



Staff	Affiliation
David Ginley (PI)	NREL
Dana Olson – Team Lead	NREL
Matthew Lloyd – Lifetime	NREL
Zbyslaw Owczarczyk – Synthesis	NREL
Joseph Berry – HTL/ETL	NREL
Ross Larsen – Computation	NREL
Garry Rumbles – Characterization	NREL
Nikos Kopidakis – Characterization	NREL
<b>Julia Hsu – Organic/inorganic interface</b>	<b>Sandia</b>
Andres Garcia (PD)	NREL
Scott Hammond (PD)	NREL
Wade Braunecker (PD)	NREL
<b>3 Graduate Students</b>	<b>CSM, CU and DU</b>

## Organic Photovoltaics

PV

**Presented by Matthew T. Lloyd**

National Renewable Energy Laboratory

matthew.lloyd@nrel.gov

May 25, 2010

This presentation does not contain any proprietary, confidential, or otherwise restricted information

## Timeline

- Project start date – FY2008
- Project end date – Ongoing
- Percent complete – Ongoing

## Budget

- Total project funding FY10  
DOE share – \$1,895K + (\$230K SNL)  
Contractor share – \$500K
- Funding received in FY09:  
\$1,751K

## Barriers

- Barriers addressed
  - Materials Utilization and Cost
  - Design & Packaging
  - Efficiency

## Partnerships Current

Partner	Project
Plextronics	Develop new geometries for enhanced lifetime
Konarka Technologies	Materials characterization, packaging, new materials
Luna Innovations	Device development for new contact materials
TDA Research	Device development for new acceptor materials
Solarmer	Lifetime of high performance OPV active layer materials
Sandia National Laboratories	Characterization of organic/inorganic interfaces
Colorado School of Mines	Students and collaborations on nanostructured materials for PV
University of Colorado	Student collaboration on new contact materials
University of Denver	Device modeling and TCO characterization

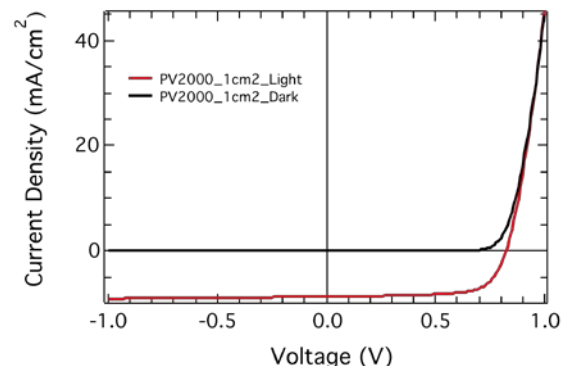
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- OPV potentially offers an approach to power production at LCOE
  - Challenges to achieving this:
    - Demonstration of a pathway to get efficiencies of >10%
    - Demonstration of a pathway to get lifetimes >10,000 hours
    - Demonstration of scalable results by very low cost manufacturing approaches
- State the importance of solving the problem in terms of its relationship to the Program's mission.
  - Increasingly OPV represents a viable near term next generation technology for direct power production. A collaborative community world wide is developing to address the technical challenges. NREL is playing a key integrating role.

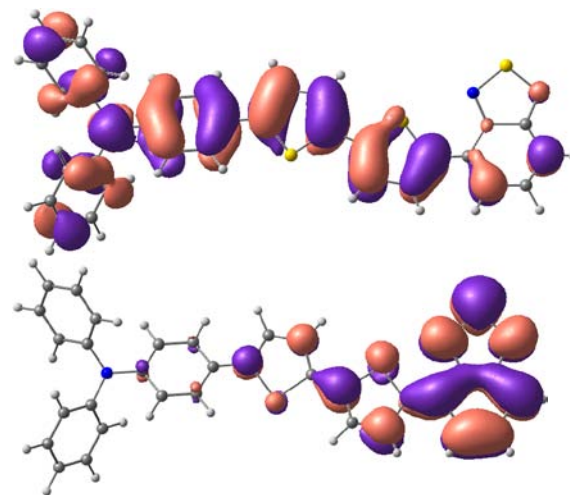
*Task#	Tasks
1	Molecular Structure, Interface and OPV Device Modeling (b,c)
2	New Absorber and Acceptor Materials Synthesis (a)
3	HTL,ETL, TCO/ Nanostructured TCOs and Contact Development (SNL +\$250k) (d)
4	Device and Packaging Reliability and Lifetime (g)
5	Scale-up Process Development (e)
6	Materials Characterization Specific to OPV Materials and Devices (f)

Milestones <sup>1</sup>	Level <sup>1</sup>	CPS <sup>1</sup>	CR <sup>2</sup>	EN <sup>2</sup>	Tasks <sup>3</sup>	Date <sup>4</sup>	CE/SC <sup>5</sup>
Development of a 5% efficient OPV device with 1 cm <sup>2</sup> area and <10% loss over 2,000 hours	<u>3</u>				<u>1-6</u>	<u>8/2009</u>	
Synthesis of a new donor molecule with a bandgap of 1.4 eV.	<u>4</u>				<u>1, 2</u>	<u>5/2009</u>	
Develop improved organic HTL that is not PEDOT:PSS-based.	<u>4</u>				<u>3, 6</u>	<u>3/2009</u>	
Demonstration of printing/processing of device with ~25 cm <sup>2</sup> area and >4% efficiency.	<u>4</u>				<u>1, 3, 5, 6</u>	<u>7/2009</u>	
Development of predictive device model to guide development.	<u>4</u>				<u>1</u>	<u>7/2008</u>	

- Modeling
  - The project has develop an increasing set of predictive tools for new polymers
  - Experiemnts confirmed the ability to predict HOMO/LUMO
- Devices
  - Demonstrated PCE of 5% for 1 cm<sup>2</sup> devices
  - Performed initial lifetime characterization for NREL as well as devices and materials from collaborative partners
  - Demonstrated >1500 hr stability with inverted devices
  - Identified primary degradation mechanism for dark storage

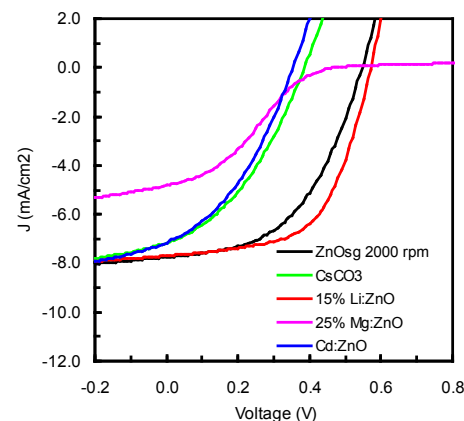


5% 1 cm<sup>2</sup> cell produced at NREL using Plextronics materials



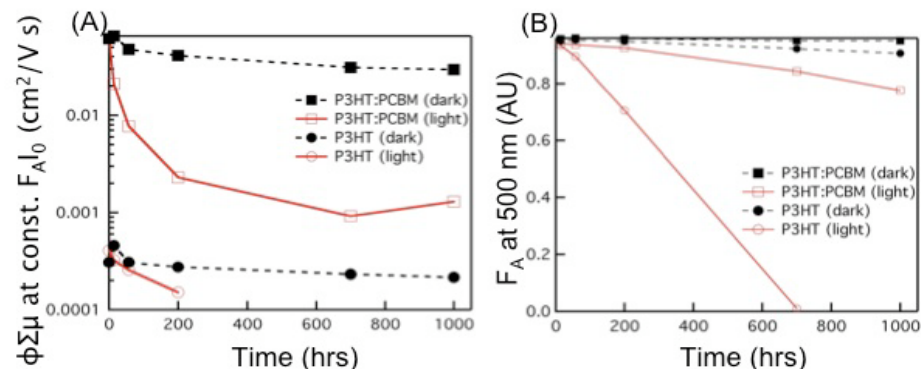
DFT-calculated HOMO (top) and LUMO (bottom) orbitals of 1-arm molecule. The remaining arms (not pictured) show degenerate states of equivalent energy and electron density.

- Contacts
  - We investigated the effects of doping ZnO in inverted devices
  - We developed initial lifetime data on the mechanisms of degradation in active layer films



Current density – voltage curves for inverted OPV devices with different dopants incorporated into the ZnO electron transport layer.

- Packaging and processing
  - Developed initial low-cost, solution-based packaging approaches
  - Developed PDIL tool for OPV and performed slot coating experiments at Konarka



(A) The product of the yield for free carrier generation times the mobility of free carriers versus degradation time in air, for a P3HT:PCBM blend under illumination (red squares) and a control sample that was kept in the dark (black squares). (B) Absorbance of the films from A at 500 nm.

- Organic photovoltaics (OPV) is an emerging PV technology that has the potential to significantly alter the LCOE paradigm for solar energy production. **Its great strength lies in the diversity of organic materials that can be designed and synthesized for the absorber, acceptor, interfaces and even packaging.** There exists a need to understand the charge separation processes, the device physics, and the interfacial effects so as to develop optimized, stable devices based on materials with improved spectral response and transport properties.
- As per the previous slide the major challenges in OPV are increasing conversion efficiency, lifetime and device area our proposed tasks specifically address these areas:

## **Task number/Description**

- OPV-1: Device, Interface, and Molecular Structure Modeling
- OPV-2: Absorber and Acceptor Materials Development
- OPV-3: HTL, ETL, Nanostructured Inorganic Acceptors and Contacts  
(In cooperation with Sandia who are separately funded for this effort through the AOP)
- OPV-4: Lifetime and Device Packaging
- OPV-5: Scale up and Large Area Processing
- OPV-6: OPV Specific Characterization Techniques and Measurements

- Our approach is focused on utilizing the key skills and infrastructure at NREL
  1. We use computational tools to develop predictive models for both materials development and device performance.
  2. We then leverage the NREL synthesis team to develop new organic materials for donors and acceptors and inorganic materials for contacts. **The synergy between task 1 and 2 is critical.**
  3. We have developed one of the leading capabilities world wide for analyzing the lifetime and the mechanisms of degradation in OPV devices which feeds back into tasks 1 and 2.
  4. We have developed a suite of OPV characterization tools specifically suited to analyzing these excitonic devices. This allows us to far better understand the specifics of the complex BHJ and interfaces.
  5. We collaborate extensively with academia and industry bilaterally and in teams to both provide and receive new materials and to evaluate them independently and their application in devices.

