

Bulk Heterojunctions Based on Native Polythiophene

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Three different bulk heterojunctions were prepared by solution processing from the same precursor film. The procedure employs standard film-forming processing methods from solution whereby bulk heterojunctions of poly-(3-(2-methylhexan-2-yl)-oxy-carbonyldithiophene) (P3MHOCT) and the fullerene derivatives [60]PCBM or [70]PCBM were prepared. The films were subjected to temperatures of 200 °C whereby P3MHOCT is converted to the more rigid and insoluble poly-3-carboxydithiophene (P3CT); films subjected to a temperature of 310 °C lead to decarboxylation of P3CT giving native unsubstituted polythiophene (PT). The same precursor film prepared by standard solution processing thus gave access to three chemically different bulk heterojunctions that were studied in terms of performance and stability. The device with a bulk heterojunction of PT/[70]PCBM and an active area of 3 cm² showed the best efficiency of 1.5% (1000 W m⁻², AM1.5G, 70 °C) as well as a slow decay of the performance over 500 h of continuous illumination in a nitrogen atmosphere (330 W m⁻², AM1.5G, 25 °C).

Introduction

Plastic photovoltaics^{1–4} present an alternative to conventional solar cells that are typically based on inorganic materials such as silicon. They offer new possibilities in terms of processing conditions, processing speed, and cost. The fabrication of the photovoltaic devices is envisaged to be entirely using low temperature solution-based roll-to-roll processing on flexible substrates. This is in stark contrast to solar cells based on inorganic materials that typically involve rigid substrates, high temperatures, and by comparison slow processing. The polymer solar cells remain inferior to the inorganic cells in terms of both efficiency and stability, but significant and consistent advances have been documented during the past decade, and today the state of the art offers power conversion efficiencies (PCEs) of around 5% for single junctions^{5,6} and 6.5% for stacked tandem cells,⁷ stabilities under accelerated conditions for thousands of hours,^{8,9} morphological stability,¹⁰ and processing on a scale of up

to 0.1 m².¹¹ While most focus has been on the power conversion efficiency, the issues of stability, operational lifetime, and processing are gaining attention, and it should be emphasized that the combination of high efficiency, long lifetime, and large area processing has not been achieved for the same material currently. To meet this challenge of unification, the delicate interplay between many parameters such as processing, morphology, carrier transport, photochemistry, and chemistry at interfaces needs to be controlled. The current state of the art is well exemplified with bulk heterojunctions based on the conjugated polymer poly-3-hexylthiophene (P3HT) and a soluble fullerene derivative (PCBM).^{5,6} The formation of devices with high power conversion efficiency is achieved through careful control of the processing conditions where the choice of solvent and

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the rate of evaporation during film formation play a very influential role.^{5,6} After the device film has been formed, thermal annealing can be employed to further increase the PCE.^{5,6} It should however be emphasized that the use of solvent and/or thermal annealing does not generally apply to all materials as a means of improving device performance. Processing from solution requires that the materials are made soluble, and this is normally achieved by attaching solubilizing side chains such as alkyl groups onto the conjugated polymer backbone. Once the film is formed, there is in principle no longer any need for the solubilizing side chains that make up a significant proportion of the active material. In the case of P3HT, the hexyl groups account for ~50% of the material weight and are passive in terms of light harvesting and charge transport. Furthermore, the side chains make the material soft and allow for diffusion of small molecules and constituents.^{8b,12} The softness that alkyl groups purvey has been linked to the instability of plastic photovoltaics, and more rigid systems generally give devices with a better stability.⁸ From this point of view, it is of some interest to prepare bulk heterojunctions via solution processing where the final device film does not have solubilizing side chains. From a fundamental point of view, a bulk heterojunction between native polythiophene and a soluble fullerene derivative such as [60]PCBM or [70]PCBM represents a challenge that cannot be met using known procedures as native (unsubstituted) polythiophene is an insoluble and intractable material.

In this work, we present an efficient procedure for the preparation of bulk heterojunctions based on solution processing of the device film and subsequent chemical conversions of the device film through thermal processing. Bulk heterojunctions of native polythiophene are presented.

