Improving Nanoparticle Organic Photovoltaic Device Performance

By

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Discipline of Physics
School of Mathematical and Physical Sciences
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Declaration

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I hereby certify that the work embodied in this thesis has been done in collaboration with other researchers. I have included within this thesis statements clearly outlining the extent of collaboration, with whom and under what auspices.

________________________________________
M. Syahrul Ulum
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May God almighty give them all peace and success in their life. Amen.
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Abstract

Recently, the fabrication of organic photovoltaic devices from water-dispersed nanoparticulate materials (solar paint) has attracted increasing interest since it offers the potential of morphological control coupled with device processing in the absence of organic solvents which are toxic to human beings and the environment. However, to date the reported efficiencies of nanoparticulate organic photovoltaic (NP-OPV) devices have been disappointingly low compared to the standard organic photovoltaic devices. This low efficiency reflects a lack of understanding of the structural motif of NP-OPV devices. Furthermore the fabrication conditions used for NP-OPV devices are not well determined as yet. To improve NP-OPV device performance, understanding the structural motive of NP-OPV devices is necessary and OPTIMISED fabrication conditions for NP-OPV need to be determined. By using relevant techniques such as X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning transmission X-ray microscopy (STXM), and differential scanning calorimetry (DSC), we analyse and optimise the conditions for fabricating NP-OPV devices and show a significant improvement in efficiency as compared to previous work. Using calcium and lithium fluoride interface layers between the aluminium and the active layer were also investigated in this project. It is found that proper thickness of the interface also contributes to improving the performance of NP-OPV devices. In this project poly(3-hexylthiophene) (P3HT) is used as the electron donor and phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM), phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM), and indene-C₆₀-bisadduct (ICBA) as the electron acceptors. The highest efficiency of nanoparticle devices fabricated for P3HT:PC₆₁BM is 1.36 %; for P3HT:PC₇₁BM is 2.00 %; and for P3HT:ICBA is 3.29 % which are by far the highest efficiencies reported so far for each system. Moreover an efficiency of 3.29 % is the highest efficiency for NP-OPV devices reported. In this project we also investigate the structural motive of NP-OPV devices and find that for P3HT:PC₆₁BM nanoparticles, the particles are core-shell in nature with a PC₆₁BM-rich core and a P3HT-rich shell. For P3HT:ICBA nanoparticles, the particles are also core-shell in nature with a P3HT-rich shell and ICBA-rich core but upon annealing a highly intermixed P3HT:ICBA is formed, which is driven by the enhanced miscibility of ICBA
in crystalline P3HT and this morphological change results in much higher device efficiencies.
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>AM1.5</td>
<td>Air Mass 1.5: Reference Solar Spectrum for OPV Characterisation</td>
</tr>
<tr>
<td>BHJ</td>
<td>Bulk Heterojunction</td>
</tr>
<tr>
<td>CMC</td>
<td>Critical Micelle Concentration</td>
</tr>
<tr>
<td>CPS</td>
<td>Count Per Second</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic Light Scattering</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>EQE</td>
<td>External Quantum Efficiency</td>
</tr>
<tr>
<td>F8BT</td>
<td>Poly(9,9'-dioctylfluorene-co-benzothiadiazole)</td>
</tr>
<tr>
<td>FF</td>
<td>Fill Factor</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>ICBA</td>
<td>Indene-C$_{60}$ bis-adduct</td>
</tr>
<tr>
<td>ICMA</td>
<td>Indene-C$_{60}$ mono-adduct</td>
</tr>
<tr>
<td>$I_{\text{max}}$</td>
<td>Current at Maximum Power Point</td>
</tr>
<tr>
<td>$I_{\text{sc}}$</td>
<td>Short Circuit Current</td>
</tr>
<tr>
<td>$J_{\text{sc}}$</td>
<td>Short Circuit Current Density</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium-tin Oxide</td>
</tr>
<tr>
<td>I-V</td>
<td>Current-Voltage Characterisation</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>NP-OPV</td>
<td>Nanoparticle Organic Photovoltaic</td>
</tr>
<tr>
<td>OPV</td>
<td>Organic Photovoltaic</td>
</tr>
<tr>
<td>P3HT</td>
<td>Poly(3-hexylthiophene)</td>
</tr>
<tr>
<td>PC$_{61}$BM</td>
<td>Phenyl-C$_{61}$-butyric acid methyl ester</td>
</tr>
<tr>
<td>PC$_{71}$BM</td>
<td>Phenyl-C$_{71}$-butyric acid methyl ester</td>
</tr>
<tr>
<td>PCE</td>
<td>Power Conversion Efficiency</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate) 1,4-phenylenediamine</td>
</tr>
<tr>
<td>PFB</td>
<td>Poly(9,9'-dioctyfluorene-co-bis-N,N'-(4-butylphenyl)-bis-N,N'-phenyl-1,4-phenylenediamine)</td>
</tr>
<tr>
<td>$P_{\text{max}}$</td>
<td>Maximum Power Point of I-V Curve</td>
</tr>
<tr>
<td>QCM</td>
<td>Quartz Crystal Microbalance</td>
</tr>
<tr>
<td>$R_s$</td>
<td>Series Resistance</td>
</tr>
</tbody>
</table>
$R_{sh}$ Shunt Resistance
SDS Sodium Dodecyl Sulfate
STDEV Standard Deviation
STXM Scanning Transmission X-ray Microscopy
TEM Transmission Electron Microscopy
UV-Vis UV-Visible Spectroscopy
$V_{max}$ Voltage at Maximum Power Point
$V_{oc}$ Open Circuit Voltage
XPS X-ray Photoelectron Spectroscopy
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This thesis will report the fabrication, characterisation and optimisation of nanoparticulate organic photovoltaic cells fabricated from conducting polymers. As a consequence, the following introduction will be restricted to a brief discussion of solar energy, conducting polymers and organic photovoltaic devices, in general, and then more specific literature referring to the fabrication and optimisation of these devices. The fabrication and optimisation conditions for standard OPV devices reported in these papers will then set a basis for the initial fabrication and optimisation conditions for their nanoparticulate analogues.

1.1 Solar Energy

The world energy consumption, particularly electrical energy is increasing rapidly, even beyond predicted estimates, due to the impact of growing populations and increased life activities that use electric energy. So far, energy consumption still almost exclusively relies on oil as the primary energy source and it is inevitable that this source will become increasingly scarce and expensive. Figure 1.1 shows a model of world oil production based on a multicyclic Hubbert model [13].
As shown in Figure 1.1 the actual rate is very close to the model rate. Therefore production rate of oil as predicted will start to decline within the next 10-20 years. To address this situation, renewable energy sources such as solar, hydroelectric, and wind turbine energy need to be optimized and implemented.

Compared to other renewable energy sources, the potential of solar energy is far greater than the others. The sun continuously emits energy (as much 3.8 x 10^{14} TW) and the earth continuously receives as much 1.2 x 10^{5} TW of energy from the sun, which is approximately 10,000 times the energy that mankind consumed in the whole of the year 2004 [27]. Unfortunately, this solar energy is not yet well utilised. Whilst there are photovoltaic devices based on inorganic semiconductors which can efficiently convert the solar energy to electric energy, their fabrication costs are currently too high to be used in mass.

High manufacture cost and cumbersome fabrication processes to produce inorganic semiconductors have motivated researchers to find other materials for solar cells which can be easily produced at low cost. Recently, conducting polymers have

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*Figure 1.1*: World-wide oil production. Units of MMSTB/D = million stock tank barrels per day and BSTB = billion stock tank barrel [13].
attracted researchers due to their potential for low cost, light weight and, mechanically flexible devices and the abundance of raw materials.

1.2 Conducting Polymer

Generally organic polymers are insulators due to the sp$^2$ hybridised orbitals and localised electrons in their carbon-based σ bonds. For conductive polymers, the backbone consists of sp$^2$ hybridised carbons which means a remaining p$_z$ orbital with a single valence electron remains. In this case double bonds can occur and lead to formation of a π bond due to overlap the p$_z$ orbitals. When many of these conjugated bonds are present, the π band gives rise to delocalised electrons which are able to move freely along the polymer backbone. The π band is then split into π and π* bands. Since each band can hold 2 electrons per atom, the π band is filled and π* band is empty. The energy difference between π band and π* band is known as π-π* energy gap, $E_g$ [28]. However, whilst the π band and π* band may be considered to define the energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is generally considered as the actual energy gap. The HOMO and LUMO levels in organic semiconductors are analogous to the valence and conduction bands in inorganic semiconductors.

In 1977 McDiarmid et al. discovered conducting polymers and showed that the conductivity of polyacetylene could be increased several orders by doping the polymer with iodine [29]. For this discovery Alan McDiarmid, Alan Heeger, and Hideki Shirakawa won the Nobel Prize for Chemistry in year 2000. In actuality, John Pople and S.H. Walmsley predicted the possibility of making polyacetylene conductive and introduced their concept of the “soliton”, in 1962.
The advantages of using conductive polymers are that they are light, flexible, inexpensive, and the raw materials are abundantly available. To date, conductive polymers have been studied and applied in a variety of applications and have produced devices such as organic light emitting diodes (OLEDs), organic field effect transistor (OFETs), and organic photovoltaics (OPVs).

![Application of conductive polymer](image)

**Figure 1.2:** Applications of conductive polymer (a) OLED [3], (b) OPV [18], (c) OFET [25, 26].

### 1.3 Organic Photovoltaic

One interesting field of research related to conducting polymers is research into organic photovoltaics. Research in this field has attracting increasing interest due the possibility of applying the potential low cost, mechanical flexibility, and abundant availability of the raw materials to the manufacture of large scale organic photovoltaics. There are very different mechanisms for inorganic photovoltaics and organic photovoltaics in terms of charge carrier generation. In a conventional photovoltaic device, the absorption of light directly creates free charge carriers, whilst in organic photovoltaics the absorption of light creates coulombically bound electron-hole pairs. These electron-hole pairs are known as excitons. The exciton then is dissociated and creates free charge carriers only at an interface between the donor material and acceptor material in a device. In an organic photovoltaic material, the donor material generally consists of a conjugated polymer that produces excitons when it absorbs light energy and donates electrons to an
acceptor material at the donor-acceptor interface. Some examples of these conjugated polymers include poly(3-hexylthiophene), (P3HT), poly(9,9'-dioctylfluorene-co-bis-N,N'-(4-butylphenyl)-bis-N,N'-phenyl-1,4-phenylenediamine), (PFB) and poly(2-methoxy-5-(3',7'-dimethyl-octyloxy))-p-phenylene vinylene, (MDMO-PPV). The acceptor material accepts electrons from the donor material and is most often made from C$_{60}$ or one of its derivatives. Some examples for donor materials are phenyl-C$_{61}$-butyric acid methyl ester, PC$_{61}$BM, phenyl-C$_{71}$-butyric acid methyl ester, PC$_{71}$BM, indene-C$_{60}$ bis-adduct, (ICBA), and indene-C$_{60}$ monoadduct, ICMA. High solubility, appropriate LUMO energy level, and visible light absorption are factors for choosing a material as an acceptor.

The diffusion length of excitons is relatively short (8 nm) [30] and this means that only excitons created within 8 nm of an interface can reach the interface and produce free charge carriers. Consequently, any excitons created beyond 8 nm of the interface recombine and are lost. Therefore, the architecture of junction between the donor and acceptor is very important. In 1986, Tang built a bilayer device where the donor and acceptor material were sequentially stacked on top of each other (Figure 1.3a) [31]. In such a device, the interface size is limited and leads to the loss of absorbed photons. To create more interfaces, Yu et al. demonstrated the concept of the “bulk heterojunction” in 1995 [32]. A bulk heterojunction structure consists of a blend of the acceptor and donor material in a bulk volume (Figure 1.3b). By blending the acceptor and donor material many interfaces are created and this leads to more efficient free charge generation.
To date performance of OPVs have reached efficiency exceeded 10 %. This achievement has been achieved as a result of the use of low band gap materials. Low band gap materials can absorb broader light spectrum resulting high current density and eventually increased device performance. Chen et al. [33] have achieved an efficiency of ~8% using low band gap materials poly[4,8-bis-substituted-benzo[1,2-b:4,5-b’]dithiophene-2,6-diyl-alt-4-substituted-thieno[3,4-b]thiophene-2,6-diyl] (PBDTTT) combined with stronger electron-withdrawing groups. Dou et al. [34] also fabricated OPV devices from low band gap materials poly{2,6’-4,8-di(5-ethylhexylthienyl)benzo[1,2-b;3,4-b]dithiophene-alt-5-dibutoxyoctyl-3,6-bis(5-bromo thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4-dione} (PBDTT-DPP). Dou et al. achieved efficiency of 8.62 % by using an inverted tandem PSC method. Recently, Heliatek have reported OPV devices with efficiency of 12 % [35]. With efficiencies reaching these levels (12 %) OPVs now show great promise as a future source of energy.

### 1.3.1 Operating Principles of Organic Photovoltaic

Generally the structure of an organic photovoltaic device is an active layer sandwiched between a cathode and an anode. The anode is typically made from a transparent conducting material like indium tinoxide (ITO) and the cathode is usually composed of a metal like aluminium. For better performance, the anode is modified by an interfacial layer, a hole blocking material like poly(3,4-ethylenedioxy-thiophene):poly(styrene-
esulfonate) (PEDOT:PSS). PEDOT:PSS functions as an exciton and electron blocker, smooths out the surface of the ITO electrode, and also prevents indium from leaching into the active layer [36, 37].

![Diagram of an organic photovoltaic device]

**Figure 1.4:** Common structure of an organic photovoltaic device.

Figure 1.4 shows the common structure of an organic photovoltaic device. The glass functions as a transparent substrate onto which the ITO is deposited. The ITO functions as a transparent anode electrode. Deposited onto the ITO there is a PEDOT:PSS layer which functions as a hole transporter and electron blocker. On top of the PEDOT:PSS there is an active layer where the electrons and holes are generated by incident light. Finally, aluminium as the top electrode functions as a cathode.

Generally, there are five steps in the process of conversion of light into electricity by an organic photovoltaic device. The first step is the absorption of incident photons. The second step is the production of an electron-hole pair also known as an “exciton”. In the third step the exciton diffuses to a material interface. When the exciton reaches the interface it is split and generates a free electron and a free hole. Finally, the free
electron travels to the cathode and the free hole goes travels to the anode. The five steps are described schematically in Figure 1.5.

**Figure 1.5:** Schematic of conversion of light into electricity. (a) The electron absorbs the photon. (b) An exciton is created. (c) The exciton diffuses to an interface. (d) The exciton splits into a free electron and a free hole. (e) The free electron travel to the cathode and the free hole to the anode.

When light shines on an organic photovoltaic device, the active layer of the device absorbs the incident photon’s energy and creates an exciton. The exciton is a paired electron and hole so electrically it is neutral. Therefore, the exciton is not affected by the external electric field. The exciton moves to the interface by diffusion which is determined by the electrochemical potential gradient of the device [38]. The diffusion length of the exciton can vary from 5-14 nm and depends on the active layer material.
Therefore, the exciton must be created at a distance from the interface less than the exciton diffusion length otherwise recombination takes place and the energy is lost.

When the exciton reaches the interface, it will be dissociated and generate free charges; an electron and a hole. However, not all the free charges will become free charge carriers. There are several possibilities which can happen. Figure 1.6 shows the possibilities that can happen at the interface.

Figure 1.6 shows an electron-hole bound pair reaching the interface with constant rate $k_s$. The electron-hole pair can move back into the bulk phase with the rate constant $k_{ex}$. The electron-hole pair can also become free charge carriers with rate constant of $k_D$. These free charge carriers can reform an electron-hole pair, with rate constant $k_R$. If no dissociation occurs, the electron-hole pair can decay back to the ground state with a rate constant of $k_F$. Equation 1.1 shows the reliance of dissociation on temperature, $T$, binding energy, $E_B$, and charge separation distance, $a$.

\[
\frac{k_D}{k_R} = \frac{3}{4\pi a^3} e^{-E_B/kT} \left[ 1 + \frac{b^2}{3} + \frac{b^2}{18} + \frac{b^2}{180} + \cdots \right]
\]  

\[\text{(1.1)}\]  

**Figure 1.6:** Free charge carrier generation model for OPV devices. The wavy line denotes an interface and the dotted ellipse denotes a coulombic binding between an interface separated electron–hole pair [22].
For a given field, $E$, relative permittivity, $\varepsilon$, and temperature, $T$, $b$ is a constant defined by:

$$b = \frac{e^3 E}{8\pi \varepsilon \varepsilon_0 k^2 T^2} \quad (1.2)$$

Where $e$ is the electron charge, $k$, is Boltzmann’s constant, and $\varepsilon_0$ is the permittivity of free space. $E_B$ is defined as:

$$E_B = \frac{e^2}{4\pi \varepsilon \varepsilon_0 a} \quad (1.3)$$

Substitution of Equation 1.3 into Equation 1.1 and rearranging gives:

$$\frac{k_D}{k_R} = A \frac{1}{a^3} \exp \left[ -\frac{B}{a} \left( \frac{1}{kT} \right) \right] \quad (1.4)$$

where,

$$A = \frac{3}{4\pi} \left[ 1 + b + \frac{b^2}{3} + \frac{b^2}{18} + \frac{b^2}{180} + \cdots \right] \quad (1.5)$$

and

$$B = \frac{e^2}{4\pi \varepsilon \varepsilon_0} \quad (1.6)$$

Equation 1.4 shows that the ratio $k_D/k_R$ is dependent on the initial charge separation distance, $a$, and the thermal energy of the bound state, $kT$.

When the bound charges successfully become free charge carriers, they are transported by a hoping mechanism towards the collection electrodes and this only happens if the energy levels of the transporting materials are appropriately aligned [6]. Therefore controlling device morphology is very important and it has been the focus of many researchers [15, 23, 40, 41].

1.3.2 Characteristics of Photovoltaic Devices

The current-voltage characteristics of a photovoltaic in the dark and under illumination can be obtained in a laboratory using a solar simulator lamp. The spectrum of a solar
simulator lamp is adjusted to match the AM1.5 spectrum which is the primary worldwide standard for testing solar devices. AM1.5 describes the spectrum of sunlight which has travelled through the atmosphere to reach the earth’s surface at an angle of 48.2° from the zenith. Figure 1.7 shows the schematic for AM1.5 together with the AM1.5 spectrum.

Figure 1.7: Schematic of the definition of the AM1.5 spectrum together with the spectral power at each wavelength [10].

Figure 1.8 shows a typical IV characteristic of a photovoltaic device. The red plot is the real characteristic of the device where its serial resistance ($R_s$) is defined by the slope at the open circuit voltage, $V_{oc}$, and its shunt resistance, ($R_{sh}$) is defined by the slope at the short circuit current, $I_{sc}$. The dashed blue line is an ideal characteristic for the device where $R_s = 0$ and its $R_{sh} = \infty$. The power conversion efficiency ($PCE$) of the device is determined by the following formula:

$$PCE = \frac{V_{oc \text{ (ideal)}} \times I_{sc \text{ (ideal)}}}{P_{in}}$$
\[ PCE = \frac{V_{OC} \ast I_{SC} \ast FF}{P_{in}} \]  

(1.7)

where \( P_{in} \) is the incident light power density and \( FF \) is the fill factor which is equal to:

\[ FF = \frac{A_{1}}{A_{2}} = \frac{V_{mpp} \ast I_{mpp}}{V_{oc} \ast I_{sc}} \]  

(1.8)

where \( V_{mpp} \) and \( I_{mpp} \) are voltage and current at the maximum power point.

Open circuit voltage, \( V_{oc} \), is the voltage across the device when it is illuminated and no current is flowing. This is the maximum possible voltage the device can produce and it is dependent on several factors such as the highest occupied molecular orbital, HOMO, level of the donor and lowest unoccupied molecular orbital, LUMO, level of the acceptor \([42]\), the morphology of the active layer \([43]\), and the intensity of the incident light \([44]\).

Short circuit current, \( I_{sc} \), is the current produced by the device when there is no external voltage applied across the device. This is the highest current the device can
produce and the voltage of the device is zero. $I_{sc}$ can be calculated by equation as follows:

$$I_{sc} = n e \mu E$$  \hspace{1cm}(1.9)

where $n$ is the density of charge carriers, $e$ is the elementary charge, $\mu$ is the mobility, and $E$ is the electric field [45].

### 1.4 Fabrication Conditions

The standard OPV device utilises a bulk heterojunction (BHJ) structure (Figure 1.9). That is the active layer of the device contains a blended mixture of both electron donor and electron acceptor materials. During fabrication these materials tend to partially phase segregate to form a network of electron and hole transport materials. The advantage of this structure is that it contains pathways for both electron and hole transport to the appropriate electrodes, whilst simultaneously maximising the density of interfaces within the active layer for charge separation to occur across.

![Figure 1.9: OPV BHJ structure.](image)

The BHJ structure is generally far from ideal however and increasing an OPV devices performance can be achieved by optimising the appropriate fabrication conditions such thermal annealing, materials ratio and concentration, and active layer
thickness. The following sections discuss how these optimisations have been achieved for standard organic photovoltaic by some research groups.

1.4.1 Annealing Temperature and Time

One of the ways that the efficiency of an organic photovoltaic device can be improved is by annealing. The basic annealing process can be described in three stages: (1) removal of crystal defects (that cause internal stress) resulting in softening of the material; (2) recrystallization by nucleation and initial growth of new grains that replace those deformed by the internal stresses; (3) further grain growth, resulting in a coarsening of the microstructure that continues until a state of equilibrium is reached [27].

Kim et al. [46] have investigated the annealing effect on device efficiency. They made devices from regioregular poly(3-hexylthiophene) (P3HT) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C_{61} (PC_{61}BM). The P3HT and the PC_{61}BM were mixed (P3HT:PC_{61}BM = 1:1 by weight) using chlorobenzene and 1,2-dichlorobenzene as solvents. The finished devices were then tested under AM1.5 simulated solar illumination (100 mW/cm²). They found that the highest power conversion efficiency (PCE) was achieved when they annealed the devices at a temperature 140 °C for 15 mins. They got PCEs of 3% for devices prepared from chlorobenzene and 2.3% for those prepared from 1,2-dichlorobenzene.

Figure 1.10 shows two graphs of the annealing effect on P3HT:PC_{61}BM organic photovoltaic devices. These graphs were obtained by Ma et al. [15]. When they investigated the effect of annealing temperature on device performance, the highest efficiency was obtained when the device annealed at a temperature 150 °C for 15 minutes (Figure 1.10 A) which is in good agreement with the 140 °C found by Kim et al. Furthermore, using the optimum temperature (150 °C), Ma et al, also did varied
annealing time (Figure 1.10 B) and found that the efficiency tends toward a maximum after ~30 mins.

Figure 1.10: (A) Device efficiency versus annealing temperature. For this data, the annealing time was 15 min. (B) Evolution of device efficiency with thermal annealing time at 150°C. The device is composed of Al/P3HT:PCBM/PEDOT:PSS/ITO [15].

Ma et al. also compared the performance of devices annealed before and after electrode deposition. By using their optimum temperature and time, Ma et al. performed another interesting experiment wherein it was shown that the Al/P3HT:PC61BM interface plays an important role in the annealing process in regard to the efficiency. Two sets of devices were prepared: one where the annealing was carried out before deposition of the Al electrode, and one where the annealing was carried out after deposition of the Al electrode. The efficiency was measured for both sets of devices as a function of annealing temperature. The results are shown in Figure 1.11.
It is clear from Figure 1.1 that annealing after the Al electrode deposition improves the efficiency at higher temperatures. The authors suggest that at elevated temperatures, processes such as Al diffusion and formation of chemical bonds between Al and P3HT:PCBM (e.g., C-Al or C-O-Al)\[47\] could result in stronger contacts and increased interfacial contact area.

1.4.2 Ratio and Concentration of Donor/Acceptor Materials

The ratio between donor material and acceptor material is very important in organic photovoltaics. Chirvase et al.\[23\] studied the effect of different weight ratios of active layer materials on photovoltaic device performance in 2004. The devices were made from regioregular poly(3-hexylthiophene) (P3HT) and the fullerene derivative [6,6]-phenyl-C$_{61}$ butyric acid methyl ester (PC$_{61}$BM) with weight ratios of 1:0.7, 1:0.8, 1:0.9, 1:1, 1:1.5, 1:2, and 1:3. The results, which show the best device for each ratio, are shown in table 1.1.
As shown in Table 1.1, devices with PC$_{61}$BM concentration 67% and 75% have poor performance. After doing AFM measurement, Chirvase et al. concluded that the poor performance of devices with PC$_{61}$BM concentrations of 67% and 75% was due to the formation of large PC$_{61}$BM crystallites upon annealing. The PC$_{61}$BM crystals provide mechanical stress on the metal electrode and possibly damage the interface. Figure 1.12 shows the AFM images of devices with PC$_{61}$BM concentrations of 50% and 75%.

**Table 1.1**: Electrical device parameters: short circuit current density, $J_{sc}$; open circuit voltage, $V_{oc}$; fill factor, $FF$; power conversion efficiency, $η$; series resistance, $R_s$; parallel resistance, $R_p$ (for dark and illuminated devices), as a function of the PC$_{61}$BM concentration [23].

<table>
<thead>
<tr>
<th>PCBM (%)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>$FF$ (%)</th>
<th>$η$ (%)</th>
<th>$R_s$ (Ω cm$^2$)</th>
<th>$R_p$ (Ω cm$^2$)</th>
<th>Dark</th>
<th>$R_s$ (Ω cm$^2$)</th>
<th>$R_p$ (Ω cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>0.9</td>
<td>0.58</td>
<td>35</td>
<td>0.18</td>
<td>423</td>
<td>566</td>
<td></td>
<td>3099</td>
<td>290235</td>
</tr>
<tr>
<td>67</td>
<td>3.08</td>
<td>0.57</td>
<td>43</td>
<td>0.75</td>
<td>9.8</td>
<td>593</td>
<td>22</td>
<td>977756</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>5.51</td>
<td>0.576</td>
<td>54.87</td>
<td>1.74</td>
<td>2.66</td>
<td>215.51</td>
<td>2.91</td>
<td>239997</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>6.35</td>
<td>0.60</td>
<td>63.2</td>
<td>2.39</td>
<td>3.4</td>
<td>514</td>
<td>3.5</td>
<td>29330</td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>7.23</td>
<td>0.60</td>
<td>45.9</td>
<td>2.01</td>
<td>1.8</td>
<td>298</td>
<td>1.9</td>
<td>93748</td>
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</tr>
<tr>
<td>44</td>
<td>7.17</td>
<td>0.58</td>
<td>39.8</td>
<td>1.64</td>
<td>1.6</td>
<td>219</td>
<td>1.6</td>
<td>374998</td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>6.21</td>
<td>0.60</td>
<td>53</td>
<td>1.94</td>
<td>1.9</td>
<td>680</td>
<td>1.8</td>
<td>39472</td>
<td></td>
</tr>
</tbody>
</table>
Based on the images displayed in Figure 1.1 we realize the following: due to thermal annealing, PC61BM crystallizes, forming relatively large clusters in the P3HT:PC61BM mixture, the vertical extension of which sometimes surpasses 500 nm. When comparing the surfaces of P3HT:PC61BM based solar cells with PC61BM concentrations of 75%, 67%, 60%, and 50%, both density and size of the crystal grains are larger for 75% and 67% PC61BM, whereas they strongly decrease in the other two cases.

AFM images taken on the aluminium contact surface of the cell in Figures 1.12b and 1.12d demonstrate that PC61BM clusters grown on the polymer surface are not suppressed by the coating metal layer.

Chirvase et al. also observed the aluminium surface of annealed devices with a PC61BM weight percentage 50% (Figure 1.13a), 67% (Figure 1.13b), and 75% (Figure 1.13c), respectively, taken with a digital camera. They found that cracks on

Figure 1.12: AFM images in tapping mode (phase) of the P3HT:PC61BM absorber surface (a), (c) as well as of the aluminium electrode (b), (d) for a PC61BM concentration of 50% and 75%, respectively. Scan area 50 × 50 μm² [8].
the aluminium were larger at higher PC{sub}61BM concentrations and yield poor device performances.

**Figure 1.13:** Photographs of annealed ITO/PEDOT:PSS/ P3HT:PCBM/Al solar cells with PCBM concentrations of 50% (a), 67% (b), and 75% (c). \( T_A = 130 \, ^\circ \text{C}, \, t = 20 \, \text{s} \).

In 2005, Ma et al. [15] reported that the best device performance for the P3HT:PC{sub}61BM system was achieved when the mixed solution had a P3HT:PC{sub}61BM ratio of 1.0:0.8, i.e., with a concentration of 1 wt.\% P3HT (10 mg mL\(^{-1}\) ) plus PC{sub}61BM (8 mg ml\(^{-1}\) ) in chlorobenzene and small variations in the ratio resulted in significant changes in the device efficiency. They also found that films cast from solutions with higher concentrations or smaller P3HT:PC{sub}61BM ratios exhibited "overgrown" PC{sub}61BM crystals after high-temperature annealing, leading to degradation of the morphology and poor device performance.

Ma et al. suggest that solution concentration is the reason previous groups had found longer anneal times to be detrimental to device performance [48]. With the concentrations noted in the previous paragraph, Ma et al. found their devices to be extremely thermally stable, with device performance reaching a plateau after 30 minutes of annealing at 150\(^\circ\)C. Devices annealed for several hours were found to maintain this plateau of performance.
1.4.3 Layer Thickness

The active layer thickness is one of major factors that affect the performance of OPV devices. A thicker film would be expected to harvest more photons, leading to a higher absorbance and better performance. However this is offset by the mobility of charge carriers within the active layer. If the active layer is too thick, the efficiency drops due to poor charge carrier transport.

