SOLID-STATE NMR CHARACTERIZATION OF THE STRUCTURE AND
MORPHOLOGY OF BULK HETERJUNCTION SOLAR CELLS

A Thesis
Presented to
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In Partial Fulfillment
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Master of Science

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A bulk heterojunction, organic solar cell, composed of a blend of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) was studied to determine the structure at the interface of the two compounds. Films of neat P3HT and the P3HT:PCBM composite where cast and annealed at elevated temperatures in order to determine the impact of sample annealing on the interface structure and interface volume of the blend. The films were characterized with 1D $^{13}$C solid-state NMR and 2D $^1$H-$^{13}$C heteronuclear correlation (HETCOR) NMR. HETCOR NMR, with Lee-Goldburg cross polarization, was used to observe discrete intermolecular interactions between the alkyl side chain of P3HT and the C_{60}, phenyl ring, and alkyl groups of PCBM. From these intermolecular interactions, a model of the structure at the P3HT:PCBM interface was constructed, which reveals the presence of stabilizing π-stacking between the thiophene ring of the P3HT and the phenyl ring of PCBM. Also, the C_{60} species interacts extensively with the alkyl groups of P3HT. The data indicates a phase separation after annealing that reduces the volume of the interface without disturbing the interface structure. A HETCOR NMR method using tangent cross polarization was used to confirm the phase separation of the P3HT and PCBM layers after thermal annealing.
DEDICATION

In memory of my uncle, Ricky L. Hayes,
who showed me the importance of
curiosity, dedication, and humility.
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CHAPTER I

INTRODUCTION

1.1 Photovoltaic Cells

The world consumes about 477 EJ of energy a year and this value is expected to increase at least 40% by 2035.¹ Less than 20% of the energy used comes from renewable energy sources. The share from renewable sources (solar, wind, geothermal, etc.) is anticipated to rise as finite fossil fuel reserves are exhausted and renewable energy sources become more efficient and cost effective.²

1.1.1 Overview

Today’s dominant renewable energy sources include geothermal, hydropower, solar, and wind. While most electricity from renewable sources is generated through hydropower, wind and solar power installations continue to approximately double each year. From the available sources of renewable energy, solar power provides the highest potential of harvestable energy with about 3.9 x 10²⁴ J of energy per year. This is roughly 8,000 times the amount of energy currently consumed worldwide.³
A usable current can be generated from solar energy using a solar cell through the photovoltaic effect. A simple photovoltaic (PV) system is illustrated in Figure 1.1.

![Diagram of a simple PV cell system](image)

**Figure 1.1. Mechanism of a simple PV cell system**

The process of generating a current in the PV cell is as follows: (1) a photon (sunlight) is absorbed by a material; (2) electrons in the highest occupied molecular orbital (HOMO) of the absorbing material are excited to the lowest unoccupied molecular orbital (LUMO); (3) the excited electrons are transferred to the cathode; and (4) the electrons travel through an external circuit to the anode to fill the hole in the light absorbing material, generating a current. In this system, a single material acts as both the electron donor and electron acceptor.

Photovoltaic production has rapidly grown over the past decade to become a $71.2 billion industry. The technology in this area has not seen much growth, relying largely on crystalline silicon cells, which have high power conversion efficiencies of 25-
30%. Due to the high material and manufacturing cost of these panels, development focus has shifted to organic materials. Organic-based solar cells have a large variety of chemical compositions that allow for a more dynamic control of functionality and production cost. They are also known for their physical flexibility, low weight, and mechanical strength.

1.1.2 Organic Photovoltaic Systems

Organic photovoltaic (PV) cell design greatly affects the power conversion efficiency (PCE). The most common designs include single-layer, double-layer heterojunction, and bulk-heterojunction PV cells. In a single-layer design, a single polymer layer is placed between two electrodes, Figure 1.2. This polymer acts as both an electron donor and an electron accepter. The most common electrodes are made from indium tin oxide (ITO) and aluminum, though other metals have also been used. Figure 1.3 shows the mechanism for generating a current in a single-layer PV cell.

![Figure 1.2. Illustration of a single polymer layer PV cell design](image-url)
Figure 1.3. Mechanism of a single polymer layer PV cell

Light, absorbed by the polymer, excites an electron from the HOMO into the LUMO, leaving a hole in the HOMO and creating an exciton (a bound electron-hole pair). The exciton dissociates, moving the electron in the LUMO towards one electrode and the hole of the HOMO towards the other. Reported power conversion efficiencies of this design are very low. A PV cell of poly (2-methoxy, 5-(2’-ethyl-hexyloxy)-p-phenylenevinylene) (MEH-PPV) only achieves a PCE of about 0.1%.  

A double-layer heterojunction cell, Figure 1.4, comprises an electron donor layer and an electron acceptor layer between two electrodes. A double-layer system presents more flexibility in PV design by allowing for optimization of the electron donor and electron acceptor components separately. By separating the electron donor and electron acceptor into two layers, a larger variety of polymers can be utilized. The mechanism for current generation in this device is shown in Figure 1.5. As before, light is absorbed by the electron donor polymer and generates a charged separated state. Increasing the amount of light absorbed increases the number of excitons generated. The excitons
diffuse across the electron donor towards the electron donor/acceptor interface and transfer to the lower energy LUMO of the electron acceptor. The excitons in the electron acceptor and the holes of the electron donor are then transferred to the electrodes. In order to avoid non-radiative relaxation, diffusion of excitons within the electron donor polymer and electron transfer between the polymers and to the electrodes needs to be fast. The diffusion time can be decreased and rate of electron transfer increased by increasing the amount of electron donor-acceptor interface. The increased amount of interface allows for increased interaction between the two layers. Additionally, the system must also have fast electron and hole migration to the electrodes to avoid back electron transfer and/or charge recombination. Under ideal conditions, all absorbed photons will be converted into a usable current. When back electron transfer or charge recombination occurs, the absorbed photon energy does not contribute to the current and is released as heat.\(^6\) Double-layer devices composed of electron-donating MEH-PPV and electron-accepting \(\text{C}_6\text{O}\) have shown improvement over the single-layer PV cell despite the presence of non-radiative relaxation and charge recombination, with an increased PCE of up to 1.85\%.\(^8\)

