



**NREL**

**National Renewable Energy Laboratory**

*Innovation for Our Energy Future*



**David Ginley, Research Fellow  
NREL**

**Progress, Trends and Challenges for PV  
Towards the Terrawatt Challenge**

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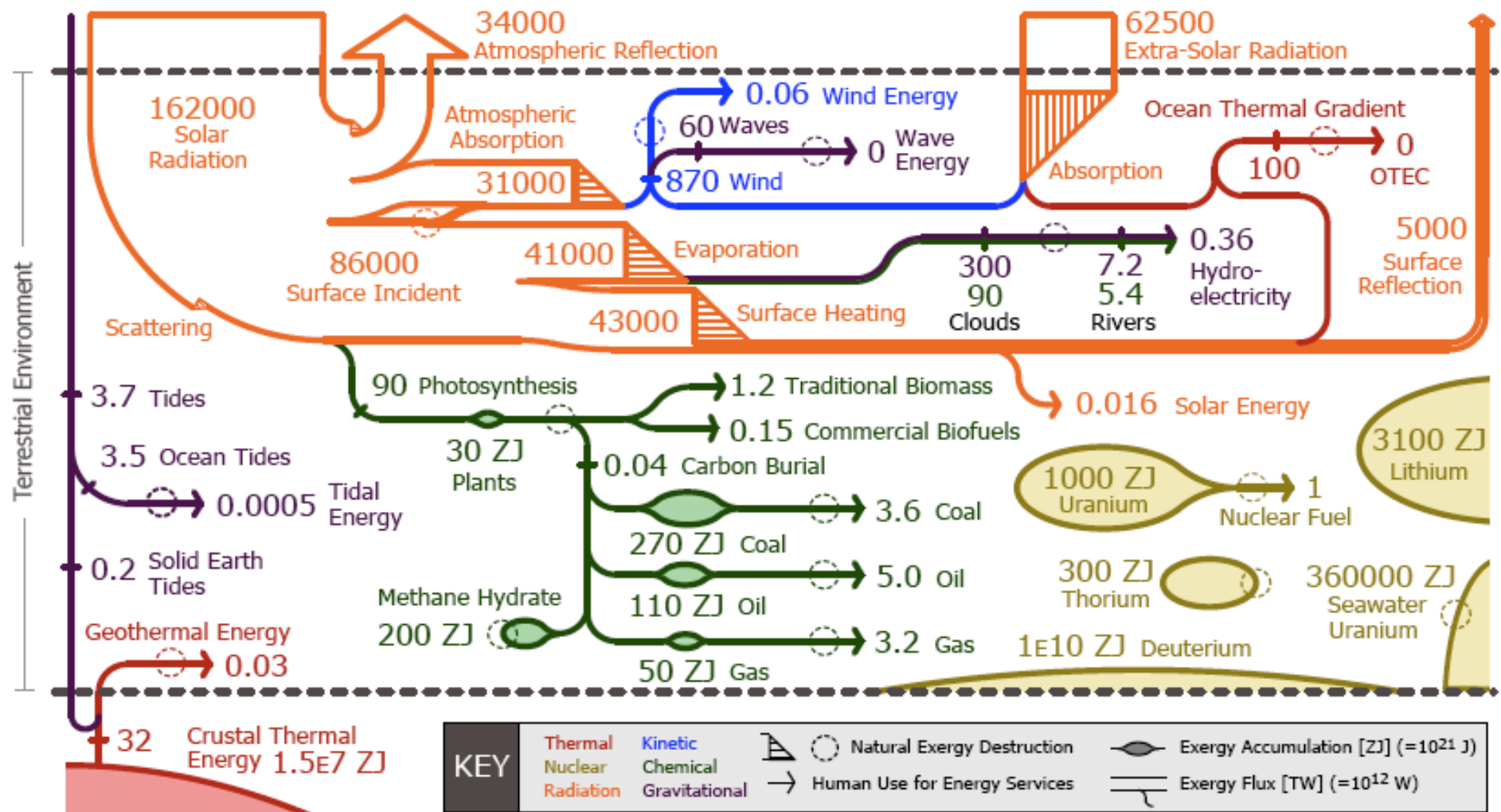
AJ Sigdel

Funding

DOE EERE AOP & Seed Fund, NREL Laboratory Directed Research and Development program (LDRD) and OS EFRC UCSB and Arizona



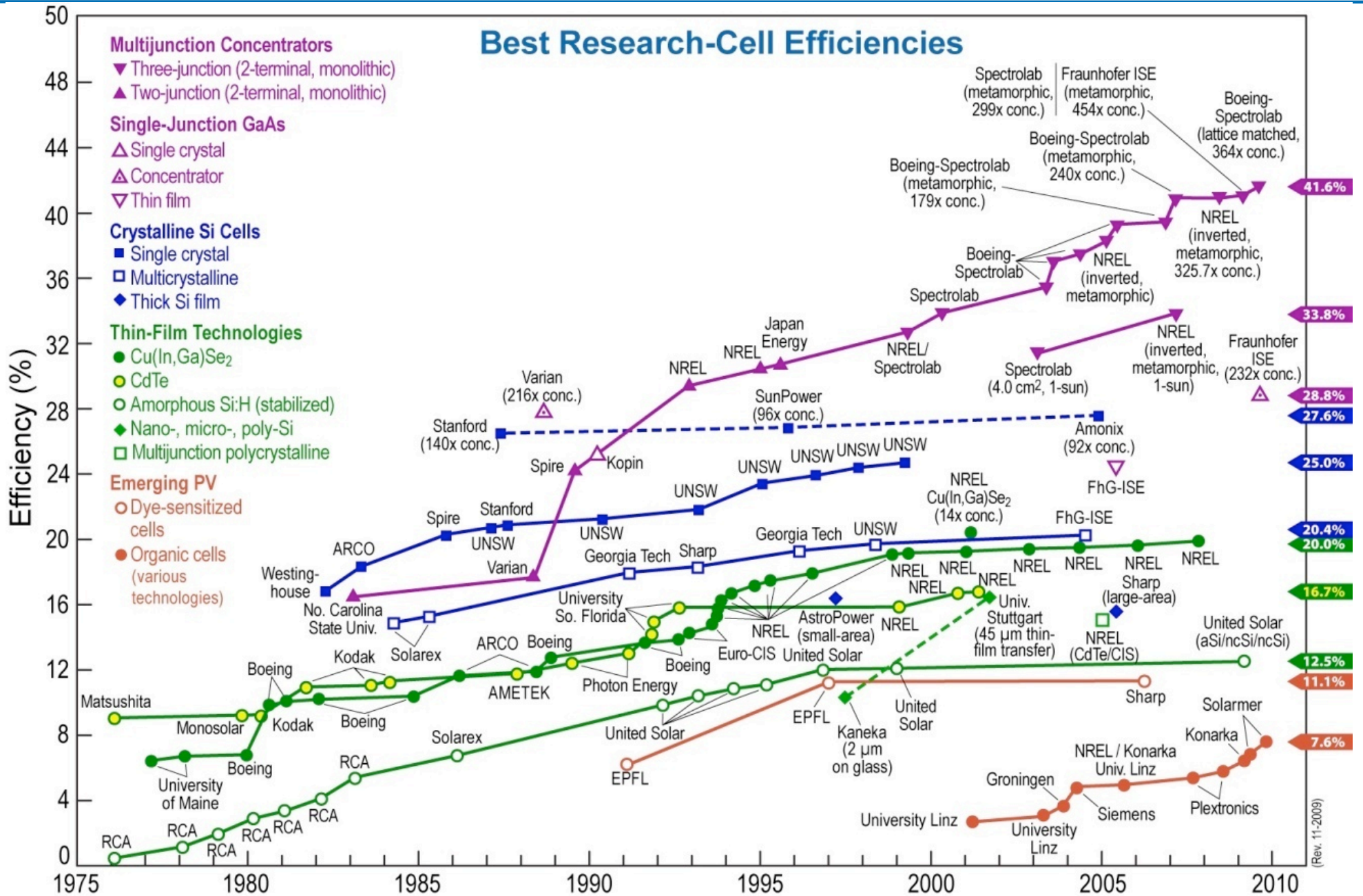
# Global Exergy Flux, Reservoirs, and Destruction



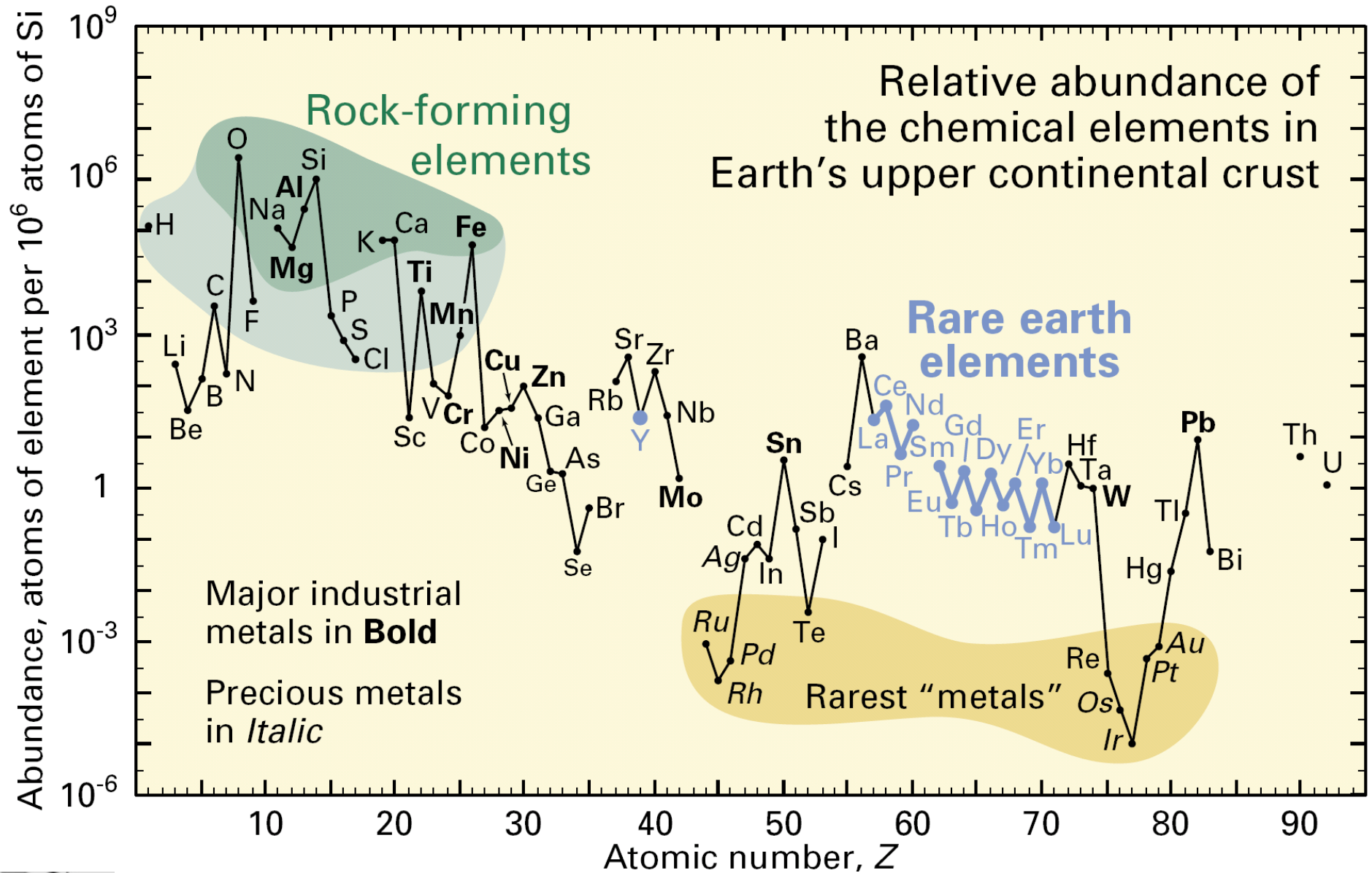
Exergy is the useful portion of energy that allows us to do work and perform energy services. We gather exergy from energy-carrying substances in the natural world we call energy resources. While energy is conserved, the exergetic portion can be destroyed when it undergoes an energy conversion. This diagram summarizes the exergy reservoirs and flows in our sphere of influence including their interconnections, conversions, and eventual natural or anthropogenic destruction. Because the choice of energy resource and the method of resource utilization have environmental consequences, knowing the full range of energy options available to our growing world population and economy may assist in efforts to decouple energy use from environmental damage.



# A story of many possibilities



# But for Terrawatts - abundance is key

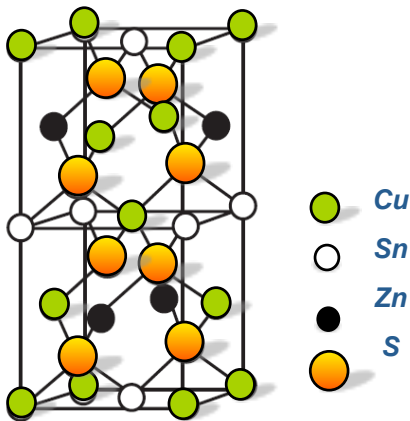


# Approaches to Abundant Green Systems



# Green Systems

- $\text{CuInGaSe}_2$  – 19.5% efficient – thin film architecture
- $\text{Cu}_2\text{ZnSnS}_4$  (CZTS)
  - 6.7% efficiency (Katagiri et al.)
  - 1.45 eV  $E_g$
- CZTS has kesterite structure



## Raw Material Costs

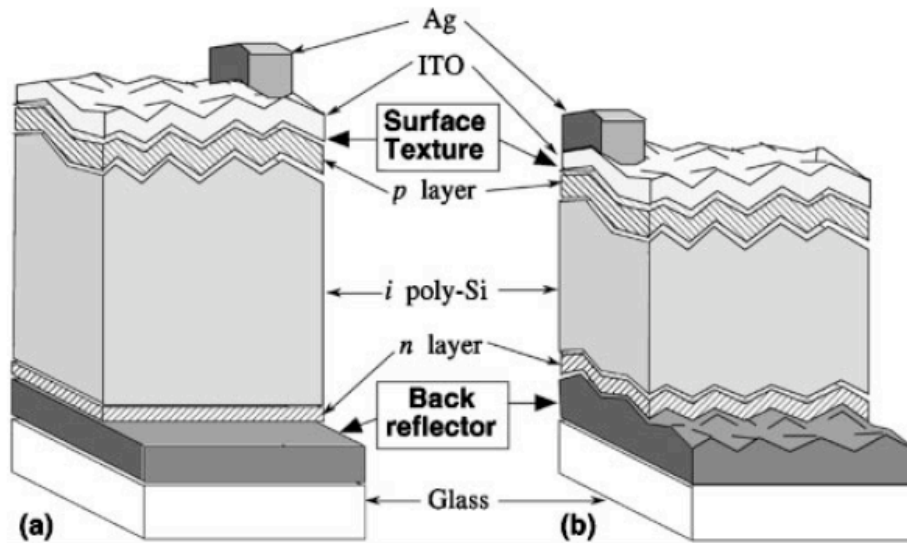
Cu - \$3.35/lb
Zn - \$1.59/lb
Sn - \$6.61/lb
S - \$0.02/lb
Ga - \$209/lb
In - \$361/lb
Se - 2002 \$4, 2007 \$33/lb

## Relative Abundance

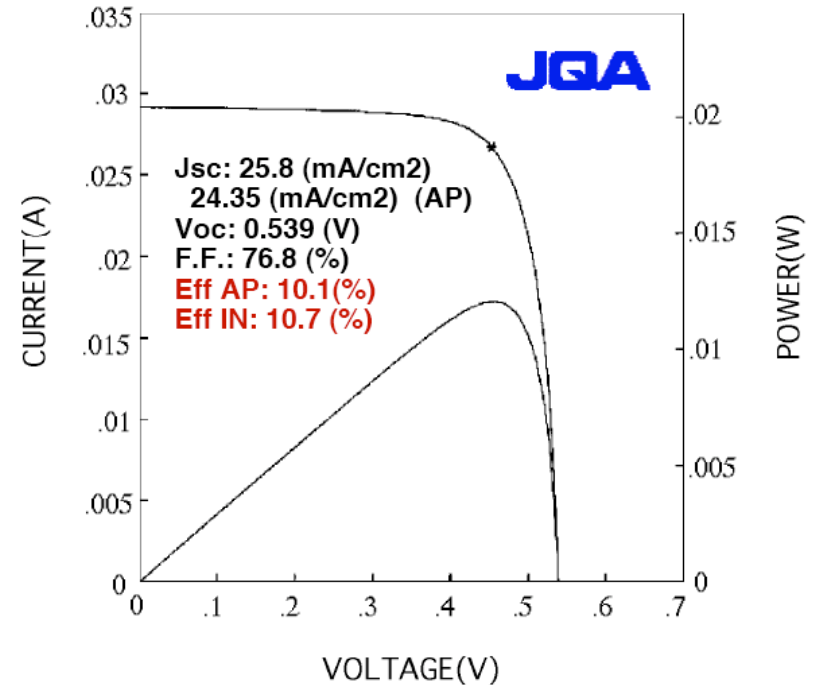
Cu - $6.0 \times 10^{-5}$
Zn - $7.0 \times 10^{-5}$
Sn - $2.3 \times 10^{-6}$
S - $10^{-4}$
Ga - $1.9 \times 10^{-5}$
In - $2.5 \times 10^{-7}$
Se - $5 \times 10^{-8}$

Source: [www.usgs.gov](http://www.usgs.gov) (2007 data)

# Thin/Thick Film Si on Glass



**Fig. 1a,b.** Schematic view of our thin-film poly-Si solar cell with STAR (natural surface texture and enhanced absorption with back reflector) structure. **a** First generation of poly-Si cell with flat back reflector. **b** Second generation of poly-Si cell with rough back reflector for thinner cell



**Fig. 3.** The performance of the 2.0- $\mu\text{m}$ -thick poly-Si solar cell with STAR structure as independently confirmed by Japan Quality Assurance (JQA). The numbers for  $\eta_{\text{int}}$  and  $\eta_{\text{ap}}$  represent the intrinsic and the aperture efficiency, respectively. The difference between the intrinsic and aperture efficiency originates from the Ag grid electrode on the ITO

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# OPV for Low Cost Power Production

## Efficiency, Lifetime and Scalability The Challenges

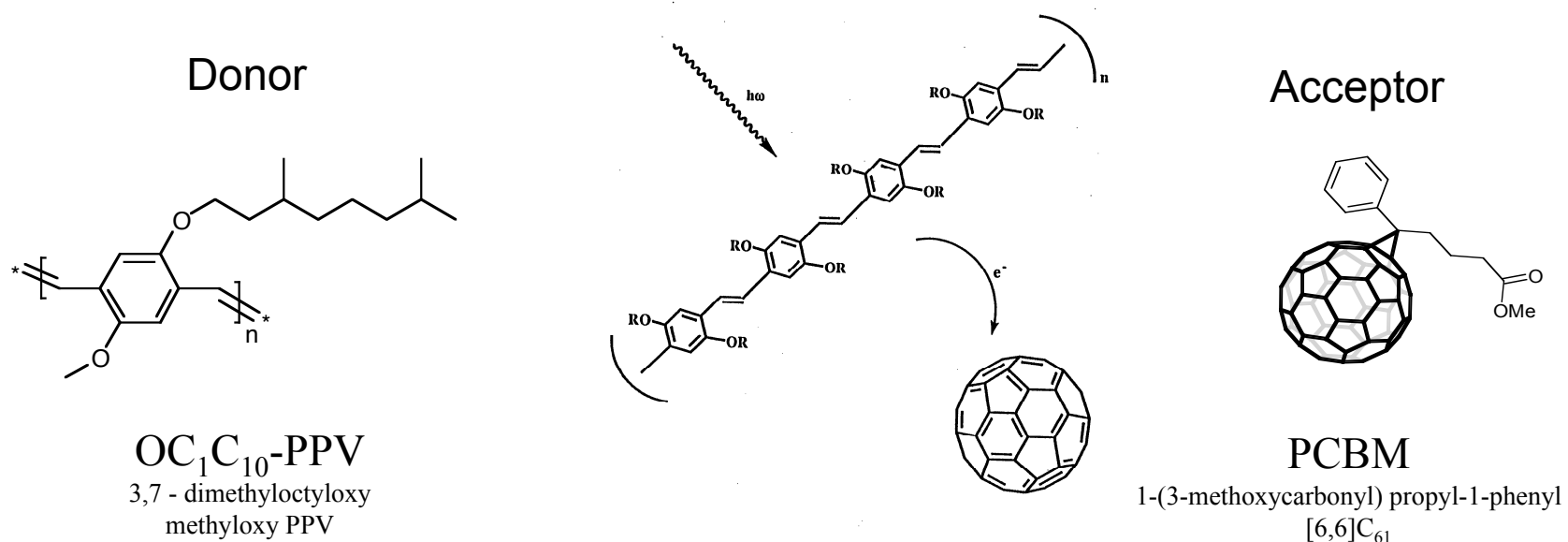
### Excitonic Solar Cells

APS



# The Basis for Polymer Organic Solar Cells

Ultrafast photoinduced electron transfer between a conjugated polymer and a fullerene was discovered in 1992\*.



