Morphology and material stability in polymer solar cells

The performance of polymer solar cells depends strongly on the distribution of electron donor and acceptor material in the active layer. Understanding the connection between morphology and performance as well as how to control the morphology, is therefore of great importance. Furthermore, improving the lifetime has become at least as important as improving the efficiency for polymer solar cells to become a viable technology.

In this work, the relation between morphology and solar cell performance is studied as well as the material stability for polymer:fullerene blend films. A combination of microscopic and spectroscopic methods is used to investigate the lateral and vertical morphology as well as the surface composition. Lateral phase-separated domains are observed whose size is correlated to the solar cell performance, while the observed surface enrichment of polymer does not affect the performance. Changes to the unoccupied molecular states as a result of illumination in ambient air are observed for the fullerene, but not for the polymer, and fullerenes in a blend change more than pristine fullerenes. Solar cells in which the active layer has been illuminated exhibit greatly reduced electrical performance, mainly attributed to fullerene degradation at the active layer surface.
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LICENTIATE THESIS

Karlstad University Studies | 2015:44

urn:nbn:se:kau:diva-37843

ISSN 1403-8099


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Distribution:
Karlstad University
Faculty of Health, Science and Technology
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SE-651 88 Karlstad, Sweden
+46 54 700 10 00

Print: Universitetstryckeriet, Karlstad 2015

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Angest, ångest är min arvedel

Per Lagerkvist
Abstract

Polymer solar cells are promising in that they are inexpensive to produce, and due to their mechanical flexibility have the potential for use in applications not possible for more traditional types of solar cells. The performance of polymer solar cells depends strongly on the distribution of electron donor and acceptor material in the active layer. Understanding the connection between morphology and performance as well as how to control the morphology, is therefore of great importance. Furthermore, improving the lifetime of polymer solar cells has become at least as important as improving the efficiency.

In this thesis, the relation between morphology and solar cell performance is studied, and the material stability for blend films of the thiophene-quinoxaline copolymer TQ1 and the fullerene derivatives PCBM and PC<sub>70</sub>BM. Atomic force microscopy (AFM) and scanning transmission X-ray microscopy (STXM) are used to investigate the lateral morphology, secondary ion mass spectrometry (SIMS) to measure the vertical morphology and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy to determine the surface composition. Lateral phase-separated domains are observed whose size is correlated to the solar cell performance, while the observed TQ1 surface enrichment does not affect the performance.

Changes to the unoccupied molecular orbitals as a result of illumination in ambient air are observed by NEXAFS spectroscopy for PCBM, but not for TQ1. The NEXAFS spectrum of PCBM in a blend with TQ1 changes more than that of pristine PCBM. Solar cells in which the active layer has been illuminated in air prior to the deposition of the top electrode exhibit greatly reduced electrical performance. The valence band and absorption spectrum of TQ1 is affected by illumination in air, but the effects are not large enough to account for losses in solar cell performance, which are mainly attributed to PCBM degradation at the active layer surface.
List of publications

The thesis is based on the following papers:

I.  Vertical and lateral morphology effects on solar cell performance for a thiophene-
    Journal of Materials Chemistry A, 2015, 3, 6970-6979

II. Photo-degradation in air of the active layer components in a thiophene-quinoxaline 
    copolymer:fullerene solar cell
    R. Hansson, C. Lindqvist, L. K. Ericsson, A. Opitz, E. Wang, 
    E. Moons
    Manuscript

Related papers not included in this thesis:

III. \textit{V}_{oc} from a Morphology Point of View: the Influence of Molecular Orientation on 
    the Open Circuit Voltage of Organic Planar Heterojunction Solar Cells, 
    U. Hörmann, C. Lorch, A. Hinderhofer, A. Gerlach, M. Gruber, J. 
    Kraus, B. Sykora, S. Grob, T. Linderl, A. Wilke, A. Opitz, R. Hansson, 
    A. Anselmo, Y. Ozawa, Y. Nakayama, H. Ishii, N. Koch, E. Moons, F. 
    Schreiber, W. Brütting 

IV.  The influence of oxygen adsorption on the NEXAFS and core-level XPS spectra 
    of the C$_{60}$ derivative PCBM, I. E. Brumboiu, L. K. Ericsson, R. Hansson, 
    E. Moons, O. Eriksson, B. Brena 
    Journal of Chemical Physics, 2014, 142, 054306

V.  Fluorescence Spectroscopy Studies on Polymer Blend Solutions and Films for 
    Photovoltaics, J. van Stam, R. Hansson, C. Lindqvist, L. K. Ericsson, 
    E. Moons 
VI. Fluorescence and UV/Vis absorption spectroscopy studies on polymer blend films for photovoltaics, J. van Stam, C. Lindqvist, R. Hansson, L. K. Ericsson, E. Moons.
Proc. SPIE, 2015, 9549, 95490L.
Acknowledgements

First of all, I would like to thank my supervisor Ellen Moons and co-supervisor Andreas Opitz for all the guidance, support and encouragement. I would also like to thank Jan van Stam, Leif Ericsson, Camilla Lindqvist, Sudam Chavhan, and Ana Sofia Anselmo. You have all provided an excellent atmosphere to perform research in and I have thoroughly enjoyed my time working together with you.

I would like to thank my colleagues at the Department of Engineering and Physics for making my time here pleasant.

I wish to thank Paul Dastoor, Natalie Holmes, and Xiajing Zhou, for introducing my to the STXM technique and also for the nice time spent together in Berkeley.

I would like to thank Ulrich Hörmann, Ergang Wang, Christian Müller, Jakub Rysz, Monika Biernat, Jasper Michels, Barbara Brena, Iulia Brumboiu, and Mariano Campoy-Quiles. This work would not have been what it is without your help.

Many thanks to Alexei Preobrajenski, Alexander Generalov, Ben Watts, and David Kilcoyne for all the help during synchrotron beamtimes.

Last, but certainly not least, I would like to thank my family and friends for making sure that my time spent outside the confines of the laboratory also has been pleasant.
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Chapter 1
Introduction

Since the industrial revolution two centuries ago, the world has seen a tremendous increase in energy consumption. In 2010 the total global energy need was 17.5 TW and has been predicted to grow to 27.4 TW by 2040. A significant part of that energy has so far come from burning fossil fuels. Environmental issues associated with fossil fuels aside, at the current consumption rate it is only a matter of time before easily attainable fossil fuel sources are depleted. In order to meet the demands for energy in the future, alternative sources of energy must be utilized more.

By far the largest source of energy currently available on Earth is sunlight. The sun transfers 1.36 kW/m\(^2\) to the outer atmosphere which leaves, after accounting for energy losses due to sunlight being reflected and absorbed by the atmosphere, enough power that the sunlight hitting the surface of the Earth in one and a half hour exceeds the world’s annual energy consumption. It is of course unfeasible to capture all of that energy, but the sheer amount of available energy alone shows that merely a small fraction would be enough for conversion to desired energy forms.

There exists a multitude of ways in which the power from sunlight can be harnessed. Green plants and cyanobacteria convert solar energy into chemical energy through photosynthesis. Sunlight unevenly heating the surface of the Earth creates pressure differences that set air in motion, creating wind, a form of kinetic energy. Sunlight also heats the oceans causing water to evaporate, allowing it to later fall out of the atmosphere as precipitation and accumulate in e.g. dams, a form of potential energy. To produce electricity, these aforementioned forms of energy would need to be converted further, and involves additional energy losses of varying degree which not seldom require rather bulky equipment. Solar cells, on the other hand, provide means to convert the energy of light into electrical energy in a one-step process.