Experimental Section

Regiorandom poly-(3-(2-methylhex-2-yl)-oxy-carbonyldithiophene) (P3MHOCT) was prepared as described in the literature.¹³ The polymer had the following properties: $M_n = 11\,624\text{ g mol}^{-1}$, $M_w = 28\,266\text{ g mol}^{-1}$, $M_p = 27\,505\text{ g mol}^{-1}$, PD = 2.564. [60]PCBM and [70]PCBM were obtained from Solenne and had a purity of 99%. Glass substrates with pre-etched 100 nm thick layer of ITO and a sheet resistivity of 8–12 $\Omega\text{ }\square^{-1}$ purchased from LumTec were cleaned by consecutive ultrasonication in isopropanol and distilled water for 10 min each followed by drying immediately prior to use. A layer of PEDOT:PSS purchased from Aldrich as a 1.3 wt % aqueous solution was spin-coated on top of ITO at a rotational speed of 2800 rpm, and the slides were annealed at 160 °C for 5 min. Subsequently, the samples were transported into the glovebox and an active layer of a mixture containing P3MHOCT and [60]PCBM or [70]PCBM (25 mg/mL in dichlorobenzene) was spin-coated onto the PEDOT:PSS covered glass-ITO substrates. The samples were then annealed at the different temperatures chosen in the range between room temperature and 310 °C. The annealing time was kept at 30 s for the temperatures up to 250 °C and at 10 s for temperatures above 250 °C. Longer annealing times lowered the V_{oc} . The aluminum metal electrode was evaporated on top after

the thermal annealing to complete the devices. The devices had an active area of 3 cm² and were tested for photovoltaic performance and stability. The photovoltaic performance was tested under a solar simulator where the irradiance and emission spectrum were checked carefully using an optical spectrum analyzer in conjunction with a precision radiometer from Eppley Laboratories. The spectrum during characterization of the solar cell efficiency was AM1.5G with an incident light power of 1000 W m⁻². The solar simulator is Class AAA from 400–800 nm, over the area of the cell and for the duration of the experiment. The stability measurements were performed in a stainless steel chamber with quartz windows and controlled atmosphere.¹⁴ The atmosphere consisted of nitrogen with an oxygen content of <1 ppm and a humidity of 0% relative. The oxygen and humidity level was monitored continuously.

Results and Discussion

The current state of the art in plastic photovoltaics is represented by the bulk heterojunction that comprises a mixture between a conjugated polymer material such as P3HT and a soluble fullerene material such as [60]PCBM or [70]PCBM (Scheme 1).^{5,6} The active layer in the devices reported has been prepared almost exclusively by the spin-coating technique whereby a solution containing the active components is applied to a rapidly rotating substrate. The spin-coating technique excellently allows for the reproducible formation of very even films with a well-defined thickness and a smooth surface. The thickness essentially only depends on the viscosity of the coating solution and of the angular speed of the substrate. However, the as-formed film rarely gives the best devices, and additional post preparation treatments need to be performed such as slow drying of the film or thermal annealing whereby the structure and the morphology of the film are altered.^{5,6} The most efficient devices require a well-ordered state with a phase segregation at the scale of the exciton diffusion length (~10 nm scale). The chemistry in the film does not change as a function of the various post treatment and annealing steps that have been reported. In the case of bulk heterojunctions based on P3HT and [60]PCBM, the nanomorphology is quite stable at room temperature and at slightly elevated temperatures.⁹ High temperatures can lead to rapid changes in the morphology for bulk heterojunctions.¹⁵ This is the effect that is efficiently explored to improve the performance of these devices. To achieve thermal stability at higher temperatures, there is a necessity for processing methods that offer advantages of higher thermal and morphological stability¹⁶ without any compromise of the processing ease and ideally also without decrease in device performance.

One way to increase thermal stability is by increasing the glass transition temperature of the material through increasing the rigidity of the molecules, but this is normally associated with adverse changes in materials properties. It is thus difficult to envisage an efficient solution to the problem that relies solely on physical transformations (i.e., thermal annealing), and a chemical methodology whereby the

