Functional multi-layer solution processable polymer solar cells

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UC Davis

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Original Objectives

- 1) Develop a method to deposit multiple conjugated polymer film layers and avoid the problem of dissolution from mutually solubility
- 2) Use this deposition method to develop multi-layer polymer based solar cells with layers that are function specific
- 3) characterize these layers and devices
- 4) develop electrical and optical models that describe and predict the properties of the multi-layers
- 5) Ultimate efficiency goals are ~6.75% with $J_{sc} = 12 \text{ mA/cm}^2$, $FF = 0.75$, and $V_{oc} = 0.75$.

Accomplishments on Original Objectives

- 1) Objective Achieved – we developed a method using interface mixing that allows deposition of function specific layers at both interfaces of an organic PV layer.
- 2) Objective Achieved – we fabricated devices based on our deposition method that achieves the goal of blocking dark current and raising FF and V_{oc}
- 3) Objective Over Achieved – we not only characterized the devices based on known methods, we developed several new methods to detect
 - a. Vertical segregation of materials under a metal electrode using Neutron Reflectometry
 - b. Whether doping occurs using NEXAFS
 - c. Whether doping occurs using detection of H_2 in a GCMS
- 4) Objective Over Achieved – We developed accurate optical models and also performed kinetic optical studies that lead to a suggestion of a new charge separation mechanism (independently verified by Heeger group). There was considerable discussion at the Spring 2012 MRS about the mechanism. We are currently developing an inclusive electrical model in collaboration with the Reide group from Dresden, Germany. This model takes doping at interfaces into account and is an extension of work on small molecule OPV. The model correctly predicts formation of partial layers of polymer between PEDOT:PSS and the active PV layer, even when the interlayer polymer is different from the PV layer polymer.
- 5) Objective Not Achieved – Although we spent over \$10,000 on new polymers and fullerenes, investigated new interface materials and several new materials from collaborators, we did not find a new material that increased the efficiency to over 6%. Much of the problem is that the purchased materials are of very low quality with large impurity content. We have presented analytical chemistry data about the quality problem at several conferences in 2011-12.

Detailed Accomplishments - 08

- Purchased and setup of most equipment
- Preparation of film samples and measurements using atomic force microscopy (topography, phase, conduction and Kelvin probe modes), neutron reflectometry, ultra-fast pump-probe optical laser spectroscopy, and scanning electron microscopy.
- Setup of optical and electrical modeling of multi-layer films. First publication is in preparation.

Detailed Accomplishments - 09

- Hired 3 students + cost share postdoc at 50% time
- Developed a multiple layer deposition method and test to make sure layers don't mix
- Determined that material layers mix upon heat tempering + electrical consequences
- Developed a method for using mixed electrode-active layer interlayer to fix work function
- Perform optical and electrical measurements of organic electrode materials from Plextronics
- Determine that published methods for making bi-layer devices from solution ineffective
- Determine kinetic difference between various fullerene acceptors

- Determine that PCBM crystallization is controlled by trace solvents and that the non-solvent additives can be used to increase the stability of polymer/fullerene morphology
- Published 4 articles on optical modeling and morphology + 5 articles in preparation

Detailed Accomplishments – 10

- Published two articles and submitted two more which were accepted in FY11
- Postdoc David Huang accepts faculty position at the University of Adelaide, Australia.
- Detailed work on PTMESS, a replacement for PEDOT:PSS (two papers in preparation)
- Developed method to create doped interface layers that regulate Voc (article accepted)
- Performed optical and electrical measurements of organic electron donor materials from Plextronics (two papers in preparation)
- Performed optical and electrical measurements of organic electron acceptor materials from Plextronics
- Prepared method to determine mixing between donor and acceptor materials using fluorescence, neutron reflectometry, and x-ray reflectometry (paper in preparation).
- Developed Kinetic model for recombination to fullerene acceptors (paper in preparation)
- Determine role of co-solvents on PCBM diffusion (paper in press)
- Determine best co-solvent for device longevity (paper in preparation)