Milestones 2010	Progress to Date 2010	FY 2011 Goals
1. Development of 5.5% efficient OPV device.	Accomplished new 7% device developed	2011 Goal 8% 1 cm <sup>2</sup> cell
2. Develop models for materials design and device operation.	Device Model under development and computational tool for new materials prediction in use	Couple predicted materials properties from computation with experimental values. Improve methods for calculations
3. Synthesis and utilization of lower band gap absorbers with reduced donor – acceptor band offset.	New polymers and dendrimers synthesized with new polymer route looking attractive	Demonstration of new polymer with enhanced red response (>700nm) with efficiency of 4 %
4. Develop ETL contact material with enhanced doping control for high efficiency inverted OPV devices.	New low temperature ZnO precursor developed with higher efficiency and lifetime. NiO superior to PEDOT:PSS for high Voc polymers ( PCDTBT) with increased lifetime	Demonstrate ETL/HTL deposited on the active layer for improved device efficiency and lifetime of inverted or standard device architectures
5. Initial correlation of lifetime and cell design/encapsulation with combinatorial lifetime testing	Combinatorial system (Air) fully operational and new key results obtained for normal and inverted devices identifying key degradation mechanisms	Demonstration of T <sub>80</sub> Lifetime >10,000 hours for a cell with efficiency greater than 5 percent
6. Determine the intrinsic degradation mechanisms important for resulting device lifetime.	Identification of oxidation of electrode and contact materials as well as photo-oxidation of polymer and fullerene. Electrode acts as first barrier to device degradation.	Evaluate degradation mechanisms in operating devices as compared to unencapsulated films. Are these different when device is operating? Also effect of UV illumination.
7. Demonstrate scalability of devices larger than 10 cm <sup>2</sup> through techniques such as slot die coating.	Slot die coater obtained and PDIL tool completely functional.	Initial data on uniformity issues for 100 cm <sup>2</sup> area cells

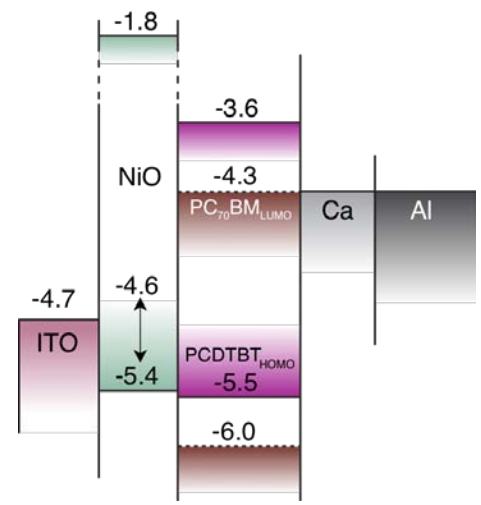
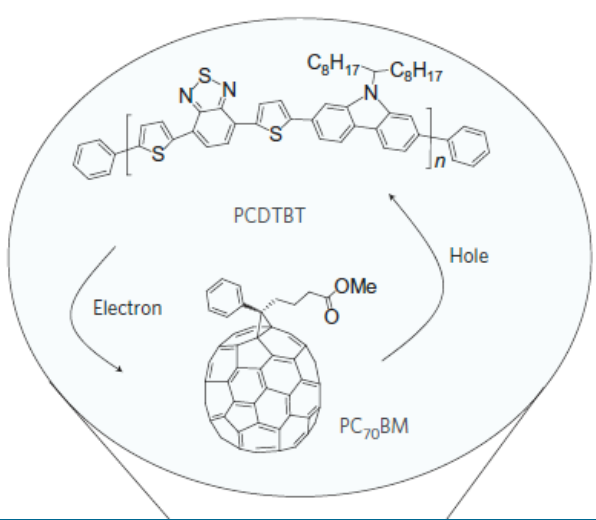
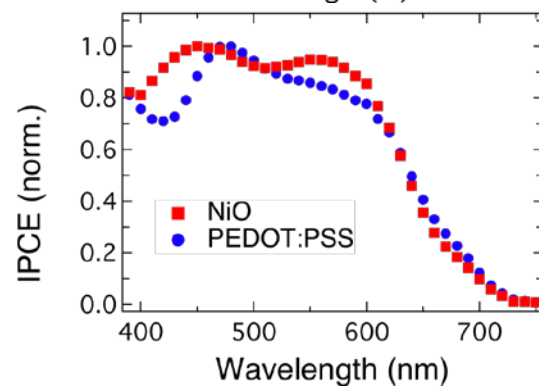
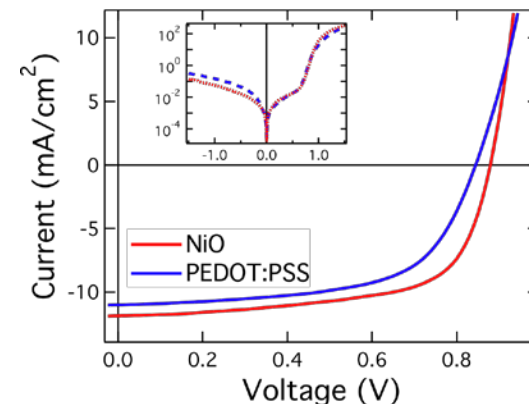
# Agreement Level Milestones FY10

Milestones	Tasks	Date	Progress to Date	Status
1. Development of 5.5% efficient OPV device.	1-6	6/10	Demonstrated new 6.7-7% device (1 cm <sup>2</sup> ).	Exceeded
2. Develop models for materials design and device operation.	1, 2, 3, 4	9/10	Device model under development and computational tool for new materials prediction in use.	On Schedule
3. Synthesis and utilization of lower band gap absorbers with reduced donor – acceptor band offset.	1, 2	7/10	New polymers and soluble small molecules synthesized. Demonstrated attractive properties for polymer route.	On Schedule
4. Develop ETL contact material with enhanced doping control for high efficiency inverted OPV devices.	3, 4	9/10	Low temperature solution deposited ZnO developed for inverted device. NiO shown superior (in efficiency) to PEDOT:PSS for some polymers (PCDTBT) with increased lifetime.	Achieved/On Schedule
5. Initial correlation of lifetime and cell design/encapsulation with combinatorial lifetime testing	1, 2, 3, 4	12/09	Combinatorial system (air) fully operational and new key results obtained for normal and inverted devices identifying primary degradation mechanisms.	Achieved
6. Determine the intrinsic degradation mechanisms important for resulting device lifetime.	1, 2, 3, 4	6/10	Key mechanisms identified (contact evolution, PCBM oxidation) and mitigation approaches demonstrated.	Achieved
7. Demonstrate scalability of devices larger than 10 cm <sup>2</sup> through techniques such as slot die coating.	2, 3, 5	8/10	Slot die coater obtained and PDIL tool completely functional.	On Schedule

# Highlights of the OPV Agreement

# Task 2,3,5 - 6.7% Efficiency with Solution Processed NiO Hole Transport Layer

- Solution processed NiO makes Ohmic contact to deep HOMO level of PCDTBT
- **6.7%** average PCE for 0.11 cm<sup>2</sup> devices
- **7.0%** PCE observed for larger area **1.0 cm<sup>2</sup>** devices (to be submitted for certification)
  - Solution NiO in press: X. K. Steirer et al., *Organic Electronics*
  - NiO/PCDTBT manuscript in preparation: X. K. Steirer et al., *Nature Materials*

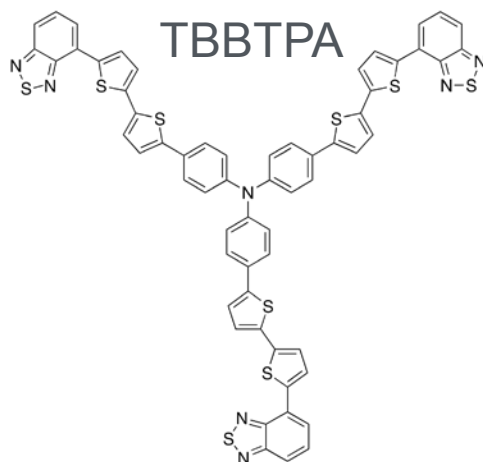


HTL	V <sub>oc</sub> (mV)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	Fill Factor (%)	PCE (%)
sNiO	879	-11.5	65	<b>6.7</b>
PEDOT:PSS	845	-11.1	60	5.7

