Diploma thesis

Microstructure and Temperature Stability of APFO-3:PCBM Organic Photovoltaic Blends

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In this thesis, the microstructure of organic photovoltaic APFO-3:PCBM bulk-heterojunction blends was examined. Earlier studies have focused on the microstructure after spin coating. This thesis aims to give a better insight into microstructural degradation as the films are annealed above the glass transition temperature, $T_g$, and the mixture approaches thermodynamic equilibrium. Electro- and photoluminescence studies indicate that the polymer and PCBM are intermixed on a scale shorter than the exciton diffusion length of 10 nm, even when annealed above $T_g$. The temperature stability of APFO-3:PCBM was also investigated with respect to the molecular weight of the polymer. The photovoltaic performance of these blends was found to be stable up to temperatures approaching the glass transition temperature, especially if a high molecular-weight APFO-3 grade was used.

The crystallization of PCBM was also investigated. Above $T_g$, PCBM crystallization was found to commence, albeit slowly at temperatures close to $T_g$. At elevated temperatures instead, micrometer sized crystals were observed to form. It was also noted that illumination while annealing APFO-3:PCBM thin films above $T_g$ affected PCBM crystallization, the origin of which is so far unclear although chemical degradation could be largely excluded.
Abstract

In this thesis, the microstructure of organic photovoltaic APFO-3:PC_{61}BM bulk-heterojunction blends was examined. Earlier studies have focused on the microstructure after spin coating. This thesis aims to give a better insight into microstructural degradation as the films are annealed above the glass transition temperature, T\textsubscript{g}, and the mixture approaches thermodynamic equilibrium. Electro- and photoluminescence studies indicate that the polymer and PC_{61}BM are intermixed on a scale shorter than the exciton diffusion length of 10 nm, even when annealed above T\textsubscript{g}. The temperature stability of APFO-3:PC_{61}BM was also investigated with respect to the molecular weight of the polymer. The photovoltaic performance of these blends was found to be stable up to temperatures approaching the glass transition temperature, especially if a high molecular-weight APFO-3 grade was used.

The crystallization of PC_{61}BM was also investigated. Above T\textsubscript{g}, PC_{61}BM crystallization was found to commence, albeit slowly at temperatures close to T\textsubscript{g}. At elevated temperatures instead, micrometer sized crystals were observed to form. It was also noted that illumination while annealing APFO-3:PC_{61}BM thin films above T\textsubscript{g} affected PC_{61}BM crystallization, the origin of which is so far unclear although chemical degradation could be largely excluded.
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1 Introduction

Accelerating global warming has been a hot topic in recent years. Although there are diverging opinions of the cause, precautious actions are taken worldwide. Combined with an increasing energy demand as developing countries strive to increase their living standards and a finite oil reserve, the need for new, especially renewable, energy resources are bigger than ever.

The sun is contributing vast amounts of energy in the form of photons to earth every day. If a share of these where to be converted into electric energy in an efficient way much of earth’s energy demand would be met.

The photovoltaic effect was discovered in 1839 by Edmund Bequerel. However, until the 1950s the usage was limited to photographic light meters, conveniently self powered. From then solar cells, or photovoltaic devices, were constructed mainly from silicon, but the cost per watt was much too high.

Currently there are solar cells made of silicon, which are able to convert 28%\(^1\) of the solar power. This is very close to the Shockley-Queisser limit at 30%\(^2\), which is the theoretical limit for power conversion. Still though, the cost per produced watt is limiting the usage to remote locations without a power grid.

The quest to lower the cost has put focus on organic materials since they are processable from solution, and thereby possible to produce at a low cost by large scale printing techniques. However, the efficiencies of these cells need to improve above 10%, compared to the 2-7%\(^1\) achieved so far, to compete on a cost per watt basis\(^3\).

Organic solar cells are composed of an active layer sandwiched between two electrodes. The active layer is a mixture of light absorbing donor molecules and electron accepting molecules. By tuning the bandgap of the donor molecules it is possible to affect the colour of the devices. This gives an artistic possibility for the use of organic solar cells, which can be integrated in roofs and facades of buildings.

Solar cells are current generators and the generation of photocurrent in organic solar cells depends strongly on the microstructure of the donor and acceptor blend. This can be affected by annealing to thermodynamically induced larger or smaller pure domains of donors and acceptors by phase separation or crystallization.

No matter what material a solar cell is made of, on a hot sunny day the temperature of the device approach 80\(^4\) degrees Celsius. Organic materials risk degradation at elevated temperatures, which makes it important to study the behaviour at temperatures close to the operating temperature.

This thesis will investigate how the morphology of an active layer composed of the donor:acceptor blend APFO-3:PC\(_{61}\)BM is affected by thermal annealing, particularly with respect to the glass transition temperature.
2 Background
The following section outlines the basic working principles of organic solar cells and discusses relevant aspects with regard to the electronic and thermodynamic properties of conjugated polymers.

2.1 Organic solar cells
The most promising organic photovoltaic (OPV) device architecture is the bulk-heterojunction (BHJ), whose active layer comprises an intimately mixed and interpenetrating electron-donor/-acceptor blend. It is necessary to provide for a large donor-acceptor interfacial area crucial for charge generation as well as good percolation for efficient charge extraction.

The light absorbing active layer is usually sandwiched between two electrodes, as illustrated in figure 2.1. Commonly, in test device configurations the anode is made of a layer of optically transparent conducting oxide, usually Indium Tin Oxide (ITO), which is coated with a thin layer of the polymer mixture polyethylenedioxythiophene:polystyrenesulfonate (PEDOT:PSS). This intermediate layer is required as it permits to smoothen the somewhat rougher ITO surface as well as to enhance the charge collection by introducing an intermediate energy level. A low work function metal such as aluminum is usually chosen as the cathode material and deposited by thermal evaporation. A thin buffer layer of, e.g., Lithium Fluoride (LiF) can be inserted between the active layer and the cathode to increase the photovoltage.
2.1.1 J(V) characteristics

The key parameters used to characterize the performance of photovoltaic devices are the open circuit voltage $V_{OC}$, short-circuit current density $J_{SC}$, fill factor $FF$ and the maximum power point MPP. The MPP is given by the maximum obtainable output power of the device divided by the power of the incident light and is related to the other key characterisation parameters as

\[
MPP = \frac{P_{\text{max}}}{P_{\text{light}}} = \frac{V_{OC} \times J_{SC} \times FF}{P_{\text{light}}}
\]

where $P_{\text{light}}$ is the power of the incident light. Clearly, maximising the $V_{OC}$, $J_{SC}$ and $FF$ is essential to achieve good photovoltaic performance.