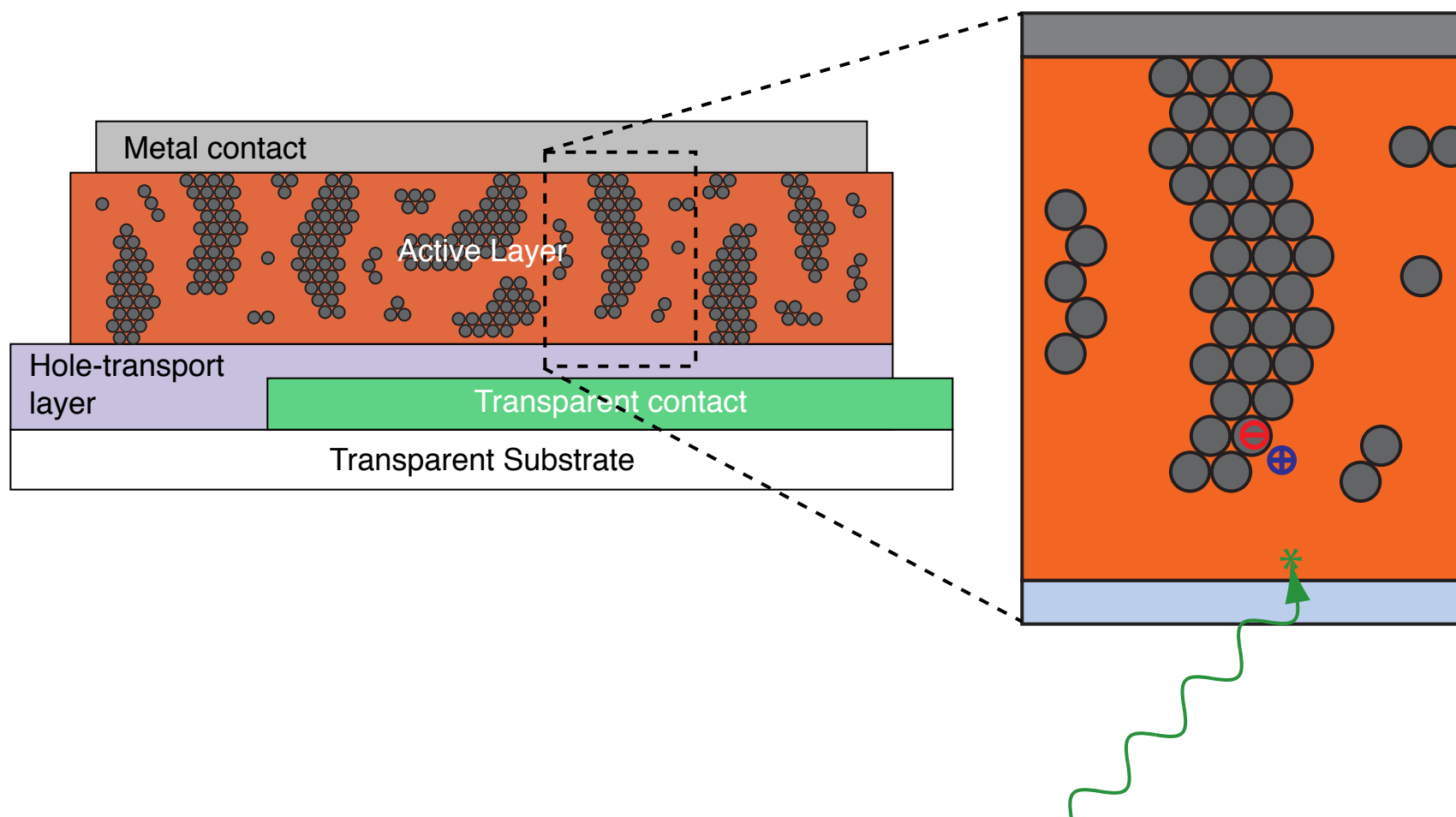
Forward electron transfer rate: 45 fs<sup>†</sup>

Backward electron transfer rate: ~1 μs

\*N. S. Sariciftci, L. Smilowitz, A. J. Heeger, and F. Wudl, *Science* **258**, 1474 (1992).

†C. J. Brabec, G. Zerza *et al.*, *Chem. Phys. Lett.* **340**, 232 (2001).

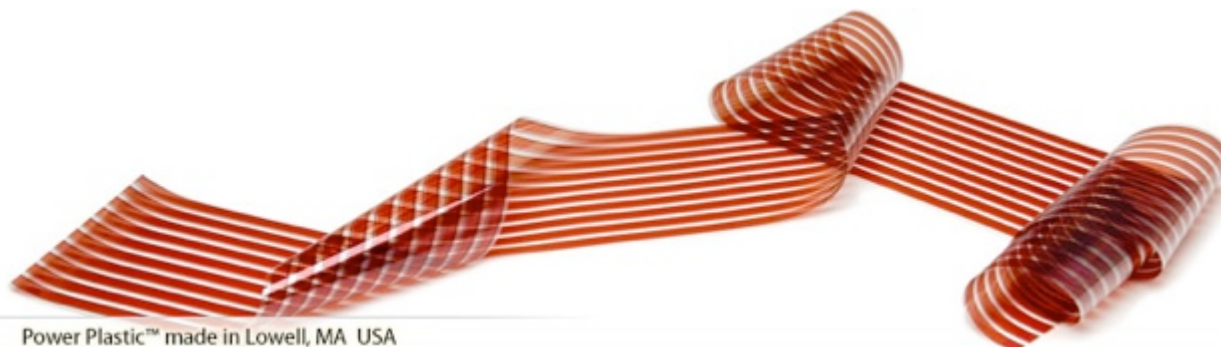
# How Do Organic Solar Cells Work?



# What are the Drivers for Organic Solar Cells

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- Terrawatt Power Production from Solar will require a number of key features:
  - Very high production capacity - **Konarka and DTU have proof of principle**
  - Reasonable Efficiency - rapid progress in devices and modules - update this talk
  - Lifetime sufficient to Commercialize - update this talk - is the paradigm different?
  - Low energy payback times -- low temperature processing - **Konarka, NREL, DTU, Plextronics - as low as 2 months possible**
  - Low capital investment - still to be proven
  - Abundant Materials - **yes** but cost still being resolved
  - Green Processing - yes a possibility
  - Low Balance of Systems Cost - **Konarka and Plextronics new ways to make cells**
  -

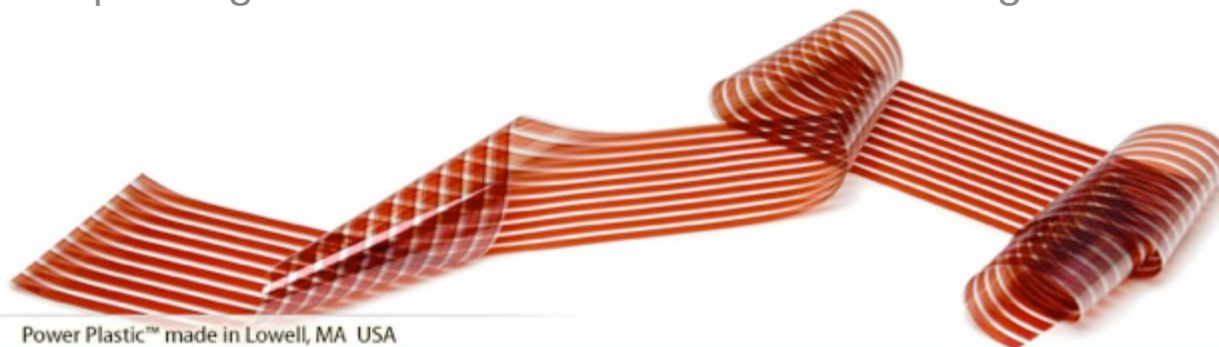




# Progress in Organic Solar Cells

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- Demonstration of low cost organic photovoltaic (OPV) devices
  - Printed or solution processed at high speed on flexible substrates
  - Using roll-to-roll processing for dramatic reduction in production costs
  - Low materials and balance of systems costs
- Near term goal: 5 - 10% efficiency, lifetime up to 10,000 hours
  - “Niche” applications in consumer electronics, autonomous sensors, RFID, etc.
- Long term goal: 15% efficiency, lifetime > 5 years
  - Grid connected - roof top power generation & solar farms
  - Building Integrated PV
  - Large scale power generation to meet the terawatt challenge



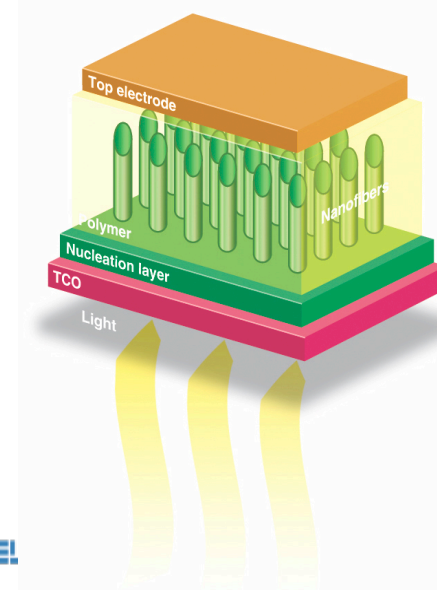
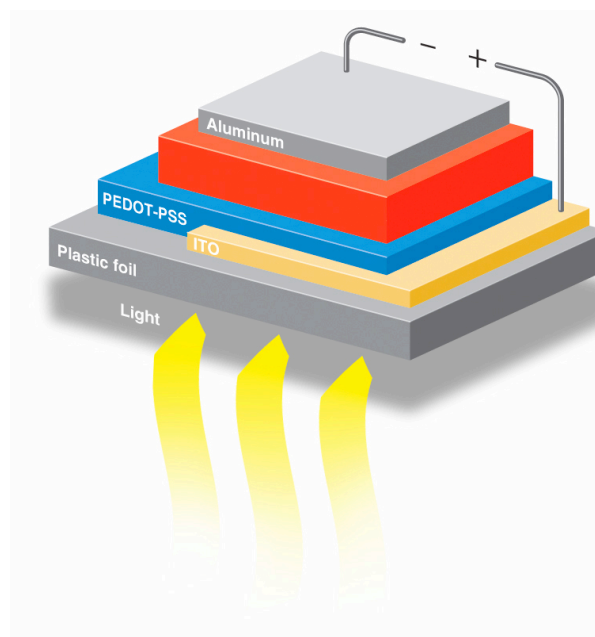
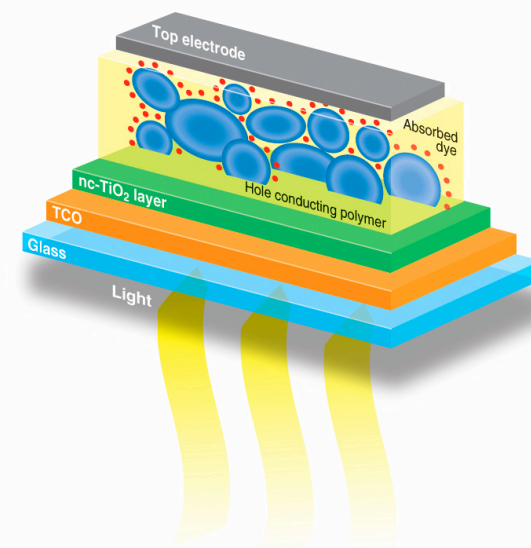
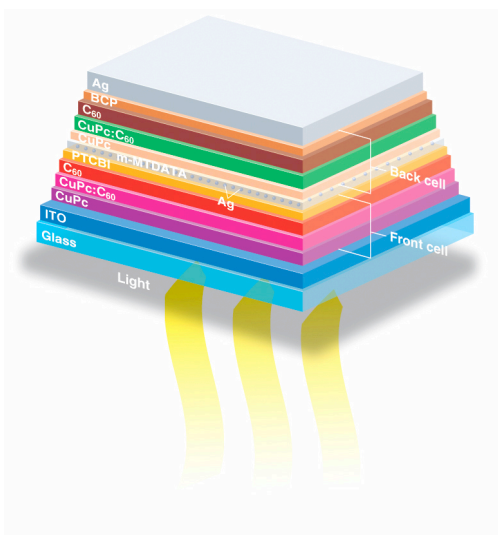
Power Plastic™ made in Lowell, MA USA

Konarka Technologies, <http://www.konarka.com/>

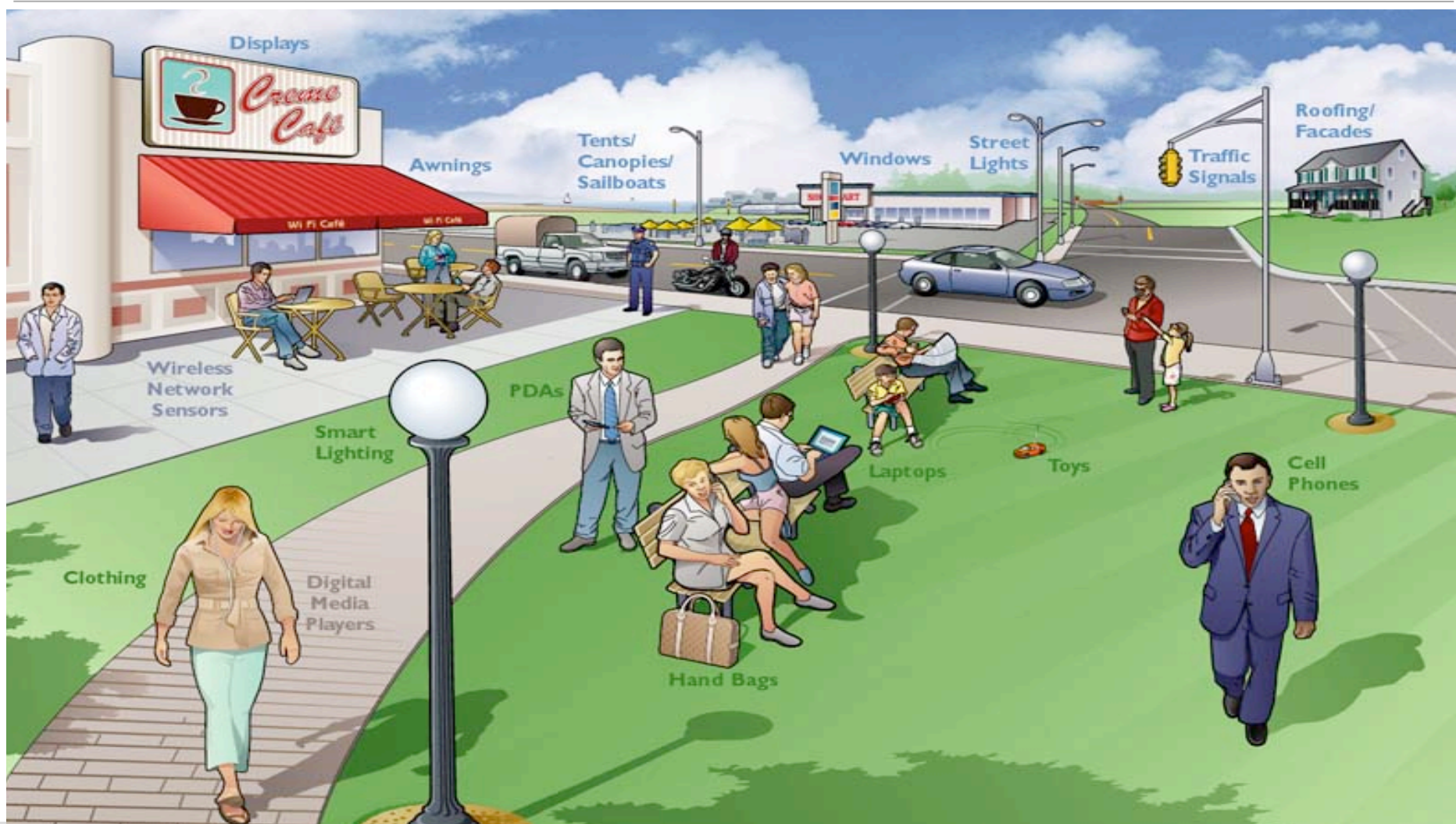
# What are Excitonic Solar Cells?

