Morphology and performance of nanoparticle organic photovoltaics

by

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A THESIS SUBMITTED TO THE UNIVERSITY OF NEWCASTLE FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY

June 2015
Declaration

The thesis contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. I give consent to the final version of my thesis being made available worldwide when deposited in the University’s Digital Repository**, subject to the provisions of the Copyright Act 1968.

**Unless an Embargo has been approved for a determined period.

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

__________________________
Natalie P. Holmes
Acknowledgements

I would like to first thank my supervisors, Dr Warwick Belcher, Professor Paul Dastoor and Dr Xiaojing Zhou, for their guidance, as well as the additional opportunities they gave me during my PhD which have only strengthened my research experience. I especially want to thank them for the support and positive feedback they gave me in the last 7 months in particular which really made the difference to my experience, and getting finished.

Thank you to the Australian Renewable Energy Agency (ARENA) for providing me with a PhD top-up scholarship, this support meant that I could focus on my work without the worries of financial hardship which I know to be a common setback for research students.

Thank you to Ms Melissa Marks, Dr Pankaj Kumar, Dr Renee Kroon and Mr Nicolas Nicolaidis for their collaborative work in the TQ1:PC$_7$BM NP OPV study in Chapter 6, and to Dr Prakash Sista and Associate Professor Mihaela Stefan for synthesising the various P3HT batches used throughout Chapters 3 – 5.

Thank you to all of the other members of the Centre for Organic Electronics that I haven’t mentioned yet, you made the group such a helpful learning environment to complete my PhD. A big thank you to the members of our writing circle – ‘Write-ho, chaps!’ – often sitting down to write was difficult but having such a positive environment with plenty of tea, coffee, snacks and humour made it that little bit easier.

I’d like to thank my mum and dad for always reminding me that they were there if I needed them, a caring and loving support network is crucial to getting through a PhD.

Matt, so many helpful discussions, be they scientific or philosophical. In addition to that the mental and emotional support you gave me through this challenging time in both of our lives. I think the biggest thank you is reserved for you.
Publications arising from this thesis

A. Publications included in this thesis


B. Publications not included in this thesis


# List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>ALS</td>
<td>Advanced Light Source, Berkeley</td>
</tr>
<tr>
<td>AM1.5</td>
<td>Air mass 1.5</td>
</tr>
<tr>
<td>B</td>
<td>Blended</td>
</tr>
<tr>
<td>BHJ</td>
<td>Bulk heterojunction</td>
</tr>
<tr>
<td>BSE</td>
<td>Back scattered electron</td>
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<tr>
<td>BT</td>
<td>Benzothiadiazole</td>
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<tr>
<td>CMC</td>
<td>Critical micelle concentration</td>
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<tr>
<td>CN</td>
<td>1-chloronaphthalene</td>
</tr>
<tr>
<td>CS</td>
<td>Core-shell</td>
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<tr>
<td>CT</td>
<td>Charge transfer</td>
</tr>
<tr>
<td>D-A</td>
<td>Donor-acceptor</td>
</tr>
<tr>
<td>DIO</td>
<td>Diiodo octane</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic light scattering</td>
</tr>
<tr>
<td>DpN</td>
<td>Degree of polymerisation</td>
</tr>
<tr>
<td>DPP</td>
<td>Diketopyrrolopyrrole</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>E&lt;sub&gt;g&lt;/sub&gt;</td>
<td>Band gap</td>
</tr>
<tr>
<td>EQE</td>
<td>External quantum efficiency</td>
</tr>
<tr>
<td>F8BT</td>
<td>poly(9,9-di octylfluorene-co-benzothiadiazol)</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused ion beam</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field emission scanning electron microscopy</td>
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<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
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<tr>
<td>GHG</td>
<td>Greenhouse gas</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
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<tr>
<td>--------------</td>
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<tr>
<td>GPC</td>
<td>Gel permeation chromatography</td>
</tr>
<tr>
<td>GPS</td>
<td>Gross phase segregation</td>
</tr>
<tr>
<td>GRIM</td>
<td>Grignard metathesis</td>
</tr>
<tr>
<td>$^1$H NMR</td>
<td>Proton nuclear magnetic resonance spectroscopy</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>ICBA</td>
<td>Indene-$C_{60}$ bisadduct</td>
</tr>
<tr>
<td>IPCC</td>
<td>Intergovernmental Panel on Climate Change</td>
</tr>
<tr>
<td>IQE</td>
<td>Internal quantum efficiency</td>
</tr>
<tr>
<td>$I_{SC}$</td>
<td>Short circuit current</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>I-V</td>
<td>Current-voltage</td>
</tr>
<tr>
<td>JS</td>
<td>Joined shell</td>
</tr>
<tr>
<td>$J_{SC}$</td>
<td>Short circuit current density</td>
</tr>
<tr>
<td>J-V</td>
<td>Current density-voltage</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>MALDI-ToF</td>
<td>Matrix-assisted laser desorption/ionisation time-of-flight mass spectrometry</td>
</tr>
<tr>
<td>MEH-PPV</td>
<td>poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]</td>
</tr>
<tr>
<td>$M_n$</td>
<td>Number average molecular weight</td>
</tr>
<tr>
<td>$M_w$</td>
<td>Weight average molecular weight</td>
</tr>
<tr>
<td>NEXAFS</td>
<td>Near edge X-ray absorption fine structure</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticle</td>
</tr>
<tr>
<td>O-DCB</td>
<td>Orthodichlorobenzene</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic light emitting diode</td>
</tr>
<tr>
<td>OPS</td>
<td>Onset phase segregation</td>
</tr>
<tr>
<td>OPV</td>
<td>Organic photovoltaic</td>
</tr>
<tr>
<td>P3HT</td>
<td>Poly(3-hexylthiophene)</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</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(styrene) sulfonate</td>
</tr>
<tr>
<td>PFB</td>
<td>Poly(9,9-dioctylfluorene-co-N,N-bis(4-butylphenyl)-N,Ndiphenyl-1,4-phenylenediamine)</td>
</tr>
<tr>
<td>PDI</td>
<td>Polydispersity index</td>
</tr>
<tr>
<td>$P_{in}$</td>
<td>Incident light intensity</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>PS</td>
<td>Poly(styrene)</td>
</tr>
<tr>
<td>PSF</td>
<td>Point spread function</td>
</tr>
<tr>
<td>RR</td>
<td>Regioregularity</td>
</tr>
<tr>
<td>rr-P3HT</td>
<td>Regioregular-poly(3-hexylthiophene)</td>
</tr>
<tr>
<td>$R_s$</td>
<td>Series resistance</td>
</tr>
<tr>
<td>$R_{sh}$</td>
<td>Shunt resistance</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium dodecyl sulphate</td>
</tr>
<tr>
<td>SEC</td>
<td>Size exclusion chromatography</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>STXM</td>
<td>Scanning transmission X-ray microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>$T_{g_r}$</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TQ1</td>
<td>Poly[2,3-bis-(3-octyloxyphenyl)quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl]</td>
</tr>
<tr>
<td>UV-vis</td>
<td>UV-visible spectroscopy</td>
</tr>
<tr>
<td>$V_{OC}$</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
Contents