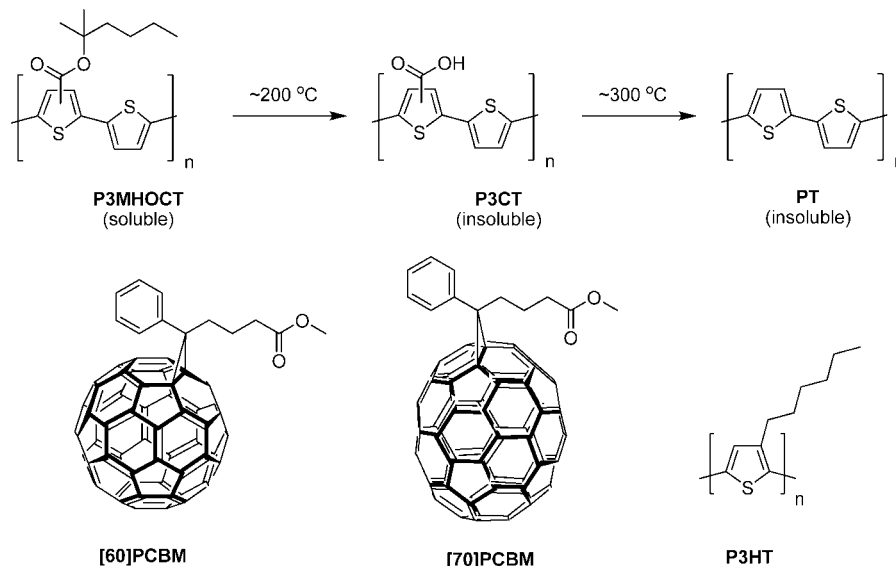
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Scheme 1. Chemical Transformation of P3MHOCT to P3CT at ~ 200 °C and Further Transformation to PT at ~ 300 °C^a

^a The soluble fullerene derivatives employed in this work are shown in the lower part of the scheme along with the conjugated polymer P3HT. chemistry of the material is altered during the process is needed. The polymer material P3MHOCT developed by the group of J. M. J. Fréchet was shown to convert to P3CT at temperatures of ~ 200 °C through elimination of 2-methylhexene.¹³ It was later shown by ¹³C labeling studies and solid-state NMR that P3CT could be further converted to PT at temperatures of ~ 300 °C by decarboxylation.¹⁷ P3MHOCT is readily soluble in common organic solvents and is easily processed into thin films on its own or as mixtures with fullerene molecules prototypical of bulk heterojunctions. The advantage of bulk heterojunctions based on P3MHOCT and [60]PCBM or [70]PCBM is thus that they can be characterized as photovoltaic devices or processed to bulk heterojunctions of P3CT or PT and the aforementioned fullerenes by simple heating for a brief period of time (seconds to minutes) to the specific temperature where the chemical transformation takes place. In this work, we simply explored these three different bulk heterojunctions (P3MHOCT, P3CT, and PT) for each of the fullerene derivatives [60]PCBM or [70]PCBM. For that reason, the samples with a freshly spin-coated active layer containing P3MHOCT were annealed correspondingly at temperatures from 190 to 270 °C for about 30 s to obtain P3CT, more than 300 °C (technically limited by 310 °C) for about 10 s to obtain PT. For P3MHOCT itself, the devices were just left at room temperature to dry or were heated to annealing temperatures below the cleavage temperature. During the annealing, it was possible to visually see the color change of the sample from red to orange (conversion from P3MHOCT to P3CT) and then from orange to purple-red (conversion from P3CT to PT). The brief periods of heating time involved here possibly do not give rise to full chemical conversion of the device film, and it is reasonable to assume that the films are composite mixtures representative of the chemistry that is accessible at the given processing temperatures. Figure 1 shows the results of UV-vis analysis of P3MHOCT and

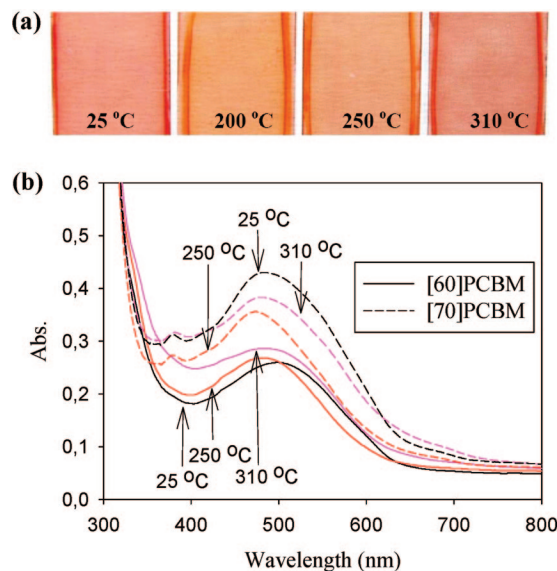


Figure 1. (a) A photograph showing the appearance of films based on [70]PCBM when heated to different temperatures. (b) UV-vis spectra of films based on P3MHOCT and [60]PCBM or [70]PCBM mixtures spin-coated on glass slides and annealed at three different temperatures (25, 250, and 310 °C). Vertical axes correspond to the absorption of the films as measured in transmission geometry neglecting the reflection losses.