The first observation of an electrical current being generated in a material by light exposure was made in 1839 by Becquerel working on silver coated platinum electrodes in electrolytes. In 1873 photoconductivity was discovered by Smith in selenium and in 1883 a solar cell made from gold coated selenium was built by Fritts that had a power conversion efficiency (PCE) of 1%. Due
to the high material cost and the low PCE, this kind of solar cell never found use in any large scale power generation. The next big step in the development of solar cell technology was taken in 1954 at Bell Labs when the first silicon solar cell displaying a PCE of 6% was developed. As of today, silicon solar cells are by far the most prevalent type of solar cell with the record efficiency just above 25% for monocrystalline silicon.

For the last two decades there has been an exponential increase in electrical power produced by solar cells, increasing from 0.1 GW in 1992 to at least 134 GW in 2013. Arguably one of the most important reasons for this increased solar cell usage is the reduction in production costs and various national measures of economic support for the end users. Despite that, power from solar cells still accounts for less than 1% of the total global power production.

For any type of solar cell to become more commercially viable, efficiencies need to increase or fabrication costs need to decrease. Today the best performing silicon solar cells have a PCE that is not very far from the theoretical limit for single junction devices, known as the Shockley-Quessier limit, which is 30% for silicon. This means that the potential benefits that could be had by reducing the fabrication costs are greater than those from improving the efficiency.

In order to reduce the production costs, several alternative solar cell technologies have been developed over the years. Particularly promising are organic solar cells, mainly because of the compatibility with inexpensive printing techniques, similar to those used to print newspapers. The mechanical flexibility and low weight together with the chemically tunable properties of organic materials allow for novel applications such as integration with textiles and transparent solar cells.

Currently the record PCE for organic solar cells has reached 11.1%. This progress is the result of great effort, largely owing to the development of new photoactive materials, but also to the increasing understanding of and control over the morphology of the solar cell’s active layer.

No matter how efficient a solar cell is or how inexpensive it is to produce, it will never see any widespread use unless the lifetime also is reasonably long. As it stands today, device stability is one of the greater challenges that organic solar cells face. For printed organic solar cells to be able to compete with silicon, it is
estimated that a module PCE of 7% and 5 years lifetime would be sufficient.\textsuperscript{19} With the record PCE for mini modules currently at 9.5\%\textsuperscript{A} and record outdoor lifetimes of modules surpassing two years,\textsuperscript{20} we are now at a point where it has become at least as important to improve the lifetime as it is to improve the PCE. Further improvement requires an increased understanding of the fundamental processes behind efficiency and stability.

The work presented in this thesis deals with i) the morphology of the active layer in polymer solar cells, and ii) the photo-degradation of the active layer and their respective influence on the solar cell device performance.
Chapter 2
Polymer solar cells

2.1 Organic semiconductors

Although organic electronics is a relatively new technology, semiconducting properties of organic materials were discovered already in 1906 when Pochettino observed photoconductivity in anthracene.\textsuperscript{21} Anthracene was also the first organic material in which the photovoltaic effect was observed,\textsuperscript{22} although with a PCE on the order of $10^{-6}$. The first polymer to display photoconductivity, polyvinylcarbazole, was described in 1957 by Hoegl et al.\textsuperscript{23,24} A breakthrough was made in 1977 when Heeger, MacDiarmid and Shirakawa discovered and developed conducting, conjugated polymers,\textsuperscript{25,26} which they were awarded the Nobel Prize in Chemistry for in 2000. Ever since, there has been a growing interest in optoelectronic technology based on organic semiconductors.

The difference between a semiconducting and a non-conducting polymer lies in the nature of the chemical bonds along the molecule backbone. Single bonds normally consist of $\sigma$-bonds formed by head-on overlap of atomic or hybrid orbitals. Electrons that take part in $\sigma$-bonds are localized and unable to move along the molecular backbone; hence a polymer with only single bonds along the backbone will be an electrical insulator. If instead, there are alternating single and double bonds (\textit{i.e.} a conjugated system), each carbon atom along the backbone will form three $sp^2$ hybridized orbitals and one unhybridized $p$-orbital. The overlapping $sp^2$ orbitals form $\sigma$-bonds and the overlapping $p$-orbitals form $\pi$-bonds (see Figure 2.1.1). In contrast to $\sigma$-bonds, electrons partaking in $\pi$-bonds are delocalized and overlap of the $\pi$-orbitals allows them to be delocalized along the conjugated backbone. When the two $p$-orbitals combine, a lower energy, bonding $\pi$-molecular orbital as well as a higher energy, antibonding $\pi^*$-molecular orbital can be formed.\textsuperscript{27,28} The energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) determines the HOMO-LUMO gap and is for conjugated polymers usually in the range of 1-4 eV,\textsuperscript{29} in other words, in the same range as the bandgap of inorganic semiconductors.
There are several fundamental differences between organic and inorganic semiconductors. In contrast to inorganic semiconductors, every molecule in an organic semiconductor is an individual semiconductor. Unless the material is ordered and ultrapure, electrical transport requires the charge carriers to be thermally activated in order to move from molecule to molecule by hopping. Consequently, the charge carrier mobility in organic semiconductors is much lower than in most inorganic semiconductors. On the other hand, the absorption coefficients of organic semiconductors are relatively large. For solar cell applications, low charge carrier mobilities can therefore, at least partly, be compensated for by using thin films (~100 nm) that still give high light absorption.

Another important difference between organic and inorganic semiconductors is related to excitons. An exciton is a quasiparticle created upon light absorption and consists of an excited electron and hole held together by Coulomb forces. Since organic materials generally have a low dielectric permittivity, the screening of charges is weaker and the exciton binding energy higher than for inorganic materials. Inorganic materials have exciton binding energies low enough that the thermal energy available at room temperature of about 25 meV is sufficient to dissociate the exciton into free charges, whereas organic materials typically have exciton binding energies in the range of 0.5-1 eV, and hence cannot be dissociated by thermal excitation alone.
2.2 Device operation

A polymer solar cell is a layered structure (see Figure 2.2.1), where the organic photoactive layer, often along with interlayers, is sandwiched between two electrodes. At least one of the electrodes needs to be transparent for obvious reasons. Commonly used transparent electrodes include indium doped tin oxide (ITO) or metal grids.

![Figure 2.2.1. Typical organic solar cell device structure.](image)

As mentioned previously, the exciton binding energy in organic materials is high compared to the thermal energy at room temperature. A common approach to dissociate the excitons is through the use of two different materials that form a heterojunction. For this to be effective there should be a LUMO-LUMO and a HOMO-HOMO energy level offset between the two materials that provide enough driving force for the exciton dissociation, and additionally the energy levels should be such that a staggered (type II) heterojunction is formed (see Figure 2.2.2). The material with the higher LUMO energy level will act as an electron donor and the other material as an electron acceptor. That way, if light is absorbed in the donor, the exciton can be dissociated by the transfer of an electron from the donor to the acceptor, and if light is absorbed in the acceptor, the exciton can be dissociated by the transfer of a hole from the acceptor to the donor. This, however, requires that the exciton is able to reach the donor/acceptor interface before it recombines and the absorbed energy is lost as heat. The exciton diffusion length in organic materials is about 5-20 nm, so efficient exciton dissociation also relies on the distribution of donor and acceptor materials (i.e. the morphology) being such that ideally everywhere...
in the photoactive layer there is a donor/acceptor interface within the exciton diffusion length.

![Diagram of energy levels in an organic solar cell.]

**Figure 2.2.2.** Energy levels of the donor, acceptor and electrodes of an organic solar cell, before electrical contact has been made.