Declaration ........................................................................................................................... iii

Acknowledgements ........................................................................................................... v

Publications arising from this thesis ................................................................. vii

List of abbreviations ..................................................................................................... ix

Contents ........................................................................................................................ xiii

Abstract ........................................................................................................................ xvii

List of figures .................................................................................................................. xx

List of tables .................................................................................................................... xxxii

Introduction ..................................................................................................................... 1

1.1 Background ........................................................................................................... 1

1.1.1 Population, climate change and renewable energy .................................. 1

1.1.2 Organic photovoltaics (OPVs) ................................................................. 2

1.2 Principles of OPV operation ........................................................................... 3

1.2.1 Photoconversion mechanism ................................................................ 5

1.3 Materials ............................................................................................................. 9

1.3.1 Semiconducting polymer donor materials ........................................ 9

1.3.1.1 Polymer material properties ..................................................... 10

1.3.1.2 Polymer morphology ................................................................ 15

1.3.2 Fullerene acceptor materials ............................................................... 18

1.4 Key avenues for improving OPV performance ...................................... 19

1.4.1 The structure of the donor polymer .................................................. 19

1.4.2 Photoactive layer morphology ......................................................... 24

1.4.2.1 Annealing, phase separation and other morphological changes 28

1.4.2.2 Miscibility and its influence on morphology .......................... 29

1.4.2.3 Effect of polymer material properties on film morphology .. 31

1.4.2.4 Utilising solvents and solvent additives to alter morphology 33

1.4.3 Ratio of donor to acceptor material ............................................... 34

1.5 Nanoparticles ................................................................................................. 35

1.5.1 Preparation of nanoparticles .............................................................. 35

1.5.1.1 Miniemulsification via ultrasonication ................................ 36

1.5.1.2 Background on miniemulsions, surfactants and micelles .... 37

1.5.1.3 Precipitation method .............................................................. 38
1.5.2 Morphology of nanoparticles and nanoparticle films .......... 40
1.6 Nanoparticulate organic electronics ........................................ 41
   1.6.1 Nanoparticles: A ‘solution’ to solubility issues .......... 41
   1.6.2 Early work on colloidal dispersions of conjugated polymers .. 41
   1.6.3 Recent developments in nanoparticulate OPVs ................. 42
1.7 Motivation and outline of thesis ........................................... 45

Experimental ................................................................................. 46
2.1 Materials .................................................................................. 46
   2.1.1 Donor polymers ................................................................. 47
   2.1.2 Characterisation of polymer material properties ............... 49
      2.1.2.1 Gel permeation chromatography (GPC) ....................... 49
      2.1.2.2 Proton nuclear magnetic resonance spectroscopy (^1H NMR) ..... 53
   2.1.2.3 Differential scanning calorimetry (DSC) ......................... 56
2.2 Nanoparticle fabrication .......................................................... 57
2.3 Nanoparticle characterisation and morphology ......................... 60
   2.3.1 Transmission electron microscopy (TEM) ......................... 60
   2.3.2 Scanning electron microscopy (SEM) ................................. 61
   2.3.3 Near-edge X-Ray absorption fine structure (NEXAFS) .......... 67
   2.3.4 Scanning transmission X-ray microscopy (STXM) .............. 68
   2.3.5 Photoluminescence (PL) ................................................... 74
   2.3.6 Dynamic light scattering (DLS) .......................................... 76
2.4 OPV device fabrication ............................................................ 76
   2.4.1 Device architecture, preparation of ITO substrates .......... 76
   2.4.2 Film formation (spin coating) and film thickness ............. 77
   2.4.3 Cathode deposition .......................................................... 79
   2.4.4 BHJ OPV device fabrication for comparative purposes ...... 80
2.5 OPV device characterisation .................................................... 81
   2.5.1 I-V characterisation ......................................................... 81
   2.5.2 Spectral response (external quantum efficiency) ............ 82

The effect of polymer material properties on nanoparticle and
nanoparticle film morphology ....................................................... 84
3.1 Overview .................................................................................. 84
3.2 Introduction ............................................................................... 85
   3.3 Experimental .......................................................................... 87
      3.3.1 P3HT synthesis and characterisation .............................. 87
      3.3.2 Nanoparticle fabrication ................................................. 87
      3.3.3 Microscopy ..................................................................... 88
3.4 Results and discussion ............................................................... 89
   3.4.1 Nanoparticle fabrication .................................................. 89
   3.4.2 STXM morphological characterisation ............................ 90
   3.4.3 Compositional analysis .................................................... 96
   3.4.4 SEM morphological characterisation ............................... 102
3.3.5 Annealing duration study ........................................................... 105
3.4.6 A simple model for the evolution of morphology ..................... 109
3.5 Conclusions ...................................................................................... 111

The effect of polymer molecular weight on NP OPV device performance
.................................................................................................................... 112
4.1 Overview .......................................................................................... 112
4.2 Introduction ...................................................................................... 113
4.3 Experimental .................................................................................... 114
  4.3.1 Materials .................................................................................... 114
  4.3.2 Nanoparticle fabrication ............................................................ 114
  4.3.3 Nanoparticle characterisation .................................................... 115
  4.3.4 Device fabrication (Nanoparticulate and BHJ) ......................... 115
4.4 Results and discussion ...................................................................... 116
  4.4.1 Nanoparticle fabrication ............................................................ 116
  4.4.2 NP and BHJ OPV device performance ...................................... 117
  4.4.3 Spectroscopy study ................................................................. 123
  4.4.4 Morphological study ............................................................... 128
  4.4.5 Explanation of device performance trends ......................... 133
4.5 Conclusions ...................................................................................... 134

Functionality of a core-shell nanoparticle active layer morphology ... 135
5. 1 Overview ......................................................................................... 135
5.2 Introduction ...................................................................................... 136
5.3 Experimental .................................................................................... 138
  5.3.1 Materials .................................................................................... 138
  5.3.2 Nanoparticle fabrication ............................................................ 138
  5.3.3 Nanoparticle characterisation .................................................... 138
  5.3.4 Nanoparticle OPV device fabrication ........................................ 139
5.4 Results and discussion ...................................................................... 139
  5.4.1 Nanoparticle OPV devices ......................................................... 139
  5.4.2 Morphological investigation ...................................................... 146
  5.4.3 Photoconversion processes in a core-shell NP photoactive layer ......................................................................................... 154
  5.4.4 STXM compositional analysis ................................................... 157
  5.4.5 Explanation for NP OPV device performance trend with varied D-
                A ratio ................................................................................................. 161
5.5 Conclusion ........................................................................................ 165