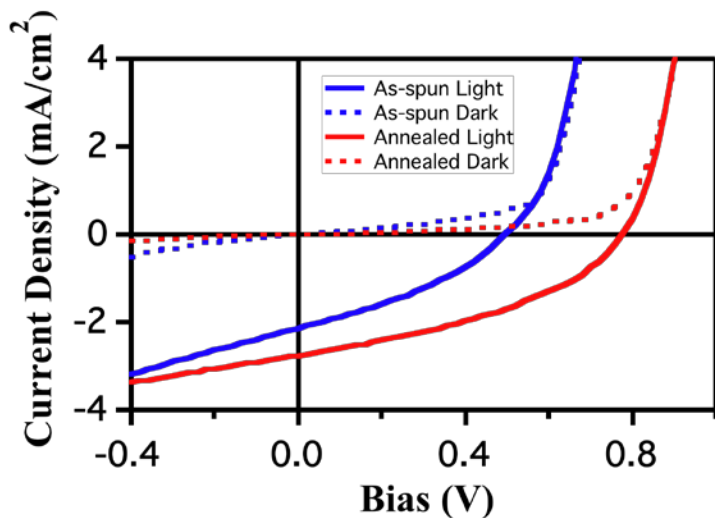
\*Avg. performance parameters



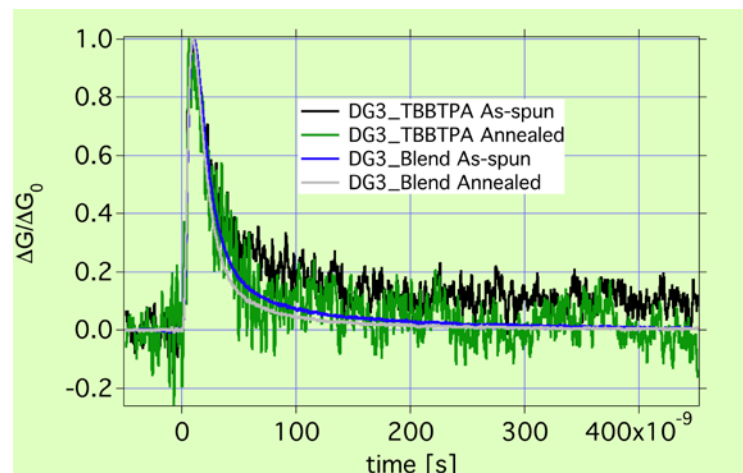
# Task 2,6 - TBBTPA:PCBM Performance Morphology-Limited but excellent Voc



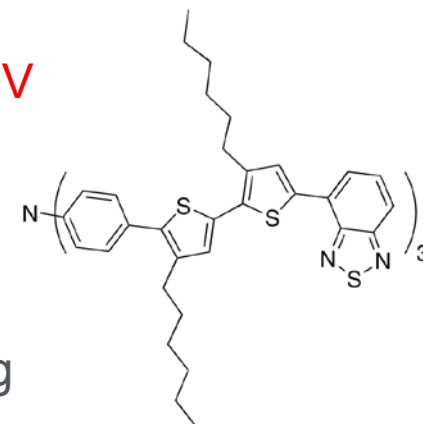
Tris(4-(5-(Benzo[c][1,2,5]thiadiazol-4-yl)-2,2'-BiThiophen-5-yl)Phenyl)Amine  
 Chemical Formula:  $C_{60}H_{33}N_7S_9$   
 Exact Mass: 1139.03  
 Molecular Weight: 1140.54  
 Elemental Analysis: C, 63.18; H, 2.92; N, 8.60; S, 25.30



## Fast free-carrier decay (TRMC)

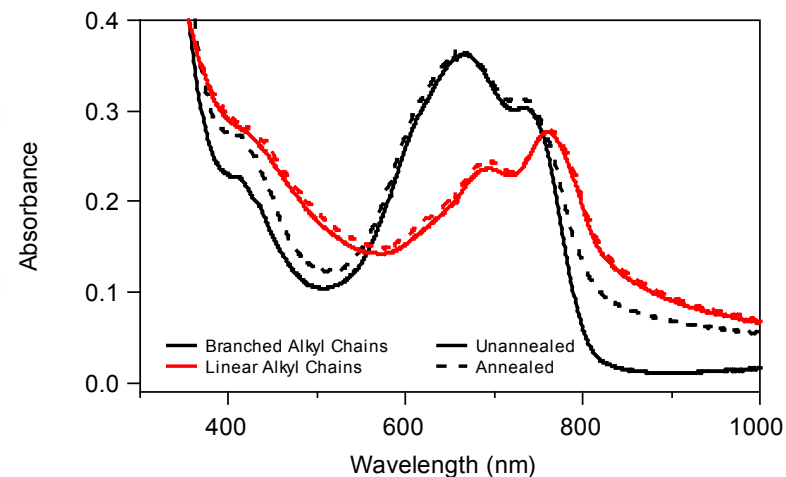
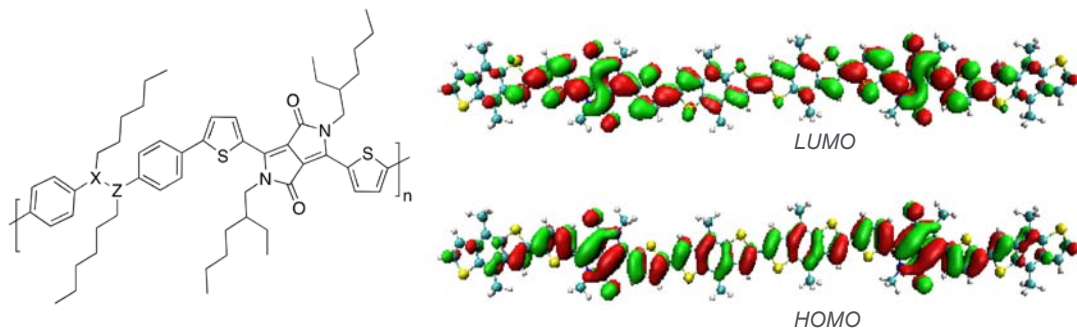


Device performance:  
 Excellent  $V_{oc} = 780 \text{ mV}$   
 Poor  $J_{sc} = 2.8 \text{ mA}$   
 Poor  $FF = 40\%$   
 PCE = 0.86%

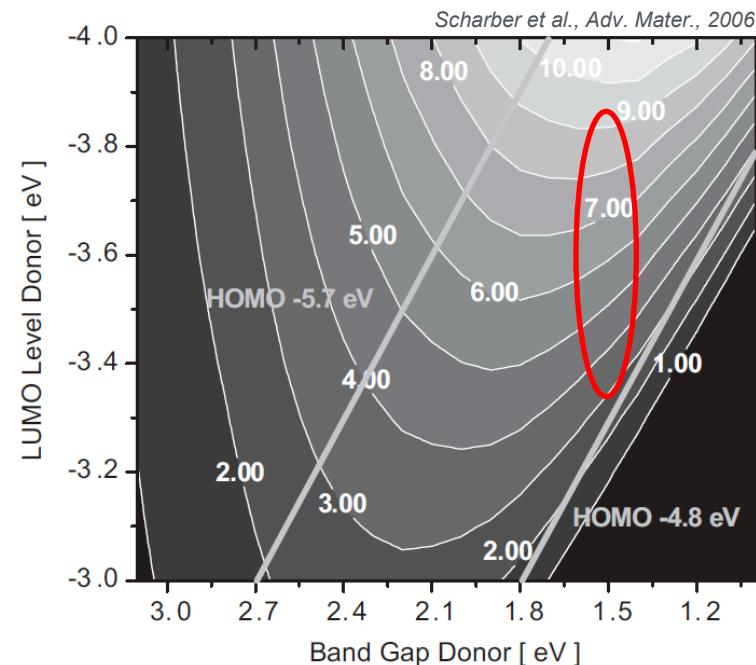


Currently synthesizing alkyl derivative to improve solubility and phase separation

# Task 1,2,5 – NREL Developed Novel Low Bandgap Polymer Absorbers

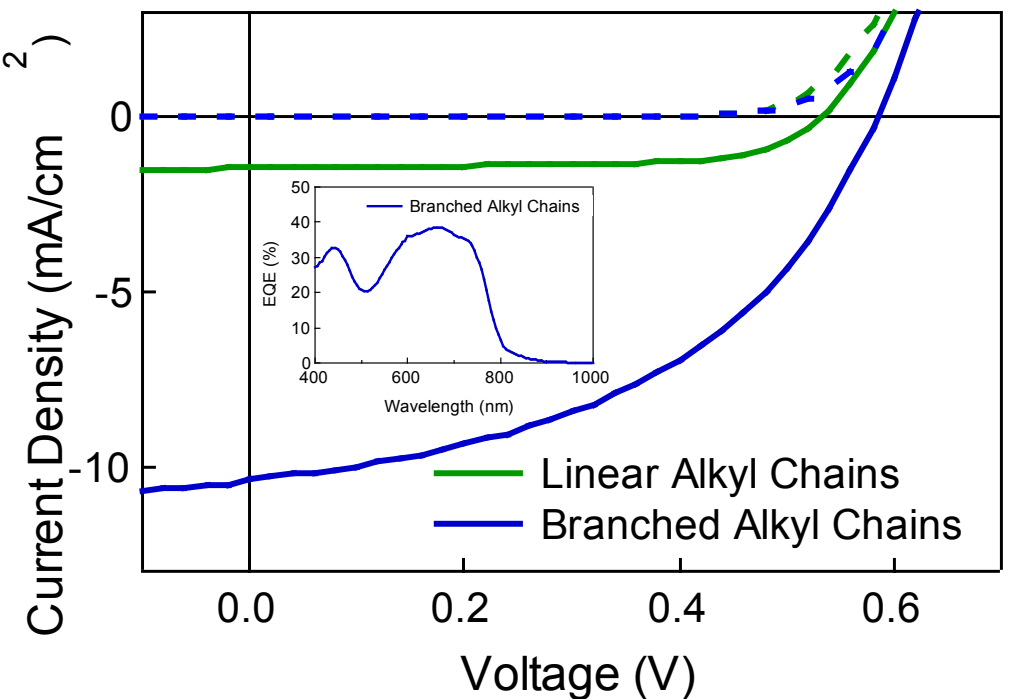
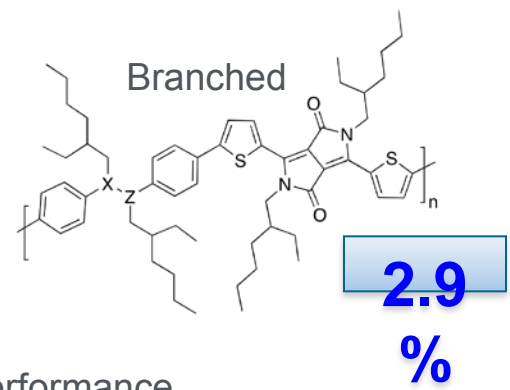
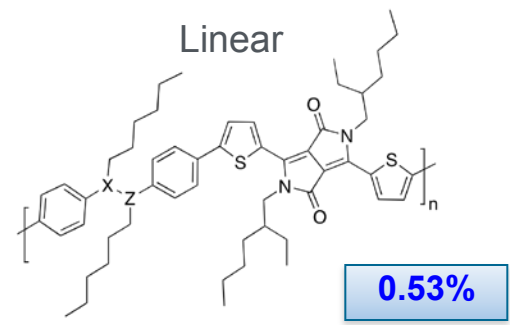