![Image](image.png)

Figure 1.4. Illustration of a double polymer layer PV cell design
Efforts to increase the PCE of these cells recently has led to the fabrication of bulk heterojunction PV cells, Figure 1.6, which are prepared as a blend of photon-absorbing and electron-accepting semiconductors. The blending helps to increase the amount of interface while maintaining phase dimensions to match the short exciton diffusion length (8-17 nm) and compensating for the 80 nm optical path length needed for sunlight absorption.\textsuperscript{9–11} Optimized, these blends would consist of co-continuous phases with an absorption phase dimension smaller than the exciton diffusion length.\textsuperscript{9,11} The increased amount of interface results in more electron transfer and thus a higher PCE for the cell. In this system, the donor-acceptor blend is placed between two electrodes. In order to generate a current, the materials must be in contact with their respective electrodes or the circuit will not be complete, resulting in primarily non-radiative
relaxation. Efficiencies up to 3% have been achieved for the bulk heterojunction cell composed of the MEH-PPV donor and C₆₀ acceptor.¹⁰ Bulk heterojunction systems have shown power conversion efficiencies as high as 5% when electron-donating poly(3-hexylthiophene) (P3HT) and the electron-accepting, soluble C₆₀ derivative, [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) are used.¹² Fullerenes are favored electron acceptors because they exhibit fast electron transfer. Substituted fullerenes, such as PCBM, have enhanced solubility that allows the fullerenes to diffuse into the polymer matrix, increasing the interactions at the interface.

Figure 1.6. An illustration of a bulk heterojunction PV cell where the donor and acceptor layers are blended together and placed between two electrodes.

1.2 Bulk Heterojunction P3HT:PCBM

Organic solar cells composed of P3HT and PCBM (Figure 1.7) have been widely studied in order to understand the effects of morphology on the physical properties of a bulk heterojunction system. Initially P3HT:PCBM gained interest because of its improved PCE over MEH-PPV based systems, and since has been used as the standard
system for studying the effects of various fabrication methods on bulk heterojunction morphology and PCE.

An optimized PV cell film begins with an ideal electronic match between the electron donor and acceptor. An ideal system would minimize the energy difference between the LUMOs of the two species in order to minimize the energy required to excite an electron to the LUMO from the HOMO, for the photon absorber. The energy needed to make exciton formation favorable must be greater than the Coulombic attraction of the electron-hole pair, estimated to be 0.4-0.5 eV. Thermal effects and the intrinsic electric field of a solar cell composed of a PCBM electron accepter reduce the minimum LUMO energy difference needed for exciton formation to 0.3 eV. Therefore an ideal donor, relative to PCBM, would have a LUMO at 3.9 eV as illustrated in Figure 1.8. The HOMO energy difference of an ideal donor relative to the accepter would be as low as possible to maximize the amount of attainable voltage from the PV cell. However, too

Figure 1.7. Molecular structures of P3HT (A) and PCBM (B)

1.2.1 Electron Transfer

An optimized PV cell film begins with an ideal electronic match between the electron donor and acceptor. An ideal system would minimize the energy difference between the LUMOs of the two species in order to minimize the energy required to excite an electron to the LUMO from the HOMO, for the photon absorber. The energy needed to make exciton formation favorable must be greater than the Coulombic attraction of the electron-hole pair, estimated to be 0.4-0.5 eV. Thermal effects and the intrinsic electric field of a solar cell composed of a PCBM electron accepter reduce the minimum LUMO energy difference needed for exciton formation to 0.3 eV. Therefore an ideal donor, relative to PCBM, would have a LUMO at 3.9 eV as illustrated in Figure 1.8. The HOMO energy difference of an ideal donor relative to the accepter would be as low as possible to maximize the amount of attainable voltage from the PV cell. However, too
large of an energy gap decreases the amount of spectral overlap with the photon flux from the sun. This limits the HOMO energy difference to 1.5 eV, resulting in an ideal donor with a HOMO energy of 5.4 eV. One polymer that meets these energy level requirements is poly(2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene)-alt-(vinylene) (MDMO-PPV). However due to the unfavorable miscibility between MDMO-PPV and PCBM, a high weight ratio of 1:4 for MDMO-PPV:PCBM is needed to prevent large phase separation during fabrication. The dominance of PCBM in this ratio limits the interface volume and reduces the theoretical efficiency of the system. While P3HT has slightly less optimal electronic properties, it is more miscible with PCBM than MDMO-PPV. This advantage allows for lower P3HT:PCBM weight ratios of 1:1 or less, which increases the total possible interface volume between the polymers. With additional processing, such as thermal annealing, the morphology of donor-acceptor interface can be optimized.\textsuperscript{12}
1.2.2 Controlling Morphology with Synthesis

Controlling the morphology of the P3HT:PCBM composite is important to ensure the maximum exciton exchange at the interface. Solvent selection greatly influences the resulting power conversion efficiency of the film. A film prepared by mixing P3HT and PCBM in toluene results in a PCE of about 0.9%, whereas a film prepared from chlorobenzene can achieve efficiencies around 2.5% before thermal annealing. The increased solubility of PCBM in chlorobenzene allows it to form smaller, crystalline, ~100 nm diameter clusters. This improves electron movement within PCBM domains and produces a homogenous P3HT:PCBM film after casting. Films cast from
chlorobenzene have nanometer-length scales of phase segregation equal to the exciton diffusion length, 8-17 nm, unlike toluene-casted films that form large, micrometer-sized clusters.\textsuperscript{11,13} The use of chlorobenzene results in films close to the ideal morphology and yielding a higher PCE.\textsuperscript{13}

The weight ratio of P3HT:PCBM is also important in controlling the efficiency of the PV cell. The optimized morphology is achieved with a composition of 40-50\% PCBM, or a 1:0.8 to 1:1 P3HT:PCBM weight ratio.\textsuperscript{10,15–17} In addition, P3HT with a molecular weight between 30,000 and 70,000 g/mol produces a blend of crystalline and amorphous regions which allows for the use of thermal annealing to more precisely control the morphology of the P3HT and PCBM domains and their interface. Lower molecular weight P3HT has too high of a crystalline content, resulting in a low molecular mobility that makes thermal annealing ineffective. At higher molecular weights, P3HT becomes almost completely amorphous, raising the required temperature and annealing time necessary to achieve morphological optimization.\textsuperscript{10}

1.3 Controlling Morphology with Processing

Thermal annealing is the processing technique that has had the largest impact on the P3HT:PCBM system, raising the PCE from about 3\% before annealing to up to 5\% after.\textsuperscript{18} In this process, films are annealed for a set period of time (typically 5-30 minutes) at temperatures between 110-160°C.\textsuperscript{18,19} By adjusting the annealing temperature and time, well-blended films colligate into larger domains in a controlled
manner. This produces a co-continuous bilayer system with a maximum amount of interface.