TQ1:PC71BM nanoparticles, a new material system ......................... 166
6. 1 Overview .......................................................................................... 166
6.2 Introduction ...................................................................................... 167
6.3 Experimental .................................................................................... 170
  6.3.1 Materials .................................................................................... 170
  6.3.2 Polymer characterisation .......................................................... 170
  6.3.3 Nanoparticle fabrication ............................................................ 171
  6.3.4 Nanoparticle characterisation .................................................... 172
Abstract

Nanoparticle organic thin films are an emerging area of organoelectronic research which offer the prospect of printing large area solar cells from water-based inks, as well as the ability to control the semi-conducting polymer morphology on the nanoscale. However, to date there has been little research into the composition and morphology of the photoactive layers in these devices. To realise the potential for nanoscale control of these films we must first develop an understanding of the factors which affect morphology in these devices. This thesis works on unravelling the material-morphology-performance relationships in NP OPV systems.

This thesis first explores the intra- and inter-particle morphology of P3HT:PC61BM nanoparticles prepared from a range of P3HT molecular weights (5 to 72 kg mol\(^{-1}\) M\(_w\)), and reports a common core-shell structure. When thermal annealing treatments were applied to these nanoparticles and nanoparticle films, we found that the morphological changes which occurred were highly dependent upon the polymer molecular weight, from subtle changes at high P3HT molecular weight to more pronounced changes at low P3HT molecular weight. Diffusion of PC61BM in the polymer matrix was found to govern the morphological evolution of annealed NP films, with both molecular PC61BM diffusion as well as diffusion of PC61BM NP core units observed, the latter only occurring after sufficient thermal energy had been supplied to the system.

The lessons learnt from the molecular weight–morphology investigation were then applied to the fabrication of P3HT:PC61BM nanoparticulate OPV devices, for the various molecular weight batches of P3HT. Power conversion efficiencies (PCEs) were observed to peak for the mid-range of
molecular weights tested, this behaviour differed from the trend generally observed for bulk heterojunction (BHJ) devices, where high molecular weight polymers deliver the highest PCEs. A balance of competing phenomena account for the optimal NP OPV device performance with mid-range molecular weight P3HT.

The functionality of a core-shell nanoparticle photoactive layer morphology was then investigated in detail, made possible by varying the ratio of donor-to-acceptor material in the nanoparticles and probing the origin of photocurrent. The new morphological variety that nanoparticles present further increases the complexity of the exciton dissociation, exciton separation and charge transport processes. Due to the core-shell domain structure in the OPV photoactive layer, charge separation at core-shell material interfaces and transport through percolation pathways in the joined shell network become increasingly more complicated processes. It was shown that when PC<sub>61</sub>BM loading exceeded a 1:1 donor-acceptor ratio, the PCE was maintained, which is opposite to that reported in similar BHJ OPV studies. This difference was due to both an increase in functional PC<sub>61</sub>BM volume and an improvement to charge percolation pathways through the joined shell network for charge extraction.

Finally, the application of the low band gap polymer TQ1 to nanoparticle OPVs was investigated. This polymer proved to be more applicable to nanoparticle OPV fabrication than P3HT due to its more desirable material properties; namely a high glass transition temperature (T<sub>g</sub>) and non-crystalline nature. TQ1:PC<sub>71</sub>BM NP OPV device performance was optimised by the application of mild thermal annealing treatments in the range of the T<sub>g</sub> (sub-T<sub>g</sub> and post-T<sub>g</sub>), both in the photoactive layer drying stages and post-cathode deposition annealing stages of device fabrication. In addition, the morphological changes caused by thermal treatments were investigated. We observed a type of morphological evolution in nanoparticle
films for OPV photoactive layers that has not previously been reported: that of PC_{71}BM nano-pathway formation between dispersed PC_{71}BM-rich nanoparticle cores. These have the benefit of making the bulk film more conducive to charge percolation and extraction.
List of figures

Figure 1.1 OPV device architecture ................................................................. 3

Figure 1.2 Simplified diagram of the electronic band structure of metals, semiconductors and insulators .......................................................... 4

Figure 1.3 Energy level diagram showing the transport of electrons (e-) and holes (h+) at an electron donor/electron acceptor material heterojunction in an OPV device active layer. Once the exciton splits into electron and hole, the electron moves to the LUMO/conduction band (CB) of the acceptor material and then to the cathode (PC); the hole moves to the anode (PAn). The HOMO/valence band (VB) of the acceptor material is lower in energy than that of the donor material. The band gap (E_g) is the energy difference between the HOMO and LUMO, with the electron affinity (x) constituting the difference between the band gap and the ionisation potential (IP). Reproduced from Ref. [10], with permission from Elsevier ............................................. 5

Figure 1.4 Schematic depicting the cross-sectional structure of a bulk heterojunction (BHJ) OPV device. (a) Light is absorbed generating an exciton, (b) diffusion of the exciton to an interface of the donor (blue) and acceptor (yellow) material, (c) dissociation of the exciton, (d) free carrier charge transport to the cathode and anode, (e) charge collection at the cathode and anode. Reproduced from Ref. [12], with permission from Annual Reviews .............................................................. 6

Figure 1.5 Coupling regiochemistry of P3HT isomers. Reproduced (in part) from Ref. [30], with permission of The Royal Society of Chemistry ................................................................. 14

Figure 1.6 Chemical structure and arrangement of regioregular P3HT. Reproduced (in part) from Ref. [31], with permission from Elsevier .......... 14

Figure 1.7 Schematic representing various polymer (and oligomer) microstructures. (a) Perfect folded chain crystal; (b) extended-chain crystal structure characteristic of oligomers; (c) semi-crystalline microstructure adopted by many high molecular weight polymers, composed of lamellar aggregates embedded in an amorphous matrix and characterised by extensive chain entanglement and folding. Reproduced from Ref. [34], with permission from The American Chemical Society ................................................................. 16

Figure 1.8 Schematic depicting the reversible formation of P3HT nanofibre. Reproduced from Ref. [35], with permission from Beilstein Journals ................................................................. 17
Figure 1.9 Conceptual diagram showing the options of down-shifting the HOMO level of the donor material (A) or up-shifting the LUMO level of the acceptor material (B) to increase $V_{OC}$. .............................................. 21

Figure 1.10 Active layer device architectures. (a) The first heterojunction device structure, the bilayer, the disadvantage of this architecture being the thin active layer required such that all excitons are utilised. (b) The bulk heterojunction architecture, this enables the active layer to be thicker and the possibility of the heterojunction existing within an exciton diffusion length. (c) An ordered or interdigitated structure, where the heterojunction is also within an exciton diffusion length. Reproduced from Ref. [178], with permission from Elsevier. ............................................................................ 25

