Workshop on Key Scientific and Technological Issues for Development of Next-Generation Organic Solar Cells
Arlington, VA, September 20-21, 2012
Sponsors: NSF, ONR

Materials synthesis
Device manufacturing
Device physics
Semitransparent device
Flexible device
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Workshop on Key Scientific and Technological Issues for Development of Next-Generation Organic Solar Cells

A National Science Foundation and Office of Naval Research Sponsored Workshop

Workshop Chair:

- Bin Hu, Chair (University of Tennessee, Knoxville, Materials Science and Engineering)

Co-organizers:

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- Anupama Kaul (National Science Foundation, Division of Electrical, Communications and Cyber Systems Program Director)
- Paul Armistead (Office of Naval Research, Naval Materials Division Program Officer)

Hilton at Arlington, Virginia
September 21-22, 2012
Preface

The Workshop on “Key Scientific and Technological Issues for Development of Next-Generation Organic Solar Cells” was initiated by Dr. Anupama Kaul, the Program Director for Electronics, Photonics and Magnetic Devices in the Division of Electrical, Communications and Cyber Systems (ECCS) at the National Science Foundation (NSF). The research and development of organic solar cells, an important area in the field of renewable energy, have attracted increasing national and international interests in the last two decades. With significant progress being achieved through the synergistic efforts between academic research and commercial development, the burgeoning field of organic solar cells has evolved to a critical point: concurrence of opportunities and challenges. Dr. Anupama Kaul came with a clear request: analyzing key issues and preparing strategic plans to benefit the entire community of organic solar cells. The objective of the workshop was to discuss critical issues and challenges involved in materials synthesis, device physics, and device manufacturing, three key aspects for a healthy ecosystem of organic solar cells. The goal of this workshop was to prepare a strategic report that can address key issues for the development of next-generation organic solar cells.

The workshop was organized by the organizing committee including Prof. Bin Hu (Chair) from the University of Tennessee, Prof. Wei You (Co-Chair) from the University of North Carolina, Dr. Anupama Kaul from the National Science Foundation (NSF), and Dr. Paul Armistead from the Office of Naval Research (ONR). The workshop was then held at the Hilton, Arlington, VA from September 20 to 21, 2012, with about 80 participants from academic universities, government laboratories, and federal funding agencies. Prior to the workshop, the organizing committee had held a series of telephone-conferences and one onsite meeting to determine and finalize the conference program. During the two-day event of this workshop, all attendees observed inspiring presentations and attended intensive group discussions. Specifically, the presentations were given by 23 invited speakers, all of whom are leading experts in the field of organic solar cells. The discussions were divided into 3 groups to focus on (i) device physics and modeling, (ii) materials synthesis, and (iii) device manufacturing.

The workshop was primarily supported by the NSF with complimentary supports from ONR and the University of Tennessee (Sustainable Energy Education and Research Center (SEERC) and NSF-Tennessee EPSCORE program). We would like to thank the guidance from Dr. Anupama Kaul (NSF) and Dr. Paul Armistead (ONR) for organizing this workshop. We would also like to acknowledge the local support from the University of Tennessee. Finally, we would like to express our sincere thanks to all invited speakers, guests, and program directors and officers who participated in this workshop.
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   2.2. Mechanical Flexibility
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   2.4. Design and Control of Manufacturing Processes
   2.5. Identification of Best Molecules
   2.6. Materials and Process Standards
   2.7. Understanding Degradation and Improving the Lifetime of Organic Photovoltaics
   2.8. Electrode and Module Design

3. Programmatic Recommendations

References

Acknowledgements
Executive Summary

The broadly defined research field of organic solar cells, an excellent example to showcase the true meaning of “multidisciplinary”, is probably one of the fastest growing research areas in the past decade. This relatively new addition to the portfolio of renewable-energy technologies, though still few steps away from an anticipated commercial success, has attracted an enormous amount of attention from the academic research community and the commercial sector. While both academic and commercial activities have a common and ultimate goal – to efficiently convert clean and renewable solar energy into electricity with a much lower cost, they are “enchanted” to organic solar cells for different reasons. For academic researchers, organic solar cells present a fascinating system that has a number of significant challenges, and more importantly, a fertile ground for scientific discoveries. Outstanding questions need to be addressed by researchers of different yet complimentary expertise. Just give a few examples: material chemists are actively pursuing new and better organic semiconductors through design and synthesis; physical chemists are inspecting the thermodynamic and kinetic behaviors of organic semiconductors in both pristine states and mixtures; and device engineers and physicists are optimizing photovoltaic processes for better efficiencies and for further understanding devices’ properties which are often specific to the organic semiconductors employed and related specific morphology. On the other hand, the business sector is emphasizing the potential low cost of roll-2-roll processing, which can lead to large-area flexible and semi-transparent solar cells for niche applications. During their exercise, these industrial scientists often pose interesting yet challenging fundamental questions on fundamental and practical issues to academic researchers. Nevertheless, organic solar cells have arrived at critical moment to address the great challenges in materials synthesis, device physics, and device manufacturing with collaborative multi-disciplinary efforts towards the success.

It is worthwhile to briefly review the history of organic solar cells, which can be traced back to the discovery of photoconduction in organic materials due to inter-molecular dissociation of photogenerated excitons. The first practically relevant solar cell was developed by C. W. Tang (then at Kodak), who convincingly showed a bilayer design with a donor:acceptor heterojunction structure that can produce a much enhanced photocurrent together with an appreciable photovoltage. This first milestone, set arguably in 1986, clearly indicated that such a donor:acceptor interface was instrumental in separating these tightly bound Frenkel excitons in organic semiconductors into usable electrical current and voltage. The next milestone emerged in 1995, when Alan Heeger’s group at UC Santa Barbara successfully demonstrated a revolutionary design concept – blending donor and acceptor components in bulk to maximize the donor:acceptor interfacial areas for photovoltaic enhancement. Such bulk heterojunctions offered two significant advantages. First, it should in principle resolve the long-standing issue that had limited the photocurrent of aforementioned bilayer heterojunction solar cells: the short exciton diffusion length would require an ultra-thin film, whereas efficient light harvesting would
mandate a thick film. Second, it used a simple and facile procedure: mixing two components in solution and forming thin film via spin coating. Such a surprisingly easy process essentially set the cornerstone for the development of future low-cost solar cells via solution based roll-2-roll process.

In recent years, the research and development of organic solar cells has gained tremendous momentum. For example, the photovoltaic efficiencies have been increased by more than two folds, from 5% to over 10% (Figure 1). This significant progress came from combined efforts in materials synthesis, device physics, and device engineering. The materials synthesis has continued to develop new materials with further tailored optical absorption, electrical polarization, and energy levels. The device physics and modeling have revealed the effects of energy, polarization, and transport on photovoltaic processes at intermolecular donor:acceptor interfaces and organic/electrode interfaces. The device manufacturing efforts have led to the promising prototype devices, e.g., large-area flexible and semi-transparent plastic solar cells. Nevertheless, the community of organic solar cells has increasingly noted that organic solar cells have already come to a critical moment: coexistence of promising opportunities and great challenges in future developments. The promising opportunities come from outstanding features of organic solar cells: facile tuning of photovoltaic processes by using molecular and morphological designs, and large-area, flexible and low-cost properties by using printing techniques. On the other hand, the great challenges lie in three issues. First, molecular effects are entangled with morphological effects in controlling photovoltaic performance. This poses a serious challenge for chemists to better design donor and acceptor materials. Second, further investigation and modeling are required to understand how molecular orbital energies, local polarizations, and exciton and charge carrier dynamics affect the photovoltaic processes at molecule/molecule and molecule/electrode interfaces. Third, photophysical and photochemical processes involved in device longevities need significant further studies towards successful commercial applications. At this critical moment, these great challenges can only be addressed by collaborative and interdisciplinary efforts from all aspects, including materials synthesis, device physics, and device engineering, in order to successfully develop next-generation organic solar cells.