After an exciton has reached the donor/acceptor interface and has successfully been dissociated into free charges, the next step is for the charges to reach the electrodes. The driving force for the charge transport is provided by the internal electric field produced by the use of electrodes with different work functions. Also in this step, the morphology is of great importance. Since the electrons mainly move through the acceptor material and the holes through the donor material, continuous pathways of either material to its corresponding electrode is ideally needed for efficient charge transport.

Once the charges reach the interface to the electrode the last step is the charge extraction. Interlayers are commonly placed between the photoactive layer and the electrodes to promote ohmic contact formation and to minimize series resistance and charge recombination. Also, as will be described in section 2.4, the donor and acceptor materials in the photoactive layer are often distributed in such a way that both materials would be in direct contact with both electrodes if no interlayers were present. Therefore, the interlayers also serve as charge selective layers that prevent the charges from exiting the photoactive layer through the wrong electrode.
2.3 Device characterization

The energy band conditions of an organic donor/acceptor heterojunction sandwiched between two electrodes in darkness is shown in Figure 2.3.1 under different bias situations.

![Energy band diagrams under different bias voltage conditions.](image)

**Figure 2.3.1.** Energy band diagrams under different bias voltage conditions. Under reverse bias (a) the applied electric field tilts the bands, but due to the large energy barriers very few electrons are injected from the anode and very few holes are injected from the cathode and only a very small current can flow across the device. Under short circuit conditions (b) the bands are still tilted due to the built-in electric field. Under sufficiently high forward bias, the bands tilt the opposite way and electrons can be injected from the cathode and holes from the anode and a current can now flow across the device. (d) Dark current as a function of applied bias voltage.
Under reverse bias (Figure 2.3.1a) electrons trying to enter the active layer from the anode (and holes trying to enter from the cathode) will experience a barrier that hinders the charge injection. Hence, in darkness only a very small current will flow under reverse bias.

Without any applied bias, i.e. at short circuit conditions, the HOMO and LUMO will still be tilted the same way as under reverse bias because of the built in electric field due to the different work functions of the electrodes, but not tilted as much. With increasing forward bias, the bands tilt less and eventually start tilting in the opposite direction. As this happens, electrons will be able to enter the active layer from the cathode and holes can enter from the anode and a much larger current can flow through the device than under reverse bias. In other words, the device has rectifying properties and will work as a diode in the dark. Figure 2.3.1d shows current as a function of applied bias (known as a J-V curve) for a solar cell in darkness; this current is called the dark current.

As previously described in section 2.2, if light enters the active layer, an exciton can be created and subsequently separated into free charges. If the device is under reverse bias, these free charges will experience a strong electric field and the device works as a photodetector. As the applied bias voltage changes from negative to positive and the fourth quadrant of the J-V diagram is entered (see Figure 2.3.2), there is still an internal electric field present due to the work function difference of the electrodes and the photocurrent still flows in the same direction as before, but the dark current increases and flows in the opposite direction to the photocurrent. Thus, as the forward bias voltage increases the dark current increases and the total current decreases (Figure 2.3.2).
The current voltage characteristics of a solar cell can be modelled as a current generator in parallel with a diode. A variety of processes that modify the current and voltage output can be taken into account by resistances added in parallel, $R_p$, and in series, $R_s$. Figure 2.3.3 shows the equivalent circuit of a solar cell.

![Solar cell equivalent circuit](image)

The diode can be modelled by the Shockley diode equation:

$$j_D = j_0 \left[ \exp \left( \frac{eV_D}{n k_B T} \right) - 1 \right]$$

(2.1)

where $j_0$ is the current density through the diode, $j_0$ the reverse bias saturation current density of the diode, $e$ the elementary charge, $V_D$ the voltage across the diode, $n$ the ideality factor, $k_B$ Boltzmann’s constant and $T$ the absolute
The current output $j$ from the solar cell under illumination as a function of applied voltage $V$ can then be written as

$$j = j_0 \cdot \exp \left[ \left( \frac{e(V - jR_S)}{n k_B T} \right) - 1 \right] + \frac{V - jR_S}{R_p} - j_p \quad (2.2)$$

In equation (2.2) above, the photocurrent $j_0$ is assumed to be constant, even though, strictly speaking it is not entirely constant, but is nevertheless often a good approximation.\textsuperscript{41}

The performance of a solar cell is evaluated from an experimentally measured current-voltage characteristic curve. Figure 2.3.4 shows a J-V curve of a solar cell under illumination where several important solar cell parameters are highlighted as well as a power-voltage curve.

![Solar cell J-V characteristics under illumination (left). Power density (right)](image)

The current density that flows through the solar cell when no voltage is applied, or equivalently, when the resistance of the external load is zero, is called the short circuit current density ($J_{SC}$). There are several factors that influence the $J_{SC}$, such as the intensity and spectrum of the incoming light, the absorption coefficients of the materials in the active layer, as well as the efficiency of the exciton dissociation, charge transport and charge extraction.

The voltage where the photocurrent and the dark current are equal and cancel out so that the total current through the device is zero is called the open circuit voltage ($V_{OC}$). Equivalently, this is the voltage that develops between the
electrodes when they are not electrically connected, hence its name. The $V_{OC}$ depends on the materials combination in the active layer and is linked to the difference between the LUMO of the acceptor and the HOMO of the donor. Using [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PCBM) as the acceptor material, the following empirical relation was obtained for a number of different conjugated polymers as donors:

$$V_{OC} = \left[ \frac{E_{HOMO}^{Donor} - E_{LUMO}^{PCBM}}{e} \right] - 0.3 \text{ V}$$  \hspace{1cm} (2.3)$$

Using high band gap materials will thus result in a high $V_{OC}$. However, since high band gap materials also absorb a smaller part of the solar spectrum, the $J_{SC}$ would be lower than for low band gap materials. Therefore, the effect of the band gap on both the $V_{OC}$ and the $J_{SC}$ needs to be taken into account when choosing the solar cell materials.

The power density $P$ generated from a solar cell is given by

$$P = jV$$  \hspace{1cm} (2.4)$$

Different loads correspond to different points along the J-V curve, and the point $(V_{max}, j_{max})$ where the solar cell generates the most power is called the maximum power point (MPP), (see the right hand side of Figure 2.3.4).

The fill factor (FF) is defined as the ratio

$$FF = \frac{j_{max} \cdot V_{max}}{J_{SC} \cdot V_{OC}}$$  \hspace{1cm} (2.5)$$

and gives a measure of how easily photogenerated charge carriers are extracted from the solar cell. Since $j_{max} \cdot V_{max}$ is equal to the area of the largest rectangle that will fit inside the J-V curve and the coordinate axes (see Figure 2.3.4), the FF can be visualized as the ‘squareness’ of the J-V curve; the more square shaped the J-V curve is, the closer the FF is to unity. The FF is strongly affected by parasitic resistances, and also depends on interface recombination and the balance between electron and hole mobilities.
The power conversion efficiency (PCE) of a solar cell is defined as the ratio between the maximal generated power and the power of the incident light, $P_{in}$.

$$PCE = \frac{j_{max} \cdot V_{max}}{P_{in}} = \frac{FF \cdot j_{SC} \cdot V_{OC}}{P_{in}}$$

(2.6)

Thus, for an efficient solar cell the FF, $j_{SC}$ and $V_{OC}$ all should be as high as possible.