Figure 1.11 Schematic detailing the three different length scales at which morphological heterogeneities within the active layers of organic electronic devices commonly impact device performance. Reproduced from Ref. [12], with permission from Annual Reviews. ......... 27

Figure 1.12 Schematic depicting morphological changes within a PBDTTTPD:PC$_{61}$BM BHJ active layer upon thermal annealing. Specific to this illustration, an increase in purity of the polymer domains (red), an increase in size of the fullerene domains (black), and an increase in crystallinity and ordering of the fullerene domains. Note that the morphology of the thermally annealed film now constitutes a combination of three phases: (a) finely mixed polymer/fullerene domains ideal for exciton dissociation, (b) pure fullerene domains ideal for electron transport, and (c) pure polymer domains ideal for hole transport. Image in the style of Bartelt et al. [65]. .............................................................................................................. 29

Figure 1.13 Schematic depicting (a) P3HT crystallisation-induced PC$_{61}$BM segregation into (b) the amorphous intraspherulitic layers. (c) The amorphous intraspherulitic domains (~ 10 nm wide) swell at sufficiently high PC$_{61}$BM content. (d) Swelling of the amorphous domains saturates and concurrently PC$_{61}$BM segregates out and forms aggregates. Reproduced from Ref. [66], with permission from The American Chemical Society. ................................................................. 30

Figure 1.14 Swollen micelle or miniemulsion droplet. Reproduced (adapted) from Ref. [91]. ............................................................................. 38

Figure 1.15 Schematic of the formation of polymer:fullerene nanoparticles via the precipitation method. (a) A solution of the polymer (purple lines) and fullerene (black circles) in, for example, chloroform; (b) micro-droplets of the polymer:fullerene solution are added to a non-solvent for the semiconducting materials which is at the same time miscible with chloroform, for example ethanol; (c) the polymer precipitates forming a matrix type structure (with the fullerene interspersed) at the same time the chloroform diffuses out of
the polymer matrix into the ethanol; (d) once all of the chloroform has
diffused out a solid nanoparticle is formed................................................. 39

Figure 2.1 Schematic depicting the method of varying monomer
(green circles) to initiator (blue stars) ratio in order to achieve
different molecular weight polymer chains. .............................................. 48

Figure 2.2 Schematic representation of the dissolution process for
polymer molecules. (a) Polymer molecules in the solid state just after
being added to a solvent, (b) first step: a swollen gel in solvent, (c)
second step: solvated polymer molecules dispersed in a solution.
Image in the style of Ref. [107]. ................................................................. 49

Figure 2.3 (a) GPC column depicting elution of polymer molecules
(black) according to their hydrodynamic radius, (b) magnified cross-
sectional view of the porous GPC column beads (white) showing
selective retention of the polymer spheres with a smaller
hydrodynamic radius over those with a larger hydrodynamic radius
due to their ability to fit in the pores of the column beads, (c)
molecular weight distribution vs elution time from the GPC column.
Reproduced (in part) from Ref. [108]. .......................................................... 50

Figure 2.4 A comparison of poly(styrene) separation with (A) THF,
(B) chloroform and (C) dimethylformamide (DMF) eluent on a GPC
column. 1. PS molecular weight ~ 1,000,000; 2. PS molecular weight
~ 200,000; 3. PS molecular weight ~ 40,000; 4. PS molecular weight ~
3,000; 5. PS molecular weight ~ 500. It is evident here that PS is most
soluble in chloroform, flowed by THF then DMF, as indicated by the
height of the largest molecular weight peak (peak 1). Also, if the
solubility is highest in chloroform, the size of the solvated polymer
coils will be largest in chloroform, followed by THF then DMF. This
is reflected in the GPC elution time, where the first two peaks (the
highest molecular weight polymers) are eluted at shorter retention
times for chloroform, followed by THF and then DMF. Reproduced
from Ref. [110].............................................................................................. 52

Figure 2.5 1H NMR (500 MHz) spectra of (a) rr-P3HT H/Br
terminated; (b) expansion of rr-P3HT H/H terminated; and (c)
expansion of rr-P3HT. In addition, the scheme depicts the magnesium
halogen exchange of H/Br terminated rr-P3HT, and the table lists
integration values from the 1H NMR spectrum of rr-P3HT (or rather
PHT) H/Br and H/H terminated. Reproduced (adapted) from Ref.
[116], with permission from The American Chemical Society. ............... 55

Figure 2.6 Schematic differential scanning calorimetry (DSC) plot
showing the transitions of $T_g$ (glass transition temperature), $T_c$
(crystallisation temperature) and $T_m$ (melting temperature).
Reproduced from Ref. [117]. ....................................................................... 56
Figure 2.7 Schematic illustrating the method of sonification using an ultrasound horn to form a miniemulsion from an immiscible organic phase (purple) and aqueous phase (blue). ................................................................. 58

Figure 2.8 Schematic of nanoparticle fabrication via the miniemulsion method. Note black circles denote fullerene molecules, black lines denote polymer molecules, and white circles with an attached line denote surfactant molecules. ........................................................................ 59

Figure 2.9 SEM of 1:3 TQ1:PC71BM disperse NPs (at 2 kV and 50,000 x magnification) measured with the SE detector. Scale bar is 1 μm. This micrograph illustrates the 3D shape detail available with the use of the SE detector (compared to in-lens detector images – Figures 2.10 to 2.12). .................................................................................................. 63

Figure 2.10 SEM of high Mw P3HT:PC61BM 1:1 NPs (at 2 kV and 150,000 X magnification) measured with the in-lens detector, with visible surface roughness to the NPs, almost a wrinkled texture. Scale bar is 200 nm. ............................................................................................... 64

Figure 2.11 SEM of P3HT:PC61BM 1:1 NPs (at 3 kV and 400,000 x magnification) measured with the in-lens detector. This micrograph nicely illustrates the resolution limit of the SEM instrument when imaging organic materials. It also provides detail of the inter-particle regions showing what is likely to be the accumulation of free surfactant. Scale bar is 100 nm. ............................................................................... 65

Figure 2.12 SEM depicting the damage that can occur to nanoparticle films during SEM imaging, (a) to (b). In image (b) there are more holes, plus existing holes have grown in size, regions have been highlighted with circles. Images were taken at an accelerating voltage of 2 kV, 117,000 x magnification, and with use of the in-lens detector. Scale bars are 200 nm. ................................................................................. 66

Figure 2.13 Schematic depicting method of floating off polymer/fullerene pristine films. Note the sacrificial layer is a PEDOT:PSS film. Image in the style of He et al. [122]. ...................... 67

Figure 2.14 Section of (a) P3HT film and (b) PC61BM film floated off onto a 300 mesh copper grid (20 μm bar, 63 μm hole, 3 mm diameter) for NEXAFS measurements......................................................... 68

