

## Final Scientific/Technical Report – March 2015

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Name of Lead Institution: **The University of Arizona**

Name of Center Director: **Neal R. Armstrong, Ph.D.**  
Position or Title of Center Director: **Regents' Professor of Chemistry & Biochemistry/  
Optical Sciences**  
Mailing Address of Center Director: **Department of Chemistry & Biochemistry  
The University of Arizona  
P.O. Box 210041  
1306 East University Blvd.  
Tucson, AZ 85721-0041  
520-621-8242  
[nra@email.arizona.edu](mailto:nra@email.arizona.edu)**

Telephone of Center Director:  
E-mail Address of Center Director:

Consortium/Teaming Members: **The University of Arizona (UA)  
Georgia Institute of Technology (GT)  
National Renewable Energy Laboratory (NREL)  
Princeton University (PU)  
University of Washington (UW)**

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## Executive Summary

The Center for Interface Science: Solar Electric Materials (CISSEM) was funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences (BES) from August 1, 2009 – December 31, 2014 under Award Number DE-SC0001084, as part of a broad set of Energy Frontier Research Centers (EFRCs) designed to underpin the development of economical energy conversion platforms for the 21<sup>st</sup> century. CISSEM successfully integrated the research groups of 19 principal investigators at The University of Arizona (the lead institution), the Georgia Institute of Technology, Princeton University, the University of Washington, and the National Renewable Energy Laboratory (NREL) into a coordinated and synergistic program, while also building a highly productive collaboration with the SLAC National Accelerator Laboratory. Our mission was to advance the understanding of interface science underlying solar energy conversion technologies based on organic and organic-inorganic hybrid materials – specifically in organic photovoltaic solar cells (OPVs); and to inspire, recruit and train future scientists and leaders in the basic science of solar electric energy conversion.

CISSEM researchers focused on establishing a foundational understanding of the electronic properties of interfaces in area-scalable, thin-film photovoltaic platforms. Metal oxide interlayers used in OPVs to improve the efficiency of charge harvesting at electrodes was our central focus. A key feature of CISSEM research has been our ability to develop a comprehensive understanding of interfaces and interfacial processes at the atomic and molecular scales. This is a scientific foundation for thin-film photovoltaic technologies and our nation’s pursuit of lowering the costs of transforming the sun’s energy into electricity. Our efforts combined: *i*) theoretical modeling; *ii*) new materials development; *iii*) developing new measurement science approaches to characterize composition, molecular and supramolecular structure, band edge energies, electrical properties, and charge harvesting or injection; and *iv*) integrating our use-inspired new materials and enhanced knowledge of interfaces and interfacial processes into OPV platforms.

The strengths of the characterization methodologies developed in CISSEM were recognized within the EFRC network, and were a major component of our interactions with other DOE-funded programs including EFRCs. CISSEM research has resulted in a legacy of 120+ peer-reviewed publications describing our basic science. Much of this highly collaborative research will now be built upon at CISSEM member institutions, with other extramural funding sources. Furthermore, the state-of-the-art facilities and expertise created for modern interface science, especially as they pertain to energy conversion and energy storage challenges, will ensure their broadest continued impact.

DOE EFRC funding has positively impacted and enhanced the training and development of more than 140 graduate students, postdoctoral researchers and research scientists at the five CISSEM institutions, and students from three Colorado universities associated with NREL. Our legacy also includes these student, postdoctoral researcher and scientist alumni who have taken positions of impact and responsibility in technology industries, government agencies and academia in the U.S., Asia and Europe.

## Comparing Actual Accomplishments with the Goals and Objectives of the Project

**Goals and Objectives of the Project:** The Center for Interface Science: Solar Electric Materials (CISSEM) was funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences (BES) from August 1, 2009 – December 31, 2014 under Award Number DE-SC0001084. CISSEM connected researchers in an integrated multi-investigator program at The University of Arizona (UA, the lead institution), the Georgia Institute of Technology (GT), Princeton University (PU), the University of Washington (UW), and the National Renewable Energy Laboratory (NREL). CISSEM's mission was to advance the understanding of interface science underlying solar energy conversion technologies based on organic and organic-inorganic hybrid materials – specifically in organic photovoltaic solar cells (OPVs); and to inspire, recruit and train future scientists and leaders in the basic science of solar electric energy conversion. Students, postdoctoral researchers (postdocs), research scientists and research engineers under 19 principal investigators (PIs) were successfully integrated into a coordinated and integrated multi-investigator EFRC program. Sub-awards from UA were in effect with GT, PU, and UW. NREL was funded directly by BES.

The CISSEM management team focused our research on creating an understanding of the electronic properties of interfaces between molecular semiconductors and (predominately) metal oxide electrical contact or interlayer materials, in order to improve the efficiency of charge harvesting at electrodes. Pursuing this fundamental science to ultimately improve area-scalable, thin-film PV energy conversion technologies was an exciting challenge that fully engaged all members of CISSEM. The molecule/atomic scale understanding of how interface composition, structure, and energetics control PV efficiency (i.e., through better contact and interlayer design and more efficient charge extraction) should ultimately provide design principles that can be used in the creation of a wide array of new energy conversion platforms, including the perovskite-based PV platform, and help extend PV efficiencies to commercially competitive levels.

An overall research management framework of four, five-year goals defined our research program to address understanding, controlling, and improving the performance of interfaces present in OPVs between organic active layers, and metallic, nontraditional-conductor, and metal oxide electrical contact or interlayer (electrode) materials, as follows:

- Goal #1*** – Develop new theories for charge transfer between molecular semiconductors and electrical contact or interlayer materials.
- Goal #2*** – Develop new methodologies for the characterization of the atomic and molecular composition of interfaces, and new approaches for the nanoscale characterization of electrical and electrochemical properties of these interfaces.
- Goal #3*** – Develop 2-D nanostructured hybrid materials that lead to the formation of chemically and physically robust interfaces, with full control of their composition, molecular architecture, and physical properties.
- Goal #4*** – Apply our understanding of interfaces to OPV platforms.

These CISSEM goals were multi-year efforts consistent with a basic science EFRC program.

**Actual Accomplishments:** Five major scientific accomplishments for CISSEM against our goals are described below, which reflect the overarching philosophy that drove our research efforts:

**a) Combined theoretical and experimental studies provided an unprecedented understanding of metal oxide/organic semiconductor interfacial energetics for harvesting or injection of electrical charges (Goals #1 and #2).**

CISSEM combined theoretical and experimental studies to develop an understanding of technologically important metal oxides (TMOs), such as zinc oxide (ZnO) and molybdenum oxide (MoO<sub>3</sub>), now routinely used to enhance efficiencies of harvesting/injection of electrical charges across active layer/electrical contact heterojunctions, in a variety of energy conversion and light-emitting platforms. We correlated atomic scale composition and defect type and density, in the near-surface region of the oxide, and the influence of these defects on interactions with organic semiconductors. Our findings highlight the overriding importance of explicitly considering defects to achieve a fundamental understanding of energy-level alignment at heterojunctions between conductive metal oxides and organic semiconductors. Deliberate control of near-surface defects and interfacial gap states is expected ultimately to lead to paradigms for control of the electronic properties of hybrid interfaces.

Brédas, Kahn and coworkers characterized the adsorption of donor molecules, which are models for hole-transport layers, on MoO<sub>3</sub> (010) surfaces [Li 2014 [10.1021/cm402113k](https://doi.org/10.1021/cm402113k); Papadopoulos 2013 [10.1002/adfm.201301466](https://doi.org/10.1002/adfm.201301466)]. Density functional theory (DFT) was combined with ultraviolet (UPS), inverse (IPES) and X-ray (XPS) photoelectron spectroscopies to explore the nature of the interface between MoO<sub>3</sub> (with intrinsic oxygen vacancies), and 4,4'-N,N'-dicarbazole-biphenyl (CBP). The near alignment of the CBP highest occupied molecular orbital with the Fermi level and conduction band edge of MoO<sub>3</sub> points to facile hole collection or injection. Because of the large initial work function of MoO<sub>3</sub>, electron transfer takes place at the interface from the organic molecules to the oxide upon deposition of CBP, inducing a reduction of MoO<sub>3</sub> at the interface. The reduced species uniquely probed by UPS are at the origin of the increased gap state density.

Monti, Brédas, Graham, Kippelen, Berry, Ginley, and Kahn integrated theory and spectroscopic characterization to fully describe, for the first time, the heterojunction between prototypical electron transport materials such as 3,4,9,10-perylenetetracarboxylic diimide (PTCDI), and C<sub>60</sub>, and ZnO [Winget 2014 [10.1002/adma.201305351](https://doi.org/10.1002/adma.201305351); Schulz 2014 [10.1002/adfm.201401794](https://doi.org/10.1002/adfm.201401794)]. The type and concentration of defects in the ZnO near-surface region critically impact its energy-level alignment with PTCDI, and the appearance of a new interface states inside the ZnO band gap. Combining DFT with UPS and XPS, we successfully predicted and observed, for the first time, the interfacial gap states that arise from ZnO-to-PTCDI partial charge transfer; caused by interstitial-zinc defects near the ZnO surface. For C<sub>60</sub>/ZnO interfaces we have been able to describe the electronic structure of ZnO films intentionally modified with near-surface defects, revealing the profound effect of this tailoring on the interfacial electronic structure of C<sub>60</sub>, and changes to interfacial band alignment and injection barriers, showing for the first time the formation of hybridized interface states and charge-transfer between shallow donor defects in ZnO and the C<sub>60</sub>.

**b) Amine-containing polymers modified the work function of electrodes to achieve the effective harvesting or injection of electrons (Goals #1, #3 and #4).**

Massively scalable (printed) electronic materials and device platforms, such as OPVs, require air-stable electrical contacts with work functions low enough to ensure efficient electron collection/injection at interfaces with organic semiconductors. Low-work function metals are not stable, requiring inert atmosphere fabrication and additional encapsulation, increasing cost and

complexity. In a remarkable effort led by Kippelen, Brédas, Graham, Marder, and Kahn, reported in *Science*, interface modifiers based on polymers containing simple aliphatic amine groups substantially reduce the work function of a variety of conductors including metals, TMOs, polymers, and graphene to as low as ca. 3.2 eV [Zhou 2012 [10.1126/science.1218829](https://doi.org/10.1126/science.1218829)]. An easily processed, air-stable ultrathin (1-to-10 nm) layer of polyethylenimine ethoxylated (PEIE) or branched polyethylenimine (PEI) produced effective work functions as low as those of alkali metals (Cs) while retaining air stability and ease of processing [U.S. Patent Appl. 2014/0131868 A1]. The work function reduction appears to arise from interface dipoles that are attributed to partial charge transfer from the amine to the electrode surface.