Since the intensity and spectrum of the incident light can affect many of the aforementioned photovoltaic parameters, it is important to have clearly defined illumination conditions for any given $J-V$ measurement. Commonly used is the Air Mass 1.5 (AM1.5) solar spectrum. The AM1.5 global spectrum (shown in Figure 2.3.5) corresponds to sunlight attenuated by passing through the atmosphere at an angle of 48° from zenith, equivalent to passing through 1.5 times the length of atmosphere compared to from zenith. For convenience, the intensity of the AM1.5 spectrum is normalized so that the integrated irradiance is 1000 W/m².

Figure 2.3.5. AM1.5 solar spectrum.44
2.4 Morphology

How the donor and acceptor materials are distributed within the active layer of an organic solar cell is of great importance for the device performance. The first successful organic solar cell, reported by Tang et al. in 1986 had an active layer that was a bilayer of copper phthalocyanine and a perylene tetracarboxylic derivative. As previously mentioned in section 2.2, only excitons that are generated close enough to a donor/acceptor interface to reach it by diffusion will contribute to the photocurrent. Therefore, a bilayer should not be thicker than twice the exciton diffusion length in order to avoid exciton recombination. Since the exciton diffusion length in organic semiconductors is in the range of 5-20 nm, this means that the bilayer then would be too thin to efficiently absorb light.

In 1995 the concept of the bulk heterojunction was introduced, in which the donor and acceptor materials are mixed within the same layer. Figure 2.4.1 shows typical bilayer and bulk heterojunction morphologies.

Figure 2.4.1. Illustration of typical bilayer (a) and bulk heterojunction (b) morphologies.

Compared to the bilayer heterojunction, the bulk heterojunction has significantly more interfacial area between the donor and acceptor materials and the interfaces are distributed throughout the film. Consequently, excitons can be efficiently dissociated in a larger fraction of the active layer even if the film is thicker than twice the exciton diffusion length. On the other hand, since the electrons are mainly transported through the acceptor material and the holes
through the donor material, efficient charge transport requires that once the exciton has been dissociated there exists continuous pathways of both donor and acceptor materials to the respective electrode. If the materials are too intimately mixed, there will be plenty of dead ends and bottlenecks that prevent the charges from easily reaching the electrodes. Considering this, the bulk heterojunction and the bilayer heterojunction excel at different aspects; in the bulk heterojunction the exciton dissociation is efficient whereas in the bilayer heterojunction the charge transport is efficient. However, comparing the device performance of the two, it is the bulk heterojunction that to date is the superior one.

For solution-processed materials, a bulk heterojunction is relatively simple to obtain through a one-step process in which the donor and acceptor materials are dissolved in the same solvent and mixed with each other before being coated onto a substrate. There are many ways to control the morphology of the bulk heterojunction such as through the choice of solvent, annealing, materials combination, blend ratios, type of substrate, and deposition method.\textsuperscript{45, 52-59} For vacuum-processed films, bulk heterojunctions can be obtained by co-evaporation.

Before the film is formed, when both materials are still in solution they form a homogenous mixture, but as the solvent evaporates the donor and acceptor materials will interact and generally start to phase separate into domains which are rich in either of the components. The extent of the phase separation will for a given materials combination depend on the film formation process. If the film dries slowly there will be sufficient time for the phases to form large domains, but if the drying is quick the system can be quenched into an intermediate state where the domains have not yet had the time to grow large before the structure is frozen in. This can be seen when comparing the morphologies of quickly drying spincoated films to more slowly drying drop cast films where the drop cast films exhibit larger domains.\textsuperscript{59} The phase separation can later be reactivated by thermal annealing or solvent annealing.

The choice of solvent often has an effect on the morphology, not only because of the different drying time due to the difference in solvent vapor pressure, but also because of the solubility of the donor and acceptor materials in the solvents. If the solubility limit is lower in one solvent compared to another, the
phase separation will start earlier, giving more time for the phase separation and resulting in larger domain sizes.

In the early stages of the film formation, driven by differences in surface energy, the component that has the lowest surface energy will tend to move towards the free surface in order to minimize the total energy. As a result, a wetting layer rich in one of the components is commonly formed at the free surface. Depending on how strongly the components interact and how much time they are given before the film is dry, interfacial instabilities may break up this layered structure into lateral domains, see Figure 2.4.2.

**Figure 2.4.2.** Schematic model illustrating morphology formation during drying. Starting from a homogeneous mixture (a), as the film dries, phase separation starts and initially creates a double layer due to surface energy differences (b). The layered structure can either be frozen in or develop further into a lateral structure (c).

Because of the impact morphology has on the performance of organic solar cells, it is of great importance to have proper tools for characterization. Structural as well as chemical information can be readily acquired via various microscopic and spectroscopic methods. A selection of experimental methods that can be used to probe the morphology is treated in more detail in chapter 4.
2.5 Degradation

As the efficiencies of polymer solar cells have steadily improved over the last years, we are reaching a point where stability rather than efficiency is becoming one of the major impediments for commercialization. Polymer solar cells degrade via several chemical and physical pathways that affect different parts of the device; the donor and acceptor materials, the active layer morphology, as well as the interlayers and electrode materials. Water and oxygen, often in combination with light, play a key part in many of the degradation processes.

The active layer components are known to be susceptible to photo-degradation in combination with oxygen or water that has leaked into the device. Hence, encapsulating the devices, protecting them from the ambient atmosphere is necessary. Recently, large area (100 cm²) modules, encapsulated using a simple low-cost packaging barrier, successfully maintained over 80% of the initial efficiency after more than 2 years of outdoor operation.

When conjugated polymers are photo-oxidized they tend to bleach as the loss in conjugation destroys the chromophores, leading to reduced photon absorption. By comparing the UV-Vis spectra of films of poly[2,3-bis-(3-octyloxyphenyl)quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl] (TQ1) of different molecular weights to degraded films, Henriksson et al. assigned the bleaching to chain scission due to photo-induced oxidation. Reese et al. have shown that the photobleaching of P3HT blended with PCBM is much slower than that of pristine P3HT and rationalized this by a process where PCBM quenches the photoexcited state of the polymer, hence protecting it from photo-oxidation. Apart from photochemical reactions, oxygen can also p-dope the active layer, forming a space charge region in front of the cathode that shields the electric field and hinders charge extraction.

Manceau et al. investigated the photochemical stability of 24 different conjugated polymers using UV-Vis and infrared spectroscopy and were able to find some general rules connecting the chemical structure to stability. Several common monomers were ranked by their degree of stability. Fluorene units were shown to be far less stable than e.g. thiophene units. It was also found that the position and number of side chains affected the stability; with high numbers of sidechains leading to low stability.
As mentioned in section 2.4, the active layer typically forms a metastable blend of the donor and acceptor materials. During illumination the active layer may reach temperatures high enough to initiate further phase separation, leading to larger domains, less effective exciton dissociation and a smaller photocurrent as a result. High temperature can also trigger the growth of large, micrometer sized PCBM crystals that will hamper the solar cell performance considerably.

Although most work on the degradation of the active layer has been focused on the polymers, PCBM has also been shown to degrade when exposed to light and air. Reese et al. observed oxidation of PCBM after exposing a P3HT:PCBM blend film to light in ambient air for 1000 hours. It has also been shown by Chambon et al. that the photo-oxidation of PCBM mainly involves the oxidation of the C60 moiety. Anselmo et al. recently used near-edge X-ray absorption fine structure (NEXAFS) and X-ray photoelectron spectroscopy (XPS) to study the effect of light exposure in air on the electronic structure of PCBM, they found distinct changes to both the occupied and unoccupied molecular states already after 30 minutes of exposure. The influence of ambient atmosphere on PCBM has been investigated by Bao et al. who exposed PCBM films to oxygen gas and water vapour in darkness. Changes to the PCBM work function were observed, more pronounced for water vapour than for oxygen exposure, and the valence band spectrum was strongly affected by the exposure to water vapour.