Figure 2.15 STXM fractional composition maps showing the concentration of (A) PFB and (B) F8BT for 1:1 PFB:F8BT blend nanoparticles. (C) NEXAFS spectra for the pure materials PFB and F8BT. Reproduced (in part) from Ref. [62]. © IOP Publishing. Reproduced with permission. All rights reserved. ........................................ 69

Figure 2.16 Visible light micrograph of silicon nitride window (250 x 250 μm dimension) containing P3HT:PC61BM disperse nanoparticle film, demonstrating suitable sample preparation for STXM imaging. ....... 70
**Figure 2.17** Illustration depicting the STXM beam profile raster scanning a core-shell nanoparticle sample. Reproduced (in part) from Ref. [62]. © IOP Publishing. Reproduced with permission. All rights reserved. ........................................................................................................................................ 71

**Figure 2.18** The beam profile of the STXM 5.3.2.2 at the Advanced Light Source. Depicted is the line spread function in the horizontal direction, plotted with an Airy function fit. Reproduced from Ref. [125]. ........................................................................................................................................ 72

**Figure 2.19** Matching STXM and TEM showing method of locating corresponding nanoparticles with TEM. Note the slight clockwise rotation of the TEM images compared to the STXM images due to the difficulty in loading the sample into the second instrument in exactly the same orientation. .................................................................................................................. 73

**Figure 2.20** Photograph of (a) PC\textsubscript{71}BM, (b) 1:3 TQ1:PC\textsubscript{71}BM BHJ and (c) TQ1 films spin coated from 22 mg/ml solutions in chloroform onto quartz for UV-vis characterisation. Replicate films are pictured to ensure repeatability/consistency................................................................................ 74

**Figure 2.21** Chemical structure of the poly(3,4-ethylenedioxythiophene) :poly(styrene) sulfonate (PEDOT:PSS), used as a transparent, conductive polymer. Reproduced from Ref. [129], with permission from Hindawi........................................................................................................ 77

**Figure 2.22** Schematic depicting the spin coating process where the liquid is a nanoparticle colloidal dispersion. Reproduced (in part) from Ref. [57], with permission from The American Chemical Society. ................. 78

**Figure 2.23** Photograph of TQ1:PC\textsubscript{71}BM 1:3 nanoparticle OPV devices during the nanoparticle film drying step, pre-cathode deposition. Note the film imperfections (e.g. comets from ink aggregates) visible in this image (indicated by arrows).................................................................................. 79

**Figure 2.24** Schematic of a typical I-V curve of an OPV device annotated with $V_{OC}$, $J_{SC}$, $V_{max}$, $I_{max}$, $P_{max}$, $R_{sh}$ and $R_{s}$. .................................................................................................................. 82

**Figure 3.1** DLS size measurements for P3HT:PC\textsubscript{61}BM nanoparticles fabrication with P3HT of varying molecular weight (5K light dotted line, 9K heavy dotted line, 12K light dashed line, 16K heavy dashed line, 44K light line, 72K heavy line). .................................................................................. 90

**Figure 3.2** STXM fractional composition maps showing P3HT concentration (first column) and PC\textsubscript{61}BM concentration (second column) and TEM images (third column) for unannealed P3HT:PC\textsubscript{61}BM nanoparticles prepared from P3HT molecular weights of 5K (a to c), 9K (d to f), 12K (g to i), 16K (j to l), 44K (m to o) and 72K (p to r). All scale bars are 1 µm. The colour contrast is scaled such that light colours correspond to higher component
concentrations. Minima and maxima for the colour scale are black = 0 and white = 100%.

Figure 3.3 TEM of 5K P3HT:PC61BM nanoparticle spin coated film. Scale bar is 1 µm.

Figure 3.4 STXM fractional composition maps showing P3HT concentration (first column) and PC61BM concentration (second column) and TEM images (third column) for annealed (140 °C 4 min.) P3HT:PC61BM nanoparticles prepared from P3HT molecular weights of 5K (a to c), 9K (d to f), 12K (g to i), 16K (j to l), 44K (m to o) and 72K (p to r). All scale bars are 1 µm. The colour contrast is scaled such that light colours correspond to higher component concentrations. Minima and maxima for the colour scale are black = 0 and white = 100%.

Figure 3.5 (a) P3HT composition map of 16K P3HT:PC61BM NPs with the arc showing rotationally averaged radial composition profile, as plotted in (b). (c) Three-phase model for the NP morphology.

Figure 3.6 STXM mass plots of P3HT (first column) and PC61BM (second column) for 16K (a-b), 44K (c-d) and 72K (e-f) annealed (140 °C 4 min.) P3HT:PC61BM nanoparticles. All scale bars are 1 µm. The colour scale bar indicates concentration of component in µg/cm².

Figure 3.7 SEM image of 9K P3HT:PC61BM NPs unannealed (a) and annealed (b); 16K P3HT:PC61BM NPs unannealed (c) and annealed (d); and 72K P3HT:PC61BM NPs unannealed (e) and annealed (f). Annealing was performed at 140 °C for 4 min. All scale bars are 1 µm.

Figure 3.8 SEM of annealed 16K P3HT:PC61BM disperse nanoparticle film depicting two film morphology types, namely (1) PC61BM micron-sized aggregates surrounded by hollow core nanoparticles and (2) joined shell nanoparticles. Scale bar is 1 µm.

Figure 3.9 SEM image of 9K P3HT:PC61BM NPs with 140 °C thermal annealing treatment for 0 min., 1 min., 2 min., 4 min., 7 min. and 10 min. All scale bars are 1 µm. Note that the micrographs in this figure are not all of the same region, but of similar regions.

Figure 3.10 SEM image of 16K P3HT:PC61BM NPs with 140 °C thermal annealing treatment for 0 min., 1 min., 2 min., 4 min., 7 min. and 10 min. All scale bars are 1 µm. Note that the micrographs in this figure are not all of the same region, but of similar regions.