Detailed Accomplishments – 11+12

- Published five articles in FY11 and one in FY12
- 5 more articles are either submitted or in Preparation for FY12
- Detailed work on PTMESS, a replacement for PEDOT:PSS – one paper published and two more in prep. (all work here with Plextronics Materials)
- Developed method to deposit p-type interlayers at the PEDOT:PSS interface, to determine whether the interlayer is doped, and device IV fitting to explain how charge density at the interface affects IV properties. The main result is that we show two separate doping mechanisms in the PTMESS matrix. Discussions are underway with Plextronics for a long term research funding for Moule students to develop a surface doping system.
- Published two laser studies on exciton dynamics and recombination dynamics. Our recombination paper was published in 2011 – Heeger group has since verified our new recombination mechanism that shows direct separation of excitons to free charges without first going to CT state.
- Prepared method to determine mixing between donor and acceptor materials using fluorescence, neutron reflectometry, and x-ray reflectometry.
- Determine role of co-solvents on PCBM diffusion
- Determine best co-solvent for device longevity – all co-solvents affect the Polymer and fullerene molecular differently. We categorize the effects and verify using NMR and DSC (paper in Prep)
- We show that bilayers of P3HT and PCBM cannot be made from solution and determine the vertical distribution of materials using Neutron Reflectometry (published in FY12)
- We show that low work function metals can dope fullerenes and that the doping has a large effect on the distribution of materials in the BHJ layer. (submitted)
- We show that PEDOT:PSS itself is an anisotropic material and will only act to dope the BHJ polymer if the PEDOT:PSS is deposited first. (in prep)
- S. Mauger and C. Rochester, the students supported on this grant are scheduled to Graduate before June 2013.

1. Introduction

The question of whether photovoltaic (PV) cells will ever be able to replace fossil fuels as the main provider of electrical power is not just a

question of device efficiency; it is a question of how much power can be provided for what price. It has been well documented¹ that PV devices at 10% power efficiency can provide for all of the world's power needs without covering too much of

the earth's surface. Assuming desert like cloud coverage, an area equivalent to the land area of Texas would have to be covered. However, it has also been shown that using the current state-of-the-art silicon devices, the price-per-Watt will never be low enough to be economically feasible for large-scale development. Solution-processable PV devices based on polymers are a very attractive alternative to traditional Silicon PV because this technology is much lower in materials cost and in environmentally toxic waste production. Solution-based polymers can be rapidly deposited using printing technologies and are compatible with light-weight flexible substrates that can increase the range of available PV applications.^{1,2} In the past ten years, the efficiency of polymer based PV devices has increased from ~1%³ to over 10%.

The highest efficiency organic solar cells are based upon a single layer than consists of a mixture of donor and acceptor moieties. This one layer has multiple optical and electrical functions, so the design of a single heterojunction layer is based upon the idea of balancing good and bad properties within a single film. This proposal addresses the idea that the use of multiple layers that have differing electrical and optical functions could lead to greater efficiency because fewer materials compromises must be made. This idea is not new, multiple functional layer have been successfully used in cross-linked OLED's^{4, 5} and organic small molecule evaporated PV devices.⁶ The main reason that multiple layers of polymers are not commonly deposited is that most conjugated polymers are mutually soluble in the same solvents. The work outlined in the proposal was intended to develop a new deposition strategy that would allow multiple organic layers to be deposited from solution using spin coating.

The deposition method that we proposed was successful, sometimes, but ultimately not reliable. Instead we focused on more reliable methods to implement doping along the interface between layers. This work has been very successful. We found that using PEDOT:PSS, the PSS would form a surface layer of ~2-3 nm thickness that would mix with and electrochemically react with P3HT upon heating. This mechanism is also a crosslinking reaction in that H₂ is released and permanent new bonds are formed. Using the Plextronics Inc. replacement to PEDOT:PSS, for which there are no mobile dopants, we were able to show that a second and different mechanism can be used to p-type dope organic materials. We are currently working with Plextronics to develop a

new product. Finally we produced n-type doping of a thin fullerene layer near the cathode also using a self-assembly method. Low work function metals will diffuse into the BHJ layer and dope the fullerene upon heating. This doping also affects the vertical segregation of BHJ materials in a predictable way.

We accomplished all of the scientific goals that we set out in the proposal written in May 2007. Some of the methods we proposed were not fully successful, but we did come up with better methods to achieve the same goal. We did not achieve the efficiency goal for this proposal. We did increase V_{oc} and explain why, but the same effect did not affect FF or J_{sc} as we had proposed.