$V_{OC}$ is the potential difference between the electrodes as the net current through the device is zero. This occurs when the photocurrent cancel out the dark current. The dark current is the current through the device in absence of light illumination due to room temperature black body radiation from the surroundings.

The short circuit current $J_{SC}$ is the current measured between the electrodes at zero voltage. The fill factor is a measure of the “squareness” of the JV-curve (figure 2.2) and is affected by the series and shunt resistance. For an ideal solar cell the fill factor equals 1, implying zero series resistance and infinite shunt resistance. In this case the square at $J_{\text{max}} \times V_{\text{max}} = V_{OC} \times J_{SC}$.

It is important to note that the device characteristics of a solar cell have to be measured under standard conditions regarding light intensity and wavelength distribution to be able to compare with other devices. Laboratory specific calibration is usually indicated by referring to the maximum power point, whereas externally verified device characterisation allows to define actual power conversion efficiencies.\(^6\)
2.1.2 HOMO/LUMO and photovoltage

Conjugated polymers, polymers with alternating single and double bonds, are commonly used as donors in OPV. This alternating structure results in three atoms strongly bound through sigma bonds to every carbon atom in the backbone and is called sp² hybridization. Since carbon has four valence electrons it leaves one electron in every carbon atom unhybridized. This p-shell electron will form a weaker pi-bond between two adjacent main chain carbon atoms and the original energy levels are split to a bonding \( \Pi \)-orbital and an anti-bonding \( \Pi^* \)-orbital. As more carbon atoms are added, further energy level splitting will occur and eventually form a \( \Pi \)-band and a \( \Pi^* \)-band, equivalent to inorganic valence and conduction bands.

The top of the \( \Pi \)-band is referred to as the highest occupied molecular orbital HOMO or the ionization potential and the bottom of the \( \Pi^* \)-band as the lowest unoccupied molecular orbital LUMO or the electron affinity.

Provided a polymer segment is planarised, electrons will delocalize over its entire length, i.e. the conjugation length, which influences the energy gap, or band gap, between the HOMO and the LUMO. Longer conjugation length results in a lower bandgap, which lies somewhere between 1 and 3 eV in polymers used for solar cells. The band gap decides the lowest optical excitations.

\( V_{OC} \) in BHJ OPV devices have been found to depend on the ionization potential of the donor and it scales with the difference in energy between the HOMO of the donor and the LUMO of the acceptor (figure 2.3).

\[
e V_{OC} = E_{LUMO,acceptor} - E_{HOMO,donor} - 0.3 \text{ eV}
\]

where e is the elementary charge. A recent theory explain that this potential loss is due to recombination via the charge transfer state (see 2.1.3) and that the loss would be minimized if charge transfer recombination could be limited to be radiative only. Studies have shown that also the microstructure can affect \( V_{OC} \). For amorphous materials \( V_{OC} \) will be larger than for crystalline compounds because charges can delocalize over several molecules in ordered systems, which raises the HOMO of the donor, thereby reducing the gap to the acceptor LUMO.
2.1.3 Microstructure and photocurrent

The first step towards photocurrent generation is efficient light absorption by the active layer materials, primarily by the p-type conjugated polymer in polymer:small-molecule OPV blends, which creates a strongly bound electron-hole charge-pair (exciton). Good light absorption can usually be achieved with an active layer thickness around 100 nm or more. Subsequently, the exciton has to diffuse to a donor/acceptor interface where it can dissociate into a weakly bound charge-pair (charge transfer state). Here, it is necessary that the donor and acceptor are intimately mixed as excitons can only diffuse across a distance of about 10 nm in conjugated polymers before recombining. The driving force for dissociation is the energy reduction from donor LUMO to acceptor LUMO. The charge transfer (CT) state is then required to split up into free charge carriers, that is electrons and holes, a process which is assisted also by sufficient delocalization of charges across reasonably pure semiconductor domains\textsuperscript{13,14}. Finally, enabled by the interpenetrating electron-/hole conducting domains of a bulk-heterojunction free charge carriers must travel to the electrodes in order to contribute to the produced photocurrent. Unfortunately, during each step recombination losses can occur, which reduce the number of extracted charges and thus the collected photocurrent (figure 2.4).

Figure 2.4. Illustration of energy levels corresponding to photocurrent generation. 1 – Light is absorbed and an exciton is created. 2 – The exciton diffuses to the donor/acceptor interface. 3 – Exciton dissociation. The CT exciton is created. 4 – Charge separation and transfer to the electrodes.

The composition and microstructure of the active layer is crucial for efficient photocurrent generation. The fraction of the strongest absorbing component should be maximized in order to achieve the largest possible exciton generation. Furthermore, as the active layer is usually required to be thin to avoid high resistive losses, it is important to tune its thickness, in order to avoid destructive interference between the incident light and the light reflected by the back electrode.

The short exciton diffusion length limits the possible dimension of pure domains, in addition to the demand for a high interfacial area, necessary for exciton dissociation to the CT state. This suggests a complete miscibility. However, pure domains are necessary to enhance charge separation. Furthermore, there have to be sufficient percolation pathways reaching the electrodes for efficient charge transport.
2.1.4 Choice of BHJ materials

Organic BHJ solar cells can be categorized into three classes, which differ in the choice of active layer donor - acceptor materials:

1. Polymer - Polymer\(^ {15}\)
   These blends readily permit efficient charge transport pathways throughout the bulk enabled by the macromolecular nature of both the hole- and electron-conductor. However, owing to entropy reasons the miscibility of the two polymers is low, which encourages large scale phase separation and results in a low interfacial area.

2. Small molecule – Small molecule\(^ {16}\)
   Provided they are solution processable, high miscibility can be achieved but charge-transport by the minority fraction is restricted because of insufficient percolation.

3. Polymer – Small molecule\(^ {17}\)
   Such mixtures combine the advantages of the two previous types of BHJ blends, that is an acceptable miscibility of the two components as well as efficient percolation of either species, especially if the small-molecular semiconductor is chosen to be the majority fraction. Furthermore, the microstructure of such blends is relatively easy to manipulate. Hence, polymer-small molecule mixtures are the most widely studied BHJ systems and are also the focus of this thesis.
2.1.5 Donor and acceptor materials used in this thesis

The donor and acceptor materials used in this study are the polymer APFO-3 and the small-molecular fullerene derivative PC₆₀BM (figure 2.5).