Kumar et al. [14] investigated the effect of active layer thickness on open circuit voltage $V_{oc}$. They found that $V_{oc}$ varies nonlinearly with the active layer thickness even with the same donor/acceptor materials. They proposed a model to show a nonlinear variation of built-in voltage, $V_{bi}$, with active layer thickness (see Figure 1.14). The nonlinear variation of $V_{oc}$ with active layer thickness has been attributed to the variation of $V_{bi}$ in the samples.

![Figure 1.14: The variation of Voc with the active layer thickness (donor + acceptor) in OPV devices based on two different donor/acceptor combinations. Symbols represent the experimental data whereas the solid curves have been plotted to guide the eye for the trend of experimental data [14].](image)

Lenes and Koster in 2006 studied the thickness dependence of the performance of BHJ solar cells based on poly[2-methoxy-5-(3’,7’-dimethyloctyloxy)-1,4-pheny-
lenevinylene] as electron donor and [6,6]-phenyl C_{61} butyric acid methyl ester as electron acceptor [17]. They observed that when the thickness of the device active layer increased, the short circuit current increased, but the fill factor decreased. Therefore the overall power conversion efficiency does not increase. Lenes et al. demonstrated that the decrease in fill factor is due to a combination of charge recombination and space-charge effects. Figure 1.15 shows the increasing active layer thickness effect on efficiency ($\eta$), open circuit voltage ($V_{oc}$), short current density ($J_{sc}$) and fill factor ($FF$).

![Graph](image)

**Figure 1.15:** Overall power conversion efficiency $\eta$, open circuit voltage ($V_{oc}$), short circuit current ($J_{sc}$), and fill factor ($FF$) as a function of active layer thickness under 1 kW/m$^2$ illumination [17].

By using thin-film optical simulation modelling, Boland and Gon [8] demonstrated that optimizing device efficiency is strongly dependent on the
simultaneous control of active layer thickness and the charge carrier mobility as seen in Figure 1.16.

Reidel and Dyakonov also investigated increasing the active layer thickness in 2004 [21]. They created a P3HT:PC$_{61}$BM bulk heterojunction device with an active layer thickness of 350 nm. The device was tested under white-light conditions at 100 mW/cm$^2$. The efficiency of this device was 3.1 %, with a short circuit current of 15.2 mA/cm$^2$. The short circuit current is the highest reported for organic solar cells. However, the fill factor for this device was only 0.37, as compared to 0.60 for a similarly prepared 100 nm thick active layer device. This illustrates the trade-off between higher absorbance and charge carrier mobility that active layer thickness must make. The absorbance of the 350 nm thick device has been increased, illustrated by the very high short circuit current. Whereas the fill factor has been reduced, indicating a rise in series resistance and a subsequent reduction in charge carrier mobility.

![Figure 1.16: P3HT:PC$_{61}$BM device efficiencies as a function of active layer thickness for (a) $\mu_e = \mu_h = 10^{-3}$ cm$^2$/V.s, $\mu_e = 10\mu_h$, $\mu_e = 100\mu_h$ and (b) $\mu_e = \mu_h = 10^{-4}$ cm$^2$/V.s, $\mu_e = 10\mu_h$, $\mu_e = 100\mu_h$ [8].]
1.5 Metal Electrodes

Metal electrodes play a significant role in determining the performance of organic photovoltaic devices. Typically their function is to extract electrons from the active layer and therefore act as the device cathode. Therefore, the selection of appropriate metal electrodes is very important. Work function of the metal is a major consideration in choosing the metal electrode since this will determine how facile electron injection into the electrode is. Some of metals usually used for metal electrode in organic photovoltaics are Al, Ca, Mg, Au, and LiF/Al with work functions of -4.2 eV, -2.89 eV, -3.66 eV, -5.1 eV and -4.3 eV respectively [16].

Eo et al. [16] studied the influence of the metal cathode on organic photovoltaic performance. They used electrode metals with different work function for devices and compared their performance. Electrode metals were chosen to have energy levels above, below and between the energy levels of the HOMO of donor material and LUMO of acceptor material. For the electrode metal they used calcium (Ca), Magnesium magnesium (Mg), aluminium (Al), lithium fluoride/aluminium (LiF/Al). They used P3HT as the donor material and PC$_{61}$BM as the acceptor material in their devices. Figure 1.17 shows the energy levels of the materials and Table 1.2 shows the results.

![Figure 1.17: Energy band diagram of OPV device [16].](image-url)
Table 1.2: Characteristics of different metal electrode devices [16].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Metal electrode</th>
<th>Work function (eV)</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>Efficiency (%)</th>
<th>$R_s$ (Ωcm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ca</td>
<td>-2.89</td>
<td>0.37</td>
<td>-8.21</td>
<td>0.52</td>
<td>1.59</td>
<td>8.28</td>
</tr>
<tr>
<td>2</td>
<td>Mg</td>
<td>-3.66</td>
<td>0.40</td>
<td>-9.17</td>
<td>0.51</td>
<td>1.85</td>
<td>8.96</td>
</tr>
<tr>
<td>3</td>
<td>Al</td>
<td>-4.20</td>
<td>0.52</td>
<td>-9.27</td>
<td>0.53</td>
<td>2.54</td>
<td>3.24</td>
</tr>
<tr>
<td>4</td>
<td>LiF/Al</td>
<td>-4.30</td>
<td>0.60</td>
<td>-9.74</td>
<td>0.61</td>
<td>3.54</td>
<td>2.87</td>
</tr>
<tr>
<td>5</td>
<td>Au</td>
<td>-5.10</td>
<td>0.26</td>
<td>-8.28</td>
<td>0.44</td>
<td>0.94</td>
<td>7.06</td>
</tr>
</tbody>
</table>

From Table 1.2, Eo et al. concluded that high performance of devices using Al and LiF/Al as the metal electrode was due to their work function energy being close to the HOMO energy of the acceptor material (PC$_{61}$BM). Moreover, the work function of LiF/Al is the same as the HOMO energy of PC$_{61}$BM and as a result, no barrier energy for electron injection exists between LiF/Al electrodes with PC$_{61}$BM. Therefore devices with LiF/Al as a metal electrode have higher performance compared to other metal electrodes. For devices using gold as the electrode metal, they concluded that they have low performance due to the formation of a Schottky type contact between the active layer and the electrode which leads to low charge extraction.

Brabec et al. [49] coated the active layer with thin insulating interlayers of lithium fluoride (LiF) before deposited a metal electrode of Al and Au. For comparison, they also made devices without LiF and devices with SiO$_x$ as insulating interlayers. They found that inserting LiF significantly enhanced the fill factor and stabilizes high open circuit voltages for both electrode metals, Al and Au. In contrast, inserting SiO$_x$ results in lower overall efficiencies.

Zhao et al. [19] investigated the effect of thermal annealing before and after cathode deposition on poly(3-hexylthiophene)P3HT/[6,6]-butyric acid methyl ester (PC$_{61}$BM) blend photovoltaic cells with different cathode buffer layers. They used LiF
and CaO as buffer layers with the thickness of each 1 nm. The results as shown in Figure 1.18.

![Comparison of the V_{oc} (a), J_{sc} (b), PCE (c), and FF (d) of the photovoltaic cells with Al, LiF/Al and CaO/Al cathodes, where the P3HT:PCBM blend were thermally annealed before or after cathode deposition [19].](image)

**Figure 1.18:** Comparison of the $V_{oc}$ (a), $J_{sc}$ (b), PCE (c), and FF (d) of the photovoltaic cells with Al, LiF/Al and CaO/Al cathodes, where the P3HT:PCBM blend were thermally annealed before or after cathode deposition [19].

Zhao et al. found that inserting a buffer layer in pre-annealed devices can increase the open-circuit voltage and the power conversion efficiency (PCE). This enhancement was attributed to two reasons. Inserting a thin buffer layer of LiF or CaO prohibits dipole formation at the PC$_{61}$BM/Al interface and blocks exciton quenching by the Al cathode. Devices annealed after cathode deposition further increase the Al and LiF/Al device performance but decrease the performance for CaO/Al devices. Further improvement of Al and LiF devices post-annealing is because the dipole or chemical reaction may become stronger. For CaO devices, post-annealing may cause a
discontinuous CaO film and destroy its connection between the P3HT:PC\textsubscript{61}BM layer and Al cathode, and therefore the performance is not further improved.

Zhao et al. also made post-annealed devices with cathodes of Al, Ca/Al, and CaO/Al (Ca/Al devices were exposed to air for 60 minutes post-annealing to form CaO/Al devices). Figure 1.19 shows the IV curve of the devices.

![IV curve of devices](image)

**Figure 1.19:** The illuminated $J$–$V$ curves of the P3HT:PCBM photovoltaic cells with Al, Ca/Al and Ca/Al (exposed to the air for 60 min) cathodes [19].

As shown in Figure 1.19, the performance of CaO/Al devices increased significantly. Zhao attributed this improvement to a CaO layer which was formed after Ca/Al devices were exposed to the air, this realigned the energy level of P3HT:PC\textsubscript{61}BM/Al interface and increased the shunt resistance ($R_{sh}$) of the devices.

He et al. [21] also investigated the effect of the cathode materials (Mg, Ca, LiF/Al, Ba) on the performance of devices. They used 4,7-bis(50-[400,400-N,N-diphenylamino-styryl]thiphen-20-yl)-benzo[1,2,5-thiadiazole] (simplified as TPA-th-TPA) as the electron donor and PC\textsubscript{61}BM as the electron acceptor. They concluded that the lower work function of the cathode the better the devices performance. The results are shown in Figure 1.20.
1.6 Acceptor

The electron acceptor is also a key parameter in determining the performance of organic photovoltaic devices. Therefore many studies of electron acceptors have been conducted in order to improve the performance of organic photovoltaic devices.

Brabec et al.[7] analysed the effect of acceptor strength (potential redox) on the open circuit voltage, $V_{oc}$, of organic photovoltaic devices. The devices were made from poly(2-methoxy-5-(3’,7’-dimethyloctyloxy)-1,4-phenylenevinylene) (MDMO-PPV) as the electron donor and for electron acceptor they used PC$_{61}$BM, other fullerenes, and ketolactame. Figure 1.21 shows the chemical structures of the materials and Table 1.3 shows the relative strength of the acceptor materials.

**Figure 1.20:** I–V curves of the organic solar cells of ITO/PEDOT: PSS/TPA-th-TPA: PCBM/cathode (Mg, Ca, LiF/Al, Ba) [21].
From their investigation, they found that the open circuit voltage in plastic solar cells is directly related to the acceptor strength of the fullerenes as shown in Figure 1.22.

**Figure 1.21:** Chemical structures of the investigated compounds. (a) MDMO-PPV, (b) azafulleroid 5, (c) ketolactam 6, (d) PCBM, and (e) C60. (modified from [7])

**Table 1.3:** Redox potentials (V vs Normal Hydrogen Electrode) of C60 and fullerene derivatives [7].

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E^1_{\text{red}}$</th>
<th>$E^2_{\text{red}}$</th>
<th>$E^3_{\text{red}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCBM</td>
<td>-0.69</td>
<td>-1.09</td>
<td>-1.57</td>
</tr>
<tr>
<td>Azafulleroid 5</td>
<td>-0.67</td>
<td>-1.07</td>
<td>-1.52</td>
</tr>
<tr>
<td>Ketolactam 6</td>
<td>-0.53</td>
<td>-0.93</td>
<td>-1.41</td>
</tr>
<tr>
<td>C60</td>
<td>-0.60</td>
<td>-1.01</td>
<td>-1.46</td>
</tr>
</tbody>
</table>
Zhao et al. [20] reported that the alkyl chain length has an effect on the photovoltaic properties of fullerene acceptors. In their study, they designed and synthesized a series of PCBM-like C₆₀ derivatives, F1, F2, F3, F4, and F5. The molecule structures of the derivatives are shown in Figure 1.23. They made devices using P3HT as electron donor and F1-F5 as electron acceptor in a ratio 1:1 by weight. The device structure is ITO/PEDOT:PSS/P3HT:F1-F5 (1:1, w/w)/Ca/Al. Table 1.4 shows the performance of the devices.

Zhao et al. concluded that the variation in device performance shown in Table 1.4, was due to the different alkyl chain length which influence the absorption, electron mobility, morphology of the films, and the interface structure of P3HT/fullerene derivative.

Figure 1.22: $V_{oc}$ versus acceptor strength. The slope $S_1$ was derived from the fitting procedure. (modified from[7])

Figure 1.23: Molecular structures of the five fullerene derivatives F1-F5[20].
He et al. [12] studied the effect of the LUMO energy level of acceptor materials on organic photovoltaic device performance. They used [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM), indene-C_{60} monoadduct (ICMA), and indene-C_{60} bisadduct (ICBA) as electron acceptor materials. Figure 1.24 shows the chemical structures of the ICMA and ICBA materials. From their experiments and calculations, they found the LUMO level energy of PC_{61}BM, ICMA, and ICBA to be -3.91 eV, -3.86, and -3.74 respectively.

<table>
<thead>
<tr>
<th>Active layer</th>
<th>$V_{oc}$ [V]</th>
<th>$I_{sc}$ [mA cm$^{-2}$]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT/F1</td>
<td>0.564</td>
<td>10.8</td>
<td>60.3</td>
<td>3.7</td>
</tr>
<tr>
<td>P3HT/F2</td>
<td>0.571</td>
<td>9.6</td>
<td>64.6</td>
<td>3.5</td>
</tr>
<tr>
<td>P3HT/F3</td>
<td>0.535</td>
<td>8.1</td>
<td>53.2</td>
<td>2.3</td>
</tr>
<tr>
<td>P3HT/F4</td>
<td>0.596</td>
<td>9.9</td>
<td>61.5</td>
<td>3.6</td>
</tr>
<tr>
<td>P3HT/F5</td>
<td>0.540</td>
<td>9.3</td>
<td>56.4</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Table 1.4: Photovoltaic performance of the PSCs based on a blend of P3HT and F1–F5 (1:1, w/w) under the illumination of AM1.5G, 100mWcm$^{-2}$ [20].

They fabricated devices using P3HT as the electron donor with a ratio donor:acceptor 1:1 by weight. The devices were prepared under the same conditions and tested under the illumination of AM1.5G 100 mW/cm$^2$. Table 1.5 shows the results.
As shown in table 1.5, the open circuit voltage ($V_{oc}$) of ICBA devices was higher than ICMA devices and ICMA devices were higher than PC$_{61}$BM devices. He et al. concluded that the higher LUMO level energy of the electron acceptor in the device, the higher the $V_{oc}$ of the resultant.

### 1.7 Nanoparticulate Organic Photovoltaics

Nanoparticulate organic photovoltaic devices are organic photovoltaic devices produced from conjugated polymer blends dispersed as nanoparticles in water. These organic photovoltaic devices have recently been attracting much attention since they offer the potential of morphological control coupled with device processing in the absence of organic solvents which are toxic to human beings and the environment. Reel-to-reel processing of water-dispersed nanoparticulate polymer solar cells has been demonstrated for a range of low band gap materials [50]. In addition, recent work has shown that nanoparticles produced by the miniemulsion technique add a level of control of active layer morphology unachievable by conventional blending and processing methods [51] and can achieve device PCEs which challenge even the corresponding BHJ devices.

Several publications now report water-based nanoparticulate OPVs. In 2003, Kietzke et al. [52] created NP-OPV devices from PFB and F8BT materials by the spin coating method. Although the power conversion of their devices is several order magnitude less than the power conversion of a PFB:F8BT BHJ OPV device, 0.2 % [53],

<table>
<thead>
<tr>
<th>acceptor</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^2$)</th>
<th>FF</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCBM</td>
<td>0.58</td>
<td>10.8</td>
<td>0.62</td>
<td>3.88</td>
</tr>
<tr>
<td>ICMA</td>
<td>0.63</td>
<td>9.66</td>
<td>0.64</td>
<td>3.89</td>
</tr>
<tr>
<td>ICBA</td>
<td>0.84</td>
<td>9.67</td>
<td>0.67</td>
<td>5.44</td>
</tr>
</tbody>
</table>

Table 1.5: Photovoltaic performance of the P3HT-Based PSCs with different acceptors [12].
the open circuit voltage was a respectable, 1.38 V. Snait et al. [54] also made NP-OPV devices from PFB and F8BT using an electroplating technique but the open circuit voltage was lower at 0.75 V and also power conversion efficiency lower than Kietzke’s. Recently, Stapleton at al. [53] reported efficiency of PFB:F8BT NP-OPV device at about 0.8 % which is 4 times higher than efficiency of PFB:F8BT BHJ device. This high efficiency was achieved by controlling both nanoparticle morphology and inter-particle interactions through a multilayer method. In his thesis [6], Stapleton also reported NP-OPV devices from P3HT and PC\textsubscript{61}BM and the highest efficiency of these devices was about 0.5 %, which is still lower than P3HT:PC\textsubscript{61}BM BHJ devices. This low efficiency indicated the need more to optimize the performance of P3HT:PC\textsubscript{61}BM NP-OPV devices.

The active layer of nanoparticle organic photovoltaic devices can be either a mixture of different nanoparticles or nanoparticles containing a blend of donor and acceptor material as shown in Figure 1.25. Nanoparticle organic photovoltaic devices can be prepared by using a spincoater.

![Figure 1.25: Spin-coating either a mixture of different particles or particles containing a blend of polymers [24].](image)

*Figure 1.25: Spin-coating either a mixture of different particles or particles containing a blend of polymers [24].*
1.7.1 Miniemulsion

In 1980, Chou et al. [55] published for the first time the properties of an emulsion they called a miniemulsion. Miniemulsions are stable droplets with a size of 50-500 nm and can be produced by mixing water, a surfactant and a water insoluble compound using ultrasound [56]. Landfester et al. used ultrasound to create aqueous dispersions of organic polymer solution droplets [56]. Figure 1.26 shows the scheme of preparation of aqueous dispersion via miniemulsion technique.

![Figure 1.26: Preparation of a dispersion of solid polymer nanoparticles in water via miniemulsion technique (modification from [24]).]

The polymer is initially dissolved in an organic solvent and introduced to an aqueous surfactant solution to obtain a macroemulsion. To get a miniemulsion, the macroemulsion is sonicated with ultrasound. The miniemulsion can then be heated to remove the organic solvent that is still retained in the droplets. Evaporation of the solvent results in a stable dispersion of solid polymer nanoparticles in water. However, this dispersion still contains surfactant molecules. Therefore, a dialysis process is needed to reduce or to remove them and also to concentrate the dispersion.

In order to keep miniemulsions stable for long periods of time, the process of degradation (which can occur through a process called Otswald ripening [57] and also coalescence, a process caused by the collision between suspended droplets [58]) must be prevented. Ostwald ripening is a process in which the interfacial area of the dispersed phase is reduced through the process of mass transfer from the high interface curvature.
to low interface curvature. The rate of Ostwald ripening depends on the polydispersity, size and solubility of the dispersed phase in the continuous (in this case aqueous) phase. Ostwald ripening can be efficiently counteracted by the addition of a hydrophobe to the dispersed phase. The most important requirement of the hydrophobe is low solubility in water. In the literature, the stability of miniemulsions is described as metastable or fully stable. The existence of a hydrophobe in emulsion droplets can provide full stability against coalescence [59].

1.7.2 Surfactant and Micelle formation

Surfactant stands for surface active agent and they are used to lower the free energy of phase boundaries. An individual surfactant molecule has a head and tail, as shown in Figure 1.27. The head of a typical ionic surfactant is hydrophilic, which means water loving, while its tail is hydrophobic which means water repelling. Therefore the surfactant is amphipathic.

![Figure 1.27: The basic structure of a surfactant molecule [6].](image)

Based on the charge present on its head, a surfactant can be classified as an anionic surfactant, a cationic surfactant, a non-ionic surfactant, or an amphoteric/zwitterionic surfactant [4]. Anionic surfactants have the head negatively charged and this is the most widely used surfactant in the cleaning industry. A cationic surfactant has its head positively charged and is most used for its disinfectant and preservative properties. Non-ionic surfactants have no head charge and are typically
used as grease/oil removers and emulsifiers. Amphoteric/zwitter-ionic surfactants can be anionic, cationic, or contain two charged group of different sign, depending on the acidity (pH) of the water. Amphoteric/zwitterionic surfactants are good for use in personal care preparations for over sensitive skins. Table 1.6 shows some examples and structures of surfactants of each class.

Table 1.6: Surfactant classifications [4].

<table>
<thead>
<tr>
<th>Class</th>
<th>Examples</th>
<th>Structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anionic</td>
<td>Na stearate</td>
<td>CH$_3$CH$_2$COO$^-$Na$^+$</td>
</tr>
<tr>
<td></td>
<td>Na dodecyl sulfate</td>
<td>CH$_3$CH$_2$SO$_4$Na$^+$</td>
</tr>
<tr>
<td></td>
<td>Na dodecyl benzene sulfonate</td>
<td>CH$_3$CH$_2$CH$_2$CH$_2$SO$_4$Na$^+$</td>
</tr>
<tr>
<td>Cationic</td>
<td>Laurylamine hydrochloride</td>
<td>CH$_3$CH$_2$NH$_2$Cl</td>
</tr>
<tr>
<td></td>
<td>Trimethyl dodecylammonium chloride</td>
<td>CH$_3$H$_2$N(CH$_3$)$_2$CT</td>
</tr>
<tr>
<td></td>
<td>Cetyl trimethylammonium bromide</td>
<td>CH$_3$CH$_2$H$_2$N(CH$_3$)$_2$Br$^-$</td>
</tr>
<tr>
<td>Non-ionic</td>
<td>Polyoxyethylene alcohol</td>
<td>C$_2$H$_4$O(OC$_2$H$_2$)$_n$OH</td>
</tr>
<tr>
<td></td>
<td>Alkylphenol ethoxylate</td>
<td>C$_6$H$_5$C$_6$H$_4$-(OC$_2$H$_4$)$_n$OH</td>
</tr>
<tr>
<td></td>
<td>Polysorbate 80</td>
<td>R = (C$<em>n$H$</em>{2n+1}$)COO</td>
</tr>
<tr>
<td></td>
<td>Propylene oxide-modified polymethylsiloxane (EO = ethyleneoxide, PO = propyleneoxide)</td>
<td>(CH$_3$)$_2$SiO$_x$((CH$_3$)$_2$SiO)$_y$(CH$_3$)$_2$Si(CH$_3$)</td>
</tr>
<tr>
<td>Zwitterion</td>
<td>Dodecyl betaine</td>
<td>C$<em>{12}$H$</em>{25}$N$^+$((CH$_3$)$_2$CH$_2$COO$^-$</td>
</tr>
<tr>
<td></td>
<td>Lauramidopropyl betaine</td>
<td>C$<em>{16}$H$</em>{33}$CONH(CH$_3$)$_2$N$^+$((CH$_3$)$_2$CH$_2$COO$^-$</td>
</tr>
<tr>
<td></td>
<td>Cocamidopropyl-2-hydroxypropyl sulfobetaine</td>
<td>C$<em>{16}$H$</em>{33}$CONH(CH$_3$)$_2$N$^+$((CH$_3$)$_2$CH$_2$CH(OH)CH$_2$SO$_4$$^-$</td>
</tr>
</tbody>
</table>
results in micelles undergoing further self-assembled transformations, forming periodic hexagonal, cubic, or lamellar mesophases as shown in Figure 1.28.

![Figure 1.28: Schematic phase diagram for cetyltrimethylammonium bromide (CTAB) in water. Arrow denotes the evaporation-driven pathway during dip-coating, aerosol processing, etc.[9].](image)

In nanoparticle organic photovoltaics, micelles are the methodology used to create the nanoparticle. Landfester et al. produced nanoparticles of semiconducting polymers dispersed in aqueous solution by micelle formation [56].

1.8 Aim and outline of thesis

To date efficiencies of nanoparticulate organic photovoltaic (NP-OPV) devices have been disappointingly low compared to standard BHJ organic photovoltaic devices. This is at least in part due to the preparation and fabrication conditions for NP-OPV not being optimised as yet. In this thesis we reveal fabrication conditions for NP-OPV devices that showed a large improvement in efficiency compared to previous work. We
also describe the structural motif of NP-OPV devices and determine how this affects their performance of NP-OPV.

In Chapter 3 we focus on optimising the ratio, concentration, and thickness of the active layer. The ratios of donor:acceptor that we use are 2:1; 1:1; 1:2. For the concentration of polymer and solvent, we use concentration 36 mg/mL; 54 mg/mL; 71 mg/mL; 89 mg/mL; 107 mg/mL; 179 mg/mL. The volume of the chloroform was kept the same, 560 µl. Different thicknesses of the active layer were obtained by adjusting the speed of the spincoater. The thickness of the active layer was measured using a profilometer.

In Chapter 4, we focus on the thermal annealing effect on nanoparticle organic photovoltaics. There are two annealing steps used in this project. The first step is annealing before electrode deposition. This step is called annealing of the active layer or sometimes simply “drying” because the solution is a water-based solution. The second step is annealing after electrode deposition and is referred to as annealing the device. In this chapter we investigate drying temperature, drying time, annealing temperature and annealing time for both of these steps to determine the optimum time and temperature for device performance.

In Chapter 5 we discuss and investigate the metal electrode. In this project we compare the performance of devices that use metal electrodes of aluminium (Al), calcium/aluminium (Ca/Al) and lithium fluoride/aluminium (LiF/Al). We will determine and discuss the effect of using these different cathode interface layers on the power conversion efficiency (PCE) the open circuit voltage, $V_{oc}$, the short circuit current density, $J_{sc}$ and the fill factor, $FF$ of the device.

Finally, in Chapter 6 we discuss the use of different acceptors in NP-OPV devices. The acceptors that we use in this project are PC$_{61}$BM, PC$_{71}$BM, and ICBA. In
this chapter we also discuss the morphology of the active layer and its effect on device performance.
2

Experimental

The following experimental section lists details of nanoparticle fabrication and characterisation, nanoparticle organic photovoltaic device fabrication and characterisation and describes the relevant techniques for both processes.

2.1 Materials

The semiconducting materials used in this project were poly(3-hexylthiophene) (P3HT) and phenyl-C$_{61}$-butyric acid methyl ester (PC$_{61}$BM) both purchased from Luminance Technology (LUMTEC), phenyl-C$_{71}$-butyric acid methyl ester (PC$_{71}$BM) and indene-C$_{60}$ bisadduct (ICBA) purchased from Solenne B.V., Netherlands. In this project we used two different batches of P3HT. Batch 1 and batch 2 have molecule weights of 22,000 Da and 18,000 Da respectively. Figure 2.1 shows the chemical structures of the materials used.

Material cathodes used during this investigation were composed of aluminium (Al), calcium (Ca), and lithium fluoride (LiF). All materials for the cathode were purchased from Sigma Aldrich. For anode electrodes, we used pre-pattern indium tin oxide (ITO) substrates which were purchased from Kintec Company, Hong Kong. Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) which was used as a hole transport layer, to smooth the ITO surface, and as an electron blocking layer on the ITO [1] was obtained from H.C Stark, U.S and used as received.

During the miniemulsion process, we used MQ water and anhydrous chloroform. MQ water is water that has been processed through a Milli-Q®plus system in which the
conductivity of the water is monitored and kept below 10 $\mu$S.cm$^{-1}$. Sodium dodecyl sulphate (SDS) used in this process was purchased from BDH Lab and Sigma-Aldrich at a purity of 90-99 % and used as received.

![Chemical structures of semiconducting materials](image)

**Figure 2.1:** Chemical structures of semiconducting materials used during this project.

### 2.2 Nanoparticle Synthesis

A total of 30 mg of semiconducting materials were dissolved in 560 $\mu$l of anhydrous chloroform. The materials were dissolved in the anhydrous chloroform by stirred the mixture at 500 rpm, at 35 °C for 25 minutes then sonicating in an ultrasonic bath (Unisons FXP10M) for 25 minutes at a temperature of 50 °C. As much as 33 mg of SDS was dissolved in 2.78 ml of MQ-water by stirring at 500 rpm for 10 minutes (until no more aggregates were observed). The chloroform solution was poured into SDS solution and then stirred at 1200 rpm for 1 hr at a constant temperature of 33 °C to form a macroemulsion. The macroemulsion was then sonicated using a Branson 450
analogue sonicator operating at 60% of maximum amplitude for 2 minutes to form the miniemulsion.

To evaporate the solvent (the chloroform), the miniemulsion was then heated at a temperature of 60 °C while being stirred at 1200 rpm for a minimum of 3 hours to obtain nanoparticles dispersed in water. The aqueous dispersion produced still contains surfactant molecules. Therefore, a dialysis process is needed to reduce or to remove them and also to concentrate the dispersion. The schematic of production of the aqueous dispersion through the miniemulsion process is shown in Figure 1.16.

The dialysis tube filters used in this project have a maximum volume of 4 ml and a filtration area of 3 cm$^2$. These dialysis tube filters were purchase from Millipore (10 kDa MWCO). The aqueous dispersions produced by the miniemulsion process were placed into the dialysis tube filters and centrifuged at 4000 rpm for 7 minutes. The filtrate collected in the bottom after centrifuging was removed and the dispersion remaining above the filter was topped up with 2-2.5 ml of MilliQ water. The tube was sealed and centrifuged again for a further 7 minutes at 4000 rpm. This process was repeated until the surface tension of the dispersion reached 38 ± 2 mN/m or its volume reach 500 μl. The dispersion was then placed into a pre-cleaned glass vial and was ready to be used.