## A wide range of possibilities!!

- Dye Sensitized Solar Cell (DSSC)
- Planar - Small Molecule
- Polymer - Fullerene Bulk Heterojunction
- Hybrid Polymer - Inorganic Ordered Bulk Heterojunction

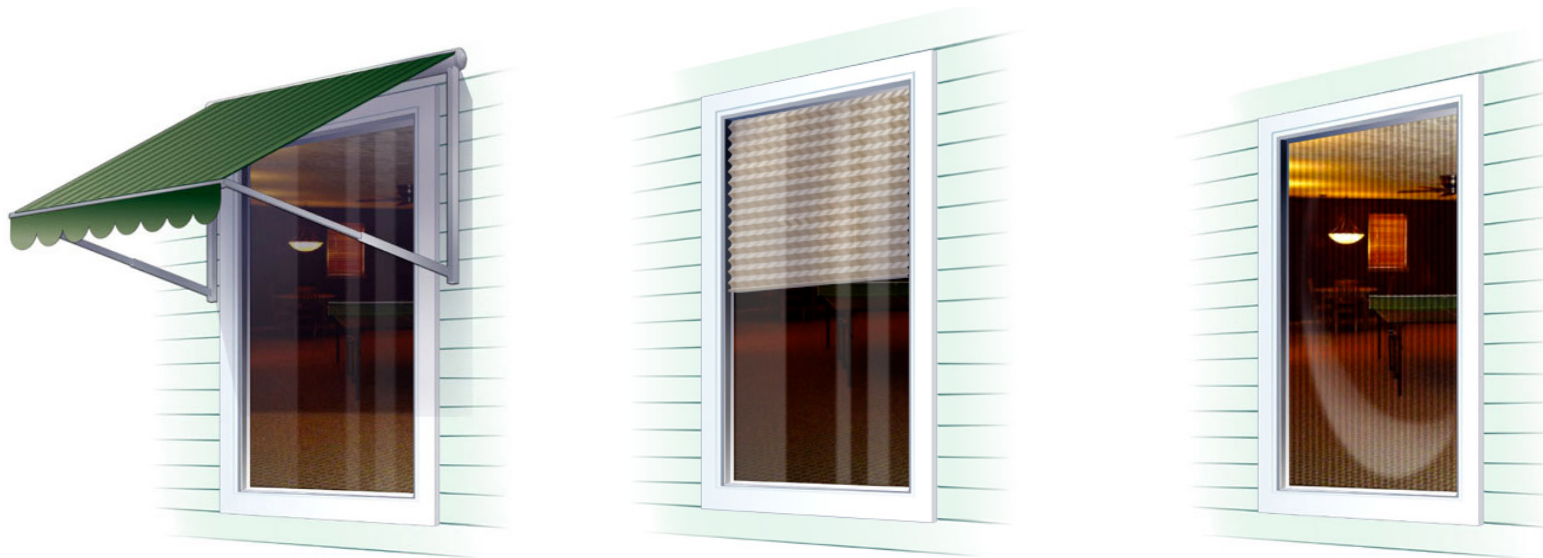


# Power Plastic® Portable to BIPV to Rooftop Applications





# BIPV Systems and Structures



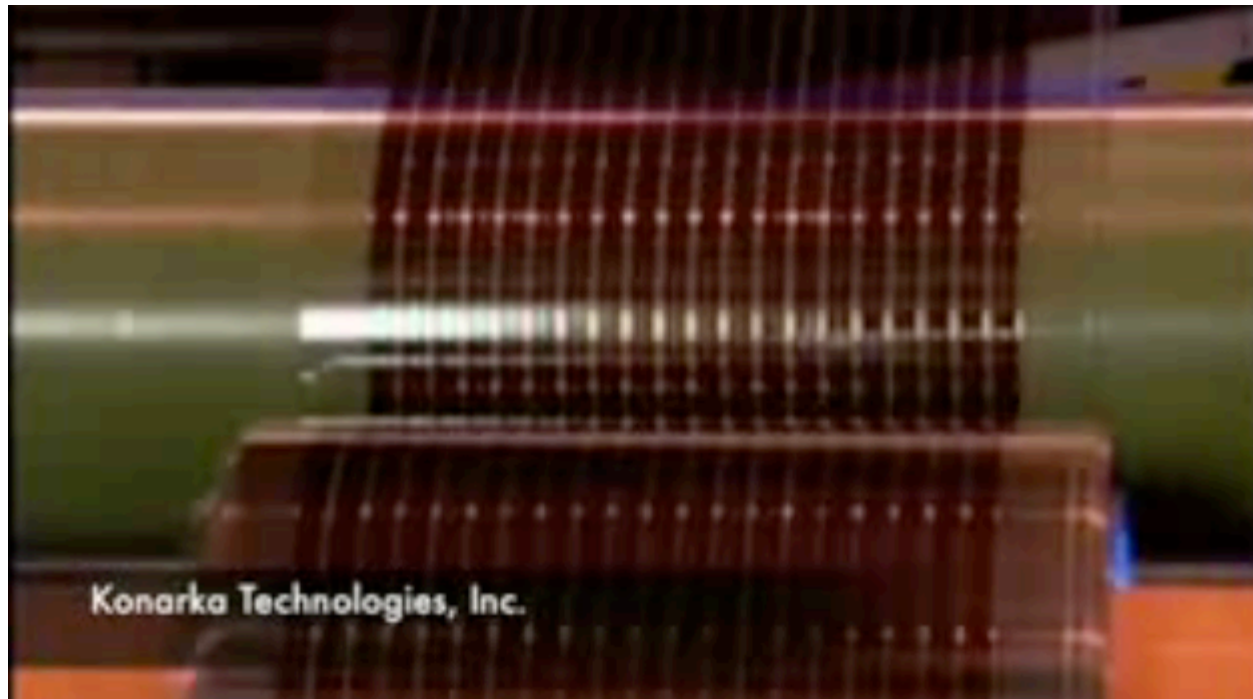
power plastic™





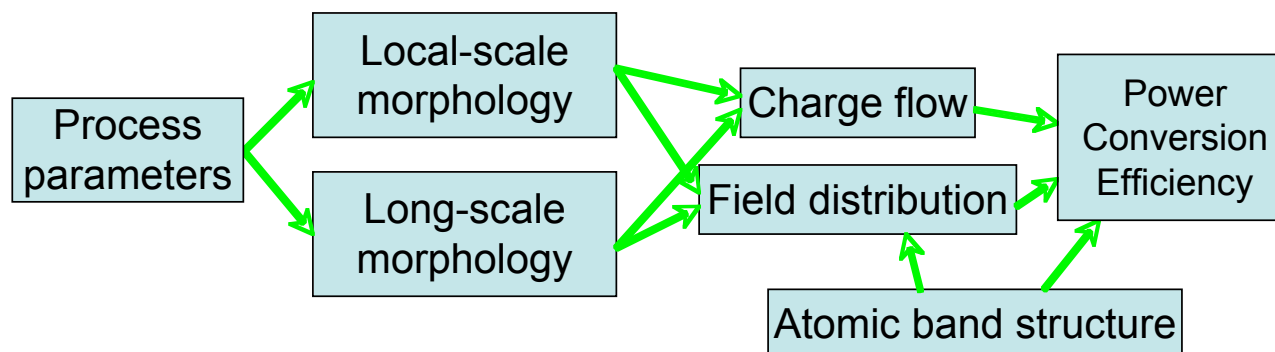
# Low Capital, Highly Scalable, Flexible or . . .

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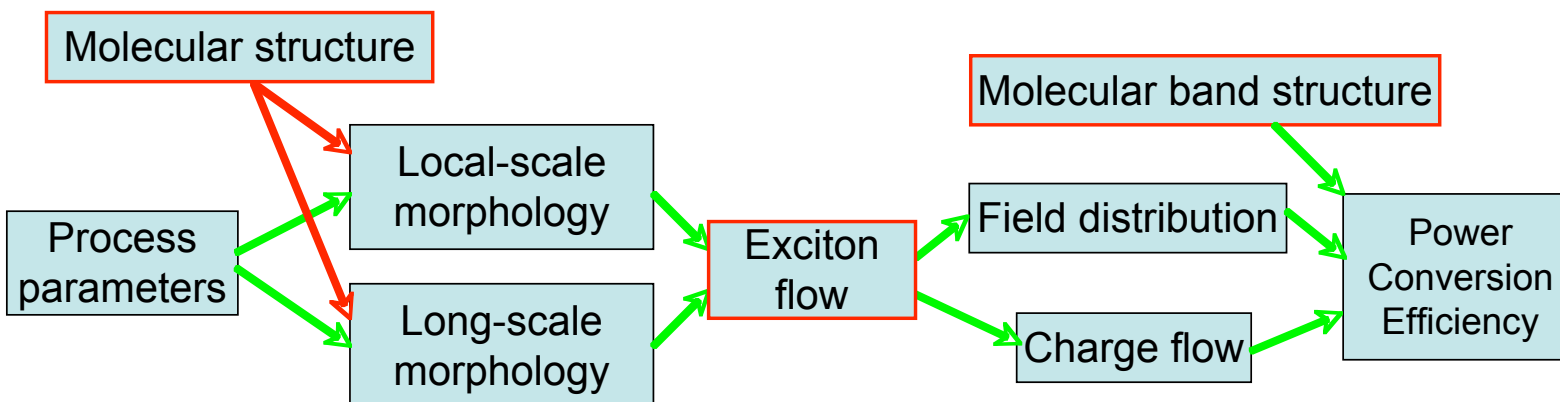


# Conventional vs. Organic Semiconductors in PV

## Conventional semiconductors (vacuum processing)

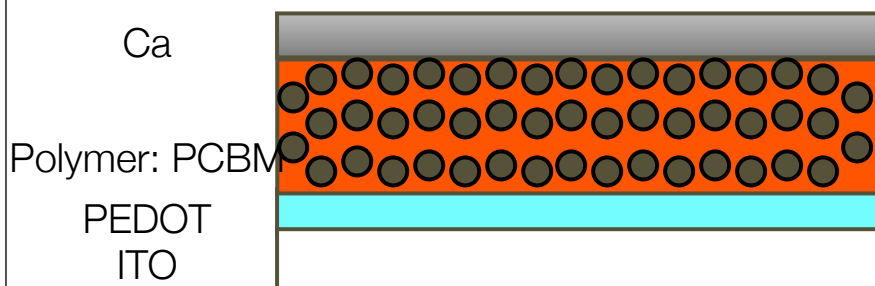


## Molecular semiconductors (solution processing)

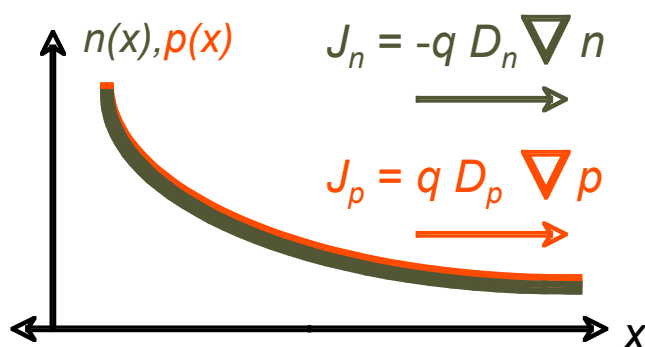


**Organic an immense plus for tunability and a minus for rapid optimization**

# Bulk Heterojunction Devices



(6,6)-phenyl C<sub>61</sub> butyric acid methyl ester (PCBM)



Chemical potential gradients for both charges are in the same direction

## • Strengths

- All excitons are effectively dissociated
- Solution processing by spin coating from a common solvent

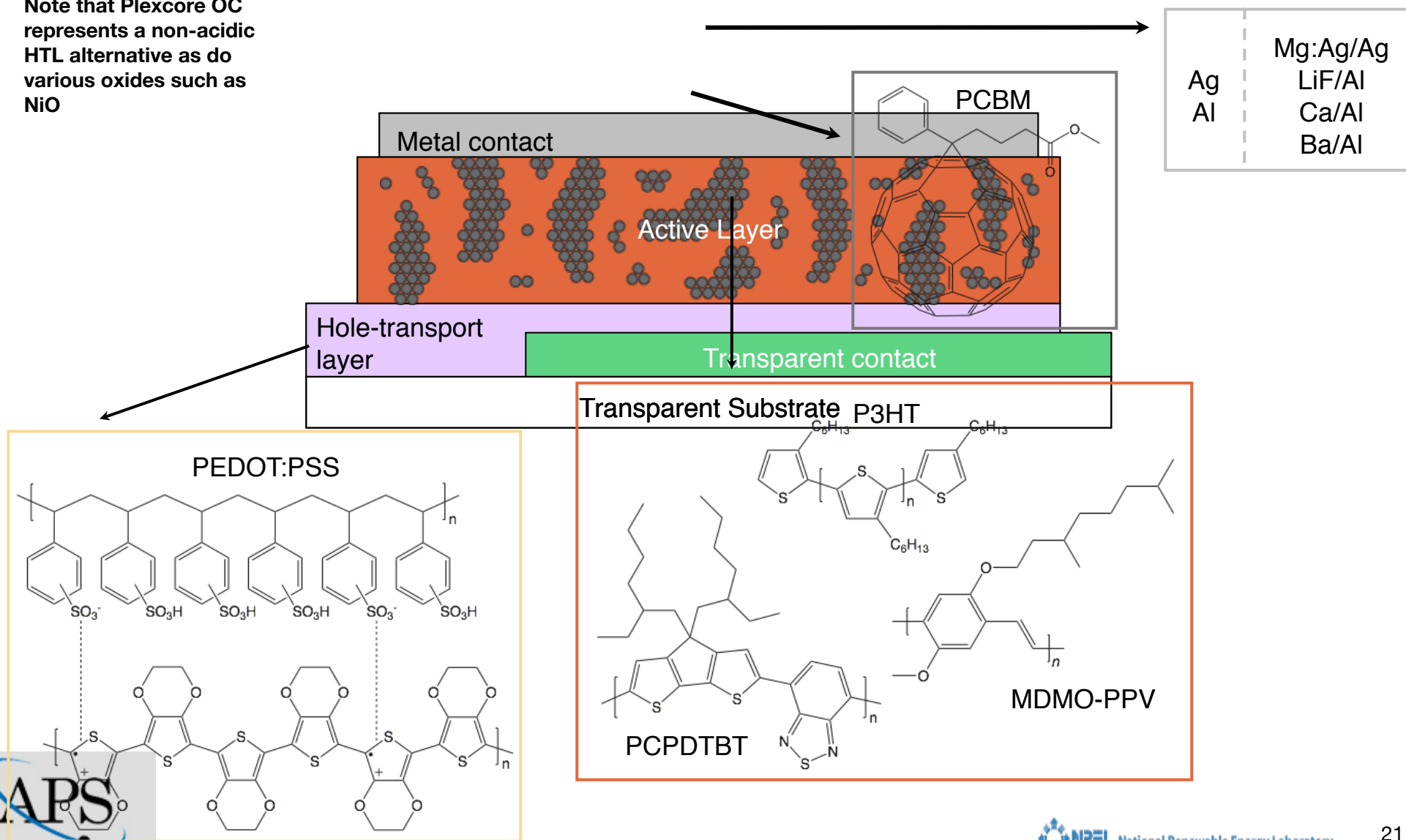
## • Weaknesses

- Chemical potential gradients do not yield diffusion current
- Recombination can occur in the bulk
- Little control over morphology

# Model Bulk Heterojunction OPV Device

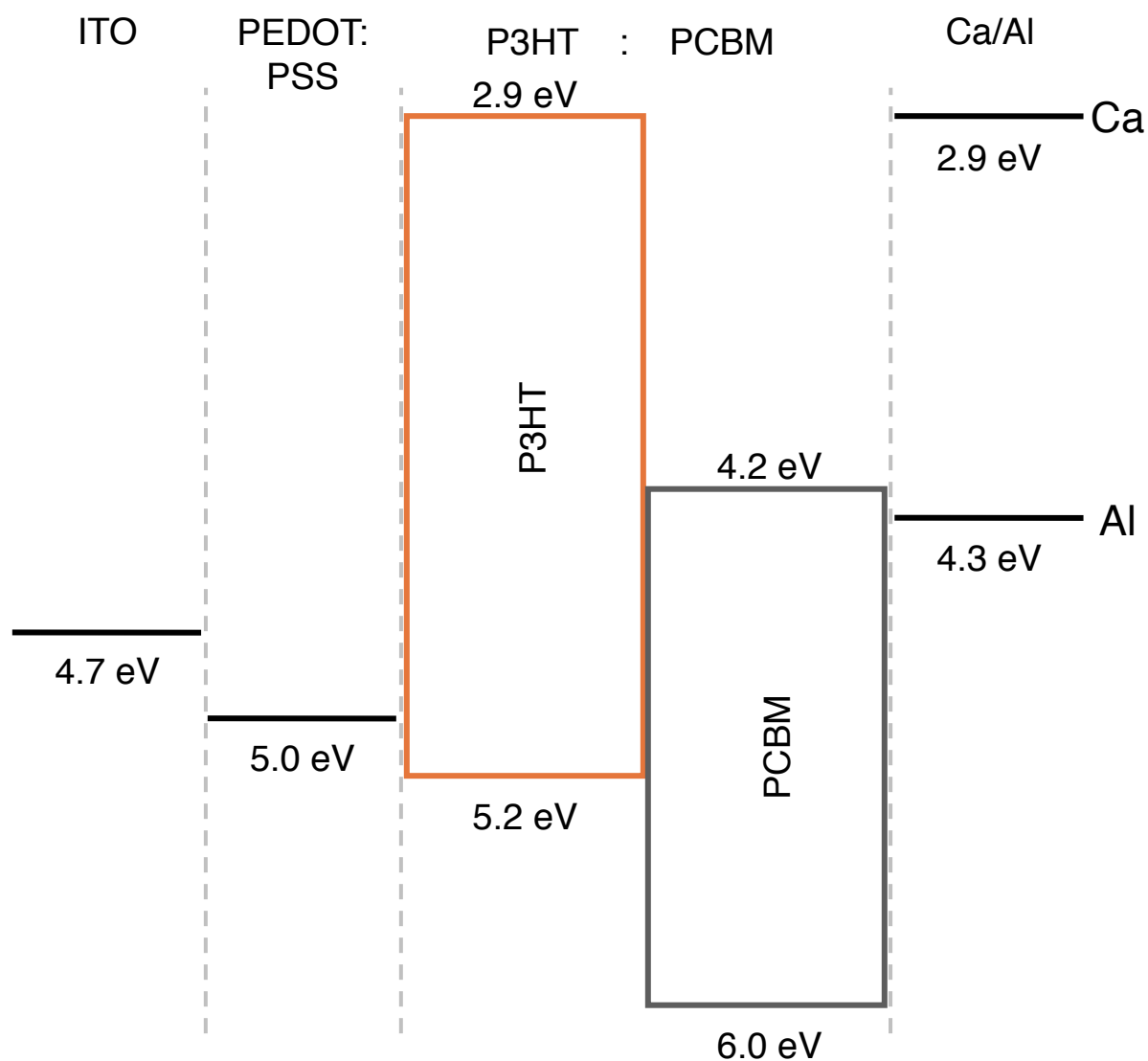
## Interfaces are key-- understanding is just developing!