Such PEIE-modified electrodes enabled the demonstration of a completely-plastic OPV on a flexible substrate [Zhou 2012 [10.1126/science.1218829](https://doi.org/10.1126/science.1218829)], and subsequently our preparation of an all-plastic OPV with high photovoltaic dynamic range [Zhou 2014 [10.1039/C3TA15073A](https://doi.org/10.1039/C3TA15073A)] for which current–voltage characteristics were successfully measured as a function of light irradiance over five orders of magnitude; from the dark to the one-sun standard solar spectrum. We also discovered how to incorporate PEIE into simple recombination layers to enable solution-processed tandem polymer solar cells with unprecedented performance [Zhou 2012 [10.1039/C2EE23294D](https://doi.org/10.1039/C2EE23294D)]. This innovative, all-polymeric recombination layer has the high work function contrast between its two opposite surfaces desired for an inverted, tandem OPV. The all-polymeric recombination layer is robust and compatible with low-cost, solution-based processing, and offers simpler fabrication of high-performance tandem OPVs. These results demonstrate the prospects of OPVs for lightweight, portable, standby power generation under room light, and even weaker, illumination.

**c) Theoretical modeling and complementary characterization techniques combined to rigorously define structure of contact-modifying molecular interlayers (Goals #1, #2 and #3).**

Work function control of electrical contacts was achieved with a unique series of dipolar and redox active small molecule surface modifiers, where it was determined that orientation, in addition to molecular composition, played a key role in control of effective work function, surface free energy, and charge collection/injection efficiencies. A variety of surface vibrational and waveguide spectroscopies were used to determine these orientations, but interactions with SLAC National Accelerator Laboratory, primarily focusing on the use of near edge X-ray absorption fine structure spectroscopy (NEXAFS), were critical. For the first time, Pemberton, Ratcliff, Brédas, Marder and Ginger combined complementary NEXAFS, polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) and DFT calculations to unambiguously quantify the tilt angle and binding modes of phenyl phosphonic acid (PA) self-assembled monolayers tethered to model, indium zinc oxide electrode surfaces [Wood 2012 [10.1021/jp3050725](https://doi.org/10.1021/jp3050725); Gliboff 2013 [10.1021/la304594t](https://doi.org/10.1021/la304594t)]. Brédas, Marder and Ginger also correlated NEXAFS spectroscopy with DFT predictions to unravel the complex, competing effects of fluorination on the molecular orientation and binding mode of alkyl and aryl PA monolayers bound to indium tin oxide [Gliboff 2013 [10.1021/jp404033e](https://doi.org/10.1021/jp404033e)]. Alkyl fluorination created a more upright orientation due to intermolecular forces and increased steric bulk, whereas aryl fluorination gave a less upright orientation due to changes in binding mode. The tilt angles and binding modes impact critical interfacial properties such as work function. Defining the interplay between binding modes, molecular dipole moment, molecular orientation, and fluorination/ molecular structure is critical for a molecular-level understanding of how self-

assembled monolayers impact charge harvesting and injection efficiencies and OPV performance, and contributes to the design rules for improved surface modifiers.

***d) Detailed characterization of nickel oxide interlayers provided invaluable insight for efficient hole harvesting or injection (Goals #1, #2 and #4).***

Interlayers based on nickel oxide ( $\text{NiO}_x$ ), a large band gap p-type oxide important for hole harvesting or injection, have been another central focus of CISSEM research.  $\text{NiO}_x$  interlayers are readily deposited from solution and often significantly outperform commercial polymeric interlayer materials. Using a combination of UPS, XPS, IPES, electronic property characterization of single junctions, and OPV measurements, Armstrong, Ratcliff, Marder, Berry, Ginley, Olson, and Kahn demonstrated for the first time selective hole-harvesting can be obtained by introducing near-surface nickel oxyhydroxide ( $\text{NiOOH}$ )-like species [Ratcliff 2011 [10.1021/cm202296p](#)] creating large interface dipoles which lead to large barriers to electron collection [Cowan 2015 [10.1002/aenm.201400549](#)]. We established design criteria for  $\text{NiO}_x$ -based hole-collecting contacts that lead to higher open-circuit voltage and improved performance in bulk-heterojunction OPVs [Ratcliff 2013 [10.1002/aenm.201200669](#)]. Detailed spectroscopic measurements of the  $\text{NiO}_x$  interlayer surface composition successfully related the observed compositional changes directly to the energy levels for charge carriers in the  $\text{NiO}_x$  interlayer [Ratcliff 2011 [10.1021/cm202296p](#)]. The key discovery is that formation of  $\text{NiOOH}$ -like entities in the near surface region of the oxide (using oxygen plasma activation) alters the critical energy levels that control hole-collection efficiency and device performance. This is likely to be an observation that generalizes across a number of oxide interlayers and device platforms.

Building on these discoveries, Olson and Kahn introduced a new bilayer that pairs  $\text{NiO}_x$  and  $\text{MoO}_3$  layers to enhance OPV efficiency [Schulz 2014 [10.1002/adfm.201302477](#)]. We exploited the outstanding hole-collection of a vacuum-deposited  $\text{MoO}_3$  layer (0.5–10 nm) and the excellent electron blocking of a solution-deposited  $\text{NiO}_x$  layer (6 nm), to greatly enhance hole-harvesting efficiency. Our UPS/XPS studies and electrical property characterization revealed the underlying energetics of the bilayer and the intricate interfacial chemistries that allows for efficient charge transfer between layers. This bilayer approach effectively and simultaneously achieves two complementary, yet challenging goals through deliberate design, with the beneficial properties of each individual material dominating.

***e) New state-of-the-art characterization techniques developed by CISSEM (Goal #2).***

Under research funded as part of CISSEM at Ginger (UW) developed a new ***time-resolved Atomic force microscopy*** (AFM) technique that successfully overcomes current limitations of commercial AFM systems when studying extremely fast sub-microsecond charge separation/recombination processes, and yet is a relatively straightforward modification to commercial AFM equipment based on custom software and low-cost external hardware [Giridharagopal 2012 [10.1021/nl203956q](#)]. This patented approach [U.S. Patent 8,686,358] avoids complex, expensive specialty hardware for niche applications. This method digitizes and data analyzes the oscillations of an AFM cantilever while a voltage pulse or light pulse is used to locally perturb a sample such as a nano-structured OPV. Fast dynamic events as short as 100–200 nanoseconds are accessible. Using this time-resolved method, the Ginger group examined a series of OPVs under realistic operating conditions, revealing for the first time sub-100 nanometer length-scale variations in photoinduced charge separation and collection efficiencies that correlate with overall device efficiency.

Under research funded as part of CISSEM at UA (Armstrong, McGrath, Saavedra), we have developed a ***new ultrafast transient absorbance spectroscopy (TAS) capability for studying charge-transfer kinetics in a polarized attenuated total reflectance (ATR) geometry***. We have successfully developed the capability to perform ultrafast Helios-based, picosecond TAS in a single-reflection ATR geometry. Our first set of experiments examined a phthalocyanine monopod adsorbed at a titanium dioxide interlayer on an indium tin oxide substrate/contact. The hole-blocking effect of the oxide interlayer was demonstrated, as well as the measurement sensitivity of ca. 0.25 monolayers, using an approach that will be generalizable across a number of charge harvesting interlayers and molecular modifiers (manuscript in preparation).

**In Summary:** Understanding how to achieve efficient charge harvesting in emerging thin-film PV solar cell platforms has been both high impact and high risk, and has required new characterization tools and detailed studies of the types highlighted in this document. The experience we have gained in this atomic/molecular-level pursuit of interface science is paramount to identifying the composition, morphology, specific interactions, and electronic properties of organic/metal oxide and organic/metal interfaces that enable efficient harvesting of electrons and holes, and the desired dramatic improvements in efficiency and lifetime in thin-film platforms. Our basic science will be foundational to DOE-sponsored efforts to create new energy conversion technologies, and transcends the five-year funding period.

## Summary of Project Activities

**Original Hypotheses and Approaches Used:** When we submitted our 2008 EFRC proposal, there had not been a concerted and coordinated multi-PI effort to understand interface properties at the atomic/molecular level, and their impact on PV performance. The contact materials, and associated organic or inorganic interlayers, which lead to the highest possible harvesting efficiencies in OPVs, were poorly understood with a lack of reliable model systems.

We recognized from the outset the need to develop the relevant model materials that would provide a better understanding of correlations between interfacial structure, energetics, and charge transfer with energy conversion efficiency. In Years 1-3, we concentrated on defining interfacial structural and compositional parameters that dictate electronic properties and charge harvesting/injection efficiencies relevant to OPV platforms. In Years 4-5, we focused on the unifying, vertically-integrated theme of advancing the understanding of the electronic properties of interfaces between molecular semiconductors and electrical contact or interlayer materials that lead to efficient harvesting of electrons and holes. It is now clear that the efficiency of charge harvesting is dictated by a competition between the desired charge transfer event (including exciton dissociation) and all other fates for the desired charge, including back charge transfer, recombination at the contact/active layer interface, drift or diffusion away from the contact/active layer interface, and bulk recombination.

The principles underlying our research program are summarized in Figures 1A-1D. We show a schematic view of an OPV active layer between contacts with widely differing work functions (Figure 1A). For an OPV, the maximum open-circuit voltage ( $V_{OC}$ ) is limited by the work function difference between the contacts, which is affected by the composition, structure and energetics (e.g., interface dipoles, local shifts in vacuum level, and charge accumulation) at both the contact/active layer interfaces.

The power conversion efficiency ( $\eta$ ) of an OPV is ultimately determined by a competition between charge harvesting and electron-hole recombinations, being reduced by: *i*) electron-hole recombination within the bulk of the active layer; *ii*) electron-hole recombination at the contact/active layer interfaces; and *iii*) other detrimental processes such as charge back injection from the contacts (Figure 1B). By incorporating thin interlayers of appropriate inorganic or organic materials between each contact and the active layer, we can increase power conversion efficiency by providing thermodynamic and/or kinetic barriers to help facilitate the desired preferential or ‘selective’ charge harvesting of either electrons or holes at each contact, while also minimizing charge back injection (Figure 1C). OPV efficiency is ultimately determined by a competition between charge harvesting and electron–hole recombinations. Dark and light current/voltage (J/V) responses showing the effects on PV efficiency of recombination and poor contact (interlayer) design (i.e., the loss of photocurrent at maximum power ( $P_{MAX}$ ) and a lower  $V_{OC}$ ) are shown by the blue plot in Figure 1D. Improving  $V_{OC}$ , the photocurrent yield at  $P_{MAX}$ , and PV efficiency through better contact-interlayer design and more efficient charge extraction are shown by the red plot in Figure 1D.