2. Technical Approach

The main scientific issues addressed in FY 2008-12 were examination of the polymer-polymer interfaces, polymer-fullerene mutual solubility, charge selective interfaces, doping levels at interfaces, and fullerene crystallization. The purpose of the solubility studies was to determine whether bi-layers of a polymer with the fullerene could be formed from solution processes. The answer is unfortunately no. The polymer interface studies were to determine how, why and with what effect dipole (doped) layers form across polymer/polymer interfaces. Naturally, if one polymer layer is to be deposited onto another, the transfer of charge across the heterojunction is an issue of high importance.

The main technical issue was developing a method to deposit multiple layers from solution without dissolving previous layers. We proposed a method using temporary protection layers which was ultimately unreliable. We find that the method would work a lot better using a slot die coater, but did not have sufficient funds to buy the necessary equipment to perform experiments using the slot die coater.

The basic question of charging across layer interfaces was addressed in the proposal and has proved to be a very interesting subject with considerable follow-up research still planned.

Active layer PEDOT:PSS interface

In a real device, one of the electrodes is made from a doped organic material called PEDOT:PSS. This material has some of the properties of a metal in that it conducts well, but the charge densities are much lower and it is not uniform in structure. In previous work, we found that light absorbed in the vicinity of the PEDOT:PSS electrode had a much lower probability of

producing photocurrent. Detailed optical modeling and electrical measurements led us to conclude that the excited states, called excitons, that are created in the ~15 nm closest to the electrode are most likely quenched by a high density of holes at this interface.⁷ This result was confirmed by the work of Ferguson et.al.⁸

The question still remains: Why do the holes build up to such a high density at this interface? To answer this question, we have been examining this interface after it is processed under different conditions. We have determined that the electrical characteristics of the interface are unique because PSS is miscible with a range of polymers upon heating but PEDOT:PSS is not. For this reason if polymers are deposited onto PEDOT:PSS a doped interface can be created upon heating, but if PEDOT:PSS is deposited onto the polymer, no mixing occurs and also no doping. The mechanism for doping is shown below.

We have used this heating trick to make interfaces with predetermined electrical characteristics and then can change the electrical characteristics of the devices prepared from these electrodes in a predictable manner.

In the last year we have re-run many experiments to determine why a charged (doped) polymer can mix with a non-polar polymer to become insoluble. Since these polymers are soluble in completely orthogonal solvents it is strange that they mix. We found that the mixing occurs because of the formation of an ionomeric mixed layer and that the formation of this ionomer results in evolution of H₂ in small quantities. This reaction creates a new <5 nm thick layer that is important in controlling the electrical device properties.

New Materials

We have obtained transparent polymer electrode materials from Plextronics Inc., improved electron acceptors from Luna Innovations Inc., experimental donor polymers from Prof. Ullrich Scherf from the University of Wuppertal, Germany

and both experimental donor polymers and functionalized electrode materials from Prof. Mihaela Iovu from the University of Texas, Dallas.

Of these materials, only the S-P3MEET from Plextronics resulted in publications and new science. The S-P3MEET (called PTMESS previously) is a series of self-doped thiophene polymers that are p-type doped. Additional (mobile) dopants are added to tune the morphology and conductivity. We showed that acidic dopants will cross-link and dope to the S-P3MEET with the same mechanism as with PSS and P3HT. By comparison, molecular dopants like F4TCNQ will also increase the doping density, but the dopants are not fixed in location and so will diffuse to other layers upon heating. Much of the work on S-P3MEET is still in preparation, partially to give Plextronics time to patent information.

3. Executive Summary

As stated in the introduction, OPV technology is exciting because there is a possibility to greatly lower the cost per Watt produced of solar energy. Also, because OPV is compatible with flexible substrates, the weight of PV modules can be greatly reduced, opening new applications for solar penetration into the market. The detailed and often mechanistic results of our studies were all designed to gain information that will improve the design of OPV devices to be either more efficient or longer lasting. We also wrote several papers to dispel literature myths created by researchers that are less careful than us. Papers 1, 5, and 12 fall into this last category. Paper 6 is a review, the subject of which is research and technology steps required to commercialize OPV. We identify the most important steps as creating of transparent flexible substrates, control of charge transport at layer interfaces, and increasing the longevity of OPV devices.

Papers 10-18 all address the problem of selective transport at layer interfaces. The problem is to collect photogenerated current while simultaneously reducing dark current and reducing recombination in a material that can be deposited from solution and that does not require heating to above 150°C. We explored several ways to accomplish this mission by introducing doped layers on either side of the active PV layer. Our work is unique because we introduce the doping using self-assembly processes that are compatible with high throughput printing. All other work in this country on selective interfaces relies on either oxide materials that require high temperature processing (not compatible with low-cost printing) or with the formation of self-assembled

monolayers (SAMs) that have been repeatedly shown to be delicate and unreliable over large areas (also not compatible with low-cost fabrication). The selective interface work performed here will have an even larger effect in tandem OPV devices.