Note that Plexcore OC represents a non-acidic HTL alternative as do various oxides such as NiO



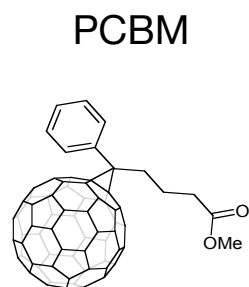
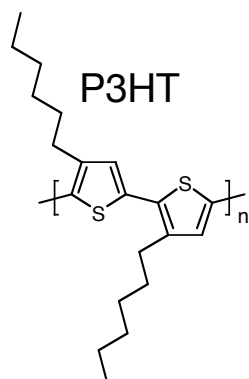
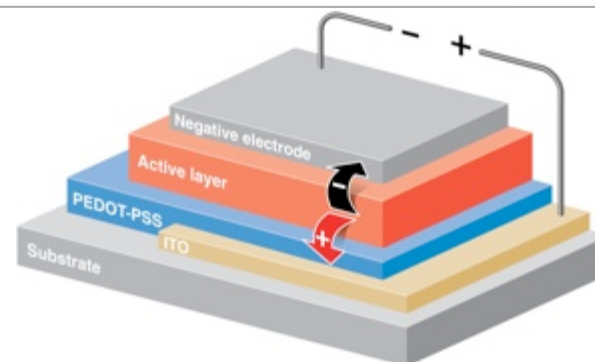


# 'Band Diagram' for OPV Devices



# Bulk Heterojunction Solar Cells - NREL Devices

glass / ITO / PEDOT:PSS / P3HT:PCBM (1:1) / Ca  
(active layer slow dried from ODCB)



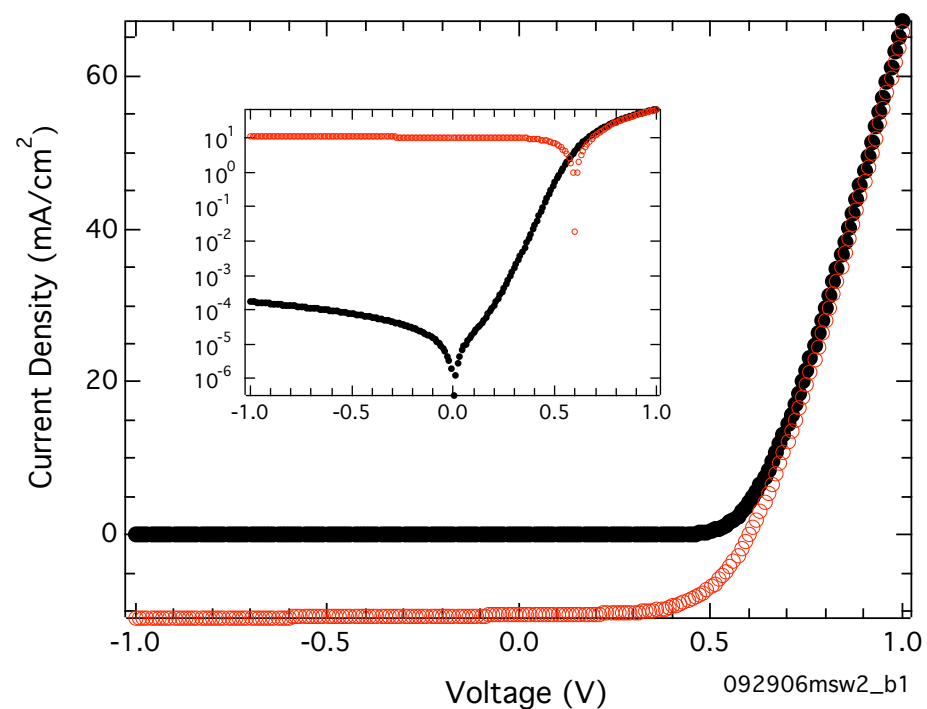
$$V_{OC} = 0.605 \text{ V}$$

$$J_{SC} = 9.3 \text{ mA/cm}^2$$

$$FF = 65.5\%$$

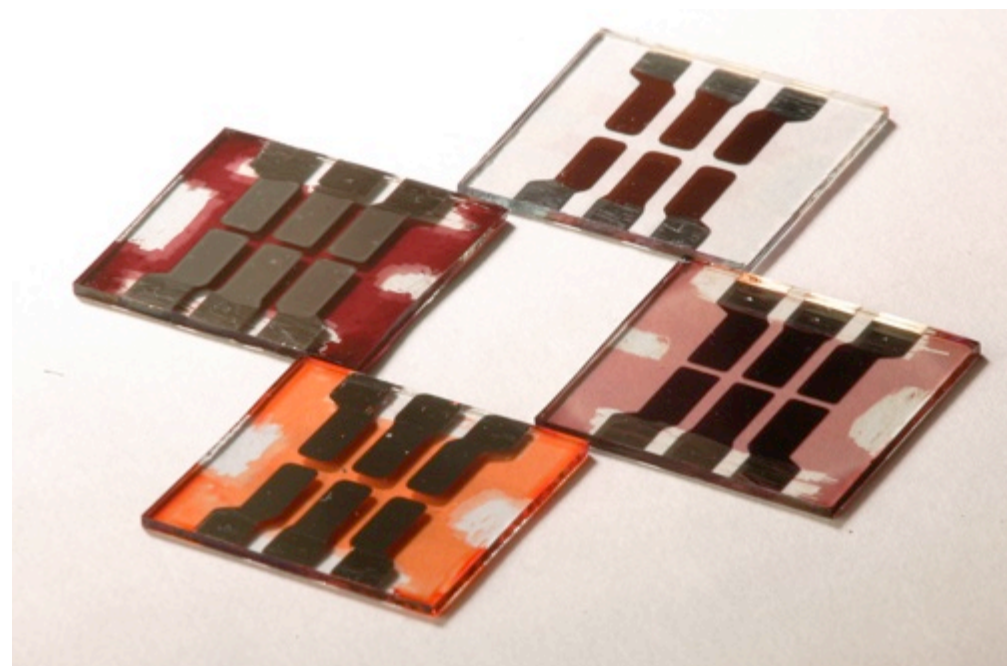
$$\eta = 3.7\% \text{ (NREL certified)}$$

$$\eta = \frac{V_{OC} J_{SC}}{P_{in}} FF$$



# How efficient are they?

- Certified measurements of  $>7\%$  in polymer / fullerene bulk heterojunction devices
- Efficiency greater than 4% with poly(3-hexylthiophene) (P3HT) donor material,  $E_g \sim 1.9$  eV
- Chemistry and materials development are important tools for increasing performance
  - Synthesis of new active layer materials
  - Development of new contact and electrode materials



# Practical Efficiency Targets for OPV devices

<u>Paper</u>	<u>Practical Efficiency Target</u>
i) “Conjugated Polymer Photovoltaic Cells”, K.M Coakley and M.D. McGehee, <i>Chem. Mater.</i> <b>16</b> (2004).	10+%
ii) “Design Rules for Donors in Bulk-Heterojunction Solar Cells - Towards 10% Energy-Conversion Efficiency”, M.C. Scharber, D. Mühlbacher, M. Koppe, <small>Text</small> Denk, <small>Text</small> C. Waldauf, A.J. Heeger, and C.J. Brabec, <i>Adv. Mater.</i> <b>18</b> (2006).	10%
iii) “Ultimate Efficiency of Polymer/Fullerene Bulk Heterojunction Solar Cells”, L.J.A Koster, V. D. Mihailetschi, and P.W.M. Blom, <i>Appl. Phys. Lett.</i> <b>88</b> (2006).	11%

**How efficient do they need to be to be practical???**



# NREL-Certified World-Class Performance through New Development

Device ID: 3393-2 pxl 1  
Aug 14, 2008 23:17  
Spectrum: AM1.5 Global

Device Temperature:  $25.0 \pm 1.0$  °C  
Device Area:  $0.043$  cm<sup>2</sup>  
Irradiance:  $1000.0$  W/m<sup>2</sup>

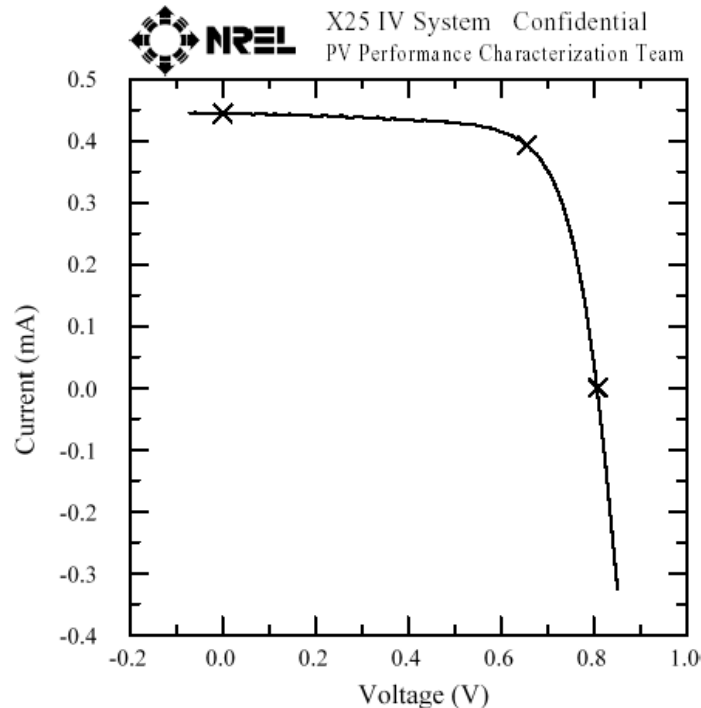
*Polymer-based OPV Solar Cell*

Single Photoactive Layer OPV Cell

NREL Certified at 5.98%

Aperture =  $0.043$  cm<sup>2</sup>

Cell Size  $\sim 0.1$  cm<sup>2</sup>



$$V_{oc} = 0.8079 \text{ V}$$

$$I_{max} = 0.39258 \text{ mA}$$

$$I_{sc} = 0.44438 \text{ mA}$$

$$V_{max} = 0.6553 \text{ V}$$

$$J_{sc} = 10.321 \text{ mA/cm}^2$$

$$P_{max} = 0.25724 \text{ mW}$$

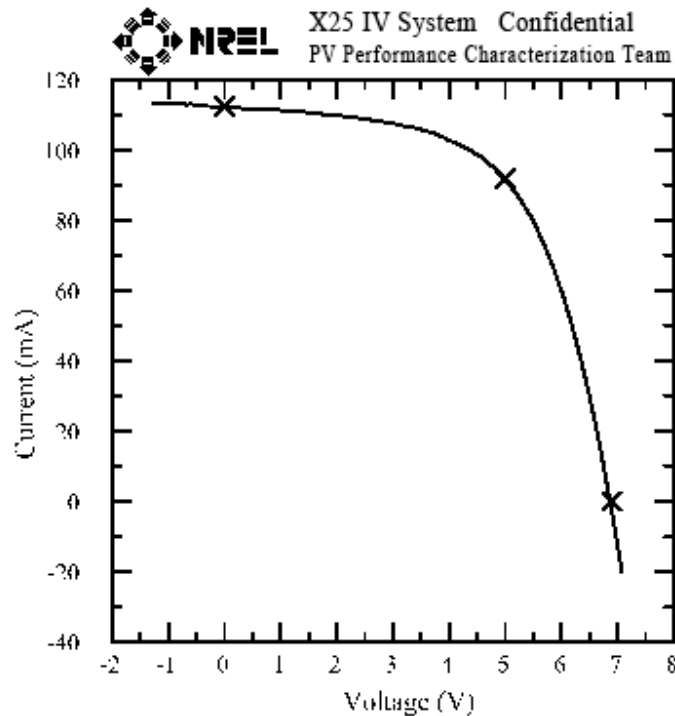
$$\text{Fill Factor} = 71.67 \%$$

$$\text{Efficiency} = 5.98 \%$$

# NREL-Certified OPV Module Efficiency using Plexcore® PV 2100 Active Layer

Device ID: 4103  
Jan 28, 2009 12:11  
Spectrum: ASTM G173 global

Device Temperature:  $24.6 \pm 0.5$  °C  
Device Area:  $223.5 \text{ cm}^2$   
Irradiance:  $1000.0 \text{ W/m}^2$



$V_{oc} = 6.9025 \text{ V}$

$I_{sc} = 0.1123 \text{ A}$

$J_{sc} = 0.502 \text{ mA/cm}^2$

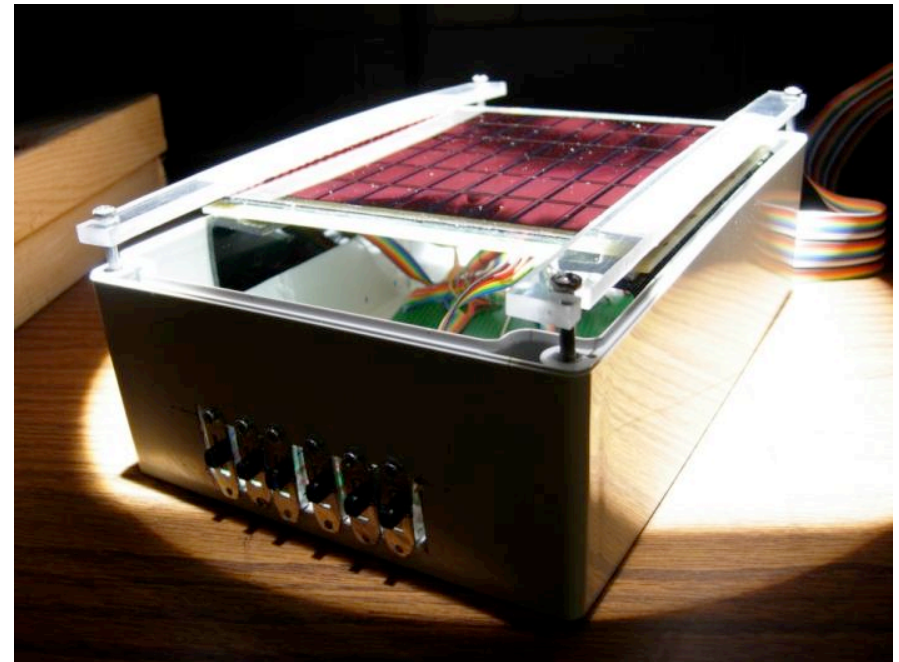
Fill Factor = 59.09 %

$I_{max} = 91.700 \text{ mA}$

$V_{max} = 4.9952 \text{ V}$

$P_{max} = 0.4580 \text{ W}$

Efficiency = 2.05 %



## Largest OPV Module certified at NREL

- 152mm x 152mm Module
- Total Area Certified at 2.05%
- Active Area coverage = 48%
- Active Area efficiency = 4.24%

## Konarka Technologies organic Cell

Device ID: EC02

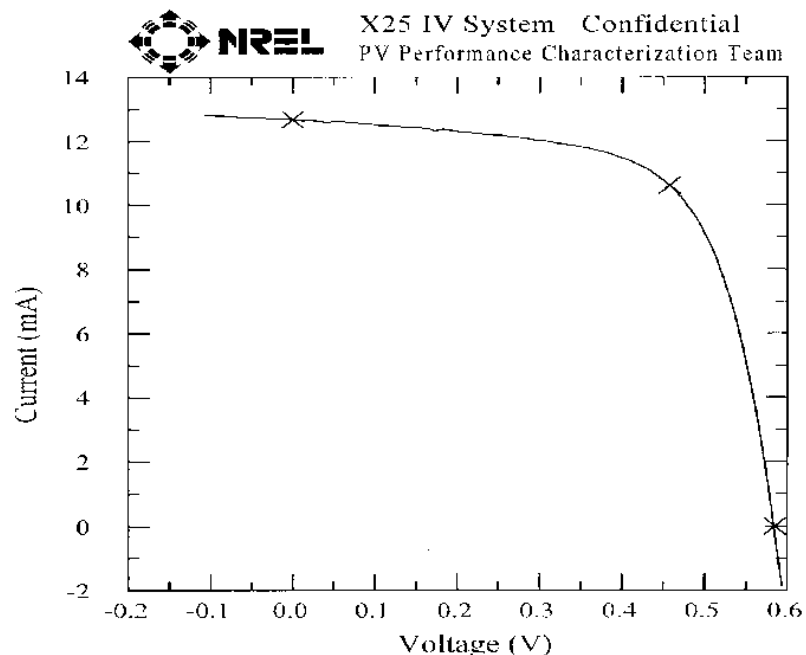
Dec 11, 2008 22:18

Spectrum: AM1.5 Global

Device Temperature:  $25.0 \pm 1.0$  °C

Device Area:  $0.759$  cm<sup>2</sup>

Irradiance:  $1000.0$  W/m<sup>2</sup>



$V_{oc} = 0.5851$  V

$I_{sc} = 12.670$  mA

$J_{sc} = 16.693$  mA/cm<sup>2</sup>

Fill Factor = 65.47 %

$I_{max} = 10.610$  mA

$V_{max} = 0.4573$  V

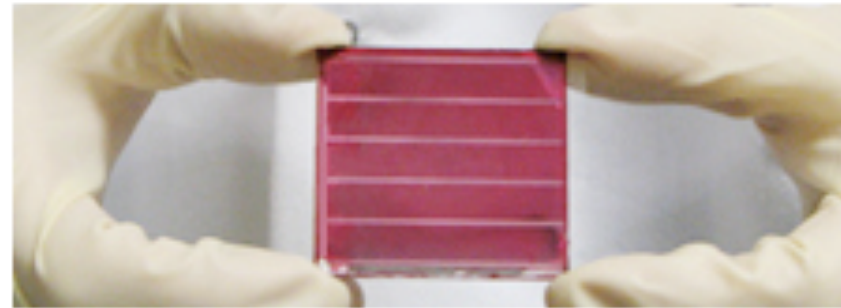
$P_{max} = 4.8530$  mW

Efficiency = 6.39 %

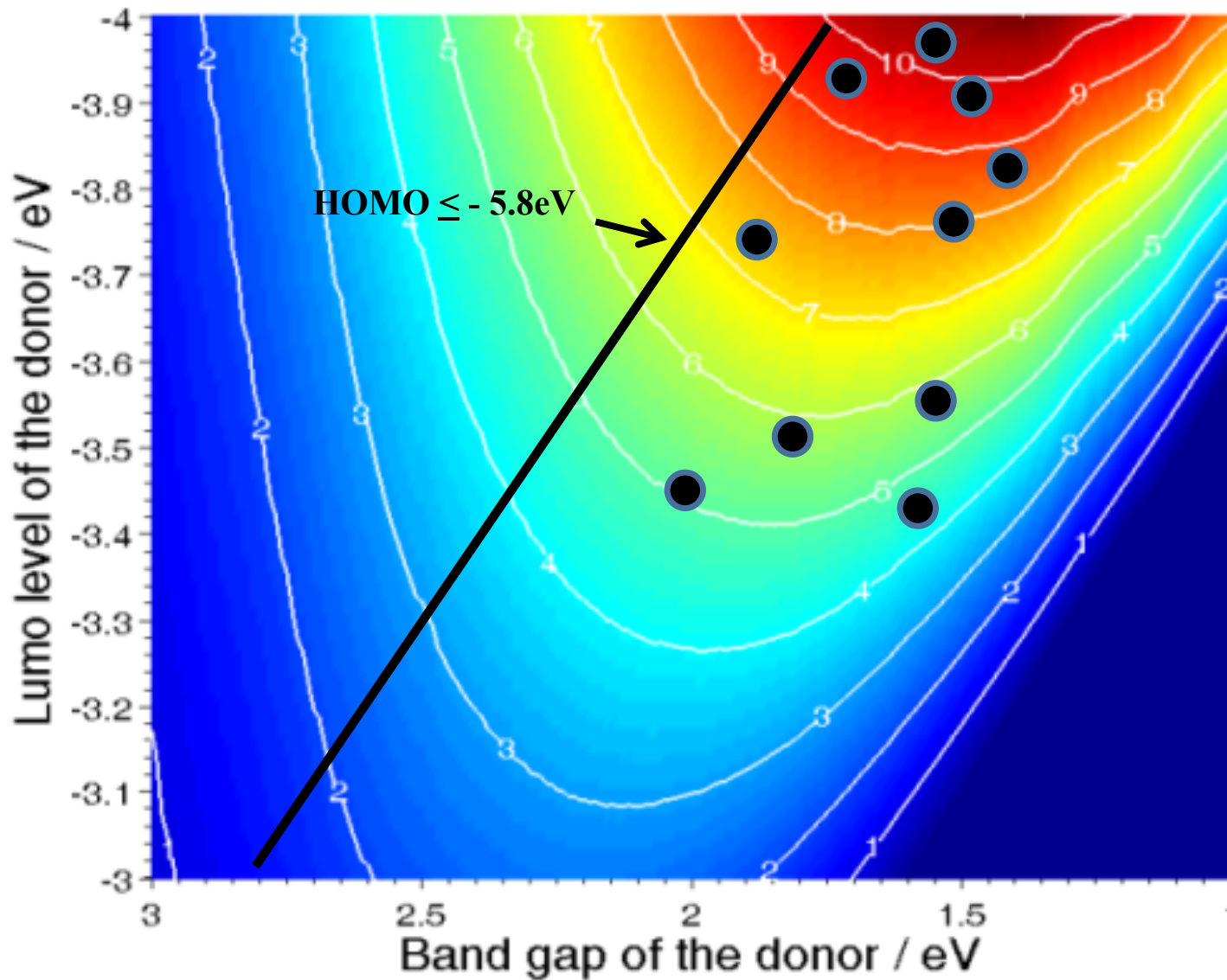
Performance  
sufficient for initial  
applications has  
already emerging