Low work function metals such as aluminium and calcium are commonly used for top electrodes in polymer solar cells. Such metals are highly reactive to oxidation and form oxides with insulating properties, thus forming barriers to charge extraction. It has been suggested that water can diffuse through pores in the metal layer and reach the interface between the electrode and the rest of the device where the metal is then oxidized. It has also been shown, using secondary ion mass spectrometry that oxygen from the surrounding atmosphere can diffuse through grain boundaries and microscopic holes in the aluminium electrode and into the device.

LiF is commonly used as an interlayer between the active layer and the top electrode known to improve the fill factor and Voc. Kawano et al showed that LiF also could improve the device stability of P3HT:PCBM solar cells during
the first 8 hours of illumination. However, thin layers of LiF have also been shown to decompose during the deposition of the aluminium top contact.

Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) is currently one of the most common materials used as a hole transport layer. However, due to its acidic nature with pH as low as 1-3, it can together with water corrode the adjacent electrode; especially those made from metals but also ITO has been shown to etch in the presence of PEDOT:PSS. PEDOT:PSS is found as one of the main sources of device degradation and alternative hole transport layers are under investigation.
Chapter 3
Materials and sample preparation

3.1 TQ1

The main polymer studied in this thesis is poly[2,3-bis-(3-octyloxyphenyl) quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl] (TQ1). TQ1 is an alternating copolymer that consists of thiophene and quinoxaline units. To make the polymer soluble in common organic solvents, two octyloxyphenyl side groups are attached to the quinoxaline unit. The molecular structure is shown in Figure 3.1.1.

TQ1 was first synthesized in 2003 by Yamamoto et al. and used for the first time in solar cells in 2010 by Wang et al. Used together with the fullerene derivative [6,6]-phenyl C$_{71}$-butyric acid methyl ester (PC$_{70}$BM), the solar cells initially displayed a PCE of up to 6%, which was later pushed to 7% by morphology control using solvent additives.

TQ1 belongs to a class of conjugated polymers called donor-acceptor polymers. By having units along the polymer backbone that are alternatingly strongly acceptor-like and strongly donor-like, the band gap of the polymer can be reduced. In TQ1, the thiophene is the donor-like unit and the quinoxaline the acceptor-like unit. The optical bandgap of TQ1 is 1.7 eV.

Being easy to synthesize and also displaying a higher thermal and chemical stability than many other commonly used electron donating polymers such as P3HT, TQ1 is a promising solar cell material for the future.
3.2 Fullerene derivatives

For solar cell applications, some of the most commonly used electron acceptors are fullerene derivatives. Fullerenes themselves have good electron accepting properties due to their high electron affinity but, owing to their low solubility in most common solvents, are not ideal for solution-processed solar cells and are normally limited to devices produced by vacuum deposition. By adding a suitable functional group to the fullerene cage, however, the issue with low solubility can be resolved. The fullerene derivative [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₀BM) was synthesized in 1995 by Hummelen et al.\(^9\) and is to date one of the most commonly used acceptor materials in polymer solar cells. The molecular structure of PC₆₀BM is shown in Figure 3.2.1a.

\[
\text{Figure 3.2.1. Molecular structure of a) PC}_{60}\text{BM and b) PC}_{70}\text{BM.}
\]

Apart from being a good electron acceptor, fullerene derivatives also have relatively good electrical transport properties with an electron mobility on the order of 10⁻² cm²/(V·s) for PC₆₀BM.\(^9\) Another widely used fullerene derivative is [6,6]-phenyl C₇₁-butyric acid methyl ester (PC₇₀BM), that exhibits stronger light absorption in the visible range than PC₆₀BM.\(^9\) The molecular structure of PC₇₀BM is shown in Figure 3.2.1b.
3.3 Spin-coating

Spin-coating is a common technique used to produce thin film coatings on flat substrates. For polymer solar cell research it has found a particularly widespread use as it provides a quick and easy way to create uniform and thin (~100 nm) films. As the name might allude to, spin-coating works by placing a solution of the coating material on a substrate and subsequently spinning it until a dry film has formed. This process can be divided into the following sub-steps\textsuperscript{99} that are illustrated schematically in Figure 3.3.1.

![Figure 3.3.1. Schematic illustration of the spin-coating process. (a) The solution is dispensed. (b) The substrate is rotationally accelerated and excess solution thrown off. (c) Solution flows off the substrate, the flow decreasing as the solvent evaporates and the film viscosity increases. (d) As the flow ceases, fluid is only lost through solvent evaporation.](image)

After an excess amount of solution has been dispensed (Figure 3.3.1a), the substrate is rotationally accelerated (Figure 3.3.1b). In this first step, about 90% of the solution is thrown off as the substrate starts spinning.\textsuperscript{99} The initial amount of solution has little or no effect on the final film thickness.\textsuperscript{100} The acceleration time until the final spin speed is reached does not affect the final
film thickness either, but can influence the radial uniformity of the film if long acceleration times are used.\textsuperscript{101}

In the next step, centrifugal forces make the solution flow radially outward (Figure 3.3.1c), reducing the film thickness while at the same time solvent evaporation also increases the viscosity of the film. Since the flow is governed by the balance between centrifugal and viscous forces, the flow decreases as the concentration and thus the viscosity of the film increases. It is mainly during this step that phase separation occurs.\textsuperscript{102}

The final step begins when the viscosity of the film has become high enough that the flow is negligible. From that point on, solvent evaporation is the dominant fluid loss (Figure 3.3.1d).

Several different factors influence the final film thickness during spin-coating. Since the final film thickness is mainly determined during step c) in Figure 3.3.1, high spin speeds that cause high centrifugal forces lead to low final film thicknesses. High initial solution concentrations on the other hand give a high solution viscosity early in the process and consequently lead to thicker films. High vapour pressure solvents evaporate quickly so that the viscosity also increases quickly, also giving thicker films. An empirical relation between film thickness $d$ and spin speed $\omega$ is given by

$$d = k \cdot \omega^\alpha$$

(3.1)

where $k$ and $\alpha$ are empirically determined constants, dependent on solution properties and substrate. $\alpha$ typically has a value in the vicinity of -0.5.\textsuperscript{100}
Chapter 4  
Experimental techniques  

4.1 Atomic force microscopy  

Atomic force microscopy (AFM) is a scanning probe technique used to characterize surfaces, most notably the surface topography. First developed in 1986 by Binnig et al., the AFM made high-resolution studies of surfaces of insulating materials possible. The scanning tunneling microscope (STM), developed a few years earlier, relies on tunneling currents and is thus restricted to conducting or semiconducting samples. Both STM and AFM utilize a very sharp tip that is scanned across the sample surface; the STM detecting electron tunneling whereas AFM detects the forces between tip and sample. The resolution of AFM images can be very high, with atomic resolution having been demonstrated, both in vacuum and on surfaces covered by liquids.

The interactions between the tip and the sample can be approximated by the Lennard-Jones potential:

\[
U = 4\varepsilon \left[ \left( \frac{n_0}{r} \right)^{12} - \left( \frac{n_0}{r} \right)^{6} \right] 
\]

(4.1)

where \( U \) is the interaction potential, \( r \) the distance between the tip and the sample, \( \varepsilon \) the depth of the potential and \( n_0 \) the finite distance where the potential is zero. The negative term in equation (4.1) is the attractive contribution from Van der Waals forces and the positive term is due to Pauli repulsion, i.e. from the overlap of electron orbitals. The Lennard-Jones potential is shown in Figure 4.1.1.
The instrumental setup of a typical AFM system is shown in Figure 4.1.2. The tip is mounted on a cantilever, allowing forces to be measured via the deflection of the cantilever. The deflection is measured by reflecting a laser beam from the top surface of the cantilever onto a position sensitive photodiode. The sample and the tip are moved relative to one another by a piezoelectric stage that can move in the x, y and z directions.