The doping mechanism shown on the figure above has large implications for device longevity. We can show that this process occurs with heating and we know that in a normal daily cycle heating to up to 80C occurs in sunlight. We can now ask, does the cross-linking reaction prevent further doping of the PV layer (which would be bad) and increase longevity or does this reaction contribute to reduced longevity. We are currently investigating this.

Paper 9 addresses longevity of the PV layer itself. We measured that trace quantities can have a large effect on the diffusion rate of fullerenes. Increased diffusion leads to crystallization and device failure. We also showed that some non-solvent additives can reduce the fullerene diffusion rate and thereby increase device longevity. We are performing follow-up work to determine the molecular mechanism at work and to design even more effective ways of fixing polymer/fullerene morphology. Paper 13 will show that non-solvent additives also have a large effect on fullerene concentration at the metal interface. We believe that controlling this interface concentration is what inhibits fullerene diffusion.

In conclusion, we worked to develop improved materials for selective charge transport at interfaces which has important implications for both device efficiency and device longevity. Most important is that our materials are compatible with low-cost and high-throughput fabrication. The materials we used react to form insoluble networks at elevated temperatures which should lead to improved device lifetime. We also worked on additives to the BHJ layer that will increase the lifetime of the BHJ layer morphology. This work was compatible with DOE-EERE's goals for higher efficiency and longer lifetime OPV devices.

Contributions from Specific group members:

Prof. Adam Moulé

- Wrote a scientific paper for the Journal of Applied Physics on the optical properties of solid state sensitized solar cells (paper 4)
- Wrote a review article for Advanced Functional Materials on morphology control in bulk-heterojunction layers. (paper 3)

- Wrote a review article for Current Opinions in solid state and materials science on the necessary steps for scale-up of OPV technology. (paper 6)
- Wrote ½ of the paper for Advanced Functional Materials doped interface layers (paper 10)
- Oral presentation results from the DOE project at:
 - 1) U Illinois (materials 10)
 - 2) U. New Mexico (chemistry 10)
 - 3) U. Houston (chemistry 10)
 - 4) U. Mass Amherst (chemistry 11)
 - 5) Stanford U. (Materials 09)
 - 6) Gordon conference on electronic properties of organic materials (08 and 10)
 - 7) MRS Spring (09, 10, 12)
 - 8) AIChE (09 2x)
 - 9) ACS (09 2x)
 - 10) SPIE (09,11)
 - 11) EMRS (11)
 - 12) HOPV-11 (11)
 - 13) Advanced Light Source workshop (11)
 - 14) NIST seminar (11)
 - 15) ICAM annual meeting (09,10)
 - 16) NSF-Egypt solar workshop (12)
 - 17) UC Solar symposium at UC Merced (11)

Total 24 presentations from A. Moule on this DOE work.

Dr. David Huang – now a Prof. in Adelaide Au.

- Performed optical modeling for (papers 1 and 4)
- Wrote paper for Journal of Applied Physics on optical modeling of dye sensitized solar cells (Paper 2)
- Co-Wrote an article about MD modeling of OPV morphology (Paper 5)
- Wrote ½ of the paper for Advanced Functional Materials doped interface layers (paper 10)
- Contributed to several other articles.

Dr. Daniela LaGrange

- Performed initial work on the formation of doped interlayers between P3HT and PEDOT:PSS.
- Is a contributing author on (paper 10) and one paper in preparation

Dr. Katie Yoon

- Is a contributing author on (paper 10)

Ms. Lilian Chang

- Wrote an article about PCBM diffusion due to trace solvents. Tied the diffusion rate to altered melting temperatures of the polymer or fullerene. (paper 9)
- Contributed to work on the anisotropic properties of PEDOT:PSS (in preparation)
- Prepared samples for (paper 7)

Mr. Chris Rochester

- Developed a method for depositing multiple mutually soluble layers using removable protection layers.
- Prepared samples and contributed to (paper 8)
- Determined that all published methods for making P3HT/PCBM bilayer devices actually cause layer mixing. PCBM can be easily washed out of a P3HT film. Has characterized the degree of mixing caused from solution and quantified the result using reflectometry. (Paper 12)
- Determined that surface tension of metal electrode causes vertical segregation in OPV layers, designed a method to test it. (submitted)
- Performed study of doping in S-P3MEET using F4TCNQ (in preparation)