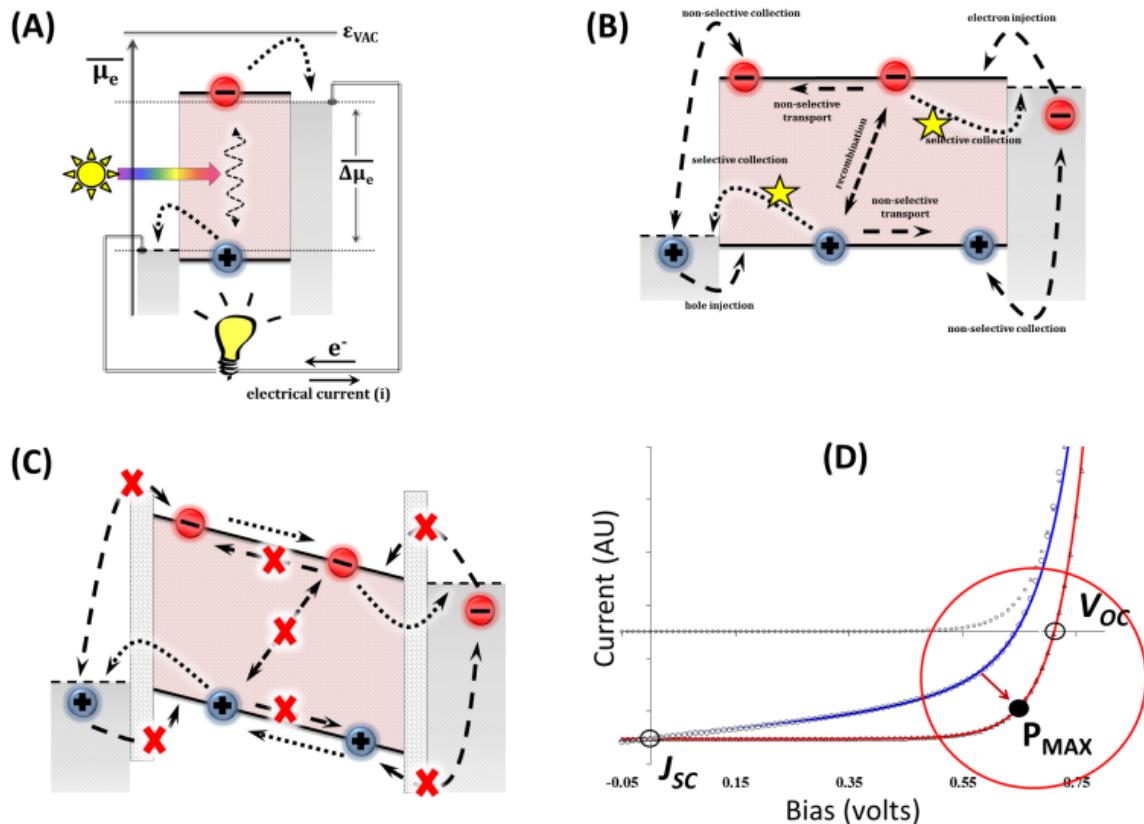


Fig. 1 – (A) Schematic view of an OPV active layer between contacts with widely differing work functions; (B)  $\eta$  for the OPV is limited by the contact work function difference and electron-hole recombinations in the bulk active layer and at both the contact/active layer interfaces; (C) The insertion of interlayer material between each contact and the active layer can provide thermodynamic and/or kinetic selectivity for charge harvesting; (D) Dark and light J/V responses show the effect of recombination and contact (interlayer) design on OPV efficiency – more efficient charge harvesting (red plot versus blue plot) improves the OPV  $V_{OC}$ , photocurrent yield at  $P_{MAX}$ , and overall  $\eta$ .

As we have pursued our research goals we have studied model material systems such as:

- NiO<sub>x</sub> hole-harvesting interlayers [e.g., Cowan 2015 [10.1002/aenm.201400549](https://doi.org/10.1002/aenm.201400549); Ratcliff 2011 [10.1021/cm202296p](https://doi.org/10.1021/cm202296p)].
- ZnO electron-harvesting interlayers [e.g., Schulz 2014 [10.1002/adfm.201401794](https://doi.org/10.1002/adfm.201401794); MacLeod 2014 [10.1039/c4ee02488e](https://doi.org/10.1039/c4ee02488e)].
- Fullerene (C<sub>60</sub>) [e.g., Jenkins 2014 [10.1039/C4TA04319G](https://doi.org/10.1039/C4TA04319G); Schulz 2014 [10.1002/adfm.201401794](https://doi.org/10.1002/adfm.201401794); Khosroabadi 2014 [10.1021/jp505364d](https://doi.org/10.1021/jp505364d); Matz 2013 [10.1021/am400640x](https://doi.org/10.1021/am400640x)]

The CISSEM Management Team initiated and used the following activities to further integrate our students and postdocs into CISSEM, and enhance their interactions and training into our day-to-day operations:

- i. The Collaborative Research Travel Program (C RTP) funded travel for graduate students and postdocs between CISSEM institutions to expand their EFRC research by allowing them to engage our center's array of facilities and expertise, and in particular interact and collaborate face-to-face with other students/postdocs. Applicants were required to identify their collaborators at another institution and propose the purpose for their travel, thereby breaking down the barriers of geographic dispersal.
- ii. The CISSEM Innovative Research Seed Awards (or CIRSAs) program was designed with the goals of: i) stimulating creativity in our graduate students and postdocs in defining important new CISSEM-related research activities and directions, and ii) providing a mechanism for enhanced engagement of our graduate students and postdocs during our annual center-wide research conferences. The CIRSA competition consisted of three steps:
  - a. During the research conference students and postdocs were tasked to find a collaborator and jointly propose a new research problem that would bring them together and fit into the strategic plan and major goals of CISSEM. We intentionally encouraged applicants to find collaborators at another institution, and to work across their disciplinary boundary.
  - b. These newly found student/postdoc collaborators submitted a brief proposal for their team's new CISSEM-funded collaborative research activity.
  - c. The proposals were judged by three of our PIs, and the winning CIRSA teams were provided with travel costs for the student/postdoc collaborators to accomplish the scientific goals of their proposed collaborative projects.

These CTRP and CIRSA programs were consistent with the BESAC recommendations for training, supporting, and inspiring the energy scientists of the future as set forth in their 2007 report *Directing Matter and Energy: Five Challenges for Science and the Imagination*, which specifically calls for the kind of training activities we achieved. The collaborative partnerships we established between PI research groups were critical to the success of the interfacial research pursued by CISSEM, and were integral and important feature of our center.

**Problems Encountered and Departure from Planned Methodology:** In 2009, to accommodate a \$10M reduction in the initial budget and scope required by the DOE grant award, CISSEM Director Armstrong and the management team scaled back research activities and the allocations of CISSEM resources versus our 2008 EFRC Proposal. As a result, the nineteen PIs funded by CISSEM were:

PI	Institution, Department	Year(s) Funded
Neal R. Armstrong, Ph.D.	UA, Department of Chemistry & Biochemistry	1-5
Joseph J. Berry, Ph.D.	NREL	1-5
Jean-Luc Brédas, Ph.D.	GT, Department of Chemistry & Biochemistry	1-5
David S. Ginger, Ph.D.	UW, Department of Chemistry	1-5
David S. Ginley, Ph.D.	NREL	1-5
Samuel Graham, Ph.D.	GT, School of Mechanical Engineering	1-5
Antoine Kahn, Ph.D.	PU, Department of Electrical Engineering	1-5
Bernard Kippelen, Ph.D.	GT, School of Electrical & Computer Eng.	1-5
Christine K. Luscombe, Ph.D.	UW, Department of Materials Science & Eng.	1-3
Seth R. Marder, Ph.D.	GT, Department of Chemistry & Biochemistry	1-5
Dominic V. McGrath, Ph.D.	UA, Department of Chemistry & Biochemistry	1-5
Oliver L.A. Monti, Ph.D.	UA, Department of Chemistry & Biochemistry	1-5
Robert A. Norwood, Ph.D.	UA, College of Optical Sciences	1-3
Dana C. Olson, Ph.D.	NREL	1-5
Jeanne E. Pemberton, Ph.D.	UA, Department of Chemistry & Biochemistry	1-5
Nasser N. Peyghambarian, Ph.D.	UA, College of Optical Sciences	1-2
Jeffrey Pyun, Ph.D.	UA, Department of Chemistry & Biochemistry	1
Erin L. Ratcliff, Ph.D.	UA, Department of Chemistry & Biochemistry	5
S. Scott Saavedra, Ph.D.	UA, Department of Chemistry & Biochemistry	1-5

Hence, several components of the research proposed in 2008 were eliminated at the onset or subsequently defunded by CISSEM, e.g.:

- Environmental barrier (encapsulation) layers – Years 1-3 support only [Graham].
- Metal nanowire/nanogrid semi-transparent electrodes – Years 1-3 support only [Pemberton].
- Nanoimprinted cells and electrodes – Years 1-3 support only [Norwood/Peyghambarian].
- Plasmonics – Year 3 support only [Norwood].
- Polythiophene brushes grafted on metal oxides – Years 1-3 support only [Luscombe/Pyun].

These changes enabled CISSEM to increase its research emphasis on exploring and characterizing the factors underpinning the energetics and dynamics of interfacial charge harvesting at organic/contact and organic/interlayer interfaces.

***Assessment of the Impact on the Project Results:*** CISSEM has focused on establishing a foundational understanding of the electronic properties of interfaces between molecular semiconductors and new electrical contact and interlayer materials, that have been designed to provide for efficient harvesting of electrons and holes in OPVs, and in some key examples, enhanced stabilities in these platforms. Our efforts have combined: *i*) theoretical modeling; *ii*) new materials development; *iii*) development of new measurement science approaches to characterize composition, molecular and supramolecular structure, band edge energies, electrical properties, and charge harvesting/injection; and *iv*) integrating our use-inspired new materials and enhanced knowledge of interfaces and interfacial processes into OPV platforms.

A key differentiator of CISSEM activities relative to other EFRCs has been our ability to develop a comprehensive understanding of interfaces and interfacial processes at the atomic or molecular scale. The strengths of the characterization methodologies developed in CISSEM have

been recognized within the EFRC network and have become a major component of our interactions with other DOE-funded programs including EFRCs [e.g., Ratcliff 2013 [10.1039/C3TC31064G](#); Garcia 2012 [10.1002/adma.201200963](#)].