[60]PCBM or [70]PCBM mixtures spin-coated on glass slides and annealed at different temperatures.

The measurements confirm a significant change of the absorption coefficient at different temperatures. Also, a slight shift of the peaks (at 500 nm) toward longer wavelengths can be seen when the samples were heated up to 310 °C. Figure 2 shows the plot of the efficiency of the cells versus annealing temperature.

The vertical lines separate regions that correspond to different polymers. The decrease of the efficiency in the first region was mostly due to the open circuit voltage of the cells being rather sensitive to thermal stresses (complete sets of *IV*-curves and graphs of V_{oc} , I_{sc} , and FF are provided in the Supporting Information). From the graph, it is clear that

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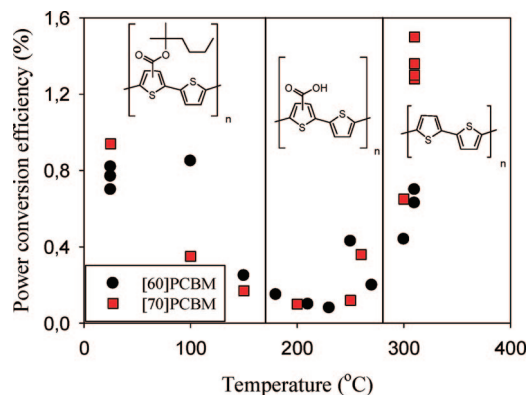


Figure 2. Efficiency versus annealing temperature for the cells with P3MHOCT polymer and [60]PCBM (●) or [70]PCBM (red ■) mixture measured under 1000 W m^{-2} , AM1.5G, 70°C conditions. The vertical lines show the temperatures at which the thermocleavage becomes significant upon increasing the temperature according to the TGA analysis reported in ref 14. The conversion is irreversible. The molecular structures for the polymers in the different temperature ranges are shown.

the performance was poorer for annealing in the temperature range where P3CT forms and best in the temperature where PT forms. The best efficiency of 1.5% (under 1 sun) could be achieved for a device with PT and [70]PCBM. SEM analysis of the surface of active layer for the same type of cells carried out after peeling off the aluminum electrode confirms (Figure 3) the formation of well-defined bulk heterojunction structure of the compound. The power conversion efficiency of the bulk heterojunctions in the as-formed films was generally observed to be in the range of 0.7–0.9% and was found to decrease as the device film was annealed in the range of temperatures below the transformation of P3MHOCT to P3CT. A broad minimum is then reached as the first cleavage temperature is reached, and the devices based on P3CT were all the poorest performing in terms of power conversion efficiency where the typical power conversion efficiency was in the range of 0.1–0.4%. When reaching the temperatures of the second transformation from P3CT to PT, a dramatic increase in power conversion efficiency was observed from the low value of 0.1–0.4% up to 0.6% in the case of [60]PCBM and as high as 1.5% in the case of [70]PCBM. [70]PCBM devices showed the largest improvement, which may be linked not only to morphology but also to better light harvesting properties of [70]PCBM as compared to [60]PCBM. It should, however, be noted that devices based on [60]PCBM and [70]PCBM generally gave the same result at processing temperatures below 300°C . One possible explanation of the decrease in performance at annealing temperatures below $190\text{--}210^\circ\text{C}$ could be that the morphology changes and that the fullerene component grows to form large crystallites. The nanomorphology plays a crucial role in the performance of polymer solar cells, and any change in morphology toward larger aggregates or crystallites could account for this.^{10,18} It is, however, not very likely seen in the light of the morphology that we observe in the SEM images (examples are shown in Figure 3). Films treated in the temperature range of $25\text{--}250^\circ\text{C}$ show a completely homogeneous nature with no observable phase separation. Films heated to 310°C do show distinct phase separation and represent traditional bulk heterojunctions of PT and the fullerene. If the performance decrease was due to changes in morphology and the formation of large fullerene crystallites, we would have expected this to be conserved in