Figure 1 Efficiency development for organic solar cells
In order to assess the critical issues and to identify future opportunities, the workshop on “Key Scientific and Technological Issues for Development of Next-Generation Organic Solar Cells” was held in September 20-21, 2012, in Arlington, VA, enabled by the generous support from NSF and ONR. This workshop has made detailed recommendations on the challenges and opportunities for materials synthesis, device physics, and device manufacturing. The recommendation for materials synthesis includes the design of donor, acceptor, and interfacial materials with desirable physical and chemical parameters. The recommendation for device physics focuses on the control on useful and non-useful photovoltaic processes at both intermolecular and organic/electrode interfaces by using absorption, polarization, and energy parameters. The recommendation of device manufacturing lies in the rational identification of photovoltaic materials and materials processing standard, photophysical and photochemical effects on device stabilities, as well as the market competitiveness. The remaining session of this report is thus dedicated to the details from these three sections: Materials Synthesis, Device Physics and Modeling, and Device Manufacturing.
Workshop Program

September 20 (Thursday), 2012

7:00-8:00 Registration and breakfast

8:00-8:30 Welcome and Introduction

Assistant Director for Engineering, NSF – Dr. Tom Peterson
Senior Engineering Advisor, ECCS Division, NSF – Dr. Larry Goldberg
Program Director, ECCS Division, NSF – Dr. Anupama Kaul
Program Officer, Office of Naval Research – Dr. Paul Armistead
Workshop Chair – Dr. Bin Hu

Technical session I: Device physics and modeling

Chair: Tobin Marks

8:30-9:15 Alan Heeger (UCSB) (Keynote presentation and discussion, Nobel Laureate)
“Plastic” Solar Cells: Ultrafast Electron Transfer in Bulk Heterojunction Solar Cells

9:15-9:40 Bernard Kippelen (Device physics)
(Georgia Tech.)
Modeling of organic solar cells: a semiconductor physics perspective

9:40-10:05 Bin Hu (Device physics)
(Univ. Tennessee)
Magneto-optic studies of internal photovoltaic processes in organic solar cells

10:05-10:30 Ashraf Alam (Modeling)
(Purdue Univ.)
Untangling the essence of organic solar cells: Why complex need not be complicated

10:30-10:45 Coffee Break
Technical session II: Device interfaces

Chair: Michael Chabinyc

10:45-11:10 Alex Jen (Interfaces/Materials)
(Univ. Washington)
Rational material Design and Interface Engineering for Highly Efficient Polymer Solar Cells

11:10-11:35 Xiaoyang Zhu (Interfaces/materials)
(Univ. Texas)

11:35-12:00 Thuc-Quyen Nguyen (Molecular solar cells)
(UCSB)
Charge transport and recombination in solution-processed small molecule bulk heterojunction solar cells

12:00-1:15 Working Lunch

Technical session III: Materials synthesis

Chair: Bernard Kippelen

1:15-1:40 Tobin Marks (Electronic properties)
(Northwestern Univ.)

1:40-2:05 Guillermo Bazan (Small molecules)
(UCSB)
Design of Small Molecules for the Solution Fabrication of Organic Solar Cells

2:05-2:30 Wei You (Materials and synthesis)
(UNC)
Materials for Polymer Solar Cells: Achievements and Challenges

2:30-2:55 Dean De Longchamp (Design and manufacturability)
(NIST)
Structure measurements for polymer-fullerene photovoltaics
2:55-3:10 Coffee Break

Technical session IV: Device technologies
Chair: Guillermo Bazan
3:10-3:35 Mike McGehee (Solar Cell Technologies) (Stanford Univ.)
A path towards stable hybrid tandem solar cells with efficiency greater than 20 %
3:35-4:00 Michael Chabinyc (Characterization/Morphology) (UCSB)
Charge Extraction from the Complex Morphologies of Bulk Heterojunctions
4:00-4:25 Jay Guo (Roll to roll processing) (Univ. Michigan)

4:30-6:30 Breakout discussions (parallel sessions)

Breakout session-1: Device physics and modeling
(Lead: Bernard Kippelen; Scribes: Bin Hu; Thuc-Quyen Nguyen; Xiaoyang Zhu; Sean Shaheen)

Breakout session-2: Materials synthesis
(Lead: Tobin Marks; Scribes: Wei You; Guillermo Bazan; Alex K-Y. Jen)

Breakout session-3: Device fabrication and manufacture
(Leads: David Carroll, Mike McGehee; Scribes: Jay Guo; Gang Li, Dean DeLongchamp)

6:30 – 8:00 Working Dinner
September 21 (Friday), 2012

7:00-8:00 Registration and Breakfast

8:00-8:05 Day 2 Introduction

Technical session V: Hybrid photovoltaic systems

Chair: David Carroll

8:05-8:30 Steve Forrest (Device physics)
(Univ. Michigan)

From Fundamental Physics to High Efficiency: The Relationship between Nanostructure and Performance of Organic Photovoltaics

8:30-8:55 Jiangeng Xue (Hybrid PV devices)
(Univ. Florida)

8:55-9:20 Vikram Dalal (Hybrid PV systems)
(Iowa State Univ.)

Hybrid, inorganic-organic multi junction solar cells for increased efficiency and stability

9:20-9:45 Zhiqun Lin (Hybrid PV system)
(Georgia Tech.)

Crafting semiconductor nanocomposites via placing conjugated polymers in intimate contact with nanocrystals for hybrid solar cells.

9:45-10:00 Coffee Break

Technical session VI: Nanostructures

Chair: Thuc-Quyen Nguyen

10:00-10:25 David Carroll (Device architecture)
(Wake Forest Univ.)

Power Generating Fabrics

10:25-10:50 Lin Chen (Structures/properties)
Correlations of electronic and molecular structures of conduction polymers with the device efficiency in BHJ solar cells

10:50-11:15 Ilia N. Ivanov (Nanostructures)

(ORNL)

Carbon nano-structures in organic photovoltaics

11:30-12:30 Working Lunch

Technical session VII: Device manufacture
Chair: Mike McGehee

12:30-12:55 Yang Yang-Gang Li (Manufacturing)

(UCLA)

Achieving OPV efficiency beyond 15%

12:55-1:20 Saiful Khondaker (Manufacturing)

(Univ. Central Florida)

Planar organic solar cell

1:20-1:45 Xiong Gong (Design)

(Univ. Akron)

Towards high performance inverted polymer solar cells

1:45-2:00 Coffee Break

Meeting wrap-up

2:00-2:20 Bernard Kippelen (Summary on breakout discussion: device physics and modeling)

2:20-2:40 Tobin Marks (Summary on breakout discussion: materials synthesis)

2:40-3:00 David Carroll (Summary on breakout discussion: Mike McGehee device fabrication and manufacture)

3:00-3:05 Anupama Kaul and Bin Hu Adjourment
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Scribes: Wei You; Guillermo Bazan (bazan@chem.ucsb.edu); Alex K-Y. Jen (ajen@u.washington.edu)

1. Introduction

Organic photovoltaic (OPV) cells offer the promise of combining the impressive properties, tunability and manufacturing scalability of modern polymer technology with all that has been learned about organic opto-electronic materials over the past two decades (e.g., consider the success of organic light-emitting diodes). Furthermore, the continued advances in reported OPV power conversion efficiencies (currently 10% ~ 11%) for both polymers and small molecules based devices provide motivation for continuing focused research on materials discovery and optimization research. Thus, if optimum materials could be developed and their properties could be understood, the possibility of light-weight, mechanically flexible organic photovoltaic materials for manufacture in low-cost roll-to-roll printing processes (or other high-throughput processes) would become a reality. However, significant challenges remain in the understanding-based development and processing of new materials for this purpose. In this section we will survey challenges and future opportunities in materials development. While the main focus will be on polymer-based bulk-heterojunction (BHJ) devices, small-molecule cells will also be discussed.

In discussing opportunities in materials synthesis, please note that such an effort cannot be truly productive if carried out in a vacuum, and that such an effort must be closely coupled to materials electronic and microstructural characterization, device fabrication and evaluation, and computational modeling in a team environment. Moreover, in the present state of organic photovoltaic development, much of the synthetic work will necessarily be exploratory, to test ideas and to investigate new, “out-of-the-box” concepts. Finally, we want to reinforce that the academic research is inextricably connected with education, and that such programs should actively encourage the development of young scientists who will form the next-generation soft matter electronics/photonics workforce.

2. Future Synthetic Opportunities: Polymeric Bulk-Heterojunction Solar Cells

Current generation bulk heterojunction solar cells have a number of crucial materials components, each of which presents challenges and opportunities; these will be discussed in sequence. Typical active layers consist of phase-separated networks of an electron donor polymer and an acceptor which is almost invariably a modified fullerene. Additional important materials components include interfacial layers which block misdirected carriers from reaching
the “wrong electrode” while enhancing electrode-active layer cohesion, perhaps shifting the electrode work function to better match active layer energy levels, and, in the case of ITO anodes, smoothing the surface. Traditionally, the $p$-type conducting polymer PEDOT:PSS has served this purpose at the cell hole-collecting electrode. In the case of tandem (“double-junction”) cells, another interconnect layer is placed between two stacked single-junction cells. The electrodes are another important materials component. More traditional cells have used ITO (tin-doped indium oxide) as the hole-extracting electrode and a low work function metals (e.g., aluminum) as the electron-extracting electrode. More recently inverted cells have used ITO electrodes to extract electrons and a higher work function/corrosion-resistant electrode material (e.g., silver) to extract holes. Not unexpectedly, different interfacial layer materials are being used in inverted cells (see section 2.4 for further discussion).

