VIII Conclusions

The two main objectives of this work were to use high resolution low voltage transmission electron microscopy (HRLVTEM) to gain a greater understanding of annealing induced morphological changes in polymer:fullerene solar cells and to use modified PEDOT:PSS anodes and novel fullerene derivatives to improve the efficiencies of polymer based photovoltaic devices.

VIII.I High Resolution Low Voltage TEM

A novel sample preparation method, involving the sonication of P3HT:PCBM flakes in dichloromethane, allowed the preparation of samples suitable for high resolution TEM from actual photovoltaic devices. In situ imaging of samples during the annealing process revealed the mechanism by which fullerene domain agglomeration occurs on the nanometre scale. The average fullerene domain size was shown to more than double during the course of a 12 minute heat treatment, while the average nearest distance between fullerene domains appeared to remain constant. In addition, the results show that fullerene domain coarsening appears to be due solely to the agglomeration of existing domains, with no evidence of PCBM mass transfer out of the P3HT matrix.

Higher resolution images of pre and post anneal device samples showed clear evidence for the annealing induced crystallization of both P3HT and PCBM, whereas no evidence of crystallites was found in the pre-anneal samples. Crystal lattice parameters were measured using two dimensional fast fourier transform analysis. P3HT crystal lamellae were directly observed for the first time, in both a- and b-axis orientation and it was calculated that P3HT crystallites occupied 12% of the image area in the annealed sample.

Focal series images through the solar cell sample appear to provide some evidence of vertical segregation within the films, but further analysis is hampered by the inherently random nature of the specimen orientation.

VIII.II Glycerol modified PEDOT:PSS anodes

Glycerol doped PEDOT:PSS anodes were incorporated into P3HT:PC$_{61}$BM solar cells in an attempt to lower the anode sheet resistance and improve photovoltaic efficiency. The glycerol modification successfully reduced the sheet resistance of PEDOT:PSS anodes from 2320 Ω/□ to 3 kΩ/□ and initial I-V results presented what appeared to be a 100% improvement of device efficiency. However, subsequent consideration of theoretical limitations and external quantum efficiency measurements proved that the I-V curves were implausible.

Spatially resolved I-V measurements showed that the glycerol modified anodes violated the assumed device area, and allowed the recruitment of photocurrent from over 4 millimetres beyond the device boundary. The use of a light-blocking mask allowed accurate I-V curves to be obtained, which showed that the glycerol modified electrodes provided no significant efficiency gains compared to the reference devices.

VIII.III Novel Fullerene Derivatives for Enhanced Open Circuit Voltage

The investigation of novel fullerene derivative proved far more successful in improving the efficiency of high performance, polymer:fullerene solar cells. The LUMO levels of seven candidate fullerene derivatives were determined by cyclic voltammetry in order to ascertain those that might prove effective in P3HT based solar cells. Of the eight, two candidates showed promise; bis-ThC$_{61}$BM and Er$_3$N@C$_{80}$, with LUMO levels 0.07 eV and 0.12eV greater than PC61BM respectively. These two candidates were then incorporated into simple bilayer photovoltaic devices where bis-ThC$_{61}$BM proved to be highly effective with a V_{OC} of 0.79V. For reasons that are not entirely clear, Er$_3$N@C$_{80}$ based devices showed no photovoltaic effect whatsoever.

Bis-ThCBM was subsequently incorporated into P3HT bulk heterojunction devices and optimised to an efficiency of 4.6% with an open circuit voltage of 0.69V. Other devices achieved V_{OC} values of up to 0.79V – one of the highest V_{OC}s reported for a P3HT based device. By comparison, P3HT:PC61BM reference devices reached 3.6% with a V_{OC} of 0.59V. Optimised processing condition included the use of dichlorobenzene as the spin casting solvent, and the incorporation of a sub nanometre thick LiF layer at the P3HT:cathode interface.

The main cause of the enhanced efficiency in the P3HT:bis-ThC$_{61}$BM solar cell was the increased open circuit voltage, however, external quantum efficiency measurements also determined an improved efficiency at the high energy end of the visible spectrum. This correlated with wavelength dependent critical field calculations which showed that the critical field, defined as the electric field required to separate 50% of excitons across the polymer:fullerene interface, was significantly lower at higher wavelengths for bis-ThCBM based devices, compared to those produced with PC$_{61}$BM.

VIII.IV Future Work

The work detailed herein presents several avenues for future exploration. The high resolution TEM techniques have the potential to be a valuable tool as researchers seek to investigate the morphological interactions of newer polymer:fullerene systems. In particular, the ability to observe and quantify phase segregation on the nanometre scale, estimate levels of crystallinity and determine agglomeration rates will aid the development of systems with optimised morphologies , and also the development of increasingly stable morphologies that remain unaffected by the thermal heating incurred by normal photovoltaic operation.

The identification of bis-ThCBM as an electron acceptor with enhanced efficacy has significant implications for the development of high efficiency devices in conjunction with the newest generation of low band gap polymers. To date, the benzothiadiazole and benzodithiophene based polymers have been reported in devices with only single adduct fullerene derivatives. One would expect the open circuit voltages of these devices could be significantly enhanced through the use of bis-adduct fullerene derivatives while still allowing a large enough LUMO-LUMO separation to facilitate efficient exciton dissociation.

In addition, there is much work to be done to improve the understanding of the kinetics at the donor/acceptor interface and how this is affected by polymer and fullerene chemistry. The wavelength dependent critical field and temperature dependent EQE work presented herein is a small step in that direction but would be greatly augmented by a range of tools such as ultra-fast spectroscopy, and computer simulations of donor-acceptor interactions.

The use of metal trimetal nitride endohedral fullerene derivatives is also a very new field with the most pressing question raised by this work being why some derivatives such as $Lu_3N@C_{80}$ should form successful photovoltaic devices, but others, such as Er3N@C80 should not. The addition of solubilising groups to $Er_3N@C_{80}$ would facilitate the fabrication of bulk heterojunction devices that could be used to further explore this question. In addition, regarding exohedrally modified fullerenes, interesting research could be conducted to minimise the negative effects on fullerene packing caused by the multiple addends. As the LUMO-raising effect appears to originate from the saturation of a carbon-carbon double bond, much smaller ‘vestigial’ molecules could conceivably be used for the second and even third addends instead of a butyric acid methyl ester. Such a strategy would maintain good solubility through the primary addend, and a heightened LUMO with hopefully less degradation of the fullerene mobility.