Figure 3.11 SEM image of 72K P3HT:PC61BM NPs with 140 °C thermal annealing treatment for 0 min., 1 min., 2 min., 4 min., 7 min. and 10 min. All scale bars are 1 µm. Note that the micrographs in this figure are not all of the same region, but of similar regions.
Figure 4.1 DLS particle size distributions of P3HT:PC_{61}BM nanoparticle dispersions fabricated with P3HT of varying molecular weight (5K light dotted line, 9K heavy dotted line, 12K light dashed line, 16K heavy dashed line, 44K light line, 72K heavy line). .................. 117

Figure 4.2 PCE vs P3HT molecular weight for average unannealed/dried (open circles) and annealed (closed circles) P3HT:PC_{61}BM NP OPV devices (a) and same plot for the corresponding BHJ OPV devices (b). Error bars represent the standard deviation for a minimum of 12 replicate devices. Note dashed/dotted lines have been included to guide the eye. ................................................. 122

Figure 4.3 J-V curves for best (a) dried and (b) annealed P3HT:PC_{61}BM NP OPV devices with varying P3HT molecular weight (5K light dotted line, 9K heavy dotted line, 12K light dashed line, 16K heavy dashed line, 44K light line, 72K heavy line). .................................. 122

Figure 4.4 Plot of EQE for the best performing annealed P3HT:PC_{61}BM NP OPV devices (a) and BHJ devices (b) fabricated with various P3HT molecular weights (5K light dotted line, 9K heavy dotted line, 12K light dashed line, 16K heavy dashed line, 44K light line, 72K heavy line). The UV-vis spectra have been normalised to the first P3HT peak. ................................................................................. 123

Figure 4.5 UV-visible absorption spectra of (a) P3HT:PC_{61}BM nanoparticle dispersions and (b) annealed P3HT:PC_{61}BM nanoparticle films, with varying P3HT molecular weight (5K light dotted line, 9K heavy dotted line, 12K light dashed line, 16K heavy dashed line, 44K light line, 72K heavy line). The UV-vis spectra have been normalised to the first P3HT peak. ................................................................................. 125

Figure 4.6 PL spectra of (a) P3HT:PC_{61}BM nanoparticle dispersions and (b) annealed P3HT:PC_{61}BM nanoparticle films, with varying P3HT molecular weight (5K light dotted line, 9K heavy dotted line, 12K light dashed line, 16K heavy dashed line, 44K light line, 72K heavy line). The film PL spectra have been normalised to film thickness. The annealed 9K PL spectrum has been excluded due to poor quality of the film for this sample. ................................................................. 125

Figure 4.7 Photograph of spin cast P3HT:PC_{61}BM blend films prepared from six different molecular weight P3HTs (5K, 9K, 12K, 16K, 44K and 72K), the change in visible light absorption with polymer molecular weight is quite clear by eye. ................................................................. 125

Figure 4.8 SEM images of low M_w (9K) P3HT:PC_{61}BM nanoparticles unannealed (a) and annealed (b), mid-range M_w (16K) P3HT:PC_{61}BM nanoparticles unannealed (c) and annealed (d), and high M_w (72K) P3HT:PC_{61}BM nanoparticles unannealed (e) and annealed (f). All scale bars are 200 nm. ................................................................................. 130

Figure 4.9 SEM image of low M_w (9K) P3HT:PC_{61}BM NPs annealed, depicting gross phase segregation (remnants of the nanoparticulate
film structure are evident from which the cores have moved to form large ∼500 nm rod-like crystallites of PC61BM). Scale bar is 1 μm. 

**Figure 5.1** DLS nanoparticle size distributions of P3HT:PC61BM nanoparticle dispersions with donor-acceptor ratio 1:0.5 light dotted line, 1:0.8 heavy dotted line, 1:1 light dashed line, 1:1.2 heavy dashed line, 1:1.5 light line, 1:2 heavy line.  

**Figure 5.2** (a) UV-visible absorption spectra of spin coated P3HT:PC61BM nanoparticulate films with donor-acceptor ratio 1:0.5 light dotted line, 1:0.8 heavy dotted line, 1:1 light dashed line, 1:1.2 heavy dashed line, 1:1.5 light line, 1:2 heavy line. (b) Nanoparticle film thickness measurements as a function of fractional PC61BM loading by mass, error bars represent standard deviation between 6 replicate film thickness measurements. 

**Figure 5.3** Trend in PCE of dried (open circles) and annealed (closed circles) P3HT:PC61BM nanoparticle OPV devices. Error bars represent standard deviation between 12 replicate devices. 

**Figure 5.4** J-V curves for best (a) dried and (b) annealed P3HT:PC61BM NP OPV devices with D-A ratio 1:0.5 light dotted line, 1:0.8 heavy dotted line, 1:1 light dashed line, 1:1.2 heavy dashed line, 1:1.5 light line, 1:2 heavy line. 

**Figure 5.5** (a) Plots of EQE for the best performing annealed P3HT:PC61BM nanoparticulate OPV devices with D-A ratio 1:0.5 light dotted line, 1:0.8 heavy dotted line, 1:1 light dashed line, 1:1.2 heavy dashed line, 1:1.5 light line, 1:2 heavy line, and (b) calculated PC61BM photocurrent contribution for annealed devices according to fractional PC61BM loading by mass. 

**Figure 5.6** STXM percentage composition maps showing P3HT concentration (first row) and PC61BM concentration (second row) and matching TEM (third row) for spin coated P3HT:PC61BM nanoparticles prepared from a P3HT:PC61BM feed ratio of 1:0.5 (a to c), 1:1 (d to f) and 1:2 (g to i). All scale bars are 600 nm. The colour contrast is scaled such that light colours correspond to higher component concentrations. Minima and maxima for the colour scale are black = 0 and white = 100%, with the exception of (e) and (h) where white is set to 85% for a clearer visualisation of morphology. 

**Figure 5.7** STXM percentage composition maps showing P3HT concentration (first row) and PC61BM concentration (second row) and matching TEM (third row) for dried P3HT:PC61BM nanoparticles prepared from a P3HT:PC61BM feed ratio of 1:0.5 (a to c), 1:1 (d to f) and 1:2 (g to i). All scale bars are 600 nm. The colour contrast is scaled such that light colours correspond to higher component concentrations. Minima and maxima for the colour scale are black = 0.
and white = 100%, with the exception of (e) where white is set to 85% for a clearer visualisation of morphology. .............................. 150

**Figure 5.8** STXM percentage composition maps showing P3HT concentration (first row) and PC_{61}BM concentration (second row) and matching TEM (third row) for annealed P3HT:PC_{61}BM nanoparticles prepared from a P3HT:PC_{61}BM feed ratio of 1:0.5 (a to c), 1:1 (d to f) and 1:2 (g to i). For each of the nine image panes, the left-hand region illustrates joining of nanoparticles and blending, the right-hand region illustrates the beginning of gross phase segregation, as the annealing treatment has led to two types of morphological change. All scale bars are 600 nm. The colour contrast is scaled such that light colours correspond to higher component concentrations. Minima and maxima for the colour scale are black = 0 and white = 100%, with the exception of (e) where white is set to 85% for a clearer visualisation of morphology. ........................................................................................... 151

**Figure 5.9** SEM of 1:1 P3HT:PC_{61}BM NP film spin coated (a) and annealed (b); (c) TEM of the annealed NP film showing that in the majority of the film the PC_{61}BM cores remain discrete and somewhat intact, with magnified region (d). Scale bars are 1 μm. ...................... 152