APFO-3 is a copolymer composed of a dioctyl-substituted fluorene unit alternating with a dithiophene benzothiadiazole-based donor-acceptor-donor segment.

PC₆₀BM is a small molecule composed of a functionalized C₆₀ cage. It is regularly used as acceptor in polymer solar cells because of its high electron affinity and electron mobility.

![Chemical structure of APFO-3 and PC₆₀BM](image.png)

Figure 2.5. The chemical structure of (left) APFO-3, poly[2,7-(9,9-dioctylfluorene)-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] and (right) PC₆₀BM, [6,6]-phenyl-C₆₁-butyric acid methyl ester

In this study APFO-3 with two different molecular weights (Mₘ) were used. The low Mₘ is referred to as APFO-3₅ₖ and the high Mₘ as APFO-3₆ₖ. Key parameters of these both and PC₆₀BM are found in table 2.1.

<table>
<thead>
<tr>
<th>Name (unit)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>Mₙ¹ (kDa)</th>
<th>Mₘ² (kDa)</th>
<th>PDI³</th>
<th>Tₘ (°C)</th>
<th>Vₜₜ (V)</th>
<th>Jₛₙ₅ (mA cm⁻²)</th>
<th>η⁵ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>APFO-3₅ₖ</td>
<td>-5.8</td>
<td>-3.4</td>
<td>5</td>
<td>12</td>
<td>2.4</td>
<td>110</td>
<td>1.02</td>
<td>4.6</td>
<td>2.2²</td>
</tr>
<tr>
<td>APFO-3₆ₖ</td>
<td>X⁶</td>
<td>X⁶</td>
<td>36</td>
<td>65</td>
<td>1.8</td>
<td>120</td>
<td>0.99</td>
<td>5.7</td>
<td>2.6²</td>
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<tr>
<td>PC₆₀BM</td>
<td>-6.6</td>
<td>-4.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>130</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

1 The molecular number Mₙ is the sum of the number fraction i of molecules with the molar mass i, Da = kg mol⁻¹
2 The molecular weight Mₘ is the sum of the weigh fraction j of molecules with the molar mass j, Da = kg mol⁻¹
3 The polydispersity index, PDI = Mₘ/Mₙ, and measure the spread of length
4 Tₘ is the glass transition temperature of the material, see 2.2.1
5 Comparative values from one unpublished study by Müller et.al. Efficiencies of 3.5% and currents of 5.7 mA cm⁻² have been seen for APFO-3₅ₖ
6 The HOMO is likely somewhat higher in APFO-3₆ₖ as a longer chain increase the probability for a longer conjugation length.
7 Blended with PC₆₀BM in a ratio of 1:4.

APFO-3:PC₆₀BM blends show high open circuit voltages, around 1V. Theoretically, this blend should be very efficient in terms of OPV performance. However, so far the photocurrents have been disappointingly low. Nevertheless, this blend is interesting for tandem or folded solar cell architectures.¹⁸
2.2 Polymer Thermodynamics

The following section outlines the thermodynamic principles that govern the phase separation of polymer/small molecule blends and discusses crystallisation of in particular the small-molecular moiety.

2.2.1 Thermal transitions and structures

In the solid state, polymers can be either of amorphous, liquid-crystalline or semi-crystalline nature. Amorphous polymer systems do not order mainly due to an irregular chain conformation with respect to pendant groups.

Polymers are in a glassy state at temperatures below the so called glass transition temperature, $T_g$. In this state the chain segments are believed to be frozen in with a very small segmental mobility. At temperatures around and above $T_g$ the chain segments will be able to slide past each other more easily, hence enabling microstructural rearrangements within the polymer system.

Amorphous polymers are considered to be in the liquid state directly above $T_g$, whereas semi-crystalline polymers only reach the liquid state after additional heating to temperatures above the melting temperature. Likewise, polymers that only display a liquid-crystalline phase such as the APFO-3 studied in this thesis can be considered liquid above $T_g$. These concepts also apply to small molecules, such as PC$_{61}$BM, which is often processed into largely amorphous structures (especially after spin-coating) but can develop a crystalline phase when heated to temperatures sufficiently higher than $T_g$.

The $T_g$ of a polymer is mainly affected by the linearity of the chain, which influences its rotation radius around sigma bonds, also known as crank-shaft motion. The side-chain flexibility and the fraction of free volume also affect the possible rotations of the chain.

The fraction of free volume depends strongly on the degree of polymerisation. Chain-ends are associated with extra free volume and thus reduce the $T_g$. Hence, higher molecular-weight polymers tend to have a higher $T_g$ than low molecular weight materials. Polymer materials usually contain a collection of chains that vary in length, expressed by the polydispersity index (PDI). As a consequence, the glass transition does not occur at a fixed temperature but rather over a range of temperatures; the $T_g$ usually indicates the midpoint of this temperature interval.
2.2.2 $T_g$ of some popular OPV polymers

The $T_g$ of different conjugated polymers can vary substantially. Primarily this is explained by the crank-shaft model, which stipulates that a large radius limits rotation due to blocking effects by adjacent polymers, thereby resulting in an increased $T_g$. Applied to the polymers in table 2.2, the linear P3HT and MDMO-PPV can rotate around the backbone axis relatively freely and thus feature a low $T_g$. APFO-3 has a significantly larger crank-shaft for rotation between the flourene and thiophene groups, hence a higher $T_g$. The high $T_g$ PPV also has stiff side groups reducing the rotation possibilities further.

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical structure</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High $T_g$ PPV</td>
<td><img src="image1.png" alt="Chemical structure" /></td>
<td>150</td>
</tr>
<tr>
<td>APFO-3</td>
<td><img src="image2.png" alt="Chemical structure" /></td>
<td>110-120</td>
</tr>
<tr>
<td>MDMO-PPV</td>
<td><img src="image3.png" alt="Chemical structure" /></td>
<td>45</td>
</tr>
<tr>
<td>P3HT</td>
<td><img src="image4.png" alt="Chemical structure" /></td>
<td>10</td>
</tr>
</tbody>
</table>
2.2.3 Phase separation
The thermodynamical miscibility of two materials is governed by the difference in Gibbs free energy between the mixed and phase separated state. A decrease in free energy upon mixing of the two materials is a necessary condition for miscibility. The Gibbs free energy of mixing is defined as

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$$

where $\Delta H_{\text{mix}}$ is the change in enthalpy and $\Delta S_{\text{mix}}$ the change in entropy upon mixing. In the case of mixing a polymer with a small molecule, as is done to create OPV BHJ blends, the miscibility is limited because of the small entropy gain upon mixing, especially if the polymer is of high molecular weight.