1.3.1 Domain level improvements

Initial studies on the effects of thermal annealing focused on the change in domain sizes and the relationship between size and PCE. A correlation between increased surface roughness due to the formation of larger domains and improved PCE is observed with atomic force microscopy (AFM) and optical microscopy.\textsuperscript{19,20} The AFM maximum vertical height (MVH) of the pre-annealed P3HT:PCBM film, relative to the substrate, was measured to be about 1.6 nm and after annealing, the MVH was increased to about 8.6 nm, indicating an increased roughness to the surface. Films of pure P3HT and pure PCBM had the opposite effect, becoming smoother with their MVH decreasing from 12.8 to 4.5 nm and 3.2 to 1.8 nm, respectively. This contrast indicates that P3HT and PCBM self-organize upon thermal annealing. In a composite film, this self-organization causes phase separation which produces larger domains that mix with the remaining smaller domains, increasing the roughness of the film.\textsuperscript{20}

With the realization that the larger domain sizes were a result of self-organization, attention shifted to understanding the crystal formation occurring within the domains. Transmission electron microscopy (TEM) revealed crystal formation of PCBM upon casting, with larger crystals forming from slow solvent evaporation and preferred smaller crystallites forming with fast solvent evaporation.\textsuperscript{18} Crystal formation in both domains was present after thermal annealing the P3HT:PCBM film. The favored packing order of
P3HT was found to be \( \pi-\pi \) intramolecular stacking of the thiophene rings parallel to the surface. Images produced from TEM showed 10 x 30 nm cylinder P3HT crystals that correspond to the exciton diffusion length.\(^{21}\) X-ray diffraction confirms these results and further indicates that when cast, P3HT contains a small crystalline phase that increases with thermal annealing, whereas PCBM increases in crystallinity from an initial amorphous phase.\(^{19,21,22}\)

1.3.2 Interface Morphology

Recent focus has turned to the interface region of P3HT:PCBM because of its importance in electron transfer. A solid-state NMR study has begun to identify the effects of thermal annealing on the interface structure. Initial studies in this area by Yang et al.\(^{23}\) utilized \(^1\)H\(^{13}\)C heteronuclear correlation (HETCOR) NMR spectroscopy to observe through-space interactions between the nuclei in P3HT and PCBM.

HETCOR NMR relies on dipolar coupling interactions between two nuclei to show spatial correlations (cross peaks). Dipolar coupling is a through-space interaction between NMR active nuclei that are separated by less than about 1 nm in space. The intensity of the dipolar coupling interaction is inversely proportional to the distance between nuclei, so as nuclei separate, the corresponding HETCOR cross peak for the interaction diminishes in intensity. Yang et al. used this technique to identify changes in the interface structure after annealing by correlating the observed change in intensity of the correlations between P3HT and PCBM with spatial distance.\(^{23}\)
Before annealing, an interaction between the alkyl side chains of P3HT and the C\textsubscript{60} of PCBM in a P3HT:PCBM blend was observed by NMR. After annealing, the cross peak in the HETCOR NMR data is significantly lower in intensity, showing that a smaller population of the P3HT is interacting with PCBM. This result is consistent with the previous studies of this composite that show an increase in the domain sizes of each component and a lowering of the interface area. Based on this single observation, the complex model shown in Figure 1.9 was proposed. This model illustrates the alkyl side chains of P3HT moving away from the C\textsubscript{60} of PCBM after thermal annealing, in addition to intramolecular rearrangement of the PCBM substituent and planar crystal formation of P3HT. Further discussion to validate structural changes within this model, other than the observed interaction between the P3HT alkyl side chain and the PCBM C\textsubscript{60}, was not presented.\textsuperscript{23}

This model is based on the current assumption that P3HT alkyl side-chains form interdigitated planes when crystalline. Recent studies have shown the alkyl side chains of P3HT are bent out of the plane and so would be in closer contact with the C\textsubscript{60} of PCBM in this model.\textsuperscript{24,25} This modification is still in agreement with residual intensity at the cross peak of C\textsubscript{60} and the alkyl side chain after annealing.\textsuperscript{23} Because the current model is established from only a single observed interaction, further data is needed to verify the specific intermolecular interactions present at the interface, and the structural changes presented, such as the formation of ring stacking after thermal annealing shown in Figure 1.9 (f).
1.4 Research Objectives

Much of the structural details of the P3HT:PCBM PV cells are still poorly characterized. To date, little information has been collected to understand the molecular interactions at the interface of these polymers. The interface is one of the critical areas of the PV cell because of its role in exciton diffusion and electron transfer. Understanding the dominant interactions of the P3HT:PCBM interface will help in the rational design of ideal polymer blends for optimized electron transfer. The structural changes in the interfacial morphology from thermal annealing can be monitored with solid state NMR. The interactions between carbons and protons can be seen through use of heteronuclear correlation spectroscopy (HETCOR). This technique can be used to see various interactions within an established radius about a specific $^{13}\text{C}$. Controlling the size of this radius ensures that the interactions viewed are located at the interface and not within the bulk of the domains.
The focus of this work is to characterize the molecular structure of the P3HT:PCBM interface before and after thermal annealing. By varying the spatial observation window of HETCOR NMR, changes to the interface structure from thermal annealing can be closely monitored. This technique yields a high number of intermolecular interaction variations that produce a clearer understanding of the effects of annealing on the interface structure.