- **Computation** → **Synthesis - A Teamed Approach**
- **First results, 2 iterations of low gap polymer:**
  - Very high extinction coefficient maximizes absorption
  - Low band gap ( $\sim 1.5$  eV) allows for enhanced overlap with the solar spectrum
  - **High yield** synthesis, scale-up feasibility
  - Strong  $\pi$ - $\pi$  interactions between the aromatic units is positive for achieving high charge mobility
  - High alkyl chain density along polymer chain reduces intercalation of PCBM enhancing phase separation and transport
  - Branched alkyl chains dramatically improve polymer solubility



# Task 1,2,5 - PV Performance of First and Second Generation Indole Based Low Bandgap Absorbers

- Linear alkyl chains optimized to 1:2 donor:PCBM
- Branched alkyl chains optimized to 1:1 donor:PCBM
- Higher solubility of branched sides chains significantly increases power conversion efficiency
- Low fill factor, reverse bias leakage point to unoptimized D/A morphology and potential for higher performance
- Evaluating and enhancing molecular weight for improved charge mobility and fill factor



Initial device performance

Donor Polymer	V <sub>oc</sub> (mV)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	Fill Factor	Efficiency
Linear Alkyl Chains	532	1.4	66%	0.53%
Branched Alkyl Chains	585	10.3	46%	2.9%

\*Avg. performance parameters

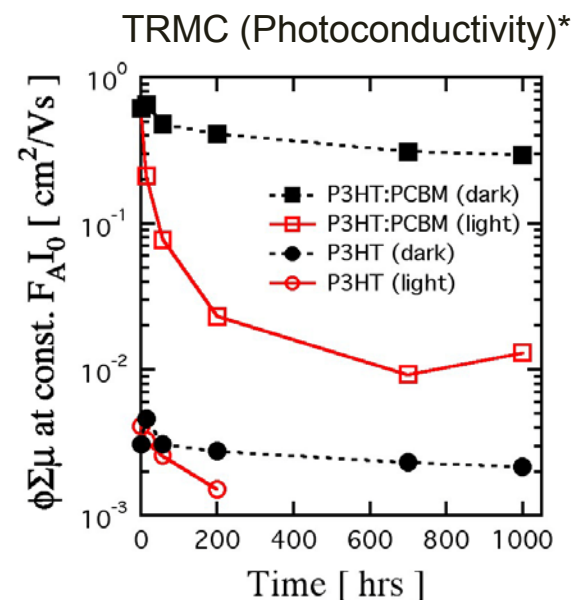
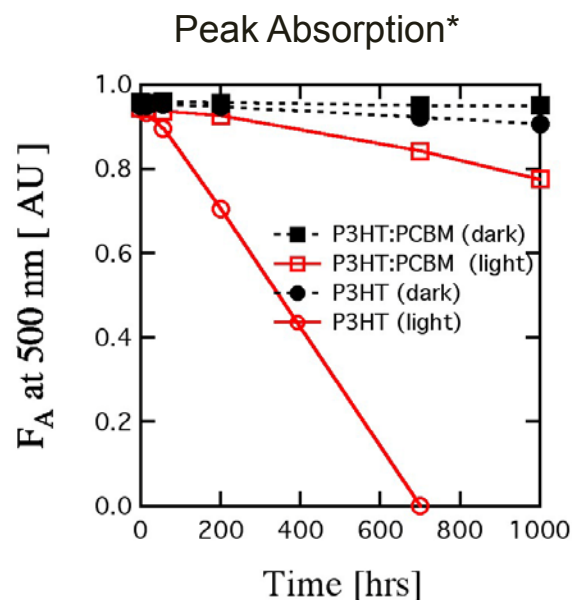
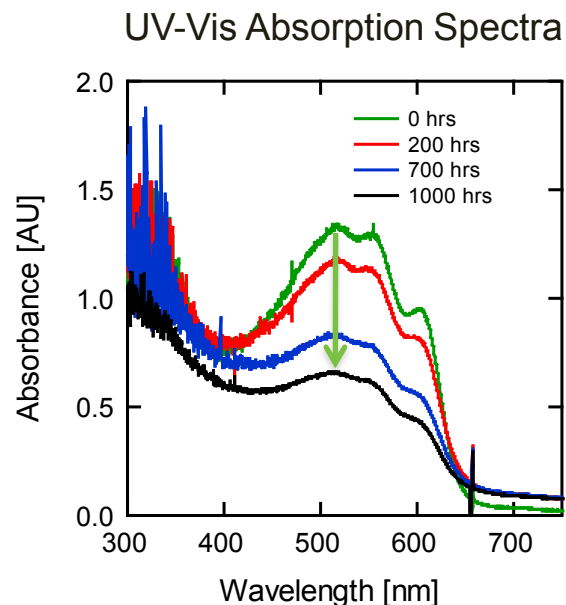


- International Summit on OPV Stability, October 2010
- NREL is a Co-organizer
- Joint US DOE/EU road mapping and establishing standards in lifetime testing
- Round-Robin efficiency calibration program



# Task 4,6 – Lifetime - Characterization by TRMC

## P3HT:PCBM Films After Extended Light Exposure

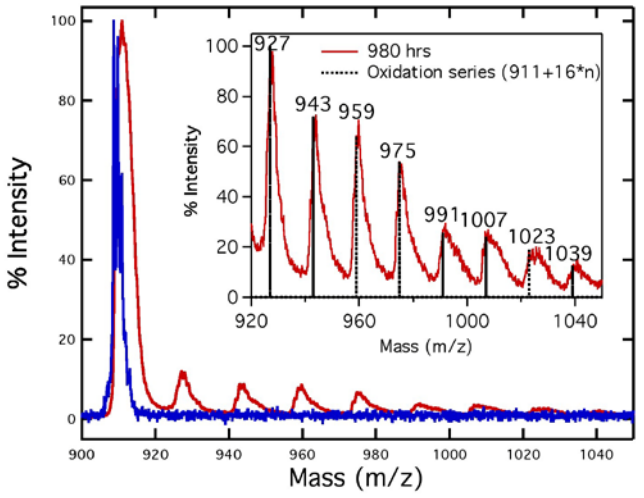


\*Initial results on UV-Vis and TRMC obtained in FY09

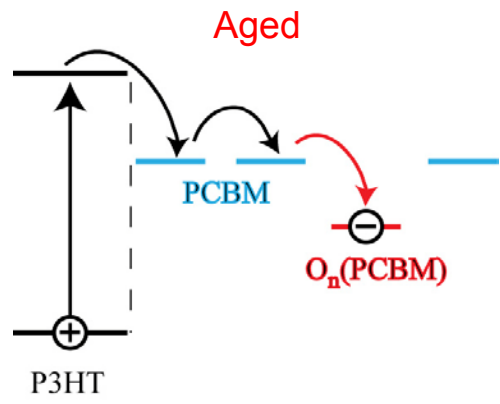
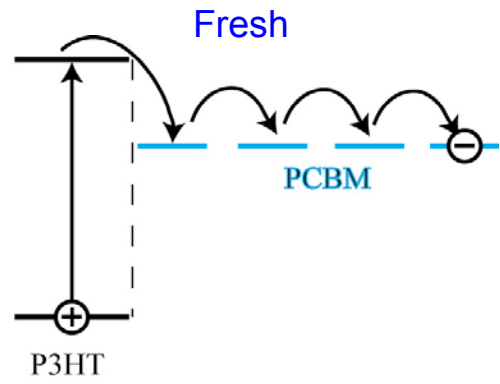
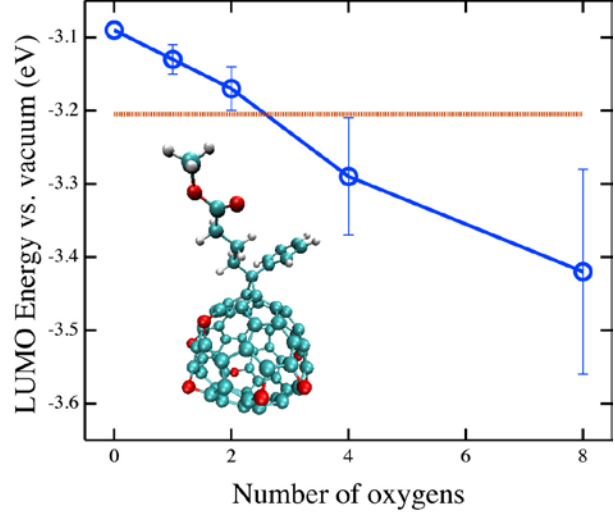
- [PCBM found to assist in stabilizing P3HT](#) against photobleaching, however, chromophore loss still linear under constant illumination (unencapsulated)
- TRMC (photoconductivity) signal: product of photoinduced free charge generation and carrier mobility, signal dominated by mobility of electrons in PCBM phase of bulk heterojunction
- Rate of decay in TRMC  $\gg$  photobleaching of the polymer
- **Degradation in photoconductivity not caused by photobleaching in P3HT!**