2.1. Active Layer Materials: Electron Donors

Since what we know about active layer materials is still evolving, synthetic research should focus on developing approaches which are efficient, concise, and flexible, to allow moving from testing ideas to ultimate materials optimization. From what has been learned to date about solution processable bulk heterojunction donor polymers, we should target syntheses which proceed with high chemo- and regio-selectivity to afford very pure products (to minimize carrier scattering), ideally for manufacture, via “green” catalytic reactions that create minimal environmentally undesirable by-products (e.g., commonly used Stille coupling reactions produce large quantities of toxic, tin-containing by-products). Syntheses must be designed to be sufficiently flexible (i) to allow sequential manipulation of HOMO and LUMO energies and band gap (to optimize environmental stability, open circuit voltage, and solar photon capture), (ii) to install solubilizing substituents for solution processing which do not block close $\pi$-$\pi$ stacking (for optimum carrier mobility) or cause mobility-degrading backbone twisting, (iii) to remove reactive chain-end functionalities by end-capping, and (iv) to afford useful molecular weights with low polydispersity. Figure 1-1 illustrates a common motif for such structures. Current thinking, which should be tested to the limits, is that ideal donor polymers should have in-chain ‘donor’ & ‘acceptor’ blocks to red-shift the optical cross-section to capture maximum solar photons, to maximize inter-chain attractions which promote order and carrier mobility, and frequently promote exciton splitting.\textsuperscript{1-3} Exciton splitting may also be enhanced by installing dipolar groups on the donor polymer in

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{A typical conjugated donor polymer structure for bulk-heterojunction OPVs. Reprinted with permission from ref 1. Copyright 2012 American Chemical Society.}
\end{figure}
regions where excitons are created. Probing the extent of in-chain donor-acceptor communication is required and the optimum location of installed dipoles should be important synthetic goals. A related approach to enhance exciton scission would be to increase the local dielectric constant in the vicinity of charge generation as illustrated in Figure 1-2. The synthetic methodology must be flexible enough to permit this capability. There are great opportunities in the development of superior donor polymers, and efforts should move from the completely empirical to a more understanding-based combinatorial/high-throughput approach, and should be pursued in conjunction with the full complement of physical and computational characterization capabilities that only a cross-disciplinary team can provide. As an example of a new experimental technique which should be applied to the materials discovery effort, time-resolved microwave conductivity (TRMC) offers an expeditious way to initially screen for photovoltaic response before the time-consuming fabrication of solar cells.

When it comes to the design of the next generation of novel materials, efforts should also be made to minimize the use of noxious, non-green solvents and additives in the OPV film processing steps. For example, toluene would be preferable to halogenated aromatics, and in principle aqueous or solvent-less (e.g., powder) processes would be preferable. Here contributions from researchers and organizations with extensive coatings/ink expertise would be invaluable, which will facilitate the materials chemists to design materials adaptable to such processes.

Hybrid systems combining organic species with high-mobility inorganic or nano-carbon phases may also offer promise as donor or acceptor (see more about acceptors below) charge transporting elements. Key challenges to overcome include achieving good wettability by the matrix, proper aspect ratio to lower the percolation threshold, means to connect efficiently with the electrodes, and passivation of surface states which may deactivate excitons or carriers. Thus, learning to use functional nanomaterials, such as inorganic nanoparticles, nanorods, nanoflakes, carbon nanotube and graphene, to compatibilize with the bulk heterojunction matrix will be an important, challenging synthetic task. It should be carried out in collaboration with high-level
physical characterization. Further, these ends must be achieved with the recognition that as solid phase loadings increase, typical composite materials become more difficult to process. Here the contribution of researchers with expertise in composite coatings processing would be extremely helpful.

2.2. Active Layer Materials: Acceptors

To date, fullerene derivatives have been by far the most effective acceptors in bulk heterojunction cells. This efficacy appears to reflect their isotropic electronic characteristics, rapid rates of charge transfer, multiple possible redox states, LUMO energies suitable for many donors, and structures apparently near-optimum for intercalating among the donor chains while still maintaining a good electron mobility. But fullerenes are very expensive and the most commonly used one, PCBM, does not absorb significantly in the visible/near-IR region of the solar spectrum. A concerted effort should be mounted to discover fullerene alternatives. Several laboratories have reported acceptor (n-type) polymers with LUMO energies compatible with a number of bulk heterojunction donor polymers, and several donor polymer-acceptor polymer blend OPVs have shown promising PCEs, up to ~5%. Opportunities in this area are great and should move from the largely empirical to the understanding-based combinatorial/high-throughput approaches. Again, such approaches to replace fullerenes should be pursued in conjunction with the full complement of physical and computational characterization efforts.

2.3. Processing Additives

It is now known that addition of various co-solvents (e.g., 1,8-diiodooctane, DIO) to bulk heterojunction blends significantly enhances blend structural order and cell performance parameters. Recent work also reveals that DIO breaks up PCBM aggregates in the blend solutions prior to film spin-coating, thus apparently enabling the smaller PCBM particles to more easily intercalate into the evolving bulk heterojunction lattice during the phase separation process. Again, opportunities in this area are great, and research should move from the empirical to the understanding-based combinatorial/high-throughput and should be pursued in conjunction with the full complement of physical and computational characterization efforts, in a team environment. Additionally, the greenness of the processing additives should be a consideration since DIO is clearly not optimum. The other reason to understand the role of processing additives here is that many commercial polymers contain a “cocktail” of additives, including UV-stabilizers, oxidation stabilizers, release agents, plasticizers, whiteners, etc. It is likely that, as OPV science moves toward scale-up and ultimate commercialization, such additives and their effect on OPV performance will become important to characterize. The more that is understood at an early stage, the easier it will be to down-select the optimum OPV additive packages.
Solvent annealing techniques to manipulate bulk heterojunction morphology and organization have also proven to be promising in enhancing OPV performance parameters, and can be considered as processing additives. More effort, both experimental and theoretical, should be placed on building an understanding base to increase the predictability of this useful processing technique, so that it can become more routine in the community.

2.4. Interfacial Layers

These are thin layers that are interposed between the cell anode (usually ITO) and the active layer or between the cell cathode (usually a metal) and the active layer to enhance OPV performance and durability. The function of interfacial layers can be multi-fold, to smooth the electrode surface, to shift the electrode work function via interfacial dipoles, to enhance electrode-active layer cohesion via either surface energy matching or covalent bonding, to passivate defects which otherwise degrade either carriers or excitons, or to block misdirected charges from leaking to the electrode and recombining with “correct” charges (Figure 1-3).

In the latter function, an anode interfacial layer would enhance hole extraction while blocking electron leakage to the anode, while the cathode interfacial layer would have the opposite function. By far, the most widely used anode interfacial layer for conventional OPVs has been PEDOT:PSS, which has the advantage of being processable from aqueous solutions/suspensions, and is insoluble in most organic solvents. This introduces a beneficial solvent “orthogonality” in terms of the subsequent spin-coating of active layer blends dissolved in organic solvents. In several cases, e.g., the high-performance donor polymer PTB7, it has been shown that PEDOT:PSS templates a “π-face down” growth orientation of the bulk-heterojunction matrix on the anode surface (the polymer π-system aligns parallel to the substrate plane), while curiously, P3HT:PCBM grows in a π-face perpendicular orientation. It is likely that these templating effects play a significant role in cell performance and should be investigated in depth.
with the goal of understanding and then controlling this growth process. Despite these attractions, PEDOT:PSS has many drawbacks, including acidic character which leads to the corrosion of ITO and reaction with basic active layer constituents, electrical and morphological inhomogeneity, hygroscopic character, and non-negligible optical absorption in the visible and near-IR.

The first PEDOT:PSS alternative interfacial layers were chlorosilane-tethered triarylamine structures which had proven effective as hole-extracting electrode interfacial layers in OLEDs and PLEDs. Either self-assembled or blended with a hole-transporting polymer and spin-coated on ITO, these robust materials greatly enhance hole transport across the OPV anode-active layer interface while blocking electron leakage/recombination at the hole-extracting electrode.\textsuperscript{14,15} Additionally, these layers are covalently bonded to the hole-extracting electrode and also enhance active layer physical cohesion as judged by metrics such as the “Scotch tape” adhesion test. Other dipolar organic self-assembled monolayer variants (e.g., phosphonic acids) have also been shown to be effective in shifting the hole-extracting electrode work function to better match active layer energy levels.\textsuperscript{16} Note that the exact surface chemistry of these coating is not well understood and should be investigated more thoroughly, to optimize interfacial charge transport and interfacial cohesion/cell durability. Adhesion tests as simple as the “Scotch tape test” should be routinely applied, and there exists an opportunity to more strongly couple (both physically and electronically) interfacial layers to OPV active layers, whether it be physical or chemical.

In addition, the emergence of inverted OPV cells (e.g., Figure 1-3) will doubtless require new interfacial layers compatible with oxides such as ZnO, MoO\textsubscript{3}, etc., thus opening up research opportunities in this area.\textsuperscript{17} For example, there may be advantages in using electrically anisotropic interfacial layers to enhance charge transport across the electrode-active layer interface. Recent work has shown that phthalocyanine nanowires grown on ITO/ZnO can enhance charge extraction in inverted PTB7:PC71BM cells.\textsuperscript{18}