**A) We developed new theoretical and experimental approaches to understand how atomic and molecular interfacial composition control band edge, frontier orbital energies, and electronic coupling, in model metal oxides and oxide/active-layer heterojunctions:**

We developed new contact and interlayer materials, based on large band gap metal oxides, providing tunability of electrical properties and control of band edge energies [e.g., Papadopoulos 2013 [10.1002/adfm.201301466](#); Ndione 2013 [10.1002/aenm.201200742](#)]. We recognized it was critical to understand how metal oxide deposition and post-deposition treatments affect energetics at metal oxide/active-layer interfaces, and the local concentrations, types and energies of defect states that may act as gap states and recombination centers. DFT calculations and a repeated slab approach were used to describe the electronic properties of several metal oxides and microscopic descriptions of metal oxide/organic or metal oxide/metal interfaces [e.g., Schulz 2014 [10.1002/adfm.201401794](#); Winget 2014 [10.1002/adma.201305351](#); Li 2014 [10.1021/cm402113k](#)]. Such knowledge forms the basis for the design and characterization of hole-selective and electron-selective interlayer materials that are foundational for new energy conversion platforms, and the selection of model contacts and interlayers.

Our studies of ZnO and related oxides included predictions (Fig. 2) of how changes in composition, at atomic scale near or at the oxide surface, lead to shifts in effective work function and electrical band gap revealed by Kelvin probe, UPS, and IPES, and the concentration and distribution of defects as revealed by O 1s photoemission peaks [e.g., Winget 2014 [10.1002/adma.201305351](#); Papadopoulos 2013 [10.1002/adfm.201301466](#)], which are sensitive to the microenvironment in the near surface region of all oxides [e.g., Li 2014 [10.1021/cm402113k](#); Li 2012 [10.1021/cm301596x](#)]. We observed a strong influence of energetically shallow donors (e.g., Zn interstitials) on ZnO interfacial electronic structure, in the presence of electron acceptors such as perylenebisimide (PDI) derivatives and C<sub>60</sub> [e.g., MacLeod 2014 [10.1039/c4ee02488e](#); Schulz 2014 [10.1002/adfm.201401794](#); Winget 2014 [10.1002/adma.201305351](#)]. Tailoring electronic structure at electron-harvesting contacts like ZnO was achieved by selectively enriching or removing near-surface defects, conclusions drawn from our DFT modeling and UPS/IPES studies for C<sub>60</sub>/ZnO heterojunctions

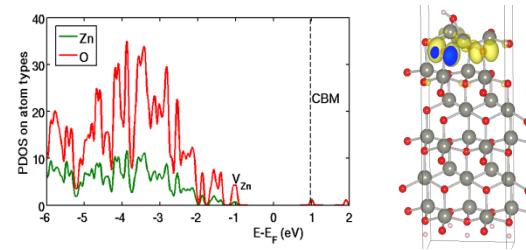


Fig. 2 – (left) DFT model of a ZnO(0002) hydroxylated surface containing oxygen and zinc vacancies donor-acceptor pairs: (right) density of states projection onto zinc and oxygen atoms with charge distributions corresponding to the valence band maximum [Li 2012 [10.1021/cm301596x](#)].

Shallow donor defects at the surface of highly-conductive ZnO thin films introduced hybrid interface states and interface dipoles, which we investigated by UPS, IPES [Schulz 2014 [10.1002/adfm.201401794](#)] and resonant photoemission (RES-PES) at SLAC, measuring carrier dynamics at C<sub>60</sub>/ZnO heterojunctions (Figs. 3-4). Charge-transfer from ZnO O 2p<sub>z</sub> orbitals to C<sub>60</sub> causes carrier trapping by emerging hybrid interface states, on a time-scale of 2 fs. We additionally studied C<sub>60</sub>/ZnO interfaces using two-photon photoemission (2PPE), describing electronic structure in the conduction band region [Monti 2012 [10.1021/jz300850x](#)], and probing

defect states near the conduction band minimum, the unoccupied manifold of  $C_{60}$ , and excited interface states that arise from hybridization.

We also explored electron-selective interlayers based on  $TiO_2$  [Ou 2013 [10.1039/C3TA10894E](#)], and closely related ternary oxides ( $Ti_xZr_yO_2$ ). The defect chemistry of  $TiO_2$  is simpler than  $ZnO$ , with a narrower range of possible vacancies and hydroxylation, and a greater ease of modification with molecular interlayers.

Interlayers based on  $NiO_x$ , a large band gap p-type oxide capable of selective hole harvesting, have been an important focus of CISSEM research [e.g., Ratcliff 2011 [10.1021/cm202296p](#); Steirer 2011 [10.1002/aenm.201100234](#)]. Using a combination of UPS, IPES, electronic property characterization of single junctions, and OPV measurements, we demonstrated for the first time selective hole-harvesting is obtained by introducing near-surface “ $NiOOH$ -like” species and large interface dipoles, accompanied by increases in the electrical and optical band gap, creating a barrier to electron collection [Cowan 2015 [10.1002/aenm.201400549](#); Ratcliff 2013 [10.1002/aenm.201200669](#)]. Defect-dense, transition metal oxide interlayers are a route to controlling active-layer/metal oxide interactions that simultaneously impact interfacial structure, energetics and the dynamics of charge transfer.

We also combined UPS, IPES and XPS to characterize the interface between the prototypical high work function n-type oxide,  $MoO_3$  (the  $<10\bar{1}>$  surface or its non-stoichiometric counterpart), and a model organic, the  $\pi$ -conjugated hole-transport layer material 4,4'-N,N'-dicarbazole-biphenyl, or CBP [Papadopoulos 2013 [10.1002/adfm.201301466](#)]. The near alignment of the CBP HOMO with the Fermi level and conduction band edge of  $MoO_3$  confirmed that charge transfers occurs from CBP to the metal oxide, inducing a reduction of  $MoO_3$  at the interface. These reduced species, at the origin of the increased gap state density observed by UPS, are a critical theme since gap states figure significantly in the competition between efficient charge harvesting and recombination, for molecular, polymeric and nanocrystalline semiconductor active layers. Inspired by these studies, entirely new  $NiO_x/MoO_x$  heterojunctions were introduced [Schulz 2014 [10.1002/adfm.201302477](#)], which took advantage of the enhanced hole-collection afforded by  $MoO_x$  and the hole-selectivity of the  $NiO_x$  layer.

#### **B) We developed new approaches to modify contact/active-layer and interlayer/active-layer interfacial regions—tailoring physical, chemical and electronic properties:**

We pursued several different approaches to modify metal or metal oxide contact and interlayer surfaces, and: *i*) control surface free energy and wettability by non-polar active layers;

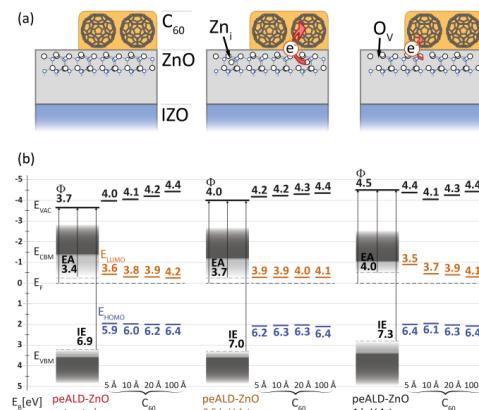


Fig. 3 – Energy level alignment at the  $C_{60}/ZnO$  interface for different surface treatments of  $ZnO$  removing electron-harvesting barriers [Schulz 2014 [10.1002/adfm.201401794](#)].

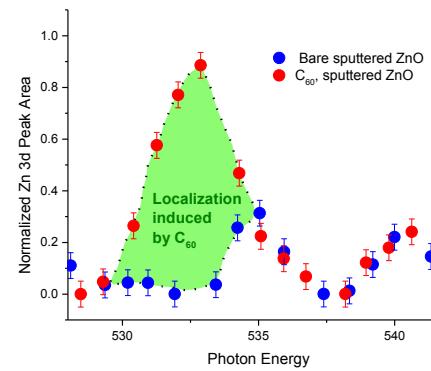


Fig. 4 – O 1s RES-PES enhancement for  $C_{60}$  on  $ZnO$  with 0.5 fs delocalization on bare  $ZnO$  (blue circles) and carrier trapping in the presence of  $C_{60}$  (red circles).

*ii)* tune the effective work function over wide ranges (changes in excess of 1.5 eV were possible); *iii)* create energy barriers against harvesting of unwanted charge carriers; and *iv)* introduce redox functionality with control of orientation and spacing of the redox-active groups near a contact/interlayer surface.

In a stunning example, we discovered that easily processed, air-stable, aliphatic-amine polymers (Fig. 5) lowers work functions of a variety of contacts to levels seen for metals such as Cs [e.g., Zhou 2012 [10.1039/C2EE23294D](https://doi.org/10.1039/C2EE23294D); Zhou 2012 [10.1126/science.1218829](https://doi.org/10.1126/science.1218829)]. Unusual interface dipoles arising from the arrangement of amine functional groups appear to control work function, and inspired our studies to produce extreme work function differences in contact materials using small molecule analogs.

We also explored a variety of substituted aryl phosphonic acid (PA) modifiers as self-assembled monolayers (SAMs) to provide a level of tunability in both effective work function and surface free energy not available in other molecular modifier systems [e.g., Li 2014 [10.1002/adfm.201303670](https://doi.org/10.1002/adfm.201303670); Knesting 2013 [10.1021/jz4021525](https://doi.org/10.1021/jz4021525); Wood 2012 [10.1021/jp3050725](https://doi.org/10.1021/jp3050725)].

Our complementary theoretical studies revealed the dipolar field established at a contact or interlayer surface is dependent upon structure, bonding and orientation of the tethered PA molecule, which control the molecular dipole projection along the normal axis – the sum of the projected molecular dipole from the core of the modifier, and bond dipoles expressed in the linker to the oxide [Li 2014 [10.1002/adfm.201303670](https://doi.org/10.1002/adfm.201303670)]. We used micro-contact printing to deposit patterned fluorinated-PAs on indium tin oxide (ITO) and characterized electroluminescence, enabling imaging of spatial variations in charge injection barrier at buried interfaces [Knesting 2012 [10.1002/adma.201102321](https://doi.org/10.1002/adma.201102321)]. Patterning of these fluorinated PAs created a tenfold enhancement in work function contrast when compared against previously patterned transparent conducting oxide surfaces. We also developed PA-tethered, redox-active modifiers for studies of charge transfer to metal oxide substrates, with a focus on phthalocyanines or Pcs [e.g., Lin 2012 [10.1021/jz3002426](https://doi.org/10.1021/jz3002426)], PDIs, prototype donors and acceptors with well-defined transition dipole moments for optical characterization, and Highest Occupied Molecular Orbital/Lowest Unoccupied Molecular Orbital (HOMO/LUMO) levels close to OPV-relevant materials.