**Solarmer breaks  
organic solar PV  
cell conversion  
efficiency record,  
hits NREL-  
certified 7.9%**

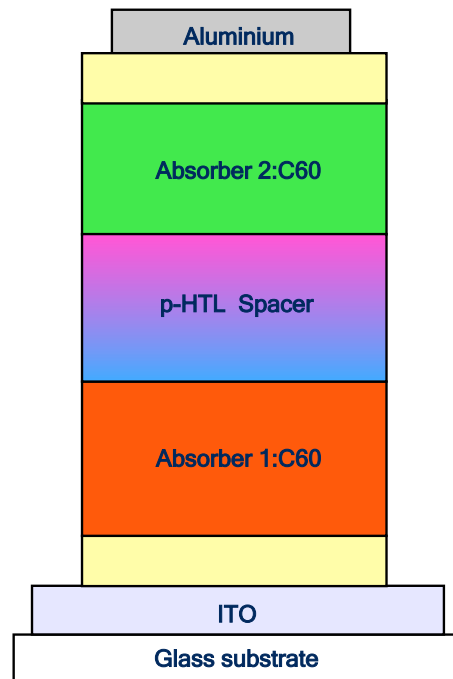






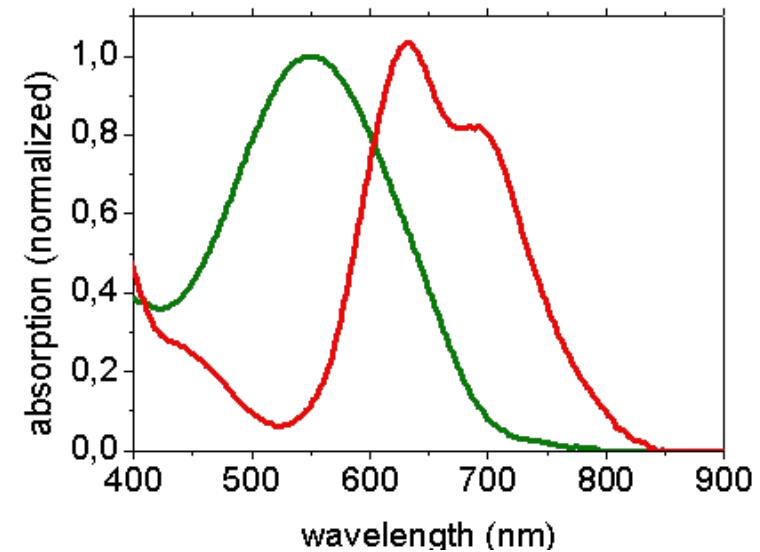
## Single Junction Devices

## Technology: p-i-n tandem solar cells



**tandem solar cell technology:**

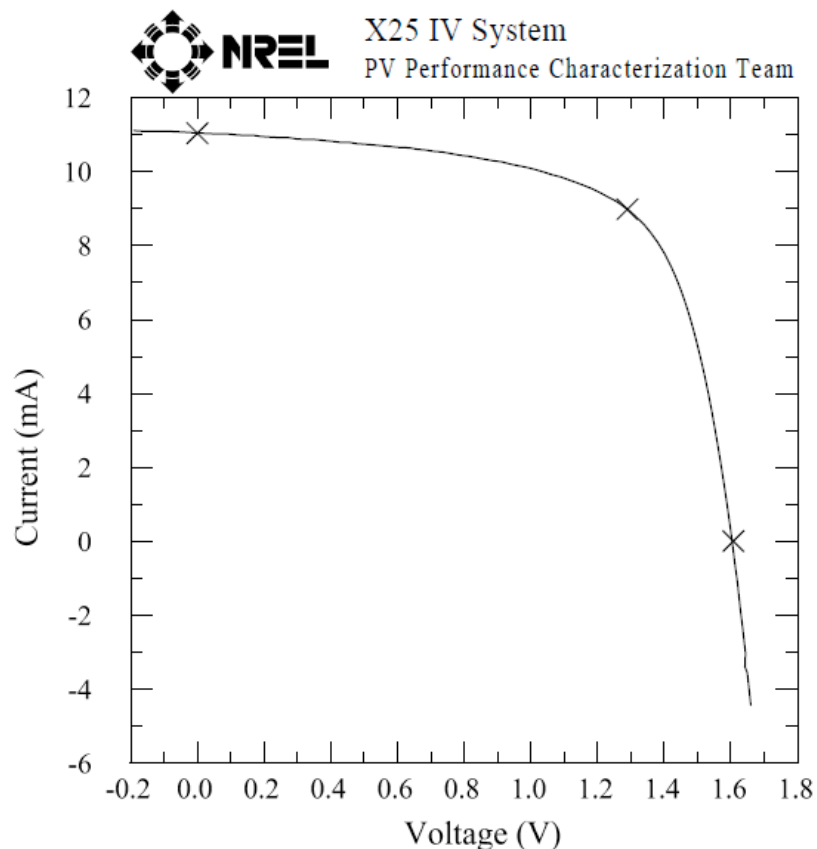
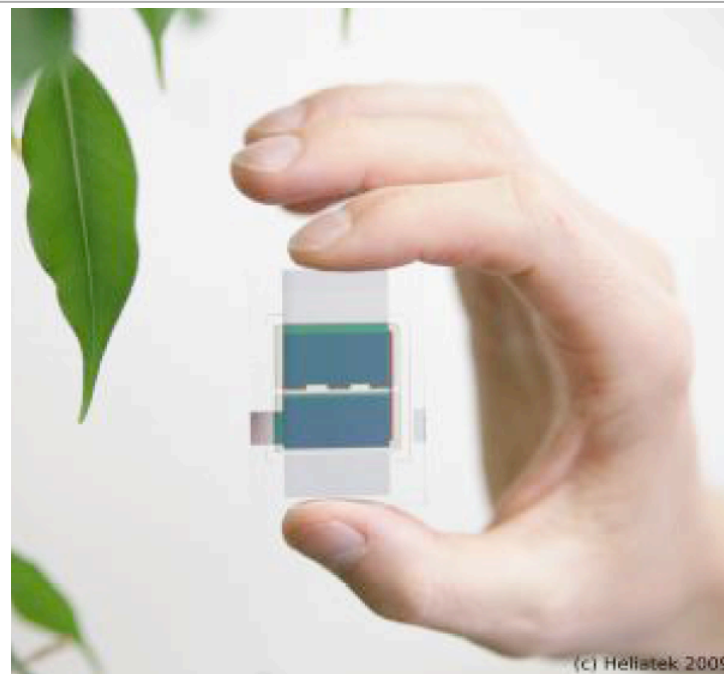
→ **optimum harvesting of complete sun spectrum**



# Record Tandem Device heliatek/IAPP/BASF



Device ID: PV17 11 e1      Device Temperature:  $24.9 \pm 0.5 \text{ }^\circ\text{C}$   
Apr 24, 2009 19:04      Device Area:  $1.974 \text{ cm}^2$   
Spectrum: ASTM G173 global      Irradiance:  $1000.0 \text{ W/m}^2$



$V_{oc} = 1.6076 \text{ V}$   
 $I_{sc} = 11.045 \text{ mA}$   
 $J_{sc} = 5.5952 \text{ mA/cm}^2$   
Fill Factor = 65.24 %

$I_{max} = 8.9829 \text{ mA}$   
 $V_{max} = 1.2896 \text{ V}$   
 $P_{max} = 11.585 \text{ mW}$

Efficiency = 5.87 %  
Device Area:  $1.974 \text{ cm}^2$

# How good can a practical double junction cell be?

## Assumptions

- Two cells are stacked in series. The total current is given by that of the subcell with the lower current.

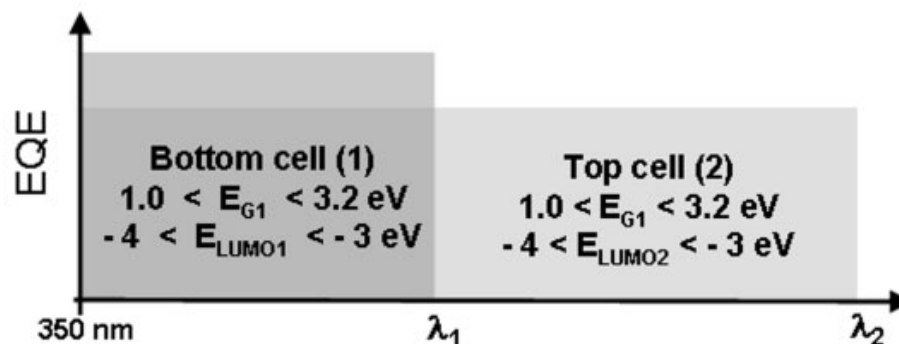
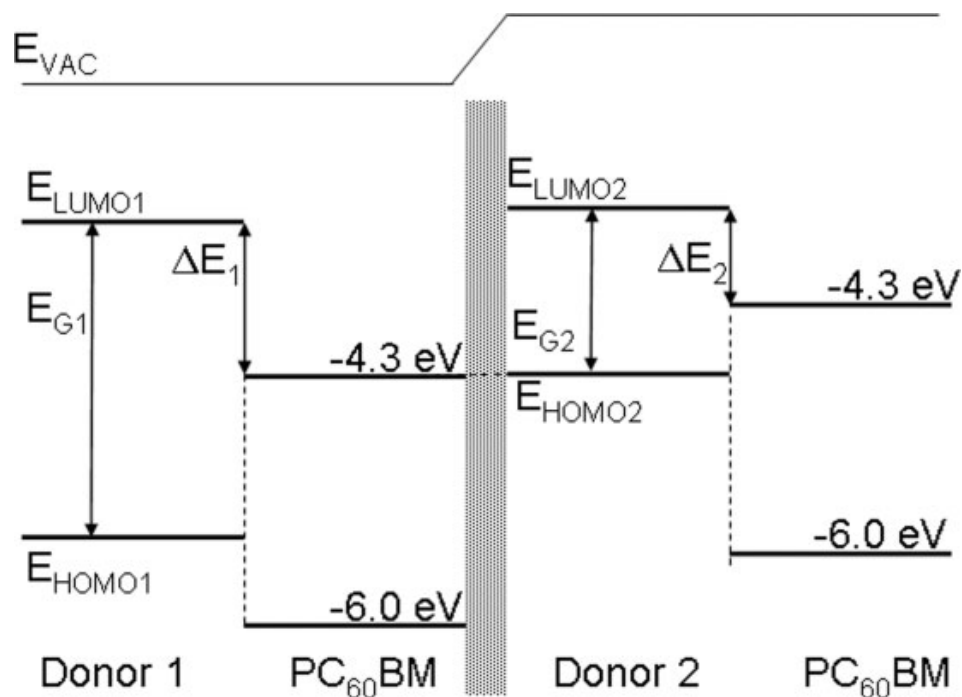
- Fill Factor = 0.65.

- EQE is approximately 85 % (see the paper for details)

- The acceptor is PCBM

- The Donor LUMO is at -4.0 eV

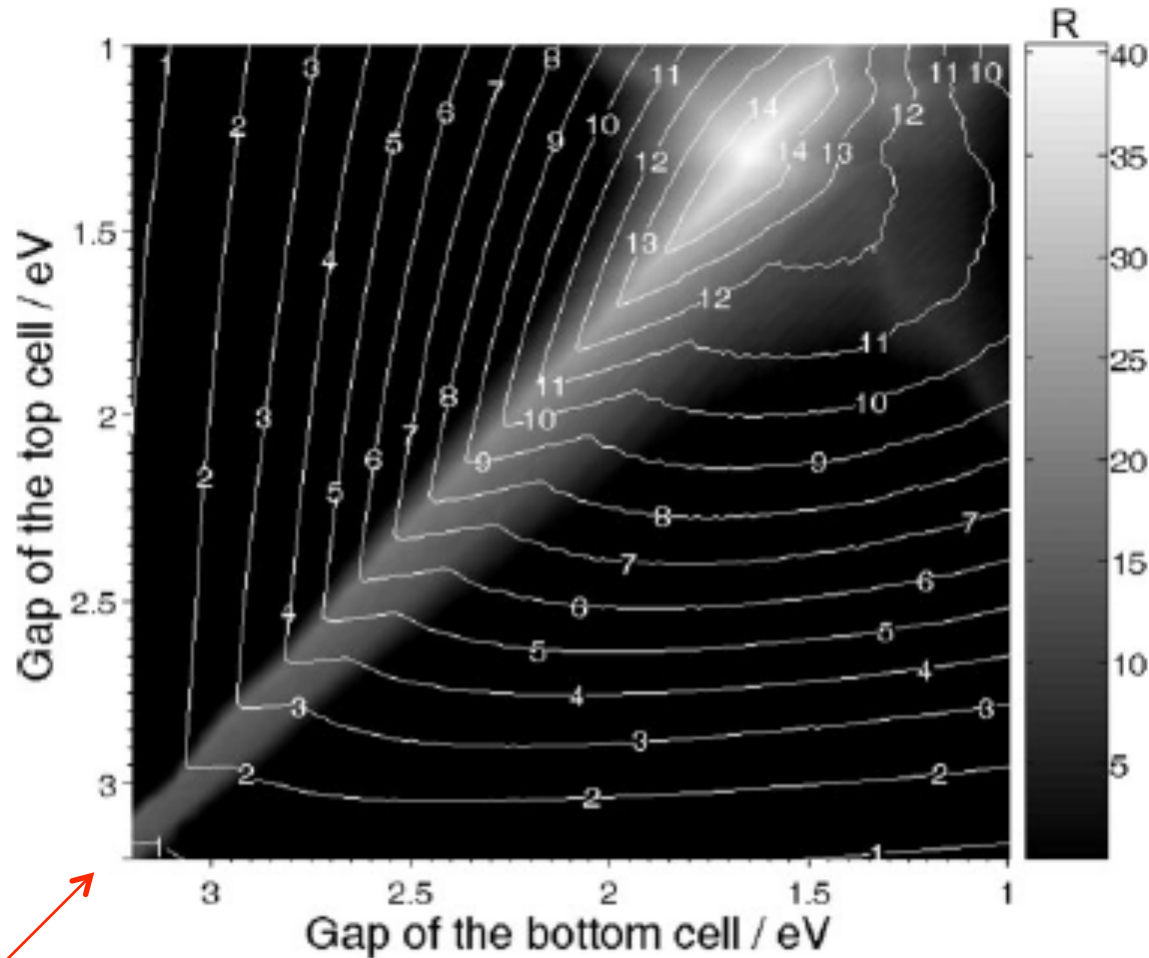
$$V_{OC} = \frac{1}{e} (|E_{HOMO}^{Donor}| - |E_{LUMO}^{PCBM}|) - 0.3$$



Dennler, Brabec et al. *Advanced Materials* 20 (2008) 579.

# Efficiency of double junction cells from previous slide

The two band gaps should be 1.3 and 1.7 eV.



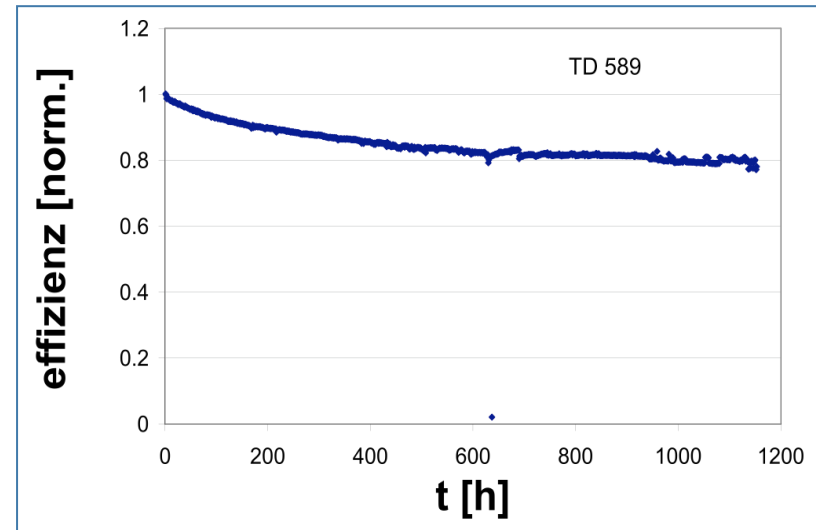
The current is matched along this diagonal.

Dennler, Brabec et al. *Advanced Materials* 20 (2008) 579.



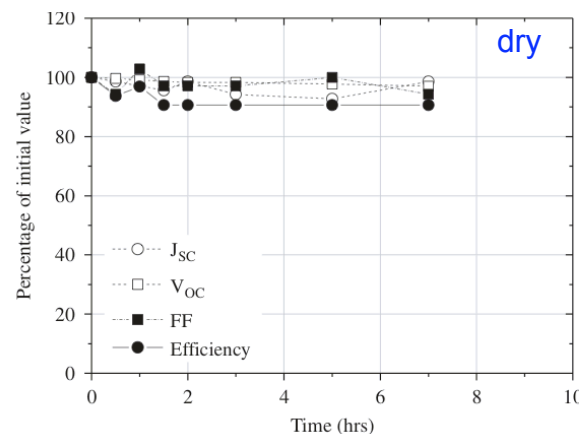
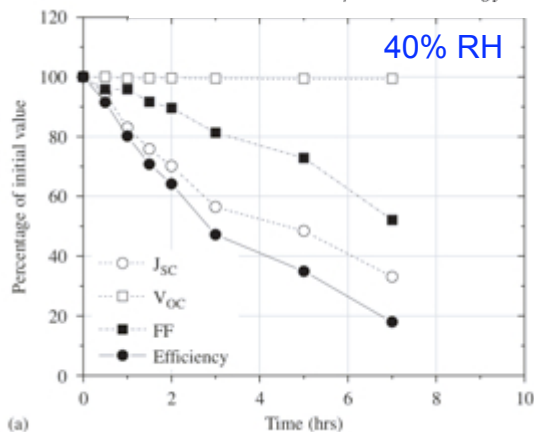
# The Next Big Question - Degradation in Organic Solar Cells

- Many pathways possible for OPV device degradation:
  - Delamination
  - Inter-diffusion of electrodes
  - Morphology changes of donor-acceptor
  - Interfacial degradation
  - Photo-oxidation of organic
  - Oxidation of electrode



Accelerated testing at 85 °C, Konarka Technologies  
Christoph Brabec, MRS Bulletin January 2005.

