency. Future work could include the investigation of porphyrins which have even lower HOMO energies, to further expand the HOMO_{donor}-LUMO_{acceptor} gap and thus increase \( V_{OC} \) beyond that of a standard binary device. Porphyrin HOMO might be lowered by the addition of phenyl-substituents having large electron-withdrawing character, such as nitro or cyano substituents.

Chapter 7 discussed the systematic study of the performance of ternary organic photovoltaic devices made from MEH-PPV, PCBM and a series of transition metal porphyrins. The effect of the transition metal in each porphyrin was examined by systematically varying the identity of the metal both across Period 4 and down Column 10 of the periodic table. We have shown that improved short-circuit current density and power conversion efficiency is a result of increasing light absorption by the porphyrin species as we progress across Period 4 of the periodic table from Co(II) to Ni(II) to Cu(II). These trends were consistent for transition metals with both octaethylporphyrins ligands and tetraphenylporphyrin ligands. In addition, we have shown a modest enhancement of approximately 5% to the efficiency of an MEH-PPV:PCBM solar cell by the addition of 2.5% by weight of the ternary dopant chromophore, Cu-OEP.

We have also shown improvements in device efficiency as we progress down Column 10 of the periodic table. This increase was driven primarily by a reduction in the degree of charge recombination in the device, leading to a significantly improved fill factor, which for the ternary blend containing Pt-porphyrin reached 0.48. Lowering the ionisation potential of the porphyrin also contributed to improved current density through more efficient exciton
generation by the porphyrin. The addition of 2.5 % by weight of Pt-TPP or Pt-OEP to a standard MEH-PPV:PCBM device resulted in an increase in device efficiency of 6 % and 11 %, respectively.

Finally, we have hypothesised that the improved performance of the OEP porphyrin structure over the TPP porphyrin structure is a result of the formation of nanostructured porphyrin domains, leading to enhanced charge transport and reduced recombination within the ternary blend system. This morphology arises due to a combination of both low porphyrin concentration, and the selection of a porphyrin species which has a strong tendency to self-associate due to low solubility properties. Further work should include AFM and NEXAFS imaging to confirm the presence and alignment of nanostructured porphyrin domains, and investigate the potential of related materials such as phthalocyanines, which are known for their strong self-association properties, to form similar morphologies.

Porphyrins form complexes with most metals, so broadening the investigation of metalloporphyrin dopants could lead to the identification of new compounds for use as efficient photosensitisers. In particular, those metalloporphyrins bearing axial ligands might be utilised as a method for controlling aggregation by preventing porphyrin-porphyrin interactions.

Finally, we suggest that future studies might investigate porphyrin species which combine the various methods we have identified for tuning the structural and electronic characteristics of the porphyrin molecule, such that enhanced ternary blend efficiency may be achieved. Such a molecule might, for example, be a metallated porphyrin, so as to minimise the hole-trapping that occurs due to the basic pyrrolic nitrogens. We suggest a platinum porphyrin as a starting compound, as the two Pt-porphyrin devices in this thesis had the highest fill factor of all compounds studied. And finally, the compound might also have sterically bulky peripheral
substituents, to minimise charge recombination by increasing the charge separation distance between donor and acceptor species.

Through the series of systematic studies in this thesis, we have established an understanding of ternary blend organic photovoltaic systems and the way in which the donor and acceptor materials interact. We have shown that porphyrinic compounds are able to be tuned such that they interact favourably with other blend components and as a consequence, broaden the spectral response of the solar cells. Through structural modification of the porphyrin we have been able to reduce charge recombination through tuning of molecular steric bulk, and also tuned the porphyrin HOMO to achieve high open-circuit voltages. But most importantly, we feel that we have demonstrated the immense value of the porphyrinoid as a molecular probe to investigate thin-film organic photovoltaic systems and thus broaden our understanding of this emerging technology.