Graphene derivatives also show great promise as OPV anode interfacial layers.\textsuperscript{19} Their attraction includes almost complete optical transparency in the important solar regions; high, tunable conductivity and work function; smooth surfaces; low cost; and surface energies well matched with those of typical active layer materials. An additional attraction is that graphene interfacial layers template the growth of many $\pi$-donor polymers such that the polymer $\pi$-systems stack face-to-face with the graphene $\pi$-system. This should be the ideal geometry for efficient hole extraction as has been demonstrated with other interfacial layers (see above and below). Challenges and opportunities here are to discover perfect ways to deposit large-area, contiguous graphene sheets directly onto ITO, followed by closely coupled physical characterization and cell fabrication. Since it is not clear that all donor polymers can be templated $\pi$-face on, the scope of these phenomenon should be explored by experimentally and theoretically.
In principle, inorganic materials should also be effective anode interfacial layers. For example, NiO is a $p$-type wide band gap oxide semiconductor with good optical transparency as thin (5 – 20 nm) films. When deposited as thin coating coatings on ITO by physical vapor deposition techniques, it significantly enhances P3HT:PCBM OPV performance, with the mechanism involving enhancing hole extraction while blocking electron leakage to the anode.\textsuperscript{20,21} This thin NiO coating also increases the anode work function, smoothies the ITO surface, and electrically homogenizes the surface. Certain NiO growth orientations appear to best enhance the P3HT:PCBM OPV performance, and grazing incidence wide angle x-ray diffraction shows that the P3HT chains align $\pi$-face down on the NiO surface, thereby enhancing cell performance (Figure 1-4). This is not true for all the current generation in-chain donor-acceptor OPV polymers, and the reason is not well understood. Developing scalable, low-cost solution-phase methods to deposit NiO or other $p$-type inorganic interfacial layers is certainly a very attractive opportunity. For emerging inverted OPVs, sol-gel derived ZnO films spin-coated directly on ITO are commonly used to extract electrons.\textsuperscript{17,22} From what has been learned from interfacial layers grown on ITO for conventional cell geometries, there are likely opportunities to enhance cell PV performance and durability by functionalizing the surfaces of these oxides. The same is likely true for the surfaces of the MoO$_3$ layers that are used to enhance hole extraction at the other electrode of inverted cells.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1-4.png}
\caption{Figure 1-4 a) Grazing incidence x-ray scattering describing the in-plane and out-of-plane structure of P3HT:PCBM on PEDOT:PSS or NiO substrates. The b) edge-on structure of P3HT on PEDOT:PSS and c) face-on structure of P3HT on NiO. Unpublished results by Tobin Marks.}
\end{figure}
Finally, promising tandem OPVs, in which two single-junction cells are stacked to capture the maximum solar light, require a connecting interfacial layer between the two cells (Figure 1-5). A number of materials have been used as such connecting interfacial layers, and the demands include both charge transport and cohesion.\textsuperscript{23,24}

2.5. Cell Electrodes

The conventional transparent conducting material for OPVs and many other types of solar cells is tin-doped indium oxide (ITO). ITO is currently produced on a huge scale, largely by sputtering, for the flat panel display industry and the thin film properties have been well-optimized. For example, one ITO property that is important for displays but probably not important for OPVs is rapid response to solution-phase etchants. Limitations of ITO include cost, since indium supplies are limited (indium is not mined, but is a by-product of zinc production), corrosion susceptibility (for the same reason it responds readily to etchants), and low conductivity. The poor corrosion resistance explains the degradation in the presence of acidic PEDOT:PSS. The rather low conductivity (typically 3000-5000 S/cm) presents a constraint on cell area, if no ancillary silver or nickel lines are used to carry current. Additionally, the surface of commercial ITO is typically rough and compositionally/electrically inhomogeneous.

Devising practical ITO replacements presents an attractive opportunity for further research, both within OPV space and beyond. To date ITO replacement approaches have been several-fold. Oxides such as indium-doped cadmium oxide (CIO) with indium at the 5 atom\% level have 3-5 times the conductivity of commercial ITO and good optical transparency. However, the surface is less corrosion resistant than ITO. One solution is to cap CVD-derived CIO films with a thin layer of ITO. The resulting films have about \( \sim 1/3 \) the sheet resistance of commercial ITO and about 1/20 the indium content, and can be used to fabricate P3HT:PCBM OPVs with

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1-5.png}
\caption{(a) Tandem polymer solar cell device structure; (b) I-V curve of a tandem polymer solar cell; (c) EQE spectra of front and rear sub-cells. Adapted from reference Jingbi You, Letian Dou, Ken Yoshimura, Takehito Kato, Kenichiro Ohya, Tom Moriarty, Keith Emery, Chun-Chao Chen, Jing Gao, Gang Li and Yang Yang. Nature Communications, 4, 1446 (2013)}
\end{figure}
performance in small cells indistinguishable from that of ITO-based cells.\textsuperscript{23,24} Another attractive approach uses networks of metallic nanowires to impart electrical conductivity while still providing a small optical cross-section, one such example shown in Figure 1-6. Various materials and network geometries have been explored. While the conductivity-transparency trade-off metrics of such materials and networks have advanced toward ITO, they have not yet reached or exceeded that of ITO.\textsuperscript{25} However, these metallic networks, in theory, should be far more flexible, corrosion-resistant, and impact-resistant than ITO, which may be advantageous for cell durability. Another promising approach is to use networks composed of the metallic fraction of sorted carbon nanotubes for fabricating transparent conducting films.\textsuperscript{26} Again, while the conductivity-transparency trade-off metrics have not reached those of ITO, respectable solar cells have been fabricated using these films as anodes. Similar to the aforementioned metallic networks, the films based on carbon nanotubes should be far more flexible, corrosion-resistant, and impact-resistant than ITO films. Therefore, this opportunity merits further research. Finally, other transparent conducting oxides such as fluorine-doped tin oxide (FTO) have been used in dye-sensitized solar cells because of the corrosion resistance; however, to date maximum achievable FTO film conductivities have been less than those of optimized ITO. The same is true of aluminum-doped zinc oxide (AZO) and a number of other binary and ternary oxides which minimize indium consumption. Coupled with modern computation/simulation to predict the properties of inorganic transparent conductors, high-throughput “phase-spread” materials growth techniques, and rapid materials evaluation techniques, this area offers significant research opportunities both for photovoltaic cells as well as for other opto-electronic technologies requiring transparent conducting electrodes. Efforts need to be leveraged and/or consolidated. For example, NREL has a large, impressive effort in the transparent conducting oxide discovery and applications area.

While transparent electrodes are required for one electrode of OPV devices (anode or cathode), metals are typically used for the other electrode. In conventional cells, the cathode has been a low work function metal such as calcium or aluminum. These materials are highly susceptible to atmospheric corrosion, and rigorous encapsulation of cells is essential for good durability and longevity of these cells. For inverted cells, a more corrosion resistant high work function metal
such as silver can be employed as the anode. While this increases cell durability and avoids corrosive, hygroscopic PEDOT:PSS, it would be desirable to replace silver with a less costly metal or metal alloy. Finding an effective, high work function electrode material represents an important research opportunity.

3. Future Synthetic Opportunities: Small Molecule Organic Photovoltaics

In terms of superior mechanical properties and microstructures which can electrically bridge grain boundaries to enhance bulk carrier mobility, polymers offer obvious attractions for solar cells. Nevertheless, polymers can be difficult to purify, are seldom monodisperse, and frequently exhibit batch-to-batch variations in physical properties. All of these heterogeneities can create scattering centers which limit OPV performance. Note that the very first organic solar cells were bilayer structures composed of vapor-deposited small molecule donors and acceptors. In regard to high levels of homogeneity, small molecules can be rigorously purified by techniques such as gradient sublimation, chromatography, and/or recrystallization (almost all the OLED displays used in commercial products are fabricated from vapor-deposited small molecules). At present, how effective scalable vapor deposition techniques would be for large-scale OPV deployment is uncertain; however, Heliatek and the Fraunhofer Institute in Germany have reported power conversion efficiencies near 12% for vapor-deposited small molecule bilayer cells. In principle, the resulting devices can have bilayer or bulk-heterojunction type structures, depending on the growth technique and mechanism. High-vacuum vapor deposition techniques can put down complex organic multilayer structures with great precision in thickness, microstructure, and composition. Furthermore, robotic equipment is being used to scale up to larger area panels. Note that this approach would be far more scalable if a CVD-like process could be developed, with suitably volatile precursors, which could conformably coat large areas without the need of high vacuum. Alternatively, perhaps active layer film growth could be achieved by a spray, electrospray, or aerosol-assisted coating technique. Exploring these possibilities presents a unique research opportunity.
Another small-molecule approach employs soluble donor precursors which are deposited by conventional solution-phase techniques along with a fullerene acceptor (Figure 1-7). As with recent polymer donor systems, the highest small molecule efficiencies have been achieved with donor molecules having both donor and acceptor cores within the same molecule, to red-shift the optical cross-section, enhance interplanar attractions, and perhaps aid exciton splitting.\textsuperscript{28,29} The highest reported power conversion efficiencies of such small molecule bulk-heterojunction devices are currently in the $6 - 7\%$ range. This area has been far less explored than that of polymer cells, and great opportunities exist to understand/exploit the role of growth solvents and techniques, processing additives, interfacial layers, alternative electrode materials, and donor-fullerene ratios. Many of these materials are highly crystalline and much structural information can be obtainable by x-ray diffraction. Nevertheless, it is not clear whether small molecule-based OPVs will have the mechanical flexibility of polymer cells and whether grain boundaries will be a major limitation or source of heterogeneity.\textsuperscript{30,31}

### 4. Values of Modeling and Simulation

Theoretical tools can play an important role in expediting the design of new materials, and the results of electronic structure calculations are being increasingly implemented to identify promising building materials blocks.\textsuperscript{32,33} However, the predictive capability of these calculations are compromised by the limitations of treating only one or two molecules or repeat units in vacuum. A major goal for theoretical efforts is the development of tools to fully model, in an ultimately predictive manner, the solid state properties of organic semiconductors. While typical methods have been developed for electronic structure analysis in the vacuum state, materials properties such as mobility, ionization potential, and electron affinity are strongly influenced by the specific intermolecular interactions of the solid state. Major strides could be made if theoretical tools could bridge the molecule to material to device, fully assessing the characteristics of materials with realistic degrees of disorder and multiple active components (Figure 1-8).