2.3 Dynamic Light Scattering (DLS)

DLS is a widely used and powerful technique in nanoparticle science since it can measure the size of particles in solution in the range of nm - μm. DLS works by measuring the intensity of light scattered by the particles in the solution. The intensity of light scattered depends on particle movement speed which is determined by solution temperature, solution viscosity, and the size of particle in the solution. If temperature
and viscosity of the solution is kept constant, then the intensity change relates directly to the particle size in the solution.

The size of particle in the solution is calculated by using the Stokes-Einstein equation;

\[ d(H) = \frac{kT}{3\pi\eta D} \]  \hspace{1cm} (2.1)

where \( d(H) \) is the hydrodynamic diameter, \( D \) is the translational diffusion coefficient, \( k \) is Boltzmann’s constant, \( T \) is the absolute temperature, and \( \eta \) is viscosity.

A typical of dynamic light scattering instrument consists of a laser, detectors, an attenuator, a cell (sample), a digital signal processor, and a computer. Figure 2.2 shows the optical configurations of the Zetasizer Nano series for dynamic light scattering measurements. A laser (1) functions as a source light to illuminate the samples in a cell (2). An attenuator (4) is used to adjust the intensity of the light so that it is compatible with the detector (3). When the cell (2) is illuminated, the light will be scattered by the particles in the solution. The detector detects the scattered light and sends a scattering intensity signal to the correlator (5). In the correlator, the scattered intensity signal is compared and this information is then analysed by the computer to determine particle size information.
To measure the hydrodynamic diameter of the particles in the nanoparticle solutions in this study, we used a NanoSeries ZetaSizer Nano-ZS (Figure 2.3) purchased from Malvern Instrument, UK. This instrument is equipped with a helium-neon laser source which was operated at a wavelength of 633 nm and a power of 4.0 mW. Samples were prepared by diluting 2.6 μl of NP solution with 3 ml of MQ-water. The diluted solution was then placed into a plastic disposable cuvette, supplied by Malvern. The disposable cuvette was then placed in the instrument. By using a computer with Malvern software to control the instrument, the average (Z-average, Z_D) particle diameter in the solution and also its polydispersity index (PDI) were obtained. PDI is a measure of the width of a Gaussian distribution and can be calculated by the following equation:

![Figure 2.2: Optical configurations of the Zetasizer Nano series for dynamic light scattering measurements [5].](image-url)
\[ PDI = \frac{\sigma^2}{Z_D^2} \] (2.2)

where \( \sigma \) is the standard deviation of the Gaussian distribution.

2.4 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is a technique used to analyse the thermal properties of materials and is widely used in chemistry [64], biotechnology [65], pharmacology [66, 67], and nanoscience [68]. It can be used to determine the temperature transitions of materials such as the glass transition temperature \( (T_g) \), crystallisation temperatures \( (T_c) \), and melting point temperatures \( (T_m) \).

DSC works based on the fact that when materials undergo phase transitions, they will absorb or release heat depending on the process. If the process is exothermic the material will release heat and if the process is endothermic it will absorb heat. A DSC instrument comprises two pans which are usually made from aluminium. One pan is for sample and another one is left empty as a reference. These two pans are heated and
controlled so that temperature difference between the two pans is kept close to zero. Therefore as the sample undergoes phase transitions either more or less energy is required to keep the temperature difference between the pans at zero. The energy difference is recorded by the instrument. The computer then plots the difference in heat output of the two heaters against the temperatures of the pans. Figure 2.4 shows a schematic of DSC system.

Figure 2.4: Schematic of DSC systems [1].

Figure 2.5 shows a typical plot of the heat flow of sample pan versus its temperature. Not all materials will have plots like Figure 2.5 since some of materials do not have crystallisation states such as completely amorphous polymers. We will not observe a crystallisation temperature transition or even melting temperature for a completely amorphous polymer.
In this investigation we used a system consisting of a Shimadzu DSC-60A instrument and a Shimadzu TA-60WS thermal analyser. The sample was prepared by firstly weighing the two empty aluminium pans. One of the pans was then filled with 2 or 3 drops of nanoparticle solution by drop casting. The other aluminium pan was left empty as a reference. The nanoparticle solution in the sample pan was then dried overnight in a laminar flow cabinet to prevent contamination of the sample. After the nanoparticle solution in the sample pan had dried, it was weighed to determine the mass of the sample. The sample pan and the reference pan were then sealed and put into the instrument and the thermal properties determined. By using a computer, the temperature rate can be adjusted and in this investigation the temperature rate was set at 10 °C/min.

2.5 UV-visible Spectroscopy (UV-Vis)

Ultra-violet and visible spectroscopy is a widely used technique in chemistry, since all inorganic and organic molecules tend to absorb electromagnetic energy in the UV-visible region. This instrument works based on the fact that light energy is absorbed by a molecule if the incident light has the same energy as an electronic transition within the molecule. The energy of the electronic transition will be different for each molecule.
Therefore the molecules can be identified by analysing the light energy absorbed. The Beer-Lambert Law states that at a given wavelength the proportion of light absorbed by a medium is proportional to the number of absorbing molecules. Mathematically, the Beer-Lambert Law can be written as:

$$\log(I_o/I) = \varepsilon cl$$  \hspace{0.5cm} (2.3)

where $I_o$ is the incident light, $I$ is the transmitted light, $\varepsilon$ is the absorption coefficient, $c$ is the concentration, and $l$ is the path length (Figure 2.6)

![Figure 2.6: Principle of UV-vis spectroscopy](image)

In this investigation a Varian Cary 6000i UV-Vis-NIR spectrophotometer (Figure 2.7) was used to investigate the absorption of films produced from nanoparticle solutions. The nanoparticles could be composed of one material or a blend of semiconducting materials. Samples were prepared by spin casting nanoparticle solutions onto quartz substrates. The wavelength of the instrument was set to record in the range of 250 to 800 nm.
X-Ray Photoelectron Spectroscopy (XPS) is a powerful technique to analyse the surface chemistry of thin films with a depth of measurement of only few nanometres. This technique provides information about the atoms or molecules present on the surface of a material. With additional ion etching, it can be used to detect elemental composition as a function of depth into a film. XPS is based on the photoelectric effect. An electron can be removed from its orbital and escapes from a material when the electron absorbs energy from a photon which is larger than its binding energy and the work function of the material. This electron is then called a photoelectron. The kinetic energy of a photoelectron can be written as:

$$KE = h\nu - BE - \phi_s$$

(2.4)

where $h\nu$ is the photon energy, $BE$ is the binding energy of the electron in its original orbital, and $\phi_s$ is the work function of material.

There were two kinds of XPS used in this investigation. Traditional XPS was used to investigate the composition of film surfaces and XPS depth profiling was used to investigate the elemental depth profile of device architectures. For the surface analysis
we used a PHI 550 XPS spectrophotometer located in the University of Newcastle (Figure 2.8).

![Figure 2.8: PHI 550 surface analysis system at the COE [2].](image)

Samples for surface analysis were prepared by spin casting nanoparticle solution onto silicon substrates (1 x 1 cm) and the substrates were then dried in the same manner as nanoparticle organic photovoltaic (NP-OPV) device preparation. Samples were then placed into a UHV chamber and illuminated with Al Kα X-rays (1486.6 eV photon energy) to collect the spectra. Survey spectra had a pass energy of 100 eV over the spectral range of 0–1100 eV and the range was traversed with a 0.5 eV step size. Higher resolution scans of elemental peaks over narrower energy bands had a step size of 0.2 eV and pass energy of 50 eV.

Depth profile investigations were performed at UNSW Sydney using an ESCALAB 250Xi (Figure 2.10). Samples for the depth profile investigation were fully functioning NP-OPV devices. Samples were put in a vacuum chamber with pressure better than 2x10⁻⁹ mbar. The sample was illuminated with Al Kα (photon energy 1486.6 eV). The pass energy for survey scans are 100 eV, 20 eV for surface region scans, and 50 eV for depth profiling.
2.7 Atomic Force Microscopy (AFM)

Atomic Force Microscopy is a useful tool to record topographic surface images at the nano scale [69-73]. It can be used in organic photovoltaics to investigate the morphology, roughness, and thickness of the active layer created by spin casting onto a substrate. Figure 2.10 shows the schematic of basic AFM operation.

The tip mounted on a cantilever scans the surface of the sample and moves up and down based on the sample surface. Consequently, the laser beam on the tip then is reflected at different angles. The photodiode detects the reflected beam and converts it into an electric signal. The computer then uses the signal as a feedback to control the tip to maintain either a constant force or constant height above the sample. The piezoelectric scanner translates the sample in the x, y, and z directions.

Figure 2.9: ESCALAB 250Xi Spectrophotometer
AFM can be operated in 3 modes: non-contact mode, contact mode, and tapping modes [74]. In non-contact mode, the tip just oscillates above the sample with a frequency little bit higher than its natural frequency. In contact mode, the cantilever tip is in contact with surface sample. In tapping mode, also called AC mode, the cantilever tip oscillates above the sample and lightly taps the sample surface.

In this project, we used an AFM from Asylum Research (Figure 2.11) operated in AC mode (for high resolution imaging of soft samples) to investigate morphology, roughness, and the thickness of nanoparticle films. It was also used to determine the size of individual nanoparticles. The cantilever used has 125 μm length and the tip has a radius of ~10 nm and a height of 17 μm.

Samples were prepared by spin casting 20 μl of nanoparticle solution onto a pre-cleaned glass silica slide (1 cm x 1 cm) which was then dried on a hot plate under the same conditions as during NP-OPV device fabrication.

Figure 2.10: Schematic diagram of the Nanoscope IIIE AFM [6].
2.8 Transmission Electron Microscopy (TEM)

The Transmission Electron Microscope (TEM) is a useful instrument to image samples on the nanoscale. In nanoparticulate samples, TEM is used to investigate nanoparticle properties such as size, structure and packing in films. TEM typically consists of an electron canon as an electron source, magnetic lenses to focus or to spread the electron beam, and a scintillator plate for display. When electrons from the electron canon bombard the sample, some of electrons will be reflected, absorbed, and transmitted by the sample. Only transmitted electrons will reach the scintillator plate. The number of electrons transmitted depends on how thick the part of the sample that is hit by the electrons is. The thinner the part of the sample that hit by the electrons, the more electrons are transmitted. Transmitted electrons are then focused or spread by magnetic lenses. Eventually, transmitted electrons reach the scintillator plate which flashes when hit by an electron. The more electrons hit an area of the plate the brighter the area. Different brightnesses on the scintillator plate then describe the sample.

During this investigation a Joel 1200EXII TEM (1992) (Figure 2.12) and digital imaging (2007) software were used to acquire TEM images of nanoparticle dispersions.
The nanoparticle dispersions for the samples were prepared by myself. Sample preparation and measurement were done by Ms. Natalie P. Holmes and Dr. Kerry B. Burke. Samples were prepared by spin cast (3000 rpm, 1 minute) 5 μl diluted nanoparticle solutions onto a low stress silicon nitride window with oxide coating. The window dimensions are 0.25 x 0.25 mm and the thickness 15 nm with a 5 x 5 mm frame. The diluted nanoparticle solution was obtained by diluting the as fabricated nanoparticle solution into 1/10 of initial concentration using MQ-water. The samples were then air dried before loading into the instrument chamber. The instrument was operated at 80 kV. Figure 2.12 shows the instrument system.

**Figure 2.12:** A Joel 1200EXII TEM (1992) 1: Electron cannon, 2: Electromagnetic lenses, 3: Vacuum pumps system, 4: Opening to insert a grid with samples into the high-vacuum chamber for observation, 5: Operation panels (left for alignment; right for magnification and focussing; arrows for positioning the object inside the chamber), 6: Screen for menu and image display, 7: Water supply to cool the instrument.
2.9 Scanning Transmission X-ray Microscopy

STXM is a powerful technique to analyse chemical composition and structure of materials in nanoscale. This technique is becoming widely used in biotechnology and polymer science [75, 76]. Scanning Transmission X-ray Microscopy is a combination of Near Edge X-Ray Absorption Fine Structure (NEXAF) and the scanning of an analysis spot size of 25 nm. Figure 2.13 shows STXM schematically. X-rays, usually from a synchrotron, are focused by a Fresnel zone plate. A thin (maximum of a few hundred nm) section of a specimen is placed in at the focus point of the X-rays. The specimen is then scanned by rastering it in front of the X-rays spot and the transmitted X-rays are recorded by the X-ray detector.

![Figure 2.13: Schematic representation of the STXM technique.](image)

STXM measurements were performed at the Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley California, on beamline 5.3.2.2. In this project, nanoparticle dispersions for the samples were prepared by myself. Samples preparation and measurements were conducted by Ms. Natalie P. Holmes. The silicon nitride (Si$_3$N$_4$) window mounted sample is rastered with respect to the X-ray beam in helium (0.33 atm) with the transmitted X-ray signal detected by a scintillator and a
photomultiplier tube. The energy of the X-ray beam was varied between 250 and 340 eV, covering the C K-edge region at a resolution of 100 meV. The NEXAFS spectra of the pristine P3HT, PC61BM, ICBA, and SDS spectra were background corrected by dividing the signal intensity at each energy by the corresponding intensity through a clean Si3N4 window and then converted to optical density. At each pixel in the STXM image a three point spectrum was obtained and a singular value decomposition algorithm (constrained to positive solutions) was used to fit a sum of the three pristine spectra to the measured blend spectrum. Image analysis was assisted by use of the IDL widget aXis2000. Radial compositional profiles were obtained across arcs of the compositional map that were clear of neighbouring particles and then integrated to give an average composition as a function of distance from the centre of the particle.

2.10 Device Fabrication

Essentially, in this study the structure of the NP-OPV devices is an active layer sandwiched between anode and cathode as shown in Figure 1.3. Indium tin oxide oxide (ITO) is used as the anode and aluminium (Al) as a cathode. For better device performance, the ITO was modified by coating it with PEDOT:PSS and the aluminium was modified by placing an interface layer such as Ca or LiF between the aluminium and the active layer.

2.10.1 Cleaning ITO substrates

Glass slides with ITO patterns used in this project were purchased from Kinetic Company. The ITO had a sheet resistance of 15 Ω/sq and an optical transmission of greater than 80 %. There are 6 fingers/cells on one slide (Figure 2.14). Before use, the slides are cleaned in order to give better films and provide a better contact. To clean the slides, they were immersed in a detergent solution which was made by diluting 1 ml
detergent (Micro 90) with 25 ml water. The slides in detergent solution were sonicated in an ultrasonic bath (Unisonics FXP10M) for 10 minutes. The substrates were then rinsed repeatedly with hot water, cold water, and finally with MQ-water. The substrates were sonicated again in MQ-water for 10 minutes and then dried using lint free tissue (Kim Wipes®). Dried substrates were then placed in an ozone cleaner for 10 minutes. The substrates were then ready for use.

![Figure 2.14: Glass substrate coated with ITO pattern.](image)

2.10.2 Spin Coating

The PEDOT:PSS solution used in this study was purchased from H.C Stark, U.S.A. The solution has a viscosity of 60-100 mPa and a conductivity of 1 S/cm. To coat the pre-cleaned ITO slide with PEDOT:PSS, 75 µl of PEDOT:PSS solution was placed on it and spin cast at 5000 rpm for 60 seconds to give a film thickness of ~50 nm (Figure 2.16b). The spincoater used in this study was a Laurell spin coater as shown in Figure 2.15. The film was then dried on a hot plate.
The next layer deposited on the slide after PEDOT:PSS is the active layer. The active layer was made by placing 35 μl of nanoparticulate solution onto the PEDOT:PSS layer and this was then spun at 2000 rpm for 60 seconds (Figure 2.16c). The speed of the spin coater can be modified to achieve the desired active layer thickness. After spin coated the active layer, the common contact and edge of the cell contacts were then cleaned using an isopropanol soaked cotton bud (Figure 2.16d). The slides were then heated on a hot plate. Since the active layer was deposited from a water-based solution, this heating process was called “drying”. The temperature used for drying the active layer was called the drying temperature and how long to dry the active layer was called the drying time. Drying temperature and drying time are investigated fully in Chapter 4. Dried active layers were then transferred to the glovebox for metal electrode deposition.

Figure 2.15: Laurell spin-coater used in this study.
2.10.3 Metal Electrode Deposition

In the glovebox, dried active layers were placed in a sample holder with a mask (Figure 2.17) for metal electrode deposition. This mask allows the metal electrode to be deposited only on the area needed. The metal electrode can be aluminium only or a combination of aluminium and other materials. The sample holder was then placed in a vacuum chamber for metal electrode deposition. The chamber pressure for metal electrode deposition process was below $2 \times 10^{-6}$ Torr. After metal electrode deposition is finished, the devices are ready to be tested. Figure 2.16e shows the sample after metal electrode deposition. The active area of the device is determined by the intersection between the metal electrode and the ITO and in this project the active area is 5 mm$^2$.

Figure 2.17: The sample holder with the mask.
2.11 Device Characterisation

The performance of a photovoltaic device is measured by how efficiently the device converts light energy to electrical energy and this is denoted by the power conversion efficiency (PCE). The PCE of a device can be calculated from the device's IV curve which is obtained during characterisation.

In this study, characterisation of devices was performed in a nitrogen atmosphere under illumination intensity of 1 sun. Devices were tested before and after annealing of the device. Annealing the device (annealing device) means the device was heated after metal electrode deposition. The characteristics of the device before annealing of the device are called pre-annealed characteristics and after annealing of the device are called annealed characteristics. Table 2.1 summarizes the terms applied to the heating process in this thesis.
Table 2.1: The terms of heating or annealing process used in whole this thesis

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<table>
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<tr>
<td>Drying</td>
<td>Heating or annealing the active layer before cathode deposition</td>
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<td>Drying Temperature</td>
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<td>Drying Time</td>
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<td>Annealing device</td>
<td>Heating or annealing the active layer after cathode deposition</td>
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<td>Annealing Temperature</td>
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<td>Annealed characteristics</td>
<td>Characteristics of device after annealing of device</td>
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<td>(after cathode deposition)</td>
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Generally, in this project, devices were annealed at a temperature of 140 °C for 4 minutes. Pre-annealed characteristics and annealed characteristics were obtained from the same device. Devices were tested using an AM1.5G simulator as sun simulator and a Keithley 2400 as a sourcemeter. The AM1.5G simulator used was a Newport-Oriel model 92251A with a 150 W Xe lamp and an AM1.5G filter that complies with ASTM E 927-05 as a Class A characterisation product. The Keithley 240 was controlled by a computer and was used to apply current and voltage to the device and to record the device output. Parameter outputs of device in the form of $V_{oc}$ and $I_{sc}$ were used to calculate the fill factor ($FF$) and the power conversion efficiency (PCE) of the device.

Another important factor in organic photovoltaic device characterisation is external quantum efficiency (EQE). EQE is the efficiency of a device as a function of the energy or wavelength of the photon, including losses by reflection and transmission [77]. This measurement reveals how much current was generated by each incident photon at all incident energies. Therefore this type of quantum efficiency also called incident photon to current efficiency (IPCE). In equation form, EQE can be written as:
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Thickness, Concentration and Ratio Effect on NP-OPV Device Performance

3.1 Introduction

Increasing the thickness of the active layer of organic photovoltaic devices will increase their light absorption. However, increasing the active layer thickness will not increase the performance of the devices continuously. There is an optimum thickness of the active layer, which strikes a balance between light absorption and exciton diffusion length [78], and increasing the active layer thickness beyond this optimum thickness will decrease the performance of the device [79]. In bulk heterojunction organic photovoltaic devices, the optimum thickness is around 100 nm [80, 81]. However, in nanoparticle organic photovoltaic (NP-OPV) devices the optimum thickness is currently unknown and thus needs to be investigated.

Other factors which need to be studied in NP-OPV devices are the concentration of polymer in the solvent and the ratio of polymer to fullerene, since the concentration and blending ratio are likely to play a significant role in improving device performance, as has been observed in bulk heterojunction devices [23, 81]. Chirvase, D. et al. [23] investigated the blend ratio effect on bulk heterojunction devices performance, specifically the P3HT:PC61BM system, in 2004. They found that ratios between 1:1 and 1:0.9 exhibit maximum power conversions. Ratios between 1:1 and 1:0.9 were found to
be optimal because maximum photocurrent was achieved in this range ratio, suggesting that the charge carrier mobility of both donor and acceptor components is matched for these concentrations [41].

In this study, a new batch of P3HT was used. The molecular weight of this polymer was 18,000 Da which was different to the P3HT used in Chapter 4. It was therefore necessary to re-optimise the drying temperature for this experiment, as molecular weight has an effect on charge carrier mobility [82, 83] and we have established that it dramatically affects active layer morphology in NP-OPV devices [84].

3.2 Experimental

3.2.1 Nanoparticle solution synthesis

Nanoparticle dispersions were prepared as outlined in Chapter 2. The P3HT used in this study, from LUMTEC, had a different molecular weight than the P3HT (18,000 Da) used in Chapter 4. In the active layer thickness study, the active layer fabricated from solutions consisted of P3HT:PC$_{61}$BM in the ratio of 1:1 by weight. For the materials concentration study, varying concentrations of P3HT and PC$_{61}$BM were used. Table 3.1 shows the amount of P3HT and PC$_{61}$BM used in each sample. The volume of chloroform used for this experiment was identical for each sample. The highest concentration used in this study was 179 mg/mL (100 mg of material in 560 µl of chloroform), which was the upper limit due to the solubility of the polymer.
Table 3.1: The amount of P3HT and PC$_{61}$BM used in each sample. The materials ratio was 1:1 by weight.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration (mg/mL)</th>
<th>P3HT (mg)</th>
<th>PC$_{61}$BM (mg)</th>
<th>Chloroform (µl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>36</td>
<td>10</td>
<td>10</td>
<td>560</td>
</tr>
<tr>
<td>2</td>
<td>54</td>
<td>15</td>
<td>15</td>
<td>560</td>
</tr>
<tr>
<td>3</td>
<td>71</td>
<td>20</td>
<td>20</td>
<td>560</td>
</tr>
<tr>
<td>4</td>
<td>89</td>
<td>25</td>
<td>25</td>
<td>560</td>
</tr>
<tr>
<td>5</td>
<td>107</td>
<td>30</td>
<td>30</td>
<td>560</td>
</tr>
<tr>
<td>6</td>
<td>179</td>
<td>50</td>
<td>50</td>
<td>560</td>
</tr>
</tbody>
</table>

For the materials ratio study, the ratio of P3HT and PC$_{61}$BM used is shown in Table 3.2. The concentration in this study was kept constant at 30 mg of material in 560 µl of chloroform.

Table 3.2: Ratio and the amount of P3HT and PC$_{61}$BM used in each sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ratio</th>
<th>P3HT:PC$_{61}$BM</th>
<th>Chloroform (µl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2:1</td>
<td>20 mg : 10 mg</td>
<td>560</td>
</tr>
<tr>
<td>2</td>
<td>1:1</td>
<td>15 mg : 15 mg</td>
<td>560</td>
</tr>
<tr>
<td>3</td>
<td>1:2</td>
<td>10 mg : 20 mg</td>
<td>560</td>
</tr>
</tbody>
</table>

3.2.2 Device fabrication

The NP-OPV devices in this study were fabricated as outlined in Chapter 2. PEDOT:PSS layers were dried on the hot plate at 140 °C for 30 minutes. For the drying temperature experiment, the active layers were dried at temperatures of 18 °C (RT), 50 °C, 75 °C, 100 °C, 110 °C, 120 °C, 130 °C, 140 °C, 150 °C, 160 °C, 170 °C, and 180 °C on a hot plate for 4 minutes and the devices use an Al only cathode. For the active layer thickness, concentration, and ratio study, Ca was used as an interface layer between aluminium and the active layer. The thickness of Ca was 30 nm and was determined by QCM in the evaporator. This thickness was chosen as a result of the Ca thickness...
optimisation study, to be discussed in Chapter 5. For the active layer thickness study, thickness was altered by varying spin coater speed. The thickness of the film was measured by a KLA-Tencor Alpha Step 500 profilometer. To measure the film thickness, the film on the glass was scratched diagonally and a profilometry scan was conducted perpendicular to the direction of the scratch. Five locations were measured (1 at the middle and 4 at the corners) then the results were averaged together to get the final thickness. Since the film is soft, we used a stylus force of 0.2 mg. All devices were annealed at 140 °C for 4 minutes. For the material ratio study, the thickness of the active layer used was the optimum thickness obtained from the active layer thickness study.

3.2.3 UV-vis spectroscopy, XPS depth profilometry, particle size, and thickness measurement samples

For UV-vis spectroscopy and film thickness measurements, the same film samples were used. The samples were fabricated by spin casting 25 µl of nanoparticle dispersion onto quartz substrates (1 cm x 2 cm). Spin coater speed, drying temperature, and drying time used were the same as with NP-OPV device preparation. For XPS depth profile measurements, actual NP-OPV devices were used as the samples. For particle size measurement, samples were prepared as outlined in Chapter 2.

3.3 Results and Discussion

3.3.1 Drying Temperature

Full optimisation of drying temperatures is undertaken in Chapter 4, however in this chapter a different batch of P3HT has been used. Consequently re-optimisation of the drying temperature has been undertaken here. Table 3.3 shows the best and the average values of IV characteristics of NP-OPV devices dried at different drying temperature for 4 minutes. There were 20 devices for each temperature treatment.
Table 3.3: I-V characteristics of NP-OPV devices dried at different drying temperature.

<table>
<thead>
<tr>
<th>Drying Temperature (°C)</th>
<th>Pre-annealed</th>
<th>Annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$V_{oc}$ (mV)</td>
<td>$J_{sc}$ (mA/cm²)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Best</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>74.8</td>
<td>0.57</td>
</tr>
<tr>
<td>50</td>
<td>166.6</td>
<td>0.85</td>
</tr>
<tr>
<td>75</td>
<td>172.7</td>
<td>1.06</td>
</tr>
<tr>
<td>100</td>
<td>375.2</td>
<td>2.86</td>
</tr>
<tr>
<td>110</td>
<td>412.6</td>
<td>3.12</td>
</tr>
<tr>
<td>120</td>
<td>416.8</td>
<td>3.52</td>
</tr>
<tr>
<td>130</td>
<td>441.2</td>
<td>3.79</td>
</tr>
<tr>
<td>140</td>
<td>378.4</td>
<td>2.67</td>
</tr>
<tr>
<td>150</td>
<td>259.4</td>
<td>2.49</td>
</tr>
<tr>
<td>160</td>
<td>259.7</td>
<td>2.22</td>
</tr>
<tr>
<td>170</td>
<td>234.6</td>
<td>2.06</td>
</tr>
<tr>
<td>180</td>
<td>225.4</td>
<td>1.93</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>55.7±12.8</td>
<td>0.46±0.062</td>
</tr>
<tr>
<td>50</td>
<td>122.0±51.7</td>
<td>0.67±0.146</td>
</tr>
<tr>
<td>75</td>
<td>141.5±17.1</td>
<td>0.80±0.146</td>
</tr>
<tr>
<td>100</td>
<td>334.6±28.1</td>
<td>2.29±0.278</td>
</tr>
<tr>
<td>110</td>
<td>394.9±15.6</td>
<td>2.77±0.204</td>
</tr>
<tr>
<td>120</td>
<td>365.3±45.0</td>
<td>2.18±1.230</td>
</tr>
<tr>
<td>130</td>
<td>421.7±15.8</td>
<td>3.26±0.325</td>
</tr>
<tr>
<td>140</td>
<td>246.5±94.1</td>
<td>2.44±0.202</td>
</tr>
<tr>
<td>150</td>
<td>211.2±42.1</td>
<td>2.09±0.231</td>
</tr>
<tr>
<td>160</td>
<td>181.0±58.0</td>
<td>2.04±0.111</td>
</tr>
<tr>
<td>170</td>
<td>186.4±33.4</td>
<td>1.89±0.108</td>
</tr>
<tr>
<td>180</td>
<td>134.1±71.7</td>
<td>1.73±0.149</td>
</tr>
</tbody>
</table>

Thickness, Concentration and Ratio Effect on NP-OPV Device Performance
Figure 3.1 shows the IV data (in average) for the drying temperature experiment for the new batch of P3HT. We note slightly different results to those observed for the P3HT used in Chapter 4, for pre-annealed devices. The highest efficiency for pre-annealed devices has shifted to 130 °C (up from 110 °C in Chapter 4) as shown in Figure 3.1 although the smoothest film surface still occurs at a drying temperature of 110 °C (see Figure 3.3). This shifting may be due to the lower surface roughness of the films at drying temperature 130 °C (see Figure 3.2), which were not as high as the films produced in Chapter 4 (Figure 4.2) and the reduced surfactant SDS on the film surface compared to the film dried at 110 °C. In Chapter 4, Figure 4.2 shows that the difference in roughness of the film surface dried at 110 °C and dried 130 °C was 12.0 nm while in this chapter, Figure 3.2 shows that the difference in roughness of the film surface dried at 110 °C and at 130 °C was just 2.4 nm. We believe that the amount of SDS on the film surface dried at 130 °C was lower than that at 110 °C based on the XPS surface scan data in Chapter 4 (Figure 4.4) and the migration of SDS from the film surface [2]. It seems reasonable to hypothesise therefore that the combination of the smooth surface with the reduced SDS on the surface improves the performance of NP-OPV devices. The dramatic increase in rms roughness of the film surface at 140 °C suggests that, as is observed in BHJ films, major morphological changes must occur at this temperature.
Figure 3.1: IV characteristics of devices dried at different temperatures. (a) Efficiency, (b) current density, (c) open circuit voltage, and (d) fill factor. Blue square is for pre-annealed devices and red circle is for annealed devices.
3.3.2 Active Layer Thickness

In this experiment, we will determine the optimal active layer thickness for 1:1 P3HT:PC$_{61}$BM NP-OPV devices. Six devices were made for each active layer thickness treatment.