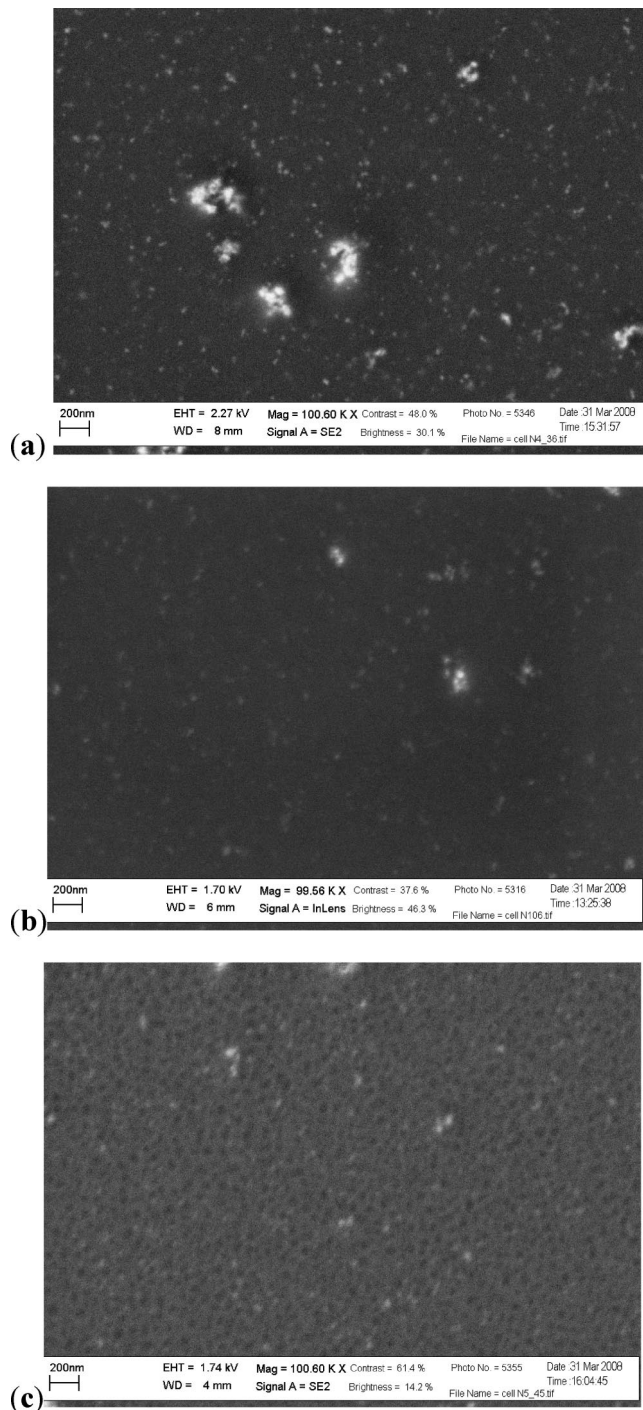


Figure 3. SEM images of the surfaces of films based on P3MHOCT and [60]PCBM compound treated at (a) room temperature, (b) 200°C , and (c) 310°C .

the rigid polymer matrix that both P3CT and PT comprise.¹⁶ We further attempted photoluminescence quenching experiments as this is a good method to probe the intimacy of the polymer–fullerene mixture. We observe a moderate photoluminescence for P3MHOCT that is completely quenched when mixed with [60]PCBM as established using spin-coated films

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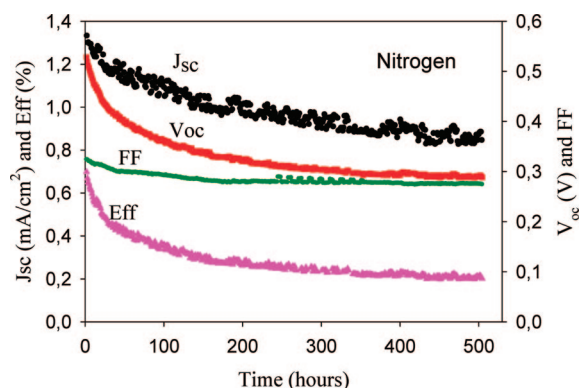


Figure 4. Variation of PV parameters of ITO/PEDOT:PSS/PT:[70]PCBM/AI device kept in nitrogen atmosphere under 1/3 sun irradiation for 500 h (330 W m^{-2} , AM1.5G, nitrogen, 0% relative humidity, $25 \text{ }^\circ\text{C}$).