K. Kawano et al. / Solar Energy Materials & Solar Cells 90 (2006) 3520–3530



PEDOT:PSS is very hygroscopic

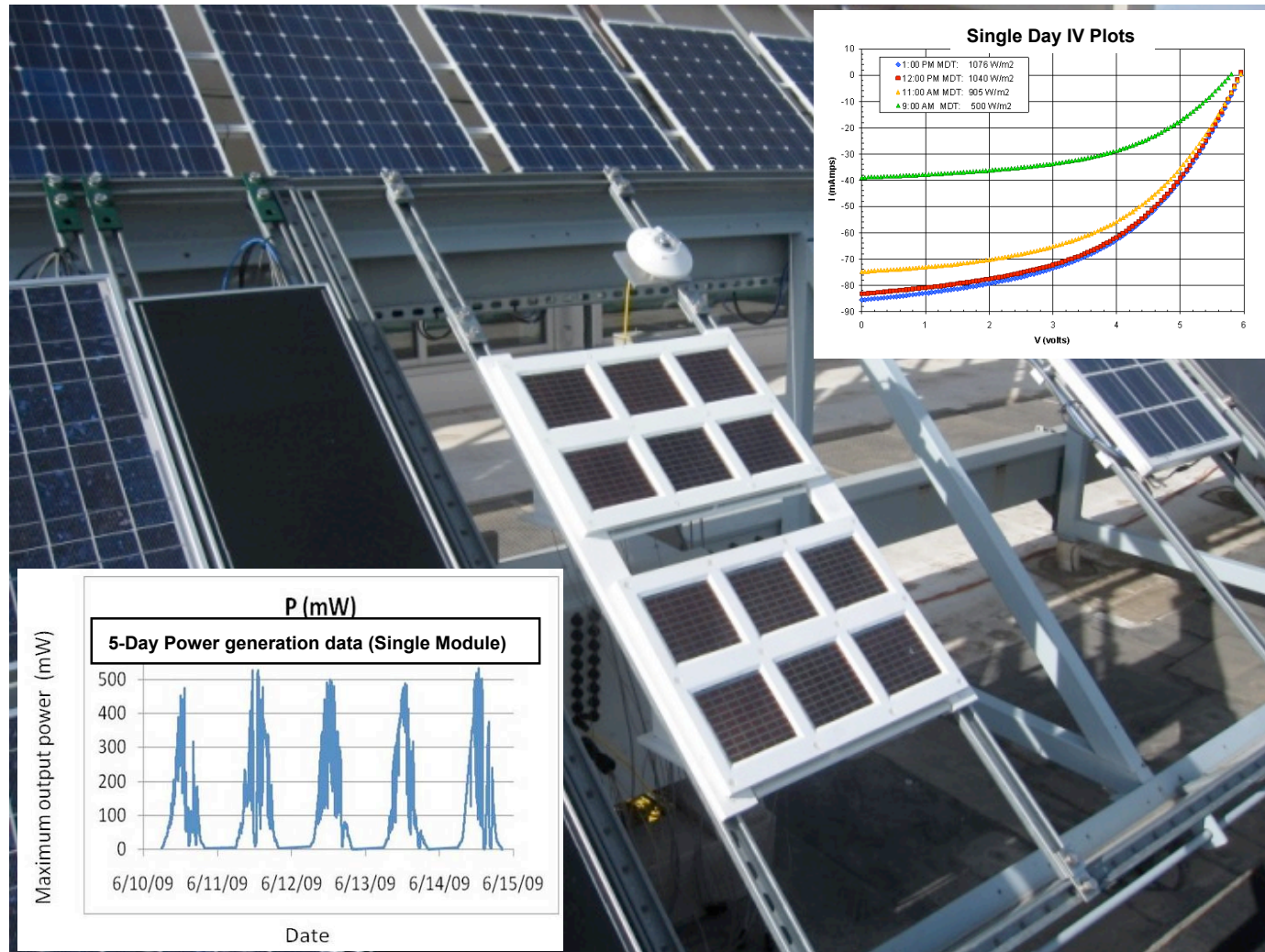
Plexcore OC, is not hydroscopic and maintains weight, resistive, and chemical stability in air and under light

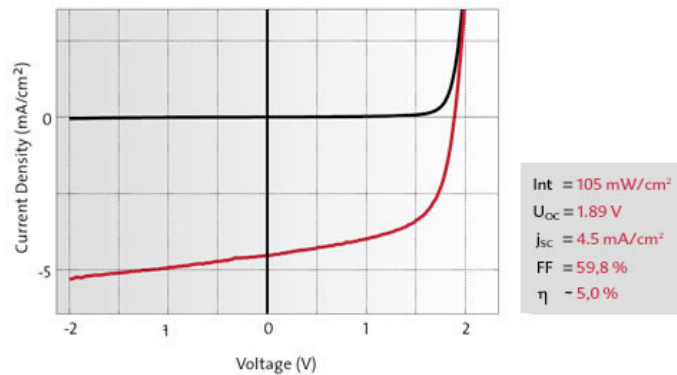
NiO, WO<sub>3</sub> offer alternatives as well

# Lifetime -- OPV outdoors



## First OPV Modules at NREL Outdoor Testing Site





Source: Heliatek, based on Novaled PIN OLED™ technology

## Organic Photovoltaics (OPV)

The application of Novaled materials to solar cells allows for highest efficiencies, just the way it does for OLEDs. It allows easy integration of tandem architecture (stacking of two solar cells on top of each other) with excellent performance:

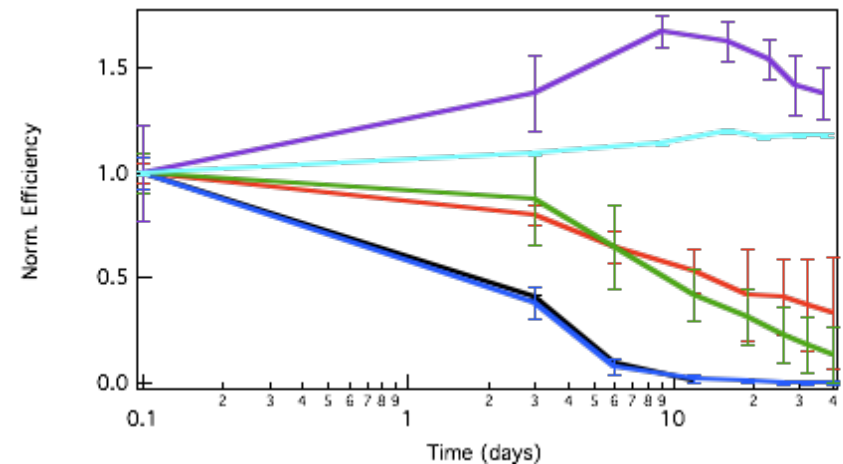
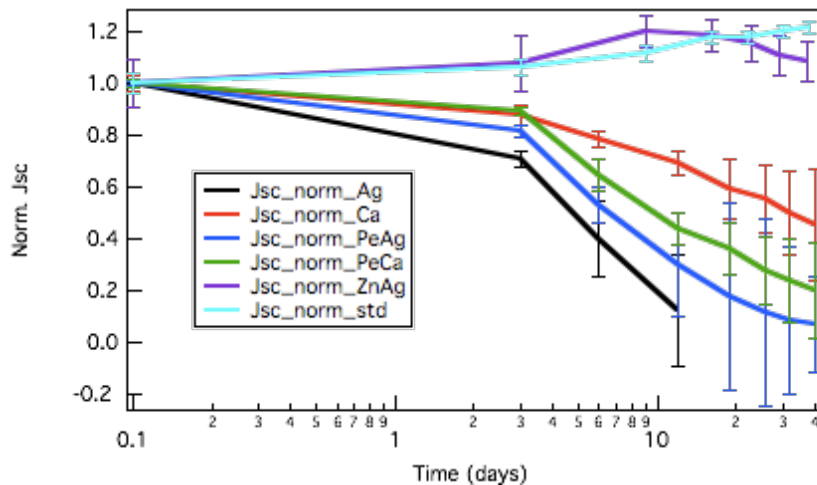
- › 5% efficiency (1cm<sup>2</sup> active area, Heliatek tandem architecture based on Novaled p- and n-dopants combining absorber materials from Heliatek and BASF)
- › High open circuit voltage (1.9V)
- › High fill factor (60%, improved fill factor with NDP9)
- › Lifetime for pin-type Heliatek solar cells with Novaled dopants: up to 16.000h (exposed to 100mW/cm<sup>2</sup> white light), very good thermal stability.

Use of doped transport layers allows for optical engineering and thus for optimized efficiency. Novaled technology is proven for highest OLED stability and this also holds for organic solar cells.

# Device and Packaging Reliability and Lifetime

## Effect of Device Architecture on Shelf Life

- Shelf life study on devices that haven't been encapsulated
- Traditional vs. inverted device architectures

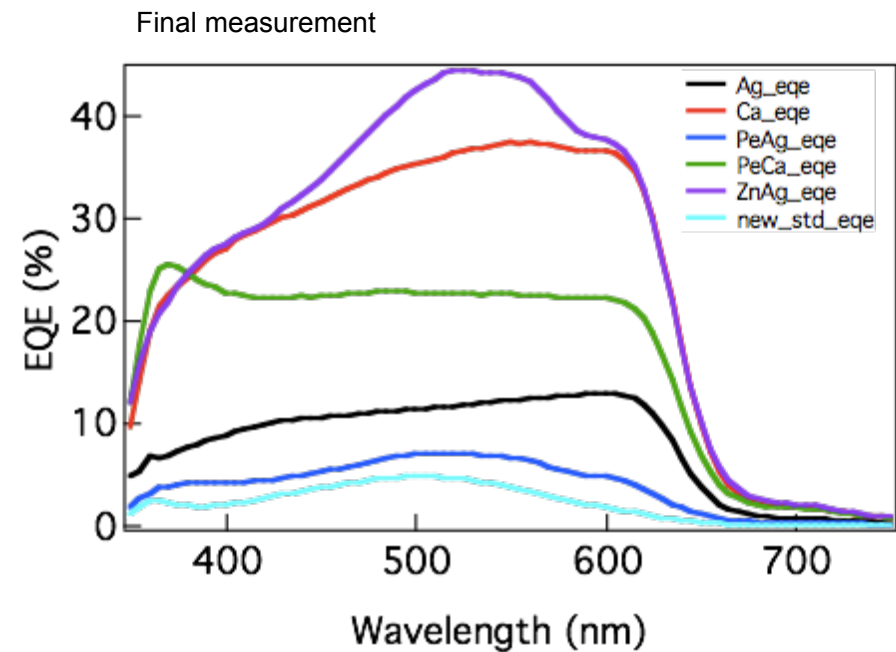
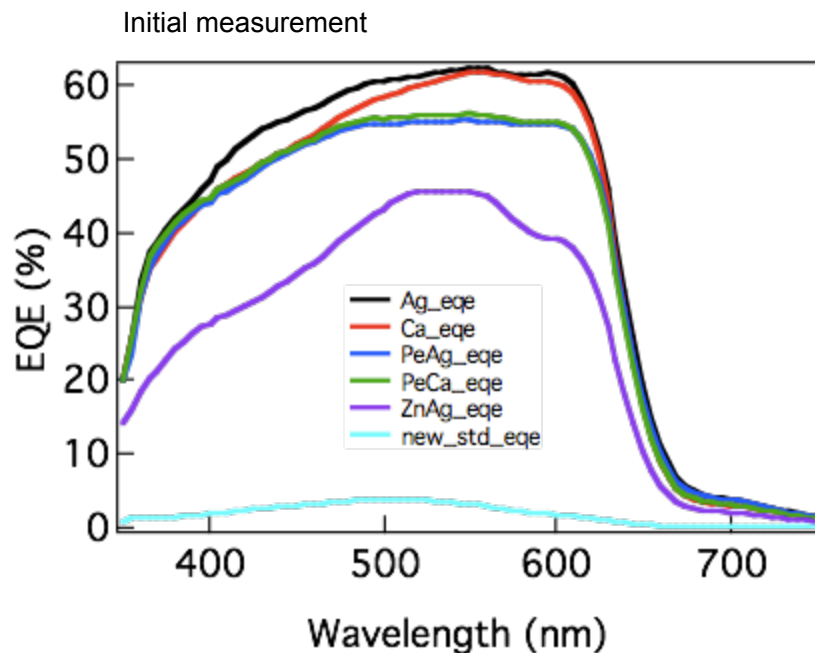


- Ca/Al electrode fails quickly, whereas inverted device is less susceptible to oxidation of the electrode materials
- Active layer is relatively stable in air when not illuminated

# Device and Packaging Reliability and Lifetime

## Effect of Device Architecture on Shelf Life

Initial & final EQE measurements (Sandia) for shelf life study



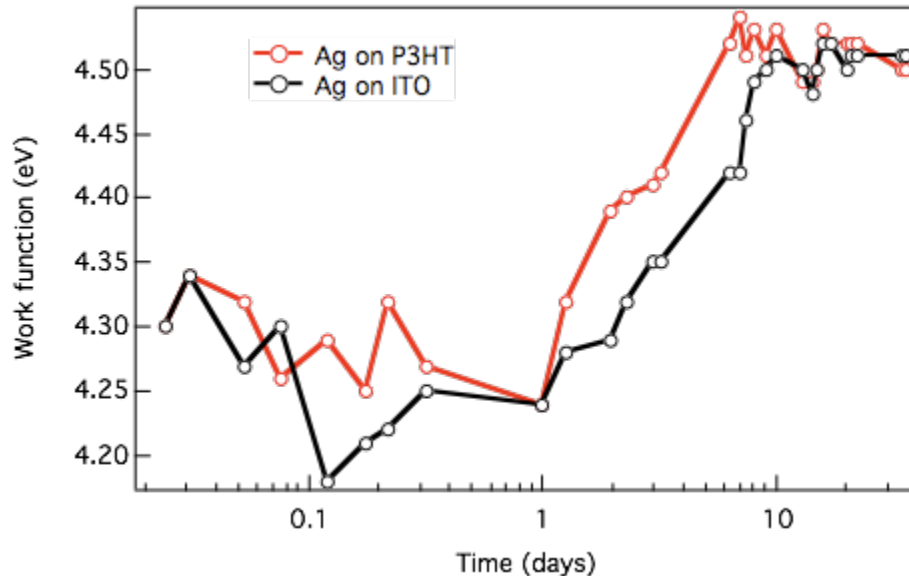
- No changes observed in current extraction efficiency from inverted (ZnAg) device after 40 days of exposure to air - large changes observed in Ca/Al (PeCa) device.
- No changes in active layer when exposed to air - electrode choice is paramount!



# Device and Packaging Reliability and Lifetime

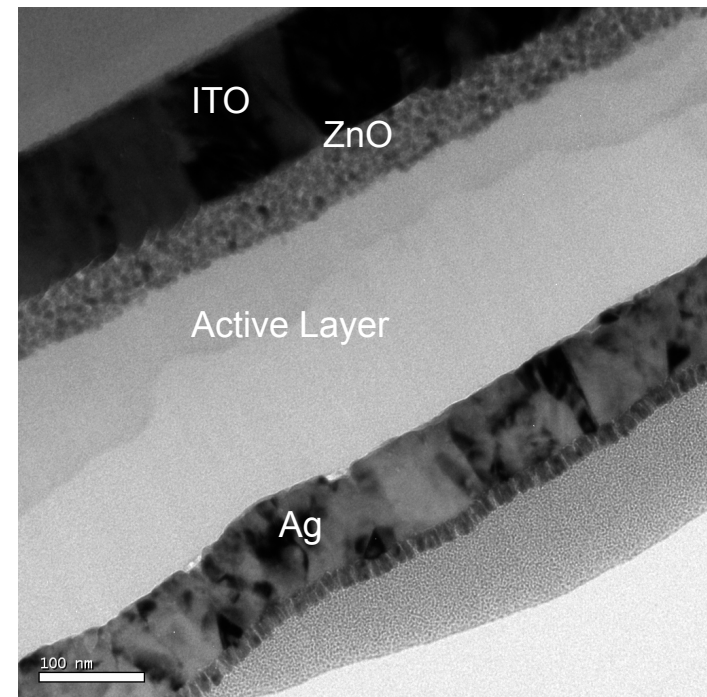
## Effect of Air Exposure on Inverted Silver Electrode

Kelvin probe measurement for Ag electrode over time exposed to air



Inconel reference, assuming a work function of 4.3 eV

- Ag work function increases over time, improving contact to donor material

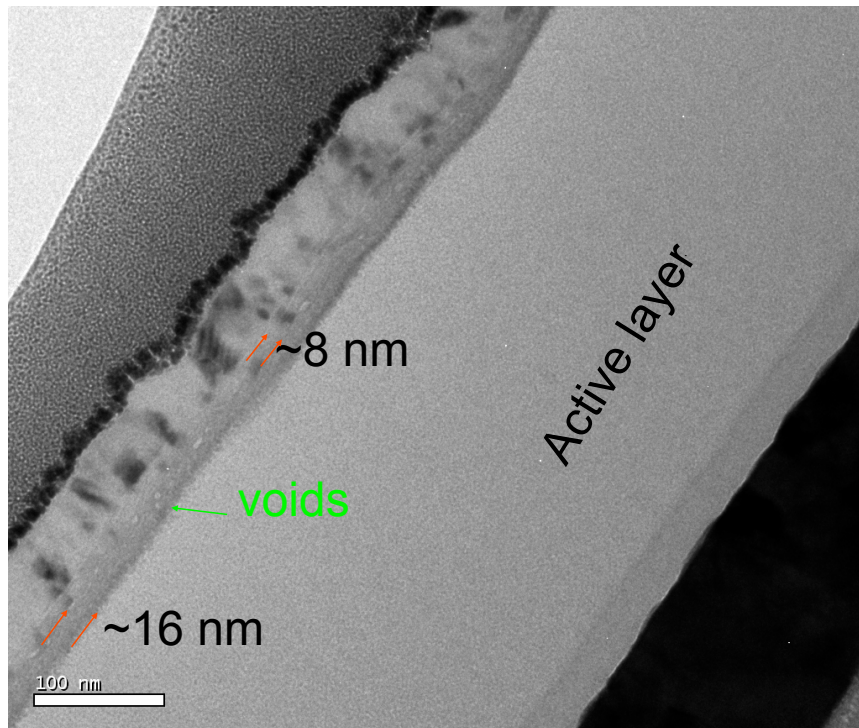


- Interface between Ag and the active layer is very sharp, with little/no sign of Ag oxidation

# Device and Packaging Reliability and Lifetime

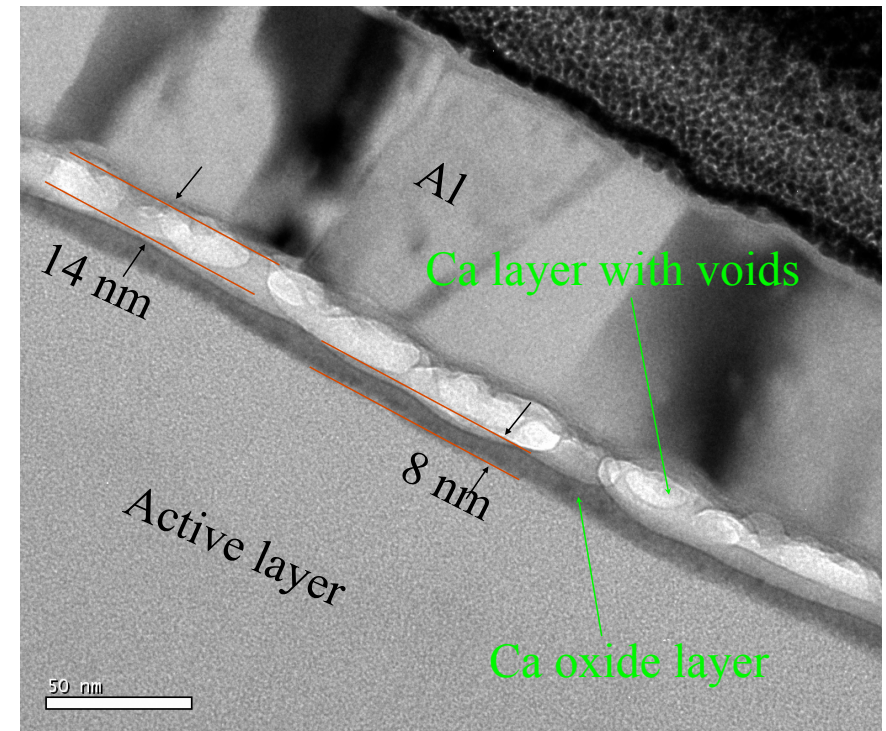
## Effect of Air Exposure on Calcium Electrode, TEM

New Sample



- At Al/Ca interface, it forms a transition layer of  $\sim 8\text{nm}$ , made of mainly Al.
- Tiny voids are often present at the interface of the transition layer and the Ca layer.
- The Ca/polymer interface is also not very sharp.

Sample After Air Exposure



- All of the Ca layer is oxidized. Very large voids are present at the interface of the transition layer and the Ca layer.
- Ca is fully oxidized after exposure to air resulting in dramatically reduced performance.