**C) We developed new measurement science approaches to characterize atomic and molecular composition, surface free energy, molecular orientation, charge transfer rates, and electrical property heterogeneity on sub-micron length scales:**

CISSEM researchers combined of complementary approaches to the characterization of interfaces between contact and interlayer materials and molecular semiconductors. Multi-group CISSEM studies demonstrated the benefits of combining angle-resolved NEXAFS at SLAC and PM-IRRAS to characterize substituent effects on molecular packing and binding modes of PA-SAMs (Fig. 6), while correlating the angles observed alkyl and benzyl PAs with predictions from DFT modeling [Gliboff 2013 [10.1021/la304594t](https://doi.org/10.1021/la304594t); Gliboff 2013 [10.1021/jp404033e](https://doi.org/10.1021/jp404033e)]. These PA-SAMs were well oriented, in agreement between with modeling studies that provided details

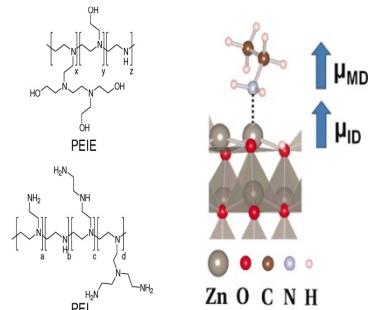


Fig. 5 – (left) Structures of poly(imines) PEIE and PEI that lower contact work functions to surprising levels; (right) modeling studies suggested enhanced interface dipoles in these physisorbed layers are the origin of low work function [Zhou 2012 [10.1126/science.1218829](https://doi.org/10.1126/science.1218829)].

regarding the binding mode for PAs on oxides. This combination of theory and experiment will guide future studies to understand molecular orientation at metal oxide/active layer interfaces.

Also of note are our collective and extensive photoelectron spectroscopies that describe transport HOMO energies of molecular semiconductors, relative to valence band energies ( $E_{VB}$ ) of the underlying contact, in combination with the breadth of IPES, 2PPE and RES-PES to describe the transport LUMO energies of these same systems – and electronic coupling induced alterations of interfaces between the contact or interlayer and active-layer components [e.g., MacLeod 2014 [10.1039/c4ee02488e](https://doi.org/10.1039/c4ee02488e); Schulz 2014 [10.1002/adfm.201401794](https://doi.org/10.1002/adfm.201401794); MacLeod 2014 [10.1002/aenm.201400073](https://doi.org/10.1002/aenm.201400073); Ratcliff 2011 [10.1021/cm202296p](https://doi.org/10.1021/cm202296p)]. We extended the sensitivity of our photoemission spectroscopy (PES) experiments to characterize band tailing of HOMO levels for organic semiconductors at interfaces with metal oxides, which revealed the dependence of bandwidth on the molecular organization and interactions between the contact and active-layer components (Fig. 7). The degree of band tailing was significant for interfacial charge trapping and PV performance (leakage currents, diode quality factors and device efficiency).

An inherent strength in CISSEM was our ability to combine reflectance spectroscopies, in both the IR and visible wavelength regions, with unprecedented sensitivity to characterize molecular orientation at interfaces. Examples include the PM-IRRAS studies described above and ATR waveguide studies for sub-mono- to multi-layer molecular assemblies coupled with electrochemical studies of electron transfer rates [e.g., Lin 2012 [10.1021/jz3002426](https://doi.org/10.1021/jz3002426); Simon 2011 [10.1021/ac2011526](https://doi.org/10.1021/ac2011526)]. Our surface Raman spectroscopies were invaluable to differentiate interactions between molecular semiconductors, such as  $C_{60}$ , and metallic contacts [e.g., Matz 2013 [10.1021/am400640x](https://doi.org/10.1021/am400640x); Matz 2012 [10.1021/ja3016186](https://doi.org/10.1021/ja3016186)].

We developed complementary approaches to characterize compositional and energetic heterogeneity on sub-micron length scales, using conductive atomic force microscopy (C-AFM), scanning probe microscopy (SPM), time-resolved electrostatic force microscopy (tr-EFM, Fig. 8) [Giridharagopal 2012 [10.1021/nl203956q](https://doi.org/10.1021/nl203956q)], and Intensity-Modulated Scanning Kelvin Probe Microscopy [Shao 2014 [10.1021/nn5045867](https://doi.org/10.1021/nn5045867)]. We demonstrated the mapping of spatial variation in electrical properties of

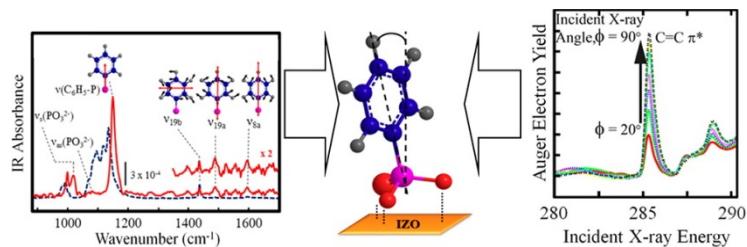


Fig. 6 – Examples of our approach to orientation determination of interface modifiers using (left) PM-IRRAS and right NEXAFS [Gliboff 2013 [10.1021/la3045941](https://doi.org/10.1021/la3045941)].

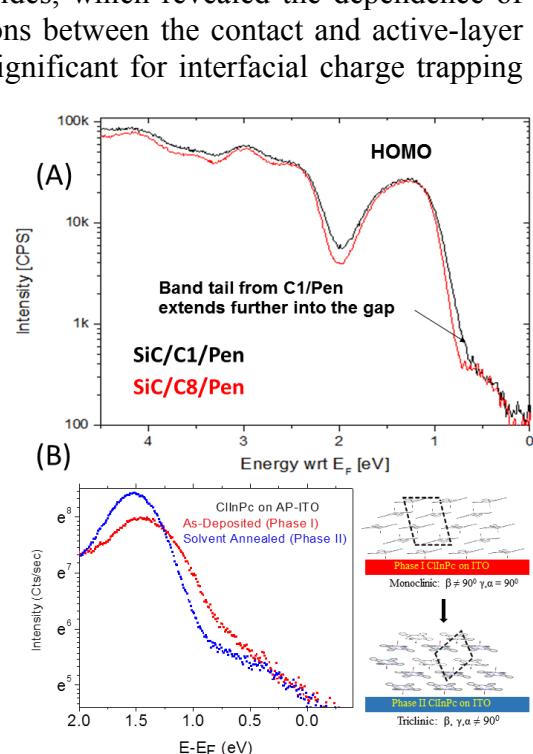


Fig. 7 – (A) log-scale UPS spectra of pentacene on SiC modified with C1 (black) or C8 (red) SAMs. C8 yields a more ordered pentacene film, with narrower VB peaks and lower tail-state densities extending into the gap; (B) UPS spectra of C60nPc films on ITO contacts, as deposited (red) and after solvent annealing (blue) converting to the Phase II polymorph. Narrowing photoemission bands accompanies changes in device impedance, due to removal of shallow trap states.

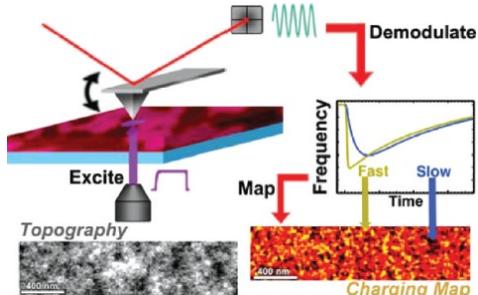


Fig. 8 – tr-EFM schematic. Local fluctuations in photo-induced charge density beneath the tip, and the rate at which they dissipate, correlate with active layer microstructure and device OPV efficiency [Giridharagopal 2012 [10.1021/nl203956q](https://doi.org/10.1021/nl203956q)].

and transient (e.g., Cowan 2015 [10.1002/aenm.201400549](https://doi.org/10.1002/aenm.201400549)) spectroscopies allowed us to extend our characterization of the dynamics of charge extraction and charge recombination at contact/active-layer and interlayer/active-layer interfaces in OPVs. These complementary characterization techniques explored the dynamics of charge harvesting over multiple time (ms to ps) and length scales (macroscopic to sub-micron) and fully integrated with other characterization capabilities within CISSEM.

For example, electrochemical and spectroelectrochemical studies of PA-Pcs bound to ITO-coated, ATR waveguide substrates provided molecular orientation information (complemented by NEXAFS at SLAC), while potential-modulated ATR (PM-ATR) spectroelectrochemistry allowed estimation of the rates of heterogeneous electron transfer ( $k_{ET}$ ) for differently oriented Pc sub-populations in a single monolayer – demonstrating the powerful molecular insight achieved by combining ATR spectroscopy and potential modulation (Fig 9). Aggregated Pcs in nearly horizontal orientations had the highest  $k_{ET}$  consistent with their closer approach to the contact surface [Lin 2012 [10.1021/jz3002426](https://doi.org/10.1021/jz3002426)]. Subsequent studies showed a tetra-PA Pc monolayer has a uniform orientation that is close to parallel to the surface plane of the contact, and the  $k_{ET}$  for this system was even higher ( $>10^4$  sec<sup>-1</sup> per molecule) – exceeding the threshold rate of charge collection we estimate to be necessary for an OPV platform at 15 mA/cm<sup>2</sup>. Indeed, the flat-lying, tetra-PA Pc has the superior performance in planar heterojunction OPVs with PA-Pc modified ITO contacts, and some degree of templating of the growth of crystalline Pc layers deposited on this modifier. We extended these studies to the ns-ps time scale to study donor-acceptor (D/A) dyads on contact/interlayer surfaces with new ultrafast transient ATR capabilities and monitor back electron transfer and recombination (Fig. 10).

contact/active-layer heterojunctions with 20-40 nm resolution under device-relevant conditions [MacDonald 2012 [10.1021/nn303043y](https://doi.org/10.1021/nn303043y)]. We also showed that, low charge mobility active layers, the separation distance between ohmic sites, and the arrival rate of photoinduced charges, determine charge collection efficiency [Zacher 2011 [10.1021/jp207471f](https://doi.org/10.1021/jp207471f)]. These studies provided pathways to understanding how heterogeneity in interfacial electronic properties is correlated with macroscopic electrical properties that limit energy conversion efficiency – key enablers for a variety of organic and inorganic electronic platforms.

Our complementary new combinations of steady state [MacLeod 2012 [10.1021/jz300283h](https://doi.org/10.1021/jz300283h)], impedance, and transient (e.g., Cowan 2015 [10.1002/aenm.201400549](https://doi.org/10.1002/aenm.201400549)) spectroscopies allowed us to extend our characterization of the dynamics of charge extraction and charge recombination at contact/active-layer and interlayer/active-layer interfaces in OPVs. These complementary characterization techniques explored the dynamics of charge harvesting over multiple time (ms to ps) and length scales (macroscopic to sub-micron) and fully integrated with other characterization capabilities within CISSEM.