The miscibility of two materials will influence $T_g$ of the blend. Strong phase separation results in two $T_g$s whereas highly miscible materials only have one $T_g$. Low molar mass materials like small molecules often have a depressive effect on the common $T_g$ with respect to the pure components.

Phase separation of a binary blend can be promoted by crystallization of one or both of the components.19
2.2.4 Crystallization kinetics

The thermodynamic condition for crystallization is given by

$$\Delta G_{\text{crystallization}} = \Delta G_{\text{Bulk}} + \sum A_i \gamma_i$$

where $\Delta G_{\text{Bulk}}$ is the change in free energy from melt to crystal and $\gamma_i$ is the surface energy of the surface $A_i$ originating from the new surfaces created by crystallization. The surface contribution is always positive and implies that the initial nucleation has to overcome an energy barrier to form a stable nucleus. This process is called primary nucleation.

Primary nucleation mainly occurs at foreign particles, which reduce the free energy barrier and thereby the critical size to form a stable nucleus. This is known as heterogeneous nucleation. This is in contrast to homogeneous nucleation, where nucleation sites are provided by the crystallising material itself.

![Figure 2.6. The bell shaped crystal growth rate depending on exponential functions. $\Delta G$ limits the primary nucleation while $\Delta \Phi$ defines the diffusion of molecules to the surface.](image)

The rate of crystallization is determined by the rate of nucleus formation as well as the diffusion of additional molecules to the nucleus. Practically, below $T_g$ there will be no diffusion since the molecules are frozen in but as temperature increases the diffusion will increase exponentially. Nucleation on the other hand tends to exponentially decrease above $T_g$. Thus, for a crystalline material, above the melting temperature $T_m$ no nucleation will occur. The resulting bell-shaped nucleation rate is illustrated in figure 2.6.\(^{20}\)
3 Results and discussion

The temperature stability of the active layer in APFO-3:PC$_{61}$BM solar cells were studied together with the evolution of the microstructure as a result of thermal treatment, particularly with respect to T$_g$. The crystallization of PC$_{61}$BM and how this process is affected by light illumination were also investigated.

3.1 Temperature stability of APFO-3:PC$_{61}$BM

In order to establish the temperature stability of APFO-3:PC$_{61}$BM blends, a series of solar cells were fabricated comprising active layers that were thermally treated at temperatures up to 190°C. This is in contrast to the established preparation route for this OPV mixture, which usually only incorporates spin-coated active layers. The donor:acceptor ratio was selected to be 1:4 APFO-3:PC$_{61}$BM as this composition has been found to yield maximum photocurrent generation. Initial experiments were done with relatively low M$_W$ APFO-3, APFO-3$_{5k}$, which has been most thoroughly studied in previous reports. Thermal treatment of the active layer in the absence of light illumination was conducted under nitrogen atmosphere before deposition of the top electrode in order to avoid possible degradation effects unrelated to the microstructure of the OPV blend.

Gratifyingly, the device performance was found to be little affected up to temperatures approaching T$_g$ of these blends, that is ~90°C (Figure 3.1).

![Figure 3.1. Performance factors versus temperature for APFO-3$_{5k}$:PC$_{61}$BM 1:4 solar cells. The standard deviation was estimated by comparing a series of 4 devices on the same substrate. V$_{OC}$ show a slight decrease while the MPP drop is more pronounced at at 110 °C, coinciding with the T$_g$ of this blend. J$_{SC}$ and FF start to decline at 90°C. An increase of J$_{SC}$ is noted at 50°C and FF increase slightly up to 90°C.](image-url)
This observation is in agreement with a previous dynamic temperature study of this blend\textsuperscript{21}, which reported an irreversible decrease in device performance after heating the solar cells to $T > 70 \text{ °C}$.

The operating temperature of solar cells approaches 80°C on warm sunny days. This indicates that APFO-3$_{3k}$:PC$_{61}$BM 1:4 OPV blends are temperature stable. However, the devices were annealed for one hour. Earlier studies have shown declining performance after extended annealing times also below $T_g$\textsuperscript{4}. The slight reduction of $J_{SC}$ at 90°C is consequently likely to be enhanced after more extended annealing periods.
The chemical stability of the active layer and especially the light-absorbing polymer was confirmed by a series of UV-vis absorbance spectra (figure 3.3), which displayed a slight blue shift of 8 nm after annealing thin APFO-3:PC_{61}BM films at T > T_g, that is 130°C. This is ascribed to the polymer adopting a somewhat more contracted chain conformation with respect to the out-of-equilibrium structure frozen in after spin-coating. Regardless, such minute changes in light absorbance are unlikely to account for the pronounced drop in photovoltaic performance.

The PDI of the low molecular polymer grade APFO-3_{5k} suggests that a fraction of polymer chains are of significantly lower chain length and thus feature a lower T_g, as confirmed by the low onset of the glass transition. From figure 3.4 it is obvious that the onset of T_g may be drastically lower than the nominal 100 – 110 °C.

![Figure 3.4.](image)

Figure 3.4. The dependence of T_g on the average molar weight for APFO-3 from an unpublished study by Müller et. al. The curve is increasing rapidly for low M_w resulting in a pronounced drop of T_g onset for polydisperse low M_w APFO-3. The curve levels out for higher M_w resulting in a T_g that is less sensitive to changes in PDI. The black dots indicate the T_g for APFO-3_{5k} and APFO-3_{36k} respectively. The grey areas represent the respective standard deviation (SD) of M_w calculated as SD = M_n(PDI – 1)^{0.5}. An onset of APFO-3_{5k} is indicated at roughly 90°C. Due to the flat behaviour above 20 kg mol\(^{-1}\) the T_g onset of APFO-3_{36k} should be at 120°C.

Thus, considering the presence of oligomeric acceptor species with much reduced T_g, it is little surprising that the photovoltaic performance of APFO-3_{5k}:PC_{61}BM blends is affected at T << T_g. This makes it interesting to study the behaviour of higher M_w APFO-3, for which the T_g should not only be elevated but also less sensitive to small variations in chain length.