\textbf{Figure 1-8.} Theoretical tools are needed to describe the effects of Intermolecular interactions and morphology in films. Obtaining materials properties of merit such as mobility ($\mu$), ionization potential (IP), and electron affinity (EA), from molecular descriptors is presently unreliable. Adapted with permission from: Savoie, B.M.; Jackson, N.E.; Marks, T.J.; Ratner, M.A., Phys. Chem. Chem. Phys. 2013,15, 4538-4547. Copyright 2013 PCCP Owner Societies.
5. Programmatic Recommendations

- Support teams that closely integrate synthesis with theory and physical characterization
- Support synthetic efforts that emphasize green, atom-efficient, environmentally benign approaches
- Support synthetic efforts that synergistically bring organic and inorganic materials together
- Support efforts to enhance OPV environmental stability
- Support efforts to find fullerene and ITO replacements
- Support efforts to define, via exploratory synthesis, the limits of polymer OPVs: what are the maximum performance metrics possible?
- Support efforts to define, via exploratory synthesis, the limits of small molecule OPVs: what are the maximum performance metrics possible?
Section 2: Device Physics and Modeling

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1. Introduction

Next-generation organic solar cells are attracting tremendous attention because of their potential to become a future renewable energy source with lighter weight and superior mechanical flexibility, earth-abundant and non-toxic materials, rapid manufacturing, and lower overall cost (as measured for instance by the Levelized Cost of Electricity) compared with other photovoltaic technologies. Great progress has been made towards increasing the power conversion efficiency (PCE) of such cells recently by implementing more sophisticated device structures, developing novel materials, and optimizing processing techniques. The improvements in performance in terms of PCE have accelerated in recent years, and several independent reports of small-area laboratory cells with PCE values above 9% can be found in the scientific literature.\textsuperscript{34,35} Likewise, private companies have announced that they achieved PCE values > 10% in champion cells.\textsuperscript{35} Recently, a record efficiency of 12% was announced by the German company Heliatek. This new world record was established in a multijunction device fabricated using vacuum deposition techniques. Recent reports by the Mitsubishi Chemical Corporation suggest similar values based on solution-deposited small molecules.

These accelerated advances in efficiency are remarkable for multiple reasons. First, the demonstration of PCE >10% in laboratory cells establish the proof-of-principle that organic photovoltaic technologies have the potential to reach a performance level where they could compete economically with well-established photovoltaic technologies based on a form of crystalline Si or some thin films of inorganic semiconductors. Second, the high pace of progress could be indicative that organic solar cells could reach efficiencies that go beyond those predicted by earlier models, in which the strong excitonic nature of the photoexcited states in organic semiconductors had been proposed as a severe limitation. These observations illustrate the importance of the gaps and needs that still exist to guide the future development of organic solar cells. A general consensus, currently prevailing in the scientific community, is that no clear and comprehensive physical model has emerged yet to explain the operation and performance of organic photovoltaic devices, let alone guiding the rational design of future materials, device architectures, and interfaces. This is in contrast with photovoltaic materials and technologies based on crystalline Si where semiconductor physics provides a solid framework to guide the modeling of these devices fabricated from materials with a morphology that is often highly crystalline and well controlled. This observation highlights the relevance and importance of this
NSF-ONR workshop that was held to bring together the best experts in the field to discuss and identify the key scientific and technological issues to be addressed to accelerate the future development of next-generation organic solar cells. Among these core issues, device physics and modeling of organic solar cells plays an important role. The goal of this section is to provide a summary of some of the gaps and needs that currently exist in the field and to discuss simultaneously opportunities and strategies to further advance this field through aspects of science and engineering that go beyond traditional considerations in the context of conventional photovoltaic technologies. The opportunities discussed in this section are by no means exhaustive but provide just a few examples. Due to the unique optical and electronic properties of organic materials, the vast possibilities of high-performance molecular structures, and the infancy of the current understanding of their physical properties, organic photovoltaics is likely to remain a vibrant and exciting field of research in the years to come. The progress and future improvements will only be limited by the imagination and creative thinking of researchers that are currently working in this field or that will enter this field in the future.

Another critical aspect that is needed to support a sustainable growth, competitiveness in an era of global competition, and an economic development in this area, is the training of a productive and competent workforce. If the field of organic photovoltaics continues on its trajectory and holds its economic promise, it is likely to have a significant societal impact. However, as will be discussed in more details in later sections, significant advances are clearly needed in demonstrating scalability, low manufacturing cost, and sufficiently long lifetime. All these aspects will have to be addressed simultaneously and will require constant important advances in science and engineering, as the technology is gradually moving down the value chain towards mass commercialization. The promise of next-generation organic photovoltaic technologies will critically depend on the willingness of the public, elected officials, and policy makers to provide federal research funding agencies with the resources needed to support a sustained progress in the field over the next decades. Hence, educating the public and various constituencies that can influence the funding of science, engineering and innovation in this field will be essential.

2. Challenges and Opportunities

There has been significant progress in the understanding of the optoelectronic behavior of OPVs using steady state measurements as a function of illumination and electrical bias. There are important opportunities using existing and emerging methodologies to characterize the energetics of states in OPVs through time-dependent measurements. Experimental methods such as impedance spectroscopy, transient photoconductivity, charge extraction in linearly increasing voltage, transient photovoltage, and others are increasingly applied to novel materials systems, and will continue to provide a more detailed understanding of the nature of charge generation and extraction in OPVs. The challenge in designing and synthesizing the next generation of donor-acceptor bulk heterojunction systems is to optimize these parameters while still retaining
optimal optical absorption, efficient charge transport, and facile processing methods of molecular semiconductors.

Despite an accelerated progress in power conversion efficiency during the past two years with values exceeding 10%, research on organic solar cells remains somewhat heuristic and relies largely on the synthesis of new organic molecules and polymers and their evaluation in single photovoltaic devices with various architectures. The device structure is varied and the new photoactive materials are combined with various interlayers and electrodes that collect holes and electrons with varying degrees of efficiency. These advances are guided by physical models that are developed in order to take into account the differences that exist in the physical properties of organic composites with complex morphologies. At the molecular level, sophisticated models have been developed that show good predictive effectiveness to correlate molecular structure with intramolecular physical properties. However, the operation of an organic solar cell requires a level of understanding at a macroscopic scale, typically of the order of a hundred nanometers. Hence, for a clear physical model to emerge, an end-to-end multiscale model from molecules to a complete solar cell or module is critically missing. There is a strong need for the development of such a model at multiple scales of length, time, and energy that is inspired by models developed by the conventional silicon semiconductor industry. Ideas on how to facilitate the elaboration of such a model include, but are not limited to: (i) follow a modular approach since no single team is likely to develop a comprehensive model; (ii) use an open-source multiscale modeling platform; (iii) create a repository for data sharing (e.g., optical properties of materials, process engineering of devices, etc.).

Another opportunity to push the frontiers of science of organic solar cells is to give more emphasis to quantum physics, coherence, and dephasing processes. As mentioned earlier, many research efforts in the OPV field have focused on increasing solar cell efficiency by tuning optical absorption, energetic alignment, and structures (nanoscale phase structures, morphologies, crystallinities). While such strategies have been successful, the community sometimes neglected a critical advantage of molecular materials: chemists’ vast capability of rationally designing and controlling physical properties at the levels of molecules and molecular assemblies based on the fundamental laws of quantum mechanics. One can learn this from nature, e.g., in the photosynthesis system, which is exquisite machinery on the nanometer scale that harvests sunlight in the production of chemical fuels and sustains life on this planet. Recent discoveries have revealed the important role of quantum coherence in efficiently channeling excitonic energy through the chromophore assembly to the reaction center. There is also evidence that such quantum coherent energy transfer may also exist in photoexcited conjugated polymers. Hence, the following question for future OPV research is relevant: Can we take advantage of quantum coherence in designing molecules and molecular assemblies to most efficiently channel excitation energy to the donor/acceptor interface for solar-to-electric conversion? Another example for quantum effects in OPVs is found in singlet fission in organic
semiconductors. The absorption of one photon in most semiconductor materials leads to the excitation of one electron-hole pair; however, this general rule breaks down in a few organic semiconductors, such as pentacene and tetracene where the absorption of one photon may lead to the formation of two electron-hole pairs. $^{37,38}$ This process is called singlet fission, in which a singlet exciton is transformed to two triplet excitons with quantum yields as high as 200%. Singlet fission may be implemented in solar cells to increase the power conversion efficiency beyond the so-called Shockley-Queisser limit. Recent discoveries have provided evidence for a quantum coherent mechanism for singlet fission, and the possibility of harvesting multiple electron-hole pairs from this quantum superposition. Likewise, quantum coherence may play a role in other multi-exciton phenomena, such as Multiple Exciton Generation, Triplet Fusion, or other phenomena yet to be discovered. Thus, one may ask: How general is this quantum superposition mechanism for multi-excitons in optically excited organic/polymeric molecules and how can we implement this for future OPVs with power conversion efficiency potentially exceeding the Shockley-Queisser limit?