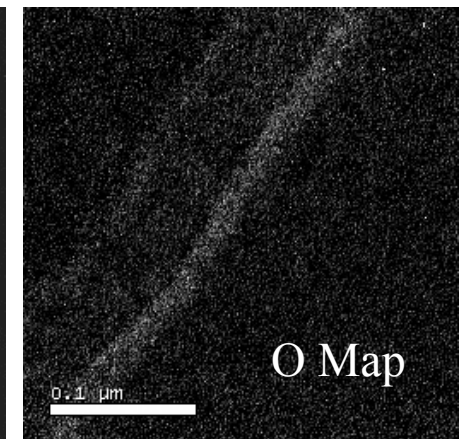
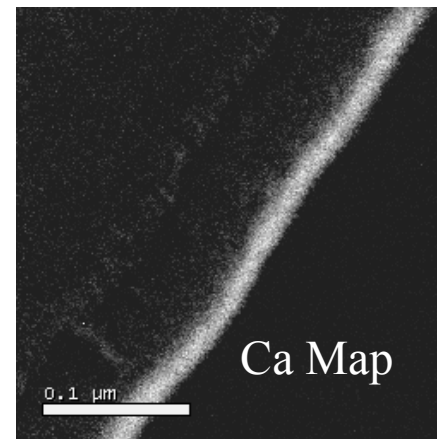
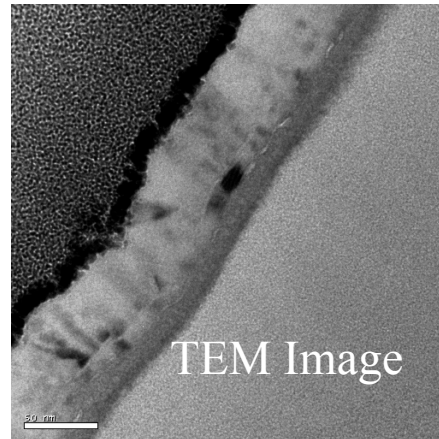


# Device and Packaging Reliability and Lifetime

## Effect of Air Exposure on Calcium Electrode, EELS Mapping

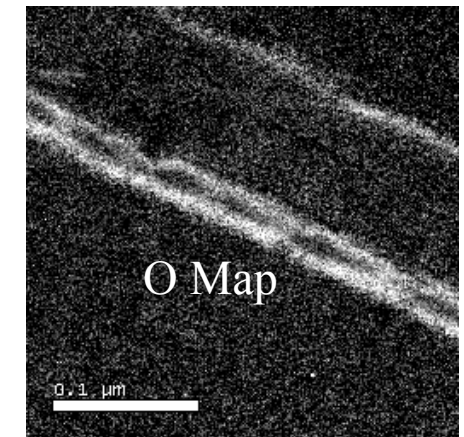
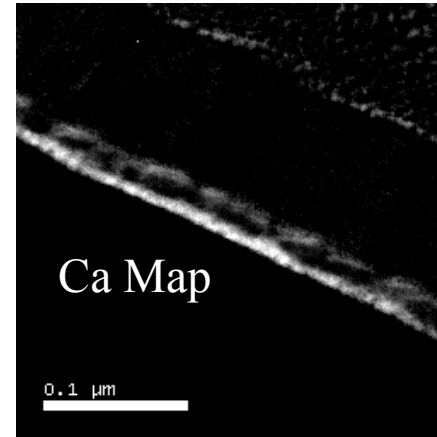
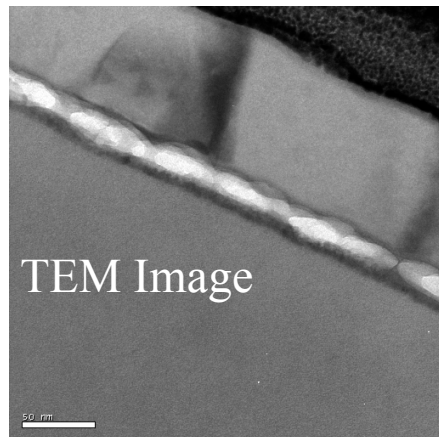
### New Sample

- The actual Ca layer thickness is about 17 nm. The Ca layer has a significant tail into the Al layer.
- O content in the Ca layer appears to be insignificant!



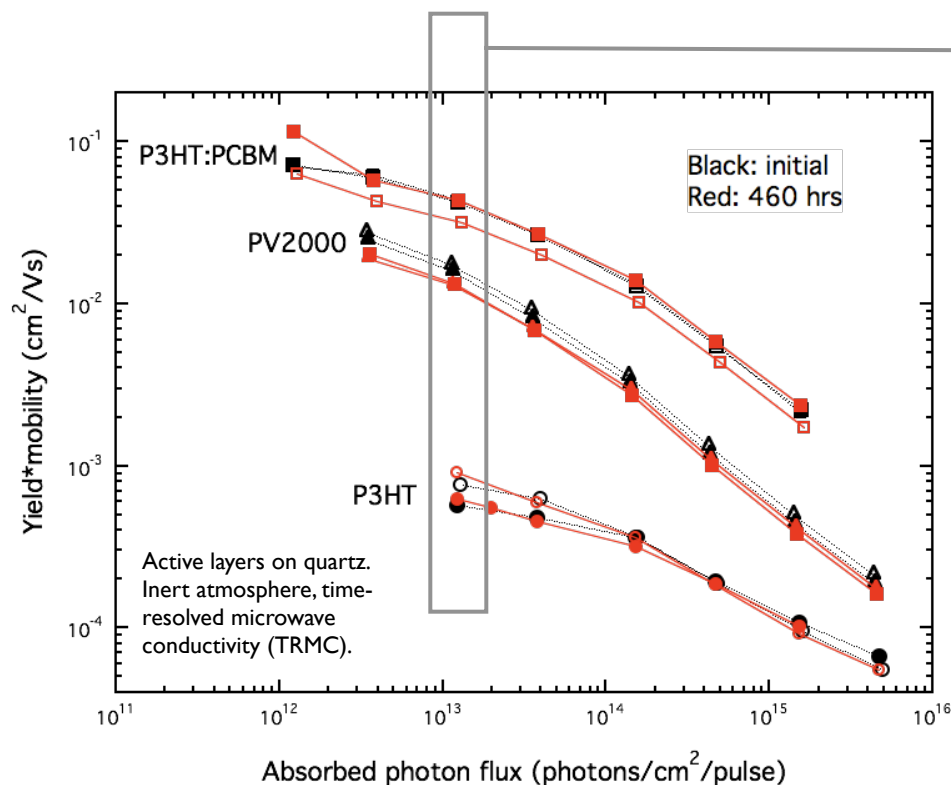
### Sample After Air Exposure

- The actual CaO layer thickness is about 8 nm. The Ca layer has a significant tail into the Al layer.
- O content in the Ca layer is significant, suggesting the Calcium is fully oxidized!

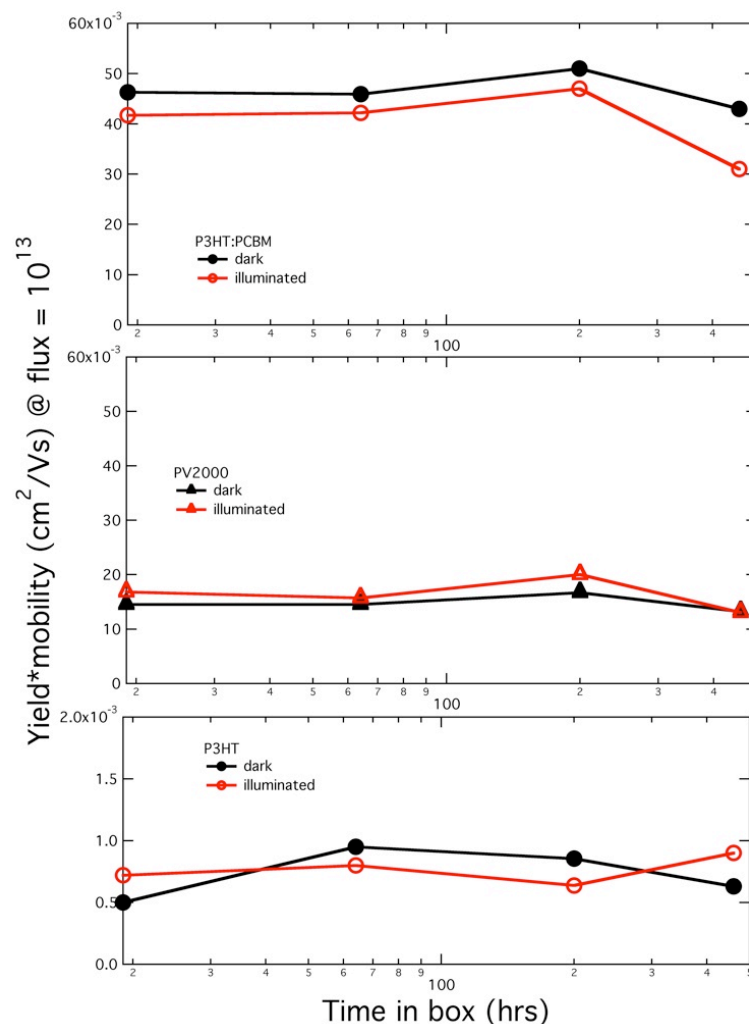


# Materials Characterization Specific to OPV

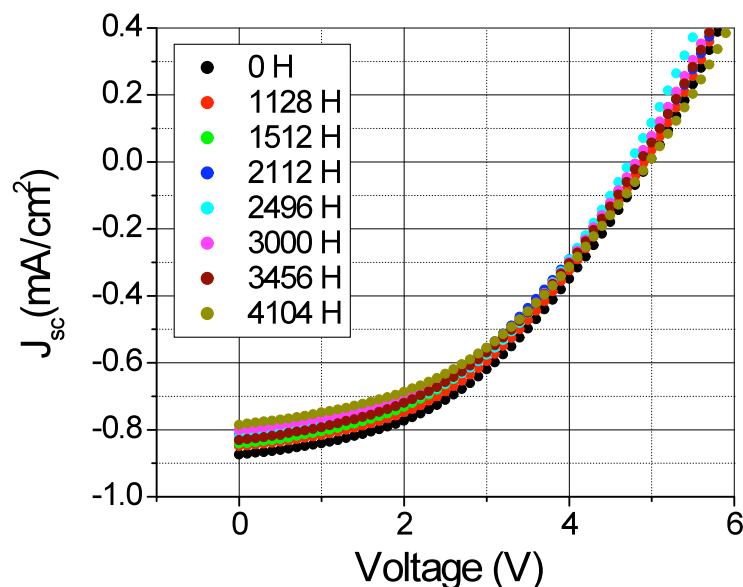
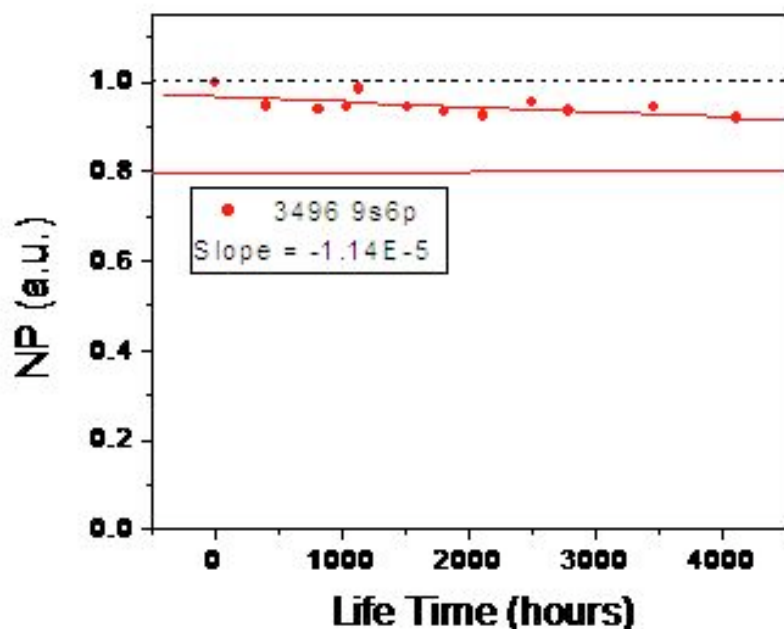
## Active Layer Degradation Studies Using TRMC



- Unique capability to assess intrinsic stability of the active layer.
- No photobleaching observed in UV-vis absorption.
- Stable active layer photoconductivity and carrier lifetimes  $\sim 500$  hrs.
- To be compared with illumination under ambient conditions.



# Champion OPV Module Lifetime Continuous Xe Light Soaking

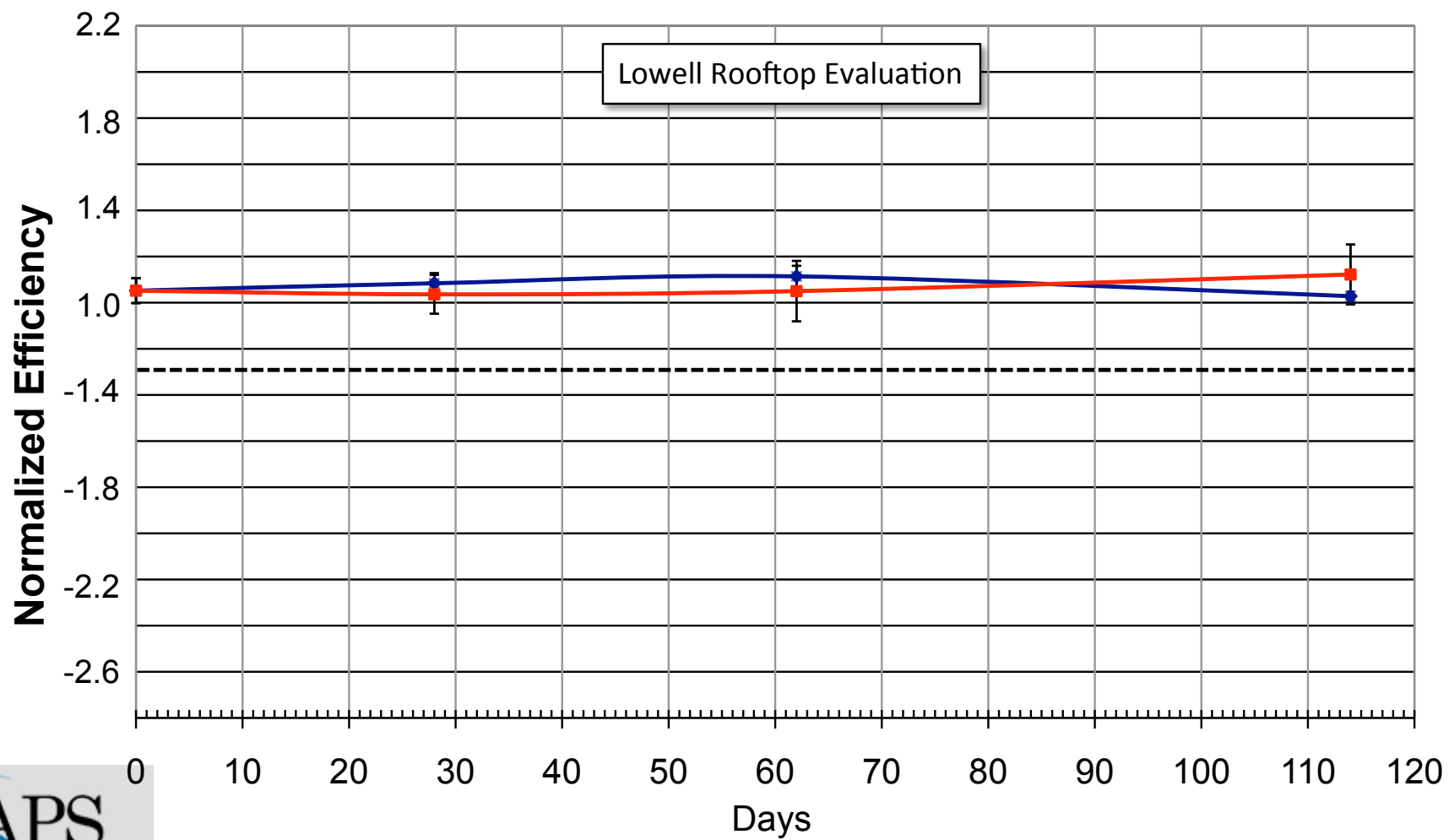


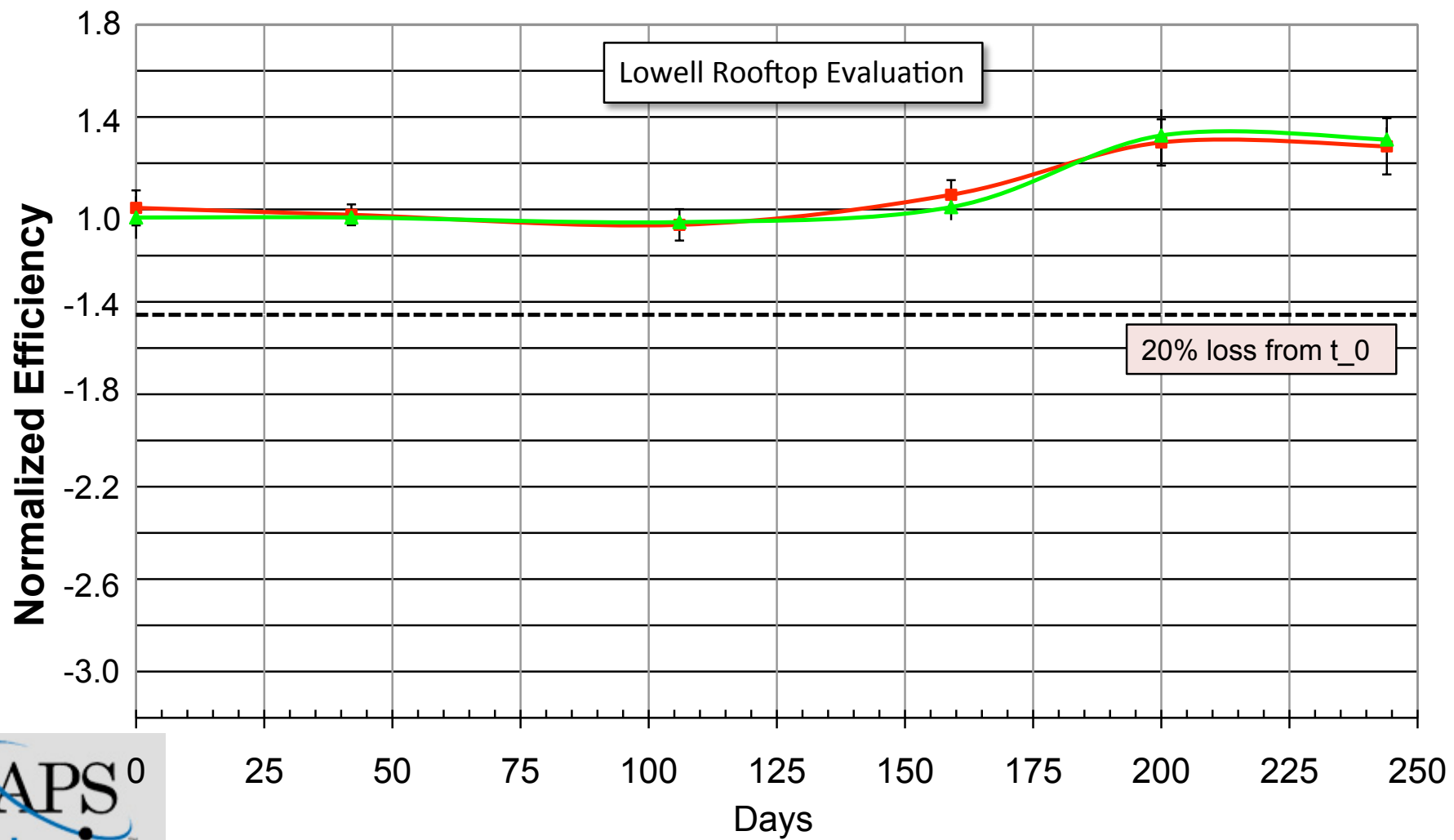
AM1.5G solar simulation JV characteristics