This work serves to define the dominant interactions at the interface before and after thermal annealing. This information has been used, along with results from previous characterization methods, to build a detailed model of the structure and structural changes at the interface. Through a better understanding of the P3HT:PCBM interface structure, a relationship between structure and efficient electron transfer can be established and this relationship can ultimately be used for the rational design of optimal PV materials.
CHAPTER II

EXPERIMENTAL

2.1 Photovoltaic films

The P3HT and P3HT:PCBM composite photovoltaic film were spin coated onto glass substrates. A portion of these films were thermally annealed at various temperatures and then characterized with solid-state NMR.

2.1.1 Photovoltaic film production

The control P3HT film was prepared by magnetically mixing 222.6 mg P3HT (Sepiolid P200) into 9 mL of chlorobenzene (25 mg/mL P3HT in chlorobenzene) at 50 °C. The composite P3HT:PCBM film was prepared by magnetically mixing 222.6 mg P3HT (Sepiolid P200) with 131 mg PCBM (ADS Chemically Modified Fullerene) into 9 mL of chlorobenzene at 50 °C, producing a 5:3 weight ratio of P3HT:PCBM. The solutions were drop cast onto 5 cm diameter Teflon® polytetrafluoroethylene casting dishes preheated to 50 °C. The dishes were set in a room temperature, nitrogen purged vacuum oven to dry for 20 min. The films were removed from the substrates and divided using a
razor blade. The annealing treatments were performed under nitrogen for 20 min at room
temperature and 145 °C.

2.1.2 P3HT:PCBM film characterization

Solid-state $^{13}$C (100.5 MHz) spectra were collected on a Varian Unity/INOVA
400 MHz (9.39 T) spectrometer using a Varian 4 mm DR-T3 probe. Samples were
packed into 4 mm zirconia rotors and all spectra were collected with magic angle
spinning (MAS) at a spinning speed of 12 kHz. The $^{13}$C chemical shifts were referenced
to HMB (17.3 ppm; methyl). A 90° pulse width of 4 µs, a recycle delay of 4 s, a cross
polarization (CP) contact time of 5 ms, and a spectral window of 40 kHz were used for all
1D $^{13}$C experiments. The numbers of transients collected are listed in the figure captions.

$^1$H-$^{13}$C Heteronuclear correlation (HETCOR) SSNMR spectra were collected on a
Varian Direct Drive 500 MHz (11.7 T) spectrometer operating at 125.62 MHz for $^{13}$C
using a Varian solids narrow-bore triple-resonance T3 MAS NMR probe. Samples were
packed into 4 mm zirconia rotors and collected with MAS at a spinning speed of 10 kHz.
A 90° pulse width of 4 µs was used with a recycle delay of 4 s. The cross polarization
time and method are listed in the figure captions. Thirty-six increments were used with
256 transients each. The $^{13}$C chemical shifts were referenced to hexamethylbenzene
(17.3 ppm; methyl) and the $^1$H chemical shifts were referenced using the aliphatic P3HT
peak (1 ppm).

Two HETCOR NMR cross polarization techniques were implemented: tangent
cross polarization (TanCP) and Lee-Goldburg cross polarization (LG-CP). Polarization
transfer from $^1\text{H}$ to $^{13}\text{C}$ in TanCP transfers all magnetization from protons within the CP observation window to the carbon of interest through a polarization relay between the protons. This wealth of polarization produces efficient magnetization transfer and results in an increase of signal intensity by a factor of about four. Due to the large range of protons capable of transferring magnetization, this technique is not optimal for determining specific structural changes at the interface and so was utilized for the observation of general morphological changes. In LG-CP, the polarization transfer relay between protons is broken so that the only magnetization that is transferred comes from the protons adjacent to the carbon of interest. The decreased magnitude of transferred magnetization results in a lower signal intensity than that produced by TanCP. This specialized polarization transfer technique was chosen to observe the behavior of the specific intermolecular interactions at the interface before and after thermal annealing.
CHAPTER III

RESULTS AND DISCUSSION

Recent growth in renewable energy sources has created a large interest in photovoltaic cells. Organic PV cells promise lower production costs and a larger variety of starting materials with which to optimize photovoltaic performance.\(^6\) Bulk heterojunction PV systems provide the ability to optimize the electron donor and electron acceptor sites separately and improve PCE with processing techniques, such as thermal annealing.\(^{12}\) One such system is the P3HT:PCBM PV cell, which is known to undergo phase separation during the annealing process.\(^{18-23,25}\) The effect of this separation on the interface structure has been examined by monitoring the interaction of the C\(_{60}\) carbons of PCBM with the protons of the alkyl side chain of P3HT using HETCOR NMR.\(^{23}\) This method shows correlation between two nuclei based on their dipolar coupling interaction. A decrease in signal intensity between the P3HT alkyl side chains and the PCBM C\(_{60}\) in the 2D HETCOR NMR data after annealing the film was attributed to the reduced volume of interface caused from phase separation. From this single intermolecular interaction, a complex model depicting numerous structural changes at the interface of P3HT and PCBM was presented.\(^{23}\) The current study focuses on locating specific
interactions at the interface in order to better understand its molecular structure and develop a rational model built on a number of distance constraints. To accomplish this, 2D $^1$H-$^{13}$C HETCOR NMR techniques at reduced cross-polarization (CP) times were used to focus on short-range carbon to proton interactions.

3.1 Chemical Shift

The different carbons within P3HT and PCBM are identified based on their $^{13}$C chemical shifts. In order to identify the particular carbons that are involved in intermolecular interactions at the interface, the chemical shifts must be determined. In the case of PCBM, there are conflicting reports on the chemical shift assignments. An initial investigation was completed to elucidate the $^{13}$C and $^1$H shifts of P3HT and PCBM.