2.1. Optical Absorption

Optical absorption is the first step towards the generation of photocurrent in organic solar cells. There are two critical parameters: absorption coefficient and absorption spectral width, which govern the essential absorption. The absorption coefficient is determined by the interaction between induced polarization and an incident electromagnetic wave. The absorption spectral width is controlled by both homogenous and in-homogenous components. The homogenous component is determined by the distribution of electronic transitions within an electronic configuration governed by electron-phonon coupling. The in-homogenous component comes from irregularities of conjugated unite structures caused defects and impurities in a semiconducting material (Fig. 2-1). Organic materials have demonstrated very good absorption coefficients up to 2~2.5/x10$^5$ cm$^{-1}$, much larger than crystalline Si. $^{39}$ Certainly, the strong absorption coefficients give a good benefit to organic thin films used in organic solar cells to absorb sunlight within a given thickness limited by low mobility values. Obviously, the strong absorption coefficients can be attributed to the facile polarization of delocalized $\pi$ electrons.

For absorption spectrum, organic materials have shown superior tuning properties by changing the band gaps through molecular design. In general, optical absorption can range from UV to near infrared wavelengths. This significant tuning on
absorption spectrum can expand the absorption spectral range in organic solar cells. The recently developed highly efficient photovoltaic polymers have all exhibited long absorption wavelengths approaching 900 nm\textsuperscript{40-42}. However, experimental results indicate that further expanding absorption beyond 900 nm often gives reduced photovoltaic efficiencies. This is a common technical problem existing in low band gap materials: \textit{infrared photovoltaic materials do not show high efficiencies}. This technical problem brings two challenging issues in low band gap materials (longer than 900 nm): (i) how do excited states get lost before the charge dissociation occurs? (ii) how can the excited states be efficiently dissociated into free charges, which are then subsequently transported to the electrodes? Clearly, addressing these two challenges require interdisciplinary investigations in device physics and modeling.

2.2. Dynamic Processes of Excited States

The purpose of optical absorption is to generate excited states towards the production of photocurrent and photovoltage in organic solar cells. Development of new methodologies to measure the dynamic processes of excited states in operating devices is essential for identification of the nature of species leading to charge trapping sites that influence loss mechanisms such as recombination and also understanding the changes during long term studies of degradation and “burn-in”. Such measurements will also help to reveal differences in the electronic structure of bulk heterojunctions formed from polymers or small molecules (Figure 2-2) in order to determine if the improvement in molecular ordering in molecular systems leads to reduction in charge trapping and thereby reduction in loss processes. In general, there is a consensus that opportunities exist to extend the number of techniques used in solid-state physics to study the physical (structural, electrical, magnetic, optical, thermal etc.) properties of photovoltaic materials and devices. There is a great potential for this community to learn from other communities.

At the molecular design level, great progress has been made in the last decade in understanding the structure-property relationship in excited states leading to tuning of optical band gaps. However, there now exist opportunities to delve into more refined design strategies that truly optimize the rates of carrier generation and recombination, both occurring at the donor-acceptor interface. A key factor in determining these rates, as dictated by the Markus theory of charge transfer\textsuperscript{43,44} is the molecular reorganization energy associated with each process. Reduction of the reorganization energy to small values (< 0.3 eV) allows the band offset energy to be small, and hence

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{donor_polymer_fullerene.png}
\caption{Efficient polymer:fullerene bulk heterojunctions comprise a mixture of relatively pure polymer and fullerene domains with molecularly mixed regions.}
\end{figure}
the photovoltage to be large, while retaining a fast rate of carrier generation. Intertwined with this Markus theory description of charge carrier dynamics is the existence of the charge transfer states that exist at the donor-acceptor interface, the role of which is not yet fully understood.

2.3. Charge generation

A photoexcitation primarily generates Frenkel excitons in organic materials due to weak dielectric constants. Dissociation of Frenkel excitons at donor:acceptor interfaces is a critical process in the generation of photocurrent in organic solar cells. There have been three important experimental points for exciton dissociation at the early stage of organic solar cell. First, it has been thought that a larger energy offset can lead to an enhanced dissociation. Second, increasing the energy offset between donor and acceptor can often cause a decrease on the open-circuit voltage (V_{oc}) and consequently becomes detrimental to the entire photovoltaic performance. Third, it has been found that a normal interpenetrating donor:acceptor network can effectively dissociate the Frenkel excitons (> 90%). Nevertheless, the early experimental findings have indicated that it is necessary to pursue a new mechanism to dissociate excitons in order to avoid the conflict requirements on the energy offset for charge dissociation and development of Voc. Recently, the new design of intrachain donor-acceptor structure in individual polymer chains has demonstrated a promising mechanism for exciton dissociation: dipoles assisted dissociation in excited states, to minimize the conflict interests for charge dissociation and development of V_{oc}. Clearly, it is important to acquire a detailed and fundamental understanding of exciton dynamics, exciton dissociation, electric charge creation, charge recombination, dipolar effects and Coulomb screening effects. Here are a few specific suggestions.

(1) We need a better understanding of the energetic landscape in terms of band structure, density of states, heterogeneity and gradients of compositions and corresponding physical properties in devices under normal operating conditions.

(2) The connection of morphological structures to the electronic density of states in organic solar cells remains challenging due to the difficulty of modeling the complex nanostructure with conventional models of semiconductor physics.

(3) The electronic density of states provides important features of the energetic landscape that the carriers traverse during charge extraction after generation as well as providing the energetics of defects (traps).

(4) Development of new models that capture the essential physics without excessive parameterization are highly desirable. Collaboration between experimentalists and computational scientists will be essential to build the most insightful models.
2.4. Charge Transport

Explicitly, the charge transport is a necessary process in the generation of photocurrent after the charge carriers are generated. Implicitly, the charge transport can affect the $V_{oc}$ and fill factor ($FF$). Fundamentally, charge conduction is the product of two parameters: charge carrier density and charge carrier mobility.\(^{49}\) In general, the carrier mobility is a limiting factor in organic electronic devices. The research efforts in the field of organic field-effect transistors have shown that molecular packing and molecular re-organization energy are key issues in the determination of charge mobility. In organic solar cells, charge transport has mainly relied on charge density in donor and acceptor interpenetrating networks. There are two major losses that can affect the charge transport after the exciton dissociation occurs: recombination and accumulation. The research effort has been devoted to morphological effects in controlling charge recombination and accumulation towards charge transport. However, the charge transport issue concerning charge recombination and accumulation still demand significant investigations in both device physics and modeling.

**Charge recombination:** The electrons and holes can partially recombine at donor:acceptor interfaces. In principle, this process is governed by two parameters: the energy diagram and the spin configuration. Concerning the energy diagram, the kinetic energy and potential energies associated with charge carriers may have appreciable impact on whether the electrons and holes should recombine. Specifically, the kinetic energy can facilitate charge transport to avoid charge recombination. The potential energy can then directly affect the interactions between electrons and holes in charge recombination. Therefore, the investigation on the effects of kinetic and potential energies of charge recombination can provide critical understanding to materials synthesis and device engineering to control charge transport by reducing charge recombination. In the spin configuration, when the electrons and holes can recombined at donor:acceptor interfaces, the recombination will lead to singlets and triplets mostly in photovoltaic domains. It is noted that the singlets and triplets have different formation rates due to spin selection rule. Therefore, it can be envisioned that manipulating spin configurations can provide additional mechanisms to control charge recombination in organic solar cells.\(^{50}\)

**Charge accumulation:** The electrons and holes can be trapped in potential wells during charge transport, generating charge accumulation. There are two possible ways to control the charge accumulation by reducing the density of potential wells and by de-trapping the trapped charge carriers. Reducing the density of potential wells comes from the control of molecular and morphological defects. De-trapping the trapped charge carriers relies on local Coulomb interactions through electrical polarizations. It is known that the potential wells can be inevitably formed in interpenetrating donor and acceptor networks. De-trapping mechanism may become essential to decrease the charge accumulation. It is noted that dielectric measurements can essentially reflect the charge accumulation with de-trapping process.\(^{51}\) However, the experimental elucidation for charge accumulation is still not sufficient. We suggest that device
physics and modeling further examine the charge accumulation in organic solar cells and provide critical understanding to materials synthesis and device engineering for the control of charge accumulation.

2.5. Charge Collection at Electrode Interfaces

Charge collection is the last process in the generation of photocurrent in organic solar cells. In principle, the interfacial energy levels as well as interfacial polarization can play an important role to control the charge collection at electrode interfaces. In general, the charge collection can directly affect each of the key factors of short-circuit current, open-circuit voltage, and fill-factor. Recent success of using dielectric interfaces suggests that the charge collection at respective electrodes is an important process in the improvement of device efficiencies. In general, the surfaces of a photovoltaic film can have certain defects formed during thin-film formation or electrode preparation. These surface defects can function as interfacial traps that can critically change the charge collection at respective electrodes. Therefore, investigating organic/electrode interfaces and understanding the charge collection at respective electrodes are among the research priorities, in order to improve the device efficiencies in organic solar cells.