There are several different imaging modes for AFM; some of the more common ones being contact mode, non-contact mode and tapping mode. Contact mode operates in the repulsive part of the interaction potential (see Figure 4.1.1). The tip is brought into contact with the sample and usually kept at a constant force as the tip is scanned across the sample. A feedback loop assures that the force is kept constant by moving the cantilever relative to the sample in the z-direction using the piezo crystal. That way, as the sample is scanned, at every point \((x,y)\), the \(z\)-position is recorded and gives a three-dimensional image of the sample surface. As the forces between tip and sample can be relatively high in contact mode, hard samples are preferable. Soft samples can easily be damaged, especially by lateral forces as the tip is dragged across the sample surface. Also, the area of contact between the tip and the sample is higher for soft samples, thus limiting the resolution.
Non-contact mode operates further away from the sample in the attractive part of the interaction potential (see Figure 4.1.1). The tip is not in direct contact with the sample and the cantilever is made to oscillate near its resonance frequency. The interactions with the sample shift the frequency of the oscillation, and this frequency shift can be kept constant by the feedback loop by varying the z-position of the cantilever, thus mapping the sample topography. Here the forces between tip and sample are lower than in contact mode so sample damage from the tip is small, as is the area of contact between the tip and the sample, allowing for very high resolutions. However, when measuring in air, the sample surface may be covered by contaminant layers (e.g. water) thicker than the range of the attractive forces being probed.\textsuperscript{108}

Tapping mode (also known as intermittent contact mode) operates within both the range of contact and non-contact mode. Just like in non-contact mode, the cantilever is made to oscillate, but now at much higher amplitude so that the tip once per oscillation is brought into contact with the sample, tapping it. Usually constant amplitude is maintained by the feedback loop while the sample is scanned. Apart from measuring the topography, the phase difference between the driving frequency and the actual oscillation frequency can also be recorded at every point. The phase difference is sensitive to the stiffness of the sample,\textsuperscript{109} so it is possible to distinguish between materials of different stiffness in the phase image. Tapping mode avoids the damage to soft samples associated with contact mode, while also being able to operate in ambient air, since any layers of adsorbed water are easily penetrated by the tip.
4.2 Secondary ion mass spectrometry

Secondary ion mass spectrometry (SIMS) is a chemically sensitive analysis method based on ion sputtering. A beam of primary ions hits the sample surface, and upon impact ejects particles from the surface (Figure 4.2.1). These particles include ions, neutral atoms and molecules, as well as electrons and photons. In SIMS, these ejected secondary ions are sent to a mass spectrometer to be analyzed. The mass spectrometer measures the mass-to-charge (m/q) ratio of the ions, thus giving information about the chemical composition of the sample. Since the secondary ions originate from very close to the surface (<1 nm), this technique gives surface sensitive chemical information.\(^\text{110}\)

![Figure 4.2.1. Illustration of the sputtering process in SIMS. Note though that in the figure, the relative amount of charged particles in relation to neutral ones is exaggerated; in a true situation only a small fraction of the secondary particles leave the surface charged.\(^\text{110}\)](image)

Sputtering using low primary ion doses to analyze the chemical composition of the topmost layer of the sample is known as static SIMS. By using higher doses, or a separate source of primary ions intended only to remove material, secondary ions can be collected throughout the sample. This mode, known as dynamic SIMS, produces depth profiles with vertically resolved compositional information. Furthermore, by scanning the primary beam laterally, composition maps can be obtained, and if used in combination with depth sputtering, complete three-dimensional maps can be created.
After the secondary ions have been generated, they are extracted and accelerated by an electric field. Because of the spread in kinetic energy from the sputtering process, the secondary ions are then sent through an energy filter before entering the mass spectrometer. There are several different types of mass spectrometers. A sector field mass spectrometer uses static electric or magnetic fields (or a combination of both) to separate ions of different m/q ratios. In a quadrupole mass spectrometer the secondary ions are sent along four parallel metal rods. Oscillating electric field are applied to the rods such that only ions having a specific m/q ratio can pass through. A time-of-flight mass spectrometer measures the time it takes the ions to travel a given distance. After being accelerated by an electric field and sent through an energy filter, ions having the same charge will also have the same kinetic energy, travelling at different speeds depending on the mass; thus allowing the m/q ratio to be obtained by measuring the time of flight. Time-of-flight mass spectrometers require that either the primary ion beam or the acceleration field is pulsed.

Although SIMS makes it possible to determine where in a sample certain chemical species are located, as well as how the concentration changes in space, the information is usually qualitative. Translating specific m/q intensities to absolute concentrations is difficult since the detection sensitivities for different elements vary.110
4.3 Synchrotron radiation

Since the discovery of X-rays in 1895 by Röntgen, a considerable number of techniques have been developed that use X-rays to characterize materials. The first X-ray sources were X-ray tubes; vacuum tubes where electrons are accelerated by a high voltage and produce X-rays as they hit the anode. The maximum photon flux that can be produced by an X-ray tube is however limited by the heating of the anode caused by the decelerating electrons, even if this problem can be reduced by using water cooling and a rotating anode. To get higher flux, synchrotrons are used. It is worth noting though, that the total photon flux from a light source is not the only factor determining how many photons ultimately will hit a sample and is therefore not the ideal quantity for comparing light sources. Brilliance (or brightness as it is also commonly referred to) is a measure related to the number of photons emitted per second per bandwidth per unit solid angle and unit area of the source. Compared to X-ray tubes, the achievable brilliance of synchrotron radiation sources can be more than 14 orders of magnitude higher.

It is well known that accelerated charges emit photons. Synchrotron radiation is produced as the trajectory of electrons moving at relativistic speeds is bent; hence the radial acceleration of the electrons causes the emission of radiation. Since the electron velocity is very close to the speed of light, an observer looking at approaching electrons will see a large relativistic Doppler shift. The radiation is emitted along the tangent of the electron path in a narrow cone, with its divergence $\theta$ given by

$$\theta \sim \gamma^{-1}$$

(4.2)

where $\gamma$ is the Lorentz factor. Since $\gamma$ typically is on the order of 1000 or more for most synchrotron facilities, the divergence is usually less than a milliradian, which is part of the reason for the high brilliance of synchrotron radiation sources.

Figure 4.3.1 schematically depicts some of the main components of a synchrotron. Electrons are normally generated from a hot cathode by thermionic emission and accelerated first by a linear accelerator (linac) before being sent into a booster ring. In the booster ring the electrons are further accelerated before they are injected into the storage ring. Modern storage rings
are generally not completely circular, but rather shaped like a regular polygon. The electron beam is bent at the corners by dipole magnets, called bending magnets, which apart from just keeping the storage ring beam in a closed path also produce synchrotron radiation.

Figure 4.3.1. Sketch of a synchrotron showing some of the main components. Electrons are generated and then accelerated before entering the storage ring where synchrotron radiation is produced as the electron beam is bent by bending magnets or insertion devices.