3.1.1 P3HT Chemical Shift

The single pulse $^{13}$C NMR spectrum for P3HT is shown in Figure 3.1 and the peaks at 136, 133, 130, and 125 ppm are assigned to C-3, C-5, C-2, and C-4 of thiophene. Resolved carbons of the alkyl side chain at 33, 24, and 15 ppm are assigned, in order, to C-9, C-10 and C-11. The peak at 31 ppm is assigned to carbons C-6, C-7, and C-8. These assignments are in agreement with previous studies.
3.1.2 P3HT:PCBM Chemical Shift

The neat PCBM was not investigated so the $^{13}$C NMR spectrum of the P3HT:PCBM composite, Figure 3.2, was used to assign the $^{13}$C chemical shifts of PCBM. From this spectrum, the peaks at 173, 146, 139, and the peak at 128 ppm are assigned to C-5’, C-C$_{60}$, C-7’, and the phenyl carbons, C-8’, C-9’, C-10’, C-11’, and C-12’, respectively.
In addition, 2D HETCOR NMR was used to resolve peak assignments for PCBM that are disputed in the literature.\textsuperscript{23,26} The $^1$H-$^{13}$C 2D NMR spectrum collected for the P3HT:PCBM film after annealing, Figure 3.3, shows strong intramolecular interactions and was used to resolve the disputed peak assignments at 56.7 and 52.6 ppm as well as the corresponding $^1$H chemical shifts. The lack of a peak correlating the $^{13}$C with a chemical shift of 56.7 ppm with protons other than the alkyl protons, H-6 through H-10, at 1 ppm shows that this peak in the $^{13}$C spectrum arises from a quaternary carbon. The peak in the $^{13}$C dimension at 52.6 ppm shows a correlation with protons at 3.2 ppm,
consistent with methyl ester protons. Based on the 2D HETCOR NMR data, the peak at 56.7 ppm is assigned to C-1’ of PCBM and the peak at 52.6 ppm is assigned to the methyl carbon, C-6’. The quaternary carbon bridgeheads of PCBM, Cα and Cβ, at 81 ppm were absent in the work by Yang et al. due to an overlap of a spinning side band caused from using a reduced MAS rate. Additional studies of PCBM confirmed the peaks at 81 ppm arise from the bridgehead carbons.²³,²⁶ The bridgehead carbon correlation at a proton chemical shift around 2 ppm indicates an intramolecular correlation with protons H-2’ through H-4’ of PCBM. The remaining carbons of PCBM fall under the strong signal intensity of the P3HT C-9 and C-10 carbons. Assignments for these carbons were based on NMR prediction and assign the peak at 35 ppm to C-2’ and C-4’ and the peak at 22 ppm to C-3’.

Figure 3.3. 11.7 T ¹H-¹³C HETCOR NMR spectrum of the P3HT:PCBM central region with 5 ms LG-CP time.
The large peak at 1 ppm in the 2D spectrum from P3HT:PCBM, Figure 3.4, is from a contribution of an overlap of signals from the alkyl protons H-7, H-8, H-9, and H-10 of P3HT. The proton peak shoulder at 0.8 ppm is consistent with methyl protons and was assigned to H-11 of P3HT. Proton H-4 was assigned to the peak at 6.5 ppm, which is the expected value for a thiophene proton. The H-6 protons are shifted downfield from the H-7 through H-11 protons by the adjacent thiophene ring to 2.5 ppm. The phenyl carbon peaks of PCBM at 129 ppm are confirmed in the 2D spectrum, with their respective protons at a $^1$H chemical shift between 7-8 ppm observed interacting with the alkyl side chain carbons and C-C$_{60}$ in Figure 3.4. The remaining $^1$H chemical shift assignments are based on NMR predictions. A summary of the $^1$H and $^{13}$C peak assignments is displayed in Table 3.1.
Figure 3.4. 11.7 T $^1$H-$^{13}$C HETCOR NMR spectra of the (A) aromatic and olefinic region and (B) aliphatic region of P3HT:PCBM prepared at room temperature with 5 ms LG-CP time.
Table 3.1. Chemical Shift Assignments

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<th>Sample</th>
<th>Group</th>
<th>$^{13}$C (ppm)</th>
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<tr>
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<td>3</td>
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<td>4</td>
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<tr>
<td></td>
<td>6</td>
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<td>24</td>
<td>1</td>
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<td></td>
<td>11</td>
<td>15</td>
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<tr>
<td>P3HT:PCBM</td>
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<td></td>
<td>1'</td>
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<td>2', 4'</td>
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<td>3'</td>
<td>22</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>5'</td>
<td>173</td>
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<td>6'</td>
<td>52.6</td>
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<td>7'</td>
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<tr>
<td>C$_{60}$</td>
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3.2 Interface Structure

The specific intermolecular interactions at the interface were studied using 2D $^1$H-$^{13}$C HETCOR with Lee-Goldburg cross polarization (LG-CP). This method shows spatial correlations between $^1$H and $^{13}$C by measuring the intensity of the dipolar coupling between them. Dipolar coupling is the direct interaction between the nuclear magnetic moments of two nuclear spins. This through space interaction occurs when the nuclei are 10 Å or closer in proximity; a molecular bond is not required. The intensity of the
dipolar coupling interaction is inversely proportional to the cubed distance between nuclei and the product of their gyromagnetic ratios. As nuclei separate, the magnitude of the dipolar coupling diminishes. In routine tangent CP (TanCP), a strong dipolar coupling between protons gives rise to correlations between $^{13}\text{C}$ and distant protons. In LG-CP, the dipolar coupling between protons is interrupted so that only protons within a few bond lengths of a specific carbon show correlations. This technique produces the localized information needed to better understand the interface structure.

3.2.1 Thermal annealing effect on P3HT structure

In order to understand the morphological changes of the P3HT:PCBM film, the effect of thermal annealing on the morphology of P3HT must be known. A sample of neat P3HT before and after thermal annealing was investigated as a control to identify changes in intramolecular interactions that occur with annealing. With these assignments, the changes in the intermolecular interactions of P3HT:PCBM can be properly assigned.

The 1D $^{13}\text{C}$ direct polarization (DP) MAS spectra for P3HT prepared at room temperature and after annealing at 145 °C are shown in Figure 3.5. The lack of difference in the chemical shifts or line widths indicates that annealing does not impact the composition or morphology of the polymer. 2D $^1\text{H}-^{13}\text{C}$ HETCOR NMR characterization was used in order to achieve higher resolution.
Figure 3.5. 9.39 T $^{13}$C DP/MAS NMR spectra of P3HT (A) prepared at room temperature (scans=16) and (B) after annealing at 145 °C (scans=18088).