# Task 1,4,6 – Lifetime - MALDI and DFT Analysis of Photo-oxidized P3HT:PCBM Films

MALDI



DFT calculated PCBM LUMO level



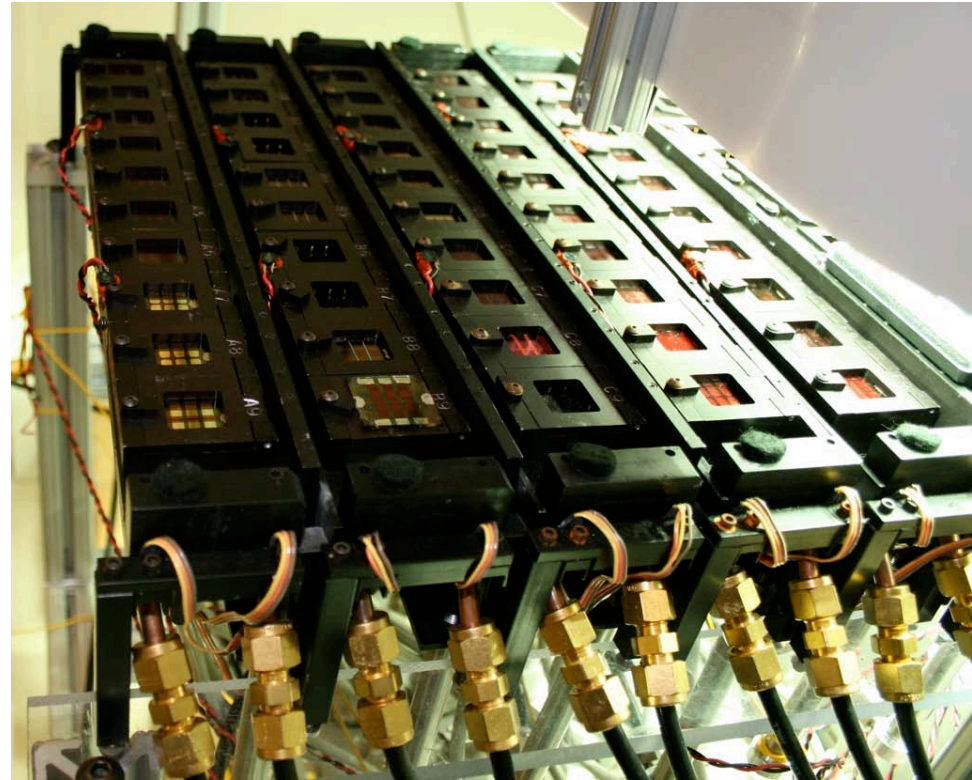
Blue - Fresh P3HT:PCBM blend, 911 peak--pristine PCBM  
 Red - Aged P3HT:PCBM blend, 8 oxidation peaks for aged PCBM

- MALDI identifies pristine PCBM in fresh blends, clearly shows up to 8 oxygen atoms on fullerene cage after 980 hrs under illumination
- DFT calculations show deepening of LUMO level for PCBM with increasing number of oxygens
- Carriers in oxidized PCBM trap states deeper than ~100 meV will not contribute to photoconductivity signal

Submitted, M. O. Reese et al., *Advanced Functional Materials*

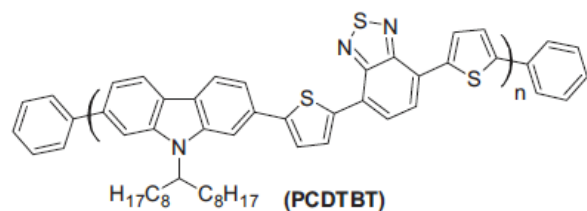
## Unique NREL PV Characterization Capability

- Concurrent measurement of 360 diodes
- Automated capture of JV
- 60 retractable (automated) spectral filters
- Substrate temperature control 0-85 °C
- LG Sulfur plasma lamp, color temp 5300K (see also Solaronix)
- Negligible UV or IR in lamp spectrum
- Approx. 0.7 sun intensity using unfiltered plasma lamp (alternatives under investigation)
- Stable temporal illumination with lamp life of 3-8 years
- Devices aged with 500  $\Omega$  load



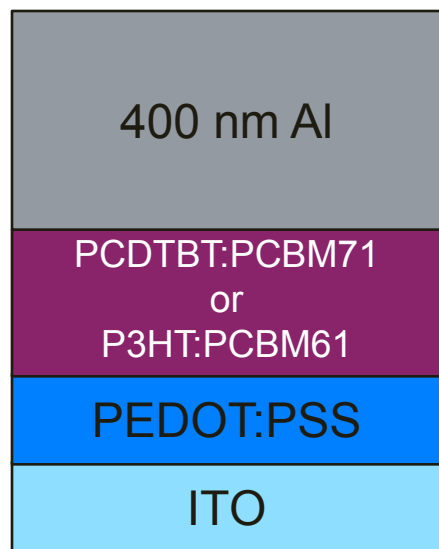
- **Parts received for “Combi II” for controlled atmosphere capability**

# Task 2,3,4 - Enhanced Lifetime in Conventional Devices with PCDTBT:PC<sub>70</sub>BM vs. P3HT:PC<sub>60</sub>BM

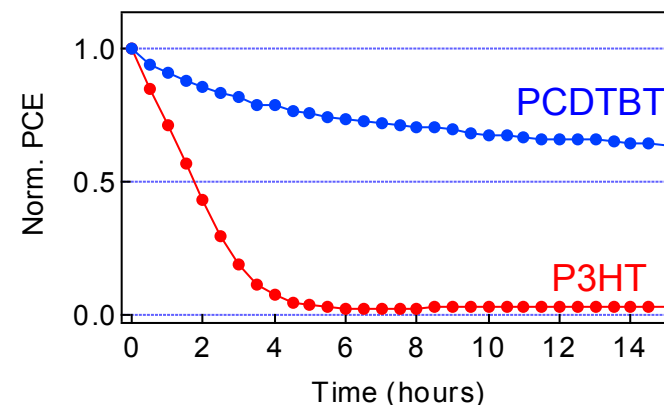
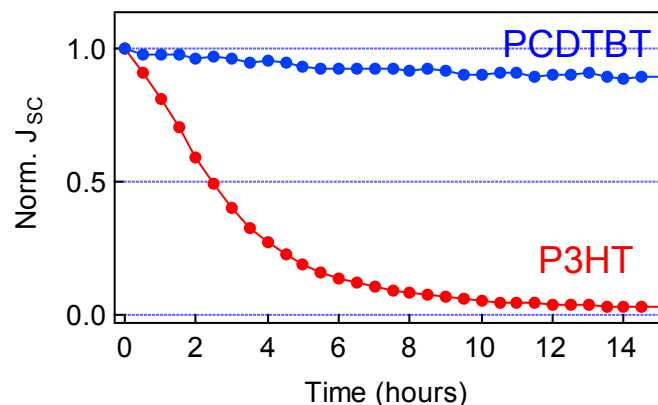


Initial device performance (note Al electrode reduces PCE)

Sample	V <sub>oc</sub> (mV)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF (%)	PCE (%)
P3HT:PCBM61 /400 nm Al	460	9.2	32	1.3
PCDTBT:PCBM71 /400 nm Al	740	10.0	46	3.4

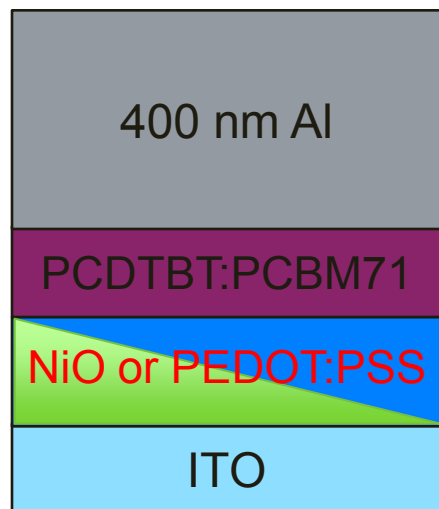
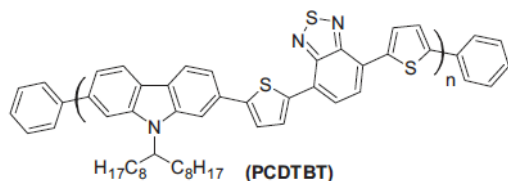