**Figure 5.10** Conceptual model with schematic of (a) 1:0.5, 1:1 and 1:2 P3HT:PC_{61}BM nanoparticle morphologies illustrating relative volume of phases, and (b) vertical cross-sectional slice of a 1:1 P3HT:PC_{61}BM OPV device as a sample to demonstrate the annealed NP film morphology, that being joined shell network-dispersed core. This model excludes gross phase segregated regions which are not the dominant morphological type in these films. ............................................. 153

**Figure 5.11** Conceptual view of exciton diffusion, exciton dissociation and charge transport in the dominant morphological phase of the annealed nanoparticle active layer. (a) Exciton generation in the P3HT-rich joined shell phase and (b) PC_{61}BM-rich core phase and diffusion to the core-shell interface for exciton dissociation and subsequent charge transport. Exciton generation, diffusion, dissociation and charge transport in (c) the P3HT-rich joined shell phase and (d) the PC_{61}BM-rich core phase. ............................................... 156

**Figure 5.12** P3HT percentage composition of P3HT-rich shell domains for spin coated nanoparticles and P3HT-rich joined shell network for dried and annealed nanoparticle films for 1:0.5 (diamonds), 1:1 (open circles) and 1:2 (closed circles) P3HT:PC_{61}BM ratios. .......................................................................................................... 158

**Figure 5.13** (a) Schematic representing the relative size of the STXM beam spot (FWHM of 120 nm) to the shell thickness (R_{s}) of 1:0.5, 1:1 and 1:2 P3HT:PC_{61}BM ratio nanoparticles with an average diameter of 270 nm. (b) Simulated nanoparticles of P3HT:PC_{61}BM ratio 1:0.5, 1:1 and 1:2 convolved with the STXM point spread function to output
the true albeit blurred STXM micrograph. Note in (b) white has been set to 100% PC$_{61}$BM and black to 0% PC$_{61}$BM for the simulated nanoparticles.

**Figure 5.14** Calculated PC$_{61}$BM photocurrent contribution (closed black circles) for annealed NP OPV devices according to fractional PC$_{61}$BM loading by mass, including calculation based on PC$_{61}$BM mass (red diamonds) and calculation based on core-shell model and STXM (blue circles). Error bars represent absolute error.

**Figure 6.1** Energy level diagram for donor polymers TQ1 and P3HT, and acceptor fullerene PCBM. [80, 167]

**Figure 6.2** (a and d) SEM showing nanoparticle size distribution, (b and e) circle identification using a Hough transform and (c and f) the output of this analysis for both small and large nanoparticle batches, respectively. Scale bars are 200 nm. Note the circle identification algorithm returns only few mismatches.

**Figure 6.3** UV-vis spectra for TQ1 pristine film (light line), PC$_{71}$BM pristine film (heavy line), 1:3 TQ1:PC$_{71}$BM BHJ film dried (heavy dashed line), 1:3 TQ1:PC$_{71}$BM NP film untreated (dot dashed line), 1:3 TQ1:PC$_{71}$BM NP film dried (140 °C 4 min.) (light dotted line), 1:3 TQ1:PC$_{71}$BM NP film dried (140 °C 4 min.) and annealed (140 °C 5 min.) (heavy dotted line). All spectra have been normalised to the same film thickness.

**Figure 6.4** Plots depicting average (a) PCE, (b) V$_{OC}$, (c) J$_{SC}$ and (d) FF for dried (open) and annealed (140 °C) (closed) nanoparticle OPV devices with varied drying temperature. Standard deviation in the data is represented by error bars. Dotted/dashed lines have been used to guide the eye. (e) J-V curves for best dried nanoparticle OPV device at 90 °C (light dotted line), 100 °C (heavy dotted line), 110 °C (light dashed line), 120 °C (heavy dashed line) and 140 °C (solid line); (f) J-V curves for best annealed (140 °C) devices with the corresponding drying treatments as in (e).

**Figure 6.5** EQE plots for dried (140 °C 4 min.) (dotted line) and annealed (140 °C 5 min.) (solid line) 1:3 TQ1:PC$_{71}$BM nanoparticle OPV device.

**Figure 6.6** SEM of 1:3 nanoparticle films (a) as spun and to match OPV device conditions: (b) dried at 110 °C 4 min., (c) dried at 110 °C 4 min. and annealed at 120 °C 5 min., (d) dried at 110 °C 4 min. and annealed at 140 °C 5 min., (e) dried at 120 °C 4 min., (f) dried at 120 °C 4 min. and annealed at 140 °C 5 min., (g) dried at 140 °C 4 min., (h) dried at 140 °C 4 min. and annealed at 140 °C 5 min. Scale bars are 200 nm.

**Figure 6.7** Plots depicting (a) average PCE (squares) and J$_{SC}$ (diamonds), (b) V$_{OC}$ (circles) and FF (triangles) for nanoparticle OPV
devices annealed at various temperatures. Dotted/dashed lines have been included to guide the eye. Standard deviation in the data is represented by error bars (a minimum of 12 devices were tested at each annealing condition). (c) J-V curves for best annealed nanoparticle OPV device at 160 °C (light dotted line), 180 °C (heavy dotted line), 200 °C (light dashed line), 230 °C (heavy dashed line) and 260 °C (solid line).

**Figure 6.8** STXM fractional composition maps showing the concentration of TQ1 (a) and PC$_71$BM (b) and matching TEM (c) with corresponding STXM mass plots (d and e) for unannealed TQ1:PC$_71$BM nanoparticles; STXM fractional composition maps showing the concentration of TQ1 (f) and PC$_71$BM (g) and matching TEM (h) with corresponding STXM mass plots (i and j) for TQ1:PC$_71$BM nanoparticles dried at 110 °C for 4 min. All scale bars are 600 nm. The colour contrast is scaled such that light colours correspond to higher component concentrations. Minima and maxima for the colour scale are black = 0 and white = 100%, with the exception of f where white is set to 70% for a clearer visualisation of morphology.

**Figure 6.9** STXM fractional composition maps showing the concentration of TQ1 (a) and PC$_71$BM (b) and matching TEM (c) with corresponding STXM mass plots (d and e) for TQ1:PC$_71$BM nanoparticles dried at 140 °C for 4 min.; STXM fractional composition maps showing the concentration of TQ1 (f) and PC$_71$BM (g) and TEM for same sample type (h) with corresponding STXM mass plots (i and j) for TQ1:PC$_71$BM nanoparticles dried at 110 °C for 4 min. followed by annealing at 140 °C for 5 min. All scale bars are 600 nm. The colour contrast is scaled such that light colours correspond to higher component concentrations. Minima and maxima for the colour scale are black = 0 and white = 100%, with the exception of b and f where white is set to 80% for a clearer visualisation of morphology.