Three types of experimental studies: electron microscopes, dielectric measurements, and photoinduced ESR have been used to study the charge collection at electrode interfaces. These experimental studies have provided critical information on interfacial energy levels, interfacial polarizations, and interfacial charge accumulations in organic solar cells. Clearly, the experimental findings indicate that the organic/electrode interfaces are a critical issue in controlling charge collection towards the improvement of device efficiencies. The workshop discussions reflect the following key questions that need to be carefully addressed. First, how photophysics and photochemistry are involved in the charge collection at electrode interfaces? Second, how can the energy levels and electrical polarizations at organic/electrode interfaces be characterized under device-operating condition? Third, how can interfacial charge collection be experimentally “visualized” during device operation?

3. Programmatic Recommendations

- Device physics modeling platforms should be developed to enable a complete multi-scale understanding of the evolution of device and module efficiencies from fundamental molecular properties.
- A variety of methodologies for creating and maintaining such platforms can be considered. For one, open-source development should be considered as an effective way to harness national and international resources to tackle the broad heterogeneity of problems to be examined.
• The development of improved theories and formalisms at each level of modeling, ranging from understanding the quantum nature of excited states to the circuit layouts of large-area modules, should be supported.
• Modeling efforts should be encouraged to interact closely with experimental work to corroborate results and verify the validity of the underlying theories and formalisms.
• The creation of databases and other data-sharing platforms would help unify and clarify the vast amount of data regarding OPV materials and devices that have been investigated.
• Education and training of the next generation of scholars, researchers, and industrial labor force should be a necessary and implicit part of any program or policy efforts.
Session 3: Device Manufacturing

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1. Introduction

It is now possible to make small organic solar cells with efficiency greater than 10% using techniques such as solution processing or small molecule evaporation. With efficiencies improving at an impressive rate, the prospects for commercialization are promising. There are, however, significant manufacturing challenges that must be addressed to support the wide-scale deployment of organic solar power modules. In this section we discuss the most promising applications for organic solar cells and the requirements of these applications. We address what will need to be done to scale up manufacturing in a cost-effective manner that avoids environmental harm. Finally, we discuss what will need to be done to attain high reproducibility and reliability such that a manufacturing line will produce consistently high yields of qualifying solar power modules that will not degrade during their intended lifetime.

2. Opportunities

2.1. Overview of Applications and Market Competitiveness

Solar cells absorb sunlight and generate electricity without generating pollution or noise. The cost of generating electricity with them has been falling rapidly and is now three times lower than it was just a few years ago. With continued research and development the cost could drop within 5 to 10 years to the point where it will be cheaper to produce electricity from unsubsidized solar cells than to obtain it from conventional power plants that run on fossil fuels. The solar industry is expected to grow explosively at that point. Affordable electricity from solar cells will not only provide power at a stable price for everyone who is currently using electricity, but it will also give the nation two attractive options for powering vehicles. One will be to switch to electric vehicles and the other will be to use the natural gas that will not be needed for power plants, and for vehicles instead. Lightweight solar cells will also be extremely beneficial to military operations when power is needed in places where it is difficult to obtain fuel. The continued advancement of solar cell technology is therefore critically important to our national security.
86% of the solar cells shipped in 2011 were based on wafers of silicon. The price of silicon solar cells has dropped remarkably over the last few years as economies of scale have been achieved, factories have been designed to produce silicon especially for solar cells instead of computer chips, and large manufacturing facilities have been established in China. Silicon modules with a power conversion efficiency of 15% are sold for approximately $1/W. The breakdown of the components in the complete system cost is shown in Figure 3-1. Currently the price to build the racks that support the solar cells and install the cell is $1.48/W. The price of the power electronics that converts the DC electricity coming out of solar cells into the AC electricity that our electricity grid uses is $0.22/W. The total price of the system is estimated to be $3.40/W.

If the total price of installing a solar system was reduced to $1/W, then the average price of generating electricity over the lifetime of the system would be approximately $0.05/kW-hr and the system would be competitive with power plants that run on fossil fuels. The U.S. Department of Energy estimates that to achieve this goal it will be necessary to drop the price of the modules down to $0.5/W, the installation to $0.4/W and the power electronics to $0.1/W. A key part of reducing installation costs will be raising the efficiency of the solar cells so that the total area that needs to be covered with solar cells can be reduced. Technologies that have at least 20% efficiency and preferably 25% efficiency are therefore highly desirable.

Although nameplate rating efficiencies are useful for comparing panels based on similar technology, they are poor indicators of real-world performance differences between organic solar cells and silicon based ones. The efficiencies quoted are those measured under full sunlight at noon at 25°C. Since the performance of silicon solar cells drops significantly under low light conditions and at the higher temperatures that solar cells typically experience, organic solar cells are much more attractive than they might at first appear. Under real-world operating conditions, an organic solar cell with an efficiency of 10% at 1 sun and 25°C will generate as much power as a silicon solar cell with an efficiency of 13%. Consequently, it might be necessary for organic solar modules to have an efficiency of only 15% to meet the cost target for competing with fossil...
fuel power plants. For all solar cell technologies there is a gap between the average efficiency of modules that come out of a factory and the world record efficiency that is obtained with one small solar cell. It is therefore likely that a world record efficiency of approximately 20% would be necessary for a company to be able to manufacture modules with 15% efficiency.

One of the most promising approaches to making solar cells with efficiency higher than 20% at low cost is to find a way to make tandem (multi junction) solar cells inexpensively. Tandems can be more efficient than single junction solar cells because a high band gap solar cell can be used to harvest the high-energy photons and generate a high voltage while a low band gap solar cell can be used to extract energy from lower energy photons as shown schematically in Figure 3-2. The world record power conversion efficiency for solar cells is 44% and was obtained by growing three p-n junctions epitaxially on each other.\(^{59}\) These solar cells cost approximately $40,000/m\(^2\) because the single crystal substrate is expensive and the deposition process is slow.\(^{60}\) In contrast, tandems can be made very inexpensively with organic semiconductors because they can be sprayed on top of each other rapidly and it is not necessary to lattice match them. At the present time, the efficiency of organic tandem solar cells is less than 11% primarily because there are no good organic solar cells based on low band gap semiconductors.

It is somewhat likely that low band gap organic solar cells will never compete on an efficiency basis with cells based on silicon or copper indium gallium diselenide (CIGS) since the open circuit voltage of organic cells seems to be limited to the band gap divided by the charge of an electron minus 0.6 V.\(^{61}\) Consequently organic solar cells with band gap of 1.1 eV will likely only have an open circuit voltage of 0.5 V, which is 0.2 V less than silicon cells generate. The most promising approach to making tandems might therefore be stacking organic solar cells with a high band gap on either silicon or CIGS cells. A recent analysis shows that it should be possible to improve the efficiency of silicon and CIGS by 15 and 30 % respectively without adding significant cost.\(^{60}\)
When solar cells are deployed in developing countries, installation costs are less important because the cost of labor is very low and the solar cells are frequently not mounted to anything. In this market, inexpensive solar cells could be very attractive even if they do not have a high-efficiency as long as they are light enough to be transported into remote villages at low cost. Organic solar cells are very attractive for this application.

There are many off-grid applications for solar cells that do not require generating electricity at a cost that is competitive with the power grid. For example, the U.S. military would greatly benefit from having lightweight flexible solar cells that could be used by soldiers to generate power in remote locations. Many portable electronic devices would have a longer battery lifetime if solar cells were used to charge the batteries. Organic solar cells are attractive for these applications because they can be deposited on extremely thin sheets of plastic.

2.2. Mechanical Flexibility

One hallmark of organic solar cells is that they tend to be more mechanically flexible than inorganic solar cells. Solar power modules that are flexible, lightweight and mechanically durable are very attractive for some portable applications. One issue with mechanical flexible organic solar cells is that current flexible encapsulation materials are prohibitively expensive and can only be used for applications where cost is not of high importance. Developing lower-cost high-performance flexible encapsulation materials is therefore a high priority and indeed would benefit a variety of consumer electronics technologies. It is important to realize, however, that most large-scale power generation applications do not require flexibility. For these applications, glass substrates and packaging can be used for organic solar cells just as they are for silicon cells. It is also possible that flexible solar cells will be manufactured on plastic in roll-to-roll coaters and then packaged in glass. Flexible yet durable glass products are also becoming available and might prove to be suitable encapsulants.

2.3. Avoiding Toxic Solvents

Almost all solution-processed organic solar cell formulations to date have required halogenated aromatic solvents that are highly toxic and/or carcinogenic. Alternative solvents will certainly be required for manufacturing on a large scale in order to comply with environmental laws. No “green” solvents that provide reasonable solvency for the most common solution-processed organic solar cell components have yet been identified. It seems unlikely that solvent reclamation via scrubbers or condensers would be practical in a low-cost manufacturing environment.

One approach to solving this problem would be to attempt molecular design with the intention of making molecules that are soluble in green solvents. Other approaches to reducing toxic solvent release include developing water-based dispersions of the organic solar cell components and
coating them from water/alcohol formulations as is done with conventional latex paint. This approach has the added difficulty of requiring specific morphological properties of the latex, while also forgoing most of the common surfactants and additives that make conventional latex paint so well-behaved. Finally, the issue of toxic liquids can be completely avoided by directly evaporating the molecules in vacuum as is done at Heliatek.