Conventional Device

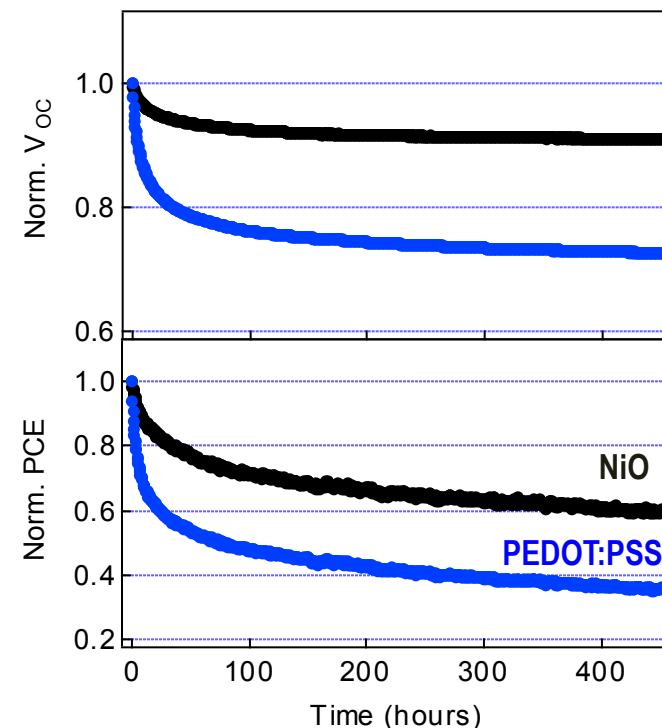
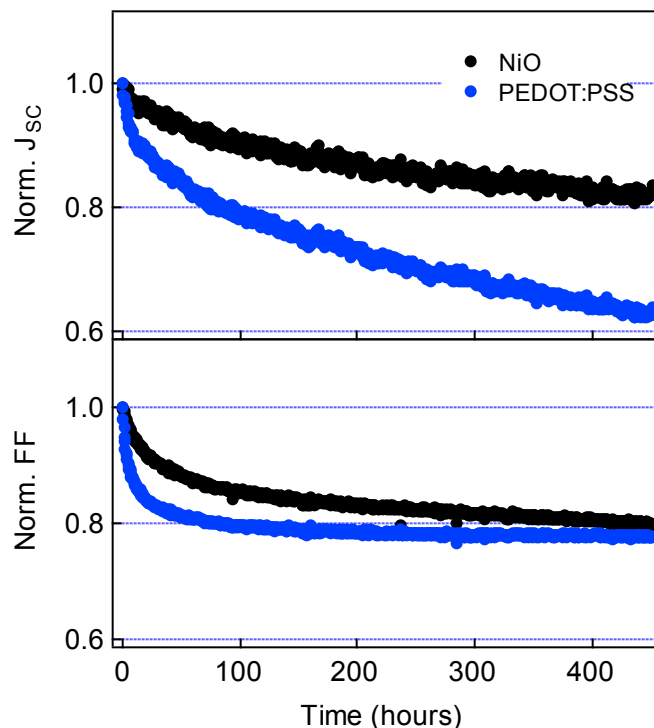


- PCDTBT shows dramatically enhanced stability over P3HT
- Tentatively explained by deep donor level of PCDTBT
- Large internal E-field maintained despite changes to the Al work function
- **Lifetime determined by complex interaction between active layer and contacts**

# Task 2,3,4 - Enhanced Lifetime in Conventional Devices with NiO HTL relative to PEDOT:PSS

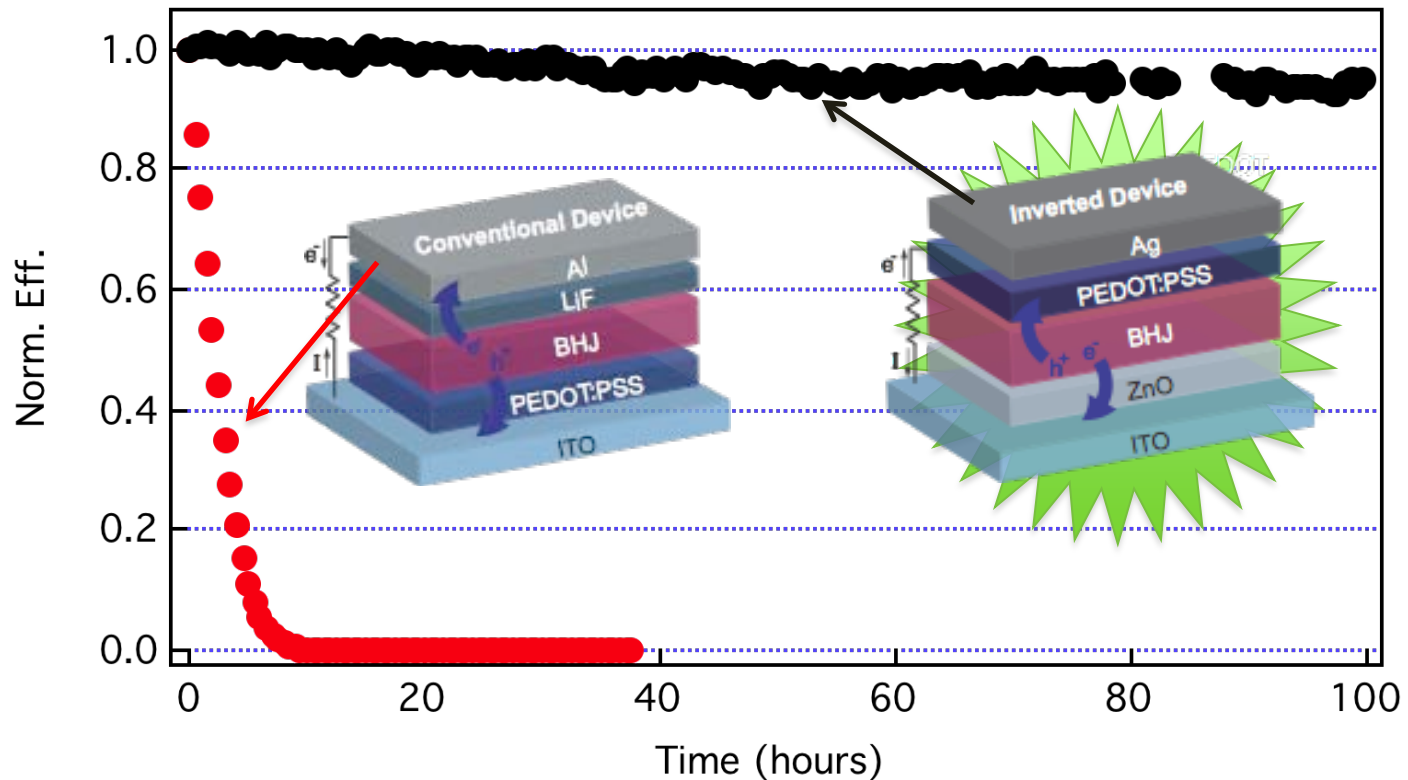


Conventional Device



- Comparable initial performance
- Solution NiO HTL shows enhanced stability compared to PEDOT:PSS
- NiO makes Ohmic contact with PCDTBT HOMO (5.4 eV)
- PEDOT:PSS documented to etch ITO, leaching In into active layer reducing lifetime
- **Lifetime also determined by complex interaction between active layer and HTL/ETL**

# Task 3,4 – Inverted Device Architecture Enables Air-Stable Contacts

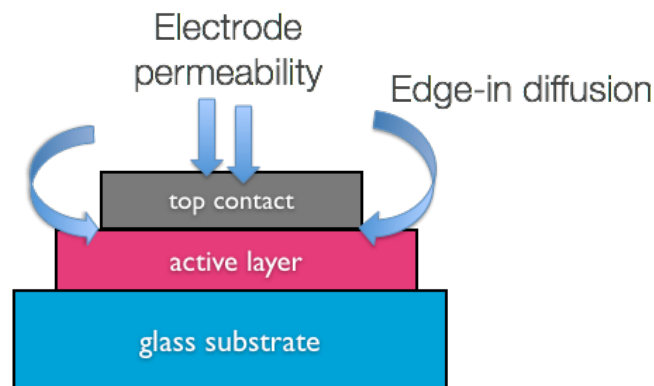


- Inverted architecture demonstrates unexpected stability in unencapsulated devices
- Points to relative stability of active layers and deterioration at contact layers only

• M. T. Lloyd et al. *Journal of Applied Physics*, manuscript in preparation

# Task 3,4 – Impact of Electrode Preparation on Lifetime

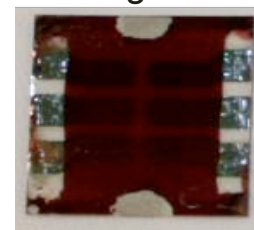
- Water vapor and/or oxygen necessary for photobleaching
- Top contacts inhibit photobleaching of active layer
- Small Ag-edge:ITO-edge ratio leads to rapid decay in photocurrent
- **Edge-in degradation clearly impacts unencapsulated device lifetime**



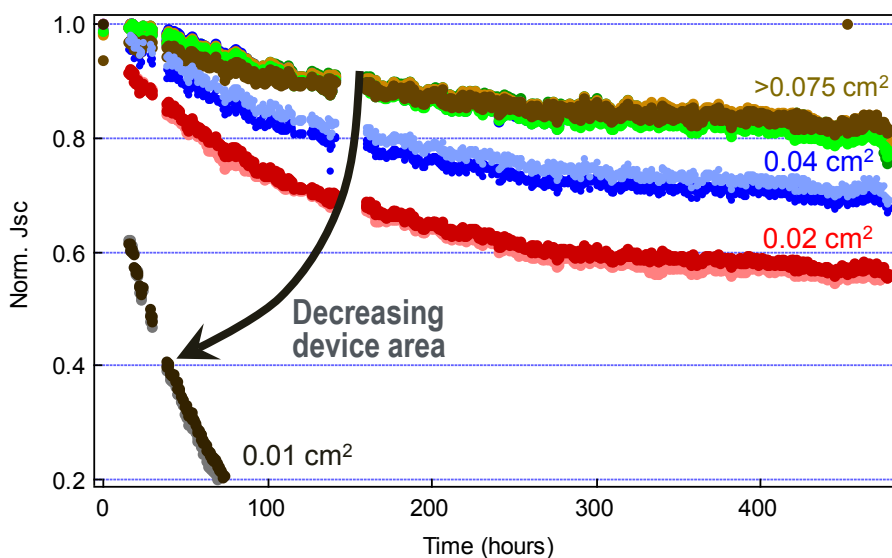
Unbleached active layer under electrodes