Thus, in a further set of experiments the photovoltaic performance of APFO3_{36k}:PC_{61}BM blends were studied. As illustrated in figure 3.5, compared to the low M_w APFO-3 blends a definitive improvement of the temperature stability can be discerned. The performance drop is postponed by 20 degrees and, in addition, is less dramatic for T > T_g.
Figure 3.5. Performance factors versus temperature for APFO-33:PC61BM 1:4 solar cells. The standard deviation was estimated by comparing a series of 4 devices on the same substrate. $V_{OC}$ show a decline at 130°C as well as $J_{SC}$. FF and MPP do not decrease below 110°C. The low FF is probably due to an active layer thickness of roughly 250 nm, which is thicker than the optimal for this blend. The large spread of $J_{SC}$ is likely due to partly uneven films with respect to thickness as valleys with thicknesses of 50 nm are present.

Figure 3.6. Representative JV-curves of thermally treated APFO-33:PC61BM 1:4 solar cells. Respective annealing temperatures in °C are plotted next to the curve.
It should be noted that the $T_g$ presented are for the pure polymers. In blends with PC$_{61}$BM $T_g$ can be depressed according to the earlier discussion of small molecule additives. However, according to unpublished results by Müller et. al. this is not the case.

This indicates that high $M_w$ APFO-3 could be as, or even more, temperature stable, than so far reported OPV mixtures, such as those based on $M_w$ PPV$^4$. However, a long time temperature study would further confirm this observation.

In conclusion the microstructure of low $M_w$ APFO-3:PC$_{61}$BM blends is likely to thermally degrade as the operation temperature on sunny days is close to the onset of degradation of $J_{SC}$. In most significant contrast, high $M_w$ APFO-3: PC$_{61}$BM blends promise exceptional temperature stability close to the $T_g = 120^\circ$C, even though a long time study should be performed. The degradation of OPV performance is clearly connected to the $T_g$ of the active layer.
3.2 Microstructure below $T_g$

Surprisingly, solar cell characteristics of devices based on APFO-3$_{35}$ appeared to be positively affected at temperatures far below $T_g$, e.g. a slight increase in $J_{SC}$ for devices annealed at 50°C and an increase of FF up to 90°C was observed (figure 3.1). In order to further investigate this observation, a series of photoluminescence (PL) spectra were recorded of thin APFO3-PC$_{61}$BM films annealed for 5 min at various temperatures in the absence of light illumination as displayed in figure 3.7. In particular the relative intensity of the PL peak at 650 nm to the CT peak at 820 nm was affected by thermal treatment.

![Figure 3.7. Absolute (left) and normalized to CT emission peak (right) photoluminescence of thermally treated APFO-3:PC$_{61}$BM 1:4 thin films. The peaks at 1060 nm are laser overtones.](image)

Evidently, the relative ratio between the CT peak and the peak at 650 nm is affected by thermal annealing even at $T \ll T_g$. The intensity of the peak at 650 nm in figure 3.7 decreases with increasing temperature below $T_g$ but after reaching its point of deflection close to $T_g$ it again increases with temperature. However, follow up studies were not able to confirm the decrease corresponding to annealing temperatures below $T_g$. Though, these where performed in situ with the laser turned on during the whole experiment affecting PC$_{61}$BM crystallization (see 3.4.1). Nevertheless, an increase of the absolute peak has been confirmed after annealing at $T > T_g$.

One possible explanation of the origin of the peak at 650 nm may be a combination of effects from the filter and the detector used in the PL setup, resulting in an increased peak as light is more efficiently spread by the sample. This would explain an increased peak as PC$_{61}$BM start to crystallize close to $T_g$ since the crystals forming will increase the spread of the light.

Another hypothesis of the origin of the peak at 650 nm is to connect it to a blue-shifted polymer emission. The increase caused by temperature is then due to PC$_{61}$BM diffusion through the polymer matrix. However, as the peak also is present in the pure PC$_{61}$BM PL spectra (figure 3.8) excited by a green laser at 530 nm, this is unlikely to be the case. If a blue laser of shorter wavelength is used to excite the same film, the peak vanishes. This further suggests filter/detector reasons for the peak as the filter is changed between blue and green lasers. Though, if this where the case, an increased peak should be seen also at 1060 nm for the green laser as PC$_{61}$BM crystals form. The lack of such observations contradicts this theory so far.
Figure 3.8. Photoluminescence of pure PC$_{61}$BM excited by a green (grey curve) and a blue (black curve) laser.

All devices were spin-coated from orthodichlorobenzene (oDCB) which generally results in a homogenous microstructure$^{22}$. If a phase separation or crystallization of PC$_{61}$BM was to occur to some extent below $T_g$ this may positively affect device performance as limited phase separation can indeed promote dissociation of the charge transfer exciton. However, extended phase separation into exceedingly coarse domains would eventually negatively affect charge dissociation resulting in a decrease in device performance as seen for the devices annealed above $T_g$.

The positive effects of solar cell performance below $T_g$ may indicate a beneficial microstructural evolution. However, it would be more trustworthy if observed in additional experiments.
3.3 Microstructure above $T_g$

Most previous studies have focused on low molecular-weight APFO-3 and hence APFO-3$_{3k}$ is employed during the remainder of this thesis, which aims to study the microstructure development of APFO-3:PC$_{61}$BM blends above $T_g$.

PL studies at room temperature have demonstrated efficient quenching of APFO-3 luminescence as PC$_{61}$BM is added, which has been ascribed to the formation of CT states$^{23}$. Blends, quenched after thermal treatment above $T_g$, in order to allow the material to approach quasi-equilibrium, were investigated (figure 3.9) and the intensity of pure polymer luminescence was shown to decrease by a factor of 100 as 20% PC$_{61}$BM was added, similar to previous studies$^{24}$. The peak position were also redshifted with the addition of PC$_{61}$BM indicating a transition to the lower energy CT state.