Figure 3.4a shows the UV-vis spectra of different film thicknesses produced from a 1:1 P3HT:PC$_{61}$BM nanoparticle dispersion and Figure 3.4b shows the relationship...
between the absorption and the thickness of a 1:1 P3HT:PC$_{61}$BM NP film at wavelength 552 nm. It is clear that increasing the film thickness will increase the light absorption of both P3HT and PC$_{61}$BM according to Beer’s Law. However, as can be seen in Table 3.1, the average power conversion efficiency (PCE) of the devices increases only until an active layer thickness of around 100–120 nm. Increasing the film (active layer) thickness beyond these thicknesses resulted in decreased power conversion efficiency. This change arises since, whilst absorption is a function of amount of material present, PCE is a complex function of absorption, exciton mobility, charge separation and charge transport. Increasing the thickness of the active layer increases the charge transport pathway which may increase recombination in the device, lowering PCE. To see the trend of devices characteristics, the IV characteristic data in Table 3.4 was plotted in graphs as shown in Figure 3.5.
**Figure 3.4:** (a) UV-Vis spectra of different film thickness of P3HT:PCBM nanoparticles. (b) Absorption (522 nm) versus film thickness obeys Beer’s Law.
Table 3.4: I-V characteristics of annealed NP-OPV devices with different active layer thickness.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt; (mV)</th>
<th>I&lt;sub&gt;sc&lt;/sub&gt; (mA)</th>
<th>J&lt;sub&gt;sc&lt;/sub&gt; (mA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Best</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>413.0</td>
<td>-0.18</td>
<td>-3.60</td>
<td>0.44</td>
<td>0.65</td>
</tr>
<tr>
<td>66</td>
<td>428.2</td>
<td>-0.18</td>
<td>-3.60</td>
<td>0.44</td>
<td>0.66</td>
</tr>
<tr>
<td>78</td>
<td>439.5</td>
<td>-0.18</td>
<td>-3.68</td>
<td>0.45</td>
<td>0.71</td>
</tr>
<tr>
<td>100</td>
<td>456.3</td>
<td>-0.19</td>
<td>-3.86</td>
<td>0.44</td>
<td>0.76</td>
</tr>
<tr>
<td>107</td>
<td>429.6</td>
<td>-0.20</td>
<td>-3.97</td>
<td>0.43</td>
<td>0.74</td>
</tr>
<tr>
<td>113</td>
<td>446.2</td>
<td>-0.20</td>
<td>-4.06</td>
<td>0.43</td>
<td>0.76</td>
</tr>
<tr>
<td>121</td>
<td>458.9</td>
<td>-0.19</td>
<td>-3.85</td>
<td>0.43</td>
<td>0.74</td>
</tr>
<tr>
<td>128</td>
<td>454.2</td>
<td>-0.18</td>
<td>-3.51</td>
<td>0.42</td>
<td>0.63</td>
</tr>
<tr>
<td>136</td>
<td>464.1</td>
<td>-0.16</td>
<td>-3.18</td>
<td>0.41</td>
<td>0.60</td>
</tr>
<tr>
<td>145</td>
<td>469.3</td>
<td>-0.16</td>
<td>-3.25</td>
<td>0.41</td>
<td>0.61</td>
</tr>
<tr>
<td>170</td>
<td>453.6</td>
<td>-0.13</td>
<td>-2.62</td>
<td>0.40</td>
<td>0.47</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>396.6</td>
<td>-0.17</td>
<td>-3.35</td>
<td>0.43</td>
<td>0.58</td>
</tr>
<tr>
<td>66</td>
<td>411.6</td>
<td>-0.17</td>
<td>-3.42</td>
<td>0.43</td>
<td>0.61</td>
</tr>
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<td>429.7</td>
<td>-0.18</td>
<td>-3.51</td>
<td>0.44</td>
<td>0.66</td>
</tr>
<tr>
<td>100</td>
<td>443.4</td>
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<td>-3.79</td>
<td>0.44</td>
<td>0.73</td>
</tr>
<tr>
<td>107</td>
<td>429.1</td>
<td>-0.19</td>
<td>-3.89</td>
<td>0.43</td>
<td>0.72</td>
</tr>
<tr>
<td>113</td>
<td>442.2</td>
<td>-0.20</td>
<td>-3.93</td>
<td>0.42</td>
<td>0.73</td>
</tr>
<tr>
<td>121</td>
<td>444.0</td>
<td>-0.18</td>
<td>-3.67</td>
<td>0.42</td>
<td>0.68</td>
</tr>
<tr>
<td>128</td>
<td>441.8</td>
<td>-0.17</td>
<td>-3.42</td>
<td>0.41</td>
<td>0.62</td>
</tr>
<tr>
<td>136</td>
<td>450.2</td>
<td>-0.15</td>
<td>-2.99</td>
<td>0.40</td>
<td>0.54</td>
</tr>
<tr>
<td>145</td>
<td>455.8</td>
<td>-0.14</td>
<td>-2.88</td>
<td>0.40</td>
<td>0.53</td>
</tr>
<tr>
<td>170</td>
<td>449.5</td>
<td>-0.12</td>
<td>-2.47</td>
<td>0.40</td>
<td>0.44</td>
</tr>
</tbody>
</table>

Power conversion efficiency decreased upon increasing the active layer thickness beyond a thickness of around 100–120 nm, which is thought to be due to increased
series resistance and charge recombination [85-87]. The increase in series resistance, $R_s$, upon increasing the active layer thickness can be seen in Figure 3.6 and shows that a thicker active layer has higher series resistance. This higher series resistance then leads to a reduction in short circuit current and reduced PCE’s.

![Graphs showing IV characteristics of NP-OPV devices with different active layer thickness](image)

**Figure 3.5:** IV characteristics of NP-OPV devices with different active layer thickness. All of the characteristics are the average values with error bars showing the STDEV devices. (a) power conversion efficiency, (b) current density, (c) open circuit voltage, and (d) fill factor.
The open circuit voltage shown in Figure 3.5(b) and the fill factor shown in Figure 3.5(d) show no significant change upon increasing the active layer thickness. The trend in current density is similar to the PCE trend. Therefore, the performance of these devices is dominated by their current density. The trend in current density shows that the balance between charge generation and charge transport is optimal at an active layer thickness of around 100 – 120 nm [41]. This optimal active layer thickness is very similar to that obtained for bulk heterojunction devices suggesting that the nanoparticulate active does not really seem to affect the optimal thickness.

### 3.3.3 Concentration

In this experiment we investigate the effect of initial material concentration on the particle size of the NP dispersion and on the performance of subsequent NP-OPV devices.

Table 3.5 shows the particle size distribution of nanoparticles produced from different concentrations of P3HT:PC$_{61}$BM in chloroform. The size of the particles was
measured by dynamic light scattering (DLS). Figure 3.7 is plot of nanoparticle size versus concentration of polymers in chloroform. As shown in Figure 3.7, particle size systematically increases with increasing concentration of polymer in chloroform. In the miniemulsion process, the core of the micelles contains a solution of polymer:fullerene. A higher concentration of polymer:fullerene therefore results in increased polymer:fullerene mass in that core. When the solvent is evaporated, only the polymer:fullerene remains. Therefore, the more polymer:fullerene in the micelles core, the larger the particle size produced. Thus higher polymer:fullerene concentration will and does result in bigger nanoparticles. Ultimately, increasing concentration was limited only by the polymers solubility, so the largest average particle size about to be produced was approximately 56 nm by this method.

Table 3.5: Particle size of nanoparticle produced from different concentration of polymers.

<table>
<thead>
<tr>
<th>Concentration (mg/mL)</th>
<th>Z-average Size (nm)</th>
<th>STDEV</th>
</tr>
</thead>
<tbody>
<tr>
<td>36</td>
<td>27.9</td>
<td>0.40</td>
</tr>
<tr>
<td>54</td>
<td>33.2</td>
<td>0.67</td>
</tr>
<tr>
<td>71</td>
<td>33.6</td>
<td>0.70</td>
</tr>
<tr>
<td>89</td>
<td>36.4</td>
<td>0.64</td>
</tr>
<tr>
<td>107</td>
<td>43.1</td>
<td>0.62</td>
</tr>
<tr>
<td>179</td>
<td>56.4</td>
<td>0.42</td>
</tr>
</tbody>
</table>
We can determine what the relationship between the initial solution concentration and particle size should be if we make some reasonable assumptions about the micelles initially formed in the particle formation process. Firstly we will make the assumption that, since throughout this experiment we do not change the volume of organic solvent added to form the micelles, and the concentration of surfactant is also held constant, the size of the liquid micelles initially formed in the microemulsion should be constant. Secondly we assume that the concentration in each micelle is the same as the initial solution. Now in the final solid particles the volume of the particle is a function of the mass in the particle and the density of the semiconducting materials:

\[ \rho = \frac{m}{V} \]  

so:

\[ V = \frac{m}{\rho} \]  

where \( V \) is the volume of the particle, \( m \) is the mass of material in the particle (and therefore the mass of the polymer and fullerene in the initial micelle) and \( \rho \) is the density of the materials.

**Figure 3.7:** Relationship between Z-average nanoparticle size and polymer:fullerene concentration in chloroform.
density of the semiconductor blend. Since the material blend ratio does not change within this experiment:

\[ V \alpha m \tag{3.3} \]

At the same time the volume of the solid particle formed is also a function of the particle radius, \( r \), according to the relationship:

\[ V = \frac{4}{3} \pi r^3 \tag{3.4} \]

so:

\[ V \alpha r^3 \tag{3.5} \]

It follows then that:

\[ m \alpha r^3 \tag{3.6} \]

Therefore a plot of the concentration of the initial solution (which is directly proportional to the mass of semiconductor in the particle) versus the particle size cubed should give a linear relationship.

Figure 3.8 shows the plot of concentration of the initial solution versus the particle radius cubed along with a linear fit to this data. Interestingly, we can see that an \( R^2 \) correlation of 0.95 is obtained fitting a line to this data and that it does not look a good linear fit. Indeed as shown in Figure 3.7 a much better linear fit is obtained by simply plotting particle size versus initial concentration. The relative closeness of these fits implies that one of our initial assumptions must be wrong with either the size of the initial micelles or the concentration of semiconducting material changing in an unknown way. Since the final composition and morphology of the nanoparticles is critical to device performance and is likely to be directly affected by these factors. These observations will require further investigation for the optimisation of device performance (which is beyond the scope of this thesis).
The thickness of nanoparticle films produced from different polymer:fullerene concentrations can be seen in Table 3.6. The films were produced using identical spincoater speed (2000 rpm for 1 minute). Plotting film thickness against polymer concentration as listed in Table 3.6 is shown in Figure 3.9a.

**Table 3.6:** Thickness and particle size of nanoparticle film produced from different polymers concentration.

<table>
<thead>
<tr>
<th>Concentration (mg/mL)</th>
<th>Z-average Size (nm)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>36</td>
<td>27.9 ± 0.40</td>
<td>86.5 ± 4.1</td>
</tr>
<tr>
<td>54</td>
<td>33.2 ± 0.67</td>
<td>92.3 ± 5.2</td>
</tr>
<tr>
<td>71</td>
<td>33.6 ± 0.70</td>
<td>109.2 ± 19.2</td>
</tr>
<tr>
<td>89</td>
<td>36.4 ± 0.64</td>
<td>93.5 ± 4.7</td>
</tr>
<tr>
<td>107</td>
<td>43.1 ± 0.62</td>
<td>111.7 ± 9.8</td>
</tr>
<tr>
<td>179</td>
<td>56.4 ± 0.42</td>
<td>177.1 ± 3.8</td>
</tr>
</tbody>
</table>

Figure 3.9a shows how the thickness of active layers increased upon increasing the polymer concentration. The increase in active layer thickness is thought to be due to increased particle size in the nanoparticle solution upon increasing the polymer concentration.

\[
y = 140.23x - 4111.6 \\
R^2 = 0.9474
\]
concentration. Interestingly, for all particle sizes, the overall thickness is $2.9 \pm 0.3$ times the radius of an average particle suggesting that three layers of particles are deposited. The relationship between particle size and thickness can be seen in Figure 3.9b.

![Figure 3.9: Relationship between (a) concentration and film thickness, (b) particle size and film thickness.](image)

The increase in the active layer thickness upon increasing concentration of polymer in the organic solvent also can be seen in Figure 3.10. Figure 3.10 shows the increase in absorption of the active layer upon increasing polymer concentration. Again there is a systematic increase with film thickness as expected.
The IV characteristics of NP-OPV devices produced from different polymer concentrations are displayed in Table 3.7, and plotted in Figure 3.11. As can be seen in Figure 3.11a, the power conversion efficiency (PCE) of devices produced from different concentrations of material in chloroform is at a maximum for a concentration of 54 mg/µl, and then begins to decline as the concentrations are increased beyond this threshold concentration. In reality this is most likely a direct effect of the changing particle size (with a size of ~33 nm being optimal). This PCE trend is similar to the trend in current density (Figure 3.11b) while the $V_{oc}$ (Figure 3.11c) and the fill factor (Figure 3.11d) show no significant change. Therefore, the highest efficiency at concentration of 54 mg/µl shows that the balance between charge generation and charge transport was optimal at this concentration and particle size.

**Figure 3.10:** UV-vis spectra of nanoparticle films produced from different concentration of P3HT:PCBM in chloroform.
Table 3.7: I-V characteristic of annealed NP-OPV devices fabricated from different polymer concentration. The best and the average characteristics are presented from a set of 6 devices.

<table>
<thead>
<tr>
<th>Concentration (mg/ml)</th>
<th>$V_{oc}$ (mV)</th>
<th>$I_{sc}$ (mA)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Best</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>509.1</td>
<td>-0.12</td>
<td>-2.45</td>
<td>0.39</td>
<td>0.48</td>
</tr>
<tr>
<td>54</td>
<td>545.5</td>
<td>-0.20</td>
<td>-4.05</td>
<td>0.42</td>
<td>0.92</td>
</tr>
<tr>
<td>71</td>
<td>526.0</td>
<td>-0.18</td>
<td>-3.63</td>
<td>0.41</td>
<td>0.79</td>
</tr>
<tr>
<td>89</td>
<td>498.5</td>
<td>-0.17</td>
<td>-3.46</td>
<td>0.38</td>
<td>0.66</td>
</tr>
<tr>
<td>107</td>
<td>486.0</td>
<td>-0.15</td>
<td>-2.98</td>
<td>0.44</td>
<td>0.60</td>
</tr>
<tr>
<td>179</td>
<td>481.3</td>
<td>-0.13</td>
<td>-2.67</td>
<td>0.42</td>
<td>0.53</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>496.9</td>
<td>-0.10</td>
<td>-2.06</td>
<td>0.38</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>9.4</td>
<td>0.017</td>
<td>0.335</td>
<td>0.004</td>
<td>0.072</td>
</tr>
<tr>
<td>54</td>
<td>539.0</td>
<td>-0.18</td>
<td>-3.56</td>
<td>0.41</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>0.019</td>
<td>0.370</td>
<td>0.005</td>
<td>0.089</td>
</tr>
<tr>
<td>71</td>
<td>521.6</td>
<td>-0.17</td>
<td>-3.36</td>
<td>0.40</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>3.7</td>
<td>0.010</td>
<td>0.196</td>
<td>0.007</td>
<td>0.055</td>
</tr>
<tr>
<td>89</td>
<td>495.2</td>
<td>-0.16</td>
<td>-3.17</td>
<td>0.38</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>2.7</td>
<td>0.013</td>
<td>0.262</td>
<td>0.002</td>
<td>0.055</td>
</tr>
<tr>
<td>107</td>
<td>470.1</td>
<td>-0.14</td>
<td>-2.85</td>
<td>0.43</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>10.1</td>
<td>0.004</td>
<td>0.078</td>
<td>0.003</td>
<td>0.018</td>
</tr>
<tr>
<td>179</td>
<td>473.8</td>
<td>-0.13</td>
<td>-2.56</td>
<td>0.41</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>5.2</td>
<td>0.005</td>
<td>0.095</td>
<td>0.003</td>
<td>0.022</td>
</tr>
</tbody>
</table>
3.3.4 Ratio

A series of nanoparticle dispersions were prepared using various ratios of polymer:fullerene in the aqueous phase. Samples containing P3HT:PC$_{61}$BM with ratios by mass of 2:1; 1:1; 1:2 were investigated. Table 3.8 shows the particle diameter in average (Z-average) of nanoparticle solutions as measured by DLS. Different ratios

![Graphs showing IV characteristics of devices produced from different polymer concentrations.](image)

**Figure 3.11**: IV characteristics of devices produced from different polymer concentrations. (a) Efficiency, (b) Current density, (c) Open circuit voltage, and (d) Fill factor, with the error bars representing the STDEV of devices produced.
gave different sizes of nanoparticle by increasing the amounts of PC$_{61}$BM (i.e. smaller ratio), the particle size is reduced systematically.

**Table 3.8:** Z-average particle diameters of P3HT:PC$_{61}$BM nanoparticles of different materials ratio as measured by DLS.

<table>
<thead>
<tr>
<th>NP Sample</th>
<th>Z-Average Size (nm)</th>
<th>STDEV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure P3HT</td>
<td>39.62</td>
<td>0.268</td>
</tr>
<tr>
<td>P3HT:PC$_{61}$BM 2:1</td>
<td>33.81</td>
<td>0.585</td>
</tr>
<tr>
<td>P3HT:PC$_{61}$BM 1:1</td>
<td>30.27</td>
<td>0.267</td>
</tr>
<tr>
<td>P3HT:PC$_{61}$BM 1:2</td>
<td>25.35</td>
<td>0.223</td>
</tr>
<tr>
<td>Pure PC$_{61}$BM</td>
<td>19.95</td>
<td>1.077</td>
</tr>
</tbody>
</table>

Figure 3.12 shows the plot of PC$_{61}$BM ratio in P3HT:PC$_{61}$BM material versus the particle size along with a linear fit to this data. It is clear that $R^2$ is very close to 1 and this implies that increasing the mass of PC$_{61}$BM in P3HT:PC$_{61}$BM will directly reduce the particle size until the size of pure PC$_{61}$BM particle.

**Figure 3.12:** Plot of PC$_{61}$BM mass fraction in P3HT:PC$_{61}$BM versus Z-Average size of nanoparticle.
Figure 3.13 shows UV-vis spectra of P3HT:PC$_{61}$BM nanoparticle films produced from P3HT:PC$_{61}$BM blends of different mass ratios. The total mass of P3HT and PC$_{61}$BM was kept constant at 30 mg. It is clear from Figure 3.13 that increasing the polymer fraction increases the relative light absorption due to P3HT at wavelengths of between approximately 450-650 nm and likewise, PC$_{61}$BM absorption increases relatively between 200-400 nm as the polymer fraction is reduced. The spectra exhibit the expected changes in relative P3HT and PC$_{61}$BM contributions.

![Figure 3.13: UV-vis spectra of P3HT:PCBM nanoparticle films produced from different material ratio.](image)

Table 3.9 and Figure 3.14 show the I-V characteristics of P3HT:PC$_{61}$BM nanoparticles with different mass ratios of P3HT and PC$_{61}$BM. Figure 3.14 shows the I-V curves for each of the best devices.
Table 3.9: I-V characteristic of P3HT:PC_{61}BM nanoparticle devices fabricated from different mass ratio of P3HT and PC_{61}BM. The best and the average characteristics are presented from a set of six devices.

<table>
<thead>
<tr>
<th>Ratio</th>
<th>V_{oc} (mV)</th>
<th>I_{sc} (mA)</th>
<th>J_{sc} (mA/cm^2)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pre-annealed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2:1</td>
<td>Best</td>
<td>412.2</td>
<td>-0.151</td>
<td>-3.024</td>
<td>0.361</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>395.4</td>
<td>-0.125</td>
<td>-2.498</td>
<td>0.347</td>
</tr>
<tr>
<td>1:1</td>
<td>Best</td>
<td>397.4</td>
<td>-0.224</td>
<td>-4.471</td>
<td>0.469</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>395.3</td>
<td>-0.199</td>
<td>-3.970</td>
<td>0.454</td>
</tr>
<tr>
<td>1:2</td>
<td>Best</td>
<td>435.8</td>
<td>-0.170</td>
<td>-3.402</td>
<td>0.446</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>422.1</td>
<td>-0.141</td>
<td>-2.830</td>
<td>0.436</td>
</tr>
<tr>
<td></td>
<td>Annealed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2:1</td>
<td>Best</td>
<td>496.9</td>
<td>-0.132</td>
<td>-2.632</td>
<td>0.364</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>472.0</td>
<td>-0.125</td>
<td>-2.497</td>
<td>0.351</td>
</tr>
<tr>
<td>1:1</td>
<td>Best</td>
<td>557.4</td>
<td>-0.220</td>
<td>-4.404</td>
<td>0.418</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>543.0</td>
<td>-0.191</td>
<td>-3.811</td>
<td>0.405</td>
</tr>
<tr>
<td>1:2</td>
<td>Best</td>
<td>579.7</td>
<td>-0.183</td>
<td>-3.669</td>
<td>0.389</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>574.1</td>
<td>-0.154</td>
<td>-3.081</td>
<td>0.374</td>
</tr>
</tbody>
</table>

Figure 3.14a shows that the highest efficiency P3HT:PC_{61}BM nanoparticle devices were obtained at a mass ratio of 1:1, driven primarily by the current density of the devices (Figure 3.14b). This optimum current density implies that an optimal balance between charge generation and charge transport occur at a ratio of 1:1.

It is interesting that at a mass ratio 1:1, the overall efficiency of devices increase after annealing although their current density and fill factor decreased after annealing. Therefore, the reason for the increased efficiency of 1:1 devices upon thermal annealing was due to an increase in open circuit voltage (V_{oc}).
Figure 3.14: Characteristics of devices produced from different material ratios. Blue bars represent pre-annealed devices and red bars represent annealed devices. (a) efficiency, (b) current density, (c) open circuit voltage, and (d) fill factor. Error bar represent the STDEV of the devices produced.

Figure 3.14c shows that the $V_{oc}$ of pre-annealed devices does not change significantly with the change in material ratio. However, after devices are annealed, the $V_{oc}$ increases systematically with increasing PC$_{61}$BM mass. Figure 3.16 shows XPS depth profile data of a 1:1 P3HT:PC$_{61}$BM nanoparticle device and shows the vertical material composition of devices from cathode to anode. There are very few changes in
the film composition between the pre-annealed and annealed devices. In both cases a partial layer of Al₂O₃ is observed at the Al/active layer interface. The size of this layer does not change dramatically upon annealing. The S and the Na peaks reach a maximum at the anode interface where the S and Na rich PEDOTT:PSS layer is located. However a systematic change in the carbon to sulphur ratio (C:S ratio) is observed for both pre-annealed and annealed devices across the active layer. This implies that there is a concentration gradient of PC₆₁BM within the device with more located near the cathode. Furthermore, the XPS depth profile data shows that after device annealing, more PC₆₁BM moves to the interface between Al and the active layer. This movement can be seen from the ratio of carbon to sulphur (C:S) at interface which increases upon annealing. This PC₆₁BM movement is advantageous for device performance since it creates a gradient in the electron conduction pathway that is maximised at the cathode, and will result in a greater charge carrier density and reduced recombination in the device [88]. As a result, $V_{oc}$ will increase [89]. Therefore this migration of PC₆₁BM concentration within the device increases the $V_{oc}$ after annealing.

Figure 3.14d shows that the $FF$ of devices that have smaller ratio of P3HT:PC₆₁BM (1:1, 1:2) decreased after annealing. As we discussed previously about XPS depth profile data, PC₆₁BM will move to the Al-active layer interface after annealing. We assume that if the concentration of PC₆₁BM is higher then more PC₆₁BM will move to the Al-active layer interface. Consequently, more PC₆₁BM will crystallize at Al-active layer interface, which may damage the interface [15, 23]. Moreover, the IV curve of the devices (Figure 3.15) shows that series resistance of the devices increase after annealing (a decrease in the slope of the IV curve at open-circuit voltage) which is in good agreement with interface damage. This interface damage is thought to be the reason for the $FF$ decreased after annealing.
Figure 3.15: IV curves of the best nanoparticle P3HT:PC$_{61}$BM devices for each different mass ratio.

Figure 3.16: X-ray photoelectron depth profile of (a) the pre-annealed P3HT:PC$_{61}$BM NP-OPV device, (b) the annealed P3HT:PC$_{61}$BM NP-OPV device.
3.4 Conclusions

Investigations to determine appropriate active layer thickness, concentration of polymers in organic solvent, and mass ratio of polymers in NP-OPV P3HT:PC$_{61}$BM devices have been performed. Optimal active layer thickness was found to be around 100–120 nm and the appropriate concentration of materials for nanoparticle synthesis is 54 mg/mL (30 mg polymer:fullerene in 0.560 mL chloroform). For a mass ratio of polymer to fullerene, the optimum ratio is 1:1. At these optimum variables, the highest performance of NP-OPV devices was observed and this was primarily driven by the highest current density suggesting that an optimal balance between charge generation and charge transport occurs at these optimum values.
4

Effect of Annealing on the Performance of Nanoparticle Organic Photovoltaic Devices

4.1 Introduction

The most extensively studied organic photovoltaic (OPV) system is based on the conducting polymer poly(3-hexylthiophene) (P3HT) and the electron-accepting fullerene phenyl-C_{61}-butyric acid methyl ester (PC_{61}BM), with power conversion efficiencies up to about 5% [90]. These materials are generally processed from organic solvents such as chloroform or chlorobenzene to form a thin film of interpenetrating domains known as a bulk heterojunction (BHJ) structure [91]. A key challenge in the large scale implementation of OPV technology is the elimination of these hazardous solvents from the device fabrication process [92, 93]. Nanoparticle organic photovoltaic devices (NP-OPV) are an alternative to traditional bulk heterojunction systems where the NP-OPVs are fabricated from aqueous dispersions of conducting polymer nanoparticles and the active layer is cast or printed from a water-based solution [94, 95]. Not only does this eliminate the use of organic solvents, the nanoparticles also provide a level of control of active layer nanomorphology that is unachievable by conventional blending and processing methods [26]. However, improving NP-OPV
devices to the point where they can match or exceed the performance of the equivalent BHJ is not without its challenges.

Traditional bulk heterojunction devices based on P3HT:PC_{60}BM have only reached efficiencies of \(~5\%\) through an extensive series of optimisations. Polymer molecular weight \([96, 97]\), polydispersity \([98]\) and regioregularity \([98]\); choice of blend ratios \([23, 99, 100]\), solvent \([31]\), electrode \([31, 101, 102]\), and interfacial layers \([16, 19]\); and treatments such as thermal \([19, 46]\) or solvent \([103, 104]\) annealing; have all been demonstrated to have an effect on the performance outcome. Furthermore, it is well documented that changing one parameter can have a significant effect of the optimal conditions of other parameters.

The NP-OPV system is even more complex, as we not only have to take into account the considerations above, but also the additional factors of control of the nanomorphology of the nanoparticles and how that affects active layer morphology and consequently device performance. It is also well documented that the existence of water in organic photovoltaic devices can decrease device performance \([105-107]\). Therefore an annealing step at a temperature above the boiling point of water may be an important consideration for NP-OPV devices. Besides drying the active layer film, annealing can increase the interfacial area between the donor and the acceptor, the active layer and the cathode, and also increase the crystallinity of the polymer leading to improved charge mobility \([47, 108]\) as well as closing pinhole defects in the active layer film \([2, 6]\). This chapter will therefore investigate the effect of annealing as it relates to NP-OPV devices.

In this chapter we specify two annealing conditions. The first is annealing before cathode deposition, which in this study is called annealing the active layer or simply
drying. The second is annealing after cathode deposition, which we call (post-assembly) annealing of the device. When discussing the results of OPV testing, we further define pre- and post-annealed states as pre-annealed and annealed, respectively. A pre-annealed result is a result before annealing the device and an annealed result is a result after annealing the device. Pre-annealed and annealed results were obtained from the same device. By using techniques such as atomic force microscopy (AFM), OPV device characterisation, X-ray photoelectron spectroscopy (XPS), and optical microscopy, we present an optimised annealing process for NP-OPV devices that demonstrates a large improvement in efficiency as compared to previous work by our group for the same system (P3HT:PC$_{61}$BM) [6].

4.2 Experimental

4.2.1 Nanoparticle synthesis

Nanoparticle dispersions were made using the procedure as outlined in Chapter 2. The semiconducting materials used in this experiment were P3HT and PC$_{61}$BM with a materials ratio of 1:1 by weight and concentration in chloroform was 0.05 mg/µl. The molecule weight of P3HT used in this experiment is 22,000 Da; P3HT and PC$_{61}$BM were purchased from LUMTEC.

4.2.2 Device Fabrication

Devices were fabricated as outlined in Chapter 2. PEDOT:PSS layers were dried on a hot plate at 140 °C for 30 minutes. For the investigation of the effect of drying temperature on device performance, the drying temperatures chosen were 50 °C, 75 °C, 100 °C, 110 °C, 120 °C, 130 °C, 140 °C, 150 °C, 160 °C, 170 °C, 180 °C, with a drying time of 4 mins in all cases. For investigation of the effect of drying time on device performance, drying times of 1 minute, 2 minutes, 3 minutes, 4 minutes, 5 minutes, 10
minutes, 15 minutes, and 30 minutes were chosen. The temperature used in the drying time investigation was the optimum drying temperature obtained from the drying temperature experiment. All of the active layers were dried in air and all of devices were annealed in a nitrogen environment (140 °C, 4 min).