The aliphatic regions of the 2D $^1$H-$^{13}$C HETCOR spectra for P3HT before and after annealing at 145 °C are shown in Figure 3.6. These spectra were collected with an LG-CP time of 1 ms, so correlations are observed for only the protons closest to each $^{13}$C. The aliphatic carbons C-6 through C-10 show correlations with $^1$H with chemical shifts around 1 ppm, consistent with the expected correlations for an alkyl chain. The methyl carbon (C-11) shows an expected correlation with a proton chemical shift slightly upfield
from the main alkyl chain around 0.8 ppm. The carbons C-6 through C-8 also show a correlation to the thiophene proton, H-4, at 6.5 ppm. In the olefinic region, Figure 3.7, the carbons of the thiophene ring C-2 through C-5 show strong correlations with H-4 at 6.5 ppm and the aliphatic protons around 1 ppm. The relative intensities of the cross-peaks of the carbons in the thiophene ring with H-4 correlate well with the relative distance between them. The closest carbon, C-4, shows the largest intensity, where as carbons C-3 and C-5 are relatively equidistant from H-4 and show similar correlation intensities. The furthest carbon, C-2, shows the smallest interaction of the carbons in the thiophene ring with H4. The additional interaction of the carbons in the thiophene ring with H-6 at 2.5 ppm becomes stronger after thermal annealing. The correlations observed with a CP contact time of 1 ms are consistent with expected ¹H and ¹³C chemical shifts of P3HT and the increasing intensity with the proton peaks at 2.5 ppm indicate a slight morphological change after thermal annealing.
Figure 3.6. 11.7 T $^1$H-$^{13}$C HETCOR NMR spectrum of the P3HT aliphatic region with 1 ms LG-CP time (A) prepared at room temperature and (B) after annealing at 145 °C.
Increasing the CP contact time results in an increase in signal intensity. The increased thiophene interaction with H-6 after thermal annealing, Figure 3.8, is more evident at a longer CP contact time of 2 ms. At this contact time, the carbons in the thiophene ring show a moderate increase in signal intensity with the C-6 adjacent protons.
A slight increase in signal intensity of the correlation between the thiophene ring carbons and H-4 is also seen. A new intramolecular interaction between C-10 and H-6 of P3HT is also observed after annealing, as shown in Figure 3.9.

Figure 3.8. 11.7 T $^1$H-$^{13}$C HETCOR NMR spectrum of the P3HT aromatic and olefinic region with 2 ms LG-CP time (A) prepared at room temperature and (B) after annealing at 145 °C
Figure 3.9. 11.7 T $^1$H-$^{13}$C HETCOR NMR spectrum of the P3HT aliphatic region with 2 ms LG-CP time (A) prepared at room temperature and (B) after annealing at 145 °C

The intensity increase in the correlations between the carbons in the thiophene ring and the protons of the alkyl side chain after thermal annealing suggests an ordering of the P3HT domain. Previous work has suggested that as the P3HT domain becomes ordered, the thiophene rings in the P3HT chains undergo π-stacking and the alkyl side chains become interdigitated. This would orient C-6 about equidistant from C-2 and C-5. The relative intensity between C-5 and C-2 with H-6 after annealing is about equal.
The short distance between C-3 and H-6 produces the largest signal intensity of the thiophene ring carbon interactions with H-6, while the long distance between C-4 and C-6 relative to the other carbons in the thiophene ring shows the weakest correlation. The presence of the correlation between C-10 and H-6 after annealing at 145 °C suggests a change in the morphology of the P3HT and is consistent with the formation of an interdigitated system.

3.2.2 P3HT:PCBM

In order to investigate the structure of the P3HT:PCBM interface and the impact of annealing on the structure and volume of the interface, P3HT:PCBM films were studied before and after thermal annealing treatment. Intermolecular interactions are assigned by identifying the correlations in the 2D NMR data that are different from the intramolecular interactions seen in neat P3HT. The assignments of the intermolecular interactions are then used to construct a model of the interface structure.

The 1D $^{13}$C direct polarization (DP) MAS spectra of P3HT:PCBM after annealing at various temperatures are shown in Figure 3.10. No large-scale changes are observed in terms of chemical shift, line width, or the presence of new peaks arising from the reactivity of P3HT and PCBM. A small drop in the signal intensity of C-C$_{60}$ is seen with an increasing intensity of thiophene P3HT peaks as the annealing temperature is increased. As annealing temperature is increased the C-9 and C-6 through C-8 peaks become more resolved. 2D $^1$H-$^{13}$C HETCOR NMR using LG-CP was implemented to better understand these changes.
Figure 3.10. 9.39 T $^{13}$C DP/MAS NMR spectra of P3HT:PCBM (A) prepared at room temperature (scans=19592) and after annealing at (B) 80 °C (scans=10800), (C) 105 °C (scans=16656), (D) 120 °C (scans=12904), (E) 145 °C (scans=10324), and (F) 160 °C (scans=15292).

The 2D $^1$H-$^{13}$C HETCOR NMR spectra before and after thermal annealing with a short CP contact time of 0.5 ms are shown in Figure 3.11. The short CP time produces correlations with protons that are closest to each $^{13}$C. The correlations between C-9 and C-10 of P3HT and protons at 2.5 ppm are reduced in intensity upon annealing. Based on observations with pure P3HT, Figure 3.7, a P3HT intramolecular interaction with H-6,
also at 2.5 ppm, would be expected to remain unchanged or increase in signal intensity with annealing. Therefore the correlations are assigned as intermolecular interactions between C-9 and C-10 of P3HT with protons H-2' and H-4' of PCBM. An increase in signal intensity for the correlation between C-6 through C-8 with H-4 at 6.5 ppm is also seen after annealing.

