

Link Foundation Fellowship Report

Efficient and cost effective solar cells:
New materials for improved recombination and
charge dissociation losses in organic photovoltaics

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1. Project narrative

Introduction

Solar energy resources are vast: more energy hits the planet in one hour than humankind consumes in entire year. However, solar technologies have only been used to a limited degree in energy production thus far because of high costs.¹ Organic solar cells²⁻²¹ offer the potential to change the landscape of how we produce and use energy. If developed into a mature technology, they present the opportunity to significantly reduce solar energy costs through earth-abundant materials, efficient installation, and roll-to-roll production.⁶⁻⁸ Their properties and designs can be tuned and optimized via materials versatility, solution-based processing, and mechanical flexibility.⁸⁻¹⁰ In recent years, there have been numerous improvements in power conversion efficiencies, with the 8% threshold recently being crossed.²²⁻²⁴ While these efficiencies continue to be notably less than today's commercial solar cells, the steady improvement in efficiencies has generated significant interest in their potential to become practical, widespread sources of energy production. However, in addition to key lifetime improvement needs, moving to power conversion efficiencies >10% is regarded as an important threshold for widespread deployment, and therefore, major materials and cell design advances are still needed. Achieving these developments will require a better understanding of organic solar cell loss mechanisms before high efficiencies can be achieved.

Organic solar cell overview and summary of findings

Fig. 1 presents an illustration of a bulk heterojunction (BHJ)¹⁴ organic solar cell (also referred to as an organic photovoltaic, or OPV, cell). The typical structure, from top to bottom, consists of a window electrode, which is generally made of glass coated with a transparent conducting oxide, usually tin-doped indium oxide (ITO). This is followed by an interfacial layer (typically an organic or metal oxide layer). Next, the absorber (active) layer, which is responsible for the photovoltaic activity of the cell, consists of an interpenetrating network of electron donor (hole-transporting, red) and acceptor (electron-transporting, green) materials. In state-of-the-art systems, the donor is generally the light-absorbing material; however, recent work has also focused on investigating light-absorbing acceptors.¹⁹⁻²⁰ Finally, the bottom contact typically consists of a second interfacial layer (e.g., LiF or TiO_x)¹⁰⁻¹⁴ and a metal electrode, such as aluminum.

Unlike the case in polycrystalline silicon solar cells, the electron-hole binding energy in organic solar cells is high (e.g., ~0.3-0.5 eV)²⁵⁻²⁷ so that light absorption leads to the generation of a bound electron-hole pair known as an exciton. To split the exciton, an energetic offset at the donor-acceptor interface is employed to overcome this binding energy. Excitons diffuse from their photogeneration point until reaching one of these interfaces. In the case where the donor (red) material is the primary

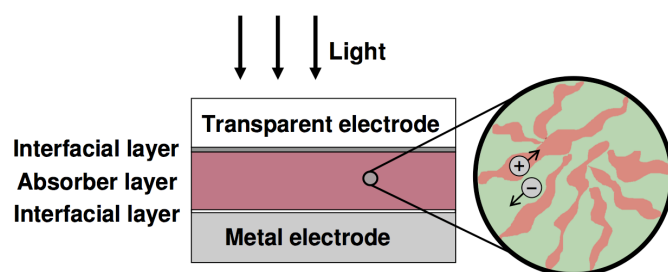


Figure 1. Diagram of a bulk heterojunction organic solar cell.

light absorber, the photoexcited electron from this bound pair is then donated to the acceptor, forming a charge transfer state at the interface with the electron on the acceptor and hole on the donor.²⁸⁻³¹ The dissociation-recombination dynamics of this “geminate pair” state are of critical importance in achieving high efficiency organic solar cells. Furthermore, the architecture of the BHJ OPV cell is unique due to two competing length scales: exciton diffusion distances are on the order of 10 nm¹⁰⁻¹⁴ before exciton decay, whereas typical active layer thicknesses required for optimum light absorption are >100 nm.¹⁰⁻¹⁴ In order to (1) position donor-acceptor sites within ~10 nm of the photon absorption site *while* (2) absorbing the majority of light with energies above the bandgap, the BHJ OPV architecture of placing donor-acceptor interfaces throughout the active layer bulk has been extensively explored and refined.¹⁰⁻¹⁴ This design has led to impressive internal quantum efficiencies approaching 100% for photons with energies greater than the absorber bandgap.¹² (Note that internal quantum efficiency is defined here as the probability that a photon absorbed by the active layer is converted into collected charge at the electrodes at $V = 0$.)