4.2.3 XPS, AFM, and microscopy samples
Thin films of P3HT:PC$_{61}$BM 1:1 nanoparticle were made by spin casting (2000 rpm for 1 minute) 20 µl of P3HT:PC$_{61}$BM 1:1 nanoparticle solution onto pre-cleaned glass substrates. The films were then dried at different drying temperatures as per the relevant NP-OPV device preparation procedure.

4.2.4 DSC samples
Samples for differential scanning calorimetry (DSC) were prepared by adding 3 drops of nanoparticle solution to an aluminium DCS pan, and drying overnight in a laminar flow cabinet to avoid contamination. DCS was then performed on the sample and compared with an empty aluminium pan as a reference.

4.3 Results and Discussion

4.3.1 Active Layer Annealing Temperature (Drying Temperature)
In this experiment we investigate the effect of the nanoparticle film drying temperature on the performance of pre-annealed and annealed devices. Table 4.1 shows a comparison of device characteristics for 1:1 P3HT:PC$_{61}$BM nanoparticle devices with an aluminium only cathode for each drying temperature. The best and the average characteristics of devices are presented in this table. To see the trend of device characteristics more clearly, the device parameters were plotted as shown in Figure 4.1.
Tabel 4.1: Comparison of characteristics for 1:1 P3HT:PC_{61}BM nanoparticle devices for each drying temperature. The best and the average characteristics are presented from a set of 10 devices.

<table>
<thead>
<tr>
<th>Drying Temperature (°C)</th>
<th>Pre-annealed</th>
<th>Annealed</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$V_{oc}$ (V)</td>
<td>$J_{sc}$ (mA/cm$^2$)</td>
<td>FF</td>
</tr>
<tr>
<td>50</td>
<td>0.44</td>
<td>1.08</td>
<td>0.28</td>
</tr>
<tr>
<td>75</td>
<td>0.46</td>
<td>1.53</td>
<td>0.29</td>
</tr>
<tr>
<td>100</td>
<td>0.50</td>
<td>3.07</td>
<td>0.33</td>
</tr>
<tr>
<td>110</td>
<td>0.43</td>
<td>4.17</td>
<td>0.37</td>
</tr>
<tr>
<td>120</td>
<td>0.42</td>
<td>3.69</td>
<td>0.45</td>
</tr>
<tr>
<td>130</td>
<td>0.26</td>
<td>1.92</td>
<td>0.27</td>
</tr>
<tr>
<td>140</td>
<td>0.25</td>
<td>2.57</td>
<td>0.31</td>
</tr>
<tr>
<td>150</td>
<td>0.35</td>
<td>1.66</td>
<td>0.34</td>
</tr>
<tr>
<td>160</td>
<td>0.17</td>
<td>1.50</td>
<td>0.27</td>
</tr>
<tr>
<td>170</td>
<td>0.23</td>
<td>1.52</td>
<td>0.29</td>
</tr>
<tr>
<td>180</td>
<td>0.18</td>
<td>1.46</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Average (± STDEV)

| 50  | 0.33 (0.17) | 0.84 (0.232) | 0.26 (0.021) | 0.11 (0.008) | 0.30 (0.099) | 0.59 (0.295) | 0.24 (0.079) | 0.09 (0.006) |
| 75  | 0.43 (0.036) | 1.33 (0.181) | 0.28 (0.009) | 0.16 (0.028) | 0.36 (0.039) | 0.90 (0.153) | 0.30 (0.025) | 0.11 (0.025) |
| 100 | 0.46 (0.0434) | 2.38 (0.7906) | 0.31 (0.0270) | 0.38 (0.0635) | 0.36 (0.0982) | 1.19 (0.6711) | 0.27 (0.0459) | 0.20 (0.0415) |
| 110 | 0.30 (0.091) | 3.82 (0.315) | 0.30 (0.037) | 0.47 (0.072) | 0.36 (0.087) | 2.13 (0.155) | 0.31 (0.027) | 0.24 (0.086) |
| 120 | 0.27 (0.154) | 1.64 (1.063) | 0.26 (0.110) | 0.43 (0.086) | 0.38 (0.064) | 1.58 (0.808) | 0.28 (0.061) | 0.30 (0.092) |
| 130 | 0.21 (0.057) | 1.00 (0.556) | 0.26 (0.012) | 0.21 (0.080) | 0.35 (0.161) | 1.78 (0.995) | 0.28 (0.062) | 0.46 (0.069) |
| 140 | 0.07 (0.075) | 1.55 (0.677) | 0.22 (0.082) | 0.22 (0.089) | 0.37 (0.071) | 2.46 (0.690) | 0.39 (0.044) | 0.55 (0.071) |
| 150 | 0.10 (0.091) | 1.22 (0.420) | 0.26 (0.028) | 0.20 (0.082) | 0.32 (0.104) | 1.51 (0.760) | 0.30 (0.057) | 0.38 (0.086) |
| 160 | 0.08 (0.060) | 0.81 (0.506) | 0.24 (0.022) | 0.02 (0.013) | 0.33 (0.105) | 1.49 (0.323) | 0.31 (0.054) | 0.17 (0.048) |
| 170 | 0.15 (0.093) | 0.69 (0.712) | 0.25 (0.028) | 0.08 (0.023) | 0.29 (0.022) | 1.64 (0.866) | 0.33 (0.058) | 0.17 (0.028) |
| 180 | 0.08 (0.061) | 0.57 (0.593) | 0.25 (0.016) | 0.03 (0.027) | 0.21 (0.058) | 0.80 (0.796) | 0.31 (0.046) | 0.15 (0.021) |
Figure 4.1 shows the performance of NP-OPV devices at different drying temperatures, both before and after annealing at 140 °C for 4 minutes. Note that this annealing temperature and time was chosen simply because it is the temperature typically employed when annealing BHJ devices [15], which was chosen as an appropriate starting point for investigation. From Figure 4.1a, we observe that for pre-annealed devices (blue squares) the efficiency increases to a maximum of ~0.6 % at drying temperature of 110 °C, after which efficiency generally declines as drying temperature is further increased. The observed trend in efficiency was driven primarily by changes in $J_{sc}$ (Figure 4.1b), and to a lesser extent, changes in $V_{oc}$ (Figure 4.1c). When the pre-annealed device of maximum performance was then annealed, its efficiency decreased, mainly due to a combination loss of $J_{sc}$ and $V_{oc}$. This observation is in contrast to what we would expect in a BHJ system of the same materials, where it is well documented that device annealing at 140 °C results in improved device performance through an almost 3-fold increase in current density [46, 109]. This result illustrates that the optimal conditions learned through study of the BHJ system do not necessarily translate to NP-OPV devices, and that reoptimisation for the NP-OPV is essential for the development of efficient devices.
Effect of Annealing on the Performance of Nanoparticle Organic Photovoltaic Devices

Figure 4.1: IV characteristic of devices dried at different temperatures. (a) Efficiency, (b) current density, (c) open circuit voltage, and (d) fill factor. Blue squares represent the average values of pre-annealed devices and red circles represent the average values of annealed devices.

From Figure 4.1a we observe that for the annealed devices, efficiency improved as drying temperature was increased, reaching a maximum efficiency at a drying temperature of 140 °C, after which it was declined with further increasing in drying temperature. Again, we note that the primary driving force of the observed efficiency is the change in $J_{sc}$ as shown in Figure 4.1b, suggesting that the morphology of the active
layer is altered during the drying regime \[110, 111\]. Fill factor is also highest at the optimal drying temperature. This highest fill factor further supports the hypothesis that the best morphology and lowest charge recombination occurs at this optimal drying temperature.

From Figure 4.1, we also note that for the annealed NP-OPV device of maximum efficiency (which had a drying temperature of 140 °C), the efficiency of the device increased after annealing due to an improved $J_{sc}$. This outcome is similar to what we would expect for a BHJ device of similar composition, and suggests that the combination of an adequate drying procedure, combined with a device annealing step, results in significant morphological changes that improve device function and performance.

Figure 4.2 below shows AFM images of device films after drying the active layer at different temperatures. The images were obtained by using the AC mode of the AFM. When the roughness of the film surfaces were plotted against drying temperature, it is clear that the smoothest film surface is achieved at a drying temperature of 110 °C, as shown in Figure 4.3. The smoothest film surface at drying temperature of 110 °C correlates well with the optimal performance of devices dried at a temperature of 110 °C. We speculate that the low roughness of the NP film dried at 110 °C results in an improved interfacial contact between the active layer and the subsequently deposited aluminium electrode. Therefore, electron transfer to the cathode is improved, resulting in the highest efficiency at this drying temperature for pre-annealed devices. To support this hypothesis, we selected two different devices (dried 110 °C and dried 140 °C) that have efficiencies (efficiency of the pre-annealed device and efficiency of the annealed device respectively) relatively the same but have different roughness film surface. The
IV characteristic of both devices is shown in Table 4.2. We can see that pre-annealed device dried at 110 °C has lower series resistance $R_s$ compared to the series resistance of the pre-annealed device dried at 140 °C. This lower series resistance implies that better contact between deposited the Al and the active layer occurs for the device dried at 110 °C.

**Figure 4.2:** Roughness of film surfaces at different drying temperature (DT). The size of all images is 20 µm x 20 µm.
As mentioned before, when devices dried at 110 °C were annealed, their efficiency decreased mainly due to a decreased in current density (Figure 4.1b). One possible reason for decreased current density could be the amount of SDS at the film surface. Figure 4.4 shows the sulphur 1s XPS spectra of P3HT:PC_{61}BM NPs dried at 75 °C, 110 °C and 140 °C. The peak at ~164 eV corresponds to sulphur in the P3HT molecule [112] whilst the peak at ~170 eV corresponds to the more electron deficient sulphur atoms in the SDS molecule [113, 114]. As we can see in Figure 4.4, the amount of SDS sulphur on the film surface dried at 110 °C is higher than that in the polymer (P3HT). The relatively high levels of SDS observed on the surface may at first appear surprising given that there should be a very thin layer of SDS bound to the polymer nanoparticle. This data reveals that there must, therefore, be relatively high numbers of individual surfactant molecules still in the dispersion and it is these molecules that remain on the surface. Consequently, when devices dried 110 °C were annealed, contact between the film surface and the Al is improved, however, surplus SDS remains on the film surface and prevents electrons getting to the Al, since SDS acts as an insulating
layer [115]. Secondly, From XPS depth profile data (discussed in chapter 5) shows that after annealing, both oxygen (O) and aluminium oxide (Al₂O₃) increase at the Al-active layer interface suggesting that there is a possibility of trapped water in the active layer which oxidises the Al when the devices were annealed. This suggestion is supported by thermogravametric analysis (TGA) on water based nanoparticle solution [6]. The presence of aluminium oxide at the Al-active layer interface, increases the interfacial (and thus device) series resistance and prevents electrons transferring into the Al electrode. These hypothesises are supported by the observed change in series resistance, which was higher after annealing the device (see Table 4.2). Therefore, the efficiency of devices dried at 110 °C decreased after annealing.

**Tabel 4.2:** IV characteristic of devices dried 110 °C and 140 °C.

<table>
<thead>
<tr>
<th>Char.</th>
<th>DT.</th>
<th>110 °C</th>
<th></th>
<th>140 °C</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td>Pre-annealed</td>
<td>Annealed</td>
<td>Pre-annealed</td>
</tr>
<tr>
<td>V_{oc} (V)</td>
<td></td>
<td>0.335</td>
<td>0.255</td>
<td>0.243</td>
</tr>
<tr>
<td>I_{sc} (A)</td>
<td></td>
<td>2.03E-04</td>
<td>9.19E-05</td>
<td>1.20E-04</td>
</tr>
<tr>
<td>FF</td>
<td></td>
<td>0.308</td>
<td>0.279</td>
<td>0.274</td>
</tr>
<tr>
<td>Eff (%)</td>
<td></td>
<td>0.418</td>
<td>0.162</td>
<td>0.160</td>
</tr>
<tr>
<td>R_s (Ω)</td>
<td></td>
<td>381.7</td>
<td>853.1</td>
<td>463.4</td>
</tr>
<tr>
<td>R_{sh} (Ω)</td>
<td></td>
<td>2449.2</td>
<td>3562.6</td>
<td>2421.9</td>
</tr>
</tbody>
</table>
In comparison, when the films are dried at a temperature of 140 °C, the film surfaces are very rough compared to 110 °C (see Figure 4.3). Therefore when Al is deposited on these surfaces, contact between Al and the film surface is poor and hence the series resistance $R_s$ in these devices is higher compared to those devices dried at 110 °C (see Table 4.2) which contributes to their low efficiency.

However, when devices dried 140 °C are annealed, the fill factor rises dramatically indicating that the contact between the Al and the film surface improved. The amount of SDS sulphur on these surfaces was also less than the amount of polymer (Figure 4.4), so the SDS had less of an insulating effect. Moreover, the possibility of the active layer traps water in this drying temperature (140 °C) is very small. Overall, the result is that electrons can be transferred to the Al electrode more easily, as evident from the observed lower series resistance after annealing (see Table 4.2).

When devices were dried at temperatures exceeding 140 °C, the efficiency of the device was decreased. We hypothesise that this decrease is due to an increase in phase

**Figure 4.4:** S 1s XPS spectra of a P3HT:PC$_{61}$BM 1:1 nanoparticle film. The spectra show that at drying temperature below than 110 °C the amount of SDS (~170 eV) on the film surface is higher than the polymer (~164 eV) while at a drying temperature of 140 °C, the amount of SDS is less than the polymer.
segregation, which is supported by optical microscopy of films dried at varying temperatures. In Figure 4.5 we can see clearly the enhanced formation of crystallites at annealing temperatures exceeding 140 °C. Moreover, a differentiated DSC thermogram of a 1:1 P3HT:PC₆₁BM NP sample (Figure 4.6) shows that at a drying temperature more than 160 °C, the polymer:fullerene material begins to degrade.

![Microscope images](image)

**Figure 4.5:** Microscope images (40x magnifications) of film surface dried at different temperature.
In this second experiment, we investigated the effect of nanoparticle active layer drying time on the performance of devices, both before and after annealing. The drying temperature used was 110 °C for pre-annealed devices and 140 °C for annealed devices. These two drying temperatures were chosen as a result of the previous experiment, where they were observed to give the most efficient devices for each annealing condition. Six devices were made for each drying time treatment. Table 4.3 shows the IV characteristics of 1:1 P3HT:PC_{61}BM nanoparticle devices dried at 110 °C for different times.

Figure 4.6: Differentiated DSC thermogram of P3HT:PC_{61}BM 1:1 nanoparticle. Exotherm process at 115-120 °C is caused by chain-melting in SDS [11]. P3HT:PC_{61}BM begin to degrade at a temperature of ~160 °C.

4.3.2 Active Layer Annealing Time (Drying Time)

In this second experiment, we investigated the effect of nanoparticle active layer drying time on the performance of devices, both before and after annealing. The drying temperature used was 110 °C for pre-annealed devices and 140 °C for annealed devices. These two drying temperatures were chosen as a result of the previous experiment, where they were observed to give the most efficient devices for each annealing condition. Six devices were made for each drying time treatment. Table 4.3 shows the IV characteristics of 1:1 P3HT:PC_{61}BM nanoparticle devices dried at 110 °C for different times.
**Table 4.3:** IV characteristic of 1:1 P3HT:PC₆₁BM nanoparticle devices dried 110 °C for different times. The best and the average characteristics are presented from a set of 10 devices.

<table>
<thead>
<tr>
<th>Drying Time (minutes)</th>
<th>Pre-annealed</th>
<th></th>
<th></th>
<th>Annealed</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V(_\text{oc}) (V)</td>
<td>J(_\text{sc}) (mA/cm(^2))</td>
<td>FF</td>
<td>PCE (%)</td>
<td>V(_\text{oc}) (V)</td>
<td>J(_\text{sc}) (mA/cm(^2))</td>
</tr>
<tr>
<td>Best</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.06</td>
<td>-0.47</td>
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<td>0.01</td>
<td>0.11</td>
<td>-1.24</td>
</tr>
<tr>
<td>1</td>
<td>0.42</td>
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<td>0.40</td>
<td>0.47</td>
<td>0.27</td>
<td>-2.16</td>
</tr>
<tr>
<td>2</td>
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<td>0.41</td>
<td>0.58</td>
<td>0.26</td>
<td>-2.05</td>
</tr>
<tr>
<td>3</td>
<td>0.46</td>
<td>-3.42</td>
<td>0.42</td>
<td>0.63</td>
<td>0.28</td>
<td>-2.07</td>
</tr>
<tr>
<td>4</td>
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<td>0.42</td>
<td>0.68</td>
<td>0.30</td>
<td>-2.27</td>
</tr>
<tr>
<td>5</td>
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<td>0.41</td>
<td>0.60</td>
<td>0.30</td>
<td>-2.43</td>
</tr>
<tr>
<td>10</td>
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<td>0.40</td>
<td>0.56</td>
<td>0.30</td>
<td>-2.46</td>
</tr>
<tr>
<td>Average (± STDEV)</td>
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<td></td>
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<tr>
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<td>0.00</td>
<td>0.09</td>
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<tr>
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<td>-2.66</td>
<td>0.38</td>
<td>0.41</td>
<td>0.26</td>
<td>-1.91</td>
</tr>
<tr>
<td>2</td>
<td>0.42</td>
<td>-3.12</td>
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<td>0.51</td>
<td>0.25</td>
<td>-1.97</td>
</tr>
<tr>
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<td>-3.32</td>
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<td>0.57</td>
<td>0.27</td>
<td>-2.02</td>
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<td>0.27</td>
<td>-2.37</td>
</tr>
</tbody>
</table>

*Effect of Annealing on the Performance of Nanoparticle Organic Photovoltaic Devices*
Figure 4.7 shows plots of the IV characteristics for the series of devices in this experiment. The graphs show that for pre-annealed devices the highest efficiency was achieved at a drying time of 4 minutes. After this time the annealing efficiency of devices decreased, which is similar to our observations in the previous experiment, where at a drying temperature of 110 °C, the efficiency of the devices decreased after annealing.

The trend in efficiency in Figure 4.7a is similar to the $V_{oc}$ (Figure 4.7c) and fill factor trends (Figure 4.7d). These trends suggest that charge carrier losses at the electrode [116] and series resistance, $R_s$, and shunt resistance, $R_{sh}$ [117] primarily affect device performance. Highest efficiency was obtained at a drying time of 4 minutes suggesting that at this drying time, devices have less charge carrier loss at the electrode, lowest series resistance and highest shunt resistance.

Since the optimal drying time is seen to be 4 minutes (the same time as was used in the first experiment) only modest improvements in device performance (up to ~0.7 %) are observed.
The roughness of film surfaces dried at 110 °C for different times is shown in Figure 4.8 and plotted in Figure 4.9. When the roughness of the film surfaces were plotted against the drying time, it is clear that the film surface is smoothest at a drying time of 4 minutes. This observation is in good agreement with the highest efficiency of devices dried at a temperature of 110 °C for 4 minutes. When aluminium was deposited on a film dried 110 °C for 4 minutes, contact between aluminium and the film was better (possibly due to less porosity at Al-active layer interface) resulting in low series resistance and increased device performance.

**Figure 4.7:** IV characteristics of devices dried at a temperature of 110 °C for various times. (a) Efficiency, (b) current density, (c) open circuit voltage, and (d) fill factor. Blue squares represent pre-annealed devices and red circles represent annealed devices.

The roughness of film surfaces dried at 110 °C for different times is shown in Figure 4.8 and plotted in Figure 4.9. When the roughness of the film surfaces were plotted against the drying time, it is clear that the film surface is smoothest at a drying time of 4 minutes. This observation is in good agreement with the highest efficiency of devices dried at a temperature of 110 °C for 4 minutes. When aluminium was deposited on a film dried 110 °C for 4 minutes, contact between aluminium and the film was better (possibly due to less porosity at Al-active layer interface) resulting in low series resistance and increased device performance.
Table 4.4 shows the IV characteristics of 1:1 P3HT:PC_{61}BM NP-OPV devices dried at 140 °C for different drying times, both before and after annealing. The best and the average of characteristics are presented in this table. Figure 4.10 shows the characteristic plots of this data.

**Figure 4.8:** AFM images depicting the roughness of films surface at different drying time. The size of all images is 20 µm x 20 µm.

**Figure 4.9:** Effect of drying time on the surface film roughness at 110 °C. Data was obtained from AFM image which was operated in AC mode.

Table 4.4 shows the IV characteristics of 1:1 P3HT:PC_{61}BM NP-OPV devices dried at 140 °C for different drying times, both before and after annealing. The best and the average of characteristics are presented in this table. Figure 4.10 shows the characteristic plots of this data.
<table>
<thead>
<tr>
<th>Drying Time (minutes)</th>
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<th></th>
<th>Annealed</th>
<th></th>
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<tbody>
<tr>
<td></td>
<td>$V_{oc}$ (V)</td>
<td>$J_{sc}$ (mA/cm$^2$)</td>
<td>FF (%)</td>
<td>$V_{oc}$ (V)</td>
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<tr>
<td>Best</td>
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<tr>
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</tr>
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<td>Average</td>
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</tr>
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</tr>
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</tr>
<tr>
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<td>0.25</td>
</tr>
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<td>0.06</td>
</tr>
<tr>
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<td>0.18</td>
<td>1.34</td>
<td>0.23</td>
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</tbody>
</table>

From Figure 4.10a, we observe that for pre-annealed devices (blue squares), the highest efficiency was achieved at a drying time of 3 minutes. Current density, $J_{sc}$ (Figure 4.10b) and open circuit voltage, $V_{oc}$, (Figure 4.10c) are also highest at this drying time suggesting that the optimal balance between charge generation and charge transportation (together with the lowest charge carrier losses at electrodes) occurs at a drying time of 3 minutes. For annealed devices (red bars) the highest efficiency occurs at a drying time of 4 minutes, after which efficiency generally declines as drying time is further increased. The observed trend in efficiency is driven primarily by changes in $J_{sc}$ (Figure 4.10b), and to a lesser extent, by changes in $V_{oc}$ (Figure 4.10c) and FF (Figure...
4.10d). That the highest $J_{sc}$, $V_{oc}$, and $FF$ all occur at a drying time of 4 minutes suggests that the optimal balance between charge generation and charge transport, the lowest charge carrier losses at the Al electrode, the best morphology, the lowest series resistance, $R_s$, and the highest shunt resistance, $R_s$, occurs at this drying time.

**Figure 4.10:** Characteristic of devices dried at a temperature of 140 °C for different time. (a) Efficiency, (b) current density, (c) open circuit voltage, and (d) fill factor. Blue square is for pre-annealed devices and red circle is for annealed devices.
4.4 Conclusions

Annealing the active layer, in conjunction with general drying processes, affects the roughness and both the bulk and surface composition of films produced from nanoparticle solutions. Drying can make the film surface smoother or rougher depending on the temperature used. Depositing aluminium onto a smooth surface of the active layer results good contact between aluminium and active layer possibly due to the reduced porosity of the Al-active layer interface. As a result, there is better transport for the free charges to hop into the cathode (aluminium) resulting in increased device performance. On the other hand, depositing aluminium onto a rough surface of the active layer results in poor contact although the rough surface has a larger area. The poor contact is thought to be due to a more porous Al-active layer interface. However, by annealing the device, the contact improves significantly and results in enhanced charge transport to the aluminium electrode.

The presence of SDS on the active layer surface and trapped water in the active layer appear to be detrimental to device performance especially after devices are annealed. After annealing, SDS can create better an insulating layer while trapped water appears to react at the Al-active layer interface to form aluminium oxide. The presence of SDS on the surface and trapped water in the active layer can be reduced by increasing the drying temperature and drying time. However, increasing the drying temperature and drying time beyond the optimal drying temperature and drying time increases phase segregation and is detrimental to device performance.

In these experiments with P3HT (22,000 Da) and PC$_{61}$BM as the semiconducting materials for NP-OPV devices, drying the active layer at drying temperature 110 °C for 4 minutes results in the smoothest film surface and the highest power conversion.
efficiency (PCE) for pre-annealed devices. For annealed devices, however, the highest power conversion efficiency (PCE) was achieved at a drying temperature of 140 °C for 4 minutes as drying the active layer at this drying temperature and drying time resulted in a roughened interface and controlled phase segregation.
5

Effect of an Interface layer on the Performance of Nanoparticle Organic Photovoltaic Devices

Elements of this chapter have been published in the journal “Solar Energy Materials and Solar Cells”


5.1 Introduction

The most common structure of organic photovoltaic devices is an active layer sandwiched between a metal electrode and a transparent metal oxide electrode [118-120]. The metal electrode (cathode) functions to collect electrons from the active layer. Generally, the metal electrode used in organic photovoltaic devices is aluminium (Al). The advantages of using Al as a metal electrode are low cost [121], resistance to corrosion [122, 123], and stability in air [124]. However, to get more efficient devices the Al cathode can be modified by inserting an interface layer between the Al and the active layer [124]. By modifying Al with an interfacial layer, the work function of the electrode is lowered [125], which better matches the HOMO energy level of the
acceptor material [16], and assists to better block positive charges (holes) [126, 127] passing into the cathode and causing recombination.

The use of interface layers in the bulk heterojunction system has been proven to increase the performance of the devices. Eo et al. [16] increased P3HT:PC₆₁BM device power conversion efficiency from 2.54 % to 3.54 % by inserting a thin layer of LiF between the cathode and active layer. Brabec et al. [49] have obtained power conversion efficiencies of 3.3 % (20 % higher than devices using Al only cathode) by inserting a thin layer of LiF into MDMO-PPV/PC₆₁BM. The increase in power conversion efficiency results since LiF creates a dipole moment across the junction resulting in better charge transfer across the interface. Zhao et al. [19] reached a power conversion of 4.6 % by inserting a thin layer of CaO in P3HT:PC₆₁BM devices. The CaO layer increases the devices performance by realigning the energy level at the P3HT:PC₆₁BM/Al interface and increasing the shunt resistance of the devices. Tseng et al. [125] inserted Ca between the aluminium and the active layer of a P3HT:PC₆₁BM device resulting in improvement of power conversion efficiency from 2.3 % to 3.83 %. They argued that the improvement arose since Ca widens the energy difference between the HOMO of P3HT and the LUMO of PC₆₁BM at the cathode interface.

Nanoparticle devices have significantly different active layer morphology than bulk heterojunction devices, since nanoparticle devices are produced from water based dispersions, with the morphology of the active layer critically dependent upon the size and structure of the nanoparticle. The two systems (BHJ vs NP) behave quite differently, therefore investigating the effect of inserting an interface layer in nanoparticle devices is important to understand the behaviour of nanoparticle solar cells. In this study, we investigate the effect of using LiF and Ca as interfacial layers in P3HT:PC₆₁BM nanoparticle devices.
5.2 Experimental

5.2.1 Nanoparticle synthesis

The nanoparticle solution was made as outlined in Chapter 2. P3HT and PC₆₁BM were used as the active layer materials, which were both purchased from LUMTEC. Two batches of P3HT, batch 1 and batch 2, were used in this investigation with molecular weights of 22,000 Da and 18,000 Da, respectively. 15 mg of P3HT and 15 mg of PC₆₁BM were dissolved in 560 µl of anhydrous chloroform to form the solution used in the preparation of nanoparticles.

5.2.2 Device Fabrication

NP-OPV devices in this investigation were produced as outlined in Chapter 2. PEDOT:PSS layers were dried on the hot plate at 140 °C for 30 minutes. In addition to the standard Al electrode, the effects of Ca/Al and LiF/Al electrodes were also investigated. For devices using Al only, the thickness of Al was approximately 100 nm. For Ca/Al devices, after drying the active layer, 30 nm of Ca was first deposited onto the active layer, followed immediately by the deposition of 100 nm of Al. For LiF/Al devices, 1.5 nm of LiF was deposited onto the active layer, followed by 100 nm of Al. For the interface layer and LiF thickness investigation, the active layers were dried at a temperature of 130 °C for 4 minutes based on the drying temperature experiment described in Chapter 3, using the same batch of P3HT (18,000 Da). For the Ca thickness investigation, the active layers were dried at a temperature of 110 °C for 4 minutes based on the drying temperature experiment described in Chapter 4, using the same batch of P3HT (22,000 Da). For annealed devices, annealing parameters of 140 °C for 4 minutes were employed. All of the metal electrodes were deposited by thermal evaporation at a pressure of less than 2 x 10⁻⁶ Torr and their thicknesses were controlled.
by the evaporator setting. For the LiF thickness study, LiF thicknesses of 1.5 nm, 3 nm, 5 nm, and 10 nm were used. For the Ca thickness study, Ca thicknesses of 20 nm, 25 nm, 30 nm, and 40 nm were used.

5.3 Results and Discussion

5.3.1 Interface Layer Comparison

In this experiment, we compare the performance of devices that use Ca and LiF as an interface layer, to devices that use Al only. The thickness of Ca and LiF used were 30 nm and 1.5 nm respectively, while the aluminium thickness is 100 nm. Twelve devices were made with each cathode arrangement. Table 5.1 shows the IV characteristics of devices using the different interfacial layers and Figure 5.1 shows the same characteristics as histograms.

Table 5.1: IV characteristics of 1:1 P3HT:PC$_6$BM NP-OPV devices using different interfacial layers. The best and the average characteristics are presented from a set of 12 devices.