Figure 3.11. 11.7 T 1H-13C HETCOR NMR spectra of P3HT:PCBM aliphatic region with 0.5 ms LG-CP time (A) prepared at room temperature and (B) after annealing at 145 °C.
The aliphatic region of the 2D $^1$H-$^{13}$C HETCOR NMR spectra from P3HT:PCBM with a CP contact time of 1 ms is shown in Figure 3.12. In these spectra, correlations between C-7' and H-6 (2.5ppm) and between C-C$_{60}$ and H-11 (0.8 ppm) are observed before annealing. After annealing, the signal intensity of these cross peaks is decreased. The downfield region in Figure 3.13 shows the reduction in signal intensity after thermal annealing for the interactions between C-9 and C-10 with H-2' and H-4' at 2.5 ppm. These changes are indicative of P3HT and PCBM domain segregation. Further discussion of this phase separation will be addressed below.
Figure 3.12. 11.7 T $^1$H-$^{13}$C HETCOR NMR spectra of P3HT:PCBM aromatic and olefinic region with 1 ms LG-CP time (A) prepared at room temperature and (B) after annealing at 145 °C.
Figure 3.13. 11.7 T $^1$H-$^{13}$C HETCOR NMR spectra of P3HT:PCBM aliphatic region with 1 ms LG-CP time (A) prepared at room temperature and (B) after annealing at 145 °C.

Increasing the CP contact time allows observation of correlations between $^{13}$C and $^1$H that have small dipolar couplings. These smaller dipolar couplings are a result of long intermolecular separation. By extending the CP contact time, more distant intermolecular interactions can be observed. A CP contact time of 2 ms introduces four new intermolecular interactions. With the longer CP time, C-C$_{60}$ now shows correlations with
H-6 (2.5 ppm) through H-10 (1 ppm), Figure 3.14, in addition to the previously seen cross peak with H-11. These C$_{60}$ correlation peaks diminish in intensity upon annealing. The C-7’ carbon of PCBM shows a correlation with the P3HT protons H-7 through H-10 (1 ppm) before annealing and these peaks also have low intensity after annealing. The phenyl carbons of PCBM at 129 ppm show a very weak correlation with the alkyl protons of P3HT, indicating a longer distance between these nuclei. As observed for the other intermolecular interactions, this peak has a reduced intensity with annealing. Likewise, carbons C-6 through C-8 of P3HT display an interaction with the PCBM phenyl protons around 7 ppm that is also reduced after annealing, Figure 3.15.
Figure 3.14. 11.7 T $^1$H-$^{13}$C HETCOR NMR spectra of P3HT:PCBM aromatic and olefinic region with 2 ms LG-CP time (A) prepared at room temperature and (B) after annealing at 145 °C.
Figure 3.15. 11.7 T $^1$H-$^{13}$C HETCOR NMR spectra of P3HT:PCBM aliphatic region with 2 ms LG-CP time (A) prepared at room temperature and (B) after annealing at 145 °C.

The reduction of the intensity of those peaks in the 2D NMR data that arise from intermolecular interactions upon annealing suggests a phase separation between P3HT and PCBM. As the phases separate, the volume of interface is reduced which reduces the total number of intermolecular interactions. As the intramolecular interactions become
dominant, the intermolecular interaction cross peaks, in many cases, are reduced to undetectable levels.

3.3 Long Distance Interactions

Dipolar coupling is inversely related to the distance between nuclei, and therefore long distance $^1$H-$^{13}$C interactions have small dipolar coupling. Nuclei with small dipolar coupling need additional time to build signal intensity in CP experiments. A longer CP contact time allows more polarization to build so that nuclei separated far in space can be observed. Dynamics also has an influence as molecular motions result in a reduction in the $^1$H-$^{13}$C dipolar coupling. This is the case for methyl groups that rotate rapidly around the C-C bond. The methyl group protons will then show weaker peak intensity in the $^1$H-$^{13}$C HETCOR NMR data; so longer CP correlation times are needed to detect those $^{13}$C near methyl protons.

The long CP contact time (5 ms) HETCOR spectra for P3HT:PCBM before annealing, Figure 3.4, and after annealing, Figure 3.16, include long-range interactions between the phenyl protons of PCBM (7-8 ppm) and carbons C-C$_{60}$ and C-6 through C-8. The C-10 carbons show an interaction with H-4 that fades upon annealing. The longer CP time also allows for a signal enhancement in the CP inefficient methyl groups C-11 of P3HT and C-6’ of PCBM. The C-11 carbons show correlations with H-2’, H-4’, and H-6 that diminish upon thermal annealing. The residual C-11 peak after annealing is from the interaction with H-6. The NMR data shows an interaction between H-6’ with C-6
through C-8 that increases after annealing as well as an interaction with C-C$_{60}$ with roughly equal intensity before and after annealing.

Based on the correlations observed in the 2D $^1$H-$^{13}$C HETCOR NMR data, a model for the intermolecular interactions between P3HT and PCBM has been constructed.
In addition to the presence of the correlations, the peak intensities have also been used in a qualitative manner to determine shorter and longer internuclear distances. The model, which is consistent with all of the NMR data, is shown in Figure 3.17. The arrows indicate the observed interactions between carbons and protons. Because the individual C$_{60}$ carbons of PCBM cannot be resolved, the interaction between the C$_{60}$ carbons and the alkyl side chain protons of P3HT is shown simply as an overlap of the alkyl side chains and the C$_{60}$. Likewise, the arrow representing the interaction between C$_{60}$ and the H-6’ protons is representative of all carbons of C$_{60}$. Taken together, the observed interactions suggest π-stacking between the thiophene ring of P3HT and the phenyl ring of PCBM, and this is broken after thermal annealing as the domains separate. As the domains separate, the volume of the interface is reduced leading to a drop in signal intensity for these interactions, as is observed. After annealing, the remaining volume of interface is believed to maintain this basic structure based on the residual peak intensities in the HETCOR data collected with 5 ms CP contact time, Figure 3.16. The residual peaks at a longer CP contact time verify that the reduction in signal intensity seen with shorter CP contact times was due to a reduction in the amount of intermolecular interactions present after thermal annealing and not from structural variation.
3.4 Morphology

There have been numerous studies on the impact of thermal annealing to the morphology of the P3HT:PCBM system. In the previous section, 2D $^1$H-$^{13}$C HETCOR using LG-CP was used to identify changes in the interface region of P3HT:PCBM. This section will focus on the changes to the packing of the P3HT and PCBM domains after thermal annealing. 2D $^1$H-$^{13}$C HETCOR using tangent cross polarization was chosen to observe the changes in domain morphology with solid-state
NMR. With the TanCP method of cross polarization, the polarization transfer relay between protons is used to transfer magnetization from all protons within a few bond lengths to the carbons. This results in greater signal intensity than LG-CP. Because the volume of the domains is much greater than the volume of their interface both before and after annealing, the main source of polarization transfer in TanCP comes from protons within the bulk domains. This makes the TanCP technique more sensitive to changes in domain packing than changes in interface volume.