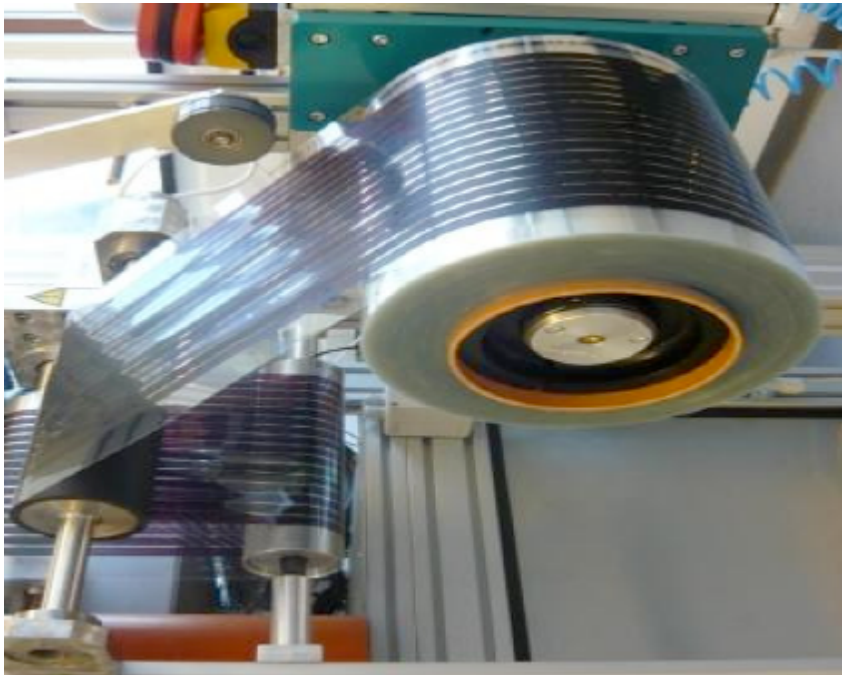
**Extrapolates to > 3 yr (27 kh) of outdoor lifetime\***

- > 4100 hrs to date (Xe-lamp, continuous, 25C)
- ~ 1.1%/1000h decay rate (stabilized efficiency, 100% duty cycle)
- 32 kWh/m<sup>2</sup>/day (6.5x ave. US insulation)

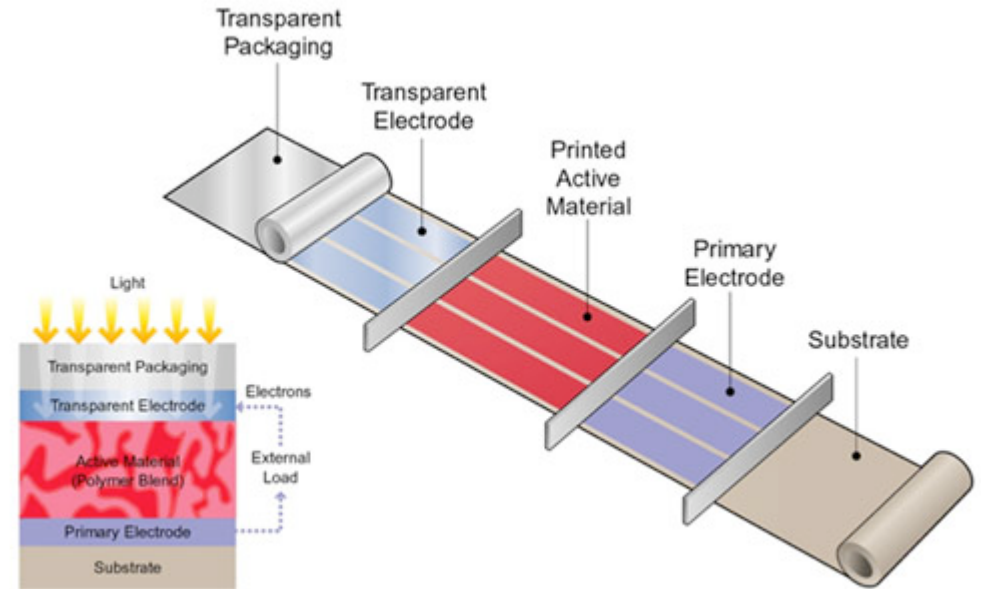








# Technology is Scalability and at Low Temperature

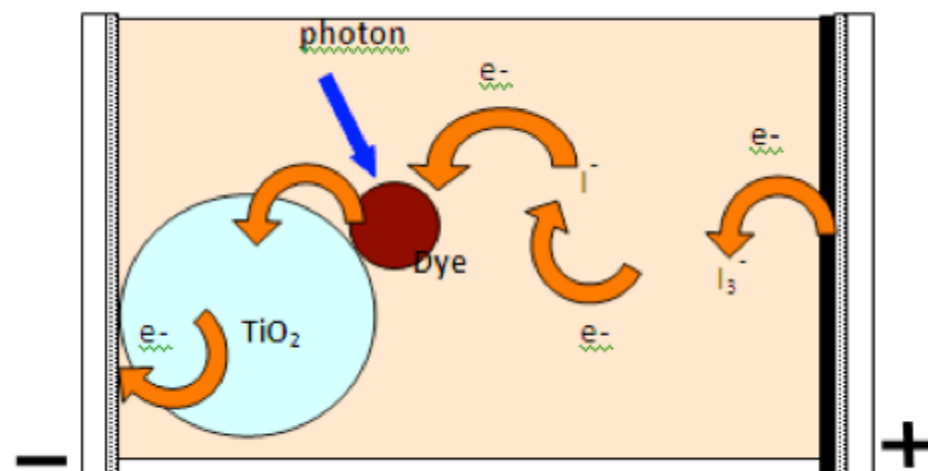
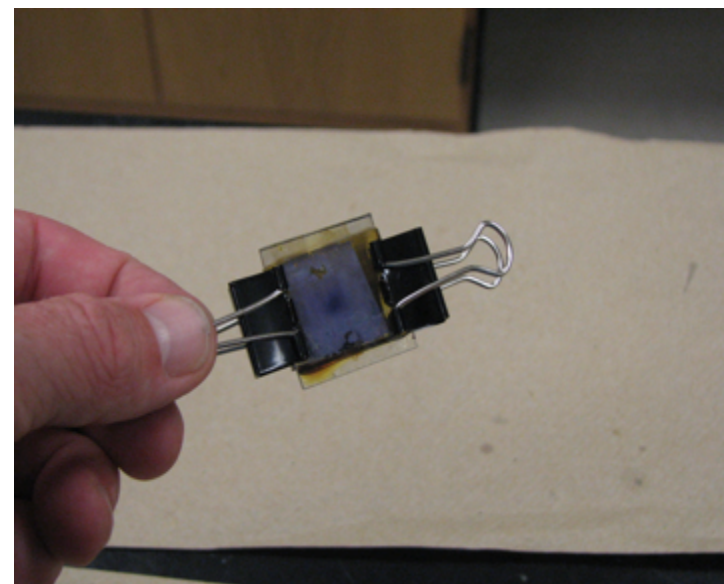
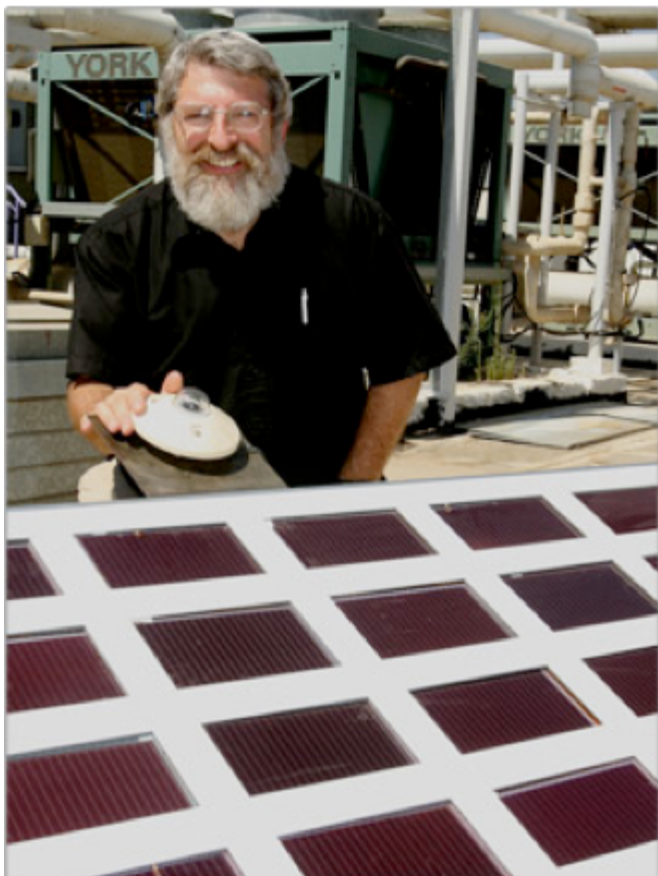


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# What Else is Coming Along??

# DSSC - The Dye Cell - Nanoscale PV



PV dye cell schematics



# Beyond the Single Junction

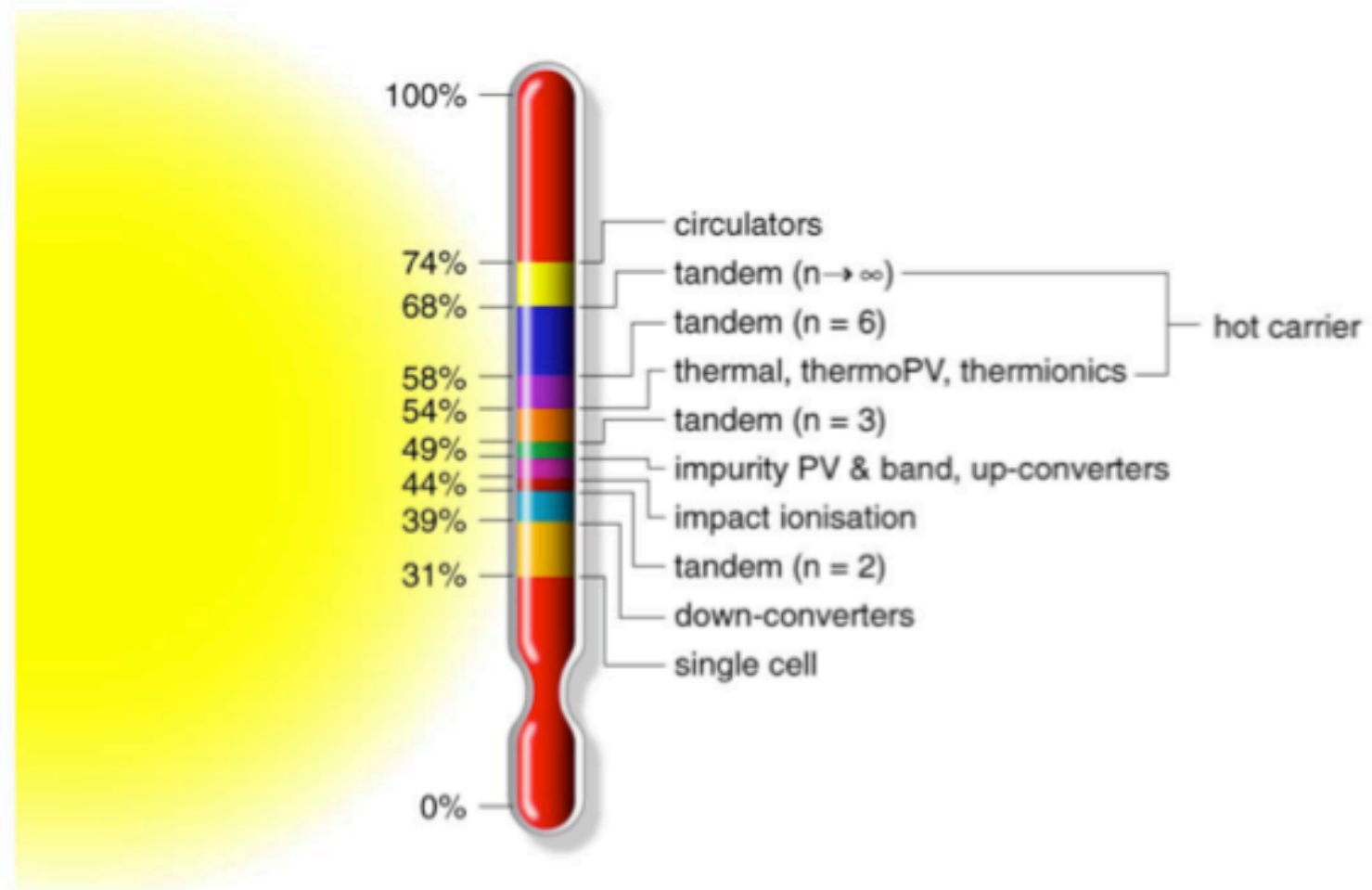
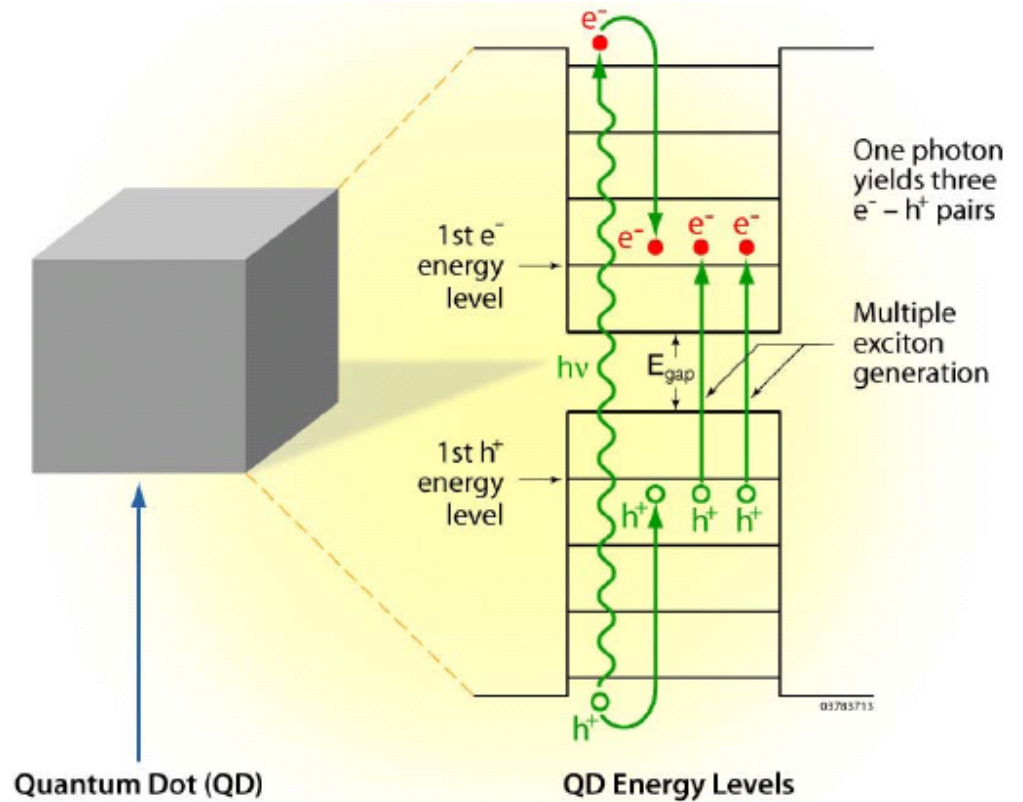
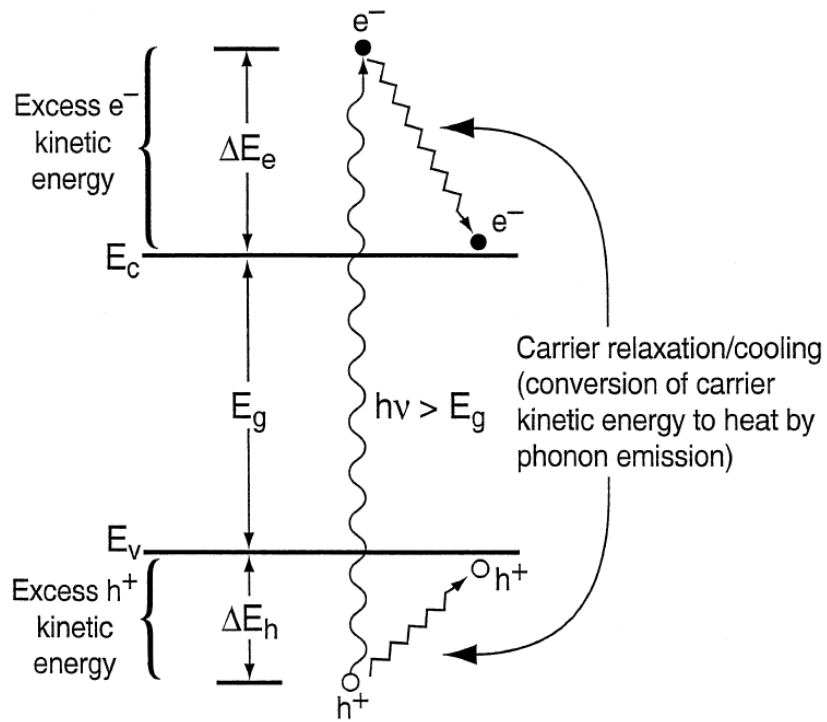


Figure 13. "Third Generation" options and thermodynamic limits on their efficiency.

# Multiple Exciton Generation in nanocrystals



# Conclusions - solar cells by design!

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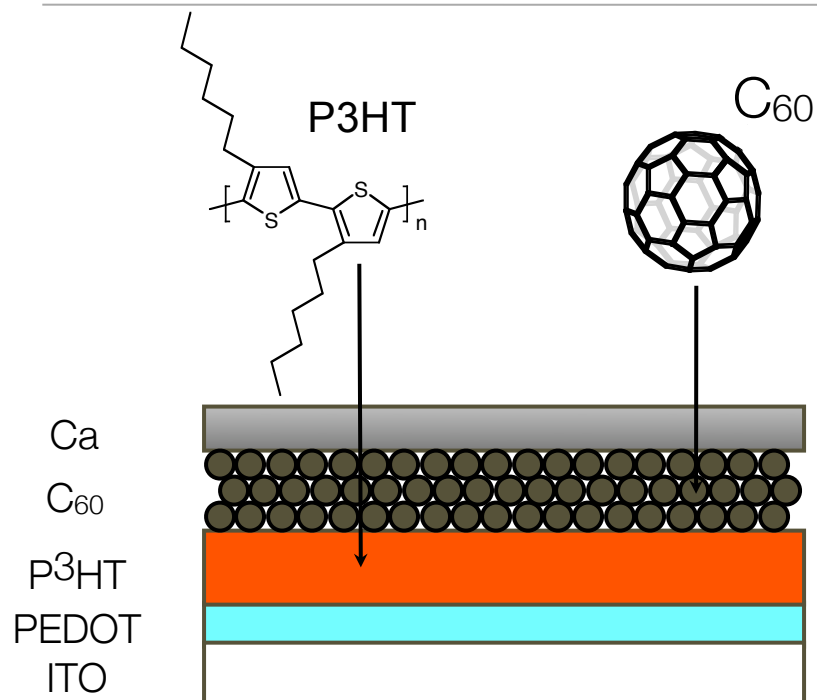
- Terawatt production will require “green approaches”
- Organic photovoltaics offer a promising technology for future low-cost, large scale renewable energy production - Progress is very rapid toward this end with scalability being demonstrated so far by low cost approaches.
- Alternatives for Earth Abundant PV exist such as CZTS, Thick Film Si, Dye Cells, 3rd Generation approaches
- Materials by Design offers tremendous potential for real breakthroughs - ie new designed donor materials are being fabricated to allow for increased light absorption - tandem devices offer great potential in this technology
- Interfacial stability seems at present the most critical area even vs efficiency. Development of new contact and electrode materials allow for enhanced performance and stability and reduced cost with increased focus on flexible substrates will be needed for new materials.

***Thank You***

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# Planar Bilayer Heterojunction Devices



## • Strengths

- Chemical potential gradients yield a net diffusion current
- Efficiently separated charges, limited recombination

## • Weaknesses

- Requires large exciton diffusion lengths
- Very little light absorption
- Often thermally evaporated