In this project, we developed OPV models and design strategies based on mechanisms for charge carrier recombination and resistances. Traditional solar cell models, originating with the work by Shockley, are widely used in understanding BHJ organic solar cell response. While these models are useful for evaluating OPVs, there are several key points of departure from traditional solar cell behavior. This project addressed areas focused on photocurrent recombination and resistance loss characteristics. We quantified how resistance effects in organic solar cells differ from traditional models due to both field and cell area dependencies. Organic semiconductor mobilities and charge densities exhibit significant sensitivity to field strength, leading to unique resistance behavior. Resistance losses are also sensitive to cell area, due to the limited conductivities of electrode materials used. With these behaviors in mind, we quantified in this project how OPVs are approaching the limit of resistance-based efficiency enhancement. Furthermore, recombination losses in organic solar cells are paramount. Since OPV materials typically have significant charge carrier binding energies (e.g., ~0.3-0.5 eV), recombination of geminate photogenerated charge carriers can be a significant issue in these cells not observed in traditional silicon solar cells. Additionally, the morphology of BHJ organic solar cells allows for dissociated charge carriers to recombine before being extracted from the cell, creating another photocurrent loss mechanism. We show in this project that geminate electron-hole pair recombination has a major impact on limiting current state-of-the-art efficiencies to ~7-8%. Achieving high efficiency OPVs (>10%) will require reducing exciton binding energies and increasing mobilities near the donor-acceptor interface. Traditional OPV design routes of reducing the optical bandgap ($E_g \approx 1.5$ eV) to achieve high efficiencies are shown to be ineffective. OPVs also employ interfacial layers that serve a unique role in BHJ organic solar cells; in addition to usual functions like photon transmission and charge injection, it was quantified here how interfacial layers often need to act as minority carrier “blocking” layers, ensuring that only majority carriers are collected at their respective electrode. Therefore, consideration of the above deviations from traditional models is imperative for the successful design and synthesis of new generation materials for high efficiency organic solar cells.

Significance and impact of the project

The development of new energy technologies is crucial for climate stability and global security. Meanwhile, solar energy resources are vast: more energy reaches our planet in one hour than humankind consumes in an entire year. However, solar technologies have thus far only been used to a limited degree in energy production because of high costs. Organic solar cells offer a potential route to large-scale solar deployment based on the possibility of large cost reductions using earth-abundant materials and inexpensive production technologies. Yet, despite recent advances, organic solar cell efficiencies lag behind their inorganic counterparts, and new materials are needed to

enhance performance. Furthermore, existing performance limitations are not completely understood and are a reason for organic solar cells not yet reaching their full potential. In this project, we propose new physical models showing how organic solar cell function differs from traditional models. Designing materials through effective new models will help this promising new solar technology achieve high performance levels and enable solar technologies to achieve large-scale energy production.

Where this project might lead

The overarching goal of this project was to provide insight for materials engineers and scientists who are designing the next generation of OPVs. Therefore, the results from this project provide an understanding of the key loss mechanisms and strategies for overcoming them in producing high efficiency OPVs. At Northwestern specifically, upon the completion of my PhD, OPV research has continued in the Marks and Ratner groups. The experimentalists are applying the findings from this project, in addition to theorists developing upon the models created during this project.

2. Journal Articles and other scholarly reports supported by this Link Fellowship

J. D. Servaites, B. M. Savoie, J. B. Brink, T. J. Marks, M. A. Ratner, "Modeling Geminate Pair Dissociation in Organic Solar Cells: High Power Conversion Efficiencies Achieved with Moderate Optical Bandgaps," *Energy & Environmental Science*, 5, 8343-8350 (2012).

J. D. Servaites, M. A. Ratner, T. J. Marks, "Organic Solar Cells: A New Look at Traditional Models," *Energy & Environmental Science*, 4, 4410-4422 (2011).

S. Dongaonkar, J. D. Servaites, G. M. Ford, S. Loser, J. Moore, R. M. Gelfand, H. Mohseni, H. W. Hillhouse, R. Agrawal, M.A. Ratner, T. J. Marks, M. S. Lundstrom, M. A. Alam, "Universality of Non-Ohmic Shunt Leakage in Thin-Film Solar Cells," *Journal of Applied Physics* 108, 124509 (2010).

"Efficiency limits in organic photovoltaics: Modeling exciton dissociation constraints based upon donor-acceptor energy offsets," Fall Meeting of the Materials Research Society, December 2011, Boston, MA.

"Practical Efficiency Limits in Organic Photovoltaic Cells," Fall Meeting of the Materials Research Society (MRS), December 2010, Boston, MA.

3. How discretionary funds were spent

The discretionary funds under this project were spent on computing fees for modeling and calculations, laboratory supplies and materials, and travel costs for presenting these results at the Materials Research Society conference.

4. How the fellowship made a difference

The fellowship made a big difference in my PhD research and ultimately my career trajectory in that it provided the support and freedom for me to tackle critical issues facing solar energy science

and technology. A key step in the development of a researcher and the production of strong research results is giving that researcher the opportunity to formulate and pursue impactful research questions. I am very fortunate to have had this opportunity, and it has had a strong influence on the quality of research and my development as an energy technology researcher.

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