Since the electrons lose energy as they radiate, the energy must be replenished so that they don’t collide with the inner wall of the storage ring. This is done by RF cavities that use a high frequency oscillating electric field. The electron beam is not continuous, but consists of electrons grouped together in bunches. Depending on how much energy an electron has lost, it will enter the RF cavity at slightly different points in time and thus experience different electric fields, which helps to keep the electron bunches together travelling at the same speed. In the transverse directions, the beam is kept together by quadrupole and sextupole magnets; the quadrupoles focus the beam and the sextupoles correct for chromatic aberrations caused by the quadrupoles.114

The synchrotron radiation is, as previously mentioned, produced by the bending magnets, but can also be produced by so-called insertion devices that
are placed along the straight sections of the storage ring. Such devices use a periodic magnetic structure that forces the electron beam to move in a transverse oscillatory motion to create synchrotron radiation. If the magnetic field is strong, the electron oscillations get large; such an insertion device is known as a **wiggl er** and produces much higher photon flux than bending magnets since the beam is bent several times instead of just once. The spectrum of the radiation from a wiggler is broad, similar to that from a bending magnet. If instead the magnetic field is weaker and the electrons oscillate within the divergence angle of the emitted radiation $\theta$, the insertion device is known as an **undulator**. The difference between a wiggler and an undulator is that the emitted synchrotron radiation from each of the bends the beam makes in an undulator overlap and only certain wavelengths interfere constructively, resulting in a spectrum with most of the photon flux narrowly concentrated around those wavelengths. By changing the magnetic field in the undulator by moving the gap between the magnets, the wavelengths that will interfere constructively can be tuned.\textsuperscript{114,117}

The synchrotron radiation emitted from a bending magnet or insertion device travels away from the storage ring and along a beamline where it can be focused, and monochromated before finally reaching the experimental endstation.
4.4 Near-edge X-ray absorption fine structure spectroscopy

X-ray absorption in matter is usually a smooth function of photon energy, but at certain energies, sharp, step-like increases in the absorption are found, as can be seen in Figure 4.4.1. These features, called absorption edges, occur at photon energies that match the energy required to ionize a core-level. Looking closer at an absorption edge, one will find that it is in fact not just a step; there is structure to be seen. The region close to the edge can have strong fluctuations in absorption, known as near-edge X-ray absorption fine structure (NEXAFS).

![Figure 4.4.1: X-ray absorption spectrum showing the carbon K-edge, the right-hand side displaying the NEXAFS region. Left figure adapted from reference 115.](image)

Since variable photon energy is required, NEXAFS measurements are normally performed at synchrotron facilities. As the photon energy is scanned across an absorption edge, core-level electrons get excited into unoccupied states. The spectrum thus gives information about the density of unoccupied states. NEXAFS spectroscopy is not only element sensitive, but also bond sensitive. For example, diamond, graphite and $C_{60}$ have very distinct NEXAFS spectra even though they only contain carbon atoms. Organic molecules have particularly rich and detailed features at the carbon edge, making it possible to use NEXAFS spectra as a way to identify a molecule by its molecular fingerprint. In addition, information about molecular orientation can be obtained from angular resolved NEXAFS since the orientation of a molecular orbital with respect to the electric field of the incident X-rays affect the absorption probability.\textsuperscript{119,121}

A NEXAFS spectrum can be recorded in a number of different ways; directly by counting the number of transmitted X-rays and comparing it to the incident
intensity, or indirectly via the relaxation processes that follow the absorption. If any transmitted signal is to be measured, however, the sample must be thin enough to provide a detectable transmission signal, and either mounted on a transparent substrate or freestanding. The relaxation processes work as follows. After a photon has been absorbed and an electron has been promoted from a core level into an unoccupied state, an electron will soon relax and fill the hole in the core level. As this happens, energy is released, either by the emission of a fluorescent photon or by the ejection of an Auger electron. By detecting the emitted photons (known as fluorescent yield) or the electrons (known as electron yield), a quantitative measure of the absorption is obtained. The different detection modes are illustrated in Figure 4.4.2. The fluorescent yield gives information from deeper within the sample than electron yield, since the escape depth of photons is much higher than for electrons. However, for molecules made of light elements (such as carbon, nitrogen or oxygen), the fluorescent yield is much lower than the electron yield.\textsuperscript{122}

![Figure 4.4.2. Different detection modes in NEXAFS spectroscopy.](image)

The electron yield can in turn be measured in various ways, giving different surface sensitivity. In total electron yield (TEY), all electrons that manage to escape the sample are counted, often by measuring the sample drain current, but can also be measured using a channeltron. In partial electron yield (PEY), a channeltron is used together with a retarding voltage that prevents low kinetic energy electrons from entering the channeltron. Since electrons originating from deeper within the sample are very likely to have lost energy to inelastic scattering on their way out, the PEY has a higher surface sensitivity than the TEY. If instead an electron energy analyzer is used to detect the electrons, the detection window can be chosen to match the kinetic energy of electrons emitted by an Auger transition; i.e. electrons that have lost no energy to
inelastic scattering can selectively be measured. This mode is called Auger electron yield (AEY) and is the most surface sensitive of the different electron yield modes.

Since NEXAFS spectra of organic materials have rich features and can be used as molecular fingerprints, it is possible to deduce the composition of multicomponent blends from the NEXAFS spectra. If the spectra of the pure components are available, the spectrum of the blend can then be fitted to a linear combination of the pure components’ spectra. The coefficients in the linear combination then give the volume ratio of the components. This requires that the pure components do not react and form new components when blended. By using detection modes with different surface sensitivities, the composition can be probed at different depths.

4.5 Scanning transmission X-ray microscopy

Scanning transmission X-ray microscopy (STXM) is a technique that combines NEXAFS spectroscopy with microscopy, providing composition maps with chemical contrast. In materials that are mixtures of components whose NEXAFS spectra differ, STXM can be used not only to distinguish between the components, but also quantitatively determine the composition. A typical STXM setup is shown in Figure 4.5.1.

![Figure 4.5.1](image-url)

Figure 4.5.1. Schematic illustration of a STXM setup. Monochromatic X-rays are focused onto the sample by a zone plate. The sample is raster scanned relative to the beam while the transmitted X-rays are detected. Unwanted diffraction orders from the zone plate are blocked by an order sorting aperture (not shown in the figure).
First of all, the NEXAFS spectra of the pure components are examined to find the photon energies where the difference in absorption is the highest. These photon energies are then selected for image scans. The X-rays are focused onto the sample and the transmitted intensity is recorded as a function of x, y position as the sample is raster scanned, forming a transmission image for a certain photon energy. The focusing is done by a Fresnel zone plate that focuses the light by diffraction, and an order sorting aperture is placed after the zone plate, only letting first order light from the zone plate through. The smallest possible spot size is obtained by using spatially coherent light, and for a given X-ray wavelength, the spot size is limited by the outer zone width of the zone plate.\textsuperscript{117} For soft X-rays, using high quality zone plates, spatial resolutions of a few tens of nanometers can be achieved.\textsuperscript{117, 124} The fine movement of the sample relative to the beam is typically done in the x- and y-directions by piezoelectric stages, course x, y and z movement by stepper motors.

The STXM composition maps are obtained from the transmission images in a similar manner to how the composition of a blend is deduced by NEXAFS spectroscopy. In the image scans, pixel by pixel, the absorption at each photon energy is fitted to a linear combination of the pure components' absorption. This way, a chemical composition map can be obtained.