![Figure 3.9. Absolute photoluminescence of APFO-3:PC$_{61}$BM with the weight % PC$_{61}$BM increasing from pure polymer to 1:4, after thermal treatment at 130°C.](image)

The transfer from pure polymer emission to the charge transfer state is further elucidated by the normalization of luminescence peaks in figure 3.10. As the PC$_{61}$BM part of APFO-3:PC$_{61}$BM ratios exceed 4:1, the CT peak is only slightly redshifted by further addition of PC$_{61}$BM and the curve level off at 1.45 eV. Temperature treatment was also performed at higher temperatures shown in the energy peak diagram (figure 3.10). No apparent difference compared to the blends annealed at lower temperatures was observed, except a possible small blueshift for the 9:1 ratio.

To further evaluate the polymer charge-transfer state transition an electroluminescence study was performed with more narrow concentration steps in the polymer emission dominated region (figure 3.11). The redshift with increasing PC$_{61}$BM is in very good agreement with the results from PL. However, all peaks are further redshifted as compared to the PL positions. This is due to the difference in excitation method used. PL excitation creates an exciton in the polymer, which have to diffuse to an interface to result in CT emission. Radiative recombination from excitons not reaching the interface contributes to polymer emission. As for the EL, the charges injected strive to minimize their energy which they do at the donor/acceptor interface, thereby resulting in CT formation and subsequent CT emission upon recombination.
The slight redshift seen at PC$_{60}$BM concentrations above a 9:1 ratio in the EL spectrum in figure 3.12 likely corresponds to the formation of enhanced pure PC$_{60}$BM domains, enabling increased delocalization of CT excitons$^{25}$, thereby reducing the emission energy. However, the possible contribution of different degrees of PC$_{60}$BM crystallization at different PC$_{60}$BM ratios and the increase of the dielectric constant from increasing PC$_{60}$BM shares should not be ruled out.

The slight redshift in the PL spectra of compositions with PC$_{60}$BM shares above 1:4 (figure 3.10) is therefore likely a combination of an increasing amount of PC$_{60}$BM further quenching the polymer emission and also the formation of larger pure PC$_{60}$BM domains delocalizing the CT exciton. The saturation of PC$_{60}$BM miscible in the polymer domains is thus likely to occur at lower PC$_{60}$BM parts than the 2:3 ratios indicated in figure 3.10.
Figure 3.12. Peak position versus wt% APFO-3. The pure polymer emission is quenched already at a APFO-3:PC\textsubscript{61}BM ratio of 19:1. The curve levels off at a ratio of 2:3, indicating phase-separated PC\textsubscript{61}BM domains at higher PC\textsubscript{61}BM fractions.

This concludes that as the microstructure reaches a thermodynamic quasi-equilibrium after annealing above $T_g$, basically no pure polymer domains larger than the exciton diffusion length of 10 nm can be found for PC\textsubscript{61}BM contents above 4:1. Phase separation in the blends studied here expresses itself by PC\textsubscript{61}BM clustering or crystallization. This is further studied in the next section.
3.4 PC<sub>61</sub>BM Crystallization

Drop cast films of APFO-3:PC<sub>61</sub>BM 20:80 were annealed for four hours above T<sub>g</sub> at 130°C under nitrogen flush to investigate the rate of PC<sub>61</sub>BM crystallization (figure 3.13).

![Optical micrograph of APFO-3:PC<sub>61</sub>BM 20:80 drop cast film annealed at 130°C. PC<sub>61</sub>BM crystals have formed on the edge (left) of the film. Crystals of smaller size could also be observed in the center (right) of the film.](image)

When blended with other conjugated polymers such as P3HT<sup>26</sup> or MDMO-PPV<sup>4</sup>, the degree of PC<sub>61</sub>BM crystallization induced by thermal treatment has been shown to depend on annealing temperature, time, concentration and/or spatial confinement due to electrodes<sup>27,28</sup>. In this study no electrodes were used; films were cast on a glass substrate. Annealing temperatures just above T<sub>g</sub> allow for efficient nucleation of PC<sub>61</sub>BM crystallites but limited growth because of restricted diffusion. Nevertheless, after annealing at 130°C small visible crystals can be seen in figure 3.13 in the thicker edge of the film, as drop-casting results in the coffee stain effect. This may also create concentration gradients in the edge enhancing the crystal growth. Largely separated smaller crystals were also present in the thinner center of the film.

To investigate whether an extensive nano sized nucleation had occurred in the thin centre, a drop-cast film of APFO-3:PC<sub>61</sub>BM annealed at 220°C was compared to a drop-cast film annealed for four hours at 130°C prior to annealing at 220°C (figure 3.14).

![Optical micrograph of drop cast films of APFO-3:PC<sub>61</sub>BM 20:80 annealed 20 minutes at 220 °C (left) and annealed four hours at 130 °C before annealing 20 minutes at 220 °C (right). The fan-like dark shapes are PC<sub>61</sub>BM crystals and the smooth parts in between are APFO-3 mixed with PC<sub>61</sub>BM. The light areas around the crystals are PC<sub>61</sub>BM depleted regions<sup>25</sup>.](image)
The fan-like crystals increased in number and their size were reduced in the pre-annealed film. This denotes crystallization at 130°C but since the crystal coverage of the both films was comparable, it is likely to be very slow and mainly nucleation favoured.

The observed PCBM crystals were of micrometer size; thus they, may short-circuit solar cells, which are roughly 100 nm thick. However, the thermal treatment of both low and high $M_w$ APFO-3 devices at 190°C indicated that this was not the case.

It has been shown that APFO-3:PC$_{61}$BM 1:4 blends roughly have a 1:1 ratio in the vicinity of the electrodes. Further studies on spin coated films of lower PC$_{61}$BM ratio, show less visible crystal coverage (figure 3.15), simply due to lower excess PC$_{61}$BM fraction available for nucleation and diffusion. If we assume that the APFO-3:PC$_{61}$BM ratio is 1:1 close to the electrodes, this would imply that crystallization is strictly hampered there, generating a finely intermixed layer between the large crystals and the electrodes. However, the 1:1 ratio close to the electrodes may strongly depend on processing conditions implying other explanations.

![Figure 3.15. Spin coated films of APFO-3:PC$_{61}$BM from oDCB of ratio 1:4 (left), 2:3 (center) and 1:1 (right). The size and number of crystals decrease with decreasing PC$_{61}$BM content.](image)
3.4.1 Light hampering crystal growth

During the study of PC$_{61}$BM crystallization, illumination was found to strongly affect the crystallization of PC$_{61}$BM (figure 3.16).