**Figure 6.10** TEM of 1:3 TQ1:PC$_71$BM disperse nanoparticle films (a) as cast, (b) dried at 90 °C, (c) dried at 100 °C, (d) dried at 110 °C, (e) dried at 120 °C, and (f) dried at 140 °C for 4 min. The progressive formation of nano-pathways connecting the PC$_71$BM-rich nanoparticle cores with increasing applied temperature is indicated with arrows. Scale bars are 200 nm.

**Figure 6.11** TEM of 1:3 TQ1:PC$_71$BM disperse nanoparticle films dried at 140°C and annealed at (a) 140°C, (c) 160°C, (e) 180°C, (f) 200°C, (g) 230°C and (h) 260°C. (b) Zoomed in region of (a) showing formation of nano-pathways connecting the PC$_71$BM-rich nanoparticle cores. Several nano-pathways have been indicated with arrows. (d) Zoomed in region of (c). All scale bars are 600 nm.
Figure 6.12 UV-vis transmittance plot of a 1:3 TQ1:PC$_{71}$BM spin cast film (prepared from chloroform) through a heating regime to a maximum temperature of 180 °C. .............................................................. 194

Figure 6.13 (a) Schematic of TQ1:PC$_{71}$BM NP film as cast and (b) TEM of the spin coated film. (c) Schematic of TQ1:PC$_{71}$BM NP film following mild thermal annealing showing movement of materials and (d) TEM of the NP film following this thermal treatment. Scale bars are 100 nm. In schematics (a) and (c) the PC$_{71}$BM-rich NP cores are coloured burgundy, and the TQ1-rich NP shells and joined shell regions are coloured grey. The insert focuses on the local movement and alignment of polymer chain segments, this allows the movement of PC$_{71}$BM molecules and hence the formation of connecting pathways between segregated PC$_{71}$BM-rich NP cores. The schematic in (d) shows exciton generation, diffusion, dissociation and charge transport mechanisms in an annealed TQ1:PC$_{71}$BM NP film. Here, percolation pathways exist due to the joined TQ1-rich NP shells and connected PC$_{71}$BM-rich NP cores. Note that the TEM image utilised in (d) depicts the lateral nanoparticle film morphology, however has been adapted here as the vertical active layer composition for conceptual purposes, considering a 100 nm film composed of 21 nm diameter nanoparticles is analogous in structure. Depictions are not to scale. ........................................................................................................... 196

Figure 6.14 TEM of TQ1:PC$_{71}$BM nanoparticles dried at 90 °C for 90 min., with no obvious morphological changes or degradation resulting. Scale bar is 500 nm total length. ................................................ 198

Figure 7.1 Depiction of the stabilisation of the polymer/PCBM BHJ network by cross-linking of the acrylate-functionalised polythiophenes. Reproduced from Ref. [139], with permission from The American Chemical Society. .............................................................. 206

Figure 7.2 Schematic representation of a diblock copolymer. Reproduced (in part) from Ref. [176], with permission of The Royal Society of Chemistry. .............................................................. 207

Figure 7.3 Illustration representing the fabrication of P3HT:PCBM reverse core-shell NPs by successive solvent displacements. Reproduced from Ref. [177], with permission of The Royal Society of Chemistry. .............................................................. 208
List of tables

Table 1.1 Chemical structure of poly(3-hexylthiophene) (P3HT) donor and poly[2,3-bis-(3-octyloxyphenyl)quinoxaline-5,8-diy-alt-thiophene-2,5-diy] (TQ1) donor polymers .................................................. 10

Table 1.2 Chemical structure of fullerene derivative acceptor materials ................................................................. 18

Table 1.3 Molecular and morphology requirements for the photoactive layer of OPVs. [39] ......................................................... 20

Table 1.4 Structure of semiconducting polymers P3HT, PCDTBT, PCPDTBT, PSBTBT, PDPP3T, PTB7 and PBDT-TT-CF ........................................... 23

Table 3.1 Material properties of P3HT of various molecular weights ....... 89

Table 3.2 Z-average particle diameters from DLS measurements for P3HT:PC61BM nanoparticles fabricated from the materials presented in Table 3.1 ........................................................................................................ 90

Table 3.3 P3HT compositions of the P3HT-rich domains and PC61BM compositions of the PC61BM-rich domains as calculated from the STXM maps for the unannealed and annealed (140 °C 4 min.) samples. The compositions presented are averages (± standard deviation). The letter code below the calculated composition denotes the sample morphology. For the 12K and 16K annealed samples, two dominant morphologies have been identified and the corresponding compositions are listed. ................................................................................ 98

Table 4.1 Particle diameters from DLS measurements for P3HT:PC61BM nanoparticles fabricated from the varied molecular weight P3HTs ........................................................................................................... 117

Table 4.2 NP OPV device characteristics for best devices, with the averages (± standard deviation) of a minimum of 12 devices in brackets. ........................................................................................................ 120

Table 4.3 BHJ OPV device characteristics for best devices, with the averages (± standard deviation) of a minimum of 12 devices in brackets. ........................................................................................................ 121

Table 4.4 Average blend ratios for P3HT:PC61BM for the different morphological domains in the NP films, prepared from the various P3HT molecular weight batches. Note that these blend ratios have associated error, please refer to Table 3.3 of Chapter 3 for associated error ........................................................................................................ 132

Table 5.1 P3HT polymer characterisation parameters. .............................................. 140
Table 5.2 Nanoparticle OPV device characteristics for best devices with varied donor-acceptor (D-A) material ratio, with the averages (± standard deviation) of 12 devices in brackets. ........................................... 143

Table 5.3 Calculated PC₆₁BM photocurrent contribution for annealed devices according to fractional PC₆₁BM loading by mass. ......................... 146

Table 5.4 R_{core} (radius of core), V_{core} (volume of core), and S_{A-C-S} (surface area of C-S interface) as a fraction of R_{NP} (radius of nanoparticle), V_{NP} (volume of nanoparticle) and S_{A-NP} (surface area of nanoparticle), respectively, calculated from spin coated NP STXM data, average values are presented with standard deviation in parentheses. ................................................................................................ 154

Table 5.5 P3HT compositions of the P3HT-rich domains and PC₆₁BM compositions of the PC₆₁BM-rich domains as calculated from the STXM maps for the spin coated, dried and annealed samples. For the annealed samples where two morphological types have been identified, these are analysed separately as shown. ........................................ 157

Table 6.1 Molecular weight characterisation data for TQ1 polymer. ....... 170

Table 6.2 NP OPV device characteristics for best devices for varied drying temperatures, with the averages (± standard deviation) in parentheses. ........................................................................................................ 178

Table 6.3 NP OPV device characteristics of best devices for varied annealing temperatures (5 min. annealing time), all devices were dried previously at 140 °C for 4 min. The averages (± standard deviation) of a minimum of 12 devices given in parentheses. ........................................ 183

Table 6.4 BHJ OPV device characteristics for best devices, with the averages (± standard deviation) of a minimum of 12 devices given in parentheses. ........................................................................................................ 185