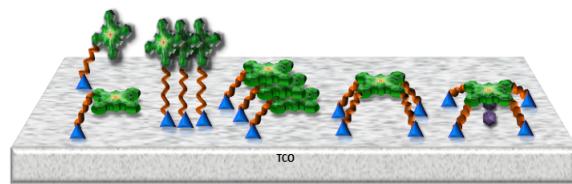


Fig. 9 – Tethered Pcs created to characterize electron transfer rates ( $k_{ET}$ ) as a function of (left to right) orientation, tether length, number of binding sites, and the introduction of an axial coordination group.

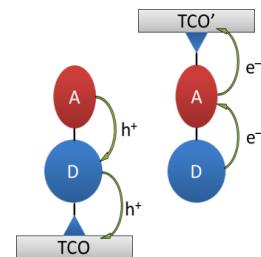


Fig. 10 – Porphyrin or Pc /PDI D/A dyads, enabling sub-ps transient ATR experiments to compare rates of charge harvesting versus recombination, and RES-PES “photon clock” experiments

## Products Developed Under the Award and Technology Transfer Activities

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### **Other Public Releases of Results**

From January 2011, monthly CISSEM highlights were submitted to the DOE and posted on the CISSEM public website, as follow:

Month	Highlight Title	Research group(s)
January 2011	Semitransparent ITO-free Organic Solar Cells	Kippelen
February 2011	Improved Synthesis of Soluble Dyes for Organic Solar Cells	McGrath
March 2011	Excellent Charge-Transport Layers from Nanoparticles	Kahn
April 2011	Controlling Polymer Growth	Luscombe, Marder
May 2011	Charge-Selective Interlayers for Thin-Film Photovoltaics	Armstrong
June 2011	New Approach for Measuring Charge Transfer Rates at Interfaces	Saavedra
July 2011	Energy-Aligned Selective-Interlayers	Armstrong, Berry, Ginley, Kahn, Olson
August 2011	Encapsulating Organic Electronics with Nano-Laminate Films	Graham

Month	Highlight Title	Research group(s)
<b>August 2011</b>	Interface-to-Face 2 (ITF2) Research Conference at NREL	All
<b>September 2011</b>	Spatially Modulating Interfacial Properties	Ginger, Marder
<b>October 2011</b>	Surfaces of Selective Interlayers	Armstrong, Berry, Ginley, Kahn, Olson
<b>November 2011</b>	Tethered Asymmetric Phthalocyanines	Armstrong, McGrath, Saavedra
<b>December 2011</b>	Surface-Initiated Polymerization	Armstrong, Luscombe, Marder
<b>January 2012</b>	Probing Nanoscale Dynamics	Ginger
<b>February 2012</b>	Nanolaminate Electrodes for OPVs	Berry, Brédas, Kahn, Kippelen
<b>March 2012</b>	Simulating Organic Solar Cells with Heterogeneous Electrodes	Armstrong
<b>April 2012</b>	Electron-Transfer Rates for Surface-Confined Chromophores	Armstrong, Ginger, McGrath, Saavedra
<b>May 2012</b>	Low-Work Function Electrodes for Organic Electronics	Brédas, Graham, Kahn, Kippelen, Marder
<b>June 2012</b>	Theoretical Modeling Reveals How Chemistry Impacts the Electronic Properties of Polar Zinc Oxide (ZnO) Surfaces	Brédas, Kippelen, Monti
<b>August 2012</b>	An Electrostatic Perspective on Interfacial Electronic Structure and Charge Transfer at Organic–Metal Interfaces	Monti
<b>September 2012</b>	How “Ohmic” is that Contact?	Armstrong
<b>October 2012</b>	Tandem Polymer Solar Cell with an All-Polymeric Recombination Layer	Kippelen
<b>October 2012</b>	CISSEM Gathers in Tucson on October 22-24, 2012 for Third Annual “Interface-to-Face” Research Conference	All
<b>November 2012</b>	Highly-Tunable Nickel Cobalt Oxide Interlayers for Solar Cells	Armstrong, Berry, Olson
<b>December 2012</b>	The Importance of Interfacial Composition and Energetics in OPVs	Armstrong, Marder
<b>January 2013</b>	Theoretical Modeling and Complementary Characterization Techniques Combine to Rigorously Define Monolayer Structure	Berry, Brédas, Ginger, Marder, Pemberton
<b>February 2013</b>	How Interfacial Contact Properties Influence Open Circuit Voltages in Organic Solar Cells	Berry, Ginley, Marder, Olson
<b>March 2013</b>	Recyclable Organic Solar Cells Based on Cellulose Nanocrystal Substrates	Kippelen

Month	Highlight Title	Research group(s)
April 2013	Probing the Selective Electron-Harvesting Properties of Titanium Dioxide Interlayers with Electrochemical Studies	Armstrong
June 2013	The Complex Effects of Fluorination on the Structure of Phosphonic Acid Self-Assembled Monolayers on ITO	Brédas, Ginger, Marder
July 2013	Combining Theory and Experiments to Study Organic Hole-Transport Layer / Molybdenum Trioxide Interfaces	Brédas, Kahn
August 2013	Understanding How Interfacial Phenomena Affect Voltage Doubling for Tandem Organic Solar Cells	Armstrong, Kahn
September 2013	Probing Bulk Heterojunction/Contact Buried Interfaces with Complementary Spectroscopies	Ratcliff (and CEEM)
December 2013	Novel Contacts Pair Nickel Oxide and Molybdenum Oxide Layers to Enhance the Efficiency of Organic Solar Cells	Kahn, Olson
January 2014	Using Interface Modifiers at Contacts to Suppress Surface Recombination in Organic Solar Cells	Ginger, Marder, Olson
February 2014	An All-plastic Solar Cell with a High Photovoltaic Dynamic Range Producing Photovoltage even Under Low Illumination	Kippelen
March 2014	Combining Theory and Experiments to Understand a Gallium- Doped Zinc Oxide Surface Modified by Organic Phosphonic Acids	Berry, Brédas, Marder, Ratcliff
April 2014	The Impact of Contact Surface Modification on The Morphology of a Model Polymer:Fullerene Bulk Heterojunction	Berry, Ginley, Kahn, Olson (and CEEM)
May 2014	Electron Harvesting, Magnesium-doped Zinc Oxide Sol-gel Layers	Ginley, Kahn, Olson
June 2014	Defect-Driven Interfacial Electronic Structure at a Metal Oxide/Organic Semiconductor Heterojunction	Berry, Brédas, Ginley, Kippelen, Monti

#### Web Site or Other Internet Sites That Reflect the Results of This Project:

The public website <http://solarinterface.org/> contained information on CISSEM and the results of our EFRC's research. The DOE's *Energy Frontier Research Center Community Website* (<http://www.energyfrontier.us>) also contained information on CISSEM and a list of CISSEM publications.

#### Networks or Collaborations Fostered

Collaborations between research groups in CISSEM were well established, engaging our PIs, students, postdocs, and scientists to address our four Major Goals including the CRTP and

CIRSA programs. In addition, the following networks or collaborations have been fostered during this award:

- The Armstrong group collaborated with EFRC research scientists at the University of North Carolina (Center for Solar Fuels) to help them set up a system to accurately measure external quantum efficiencies (IPCE) of both PV and photoelectrochemical energy conversion systems for their center.
- The Armstrong, Ginger, Kahn, Monti, and Pemberton groups collaborated Dr. Dennis Nordlund at SSRL beamlines using NEXAFS, RES-PES and XAS to characterize metal oxide surface composition, charge transfer, and tilt angles of molecular interface modifiers [Gliboff 2014 [10.1021/jp412150j](https://doi.org/10.1021/jp412150j); Gliboff 2013 [10.1021/jp404033e](https://doi.org/10.1021/jp404033e); Gliboff 2013 [10.1021/la304594t](https://doi.org/10.1021/la304594t); Lin 2012 [10.1021/jz3002426](https://doi.org/10.1021/jz3002426)].
- The Armstrong group collaborated with the groups of Prof. Dr. Christoph Brabec (i-MEET, Erlangen, Germany) and Prof. Dr. Klaus Meerholz (University of Cologne, Germany). Graduate students from these groups visited UA to carry out some of their Ph.D. research in the Armstrong laboratory.
- Berry and Ginley collaborated with Prof. Sir. Richard Friend and Prof. Judith MacManus-Driscoll (University of Cambridge, UK) to examine the impact of materials synthesis on interfacial charge generation and extraction [Gershon 2013 [10.1016/j.tsf.2013.03.041](https://doi.org/10.1016/j.tsf.2013.03.041)].
- The Brédas group collaborated with Dr. Stephen Lany (NREL) on modeling the MZO surface.
- The Graham group collaborated with Prof. Frederik Krebs (Risø DTU National Laboratory, Denmark) to investigate interfacial mechanical adhesion for thin-film PV structures using double cantilever beam tests.
- Graham collaborated with Prof. Jörg Winter (Center for Plasma Science and Technology, Ruhr-Universität Bochum, Germany).
- The Graham group collaborated with the Prof. Xiaolin Zheng group (Department of Mechanical Engineering, Stanford University) to apply a rapid flame-based process for doping TiO<sub>2</sub> films with W and C for potential use in OPVs.
- The Graham group collaborated with Prof. Mariadriana Creatore (TU Eindhoven, the Netherlands) to pursue ALD films for organic electronics.
- The Kahn group collaborated with Prof. Tobin Mark (Northwestern University) to characterize transparent conducting oxides prepared at the Northwestern EFRC ANSER Center by UPS and IPES.
- Kahn collaborated with the group of Prof. David Cahen (Weizmann Institute of Science, Israel) on interfaces of lead halide perovskites in thin-film PV.
- The Kippelen group interacted with Prof. Kenneth H. Sandhage's (GT) group to collaborate on the structural characterization of metal oxide films and nanolaminates using X-ray and transmission electron microscopy experiments [Cheun 2012 [10.1002/adfm.201102968](https://doi.org/10.1002/adfm.201102968)].
- The Marder group collaborated with Prof. Moonhor Ree (Pohang University of Science and Technology, S. Korea) and Prof. David Bucknall (GT) to study structures of organic-organic interfaces relevant to bulk heterojunction [Wunsch 2013 [10.1039/C3TC30774C](https://doi.org/10.1039/C3TC30774C)].