Mr. Scott Mauger

- Contributed to initial study of mixing between P3HT and PEDOT:PSS (paper 10)
- Performed initial study of S-P3MEET and published article in Organic Electronics (paper 11)
- Performed study of doping of S-P3MEET using Nafion (in preparation)

- Led study of anisotropic properties of PEDOT:PSS (in preparation)
- Led study of vertical segregation due to doping by the metal electrode (submitted)

Mr. Eric Busby

- Performed ultra-fast spectroscopy measurements of recombination with 5 different functionalized fullerenes. (Paper 8)
- Performed study of exciton migration and chain reorganization of optically excited P3HT (paper 7)

Mr. Khanh Do

- Wrote a paper about stability of the polymer backbone based on MD modeling (paper 5). Note that Khanh was an undergrad in my group

Eight other undergrads contributed to the work in this project. Most of them have already graduated, but several new undergrads are currently being trained to carry out this work.

Publications from this work⁹⁻²⁰

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Submitted

13. Mauger, S. A.; Chang, L.; Friedrich, S.; Rochester, C. W.; Huang, D. M.; Wang, P.; Moule, A. J., Self assembly of selective interfaces in organic photovoltaics. *submitted to Advanced Materials* 2012
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In Preparation²¹⁻²⁶

15. Mauger, S. A.; Chang, L.; Rochester, C. W.; Moule, A. J., Directional dependence of electron blocking in PEDOT:PSS. *In Preparation* 2012.
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Collaborations Fostered through this Proposal

- 1) Michaela Iovu UT Dallas - made some polymers for us, but the polymers did not produce a viable morphology with fullerenes.
- 2) Stephan Friedrich LLNL - performed all NEXAFS measurements for us at LBNL which resulted in one publication (paper 10) and three more either submitted or in press (papers 13, 16, 17)
- 3) Jarek Majewski LANL - beam line scientists at LANSCE. We have performed a lot of neutron reflectometry measurements with some collaboration from Jarek and his postdoc Peng Wen. Even if not listed they were supportive in (papers 10, 13, 16, and 17)
- 4) Moritz Riede Dresden, Germany - his groups has prepared samples and sent them to us for reflectometry measurements. Also a student from Dresden is performing IV fitting of devices with interlayers (paper 18)
- 5) Olle Inganäs Linköping, Sweden - we wrote an optical modeling paper (paper 1) together that has been well cited. Prof. Inganäs will now hire Scott Mauger (my student) for a short research stay in Linköping. This collaboration will most likely last.
- 6) Delmar Larsen UC Davis - We wrote two spectroscopy papers together (papers 8 and 7). Both papers were quite fundamental and this interaction has led to at least 10 further joint proposals written. Unfortunately, they have not been funded. We will continue to collaborate.
- 7) Plextronics Inc. Pittsburgh PA - We started working with Plextronics in 2008 and have produced one paper with their materials (paper 11). This first paper was delayed in publication due to IP issues. We have prepared two further papers based on Plextronics materials (in prep 16 and 17). We are in discussions about direct funding of Moule research from Plextronics.
- 8) Dana Olson NREL - We have recently decided to work together on reaction between the PSS group in PEDOT:PSS and materials in adjacent layers. This collaboration is very new.
- 9) Louise Berben UC Davis - an electrochemist that works on high adduct fullerenes with us. We have one or two papers in preparation.

Techniques Fostered through this proposal

- 1) H₂ detection to determine whether doping occurs was shown for the first time here.
- 2) Using GCMS to detect trace solvents in OPV layers was shown for the first time by us.
- 3) We have several papers on the use of Neutron reflectometry in OPV devices. While our article is not the first to show the use of this technique, we were showing data at conferences 2 years before the first paper. Our contacts at the neutron facility in LANL stated that user proposals for OPV are growing exponentially.
- 4) We showed, for the first time, how x-ray and electron detected NEXAFS/XANES can be used in combination to separate bulk and surface effects in OPV samples
- 5) We showed how NEXAFS can be used to determine whether doping occurs in organic samples.

- 6) Demonstration of chain relaxation in the ground state of a polymer using pump-dump-probe ultrafast spectroscopy

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