2.4. Design and Control of Manufacturing Processes

Most organic solar cells are based on bulk heterojunctions that self-assemble as the thin film forms. Since the structure that forms is not at equilibrium, it depends very sensitively to how the film is cast. Most researchers spin cast the films. In manufacturing, techniques such as slot die coating or doctor blading are more likely to be used. New process designs that produce the optimal morphology will be required. The community will need robust and reliable elucidation of the relationships between molecular characteristics, formulation properties (viscosity, surface tension), process variables (coating speed, temperature, drying environment), and the electronic and morphological characteristics of the final layer.

It is possible that modeling may have a role in this effort, provided that it can be validated against real-world manufacturing results. It may be possible using modeling to proceed from simple knowledge of the formulation characteristics toward a set of likely process variables, narrowing the range and cost of a typical design of experiments matrix.

More pragmatically, organic solar cell manufacturing could use the development of silicon electronics as a guide, and – as in that industry – invest early (now) in process development and engineering based on the current best understanding, with the expectation that deeper and more fundamental understanding will come as success expands the scope of the endeavor, to provide additional cost savings and new product opportunities. One way to accelerate this process would be to encourage researchers from academic and government labs to interact with manufacturing experts to determine as soon as possible what will need to be done to create a successful manufacturing process. There are experts who have substantial experience depositing thin films from solution or with larger operation tools which should be able to substantially reduce the time needed to develop a manufacturing process for organic solar cells.

2.5. Identification of Best Molecules

Molecular design has always been a pillar of organic solar cell research. Until recently, most molecular design has been focused entirely on obtaining higher efficiency materials. Although many of the most important discoveries were made by serendipity, consensus rules are beginning to emerge from the synthetic community on how to make stable light absorbing semiconductors from several polymer families.
It is time to expand the molecular design criteria. Some of the molecules that have been used to make the highest performing organic solar cells are very expensive and will probably always be expensive because they are made using more than 10 processing steps. As researchers make decisions on what molecules to thoroughly investigate, they should consider moving towards ones that have the potential for being synthesized at low-cost. Other worthy design criteria includes chemical stability, solubility in “green solvents,” and plastic properties.

2.6. Materials and Process Standards

Many researchers find that they are not able to reproduce results obtained by other researchers when they make organic solar cells. The most likely origins of these reproducibility issues are differences in materials or differences in process. Standardization of materials property reporting and process reporting might significantly enhance reproducibility (or at least simplify process troubleshooting) in the technical community.

It is quite common to obtain different results with organic solar cell materials (especially polymers) having nominally identical manufacturer and assay specifications. There are several reasons why different batches a polymer may have different properties. For example, the relative molecular mass of the polymer is sometimes different. The dispersity (i.e., polydispersity index) of the polymer,\textsuperscript{64} or perhaps even the exact shape of the relative molecular mass distribution, could lead to differences in its physical properties. The potential for random structural isomers is also quite common in polymers, and measurements of isomerization such as explicit numerical regioregularity\textsuperscript{64,65} are important.

Purity is perhaps the most important materials property in organic solar cell materials that does not have a consistent or universally accepted reporting standard. Because the number of charge carriers is quite dilute in organic solar devices, a small concentration of an impurity that acts, for example, as a charge carrier trap could have a significant impact on device performance.\textsuperscript{66,67} While common elemental analysis methods can provide an assay of trace metal-containing impurities such as catalysts, there is no well-developed assay method that can reliably report trace (ppm/ppb) levels of contaminants having an elemental composition similar to that of the desired product. Reaction by-products, oligomers, and doped material are all examples of potential trace impurities that could significantly influence device properties but would likely go undetected by most currently used assay methods. In the absence of reliable assays, a standard device design and fabrication process might be substituted. With very strict controls, variations in device performance might be unambiguously associated with impurities in a single material or layer.
Process reporting standards are also important. It is likely that there are important processing parameters that are not always described in manuscripts, such as the temperature of the solution during casting, the rate of acceleration of the spin coater and the atmosphere of the glove box during the film formation. It is important to do research to identify all of the factors that have an impact on the device performance so that manufacturers will be able to consistently obtain optimal results. A guide or template to process reporting that is enforced by the larger technical community (journal editors in particular) would provide enormous benefit.

It might be possible to position robust assay capabilities, the availability of standard processes / standard device designs, and standard device tests in a single U.S. facility or center. Such a facility could be used by materials developers to identify subtle differences between materials or to measure how their material behaves in a standard device design fabricated by a standard process. Perhaps it could also be of use in troubleshooting manufacturing processes or supply line issues. It would be important in such a facility to set some barrier to entry such that it is not overwhelmed with requests to test thousands of new materials. This idea is similar to the mode of operation of the European “Innovation Centers” for organic electronics, which were evaluated in an NSF-funded report “European Research and Development in Hybrid Flexible Electronics” in 2010.68

2.7. Understanding Degradation and Improving the Lifetime of Organic Photovoltaics

One of the most important manufacturing challenges that must be addressed is improving the long-term lifetime of organic solar cells. Failure mechanisms can be classified as either extrinsic or intrinsic. Extrinsic failure occurs when the packaging leaks, exposing the cells to air (in Figure 3-3), or excessive mechanical force causes the module to break. Examples of intrinsic failure are photo oxidation, changes of film morphology, reactions between the semiconductors and electrodes, or delamination that occurs when stress builds up due to mismatch in thermal expansion coefficients.

Extrinsic failure is prevented by making sufficiently robust packaging. We do not yet understand intrinsic failure well enough to know what needs to be done to make solar cells that can last for more than 25 years. When the performance of organic solar cells is monitored under steady...
illumination and constant temperature, two regimes of degradation are typically observed as depicted in Figure 3-4. In the first couple of weeks as the cells burn-in, the power conversion efficiency decays exponentially by 10 to 30%. After burn-in, the rate of degradation tends to be much slower and linear as a function of time. Several polymers have been observed to maintain 80% of their performance after burn-in for as long as 3 to 6 years. There are many important fundamental questions that need to be answered in order to figure out how to make solar cells more stable. Research should be done to address these questions.

What is the mechanism of burn-in degradation and why does it stop after a couple of weeks? Does burn-in stop when all of the oxygen is consumed, when all the polymer chain ends have undergone a reaction or all of the impurities have participated in a reaction? Does burn-in stop when reactants reach equilibrium with the products of the reaction? How is the long-term degradation different from burn-in degradation?

Can we eliminate chemical degradation with better purification procedures? Attempts to detect the impurities or degradation products have been unsuccessful in many cases. How can we detect impurities that exist at concentrations of much less than 1%? Are small molecules easier to purify than polymers?

Many molecules are less stable when they are in an excited state. It is therefore important to know if chemical degradation primarily results from molecules being in the excited singlet state, triplet state or charged state. It is also important to know which part of the molecules reacts so that more robust chemical structures can be made. At this time, it is not clear whether stability arises by having a desirable arrangement of energy levels or by avoiding reactive chemical moieties.

To determine whether bulk heterojunctions are thermally stable under typical operating conditions, we need to have phase diagrams for donor-acceptor blends and know the miscibility of the two materials with each other. In some cases we know that structures are not stable at
temperatures in the range of 110 to 150 °C, but we do not know what happens to these structures at 25-80 °C over a period of years.

The cathode in many organic solar cells is highly reactive, so it is important to understand what has to be done to make stable organic-metal interfaces. Preliminary results suggest that solar cells made in the inverted architecture are more stable.\(^{69}\)

It is critically important to find ways to speed up the testing process so that one can rapidly find out how stable solar cells will be. In order to extrapolate lifetimes from accelerated tests, we need to know how the rate of degradation scales with illumination intensity and temperature. Sometimes degradation is accelerated by exposing solar cells to oxygen. It is important to find out if oxygen is involved in the degradation that occurs in encapsulated devices to determine whether or not the information that is gained by testing solar cells in air can be used to predict what happens when cells are encapsulated. It is also important to find out how degradation depends on the energy of the photons that are used for testing. Is it possible that ultraviolet photons generate damage faster than lower energy photons and that an ultraviolet filter will be needed to stabilize organic solar cells. Understanding all of the factors that influence degradation is critically important not only so that the degradation can be prevented, but also so that different research labs will know what variables to control so experiments will be reproducible.

Do organic cells fracture cohesively or at interfaces when temperature cycling causes some layers to thermally expand more than others? What has to be done to prevent solar cells from failing mechanically?

2.8. Electrode and Module Design

The most commonly used transparent electrode for both organic solar cells and flat-panel displays is indium tin oxide. It would be desirable to find a transparent electrode that could be deposited at lower cost. Options that are currently being explored include silver nanowires, carbon nanotubes and graphene (more detailed discussion in Section 1).

Research on making modules with organic solar cells is still in the early stages. It will be important to create designs that are compatible with low-cost manufacturing, minimize power loss due to series resistance, optical losses and gaps between solar cells, and tolerant to shunt pathways that are likely to exist in some of the solar cells.

3. Programmatic Recommendations

- Provide seed funding for hybrid solar cells with organics on top of silicon or CIGS.
• Provide funding for efforts that invest now in process design and engineering, with an eye toward continual refinement of fundamental understanding.
• Provide support/enforcement for materials property and process reporting standards among grantees; provide funding for improved assay technologies.
• Consider funding a center for organic solar power manufacturing in the format and scope of the European Innovation Centers.
• Greatly increase support for studies of intrinsic degradation and accelerated testing in organic solar cell materials.
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