<table>
<thead>
<tr>
<th>Metal Electrode</th>
<th>Pre-annealed</th>
<th>Annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$V_{oc}$ (mV)</td>
<td>$J_{sc}$ (mA/cm$^2$)</td>
</tr>
<tr>
<td>Best</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>422.0</td>
<td>-3.76</td>
</tr>
<tr>
<td>Al/LiF</td>
<td>417.2</td>
<td>-4.34</td>
</tr>
<tr>
<td>Al/Ca</td>
<td>384.2</td>
<td>-3.85</td>
</tr>
<tr>
<td>Average (± STDEV)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>387.1</td>
<td>-3.20</td>
</tr>
<tr>
<td></td>
<td>19.3</td>
<td>0.386</td>
</tr>
<tr>
<td>Al/LiF</td>
<td>366.9</td>
<td>-3.92</td>
</tr>
<tr>
<td></td>
<td>62.3</td>
<td>0.287</td>
</tr>
<tr>
<td>Al/Ca</td>
<td>350.7</td>
<td>-3.53</td>
</tr>
<tr>
<td></td>
<td>22.6</td>
<td>0.236</td>
</tr>
</tbody>
</table>
Figure 5.1a shows that for pre-annealed devices, the PCE of devices using LiF/Al were slightly better than devices using Ca/Al and Al only. The PCE trend is similar to the $J_{sc}$ trend in Figure 5.1b. This trend reveals that the balance between charge generation and charge transport is slightly better when using LiF/Al. In Figure 5.1c, there is no significant change in $V_{oc}$ for pre-annealed devices but in Figure 5.1d, the fill factor of the LiF/Al devices was slightly lower than others, which is not surprising since bulk LiF is an insulator [128, 129]. Figure 5.2 shows a schematic of how LiF increases the series resistance of devices and reduces the fill factor. Electrons ($e^-$) from the active layer can reach the aluminium if it does not contact the LiF particle since LiF cannot conduct the electron to the aluminium. It is clear that the more LiF at interface, the higher the series resistance of devices.
Figure 5.1: IV characteristics of 1:1 P3HT:PCBM NP-OPV devices with different metal electrodes. Blue bars represent pre-annealed devices and red bars represent annealed devices. Error bars indicate the standard deviation (STDEV) of the devices produced. (a) Power conversion efficiency (PCE), (b) current density ($J_{sc}$), (c) open voltage circuit ($V_{oc}$), and (d) fill factor.
Figure 5.1a also shows the power conversion efficiency (PCE) of devices after annealing. After annealing, the performance of devices which use an interface layer increased significantly, while devices with only Al decreased.

The PCE of devices using only Al decreased after annealing as a result of decreasing current density, open circuit voltage, and fill factor. The series resistance increases after annealing as can be seen in Figure 5.3a which is in good agreement with the observed decrease in fill factor. The series resistance doubled from 0.11 kΩ to 0.22 kΩ. The shunt resistance ($R_{sh}$) decreased from 6.02 kΩ to 5.33 kΩ which indicates increased charge recombination after annealing [130]. The decrease in PCE of devices that use Al only, after annealing also has been discussed in Chapter 4.

For LiF/Al devices, the PCE increased after annealing. The current density and fill factor decreased after annealing but the $V_{oc}$ increased significantly. Therefore, the improvement in PCE is dominated by an enhanced $V_{oc}$. The decrease in FF reveals that the series resistance of devices had increased, and this can again be seen in Figure 5.3b. The series resistance increases from 0.06 kΩ to 0.14 kΩ. The reason is thought to be the existence of SDS on the surface of the active layer as discussed in Chapter 4, and also
because the layer formation of the insulating LiF improves after annealing (see Figure 5.2). We speculate that $V_{oc}$ for these devices increases due to the formation of a dipole across the interface which makes charge injection more facile.

![Figure 5.3: IV curves of the best 1:1 P3HT:PCBM NP-OPV devices with different metal electrodes. Blue circles represent pre-annealed devices and red squares represent annealed devices. (a) Aluminium only, (b) aluminium with lithium fluoride, and (c) aluminium with calcium.](image)

For Ca/Al devices, the PCE also increased after annealing. The current density slightly increases after annealing, but the fill factor decreased. The $V_{oc}$ however, increased significantly and is the main reason for the observed increase in PCE. The decrease in the fill factor revealed that series resistance ($R_s$) of these devices increases.
after annealing as shown in Figure 5.3c. The $R_s$ increased from 0.07 kΩ to 0.14 kΩ. However, significantly the shunt resistance ($R_{sh}$) increased from 6.17 kΩ to 8.74 kΩ, which indicates a reduction in charge recombination after annealing [130]. Series resistance was obtained through calculation of the inverse of the slope at $V_{oc}$, and shunt resistance was obtained by calculation of the inverse of the slope at $I_{sc}$.

To understand more clearly the effect of using an interface layer on NP-OPV devices performance, we conducted XPS depth profiling measurements to probe the composition as a function of depth across the interface.

### 5.3.2 XPS Depth Profiling

To investigate the vertical morphology of devices using different interfacial layers, samples were sent to the University of New South Wales, Sydney for XPS depth profile measurement using an ESCALAB 250Xi. The samples were kept in a nitrogen environment to minimise device degradation. Figure 5.4 shows the XPS depth profile plot of Al, LiF/Al, and Ca/Al devices both before and after annealing. To see clearly the composition of materials at Al-active layer interface, we zoom into the region of etch time of 250 s – 1000 s as can be seen in Figure 5.5.

We observe from Figure 5.4, that the C:S ratio for all devices decreases from cathode to anode suggesting that PC$_{61}$BM tends to segregate vertically towards the top electrode [23, 120, 131, 132]. Thus, there is a favourable vertical concentration gradient through the NP active layer (with enrichment of acceptor at the cathode and donor at the anode) which will act to assist charge transport and minimise recombination in the active layer in these devices [88]. P3HT has a molecular formula of C$_{10}$H$_{14}$S and a “monomeric” molecular weight of 166.3 g/mol, PC$_{61}$BM has a molecular formula of C$_{72}$H$_{14}$O$_2$ and a molecular weight of 910.88 g/mol. So if we ignore any contribution
from the SDS (an admittedly significant assumption) a 1:1 ratio of P3HT:PC$_{61}$BM by weight will have 910.88/166.3 or 5.477 P3HT monomers per PC$_{61}$BM. The PC$_{61}$BM contributes 72 carbons and no sulphurs, the 5.477 P3HT monomer units contribute 54.77 carbons and 5.477 sulphurs. Therefore the C:S ratio for a 1:1 mixture should be 126.77:5.477 or 23.1 carbons per sulphur in the active layer. As can be seen in Figure 5.4, the C:S ratio increases from anode to cathode and if we average the C:S ratio from anode to cathode the result agrees excellently with the C:S ratio calculation. The increase C:S ratio from anode to cathode is observed in pre-annealed devices because these devices have been dried previously.

Inserting an interfacial layer causes PC$_{61}$BM to concentrate more at the interface after annealing. Figure 5.4d and Figure 5.4f clearly show there are increases in concentration of C at the interface after annealing. The increased concentration of PC$_{61}$BM at the interface is thought to be due to the interface layer modifying the surface energy of the interface, which drives more PC$_{61}$BM to concentrate at interface relative to P3HT [133] and which results in higher charge carrier density [88]. As a result, $V_{oc}$ will increase [89] and consequently there is an overall increase in device performance.

The XPS depth profile data of a device without an interface layer (i.e. Al only) shown in Figure 5.4a and Figure 5.4b shows that the C:S ratio has changed slightly after annealing. The C:S ratio of the pre-annealed device decreases from cathode to anode more quickly than for the annealed device. The percentage of the C:S ratio close to the cathode before annealing is about 24.1 % (Figure 5.5a), which decreased to 21.2 % (Figure 5.5b) after annealing. The decrease of the C:S ratio at the interface after annealing is believed to be the reason that the $V_{oc}$ decreases upon annealing a device using only Al. Oxygen at the interface increased after annealing from 9.9 % (Figure
5.5a) to 16.3 % (Figure 5.5b). Aluminium oxide (Al\textsubscript{2}O\textsubscript{3}) at the interface also increased. Before annealing, the percentage of Al\textsubscript{2}O\textsubscript{3} at the interface is about 9.7 % (Figure 5.5a) and after annealing Al\textsubscript{2}O\textsubscript{3} this percentage increased to 13.5 % (Figure 5.5b). We hypothesise that the increase in Al\textsubscript{2}O\textsubscript{3} at the interface after annealing contributes to lower the performance of devices because Al\textsubscript{2}O\textsubscript{3} has much lower conductivity than pure aluminium.

Figure 5.5c and Figure 5.5d show the XPS depth profile of a device with LiF as an interface layer in the region of 250 – 1000 s of etch time. There is no significant change in oxygen and aluminium oxide concentration at the interface after annealing as was observed for devices using Al only. Oxygen at the interface slightly decreased after annealing from 8.9 % (Figure 5.5c) to 6.4 % (Figure 5.5d) and aluminium oxide only increased slightly from 7.5 % (Figure 5.5c) to 8.5 % (Figure 5.5d). LiF then tends to protect the aluminium layer from oxygen sources that may oxidise the aluminium of the cathode and consequently gives better transport to the free charges to hop into the pure aluminium. The C:S ratio however, has changed significantly after annealing. The C:S ratio increased significantly at the interface from 24.1 % (Figure 5.5c) to 28.7 % (Figure 5.5d). This increase after annealing revealed that the PC\textsubscript{61}BM concentration increased at the interface resulting in an increase in \( V_{oc} \) and consequently the device performance.
Figure 5.4: XPS depth profiles (region 0 s – 3000 s) for the pre-annealed (a, c, e) and annealed (b, d, f) 1:1 P3HT:PC_{61}BM NP-OPV devices different metal electrode. (a, b) Al only, (c, d) Al with LiF, and (e, f) Al with Ca.
Figure 5.5: XPS depth profiles (region 250 s – 1000 s) for the pre-annealed (a, c, e) and annealed (b, d, f) 1:1 P3HT:PC$_6$BM NP-OPV devices different metal electrode. (a, b) Al only, (c, d) Al with LiF, and (e, f) Al with Ca.
Figure 5.5e and Figure 5.5f show the XPS depth profile of a device using Ca as an interfacial layer in the region of 250 – 1000 s of etch time. As observed in the LiF devices, the oxygen and the aluminium oxide percentage also have not changed significantly after annealing. Oxygen at the interface before and after annealing is still the same, 7.5 % (Figure 5.5e and Figure 5.5f) to 6.4 % and aluminium oxide increases only a tiny amount from 6.8 % (Figure 5.5e) to 8.0 % (Figure 5.5f). As with LiF, the Ca then tends to prevent oxygen from oxidising the pure aluminium cathode. The C:S ratio increased at the interface significantly after annealing, from 24.6 % (Figure 5.5e) to 32.1% (Figure 5.5f). This increase reveals that concentration of PC\textsubscript{61}BM at the interface was also increased after annealing, which then leads to enhanced $V_{oc}$.

For comparison with bulk heterojunction devices (BHJ), we use IV characteristics data (Table 5.2) and the XPS depth profile data (Figure 5.7) of a 1:1 P3HT:PC\textsubscript{61}BM bulk heterojunction device using metal electrodes Al, LiF/Al and Ca/Al. This comparison data was obtained from Elisa Sesa of the University of Newcastle. The aluminium layer thickness for all devices was around 60 nm, while the thickness of the LiF layer and the Ca layer was around 1.5 nm and 20 nm, respectively.
Table 5.2: IV characteristics (in average) of 1:1 P3HT:PC$_{61}$BM bulk heterojunction devices using different metal electrode.

<table>
<thead>
<tr>
<th>Metal Electrode</th>
<th>Pre-annealed</th>
<th></th>
<th></th>
<th></th>
<th>Annealed</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$V_{oc}$ (mV)</td>
<td>$J_{sc}$ (mA/cm$^2$)</td>
<td>FF</td>
<td>PCE (%)</td>
<td>$V_{oc}$ (mV)</td>
<td>$J_{sc}$ (mA/cm$^2$)</td>
<td>FF</td>
<td>PCE (%)</td>
</tr>
<tr>
<td></td>
<td>(± STDEV)</td>
<td></td>
<td></td>
<td></td>
<td>(± STDEV)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>420.1</td>
<td>8.06</td>
<td>39</td>
<td>1.32</td>
<td>546</td>
<td>8.94</td>
<td>39</td>
<td>1.92</td>
</tr>
<tr>
<td></td>
<td>13.7</td>
<td>0.60</td>
<td>1</td>
<td>0.13</td>
<td>12.8</td>
<td>0.86</td>
<td>2</td>
<td>0.29</td>
</tr>
<tr>
<td>Al/LiF</td>
<td>607.2</td>
<td>7.44</td>
<td>45</td>
<td>2.05</td>
<td>604</td>
<td>9.78</td>
<td>48</td>
<td>2.84</td>
</tr>
<tr>
<td></td>
<td>21.8</td>
<td>0.62</td>
<td>2</td>
<td>0.22</td>
<td>3.1</td>
<td>0.94</td>
<td>2</td>
<td>0.37</td>
</tr>
<tr>
<td>Al/Ca</td>
<td>581.3</td>
<td>7.66</td>
<td>50</td>
<td>2.22</td>
<td>576</td>
<td>8.66</td>
<td>57</td>
<td>2.86</td>
</tr>
<tr>
<td></td>
<td>13.9</td>
<td>0.74</td>
<td>3</td>
<td>0.29</td>
<td>5.5</td>
<td>0.78</td>
<td>2</td>
<td>0.32</td>
</tr>
</tbody>
</table>

Figure 5.6 shows the IV characteristics of 1:1 P3HT:PC$_{61}$BM bulk heterojunction devices both pre-annealed and annealed. As shown in Figure 5.6a, the efficiency of devices using Al only was increased after annealing, which was opposite to the NP-OPV devices using Al only. The increased efficiency was mainly due to increased $V_{oc}$ (Figure 5.6c). Based on XPS data (Figure 5.7a and Figure 5.7b), after annealing, the concentration of C:S ratio at the BHJ interface increased and is thought to be the reason for the $V_{oc}$ increase.
For devices using LiF as an interface layer, after annealing the efficiency of the devices increased, driven by the $J_{sc}$ (Figure 5.6b) and the fill factor ($FF$) (Figure 5.6d), but not by the $V_{oc}$ (Figure 5.6c). The increase of the $J_{sc}$ and the $FF$ suggest that annealing the devices with LiF as an interface layer results in better charge extraction from the interface and lower charge recombination. $V_{oc}$ did not increase although the C:S ratio increased dramatically after annealing, as shown in Figure 5.7c and Figure 5.7d. We assume that $V_{oc}$ did not increase because prior to annealing, $V_{oc}$ had already reached the optimum value.
Inserting an interfacial layer of calcium also increased the efficiency of bulk heterojunction devices as we can see in Figure 5.6a, which was driven by the $J_{sc}$ (Figure 5.6b) and the $FF$ (Figure 5.6d) and again not because of the $V_{oc}$ (Figure 5.6c). The increase in $J_{sc}$ and $FF$ suggest that annealing the devices that use Ca as an interface results in a better active layer morphology and lower charge recombination. Figure 5.7e and Figure 5.7f show that concentration of C:S ratio was higher at interface but the $V_{oc}$ did not increase. Again we assume that the $V_{oc}$ already reached the optimum point before annealing. Thus for LiF and Ca BHJ devices, annealing the device improves performance through morphological change of the active layer but not through changes at the interface.
Figure 5.7: XPS depth profiles for the pre-annealed (a, c, e) and annealed (b, d, f) 1:1 P3HT:PCBM bulk heterojunction devices with different interface layers. (a, b) Al only, (c, d) Al with LiF, and (e, f) Al with Ca.
5.3.3 Lithium Fluoride Thickness

In this experiment we investigate and optimise the effect of LiF thickness on the performance of NP-OPV devices. Table 5.3 shows the IV characteristics of 1:1 P3HT:PC$_{61}$BM nanoparticle devices with different thicknesses of the LiF layer at the Al-active layer interface and Figure 5.8 shows the data as graphs. 12 devices were made for each LiF thickness.

**Table 5.3:** Best and average of IV characteristics of 1:1 P3HT:PC$_{61}$BM NP-OPV devices using different thickness of interface layer, LiF.

<table>
<thead>
<tr>
<th>LiF Thickness (nm)</th>
<th>Pre-annealed</th>
<th>Annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$V_{oc}$ (mV)</td>
<td>$J_{sc}$ (mA/cm$^2$)</td>
</tr>
<tr>
<td><strong>Best</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>397.5</td>
<td>-3.76</td>
</tr>
<tr>
<td>1.5</td>
<td>411.6</td>
<td>-3.84</td>
</tr>
<tr>
<td>3</td>
<td>412.6</td>
<td>-4.07</td>
</tr>
<tr>
<td>5</td>
<td>403.3</td>
<td>-3.87</td>
</tr>
<tr>
<td>10</td>
<td>393.6</td>
<td>-3.35</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(± STDEV)</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>381.8</td>
<td>-3.17</td>
</tr>
<tr>
<td></td>
<td>11.1</td>
<td>0.470</td>
</tr>
<tr>
<td>1.5</td>
<td>396.7</td>
<td>-3.49</td>
</tr>
<tr>
<td></td>
<td>11.2</td>
<td>0.346</td>
</tr>
<tr>
<td>3</td>
<td>401.6</td>
<td>-3.83</td>
</tr>
<tr>
<td></td>
<td>5.6</td>
<td>0.242</td>
</tr>
<tr>
<td>5</td>
<td>394.4</td>
<td>-3.73</td>
</tr>
<tr>
<td></td>
<td>7.9</td>
<td>0.085</td>
</tr>
<tr>
<td>10</td>
<td>386.0</td>
<td>-2.84</td>
</tr>
<tr>
<td></td>
<td>3.3</td>
<td>0.321</td>
</tr>
</tbody>
</table>
From Figure 5.8a we observe that for the pre-annealed devices, efficiency improved as the LiF thickness was increased, reaching a maximum efficiency at a thickness of 3 nm, after which efficiency declined with further increases in LiF thickness. The trend in efficiency is similar to the $J_{sc}$ trend in Figure 5.8b, while $V_{oc}$ is almost invariant across all the thickness values. The $J_{sc}$ trend leads to the conclusion that the primary driving force of the observed efficiency is changes in $J_{sc}$, suggesting that the optimal balance between charge generation and charge transport occurs at a LiF thickness of 3 nm. The fill factor trend in Figure 5.8d also shows a similar trend to the

**Figure 5.8:** IV characteristics of 1:1 P3HT:PCBM NP-OPV devices with different LiF thicknesses as blue circles represent pre-annealed devices and red squares represent annealed devices. Error bars showing the STDEV of devices produced. (a) Power conversion efficiency (PCE), (b) current density ($J_{sc}$), (c) open voltage circuit ($V_{oc}$) and (d) fill factor.
efficiency trend but with the peak shifted to 1.5 nm. Beyond a thickness of 1.5 nm, fill factor decreased sharply upon increasing LiF thickness, which is likely to be due to the formation of a more complete LiF layer (see Figure 5.2). We speculate that better LiF layer formation results in a more electrically insulating interface.

For annealed devices, the peak efficiency occurs at a LiF thickness of 1.5 nm. It is interesting to note that after annealing, the efficiency of the devices decreased except at a thickness 1.5 nm where efficiency increased after annealing, which is what we have observed in our previous investigation. At a LiF thickness of 1.5 nm, after annealing $J_{sc}$ stayed relatively constant and fill factor decreased. Only $V_{oc}$ increased significantly after annealing suggesting that efficiency was mainly driven by changes in $V_{oc}$. Moreover, the efficiency trend in Figure 5.8a is also echoed in the $V_{oc}$ trend (Figure 5.8c). Beyond a LiF thickness of 1.5 nm, efficiency decreased dramatically after annealing which is likely to be because upon annealing thicker LiF performs better as an insulator layer, leading to an increase in device series resistance $R_s$ and a reduction in device shunt resistance $R_{sh}$ [130]. These changes to series resistances $R_s$ and shunt resistances $R_{sh}$ can be readily seen in Figure 5.8 from the relative slopes of the IV plots at $V_{oc}$ and $I_{sc}$, respectively. The optimum thickness of LiF seems then to be a balance between the presence of as much LiF as possible whilst not allowing the formation of a complete insulating layer. Thus by the time we have 10 nm LiF in the device a complete insulating layer is obtained on annealing and the device is no longer functional. The increase in series resistance $R_s$ and the decrease of shunt resistance $R_{sh}$ upon increasing LiF thickness beyond 1.5 nm are in good agreement with the observed fill factor in Figure 5.8d since Figure 5.8d shows that the fill factor decreases upon increasing LiF thickness beyond of 1.5 nm.
5.3.4 Calcium Interface Layer Thickness

In this experiment we investigate and optimise the effect of Ca interface layer thickness on NP-OPV devices. In investigating the Ca layer thickness effect, the drying temperature used was 110 °C as determined in Chapter 4 for P3HT batch 1 (MW 22,000

Figure 5.9: IV curves of 1:1 P3HT:PCBM NP-OPV devices with different LiF thicknesses. (a) 0 nm, (b) 1.5 nm, (c) 3 nm, (d) 5 nm, and (d) 10 nm. Blue squares are pre-annealed devices and red circles are annealed devices.
Da). Table 5.4 shows the characteristic data of pre-annealed 1:1 P3HT:PC$_{61}$BM nanoparticle devices of different Ca thickness.

**Table 5.4:** Device characteristics of 1:1 P3HT:PC$_{61}$BM nanoparticles with different Ca thickness. The best and the average characteristics are presented from a set of 12 devices.

<table>
<thead>
<tr>
<th>Ca Thickness (nm)</th>
<th>$V_{oc}$ (mV)</th>
<th>$I_{sc}$ (mA)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Best</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>470.7</td>
<td>-0.15</td>
<td>-3.06</td>
<td>0.36</td>
<td>0.52</td>
</tr>
<tr>
<td>20</td>
<td>474.5</td>
<td>-0.20</td>
<td>-3.98</td>
<td>0.42</td>
<td>0.72</td>
</tr>
<tr>
<td>25</td>
<td>503.6</td>
<td>-0.27</td>
<td>-5.42</td>
<td>0.48</td>
<td>1.30</td>
</tr>
<tr>
<td>30</td>
<td>516.5</td>
<td>-0.28</td>
<td>-5.56</td>
<td>0.47</td>
<td>1.31</td>
</tr>
<tr>
<td>40</td>
<td>499.8</td>
<td>-0.23</td>
<td>-4.69</td>
<td>0.40</td>
<td>0.93</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(± STDEV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>460.7</td>
<td>-0.13</td>
<td>-2.56</td>
<td>0.33</td>
<td>0.40</td>
</tr>
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<td></td>
<td>12.3</td>
<td>0.038</td>
<td>0.754</td>
<td>0.036</td>
<td>0.149</td>
</tr>
<tr>
<td>20</td>
<td>410.0</td>
<td>-0.17</td>
<td>-3.39</td>
<td>0.38</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>54.8</td>
<td>0.018</td>
<td>0.357</td>
<td>0.027</td>
<td>0.097</td>
</tr>
<tr>
<td>25</td>
<td>495.4</td>
<td>-0.25</td>
<td>-5.02</td>
<td>0.46</td>
<td>1.14</td>
</tr>
<tr>
<td></td>
<td>11.6</td>
<td>0.015</td>
<td>0.309</td>
<td>0.022</td>
<td>0.095</td>
</tr>
<tr>
<td>30</td>
<td>503.8</td>
<td>-0.26</td>
<td>-5.29</td>
<td>0.45</td>
<td>1.19</td>
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<td>9.6</td>
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<tr>
<td>40</td>
<td>491.6</td>
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<td>-3.48</td>
<td>0.36</td>
<td>0.63</td>
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<tr>
<td></td>
<td>6.4</td>
<td>0.038</td>
<td>0.759</td>
<td>0.029</td>
<td>0.197</td>
</tr>
</tbody>
</table>

We observe from Figure 5.10a, that significantly improved device performance occur as the calcium thickness is increased from 20 nm to 30 nm. Figure 5.10a and Figure 5.10b shows that efficiency and $J_{sc}$ have the same trend, which suggests that the performance of the devices is dominated by the charge separation rate and transport. An optimal balance between charge generation and charge transport occurs at a Ca layer thickness of 30 nm. Increasing the Ca layer thickness beyond of 30 nm reduces the current density and the fill factor. Typically the thin layer of Ca metal deposited at the cathode interface will rapidly oxidise to CaO/CaOH species. Thicker Ca results in a better CaO layer formation which will result in a better insulator layer at the interface.
since CaO layer is an insulator. Consequently, series resistance of the device increased. The increase in series resistance upon increasing Ca thickness beyond of 30 nm is in good agreement with the decrease of the $FF$ and the $J_{sc}$. This hypothesis is supported by Figure 5.12 which confirms that thicker Ca layer have higher series resistance.

As mentioned before, a thin layer of Ca metal deposited at the cathode interface will rapidly oxidise to CaO/CaOH species. Thus the work function of the electrode is dictated by the Al and is $\sim 4.2$ eV [16]. This works adequately for electron injection from PC$_{61}$BM (see Figure 5.11). However as our Ca layer gets thicker Ca metal may be retained at the interface. The work function of Ca is $\sim 2.9$ eV [16] which is no longer ideal for electron injection from PC$_{61}$BM and device function consequently must suffer.
Figure 5.10: Characteristics of NP-OPV devices dried at 110 °C with different Ca interface layer thickness. Errors bars represent STDEV of the device values.
Figure 5.11: Energy band diagram of OPV device. (modified from [16])

Figure 5.12 shows the IV curves of 1:1 P3HT:PC_{61}BM nanoparticle devices with different Ca thicknesses. It is clear that devices with Ca thickness of 30 nm have the lowest series resistance, $R_s$, and increased current density and this leads to optimal balance between charge generation and charge transport. Series resistance $R_s$ was obtained by calculating the slope at $V_{oc}$.

Figure 5.12: IV-curve of NP-OPV devices dried 110 °C with different Ca thickness.
Figure 5.13 shows the IV curves (dark and illuminated) and external quantum efficiency (EQE) curves for the best device produced with Ca as an interface layer. This device had an efficiency of 1.31 % and a peak EQE of 35 %. The EQE shows that current generation is dominated by P3HT (450-650 nm) with a reduced PC$_{61}$BM contribution (below 400 nm) from that observed for BHJ device [23]. A reduced PC$_{61}$BM contribution to current is consistent with the core-shell morphology of these particles [26] where PC$_{61}$BM is trapped in the core and subsequently excitons generated in this material are less likely to successfully generate charges. The core-shell morphology of these particles is discussed in more detail in Chapter 6.

5.4 Conclusions

Inserting an interface layer of LiF or Ca between the Al and active layer increases the performance of P3HT:PC$_{61}$BM NP-OPV devices, particularly after annealing. The increased performance is mainly due to the $V_{oc}$ of devices increasing when using LiF and Ca as an interface layer. Based on XPS depth profile data, inserting an interface layer drives PC$_{61}$BM concentration to the cathode interface during annealing which is
thought to be the reason for the increase of open circuit voltage \( (V_{oc}) \) which ultimately increases NP-OPV device performance.

In bulk heterojunction devices when using an interface layer, higher device performance after annealing is driven by the \( J_{sc} \) and the \( FF \), whereas with NP-OPV devices that was driven by improvements in \( V_{oc} \). Based on XPS data profiles, after annealing bulk heterojunction devices, the concentration of C:S ratio increases at the BHJ Al-active layer interface. However, higher concentrations at the Al-active layer interface after annealing did not further increase the \( V_{oc} \) which was thought to be due to \( V_{oc} \) already reaching the optimum point before annealing. Therefore, an interface layer increases the performance of NP-OPV devices and bulk heterojunction devices in different ways. This highlights the importance and necessity for reoptimisation of device parameters for the NP-OPV system.

XPS depth profile data also shows that inserting an interface layer can reduce the formation of aluminium oxide at the Al-active layer interface which results in better transport of the free charges and enhanced ability to hop into the pure aluminium. In devices using aluminium only, \( \text{Al}_2\text{O}_3 \) increases significantly after annealing increasing series resistance and resulting in devices of low performance.

Investigation of the thickness variation of interface layer on NP-OPV devices shows that there is an optimum thickness of the interfacial layers. For LiF interface layer, the optimum thickness is 1.5 nm and for the Ca interface layer, the optimum thickness is 30 nm. Increasing the interface layer thickness beyond of the optimum thickness will result in lower device performance. Increasing LiF thickness beyond of 1.5 nm made the performance of the annealed devices drop due to LiF acting as an insulator layer at greater thicknesses. Increasing Ca beyond 30 nm will increase the
series resistance of the devices and alters the work function of the cathode reducing charge injection and lowering device performance.
6

Acceptors Effect on NP-OPV Device Performance

Elements of this chapter have been published in the journals “Solar Energy Materials and Solar Cells” and “Nano Energy”


6.1 Introduction

The nature of the electron acceptor is a key factor in optimizing the performance of organic photovoltaic (OPV) devices. Many studies have investigated the electron acceptor in order to improve the performance of organic photovoltaic devices [7, 12, 20]. Some factors to be considered in selecting the appropriate acceptor are solubility [134], LUMO energy [7], and visible light absorption [135]. The most common acceptor used in organic photovoltaics is PC$_{61}$BM (phenyl-C$_{61}$-butyric acid methyl ester) with more than 1000 publications since 2002 [90]. The advantages of using PC$_{61}$BM as an acceptor in organic photovoltaic devices include good solubility, high electron mobility and high electron affinity [32, 98, 136]. PC$_{71}$BM (phenyl-C$_{70}$-butyric acid methyl ester) has also been used as an acceptor in OPVs. PC$_{71}$BM exhibits stronger absorption of visible wavelengths than PC$_{61}$BM and it has been demonstrated that it
leads to higher power conversion efficiency (PCE) in OPV devices than PC\textsubscript{61}BM [135, 137]. Another acceptor material that gives a better performance than PC\textsubscript{61}BM is ICBA (indene-C\textsubscript{60} bis-adduct) driven primarily by the fact that ICBA has greater solubility and a higher LUMO energy than PC\textsubscript{61}BM [12, 138].