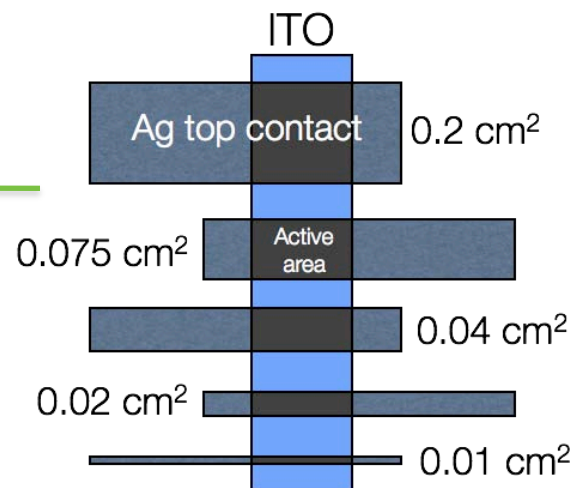
Aged



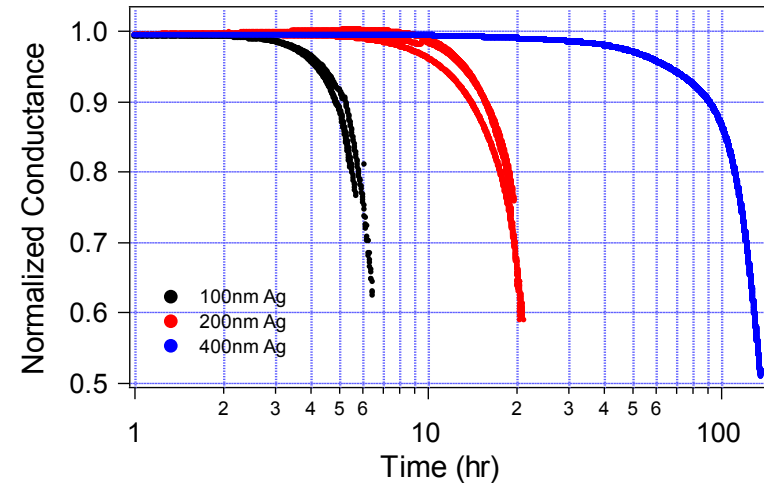
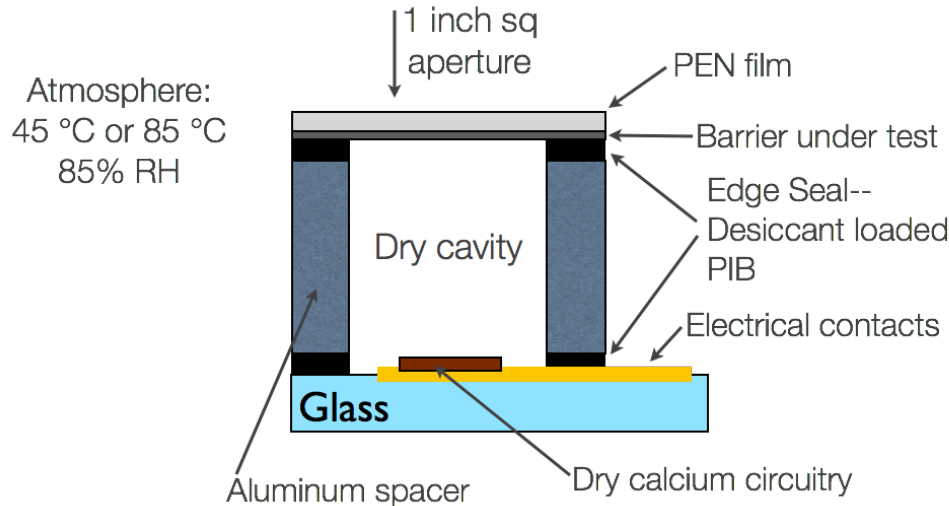
Fresh



Schematic of device geometry (top view)



# Task 3,4 – Assessment of Barrier Properties of the Top Contact

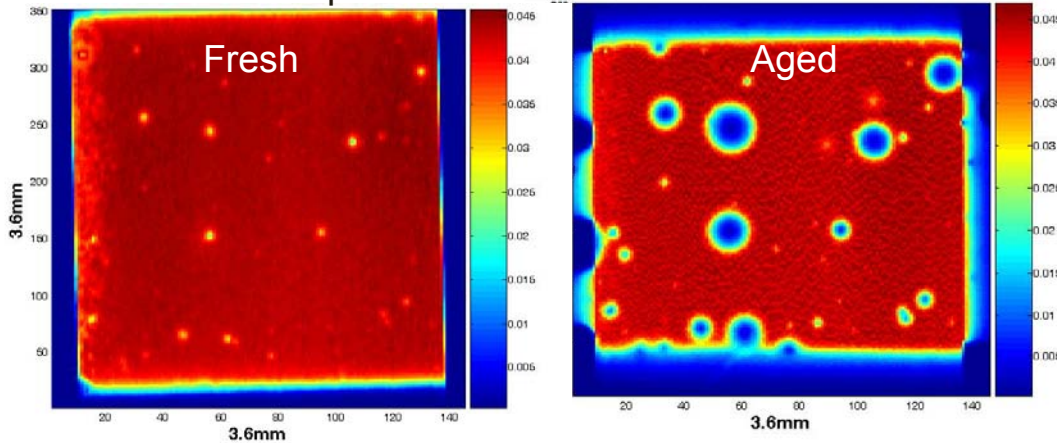


- Electrical calcium test used to determine water vapor transmission rate (WVTR) for typical device electrodes
- 1 sq. inch aperture overestimates ingress
- **Trend in lag time and WVTR for increasing electrode thickness**
- **Largely overlooked in all OPV and OLED research**
- **Electrode preparation is critical rate limiting factor in OPV lifetime**

Barrier	Lag time (hours)	WVTR (g/m <sup>2</sup> /day)
100 nm Ag	4.4	$5.2 \times 10^{-2}$
200 nm Ag	15.1	$1.9 \times 10^{-2}$
400 nm Ag	96.6	$3.6 \times 10^{-3}$

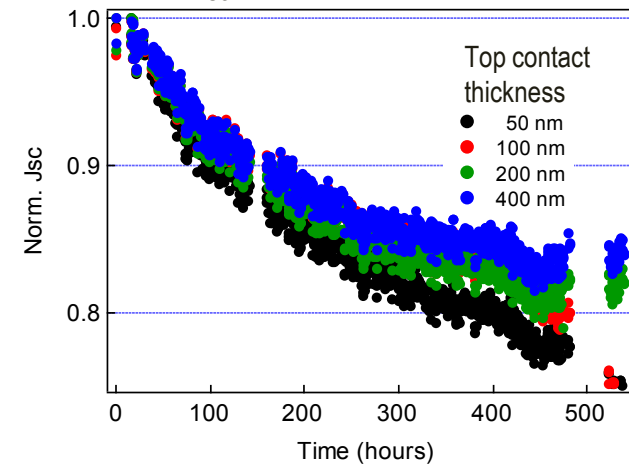
# Task 3,4 – Inverted Device Electrodes Determine Lifetime

### Photocurrent Map

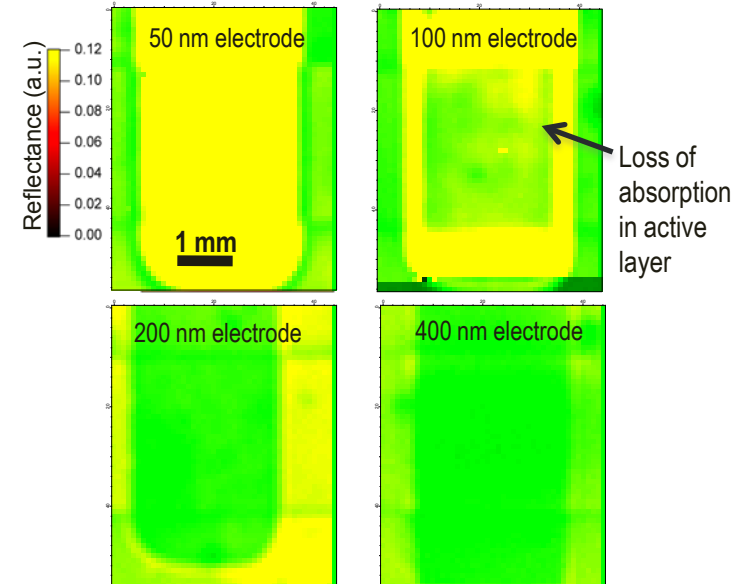


- Photocurrent maps indicate “dark spot” formation (well known in OLEDs) due to pinhole defects
- Absorption/reflectance maps indicate uniform photobleaching (TRMC decay rate  $\gg$  photobleaching, see slide 17)
- Loss in  $J_{SC}$  inversely proportional to electrode thickness
- Photobleaching of active area present for thin contacts
- Rate of ingress compounded by smaller grain size for thin films (verified by AFM, not shown)
- **Unencapsulated device lifetime critically depends on thick, pinhole-free electrodes**
- **Multilayer composite electrodes lead to stabilized efficiencies**