3.4.1 P3HT Morphology

A neat P3HT film was examined as a control to determine the effect of thermal annealing on its morphology. These results are used to confirm that the changes observed in the NMR data upon thermal annealing arise from changes of the P3HT:PCBM interface and not solely from changes in the morphology of P3HT. Thermal annealing had little effect on the morphology of the P3HT film in the aliphatic region, Figure 3.18, and the aromatic and olefinic region, Figure 3.19. No changes in chemical shift were observed, which is in agreement with the LG-CP results. The LG-CP data shows a significant increase in signal intensity between the carbons in the thiophene ring, C-2 through C-5, and H-6 that is not seen in the TanCP data, suggesting that ordering of the neat P3HT film from thermal annealing occurs on a small scale.
Figure 3.18. 11.7 T $^1$H-$^{13}$C HETCOR NMR spectra of P3HT aliphatic region with 1 ms TanCP time (A) prepared at room temperature and (B) after annealing at 145 °C.
Figure 3.19. 11.7 T $^1$H-$^{13}$C HETCOR NMR spectra of P3HT aromatic and olefinic region with 1 ms TanCP time (A) prepared at room temperature and (B) after annealing at 145 °C.

3.4.2 P3HT:PCBM Morphology

In the 2D $^1$H-$^{13}$C HETCOR spectra before and after annealing, Figure 3.20, the signal from the H-4 proton is split by a width of 0.7 ppm. Before annealing, the majority of the H-4 signal intensity lies at 5.8 ppm and most of the peak intensity shifts to a
chemical shift of 6.5 ppm after thermal annealing. This 0.7 ppm downfield shift of H-4 is also observed in the interactions with the alkyl side chain carbons, Figure 3.21. The shift in intensity of the H-4 peak reflects a change in the packing environment of P3HT.

When the film is cast, P3HT is well mixed with PCBM. The strong presence of an aromatic environment moves the chemical shift of the thiophene proton 0.7 ppm upfield to 5.8 ppm. When annealed, the P3HT strands aggregate, moving H-4 into a dominant thiophene environment. The thiophene environment returns the H-4 chemical shift downfield to 6.5 ppm. The thiophene proton also shows an increase in signal intensity with the alkyl side chain carbons, C-6 through C-11. This increase in signal intensity is indicative of an ordered P3HT domain. As the P3HT domain becomes ordered, the π-stacking and interdigitated packing of P3HT surrounds H-4 with alkyl side chains, increasing the dipolar coupling between them. As this interaction strengthens, the corresponding cross peaks increase in signal intensity.
Figure 3.20. 11.7 T 1H-13C HETCOR NMR spectra of P3HT:PCBM aromatic and olefinic region with 1 ms TanCP time (A) prepared at room temperature and (B) after annealing at 145 °C.
Figure 3.21. 11.7 T $^1$H-$^{13}$C HETCOR NMR spectra of P3HT:PCBM aliphatic region with 1 ms TanCP time (A) prepared at room temperature and (B) after annealing at 145 °C.
CHAPTER IV

CONCLUSIONS

The structure of the interface between P3HT and PCBM was studied with SSNMR. The $^1$H and $^{13}$C chemical shifts were determined with 1D $^{13}$C SSNMR and 2D $^1$H-$^{13}$C HETCOR NMR. Specific intermolecular interactions were identified with 2D $^1$H-$^{13}$C HETCOR NMR utilizing Lee-Goldburg cross polarization. This method removes the $^1$H-$^1$H dipolar coupling so only localized protons would cross polarize to the $^{13}$C. This allowed for more focus on the structural changes at the interface after thermal annealing.

A second method of 2D $^1$H-$^{13}$C HETCOR NMR using tangent CP was used to detect changes in the morphology of the composite film. Tangent CP allows for a polarization transfer from all protons within the CP window, which expands the view to the domains of P3HT and PCBM.

When using the LG-CP method, interactions between the aliphatic regions of P3HT and PCBM as well as an interaction between the thiophene region of P3HT and the phenyl ring of PCBM suggest a favored $\pi$-stacking configuration at the interface between the P3HT chains and the substituent of PCBM. Residual peaks in the NMR data at
longer CP contact time suggest that the proposed interface structure remains intact after thermal annealing.

The 2D HETCOR TanCP method showed a 0.7 ppm split in the $^1$H chemical shift of the P3HT thiophene proton. When cast, the proton on the thiophene ring is observed at a $^1$H chemical shift of 5.8 ppm and after thermal annealing, this interaction shifts downfield to 6.5 ppm as it moves into a concentrated thiophene environment. This shift reflects an environment change of P3HT from a well-mixed state with PCBM to a well-ordered P3HT domain.

The NMR analysis of this blend shows thermal annealing to cause phase separation in the P3HT:PCBM PV cell. A basic model of the structure at the interface of these domains has been constructed based on the specific interactions identified. Though the volume of interface decreases as the domains grow, the structure of the interface remains intact. Previous studies by Yang et al. have hypothesized the general structure of this interface without the support needed to confirm the resulting model. The interactions identified in the current study lead to a more confident understanding of how these domains interact at the interface when cast and after thermal annealing. This understanding can be applied to the improvement of future photovoltaic systems by designing polymers to mimic the favored interactions found in this system for better electron transfer across the domains.
REFERENCES


APPENDIX

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Author: Cuiying Yang,†, Jerry G. Hu,‡ and, and Alan J. Heeger*,†

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