In this chapter we will investigate the use of different acceptor molecules in nanoparticle organic photovoltaic (NP-OPV) devices. PC\textsubscript{61}BM, PC\textsubscript{71}BM, and ICBA will be used in this study to investigate whether, or not, changing acceptor molecule produces similar performance characteristics for NP-OPVs as they do for bulk heterojunction (BHJ) devices. We use XPS depth profile, STXM and TEM measurements to investigate the effect of using different acceptors on the performance and morphology of NP-OPV devices.

6.2 Experimental

6.2.1 Nanoparticle synthesis

Nanoparticle solutions were prepared as outlined in Chapter 2. P3HT (MW 18,000 Da) was used as the electron donor and PC\textsubscript{61}BM, PC\textsubscript{71}BM and ICBA as the acceptor with a ratio of 1:1. However in the P3HT:ICBA ratio experiment, the ratios investigated were 1:0.5, 1:0.6, 1:0.7, 1:0.8, 1:0.9, 1:1 and 0.8:1.

6.2.2 Device fabrication

NP-OPV devices were produced as outlined in Chapter 2. PEDOT:PSS with a thickness of ~60 nm was dried on a hotplate at 140 °C for 30 minutes, and the active layers with thicknesses of ~100 nm were dried on a hotplate at a temperature of 130 °C for 4 minutes (in air). Following deposition of calcium and aluminium with thicknesses of
~30 nm and ~100 nm respectively, devices were annealed on a hotplate at a temperature of 140 °C for 4 minutes (in nitrogen).

For the ICBA device optimisation study, PEDOT:PSS was dried for 20 minutes, then drying temperature, drying time, annealing temperature and annealing time for the active layer were investigated. The Ca, Al and active layer thicknesses were ~30 nm, ~100 nm and ~100 nm, respectively.

6.2.3 STXM, TEM and XPS depth profile sample
STXM and TEM samples were prepared as outlined in Chapter 2 and for the XPS depth profile samples, a functional NP-OPV device was used.

6.3 Results and Discussion

6.3.1 Applying the standard PCBM procedure for PC_{61}BM, PC_{71}BM and ICBA
In this experiment, we use the same preparation conditions for all devices, following the typical equimass PCBM procedure. In the PCBM procedure, PEDOT:PSS with a thickness of ~60 nm was dried on a hotplate at 140 °C for 30 minutes, then the active layers with thicknesses of ~100 nm were dried on a hotplate at 130 °C for 4 minutes (in air). After depositing calcium and aluminium with thicknesses of ~30 nm and ~100 nm respectively, the devices were annealed on a hotplate at 140 °C for 4 minutes (in nitrogen). Table 6.1 shows the IV data of devices and Figure 6.1 shows the data in graphs.
Table 6.1: IV data of 1:1 P3HT:PC\textsubscript{61}BM NP, 1:1 P3HT:PC\textsubscript{71}BM NP and 1:1 P3HT:ICBA NP devices. The best and the average characteristics are presented from a set of 12 devices.

| Acceptor | Pre-annealed | | | | | | Annealed | | | |
|-----------|--------------|----------------|---|---|----------------|---|---|----------------|---|---|---|
|           | \(V_{oc}\) (mV) | \(J_{sc}\) (mA/cm\textsuperscript{2}) | FF | PCE (%) | \(V_{oc}\) (mV) | \(J_{sc}\) (mA/cm\textsuperscript{2}) | FF | PCE (%) |
| PC\textsubscript{61}BM | 415.9 | -4.71 | 0.47 | 0.92 | 527.1 | -4.91 | 0.45 | 1.13 |
| PC\textsubscript{71}BM | 440.2 | -6.27 | 0.48 | 1.27 | 543.4 | -5.99 | 0.45 | 1.46 |
| ICBA | 712.7 | -5.31 | 0.37 | 1.40 | 701.8 | -7.21 | 0.40 | 2.02 |

**Average**

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>(±) STDEV</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PC\textsubscript{61}BM</td>
<td>392.2</td>
<td>-4.03</td>
<td>0.45</td>
<td>0.72</td>
<td>514.2</td>
<td>-4.05</td>
<td>0.43</td>
<td>0.90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PC\textsubscript{71}BM</td>
<td>429.7</td>
<td>-5.76</td>
<td>0.47</td>
<td>1.16</td>
<td>527.2</td>
<td>-5.58</td>
<td>0.44</td>
<td>1.29</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ICBA</td>
<td>686.8</td>
<td>-4.60</td>
<td>0.35</td>
<td>1.11</td>
<td>680.1</td>
<td>-6.34</td>
<td>0.38</td>
<td>1.66</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From Figure 6.1a we can see that both pre-annealed and annealed PC\textsubscript{71}BM and ICBA devices have higher power conversion efficiency (PCE) compared to PC\textsubscript{61}BM. The PCE of PC\textsubscript{71}BM devices was higher than PC\textsubscript{61}BM as a result of higher current density, while the higher PCE of ICBA devices than PC\textsubscript{61}BM was due to a combination of higher current density \(J_{sc}\) and open circuit voltage \(V_{oc}\). PC\textsubscript{71}BM has higher current density than PC\textsubscript{61}BM primarily because PC\textsubscript{71}BM absorbs more light energy in the visible wavelengths [135]. In ICBA, aside from its higher LUMO energy, it also absorbs more light energy at visible wavelengths than PC\textsubscript{61}BM [139]. Consequently ICBA has higher current density and, as a result of a higher LUMO energy, higher open circuit voltage.

As observed in Figure 6.1a, the PCE of PC\textsubscript{61}BM, PC\textsubscript{71}BM and ICBA devices were increased after annealing. For PC\textsubscript{61}BM and PC\textsubscript{71}BM devices, the PCE increase was driven primarily by the open circuit voltage (Figure 6.1c) as the current density
The acceptor effect on NP-OPV device performance was assessed. The current density (Figure 6.1b) and the fill factor (Figure 6.1d) did not change significantly, and some even decreased slightly after annealing. For ICBA devices, the current density (Figure 6.1b) and the fill factor (Figure 6.1d) increased after annealing while the open circuit voltage remained constant after annealing. Therefore, the increase in PCE of the ICBA devices was driven entirely by current density and fill factor.

Figure 6.1: IV characteristics of 1:1 P3HT:PC$_{61}$BM NP-OPV, 1:1 P3HT:PC$_{71}$BM NP-OPV and 1:1 P3HT:ICBA NP-OPV devices. Blue bars represent the pre-annealed devices and red bars represent the annealed devices. Error bars showing the STDEV of devices.
We can see clearly from Figure 6.1 that ICBA devices have the highest PCE after annealing, however, ICBA devices also have the lowest fill factor. Figure 6.2 shows the IV curves of PC_{61}BM, PC_{71}BM and ICBA devices. It is clear that at the open circuit voltage, ICBA devices have a lower slope (Figure 6.2c) compared with the slope of PC_{61}BM (Figure 6.2a) and PC_{71}BM (Figure 6.2b) devices suggesting that ICBA devices have higher series resistance (R_s) compared to the others and this higher series resistance is in good agreement with the ICBA devices fill factor.

As we discussed before, the improved PCE of the PCBM devices after annealing was mainly due to increased open circuit voltage, while improved PCE of ICBA devices was mainly due to their current density increasing after annealing. In an attempt to further understand these observations, we conducted XPS depth profiling, STXM and TEM experiments for this study.
6.3.2 XPS Depth Profiling

Figure 6.2: IV curves of 1:1 P3HT:PC_{61}BM NP-OPV (a), 1:1 P3HT:PC_{71}BM NP-OPV (b) and 1:1 P3HT:ICBA NP-OPV (c). Blue squares are for pre-annealed and red circles for annealed devices.

In this study, we compare the depth profile data of a 1:1 P3HT:PC_{61}BM NP device and a 1:1 P3HT:ICBA NP device. Both devices use the same preparation conditions such drying the active layer at 130 °C for 4 minutes, annealing the devices at 140 °C for 4 minutes, and using Ca as an interface layer with thickness of 30 nm.
We can see in Figure 6.3a and Figure 6.3b, there is a significant change in morphology for the 1:1 P3HT:PC$_{61}$BM NP device with Ca as an interface layer, as evident from the carbon to sulphur ratio which increased at the interface after annealing.

This increase is thought to be the reason for the observed $V_{oc}$ increase since it creates a gradient in the electron conduction pathway that is maximised at the cathode, and will result in greater charge carrier density and reduced recombination in the device [88]. For 1:1 P3HT:ICBA NP devices, it is clear from Figure 6.3c and Figure 6.3d that the carbon to sulphur ratio show no significant changes, which is why the $V_{oc}$ remains 

Figure 6.3: XPS depth profile of 1:1 P3HT:PC$_{61}$BM NP-OPV (a, b) and 1:1 P3HT:ICBA NP-OPV (c, d) devices. Pre-annealed (a, c) and annealed (b, d).
constant after annealing. However, oxygen and aluminium oxide peaks decrease significantly after annealing which is likely to be one of the reasons the current increased after annealing since this will have the effect of reducing the $R_s$ of the device. This can also be seen in Figure 6.2c in the relative slopes of the pre-annealed device at $V_{oc}$. Another factor contributing to the increasing current is thought to be due to the miscibility of ICBA in P3HT since increased miscibility has been shown to improve current density [140, 141]. The morphology and thus miscibility in this film can be investigated using STXM and TEM measurements.

6.3.3 STXM and TEM

6.3.3.1 P3HT:ICBA NPs
STXM measurements of the NP active layers were undertaken to probe directly the nanostructure of the NP-OPV devices. STXM compositional mapping of the P3HT and ICBA components for the as-spun (Figure 6.4a and Figure 6.b) and dried films (Figure 6.4d and Figure 6.4e) demonstrate that these P3HT:ICBA NPs have a core shell morphology with a P3HT-rich shell and ICBA-rich core domains and that the drying step (110 °C for 4 minutes) used for the NP-OPV device fabrication does not greatly alter this core shell structure of the as-spun nanoparticle film. The corresponding TEM images of the pre-annealed and dried nanoparticles (Figure 6.4c and Figure 6.4f respectively) confirm that these are discrete nanoparticles with a range of particle sizes. Moreover, examination of these different particle sizes indicates that the core shell morphology is preserved at all length scales down to the resolution of the STXM instrument; thus providing compelling evidence that the STXM images accurately represent the active layer morphology of the P3HT:ICBA NP-OPV device. Upon
annealing, the core-shell structure is lost (Figure 6.4g and Figure 6.4h) and the particles merge together (Figure 6.4i).

Quantitative analysis of the STXM compositional maps was completed using a combination of linear and radial profiling [26]. As shown in Figure 6.5a, the as-spun particles exhibit an ICBA core fractional composition of 0.41 ± 0.05, which is very close to the experimentally prepared value (0.5) based on the 1:1 P3HT:ICBA solution composition, and a thin shell region that is depleted in ICBA (0.23 ± 0.05). Upon

**Figure 6.4:** 2 µm x 2 µm P3HT and ICBA STXM compositional maps for: as-spun (a and b), as-dried (d and e) NP films. 1 µm x 1 µm P3HT and ICBA STXM compositional maps for an annealed (g and h) NP film. Corresponding TEM images for the as-spun (c), as-dried (f) and annealed (i) NP films are also shown.
drying, the ICBA shell fractional composition increases to $0.34 \pm 0.05$, whilst the core composition remains largely unchanged ($0.44 \pm 0.05$). Finally upon annealing, the particle shell and core compositions become effectively the same with an average composition of $0.32 \pm 0.05$. Clearly these particles are then depleted in ICBA and this observation needs explanation.

**Figure 6.5:** (a) ICBA fraction of the core and shell domains as a function of thermal treatment for NP films. The closed black circles and open red circles represent the NP ICBA core and shell fractional compositions respectively. The error bars are obtained from the standard deviation of the radial analysis. (b) 2 mm x 2 mm TEM image of an annealed NP film clearly showing presence of small crystallites in the interstitial regions between NP domains. (c) Schematic model of NP evolution during thermal treatment.

Based on the STXM and TEM images a model for the evolution of P3HT:ICBA NP composition and morphology can be proposed. During particle formation P3HT migrates into the particle shell region resulting in the observed reduction in ICBA fraction. This observation is consistent with the lower surface energy of P3HT which will tend to drive P3HT to the outermost surface of the NP during NP synthesis [142-
Upon drying, movement of ICBA into the shell region occurs raising the ICBA shell fractional composition in the as-dried particles and, due to the relative volume (~2:1) of the core to shell, this movement has little effect on the core composition. Upon annealing of the P3HT:ICBA particles there is continued movement of ICBA from core to shell and, at the higher annealing temperature, diffusion from shell to outside the particle is now activated. Consequently, the P3HT and ICBA become homogenously blended (on the scale of the STXM measurement) throughout the core and shell resulting in the observed similar compositions. A further implication of this model is that ICBA can be lost from the annealed particles due to the ICBA concentration gradient at a particle-air interface. This conclusion is supported by TEM images of the annealed particles (Figure 6.5b) which show regions of very small (less than 50 nm) crystallites between the NP domains, which we hypothesise to be ICBA. A schematic of this process is shown in Figure 6.5c.

The Flory-Huggins free energy of mixing theory states that:

\[
\Delta G_{mix} = RT \left[ n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi \right] 
\]

where \( \Delta G_{mix} \) is the change in Gibbs free energy upon mixing \( n_2 \) moles of polymer of volume fraction \( \phi_2 \) in \( n_1 \) moles of solvent (acceptor) of volume fraction \( \phi_1 \) at temperature, \( T \). The relative strength of the chemical interactions between P3HT and ICBA or PC\(_{61}\)BM can be obtained by measuring the decrease in melting point of P3HT in P3HT:ICBA and P3HT:PC\(_{61}\)BM mixtures as a function of acceptor weight fraction [145]. Using differential scanning calorimetry, it is possible to estimate the Flory-Huggins interaction parameter (\( \chi \)) using:
where $T_m$ is the melting point at a solvent (acceptor) volume fraction $\phi_s$, $T_m^0$ is the melting point of pure polymer, $R$ is the ideal gas constant, $\Delta H_f$ is the heat of fusion of polymer, $v_m$ is the monomer molar volume of polymer ($v_{m,P3HT} = 151 \text{ cm}^3/\text{mol}$) and $v_s$ is the solvent molar volume ($v_{s,PC_{61}BM} = 607 \text{ cm}^3/\text{mol}$ and $v_{s,ICBA} = 635 \text{ cm}^3/\text{mol}$) [146]. Equation (6.1) can be rewritten in the form:

$$
\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_f} \frac{v_m}{v_s} (\phi_s - \chi \phi_s^2) 
$$

(6.2)

Thus by plotting $1/T_m - 1/T_m^0$ as a function of $\phi_s$ it is possible to use linear least squares fitting to obtain a fit of the form $y = ax + bx^2$ and hence extract $\chi$ from the ratio of the fitted $b$ and $a$ parameters. Figure 6.6a shows the variation of melting point depression as a function of acceptor weight fraction for both PC$_{61}$BM and ICBA together with their associated fits. From the fits to the data in Figure 6.6a we obtain $\chi$ values for PC$_{61}$BM and ICBA in P3HT of 0.80 ($\chi_{PC_{61}BM}$) and 0.39 ($\chi_{ICBA}$) respectively. The value of $\chi_{PC_{61}BM}$ is in good agreement with that reported previously [146] and the observation that $\chi_{ICBA} < \chi_{PC_{61}BM}$ indicates that ICBA is more miscible than PC$_{61}$BM in the P3HT matrix [147].

In order for the mixed state to be thermodynamically stable, we need the condition that $\frac{\partial^2 \Delta G_{mix}}{\partial \phi^2} > 0$ and thus the value of $\chi$ that defines the boundary between the two phase and homogenous regions can be derived:
\[ \chi_{\text{spinodal}} = \frac{v}{2} \left[ \frac{\rho_1}{M_1 (1 - \phi_2)} + \frac{\rho_2}{M_2 \phi_2} \right] \]  

(6.4)

where \( v \) is the molar volume of the lattice site in the Flory-Huggins model which here is defined as the molar volume of the solvent (acceptor) [145], \( \rho_1 \) is the density of the acceptor (1.5 g cm\(^{-3}\) for both PC$_{61}$BM and ICBA), \( M_1 \) is the molecular weight of the solvent (acceptor), \( \rho_2 \) is the density of the polymer (1.1 g cm\(^{-3}\) for P3HT) and \( M_2 \) is the molecular weight of the polymer.

Figure 6.6b plots \( \chi_{\text{spinodal}} \) as a function of P3HT weight fraction for both PC$_{61}$BM and ICBA and shows that both plots have the same form with the ICBA plot slightly displaced due to its different molecular weight and hence molar volume. Also plotted are horizontal lines corresponding to the values of \( \chi_{\text{PC}_{61}\text{BM}} \) and \( \chi_{\text{ICBA}} \) indicating that whereas PC$_{61}$BM is insoluble in P3HT for \( 0.06 < \phi_2 < 0.32 \) ICBA is miscible for all P3HT weight fractions. The intersection of these horizontal lines with the actual P3HT weight fraction of the 1:1 P3HT:PC$_{61}$BM (\( \phi_2 = 0.42 \)) and 1:1 P3HT:ICBA blends (\( \phi_2 = 0.48 \)) reveals the phase of the mixture (i.e. whether the blend is in the two-phase or homogenous regions). Although both mixtures lie in the homogenous region, the 1:1 P3HT:PC$_{61}$BM blend lies close to the spinodal boundary. This model provides an explanation for the observed phase segregation of PC$_{61}$BM in annealed P3HT:PC$_{61}$BM films since, upon annealing, crystallisation of P3HT occurs [146] reducing the P3HT weight fraction of the bulk material and resulting in the intersection point being displaced into the two phase region. By contrast, ICBA remains miscible in P3HT at all weight fractions and thus is not affected by P3HT crystallisation.

The miscibility of ICBA in P3HT is thought to be the reason that the C:S ratio did not increase at the Al-active layer interface as shown in Figure 6.3c and Figure 6.3d.
after annealing and reveals that the improvement of ICBA devices efficiency is not due to change in vertical composition. The improvement is thought to be from high intermixing between ICBA and P3HT due to the miscibility of ICBA in P3HT which leads to an optimal balance between charge generation and charge transport. This optimal balance results in higher current density and ultimately increases ICBA device performance.
Figure 6.6: (a) Melting point depression of P3HT as a function of ICBA volume fraction (open red circles) and PCBM volume fraction (closed black circles), obtained from DSC experiments. (b) Plot of spinodal c as a function of P3HT weight fraction where the solvent is PCBM (dark black line) and ICBA (faint red line). The shaded area shows the two phase region. The horizontal dashed lines show the value of $\chi$ for PCBM ($\chi = 0.80$, upper black dashes) and ICBA ($\chi = 0.39$, lower red dashes) blended with P3HT derived from the melting point depression data. The vertical dotted lines show the P3HT weight fraction for the 1:1 P3HT:PCBM ($\phi_{P3HT} = 0.42$, left black dots) and 1:1 P3HT:ICBA ($\phi_{P3HT} = 0.48$, right red dots) blends as used in the NP-OPV devices discussed in the text. The arrows indicate the direction of $f_{P3HT}$ change upon crystallisation of P3HT.
6.3.3.2 P3HT:PC$_{61}$BM NPs

Phase segregation of the P3HT:PC$_{61}$BM NP film upon annealing can be seen clearly in Figure 6.7 which in good agreement with the model proposed. Figure 6.7a shows the TEM image of the pre-annealed nanoparticles and confirms that these are discrete nanoparticles with a range of particle sizes. STXM compositional mapping of the P3HT and PC$_{61}$BM components (Figure 6.7b and Figure 6.7c respectively) for the corresponding region demonstrates that the NPs also have core–shell morphology. Examination of different particle sizes indicates that this core–shell morphology is preserved at all length scales down to the resolution of the STXM instrument; again providing compelling evidence that the STXM images accurately represent the active layer morphology of NP-OPV device. Radial compositional averaging [26] of a number of NPs in the STXM maps confirms that the particles have a core–shell structure comprising of a PC$_{61}$BM-rich (∼80% pure) core surrounded by a P3HT-rich (65–70% pure) shell. These observations are consistent with the lower surface energy of P3HT (26.9 mJ m$^{-2}$) [142] compared with PC$_{61}$BM (38.2 mJ m$^{-2}$) [143], which will tend to drive P3HT to the outermost surface of the NP during NP synthesis.
Acceptor Effect on NP-OPV Device Performance

Figure 6.7: (a) TEM image of the pre-annealed P3HT:PC$_{61}$BM NP film. Corresponding STXM maps of: (b) P3HT composition and (c) PCBM composition for the pre-annealed P3HT:PC$_{61}$BM NP film. (d) TEM image of the annealed P3HT:PC$_{61}$BM NP film. Corresponding STXM maps of: (e) P3HT composition and (f) PC$_{61}$BM composition for the annealed P3HT:PC$_{61}$BM NP film. The horizontal line in the composition images is produced by a small (< 5%) beam intensity variation occurring in the P3HT mass plot. A 1 µm scale bar is shown.

Figure 6.7d shows the TEM image of the annealed nanoparticles (140 °C for 4 min) and reveals significant morphological changes. Although some NP material is retained, the majority of the film has undergone gross phase segregation to form larger domains. Figure 6.7e and Figure 6.7f show the P3HT and PC$_{61}$BM STXM compositional maps of the annealed NP film respectively. The composition of the PC$_{61}$BM domains is unchanged (∼80% pure), whilst the purity of the P3HT domains is increased (∼80% pure). Moreover, in these phase segregated domains the discrete nature of the NP structure has been lost. This observation provides an explanation of the XPS depth profile data in Figure 6.3a and Figure 6.3b where more PC$_{61}$BM moves to the Al-active layer interface which results in higher $V_{oc}$ after annealing.
6.3.4 Optimisation of Preparation Conditions for ICBA devices

6.3.4.1 Drying Time

In this experiment we investigate the effect of the nanoparticle film drying temperature on the performance of pre-annealed and annealed 1:1 P3HT:ICBA NP devices. The drying temperature used in this experiment was 150 °C. This drying temperature was chosen based on the optimum pre-thermal annealing in bulk heterojunction devices [138]. We also use the “slow up and slow down” method in drying the active layer to get better performance [148]. “Slow up” means the sample is heated on a hot plate from room temperature to set up temperature and “slow down” means the sample left on a hot plate after the hot plate is turned off until the hot plate reach room temperature. PEDOT:PSS was dried at 140 °C for 20 minutes using this slow up and slow down technique on a hotplate. Before the active layers were dried in a nitrogen environment (in a glovebox), the active layers were firstly dried in air at 110 °C for 3 minutes (slow up and medium cooling down) in order to remove water from the active layer. Medium cooling down means the sample was removed from the hot plate as soon as the setting time was reached. Devices were annealed in nitrogen at 140 °C for 4 minutes (slow up and down). Table 6.2 shows a comparison of device characteristics for 1:1 P3HT:ICBA nanoparticle devices with a Ca/Al cathode for each drying temperature. The thickness of the active layer, Ca and Al were ~100 nm, ~30 nm and ~100 nm respectively. The best and the average characteristics of devices are presented in this table. To see the trend of device characteristics more clearly, devices characteristics were plotted in graphs as shown in Figure 6.8.
Table 6.2: Comparison of characteristics for 1:1 P3HT:ICBA nanoparticle devices for each drying time. The best and the average characteristics are presented from a set of 6 devices.

| Drying Time (minute) | Pre-annealed | | | | | | Annealed | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | \( V_{oc} \) (mV) | \( J_{sc} \) (mA/cm\(^2\)) | FF | PCE (%) | \( V_{oc} \) (mV) | \( J_{sc} \) (mA/cm\(^2\)) | FF | PCE (%) |
| Best | | | | | | | | | | | | | |
| 5 | 716 | -4.37 | 0.36 | 1.04 | 677 | -5.35 | 0.36 | 1.21 |
| 10 | 697 | -4.99 | 0.40 | 1.39 | 780 | -6.34 | 0.42 | 2.07 |
| 15 | 680 | -4.98 | 0.45 | 1.51 | 797 | -6.16 | 0.50 | 2.42 |
| 30 | 653 | -4.60 | 0.44 | 1.23 | 782 | -5.81 | 0.49 | 2.22 |
| Average (± STDEV) | | | | | | | | | | | | | |
| 5 | 708 | -4.08 | 0.34 | 0.99 | 654 | -4.99 | 0.33 | 1.09 |
| 10 | 681 | -4.70 | 0.39 | 1.24 | 767 | -5.87 | 0.40 | 1.80 |
| 15 | 676 | -4.65 | 0.45 | 1.40 | 793 | -5.77 | 0.49 | 2.22 |
| 30 | 646 | -4.12 | 0.43 | 1.15 | 780 | -5.14 | 0.48 | 1.92 |

From Figure 6.8a, we observe that for pre-annealed devices (blue squares), the highest efficiency was achieved at a drying time of 15 minutes. Fill factor, \( FF \), (Figure 6.8d) was also highest at this drying time suggesting that the lowest series resistance, \( R_s \) (for pre-annealed) occurred at drying time of 15 minutes. In Figure 6.9 we can see that the highest slope (for pre-annealed) at \( V_{oc} \) occurred at a drying time of 15 minutes which is in good agreement with the fill factor.
For annealed devices (red circles) the highest efficiency also occurs at a drying time of 15 minutes, after which efficiency declines as drying time is further increased. The observed trend in efficiency is driven primarily by changes in FF (Figure 6.8d), and to a lesser extent, changes in $V_{oc}$ (Figure 6.8c). The highest $V_{oc}$ and FF at a drying time of 15 minutes suggests that this device has the lowest charge carrier losses at the Al electrode, and that the best morphology, the lowest series resistance, $R_s$, and the highest shunt resistance, $R_{sh}$, occurs at this drying time. The lowest $R_s$ and highest $R_{sh}$ are also supported by Figure 6.9 where the highest slope at $V_{oc}$ and the lowest slope at $I_{sc}$ occur.
at a drying time of 15 minutes. Figure 6.8b shows that the highest current density occurs at a drying time of 10 minutes suggesting that the optimal balance between charge generation and charge transport occurred with this drying regime.

![IV curves of 1:1 P3HT:ICBA NP-OPV devices dried for different periods of time.](image)

**Figure 6.9:** IV curves of 1:1 P3HT:ICBA NP-OPV devices dried for different periods of time.

### 6.3.4.2 Annealing Temperature

In this experiment the annealing temperatures used were 140 °C and 150 °C, both for 4 minutes. 140 °C was chosen simply because this is the standard procedure and 150 °C was chosen because we also dry the active layer at this temperature. PEDOT:PSS layer was dried on a hot plate at 140 °C for 20 minutes (slow up and slow down). The active
layers with thickness of ~100 nm were dried firstly in air at 110 °C for 3 minutes (slow up) and then in nitrogen (glovebox) at a temperature of 150 °C for 15 minutes, slow up and slow down, on a hotplate. Ca and Al thickness were ~30 nm and ~100 nm respectively. The devices were annealed on a hotplate for 4 minutes, slow up and slow down. Table 6.3 shows the IV characteristics of 1:1 P3HT:ICBA NP-OPV devices annealed at 140 °C and 150 °C for 4 minutes. The best and the average device characteristics from a set of eight devices are presented in this table. Figure 6.10 shows the characteristic plots of this data.

Table 6.3: IV characteristics of 1:1 P3HT:ICBA nanoparticle devices annealed for 4 minutes at different annealing temperature. The best and the average characteristics are presented from a set of 8 devices.

<table>
<thead>
<tr>
<th>Annealing Temperature (°C)</th>
<th>V_{oc} (mV)</th>
<th>I_{sc} (mA)</th>
<th>J_{sc} (mA/cm²)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Best</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>140</td>
<td>779.8</td>
<td>-0.39</td>
<td>-7.84</td>
<td>0.49</td>
<td>2.86</td>
</tr>
<tr>
<td>150</td>
<td>822.5</td>
<td>-0.37</td>
<td>-7.48</td>
<td>0.50</td>
<td>2.92</td>
</tr>
<tr>
<td><strong>Average (± STDEV)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>140</td>
<td>769.7 ± 5.8</td>
<td>-0.36 ± 0.026</td>
<td>-7.13 ± 0.524</td>
<td>0.47 ± 0.018</td>
<td>2.58 ± 0.199</td>
</tr>
<tr>
<td>150</td>
<td>810.1 ± 6.9</td>
<td>-0.34 ± 0.025</td>
<td>-6.86 ± 0.491</td>
<td>0.48 ± 0.016</td>
<td>2.65 ± 0.214</td>
</tr>
</tbody>
</table>

As we can see in Figure 6.10a, the efficiency of devices annealed at 150 °C were slightly better than devices annealed at 140 °C. Higher V_{oc} and FF make the efficiency of devices annealed at 150 °C slightly better although the current density of devices annealed at 140 °C was slightly higher than devices annealed at 150 °C. Higher V_{oc} and FF suggests that the devices dried at 150 °C have better morphology, lower charge carrier losses at the Al electrode, lower series resistance and higher shunt resistance. Figure 6.10 shows that the higher slope at V_{oc} and lower slope at J_{sc} occur with devices.
annealed at 150 °C, which is in good agreement the observed fill factor. Slightly higher current density at devices annealed at 140 °C suggests that the optimal balance between charge generation and charge transport occurred in this annealing temperature.