![Micrographs (a and b)](image)
![Micrographs (c and d)](image)

Figure 3.16. Optical micrographs of APFO-3:PC$_{61}$BM 1:4 drop cast, a and b, pure PC$_{61}$BM drop cast, c and d. Film b and d were illuminated during annealing at 130°C for 30 minutes in a nitrogen-flushed atmosphere. Film a and c were annealed at 130°C for 30 minutes in the dark. All films were subsequently annealed at 220°C. As for pure PC$_{61}$BM, the images indicate that the number of nucleation sites decreases resulting in larger crystals.

Clearly, illuminating APFO-3:PC$_{61}$BM thin films while annealing above $T_g$ affect the material by limiting possible PC$_{61}$BM crystallization to crystals below micrometer size. This could be due to an increased nucleation forming many nano sized crystals. However, the pure PC$_{61}$BM film has larger crystals formed after illumination pointing to other causes such as thermal or chemical degradation.

Illumination was shown to reduce crystallization also at annealing temperatures of 70°C (figure 3.17), that is far below $T_g$. This exposes a vulnerable feature of PC$_{61}$BM devices which may need to be accounted for during processing as well as device operation. However, the heat contribution from the light source may have increased the temperature to reach the onset of $T_g$. 

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Figure 3.17. APFO-3:PC₆₁BM drop cast film annealed at 70°C. The upper left part was illuminated while the other part was kept in dark. The film was subsequently annealed at 220°C.

In order to detect possible thermal degradation, UV-visible absorption spectra were recorded (figure 3.18). A slight blueshift of polymer absorption was detected between the as-cast film and the two annealed films, but no shift was seen between the film annealed in dark and the film annealed under light illumination.

Figure 3.18. Absorbance of APFO-3:PC₆₁BM 1:4 as cast, annealed at 130°C under illumination and in dark.

To further examine whether the reduced crystallization was due to chemical degradation, such as oxidation or photopolymerisation, infrared absorbance (IR) spectra were recorded for both pure and blend films annealed in dark and under illumination (figure 3.19).
The IR spectra did not show any chemical degradation of either APFO-3 or PC$_{61}$BM. However, studies of laser light effects on PC$_{61}$BM in the visible spectrum have been found to induce dimerization$^{32}$ of PC$_{61}$BM molecules. Other studies have demonstrated polymerization of C$_{60}$ fullerenes$^{33}$, also induced by laser light in the visible spectra. Though, this might be the case, it should result in a change of the chemical structure of the PC$_{61}$BM cage in the IR spectra as this dimer bonding is between the PC$_{61}$BM cages.

To determine whether the illumination, whilst annealing, effects solar cell performance, a limited series of solar cells were fabricated (figure 3.20).
Figure 3.20. Solar cell performance of annealed films under illumination (grey) compared to films annealed in dark (black).

No significant effect of illumination on solar cell performance can be detected, except a slight reduction of FF. As for previous series a pronounced performance drop is seen from annealing above $T_g$. Below $T_g$ FF increase slightly while $J_{SC}$ show a slight reduction.

Figure 3.21. Representative JV-curves of thermally treated APFO-3:PC$_6$BM 1:4 solar cells under illumination and in dark. Respective annealing temperatures in °C are plotted next to the curve. Gray curves – illuminated while annealing, Black curves – annealed in dark.
4 Conclusions
The photovoltaic performance of APFO-3:PC\textsubscript{61}BM blends that comprise low M\textsubscript{w} APFO-3 is found to be stable with respect to one hour thermal treatment at temperatures up to 90°C. This is unlikely to be sufficient for long term operation as solar cells can be expected to be exposed to this range of temperatures for much longer periods of time on hot and sunny days. However, APFO-3:PC\textsubscript{61}BM blends based on the higher M\textsubscript{w} APFO-3 were shown to be stable up to 110°C and thus are an excellent candidate for long time thermal stability studies. Most significantly, the temperature stability could be connected to softening of the OPV blends, as the onset of degradation of the devices coincided with the onset of T\textsubscript{g}. A possible explanation to the performance drop above T\textsubscript{g} is the diffusion of PC\textsubscript{61}BM into pure polymer domains that may have formed after spin-coating, as this would substantially reduce the likelihood of the CT exciton dissociating into free charge carriers.

Probably, microstructural changes were also induced by annealing below T\textsubscript{g} and may have contributed to an increased FF of solar cells. However, their origin requires further investigation. Thermal treatment above T\textsubscript{g} resulted in an almost complete transfer from polymer emission to CT emission for APFO-3:PC\textsubscript{61}BM ratios of 4:1 as evidenced by EL an PL studies. This concludes that no pure polymer domains larger than the exciton diffusion length of 10 nm are present in the blend as the microstructure approaches thermodynamic equilibrium. Provided there is sufficient molecular mobility, e.g. if T > T\textsubscript{g}, any additional PC\textsubscript{61}BM will phase-separate and eventually crystallize.

The redshift of the CT peak position at higher PC\textsubscript{61}BM ratios than 4:1 was likely due to a combination of further intermixing with the polymer and increased delocalization of the CT exciton as the excess PC\textsubscript{61}BM form pure domains.

For all investigated compositions, thermal treatment at elevated temperatures did not noticeably affect the CT peak position of APFO-3:PC\textsubscript{61}BM. This is despite of the fact that crystallization of PC\textsubscript{61}BM was shown to occur at high crystallization rates for 1:4 compositions. This may be explained by the inherent miscibility of APFO-3:PC\textsubscript{61}BM, only allowing excess PC\textsubscript{61}BM to crystallize. The drastic reduction in the number of large PC\textsubscript{61}BM crystals in blend films as the acceptor fraction is reduced strengthens this argument.

At temperatures close to T\textsubscript{g} the crystallization rate was relatively slow. However, at more elevated temperatures and thus higher diffusion rates, the increase in crystallization rate was found to be sufficient to permit growth of micrometre-sized PC\textsubscript{61}BM crystals.

Light illumination during thermal treatment in the vicinity of or above T\textsubscript{g} was found to drastically affect PC\textsubscript{61}BM crystallization in APFO-3:PC\textsubscript{61}BM films, as PC\textsubscript{61}BM crystals could no longer be observed with optical microscopy. The appearance of pure PC\textsubscript{61}BM films was affected in a similar fashion. No sign of chemical degradation could be detected and solar cells based on such treated active layers didn’t display a change in photovoltaic performance. Further studies are required to determine the effect of illumination on PC\textsubscript{61}BM solidification.
5 Outlook

The temperature stability studies of high $M_w$ APFO-3:PC$_{61}$BM blends should be extended to longer periods of time in order to better compare device operation at elevated temperatures. In addition, it may be of benefit to more closely study the temperature range around $T_g$, which would allow to narrow down the onset of performance degradation. Clearly, future studies should be conducted on active layers that feature a more optimised thickness.