on glass substrates employing front face illumination (see Supporting Information). Unfortunately, the pure films of P3CT and PT and their mixtures with [60]PCBM did not show any photoluminescence, and it was thus difficult to draw any further conclusions from these studies. While this is subject to further study, we can offer two possible explanations currently. First, slight changes in the optical properties may account for some of the degradation in performance (the effect of this is expected to be minor if present). The second and more likely explanation is that the performance of the three different devices based on respectively P3MHOCT, P3CT, PT, and [60]PCBM exhibits typical performances in the ranges of 0.7–0.8%, 0.1–0.2%, and 0.6–0.7%. For the three different devices based on respectively P3MHOCT, P3CT, PT, and [70]PCBM, typical performances in the ranges of 0.9%, 0.1%, and 1.3–1.5% are observed. At the intermediate temperatures, cleavage may take place to a small extent as evidenced from the weight loss during TGA experiments.¹⁷ We thus propose that the observed changes in performance with temperature represent a complex interplay between morphological changes and changes in the chemistry of the film.

In addition to the morphological and chemical changes that take place during the heating steps, the diffusion and partitioning of PCBM into the polymer matrix may play an important role. One possibility is, for instance, that the solubility of PCBM in the polymer matrix decreases as the material is cleaved, thus promoting phase separation. In terms of thermal stability of the materials employed, we assume that they are stable with respect to the temperatures and the duration of the thermal treatments employed. The polymer is quite stable thermally as shown earlier,¹⁷ and fullerenes are very thermally stable materials and allow for sublimation at temperatures of up to $400 \text{ }^\circ\text{C}$ in their pure state, while the derivatives such as PCBM sustain temperatures of $\sim 180 \text{ }^\circ\text{C}$ in refluxing dichlorobenzene for 7 h during the preparation.

In addition, lifetime measurements were carried out for different devices, and the cells with PT showed the most stable performance. Figure 4 shows the change of photovoltaic parameters versus time for devices based on PT and [70]PCBM kept in nitrogen atmosphere at 0% relative humidity with an incident power of 330 W m^{-2} . The short circuit current density stayed above 50% of the initial value

for more than 500 h and the fill factor showed almost no decay, while the open circuit voltage decreased significantly during the decay process, which was the major cause of the rather fast initial decay of efficiency.

The results confirm that the V_{oc} of these types of devices is rather sensitive toward stresses applied to the cells. Further investigation of the devices is needed to reveal the reason of poor performance of V_{oc} . We believe that if one could improve the stability of V_{oc} , then this type of device could certainly challenge the commonly used traditional organic materials, such as P3HT and others.

Conclusions

We have shown that a simple bulk heterojunction precursor film can be prepared by solution processing compatible with the state of the art procedures and how it can be processed into chemically different bulk heterojunctions through a simple thermal treatment. While there was no difference in the processing conditions, there was a slightly lower performance in terms of the power conversion efficiency than the current state of the art, while there was a relative increase in performance as the processing temperature was increased, and efficiencies up to 1.5% could be achieved for bulk heterojunctions based on native polythiophene and [70]PCBM under simulated sunlight (1000 W m^{-2} , AM1.5G, $70 \text{ }^\circ\text{C}$). The photocurrents of the devices showed quite stable performance in time and were studied for more than 500 h where an initial fast decay was observed followed by a long steady period where the performance remained constant. While the power conversion efficiency obtained in this work for native polythiophene is a modest 1.5% for a large area device (3 cm^2) as compared to the state of the art that gives more than twice as much, it should be borne in mind that the current state of the art did not reach the high efficiencies to begin with. In the prototypical case of P3HT/PCBM, the high efficiencies were arrived at through a massive and directed research effort over the past few years involving a detailed understanding of the relationship between film-forming process and device function. It is not unlikely that the processing of device films via thermocleavability can be extended to other polymer systems and that the processes can be developed along the same lines as has taken place for the P3HT/PCBM system such that more efficient and stable devices can be obtained. We believe that a better understanding of the complex interplay between morphological changes and the chemistry of the film as a function of temperature could lead to significant improvements in both device performance and operational stability.

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Supporting Information Available: Experimental details of device preparation and device characterization, IV -curves, plots of V_{oc} , I_{sc} , and FF as a function of temperature, and photoluminescence data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.