Figure 6.10: Characteristics of 1:1 P3HT:ICBA NP devices annealed at different temperatures. (a) Efficiency, (b) current density, (c) open circuit voltage, and (d) fill factor. Error bars represent the STDEV of the devices produced.
6.3.4.3 Annealing Time

In this experiment, we will determine the optimal annealing time for 1:1 P3HT:ICBA NP-OPV devices. PEDOT:PSS layer was dried on a hot plate at 140 °C for 20 minutes (slow up and slow down). The active layer with a thickness of ~100 nm was dried firstly in air at a temperature of 110 °C for 3 minutes (slow up) and then in nitrogen (glovebox) at a temperature of 150 °C for 15 minutes (slow up and slow down). Ca and Al thickness were ~30 nm and ~100 nm respectively. The devices were annealed in nitrogen at a temperature of 150 °C (slow up and slow down). The IV characteristics of ICBA devices produced with different annealing times are displayed in Table 6.4, and plotted in Figure 6.12. 10 devices were made for each annealing time treatment.

Figure 6.11: IV curves of 1:1 P3HT:ICBA NP devices annealed at different annealing temperature.
Table 6.4: IV characteristic of ICBA devices annealed at 150 °C for different times. 10 devices were made for each annealing time treatment.

<table>
<thead>
<tr>
<th>Annealing Time (minutes)</th>
<th>$V_{oc}$ (mV)</th>
<th>$I_{sc}$ (mA)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Best</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>772.5</td>
<td>-0.33</td>
<td>-6.58</td>
<td>0.43</td>
<td>2.12</td>
</tr>
<tr>
<td>1</td>
<td>797.9</td>
<td>-0.39</td>
<td>-7.85</td>
<td>0.47</td>
<td>2.78</td>
</tr>
<tr>
<td>2</td>
<td>800.9</td>
<td>-0.38</td>
<td>-7.65</td>
<td>0.49</td>
<td>2.88</td>
</tr>
<tr>
<td>3</td>
<td>805.2</td>
<td>-0.39</td>
<td>-7.79</td>
<td>0.49</td>
<td>2.98</td>
</tr>
<tr>
<td>4</td>
<td>807.7</td>
<td>-0.37</td>
<td>-7.44</td>
<td>0.48</td>
<td>2.51</td>
</tr>
<tr>
<td>5</td>
<td>815.9</td>
<td>-0.37</td>
<td>-7.31</td>
<td>0.50</td>
<td>2.95</td>
</tr>
<tr>
<td>10</td>
<td>796.7</td>
<td>-0.32</td>
<td>-6.38</td>
<td>0.45</td>
<td>2.18</td>
</tr>
<tr>
<td>15</td>
<td>806.4</td>
<td>-0.31</td>
<td>-6.17</td>
<td>0.44</td>
<td>2.08</td>
</tr>
<tr>
<td><strong>Average</strong> (± STDEV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>753.9</td>
<td>-0.26</td>
<td>-5.22</td>
<td>0.41</td>
<td>1.63</td>
</tr>
<tr>
<td></td>
<td>13.3</td>
<td>0.049</td>
<td>0.981</td>
<td>0.015</td>
<td>0.328</td>
</tr>
<tr>
<td>1</td>
<td>741.8</td>
<td>-0.35</td>
<td>-6.93</td>
<td>0.45</td>
<td>2.31</td>
</tr>
<tr>
<td></td>
<td>59.0</td>
<td>0.028</td>
<td>0.569</td>
<td>0.017</td>
<td>0.247</td>
</tr>
<tr>
<td>2</td>
<td>777.8</td>
<td>-0.35</td>
<td>-6.95</td>
<td>0.44</td>
<td>2.35</td>
</tr>
<tr>
<td></td>
<td>22.7</td>
<td>0.026</td>
<td>0.523</td>
<td>0.041</td>
<td>0.287</td>
</tr>
<tr>
<td>3</td>
<td>786.5</td>
<td>-0.36</td>
<td>-7.10</td>
<td>0.46</td>
<td>2.57</td>
</tr>
<tr>
<td></td>
<td>16.1</td>
<td>0.031</td>
<td>0.615</td>
<td>0.024</td>
<td>0.238</td>
</tr>
<tr>
<td>4</td>
<td>764.6</td>
<td>-0.34</td>
<td>-6.73</td>
<td>0.41</td>
<td>2.11</td>
</tr>
<tr>
<td></td>
<td>47.1</td>
<td>0.023</td>
<td>0.468</td>
<td>0.034</td>
<td>0.203</td>
</tr>
<tr>
<td>5</td>
<td>800.9</td>
<td>-0.33</td>
<td>-6.68</td>
<td>0.46</td>
<td>2.46</td>
</tr>
<tr>
<td></td>
<td>11.5</td>
<td>0.024</td>
<td>0.470</td>
<td>0.033</td>
<td>0.295</td>
</tr>
<tr>
<td>10</td>
<td>783.9</td>
<td>-0.29</td>
<td>-5.89</td>
<td>0.41</td>
<td>1.92</td>
</tr>
<tr>
<td></td>
<td>22.0</td>
<td>0.022</td>
<td>0.444</td>
<td>0.020</td>
<td>0.202</td>
</tr>
<tr>
<td>15</td>
<td>792.9</td>
<td>-0.29</td>
<td>-5.73</td>
<td>0.41</td>
<td>1.85</td>
</tr>
<tr>
<td></td>
<td>22.2</td>
<td>0.019</td>
<td>0.374</td>
<td>0.021</td>
<td>0.179</td>
</tr>
</tbody>
</table>

As can be seen in Figure 6.12a, the power conversion efficiency (PCE) of devices annealed at different times is at a maximum at a time of 3 minutes, and then begins to decline as the times are increased beyond this threshold time. This PCE trend is similar to the trend in current density (Figure 6.12b) and the trend in fill factor (Figure 6.12d) while the $V_{oc}$ (Figure 6.12c) shows no significant change. Therefore, the highest
efficiency at a drying time of 3 minutes shows that the optimal balance between charge generation and charge transport, low series resistance and high shunt resistance occurred at this drying time.

![Graphs showing IV characteristics of ICBA devices with different annealing times.](image)

**Figure 6.12:** IV characteristics of ICBA devices with different annealing times. All of the characteristics are the average values with error bars showing the STDEV devices. (a) Power conversion efficiency, (b) current density, (c) open circuit voltage, and (d) fill factor.

### 6.3.4.4 Ratio

In this experiment, devices containing P3HT:ICBA with ratios by mass of 1:0.5, 1:0.6, 1:0.7, 1:0.8, 1:0.9, 1:1, and 0.8:1 were investigated. PEDOT:PSS layer was dried on a hot plate at 140 °C for 20 minutes (slow up and slow down). The active layers with a
thickness of ~100 nm were first dried in air at a temperature of 110 °C for 3 minutes (slow up) and then dried in nitrogen at a temperature of 150 °C for 15 minutes (slow up and slow down). Ca and Al thicknesses were ~30 nm and ~100 nm, respectively. The devices were then annealed at a temperature of 150 °C for 3 minutes (slow up and slow down). Table 6.5 shows the IV characteristics of P3HT:ICBA devices at different material ratios. In this table, the best and the average characteristics of devices are presented from a set of 10 devices.

Table 6.5: I-V characteristic of P3HT:ICBA nanoparticle devices different mass ratio of P3HT and ICBA.

<table>
<thead>
<tr>
<th>Ratio</th>
<th>$V_{oc}$ (mV)</th>
<th>$I_{sc}$ (mA)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Best</td>
<td>Average (± STDEV)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:0.5</td>
<td>678.3</td>
<td>656.7 ± 17.4</td>
<td>-0.39</td>
<td>-0.33 ± 0.036</td>
<td>-6.66 ± 0.728</td>
</tr>
<tr>
<td>1:0.6</td>
<td>806.9</td>
<td>791.1 ± 10.2</td>
<td>-0.38</td>
<td>-0.35 ± 0.016</td>
<td>-7.59 ± 0.320</td>
</tr>
<tr>
<td>1:0.7</td>
<td>759.3</td>
<td>747.9 ± 8.7</td>
<td>-0.40</td>
<td>-0.37 ± 0.021</td>
<td>-8.07 ± 0.424</td>
</tr>
<tr>
<td>1:0.8</td>
<td>817.9</td>
<td>805.2 ± 7.2</td>
<td>-0.42</td>
<td>-0.38 ± 0.027</td>
<td>-8.38 ± 0.536</td>
</tr>
<tr>
<td>1:0.9</td>
<td>775.8</td>
<td>765.7 ± 6.0</td>
<td>-0.43</td>
<td>-0.38 ± 0.031</td>
<td>-8.50 ± 0.610</td>
</tr>
<tr>
<td>1:1</td>
<td>807.4</td>
<td>793.1 ± 10.7</td>
<td>-0.37</td>
<td>-0.33 ± 0.034</td>
<td>-7.42 ± 0.680</td>
</tr>
<tr>
<td>0.8:1</td>
<td>807.2</td>
<td>799.0 ± 6.1</td>
<td>-0.36</td>
<td>-0.31 ± 0.038</td>
<td>-7.13 ± 0.764</td>
</tr>
</tbody>
</table>
Figure 6.13 shows the IV characteristics of P3HT:ICBA devices plotted in graphs. We can see in Figure 6.13a, that a blend ratio of 1:0.8 shows the highest power conversion efficiency. This efficiency is driven by both $J_{sc}$ (Figure 6.13b) and $V_{oc}$ (Figure 6.13c), suggesting that optimal balance between charge generation and charge transport, and the lowest charge carrier losses at the cathode, occurred at this ratio. Figure 6.13d shows that devices with a blend ratio of 1:1 have the highest fill factor and reveals that these devices have the lowest series resistance and the highest shunt resistance.

![Graphs of IV characteristics](image)

**Figure 6.13**: Characteristics of devices produced from different materials ratio. (a) Efficiency, (b) current density, (c) open circuit voltage, and (d) fill factor. Error bars represent the standard deviation of the devices produced.
6.3.5 PCBM Procedure and ICBA Procedure Comparison

In this experiment, we compare the performance of 1:1 P3HT:PC$_{61}$BM NP-OPV devices, 1:1 P3HT:PC$_{71}$BM NP-OPV devices and 1:0.8 P3HT:ICBA NP-OPV devices produced using the optimal drying and annealing conditions for ICBA. In this study, the optimal drying and annealing conditions for ICBA are called the ICBA procedure. In the ICBA procedure, PEDOT:PSS with thickness of ~60 nm was dried at 140 °C for 20 minutes (slow up and slow down). The active layer with thickness ~100 nm was firstly dried in air at 110 °C for 3 minutes (slow up) and then dried in nitrogen (glovebox) at 150 °C for 15 minutes (slow up and slow down), after which calcium and aluminium with thickness of ~30 nm and ~100 nm respectively were deposited onto the active layer. Devices were then annealed in nitrogen (glovebox) at 150 °C for 3 minutes (slow up and slow down).

The materials ratio used for P3HT:PC$_{61}$BM, P3HT:PC$_{71}$BM and P3HT:ICBA were 1:1, 1:1 and 1:0.8 respectively. Table 6.6 shows the IV characteristics of 1:1 P3HT:PC$_{61}$BM NP-OPV devices, P3HT:PC$_{71}$BM NP-OPV devices and P3HT:ICBA NP-OPV devices produced using the ICBA procedure and Figure 6.14 shows the best device produced using the ICBA procedure. For comparison, Figure 6.15 shows the best characteristic of devices produced using the PCBM procedure.
Table 6.6: IV characteristics of 1:1 P3HT:PC$_{61}$BM NP-OPV devices, 1:1 P3HT:PC$_{71}$BM NP-OPV and 1:0.8 P3HT:ICBA NP-OPV devices produced using ICBA procedure.

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>Pre-annealed</th>
<th>Annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$V_{oc}$ (mV)</td>
<td>$J_{sc}$ (mA/cm$^2$)</td>
</tr>
<tr>
<td>PC$_{61}$BM</td>
<td>408.1</td>
<td>-4.31</td>
</tr>
<tr>
<td>PC$_{71}$BM</td>
<td>408.7</td>
<td>-5.45</td>
</tr>
<tr>
<td>ICBA</td>
<td>772.5</td>
<td>-4.89</td>
</tr>
</tbody>
</table>

**Average (± STDEV)**

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC$_{61}$BM</td>
<td>371.8</td>
<td>-3.99</td>
<td>0.36</td>
<td>0.54</td>
<td>573.2</td>
<td>-4.86</td>
<td>0.44</td>
<td>1.24</td>
</tr>
<tr>
<td></td>
<td>29.6</td>
<td>0.20</td>
<td>0.02</td>
<td>0.09</td>
<td>8.7</td>
<td>0.24</td>
<td>0.01</td>
<td>0.09</td>
</tr>
<tr>
<td>PC$_{71}$BM</td>
<td>372.4</td>
<td>-5.25</td>
<td>0.39</td>
<td>0.76</td>
<td>567.6</td>
<td>-6.91</td>
<td>0.48</td>
<td>1.87</td>
</tr>
<tr>
<td></td>
<td>23.5</td>
<td>0.15</td>
<td>0.02</td>
<td>0.10</td>
<td>6.7</td>
<td>0.24</td>
<td>0.02</td>
<td>0.11</td>
</tr>
<tr>
<td>ICBA</td>
<td>762.2</td>
<td>-4.49</td>
<td>0.40</td>
<td>1.39</td>
<td>805.2</td>
<td>-7.64</td>
<td>0.46</td>
<td>2.85</td>
</tr>
<tr>
<td></td>
<td>8.6</td>
<td>0.327</td>
<td>0.014</td>
<td>0.121</td>
<td>7.2</td>
<td>0.536</td>
<td>0.027</td>
<td>0.306</td>
</tr>
</tbody>
</table>
We can see from Figure 6.14a, that the PCE of all devices increased after annealing. For 1:1 P3HT:PC$_{61}$BM NP-OPV and 1:1 P3HT:PC$_{71}$BM NP-OPV devices, the increase in efficiency was not only because $V_{oc}$ increased but also because $J_{sc}$ and FF increased. This result was different than with devices produced using the PCBM procedure (Figure 6.15), where the increase in efficiency was driven mainly by $V_{oc}$. The increase in $V_{oc}$, $J_{sc}$ and FF reveal that using the ICBA procedure results in reduced
losses of charge carriers at electrode, better charge extraction, lower series resistance and higher shunt resistance. Similar to other devices, the increase in efficiency of 1:0.8 P3HT:ICBA NP-OPV devices was driven by $V_{oc}$, $J_{sc}$, and FF which was different than devices produced using PCBM procedure, where the increased in efficiency was driven mainly by $J_{sc}$ as can be seen in Figure 6.14.

![Graphs showing IV characteristics](image)

**Figure 6.15:** Best IV characteristics of 1:1 P3HT:PC$_{61}$BM NP, 1:1 P3HT:PC$_{71}$BM NP and 1:1 P3HT:ICBA NP devices produced using PCBM procedure. Blue bars represent the pre-annealed devices and red bars represent the annealed devices.
Compared with devices produced using the PCBM procedure, devices produced using the ICBA procedure had better performance. Table 6.7 shows IV characteristics of devices produced using the PCBM procedure and also the ICBA procedure. The data in this table is presented as average values. As we can see in Table 6.7, the PCE of annealed PC₆₁BM devices increased from 0.90 % to 1.24 %, the PCE of annealed PC₇₁BM devices increase from 1.29 % to 1.87 % and the PCE of ICBA devices increase from 1.66 % to 2.85 %. These significant improvements show great promise for NP-OPV devices in the future and show that NP devices fabricated from aqueous dispersions can exhibit performances similar to those of BHJ devices fabricated from organic solvents.

Table 6.7: IV characteristics (in average values) of NP-OPV devices produced using PCBM procedure and ICBA procedure.

<table>
<thead>
<tr>
<th>Device</th>
<th>Pre-annealed</th>
<th>Annealed</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V&lt;sub&gt;oc&lt;/sub&gt; (mV)</td>
<td>J&lt;sub&gt;sc&lt;/sub&gt; (mA/cm²)</td>
<td>FF</td>
<td>PCE (%)</td>
<td>V&lt;sub&gt;oc&lt;/sub&gt; (mV)</td>
<td>J&lt;sub&gt;sc&lt;/sub&gt; (mA/cm²)</td>
<td>FF</td>
<td>PCE (%)</td>
</tr>
<tr>
<td>PC₆₁BM</td>
<td>392.2</td>
<td>-4.03</td>
<td>0.45</td>
<td>0.72</td>
<td>514.2</td>
<td>-4.05</td>
<td>0.43</td>
<td>0.90</td>
</tr>
<tr>
<td>PC₇₁BM</td>
<td>429.7</td>
<td>-5.76</td>
<td>0.47</td>
<td>1.16</td>
<td>527.2</td>
<td>-5.58</td>
<td>0.44</td>
<td>1.29</td>
</tr>
<tr>
<td>ICBA</td>
<td>686.8</td>
<td>-4.60</td>
<td>0.35</td>
<td>1.11</td>
<td>680.1</td>
<td>-6.34</td>
<td>0.38</td>
<td>1.66</td>
</tr>
<tr>
<td>PC₆₁BM</td>
<td>371.8</td>
<td>-3.99</td>
<td>0.36</td>
<td>0.54</td>
<td>573.0</td>
<td>-4.86</td>
<td>0.44</td>
<td>1.24</td>
</tr>
<tr>
<td>PC₇₁BM</td>
<td>372.4</td>
<td>-5.25</td>
<td>0.39</td>
<td>0.76</td>
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<td>-6.91</td>
<td>0.48</td>
<td>1.87</td>
</tr>
<tr>
<td>ICBA</td>
<td>762.2</td>
<td>-4.49</td>
<td>0.41</td>
<td>1.39</td>
<td>805.0</td>
<td>-7.64</td>
<td>0.46</td>
<td>2.85</td>
</tr>
</tbody>
</table>

6.4 Conclusions

Using different acceptors in NP-OPV devices result in significantly different device performance. This study shows that P3HT:PC₇₁BM devices have better performance compared to P3HT:PC₆₁BM devices due to higher current density. Higher current
density and open circuit voltage result in P3HT:ICBA devices having better performance than both P3HT:PC_{61}BM and P3HT:PC_{71}BM devices.

The PCBM procedure increased the performance of P3HT:PC_{61}BM devices and ICBA devices in different ways. In P3HT:PC_{61}BM devices, the increase in efficiency was driven by open circuit voltage which increase after annealing, while in ICBA the increase in efficiency was driven by current density which increased after annealing. Based on XPS depth profile data, there is a difference in the annealing effect on the morphology of P3HT:PC_{61}BM and P3HT:ICBA devices. In P3HT:PC_{61}BM devices, the C:S ratio at the cathode interface increases after annealing and is thought to be the reason for the $V_{oc}$ increase. In P3HT:ICBA devices, the C:S ratio at the interface is almost unchanged before and after annealing, therefore we observe no significant change in $V_{oc}$.

STXM images and TEM images reveal that pre-annealed NP-OPV devices have active layers composed of nanoparticles with core shell morphology. Annealing P3HT:PC_{61}BM NP-OPV devices led to gross phase segregation of the components which is in good agreement with the XPS depth profile result and device data. In contrast, annealing P3HT:ICBA NP-OPV devices increased the miscibility of ICBA in P3HT which was supported by XPS depth profile data. The increased miscibility of ICBA in P3HT results in a redissolution of the ICBA in the core region resulting in a more homogenous blend and consequently increased current density and device performance.

The use of the ICBA procedure to produce NP-OPV devices results in more efficient devices compared with devices produced using the PCBM procedure. The ICBA procedure increased the power conversion efficiency of devices by increasing the
current density, the open circuit voltage and the fill factor. However, compared to the PCBM procedure, the ICBA procedure required longer (annealing and drying) times and a higher temperature to produce efficient NP-OPV devices.
Conclusions & Future Work

7.1 Fabrication Conditions

In order to increase device performance optimisation of appropriate fabrication conditions such as proper thickness, concentration, ratio, annealing, interfacial layer and acceptor material must occur. In this thesis a series of experiments have been conducted in order to find these appropriate fabrication conditions for nanoparticle organic photovoltaic (NP-OPV) devices.

The nanoparticulate system is fundamentally different from the BHJ system. The same “rules” do not apply and all device fabrications must be reoptimised to achieve optimal device performance.

Increasing film thickness increases the light absorption of both P3HT and PC$_{61}$BM according to Beer’s Law. However, the average power conversion efficiency (PCE) of the devices increases only until an active layer thickness of around 100–120 nm. Increasing the film (active layer) thickness beyond of these thicknesses resulted in decreased power conversion efficiency. Increasing the thickness of a device active layer increases the charge transport pathway which may increase recombination in the device, lowering PCE. Therefore the optimal active layer thickness was found to be around 100–120 nm. This optimal active layer thickness is very similar to that obtained for bulk
heterojunction devices suggesting that the nanoparticulate morphology does not affect the optimal thickness and is determined by the materials.

Increasing the concentration of polymer in chloroform during the NP fabrication step increases the thickness of the active layer. This increase in active layer thickness is thought to be due to particle size in the nanoparticle solution increasing systematically with increasing the polymer concentration. The power conversion efficiency (PCE) of devices produced from different concentration of materials in chloroform is at a maximum for a concentration of 54 mg/µl, and then declines as the concentration was increased beyond this threshold concentration. In reality this is most likely a direct effect of the changing particle size (with a size of ~33 nm being optimal). The PCE trend is similar to the trend in current density while the $V_{oc}$ and the fill factor show no significant change. Therefore, the highest efficiency at concentration of 54 mg/µl shows that the balance between charge generation and charge transport is optimal for this concentration and particle size.

The highest power conversion efficiency P3HT:PC$_{61}$BM nanoparticle devices were obtained at a mass ratio of 1:1 while for P3HT:ICBA nanoparticle devices a mass ratio of 1:0.8 was required. The highest power conversion efficiency was driven primarily by the current density of the devices. This optimum current density implies that an optimal balance between charge generation and charge transport occur at a ratio of 1:1 for P3HT:PC$_{61}$BM NP-OPV devices and 1:0.8 for P3HT:ICBA NP-OPV devices.

Annealing the active layer (before cathode deposition) and the devices (after cathode deposition) affects the roughness and both the bulk and surface composition of the active layer produced from nanoparticle solutions. Therefore, the performance of NP-OPV devices critically depends on the annealing treatment. For pre-annealed devices the power conversion efficiency (PCE) increases to a maximum at a drying
temperature of 110 °C (P3HT 22,000 Da) or 130 °C (P3HT 18,000 Da), after which efficiency generally declines as drying temperature is further increased. The highest PCE was achieved at these drying temperatures due to a smooth film surface and reduced SDS on the surface of the active layer. Depositing aluminium onto a smooth surface of the active layer results good contact between aluminium and active layer due to the reduced porosity of the Al-active layer interface. As a result, there is better transport for the free charges into the cathode (aluminium) resulting in increased device performance. On the other hand, depositing aluminium onto a rough active layer surface results in poor contact, although the rough surface has a larger area. The poor contact is thought to be due to more porosity at Al-active layer interface. However, annealing the device improves the contact significantly and results in enhanced charge transport to the aluminium electrode.

The presence of SDS on the active layer surface and trapped water in the active layer appear to be detrimental to device performance especially after devices are annealed. After annealing, SDS can create an insulating layer while trapped water reacts at the Al-active layer interface to form aluminium oxide. The presence of SDS on the surface and trapped water in the active layer can be reduced by increasing the drying temperature and drying time. However, increasing the drying temperature and drying time beyond the optimal increases phase segregation and is detrimental to device performance. For annealed devices, the highest power conversion efficiency (PCE) was achieved at a drying temperature of 140 °C for 4 minutes as drying the active layer at this drying temperature and drying time resulted in a roughened interface and controlled phase segregation.

Introducing LiF or Ca at the Al-active layer interface increases the performance of P3HT:PC_{61}BM NP-OPV devices, particularly after annealing. The increased
performance is mainly due to the $V_{oc}$ of devices increasing when using LiF and Ca as an interface layer. Based on XPS depth profile data, inserting an interface layer drives PC$_{61}$BM concentration at the cathode interface which is thought to be the reason for the open circuit voltage $V_{oc}$ increase and ultimately increases NP-OPV device performance.

The presence of an interface layer at Al-active layer interface reduces the formation of aluminium oxide at the interface which results in better transport of the free charges and enhanced ability to hop into the pure aluminium. The reduction of Al$_2$O$_3$ can be seen from XPS depth profile data. In devices using aluminium only, Al$_2$O$_3$ increases significantly after annealing, increasing series resistance and resulting in devices of low performance.

Increasing the thickness of an interface layer does not increase the power conversion efficiency of NP-OPV device continuously. There is an optimum thickness of the interfacial layers. For the LiF interface layer, the optimum thickness is 1.5 nm and for the Ca interface layer, the optimum thickness is 30 nm. Increasing the interface layer thickness beyond of the optimum thickness will result in lower device performances. Increasing LiF thickness beyond of 1.5 nm made the performance of the annealed devices drop due to LiF acting as an insulator layer at greater thicknesses. Increasing Ca beyond 30 nm increases the CaO layer thickness and consequently increases the series resistance of devices since CaO has low conductivity. Furthermore, with thicker Ca it is possible Ca metal remains and alters the work function of the cathode reducing charge injection. Higher series resistance and reducing charge injection, lowering device performance result.

The performance of devices is also depends on the acceptor material. Higher solubility, stronger absorption, higher miscibility and higher LUMO energy of acceptor material result in higher device performance. This study shows that P3HT:PC$_{71}$BM
devices have better performance compared to P3HT:PC\textsubscript{61}BM devices due to PC\textsubscript{71}BM have stronger absorption at visible wavelengths which leads to higher current density. Higher miscibility, higher LUMO energy (which results in higher $V_{oc}$) and higher solubility of ICBA result in P3HT:ICBA devices having better performance than both P3HT:PC\textsubscript{61}BM and P3HT:PC\textsubscript{71}BM devices.

We developed two procedures to produce NP-OPV devices. The first procedure has been called the PCBM procedure and the second procedure is called the ICBA procedure. The PCBM procedure increased the performance of P3HT:PC\textsubscript{61}BM devices and ICBA devices in different ways. In P3HT:PC\textsubscript{61}BM devices, the increase in efficiency was driven by open circuit voltage which increased after annealing, while in ICBA the increase in efficiency was driven by current density which increased after annealing.

The use of the ICBA procedure to produce NP-OPV devices results in more efficient devices compared with devices produced using the PCBM procedure. The ICBA procedure increased the power conversion efficiency of devices by increasing the current density, the open circuit voltage and the fill factor. The highest power conversion efficiency (PCE) of 1:1 P3HT:PC\textsubscript{61}BM NP-OPV, 1:1 P3HT:PC\textsubscript{71}BM NP-OPV and 1:0.8 P3HT:ICBA NP-OPV devices were 1.36 %, 2.00 % and 3.29 % respectively. Compared to previous work (~0.4 %) by our group, for the same system (P3HT:PC\textsubscript{61}BM NP-OPV devices) the efficiency has increased more than 3 fold and compared to P3HT:ICBA NP-OPV devices, the efficiency has increased more than 8 fold. These significant improvements show great promise for NP-OPV devices in the future and show that NP devices fabricated from aqueous dispersions can exhibit performances similar to those of BHJ devices fabricated from organic solvents. It will
be interesting to apply the ICBA procedure for other more efficient polymer systems since this system produces high open circuit voltage devices.

### 7.2 Morphology

Investigation of the morphology of the active layer of NP-OPV devices have been achieved using STXM, TEM, and XPS depth profile systems. STXM and TEM images reveal that pre-annealed NP-OPV devices have an active layer composed of nanoparticles with core shell morphology with donor-rich shell and acceptor-rich core domains. Annealing P3HT:PC$_{61}$BM NP-OPV devices lead to gross phase segregation of the components which was in good agreement with the XPS depth profile results that show there is PC$_{61}$BM movement from anode to cathode after annealing. This movement is thought to be the reason for the $V_{oc}$ increase. In contrast, annealing P3HT:ICBA NP-OPV devices increased the miscibility of ICBA in P3HT which was again supported by XPS depth profile data that showing there is no significant movement of ICBA from anode to cathode after annealing. Therefore we observe no significant change in $V_{oc}$. The increased miscibility of ICBA in P3HT results in a redissolution of the ICBA in the core region resulting in a more homogenous blend and consequently increased current density and device performance.

Using the ICBA procedure resulting in increased ICBA device performance due to not only an increase in current density but also open circuit voltage and the fill factor increased. It will be interesting to investigate the morphology of devices prepared using the ICBA procedure using STXM, TEM, and XPS depth profiling system since the ICBA procedure uses higher temperature and longer annealing times compared to the PCBM procedure and results in significantly different performance.
7.3 Conducting Polymer NPs

Conducting polymer NPs are now showing significant promise as a material for solar cell manufacture. All material systems tested have resulted in device performances which, while less than that of the corresponding BHJ device, approach the PCE of BHJ devices. However, the advantages of water processibility coupled with the morphological control which an NP approach allows mean that NP-OPVs are well placed to play a role in large scale energy production in the future. Efforts to use these materials in large scale reel to reel printing of NP-OPV modules are already underway. The results presented in this thesis will act as an excellent starting point for these endeavours.


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