To further investigate the microstructure of the blend annealed just above $T_g$, an atomic force microscopy (AFM) study should be performed on different compositions of APFO-3:PC$_{61}$BM in order to confirm the partial miscibility of the donor and acceptor material as well as to visualise eventual PC$_{61}$BM phase separation in blends that contain higher PC$_{61}$BM ratios. Furthermore, AFM studies of blends annealed for longer periods of time at elevated temperatures may give additional insight into the inherent miscibility of this OPV mixture. Transmission electron microscope (TEM) studies would be an appropriate complement to AFM as it would permit to investigate the blend microstructure below the thin-film surface.

The effect of illumination on PC$_{61}$BM crystallisation should be followed up. Even though the current study did not reveal any changes in OPV performance, this effect may contribute to diverging performance seen for some OPV blends. There would also be interesting to illuminate an OPV active layer before thermal treatment above $T_g$ to investigate whether the PC$_{61}$BM can be frozen in to the microstructure obtained after spin-coating.

Several signals in the IR spectra appeared to slightly change shape or intensity after illumination. Although these variations couldn’t be linked to oxidation of the semiconductors, other structural changes may have occurred. Thus, for instance Raman spectroscopy should be performed as it may yield complementary information, especially with respect to possible photopolymerization. X-ray and electron diffraction studies would allow investigating whether PC$_{61}$BM crystallization is completely restrained or if illumination results in an increase of nucleation, which would imply more but significantly smaller crystals. If this was the case, appropriate tuning of thermal treatment procedures may offer an additional tool to structure OPV blends.

![Figure 5.1. Pure PC$_{61}$BM drop-cast film annealed under illumination (left half) and in dark (right half) at 130ºC prior to annealing at 220ºC in dark.](image)

Finally, since light illumination was also found to affect pure PC$_{61}$BM, selective irradiation of thin films may represent a powerful mean to pattern this n-type semiconductor (figure 5.1).
6 Experimental
The following methods and techniques were used in the project.

6.1 OPV devices
The solar cells used in this study were constructed by spin coating\(^a\) a ~40 nm thick layer of PEDOT:PSS from a water solution on a TL1 washed ITO-coated glass substrate. The active layer of APFO-3:PC\(_{60}\)BM 1:4 was deposited on top by spin coating from 60g/L oDCB solution to a thickness of ~100 nm. For top electrode a ~6 Å thick layer of LiF were deposited by thermal evaporation\(^b\) before a ~800 Å thick Al layer. The thickness of the high M\(_w\) active layer was ~250 nm.

Thermally treating of OPV devices where carried out on a Koffler bench hotplate calibrated by heating standards. The annealing were performed in a glovebox without illumination and under nitrogen atmosphere. The thermal treatment was performed before evaporation of the top electrodes.

The IV characteristics were measured at ambient with a solar simulator, Air Mass 1.5, 1000 W m\(^{-2}\).

\(^a\)Spin coating:

The material to be deposited is dropped on to the substrate in a solution. The substrate is rotated and the solvent and parts of the solute is forced of the substrate surface. Depending on angular speed, viscosity, volatility, concentration etcetera the resulting thin film will have different thickness. Picture from: http://www.phys.tue.nl/mmn/projects/project-Klara/ (2010-05-15)

\(^b\) The cathode was deposited through thermal evaporation where the material to be deposited is heated above its vaporizing temperature. The process is done in vacuum to minimize oxidation. The substrate is kept in a mask to get the electrode at the desired location. Each substrate gets four electrodes with an area of ~4mm\(^2\).

6.2 Photoluminescence
The principle of photoluminescence is that a material will be excited as it is illuminated. When it relaxes through radiative recombination the emitted light is called luminescence. The “photo” is derived from the excitation method. The wavelength and intensity of the emitted light is detected.

All samples were spin-coated on TL-washed glass substrates to a thickness of ~100 nm. For the composition series a mean from three measurements where recorded. Thermal treatment was performed on a hot plate, calibrated by heating standards, in a glove box under nitrogen atmosphere. For the temperature series one measurement where performed on different films for every temperature.

The equipment used where an Oriel liquid light guide, a Shamrock SR 303i spectrograph and a Newton EMCCD silicon detector.
6.3 Electroluminescence
Electroluminescence spectrography is performed by injecting electrons into the material. These recombine at the lowest energy state. The wavelength and intensity of the emitted light is detected.

The samples were prepared as OPV devices according to 6.1. Thermal treatment was done on a Koffler bench, calibrated by heating standards, in a glove box under nitrogen atmosphere.

The equipment used where a Shamrock SR 303i spectrograph and a Newton EMCCD silicon detector.

6.4 UV-vis absorbance
The samples were spin-coated on glass substrates. For the temperature study the same sample were measured after thermal treatment on a hot plate calibrated by heating standards in a glove box under nitrogen atmosphere. The illuminated/dark samples were performed on a covered hot plate under nitrogen flush. A boroscope was used as light source.

Absorbance where measured with a Lambda 950 UV-vis-spectrometer.

6.5 IR Transmittance
The samples were prepared by spin-coating from solution on KBr substrates. Thermal treatment of substrates for where carried out on a hotplate calibrated by heating standards. The hotplate was covered to allow nitrogen flush. A boroscope was used as light source.

IR absorbance was measured by a Vertex 70 IR spectrometer.

6.6 Microscope study
All images, unless stated, were photographed in the vicinity of the center of the films to avoid concentration gradients. Temperature treatment for PC61BM crystallization where performed in a nitrogen flushed hot stage. Illumination was performed through a hole in the hot stage. The comparison between illumination and dark pre-treatment is subsequently noticed on one film only, eliminating film casting differences.

For the optical microscope study an Olympus BX60 and an Olympus BH2 polarizing microscope were used.

6.7 Thickness measurement
The thickness of active layers where measured with a Dektak profilometer.
7 References

1 Green, M.A., Emery, K., Hishikawa, Y., Warta, W., Solar cell efficiency tables (version 35), Progress in Photovoltaics: Research and Applications 18, 144-150, 2010