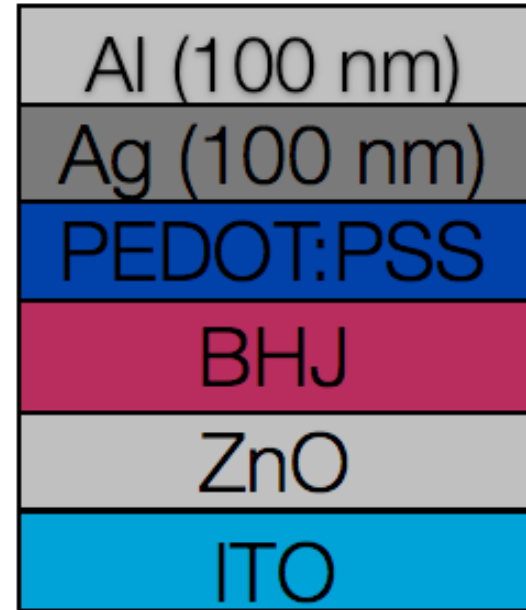
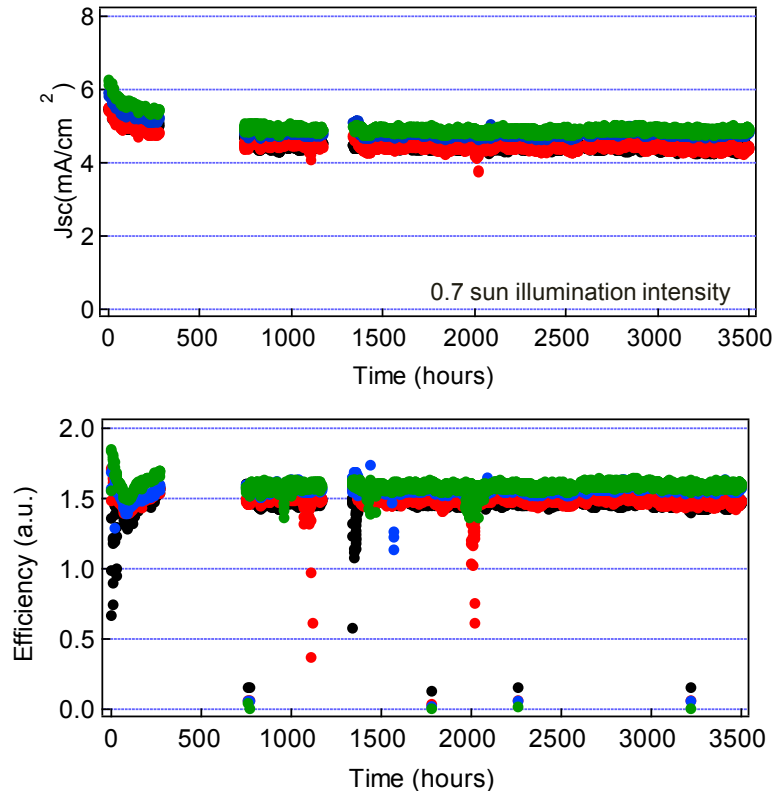
### Device $J_{SC}$ under constant illumination



### 567 nm Reflectance Map for aged devices

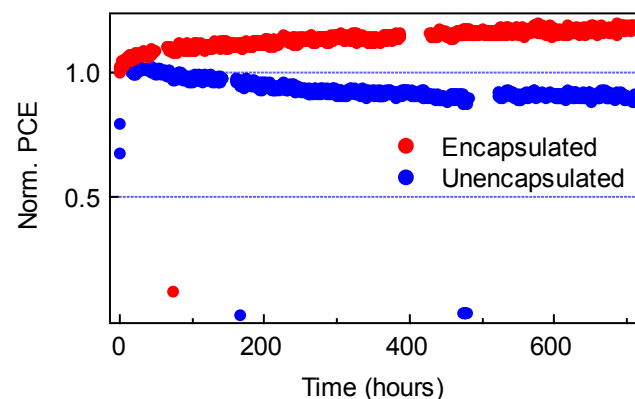
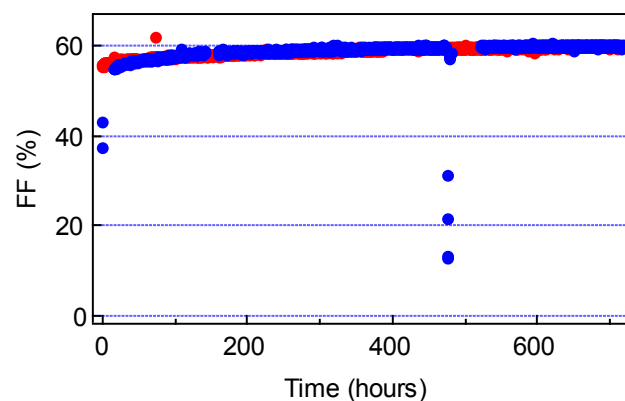
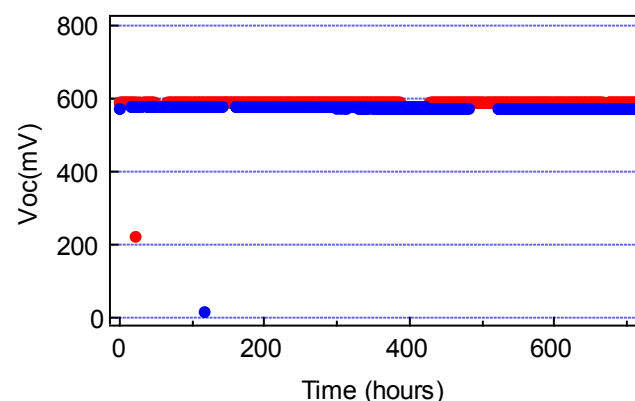
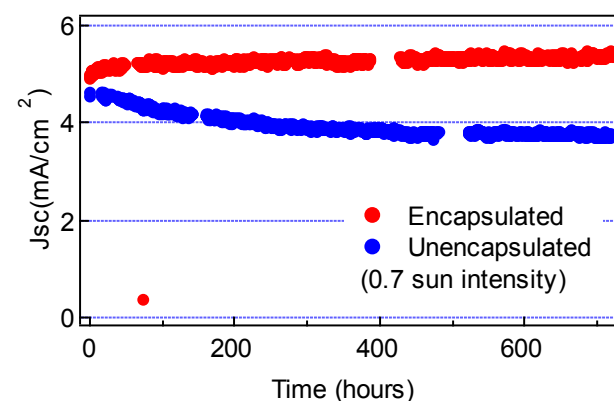


# Task 4 - Stabilized Efficiencies in Unencapsulated Inverted Devices



- Unencapsulated devices under constant illumination in air
- Al thought to fill pin holes in Ag, form stable oxide barrier
- Edge-in diffusion rate < pinhole diffusion rate (not primary lifetime limitation)
- Composite electrodes show stabilized efficiencies to 3500 hours (to date)

# Task 4 – Comparison of Unencapsulated and Encapsulated Inverted Devices



- Inverted device architecture also performs well when encapsulated
- No initial decay observed for  $J_{sc}$  in encapsulated device
- Indicates that initial degradation is related to exposure to atmosphere

Partner	Activity	Status in FY09	Status in FY10	Notes
Konarka	SAI development program – novel packaging	Funded	Ongoing	Packaging
Plextronics	Interfacial development and lifetime studies	Ongoing Funds in CRADA	Ongoing	Lifetime, interfaces, new organic materials
TDA	Assessment of new acceptor and donor materials	Funds In CRADA	Ongoing/Expansion	Device development for new organic materials
Solarmer	Device development for new polymers	No agreement in place	CRADA	Device and lifetime testing
Arizona EFRC	Basic science of TCO/Organic Interface	Funded	Ongoing	Interfacial Characterization
UCSB EFRC	Development of interfacial modifier for improve BHJ	Funded	Ongoing	Optimization of BHJ order
Dow Chemical	Development of ink based precursors for roll to roll processing	Ongoing Funds in CRADA	Ongoing	Prediction of ink based technology impact on LCOE
Luna	New Device Development	CRADA – joint project funded	Ongoing	New carbon materials for substrates and acceptors
CU/CSM/DU	Graduate Student Support	Task Orders	Ongoing	Also collaboration with MRSEC and RASEI

# Task Summary

Milestones	Tasks	Date	Progress to Date	Status
1. Development of 5.5% efficient OPV device.	1-6	6/10	Demonstrated new 6.7-7% device (1 cm <sup>2</sup> ).	Exceeded
2. Develop models for materials design and device operation.	1, 2, 3, 4	9/10	Device model under development and computational tool for new materials prediction in use.	On Schedule
3. Synthesis and utilization of lower band gap absorbers with reduced donor – acceptor band offset.	1, 2	7/10	New polymers and soluble small molecules synthesized. Demonstrated attractive properties for polymer route.	On Schedule
4. Develop ETL contact material with enhanced doping control for high efficiency inverted OPV devices.	3, 4	9/10	Low temperature solution deposited ZnO developed for inverted device. NiO shown superior (efficiency) to PEDOT:PSS for some polymers (PCDTBT) with increased lifetime.	Achieved/On Schedule
5. Initial correlation of lifetime and cell design/encapsulation with combinatorial lifetime testing	1, 2, 3, 4	12/09	Combinatorial system (air) fully operational and new key results obtained for normal and inverted devices identifying primary degradation mechanisms.	Achieved
6. Determine the intrinsic degradation mechanisms important for resulting device lifetime.	1, 2, 3, 4	6/10	Key mechanisms identified (contact evolution, PCBM oxidation) and mitigation approaches demonstrated.	Achieved
7. Demonstrate scalability of devices larger than 10 cm <sup>2</sup> through techniques such as slot die coating.	2, 3, 5	8/10	Slot die coater obtained and PDIL tool completely functional.	On Schedule

- **Modeling** - Key focus in this task will be to continue to extend our computational modeling ability to become both increasingly predictive for new materials development and for predicting device behavior.
- **New Organic Materials** - A key focus will be on development of new lower gap polymers with increased absorption and band edges that will lead to improved Voc and increased stability.
- **Contacts** - Initial results with new HTL/ETL's will be extended to to alternative materials for the HTL/ETL, and to understanding optimization for new electroactive polymers and alternative TCOs. This will be done for conventional configurations as well as inverted devices.
- **Lifetime Characterization** - Development of the *controlled atmosphere* combinatorial set up. Extended effort to delineate the key mechanisms for degradation as a function of device configuration and characterization of devices with new organic materials.
- **Characterization** - Development of new rapid assessment techniques for measuring the acceptor donor properties and the resultant device with predictive correlations to device properties.