- Marder collaborated with Prof. Udo Bach (Monash University, Australia) and Prof. Michael Grätzel (EPFL Lausanne, Switzerland) to investigate phosphonic acids as surface modifiers in dye-sensitized solar cells.
- The Marder group collaborated with the group of Prof. Larry Bottomley (GT) on cyclic square-wave voltammetry.
- The Marder group collaborated with the group of Prof. Norbert Koch (Humboldt Univ., Germany) on the use of oxidants and reductants (p- and n-dopants, respectively) to modify metal oxide work function.
- The Monti group collaborated on computational studies with Fabio Della Sala, National Nanotechnology Laboratory, Lecce, Italy [Terentjevs 2011 [10.1021/jp204720a](https://doi.org/10.1021/jp204720a)].
- The Monti group collaborated with Dr. Peter Sutter at the Center for Functional Nanomaterials, Brookhaven National Laboratory for low temperature scanning tunneling microscopy research.
- The Monti group established collaborated with Prof. Norbert Koch (Humboldt Universität zu Berlin, Germany) and Prof. Martin Wolf (Fritz Haber Institut, Berlin, Germany) in context of the Collaborative Research Centre 951 “Hybrid Organic/Inorganic Systems for Opto-Electronics” (HIOS SFB 951).
- The Monti group collaborated with Prof. Torsten Fritz (Universität Jena, Germany) to investigate the chemical nature of hybrid interface states for 3,4,9,10-perylene tetracarboxylic dianhydride on ZnO.
- The Pemberton group collaborated with Jerome Lenhard (Eastman Kodak Co.) to look at low work function metals on a series of PDI electron transport materials.
- Pemberton and Ratcliff collaborated with Prof. Robert Crabtree (Yale and ANSER EFRC) to characterize hydroxamic acids on metal oxide interlayers.
- Ratcliff collaborated with Dr. Martyn McLachlan (Imperial College London, UK) to understand the energetics of poly(3-hexylthiophene) and lead zirconate titanate heterojunctions.
- The Saavedra group initiated collaborations with Prof. Thomas E. Mallouk (Penn State University) to study photo-induced charge transfer in thin, multilayer films of chromophores designed by Mallouk’s group to harvest solar energy for water splitting.

### **Technologies/Techniques**

The following techniques have been developed through CISSEM research:

- Armstrong group – A method for characterizing the electrical properties of contact materials on sub-micron length scales, and differentiating between ohmic and non-ohmic regions [MacDonald 2012 [10.1021/nn303043y](https://doi.org/10.1021/nn303043y)].
- Armstrong, Ratcliff, and Saavedra groups – A planar waveguide-based ATR transient absorbance spectroscopy instrument to enable studies of charge transfer kinetics in interface-confined thin films of molecular chromophores [Lin 2012 [10.1021/jz3002426](https://doi.org/10.1021/jz3002426)].
- Berry, Ginley, and Olson groups – The large area deposition of high quality and high conductivity metal oxide thin films.

- Brédas group – DFT-based surface models for defect-containing metal oxides modified with organic molecules, which incorporate various surface defects based consistent with detailed experimental characterizations [e.g., Li 2014 [10.1021/cm402113k](https://doi.org/10.1021/cm402113k); Schulz 2014 [10.1002/adfm.201401794](https://doi.org/10.1002/adfm.201401794); Winget 2014 [10.1002/adma.201305351](https://doi.org/10.1002/adma.201305351); Li 2014 [10.1002/adfm.201303670](https://doi.org/10.1002/adfm.201303670)].
- Brédas, Kahn, Ginger, Graham, Kippelen, Marder, Olson, and Ratcliff groups – Organic molecule based surface treatment methodologies for reducing electrode work functions, including amine-based polymers [e.g., Li 2014 [10.1002/adfm.201303670](https://doi.org/10.1002/adfm.201303670); Knesting 2013 [10.1021/jz4021525](https://doi.org/10.1021/jz4021525); Zhou 2012 [10.1039/C2EE23294D](https://doi.org/10.1039/C2EE23294D); Zhou 2012 [10.1126/science.1218829](https://doi.org/10.1126/science.1218829); Wood 2012 [10.1021/jp3050725](https://doi.org/10.1021/jp3050725)].
- Saavedra group – A Helios-based instrument to perform ultrafast (picosecond) TAS in single reflection polarized ATR geometry.
- Ginger group – A tr-EFM scanning probe tool for local characterization of interfacial charge transfer in thin-film solar cell structures [Giridharagopal 2012 [10.1021/nl203956q](https://doi.org/10.1021/nl203956q)].
- Ginger group – An intensity-modulated scanning Kelvin probe microscopy methodology to measure variations in carrier lifetime due to buried interface chemistry in OPVs [Shao 2014 [10.1021/nn5045867](https://doi.org/10.1021/nn5045867)].
- Ginger and Ratcliff groups – Transient photocurrent and transient photovoltage approaches to measure charge extraction rates [Cowan 2015 [10.1002/aenm.201400549](https://doi.org/10.1002/aenm.201400549); Knesting 2013 [10.1021/jz4021525](https://doi.org/10.1021/jz4021525)].
- Graham group – An improved method to measure the effective water vapor permeation rate through barrier films using the calcium corrosion test.
- Graham and Marder group – A spray coating method that enables the rapid surface modification of metal oxide interfaces with phosphonic acids [Bulusu 2013 [10.1021/la303354t](https://doi.org/10.1021/la303354t)].
- Kahn and Monti groups – A methodology to investigate ultrafast charge-transfer from sorbed organic molecules to metal oxide surfaces using RES-PES and XAS – both at SSRL [Schulz 2014 [10.1002/adfm.201401794](https://doi.org/10.1002/adfm.201401794)].
- Luscombe and Marder groups – A method to grow polythiophene brushes on metal oxide surfaces from phosphonate containing initiators [Doubina 2012 [10.1021/la204117u](https://doi.org/10.1021/la204117u)].
- Marder group – New purification methodologies and syntheses of phosphonic acid dipolar interface modifiers.
- McGrath group – New synthetic routes to functionalized asymmetric phthalocyanines [Polaske 2011 [10.1021/la203126c](https://doi.org/10.1021/la203126c); Mayukh 2011 [10.1002/chem.201001427](https://doi.org/10.1002/chem.201001427); Mayukh 2010 [10.1021/jo1011637](https://doi.org/10.1021/jo1011637)].
- Monti group – The angle resolved 2PPE of metal oxide films, and oxide films interacting with organic small molecules.
- Norwood and Peyghambarian groups – A method adapting both electric field and conducting probe modes of force microscopy to study charge density and transport in nanostructured electrode systems.
- Norwood and Peyghambarian groups – A nanoimprinting by melt-processed polymers technique for making nano-patterned electrode structures [Thomas 2011 [10.1002/adma.201102834](https://doi.org/10.1002/adma.201102834)].

## **Inventions/Patent Applications, Licensing Agreements**

The following patent/patent applications have been developed through our EFRC research:

### **US Patent 8,686,358**

- “Sub-Microsecond-Resolution Probe Microscopy”
- Issued: April 1, 2014
- Filed: September 14, 2011
- Application Number: 13/232,859
- US Patent Application 2012/0079630 A1
- Inventors: Ginger, David; Giridharagopal, Rajiv; Moore, David; Rayermann, Glennis; Reid, Obadiah

### **Patent No. WO 2011/127475 A1**

- “Organic photovoltaic devices comprising solution- processed substituted metal-phthalocyanines and exhibiting near-ir photo-sensitivity”
- PCT/US2011/031970
- PCT Filed: April 11, 2011
- International Publication Date: October 13, 2011
- Inventors: McGrath, Dominic V.; Mayukh, Mayank; Placencia, Diogenes; Armstrong, Neal R.

### **US Patent Application 2013/0008503 A1**

- “Organic photovoltaic devices comprising solution-processed substituted metal-phthalocyanines and exhibiting near-ir photo-sensitivity”
- Published: January 10, 2013
- Filed: April 11, 2011
- Application Number: 13/635,324
- Inventors: McGrath, Dominic V.; Mayukh, Mayank; Placencia, Diogenes; Armstrong, Neal R.

### **Patent No. WO 2012/166366 A1**

- “Systems and methods for producing low work function electrodes”
- PCT/US2012/038125
- PCT Filed: May 16, 2012
- International Publication Date: December 6, 2012
- Inventors: Kippelen, Bernard; Fuentes-Hernandez, Canek; Zhou, Yinhua; Kahn, Antoine; Meyer, Jens; Shim, Jae Won; Marder, Seth R.

### **US Patent Application 2014/0131868 A1**

- “Systems and Methods for Producing Low Work Function Electrodes”
- Published: May 15, 2014
- Filed: May 16, 2012
- Application Number: 14/117,965
- Inventors: Kippelen, Bernard; Fuentes-Hernandez, Canek; Zhou, Yinhua; Kahn, Antoine;

Meyer, Jens; Shim, Jae Won; Marder, Seth R.

#### **US Patent Application 2014/0202517 A1**

- “Recyclable Organic Solar Cells On Substrates Comprising Cellulose Nanocrystals (CNC)”
- Published: July 24, 2014
- Filed: March 21, 2014
- Application Number: 14/221,369
- Inventors: Kippelen, Bernard; Fuentes-Hernandez, Canek; Zhou, Yinhua; Moon, Robert; Youngblood, Jeffrey P.

#### **Other Products – Videos, Tours, and News Articles**

The following videos, tours, and news articles included general information on CISSEM or the results of CISSEM EFRC research:

- **July 22, 2009:** UANews video “Project Sage: Energy Frontier Research Center Develops New Solar Cells” produced and edited by Will Holst.
- **July 22, 2009:** UANews article “Project Sage Special Report: Bringing Solar Power to the Masses” by Lew Serviss.
- **August 3, 2009:** UANews video “It's Complicated: Creating Generation Three Solar Cells” produced and edited by Will Holst.
- **March 31, 2010:** American Chemical Society – The Journal of Physical Chemistry Letters, Perspective Video, “Organic Photovoltaics”.
- **April 1, 2010:** Neal Armstrong presented an overview of CISSEM to the Arizona Leadership Solar Bus Tour at UA. The Solar Bus Tour was hosted by U.S. Rep. Gabrielle Giffords, the Arizona Economic Resource Organization, SCF Arizona, and UA.
- **June 23, 2010:** UANews article “Stimulus Funding at UA Passes \$100M” by University Communications.
- **August 18, 2010:** Catherine Zoi, Assistant Secretary for EERE, DOE and U.S. Rep. Gabrielle Giffords visited the UA campus, including a tour of Neal Armstrong’s CISSEM EFRC laboratories.
- **October 15, 2010:** Dr. Arun Majumdar, Director of the DOE ARPA-E, visited the UA campus, which included a tour of Neal Armstrong’s CISSEM EFRC laboratories and a meeting with the students of UA’s Energy Science Group.
- **October 17, 2010:** Arizona Daily Star article “Scientists look to tap sun in new ways” by Tom Beal.
- **October 27, 2010:** Solar Novus Today article “Semitransparent ITO-Free Organic Photovoltaics” by Nancy Lamontagne, Novus Media Today, LLC.
- **November 12, 2010:** Inside Tucson Business article “UA research progress: Tuning a plastic molecule to turn sunlight into energy” by Joe Pangburn.
- **November 14, 2010:** Arizona Daily Star article “Thin-film cells are solar's new frontier” by Neal Armstrong.
- **November 28, 2010:** Arizona Daily Star article “UA scientists at the frontiers of research” by Tom Beal.