Usually, the absorption is measured in transmission mode as shown in Figure 4.5.1. That way, the deduced composition at each pixel will be an average vertically through the sample. However, it is also possible to obtain maps of the surface composition by measuring the absorption from the electron yield. Watts et al. used a channeltron in addition to the more regular X-ray detector to simultaneously measure the bulk and surface composition of a polymer blend.\textsuperscript{125}


4.6 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface sensitive technique that probes the occupied electronic states of a sample. Electrons ejected from the X-ray illuminated sample are collected and their kinetic energy is measured, thus giving information about the core-level or valence band from which they originated. XPS is based on the photoelectric effect\textsuperscript{126} and the relation between the electron binding energy $E_B$ and the measured kinetic energy $E_K$ is given by\textsuperscript{127}

$$h \nu = E_B + \phi + E_K$$

(4.3)

where $h$ is Planck’s constant, $\nu$ the photon frequency and $\phi$ the work function of the detector in electrical contact with the sample.

A schematic diagram of a typical XPS experiment is shown in Figure 4.6.1. In contrast to NEXAFS spectroscopy where the photon energy is scanned, XPS uses a fixed excitation energy and measures the kinetic energies of the emitted photoelectrons. This is done by an electron energy analyzer, often a concentric hemispherical analyzer that uses two concentric hemispheres with a voltage difference between them. For a given voltage and analyzer geometry, the electrons will move in different trajectories depending on the kinetic energy, thus enabling the kinetic energy to be measured. Smaller kinetic energy ranges can simultaneously be measured by a position sensitive detector as the electrons exit the hemispheres, while larger ranges are measured by sweeping the voltage difference between the hemispheres. In practice, however, the electrons are often pre-retarded before entering the analyzer to a predetermined kinetic energy known as the pass energy, so it is instead the retarding voltage that is swept. The reason for this is to get the same relative energy resolution for all kinetic energies.\textsuperscript{114, 127}
Figure 4.6.1. Typical XPS setup. Monochromatic X-rays cause the emission of photoelectrons whose kinetic energy is measured by an electron energy analyzer.

Once the kinetic energies are determined using equation 4.3, the binding energies of the different core-level and valence band electrons can be obtained. Since each element has its core levels at unique binding energies XPS allows for the identification of the elemental constituents at a sample’s surface as well as their relative concentration. In addition, the binding energy of a core level is affected by the local chemical environment, giving rise to core-level chemical shifts. These shifts can be rather large, for example, the difference between the C1s binding energy in graphite and in carbon dioxide is more than 7 eV.128

Not all electrons leaving a sample illuminated by X-rays are directly ejected photoelectrons. After a core level electron has been removed from an atom, an outer shell electron can refill the core level, whereby energy can be released by the emission of an Auger electron. Since the kinetic energy of an Auger electron is determined just by the energy level differences in the atom from which it originated, an Auger peak is easily identified by changing the excitation energy and observing whether the kinetic energy of the peak changes or not.

Another contribution to an XPS spectrum comes from all the electrons that on their way out of the sample lose energy to inelastic scattering. A photoelectron originating from an atom deeper within the sample than the inelastic mean free path is likely to interact inelastically with its surroundings and, apart from losing kinetic energy itself, also produce a cascade of secondary electrons. These electrons will contribute to a background signal; and since electrons with kinetic energy of a few eV have comparably long inelastic mean free paths, the low kinetic energy range of an XPS spectrum is dominated by secondary electrons.
Chapter 5
Introduction to the papers

Paper I

In this paper, the effect of the choice of solvent and the use of the additive chloronaphthalene in the coating process on the morphology of thin films of TQ1:PC$_{70}$BM blends is studied. The lateral morphology of the active layer of the solar cell was probed by AFM and STXM, the vertical morphology by SIMS and ellipsometry, and the surface composition by NEXAFS spectroscopy. The results show lateral phase-separated domains in films spin-coated from single solvents, with PC$_{70}$BM rich islands surrounded by a TQ1 rich phase. The lateral domain size increases with increasing solvent vapour pressure and decreasing PC$_{70}$BM solubility. When small amounts of chloronaphthalene are added to the coating solution no such lateral domains are observed. At the surface of the film a strongly TQ1-enriched layer is found in all TQ1:PC$_{70}$BM blends, rationalized by surface energy differences between TQ1 and PC$_{70}$BM. The influence of the active layer morphology on the solar cell performance is also studied. The addition of chloronaphthalene strongly improves the photocurrent and power conversion efficiency, correlated to finer lateral domain sizes and higher TQ1-enrichment at the cathode interface. Neither the open-circuit voltage nor the series resistance of the devices are sensitive to the differences in morphology. This indicates that the TQ1 enriched surface layer does not hinder charge transport and collection.

Paper 2

In this manuscript, the photo-degradation of a TQ1:PCBM blend is studied. Changes to the electronic structure of TQ1 and PCBM caused by illumination of films in ambient air are investigated and the photo-degradation in pristine materials and the blend are compared. The effect of the photo-degradation on the solar cell performance is also studied. NEXAFS spectroscopy shows that the unoccupied molecular orbitals of TQ1 are not significantly affected, while those of PCBM are severely degraded in pristine films. PCBM blended with TQ1 is found to degrade even faster than pristine PCBM. The occupied molecular orbitals of TQ1 exhibit changes upon light exposure, seen in the valence band spectrum, and photo-bleaching of TQ1 is observed. Solar cells in which the active layer has been exposed to light in air before depositing the top electrode show a greatly reduced performance. The photo-bleaching of TQ1 is
not large enough to explain these losses, which are mainly attributed to the PCBM degradation at the surface of the active layer.
Chapter 6
Conclusions and outlook

Being able to control the nanostructure is of great importance for producing efficient polymer solar cells. The results in this thesis demonstrate how, for TQ1:PC$_{70}$BM blends, the solution formulation can influence the active layer morphology and how that, in turn, affects the solar cell performance. The laterally phase-separated structures are chemically identified, showing that PC$_{70}$BM-rich islands are surrounded by a TQ1 rich phase. The TQ1-enrichment found at the surface of the active layer does not appear to hinder charge transport and collection.

The photo-degradation of a TQ1:PCBM blend and its effect on the solar cell performance is also studied. It is shown that PCBM degrades faster in the blend film than in a pristine film rationalized by the higher light absorption and subsequent electron transfer by TQ1, and it appears that the reduced solar cell performance is mainly due to the PCBM degradation.

To understand the photo-degradation mechanisms of PCBM, further experiments are needed. Controlled exposure of PCBM to oxygen and to water vapour during the illumination, for example could provide valuable information about the underlying causes for the degradation.

Since our results show that TQ1 is less prone to photo-degradation than PCBM, photo-stability studies aimed at finding or developing alternative more stable acceptor materials would be an interesting topic for future work.

Another potential way to improve the stability of polymer solar cells could be to replace the very commonly used, and acidic, PEDOT:PSS with alternative hole transporting layers, such as nickel oxide and molybdenum oxide, aiming at increasing both the stability and efficiency.
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Morphology and material stability in polymer solar cells

The performance of polymer solar cells depends strongly on the distribution of electron donor and acceptor material in the active layer. Understanding the connection between morphology and performance as well as how to control the morphology, is therefore of great importance. Furthermore, improving the lifetime has become at least as important as improving the efficiency for polymer solar cells to become a viable technology.

In this work, the relation between morphology and solar cell performance is studied as well as the material stability for polymer:fullerene blend films. A combination of microscopic and spectroscopic methods is used to investigate the lateral and vertical morphology as well as the surface composition. Lateral phase-separated domains are observed whose size is correlated to the solar cell performance, while the observed surface enrichment of polymer does not affect the performance. Changes to the unoccupied molecular states as a result of illumination in ambient air are observed for the fullerene, but not for the polymer, and fullerenes in a blend change more than pristine fullerenes. Solar cells in which the active layer has been illuminated exhibit greatly reduced electrical performance, mainly attributed to fullerene degradation at the active layer surface.