- **December 2, 2010:** Arizona Daily Wildcat article “Research funded by stimulus” by Lívia Fialho.
- **December 7, 2010:** Materials Views article “New Concept for the Preparation of Organic Electronic Devices” by Sjef Oellers (John Wiley & Sons).
- **December 8, 2010:** Arizona Daily Wildcat article “Energy sparks conversations” by Lívia Fialho.
- **March 31, 2011:** Arizona Daily Star article “Spotlight put on technology innovations by five on UA staff” by Tom Beal.
- **May 23, 2011:** UANews article “UA Researchers Tout Solar Energy at National Summit” by University Communications.
- **August 16, 2011:** C.H. Huckelberry (Pima County Administrator) and Carmine DeBonis Jr (Development Services Director, Pima County Development Services) visited the UA campus to tour Neal Armstrong’s CISSEM EFRC laboratories.
- **August 17, 2011:** Pima County Interview with Dr. Neal Armstrong, Director of the University of Arizona’s Energy Frontier Research Center and a UA Professor of Optical Sciences and Chemistry, Solar One Stop website, by Sheryl Kornman, Pima County Communications Office.
- **August 23, 2011:** Pima County News article “Neal Armstrong: Inspiring future scientists in solar energy conversion”, Tucson Citizen.com website.
- **September 13, 2011:** National Science Board’s Annual Retreat and Site Visit at The University of Arizona included a “Tour of Energy Frontier Research Center (EFRC).”
- **December 11, 2011:** Arizona Daily Star article “Colors of the world may power your home” by Dominic McGrath.
- **December 12, 2011:** Dr. Ramamoorthy Ramesh, Department of Energy SunShot Director, visited the UA campus including a tour of Neal Armstrong’s and Jeanne Pemberton’s CISSEM EFRC laboratories.
- **February 3, 2012:** Nancy Sutley, Chair White House Council on Environmental Quality, visited the UA campus including a tour of Neal Armstrong’s CISSEM EFRC laboratories. Refer to the article “Built to Last: Energy and the Environment in the Southwest” on the [www.whitehouse.gov](http://www.whitehouse.gov) website.
- **April 19, 2012:** Georgia Tech College of Science article “Stable Electrodes for Improving Printed Electronics” by Jason Maderer.
- **April 20, 2012:** Engineerblogger article “Nanocoated stable electrodes for improving printed electronics: Method could pave way for lower cost, more flexible devices”.
- **April 25, 2012:** Forbes Magazine “New Technique Creates First Plastic Solar Cell” by Jennifer Hicks.
- **April 26, 2012:** Forbes Magazine article “Printing TVs as Thin as Paper, & 1st Completely Plastic Solar Cell” by Zachary Shahan.
- **April 2012:** UA brochure (Bold Ideas: Research at the University of Arizona) article “Creating the next generation of solar power” by Barbara Sparks.
- **July 2012:** Article “Nanometers and Nanoseconds, Together at Last” by Dr. Rajiv Giridharagopal, University of Washington, in the July 2012 U.S. DOE Frontiers in Energy Research Newsletter.

- **August 18, 2012:** Arizona Daily Star article “100 days of science: AZ scientists, utilities, gov’ts all major players in solar research” by Tom Beal.
- **September 24, 2012:** Stories of Discovery & Innovation article “Just One Word—Plastics” by Dawn M. Adin, U.S. DOE.
- **October 5, 2012:** “2012 Southern Arizona Solar Bus Tour” hosted by The University of Arizona, City of Tucson, Pima County, Pima Association of Governments, and the Sonoran Institute.
- **October 15, 2012:** Royal Society of Chemistry EES Blog article “Record breaking tandem polymer solar cells” by Heather Montgomery.
- **October 17, 2012:** Article “A Science Passport: Crossing Disciplines to Solve New Problems” by Timothy D. Courtney, University of Delaware, in the October 2012 U.S. DOE Frontiers in Energy Research Newsletter.
- **November 25, 2012:** Arizona Daily Star article “Painting the future of energy production” by Oliver Monti.
- **November 2012:** Article “Cutting Edge: Building a winning team” by Neal Armstrong in the Fall 2012 edition of the Catalyst, the UA Chemistry and Biochemistry Alumni Newsletter.
- **January 2013:** Article “Synergy Within and Beyond, Interview with Oliver Monti, Center for Interface Science: Solar Electric Materials” by Jaroslaw Syzdek, LBNL, in the January 2013 U.S. DOE Frontiers in Energy Research Newsletter.
- **March 25, 2013:** Georgia Tech News Room article “Trees Used to Create Recyclable, Efficient Solar Cell”.
- **May 17, 2013:** UANews article “UA Regents’ Professors Named in College of Science, Eller College of Management” by Daniel Stolte.
- **September 5, 2013:** Daily Wildcat article “Future of solar cells very bright at UA” by Zane Johnson.
- **November 21, 2013:** UANews article “Three UA Faculty Members Inducted as Regents’ Professors, Two as Distinguished Professors” by University Communications.
- **December 9, 2013:** UA@Work article “Why They Chose the UA: After 35 Years, Regents’ Professor Has ‘Never Been Bored’ at UA” by University Communications.

#### **Other Products – Instruments, Equipment and Facilities Brought Online**

The following developments in infrastructure (i.e., equipment costing in excess of \$50K, facilities brought online) have been successfully developed through CISSEM EFRC funding:

*Upgrade for the Kratos AXIS Ultra X-ray Photoelectron Spectrometer in the UA Laboratory for Electron Spectroscopy and Surface Analysis (LESSA) facility:* The upgrade to the UA’s Kratos AXIS Ultra X-ray Photoelectron Spectrometer involved the installation of a new state-of-the-art delay line detector system and electronics. The outcome was unprecedented energy resolution and sensitivity for the characterization of composition and frontier orbital energies of PV relevant materials. The Kratos instrument characterizes the surface and interface composition in the top 5-10 nm of a sample using XPS, and using UPS determines changes in surface potential as an interface is formed.

*XPS/UPS Fully Integrated Glovebox Sample Handling and Thin-film Deposition Capabilities in the UA Laboratory for Electron Spectroscopy and Surface Analysis (LESSA) facility:* The Kratos

AXIS Ultra XPS/UPS instrument in the UA LESSA facility was upgraded with a fully integrated glovebox sample handling and thin-film deposition capabilities (Fig. 11). This vacuum system and transfer mechanism allowed us to transport a substrate holder between deposition and analysis chambers without exposure to ambient, i.e.: (i)

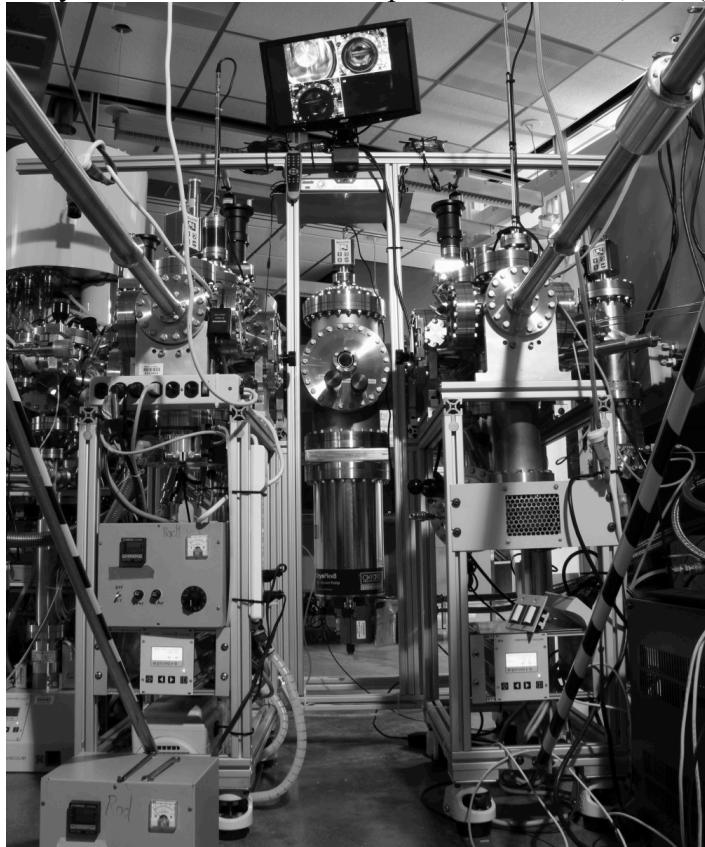


Fig. 11 – New thin-film deposition and glovebox sample handling capabilities established through CISSEM funding for the UA Kratos AXIS Ultra XPS/UPS instrument in the UA's LESSA facility.

molecule organic compounds, metal, and metal oxide deposition capabilities (electron-beam evaporation and PVD) connected through a double glovebox arrangement, and equipment to evaluate electronic properties of diode structures and OPVs including J/V characteristics.

*TAS System in the UA Saavedra laboratory:* A commercial flash photolysis instrument based on free-space optics and used to construct a planar waveguide-based TAS system. The commercial instrument included optical elements such as the monochromator, timing control with the shutters and oscilloscope, as well as the data analysis software. The TAS system was used for time-resolved spectroscopic characterization of organic films at interfaces, assemblies that could not be studied using conventional transmission-based measurements.

*PM-ATRS Instrument in the UA W.M. Keck Center for Surface and Interface Imaging:* We assembled a PM-ATRS custom instrument based on free space optical coupling of a planar waveguide platform with potential control. Components were procured from multiple vendors. The PM-ATRS instrument was used to study the charge-transfer kinetics and electrochromic response of organic molecules tethered to metal oxide surfaces.

*Expanded Capabilities for Thin-film Organic Diode Structures and OPVs in the UA Chemical Sciences Building Cleanroom Facility:* A new system for preparing thin-film organic diode structures and OPVs was assembled and installed in the cleanroom facility to expand UA's capabilities to create thin-film samples for CISSEM experiments.

The system included both small

*Solution and Thin-film Raman System in the UA Pemberton laboratory:* We assembled and installed this custom system from components procured from multiple vendors, including a laser, a monochromator, and a charge-coupled device. The Raman system was used by CISSEM to evaluate the orientation of organic films, such as self-assembled PA molecules, on metal oxide thin films.

*Time-resolved Spectroscopic Characterization in the GT Kippelen laboratory:* The Kippelen group at GT acquired a commercial low-repetition rate regenerative amplifier system coupled with a tunable femtosecond optical parametric amplifier capable of computer controlled operation from the visible to the IR range as a versatile tool for the characterization and optimization of organic/inorganic materials and interfaces.

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